Induction of Higher Coordination States in Phenyl Grignard Reagents by Intramolecular Coordination. Crystal Structures of *o*-$CH_2(OCH_2CH_2)_nOCH_3$-Substituted Phenylmagnesium Bromides (n = 0–3)

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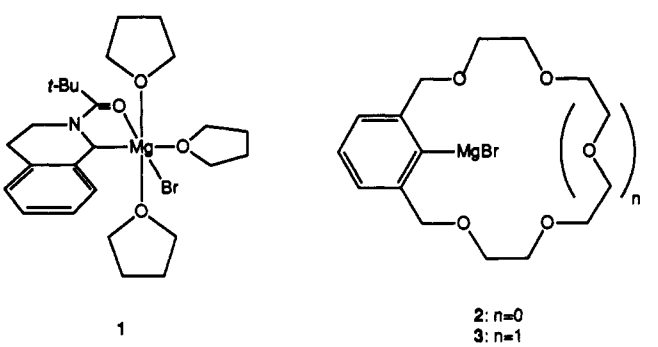
A series of phenylmagnesium bromides with intramolecularly coordinating substituents $CH_2(OCH_2CH_2)_nOCH_3$ at one [n = 0–4 (**14–18**)] or both [n = 1, 2 (**19, 20**)] ortho positions has been investigated. The pure Grignard reagents were obtained from the exchange reaction of the corresponding arylmercury bromides (**35–39**) with magnesium, since their synthesis from the analogous bromides (**7–13**) and magnesium was accompanied by extensive ether cleavage in the substituents if $n > 1$. The Grignards exhibit intramolecular coordination both in solution and in the crystalline state, as was concluded from ^1H NMR spectroscopy and from X-ray crystal structure determinations. The structures of four complexes with one ortho substituent (n = 0–3) were determined. They show higher coordination numbers than normally encountered in organomagnesium compounds. The structure of **14** can be related to those of normal, halogen-bridged, dimeric Grignard reagents, though with a pentacoordinated rather than a tetrahedral magnesium due to additional coordination of the CH_2OCH_3 oxygens. From **15** on, hexacoordination of the magnesium is found: additional THF molecules serve to complete the pseudooctahedral surrounding in the case of **15** (+2 THF) and **16** (+1 THF), until a completely solvent free species is obtained in **17**. Crystal data: complex **14** monoclinic space group $P2_1/a$, a = 7.804 (4) Å, b = 18.224 (8) Å, c = 9.152 (5) Å, β = 94.51 (2)°, V = 1298 (1) Å^3, Z = 2; complex **15** orthorhombic space group $Pbca$, a = 14.975 (2) Å, b = 13.490 (2) Å, c = 20.712 (3) Å, V = 4184 (1) Å^3, Z = 8; complex **16** monoclinic space group $P2_1/n$, a = 8.555 (1) Å, b = 13.221 (2) Å, c = 17.292 (2) Å, β = 101.86 (1)°, V = 1914.0 (4) Å^3, Z = 4; complex **17** monoclinic space group $P2_1/n$, a = 11.817 (2) Å, b = 7.861 (2) Å, c = 18.111 (3) Å, β = 105.23 (2)°, V = 1623.3 (6) Å^3, Z = 4. The final R values were 0.073 (**14**), 0.067 (**15**), 0.055 (**16**), and 0.065 (**17**).

Introduction

The complexation of the metal atom by electron-donating ligands like ethers plays an important role in the chemistry of Grignard reagents.[1] Normally, Grignards have a tetrahedral coordination geometry with one (dimeric structure) or two (monomeric structure) ether oxygens bonded to the metal atom. Higher coordination numbers are seldom encountered; as an example, the trigonal-bipyramidal $MeMgBr\cdot(THF)_3$ may be mentioned.[2] If, however, intramolecular substituents are present, capable of the formation of (several) coordinative bonds, unusual coordination geometries may result. Even hexacoordination is found as shown in the pseudooctahedral structure of the intramolecularly coordinated Grignard reagent 1-bromomagnesio-2-pivaloyl-1,2,3,4-tetrahydroisoquinoline tris(tetrahydrofuranate) (**1**, see Chart I).[3] In this specific complex, the high coordination number may be caused by the increased polarity of the magnesium–carbon bond, since the α-carbon atom is benzylic and has a direct bond to an electronegative nitrogen atom.

The higher coordination states can result in both higher and lower reactivities of the organomagnesium compounds.

Chart I



1 **2**: n=0 **3**: n=1

Lower reactivities may arise from a more efficient coordination of the magnesium as compared with "normal", solvent-coordinated compounds. The magnitude of this thermodynamic stabilization can be quantified by thermochemical measurements: less exothermic enthalpies will be found for the reaction with a proton donor (vide infra). Increased reactivities may be caused by stronger polarization of the Mg–C bond, induced by strong coordination of the magnesium with a Lewis base. This effect leads eventually to complete dissociation into highly reactive magnesiate species, as found on the complexation of diorganomagnesium compounds with cryptands. Two such complexes, $[EtMg^+(2,2,1\text{-cryptand}]_2\cdot Et_6Mg_2^{2-}$ and $[NpMg^+(2,1,1\text{-cryptand})]\cdot Np_3Mg^-$, were characterized by their crystal structures; here, polycoordination of the alkylmagnesium cation in the cryptand incites the formation of the very reactive magnesiate counterions.[4] To our

(1) (a) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 1, p 155. (b) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. C. *Adv. Organomet. Chem.*, in press. (c) Markies, P. R.; Akkermann, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Van Der Sluis, P.; Spek, A. C. *J. Organomet. Chem.* **1990**, *393*, 315.

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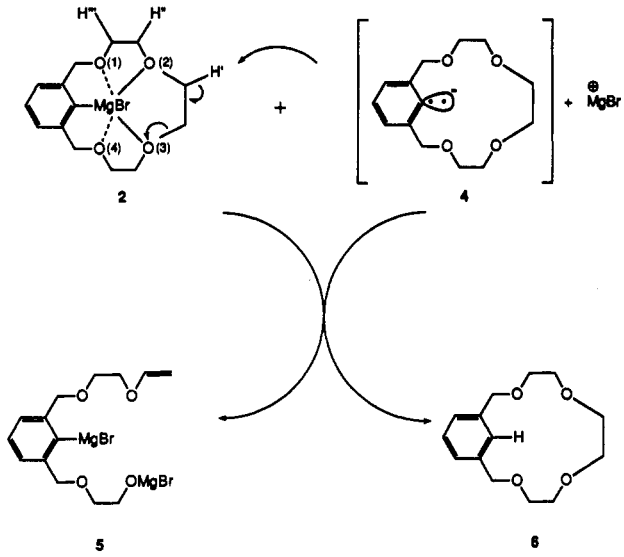
Scheme I



knowledge, an analogous dissociation of a Grignard reagent into RMg^+L_n and Br^- has no yet been observed.

Recently, we reported on the crown ether substituted aryl–Grignard 2-(bromomagnesio)-1,3-xylyl-15-crown-4 (**2**) and its 18-crown-5 analogue (**3**) and the crystal structure of **2** (Chart I).[5] These compounds are of interest because of the strong intramolecular coordination of the magnesium by the crown ether oxygens. In **2**, the magnesium atom at the xylyl 2-position is surrounded by four oxygen atoms, which compel its hexacoordination.

During the formation of **2** and **3** from the corresponding aryl bromides and magnesium, a remarkably selective ether cleavage reaction of the crown ether ring occurred. This reaction was attributed to the activation of specific crown ether ethylene groups by coordination of the adjacent oxygen atoms by the magnesium. During the Grignard formation process, a reactive intermediate selectively abstracts a proton from a previously formed Grignard molecule. In the case of **2**, the selectivity of the cleavage reaction was related to its crystal structure. This Grignard crystallizes solvent-free from a THF solution with two normal [O(2) and O(3)] and two weak [O(1) and O(4)] coordinative bonds to the magnesium (Scheme I). The hydrogen atoms H′ of the ethylene group surrounded by O(2) and O(3) are more strongly activated than hydrogens H″ and H‴ due to polarization of the C–H bonds and by the strongly coordinated oxygens O(2) and O(3); the latter are, for the same reason, better leaving groups in the E2 reaction. Thus, during the Grignard formation reaction, intermediate **4** was postulated to abstract proton H′ from **2**, to yield the apparent "hydrolysis" product **6**. Grignard **2** is converted to **5**, the crown ether ring being cleaved at C–O(3) under formation of an alcoholate and a vinyl ether function. The cleavage reaction of **3** takes an analogous, though slightly more complicated course.

In this paper, the results of the study of "open" analogues of crown ether compounds **2** and **3** are reported. The compounds investigated have long chainlike polyether substituents instead of a crown ether ring. They were synthesized with a substituent $CH_2(OCH_2CH_2)_nOCH_3$ at one [n = 0–4 (**14–18**)] or both [n = 1, 2 (**19** and **20**)] ortho positions (see Scheme II). The choice of the compounds was made on the basis of the following considerations.

The polyether substituents in the new compounds are much more flexible than the crown ether ring in **2** and **3**. Therefore, the intramolecular coordination is no longer imposed by the conformational rigidity of the molecule but the substituent will (within certain limits dictated by bond length) be able to find its enthalpically most favorable conformation. The variation of the number of oxygen atoms (1–6) makes the whole range from "simple" solvent coordinated to completely intramolecularly coordinated arylmagnesium species accessible. In principle, the magnesium might even be coordinated by (extra) solvent molecules, resulting in new coordination geometries with high coordination numbers. This should be revealed by crystal structure determinations of the complexes, while in solution, their structure could be studied by ^1H NMR spectroscopy.

During the formation reaction of the Grignard compounds from the polyether-substituted bromides with magnesium, ether cleavage reactions can be expected, similar to those found for **2** and **3**, and relations were expected between the (crystal) structures of the Grignards and the selectivity of the ether cleavage reaction.

The smallest members of the series (**14**, **15**, and **19**) had already been investigated thermochemically in our laboratory.[6,7] The results, which have to be regarded as preliminary due to the great experimental problems met in their determination, suggest an appreciable thermodynamic stabilization by intramolecular coordination. Compared with unsubstituted phenylmagnesium bromide, these aryl–Grignard compounds show a lower heat effect (less exothermic) upon hydrolysis with acetic acid in THF solution [PhMgBr, −200.0 (4.2) kJ mol^{-1}; **14**, −183.1 (1.7) kJ mol^{-1}; **15**, −168.7 (1.6) kJ mol^{-1}; **19**, −147.7 (2.3) kJ mol^{-1}]. This stabilization must originate from better coordination of these Grignards in solution, as compared with the "normal" tetrahedral complexes of PhMgBr with THF or diethyl ether.[8,9]

Results and Discussion

The synthesis of the aryl bromides **7–13** from *o*-bromobenzyl bromide or 1-bromo-2,6-bis(bromomethyl)-benzene and the appropriate oligoethylene glycol monomethyl ether in toluene with potassium hydride at room temperature was straightforward (see Scheme II).[6,10]

Grignard Reagents from Aryl Bromides. Ether Cleavage Reactions. The reaction of **7** with magnesium is known to proceed normally.[6] Bromides **8–12** were reacted with magnesium in [D_8]THF on a NMR scale to investigate the occurrence of ether cleavage during the Grignard formation. The resulting solutions were analyzed by ^1H NMR spectroscopy. The Grignard reactions of **8** and **12** proceeded in a normal way: one ethylenoxy unit in the sidearm is obviously not sufficient to induce ether cleavage. Hydrolyzed material (the "aryl–H" compound carrying hydrogen at position 2; <10%) was the only observable side product; on the extremely small scale of the reactions, even minimal traces of water will give a significant amount of hydrolysis. Cleavage reactions analogous to those occurring with the 1,3-xylyl crown ether bromides were found for the bromides **9–11**, but the cleavage process was nonselective, contrary to that found for Grignards **2** and **3**. Next to signals from the desired Grignard and the aryl–H compound, a large number of unidentified signals

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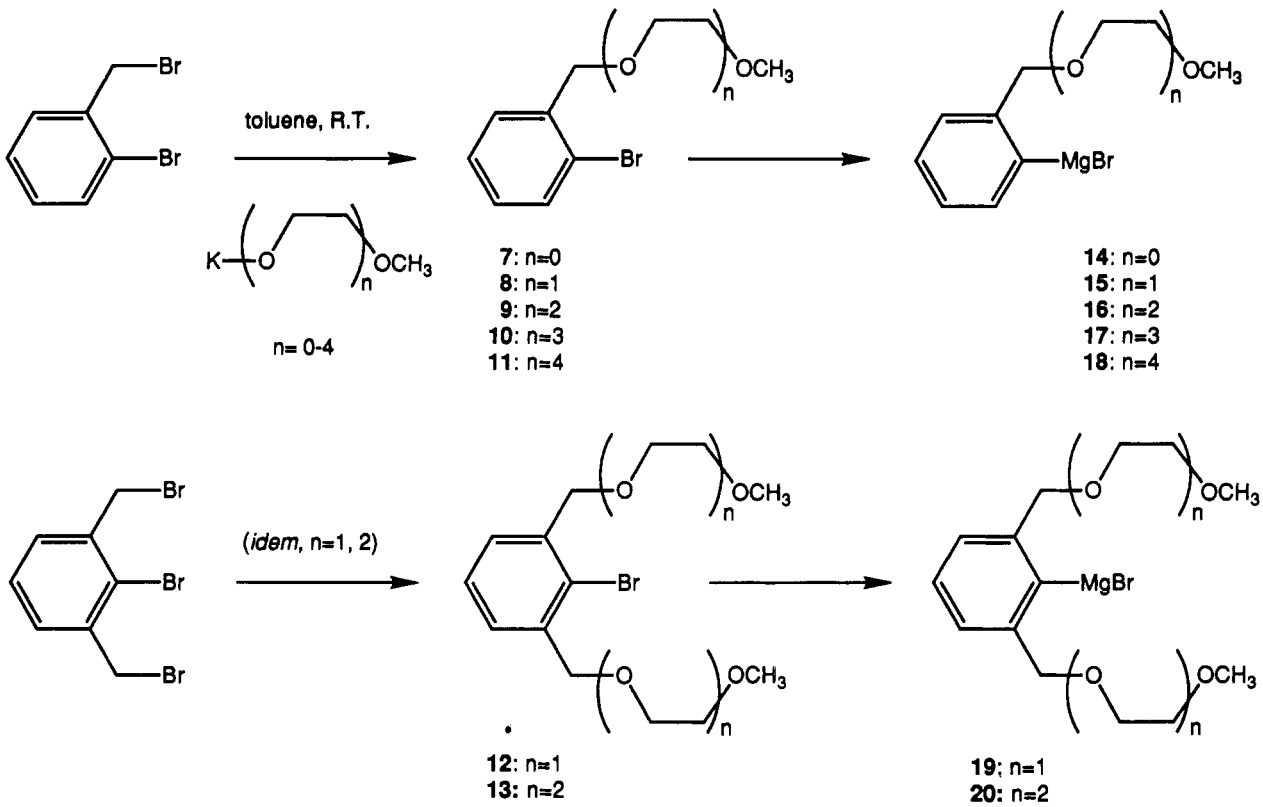
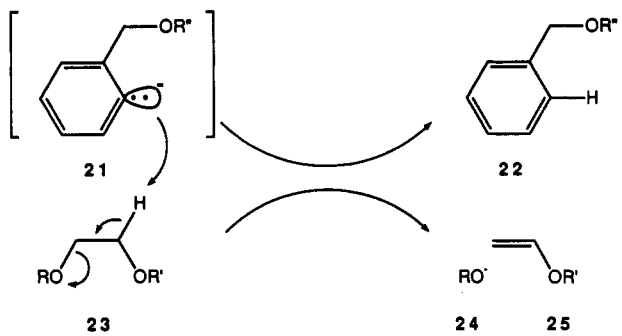
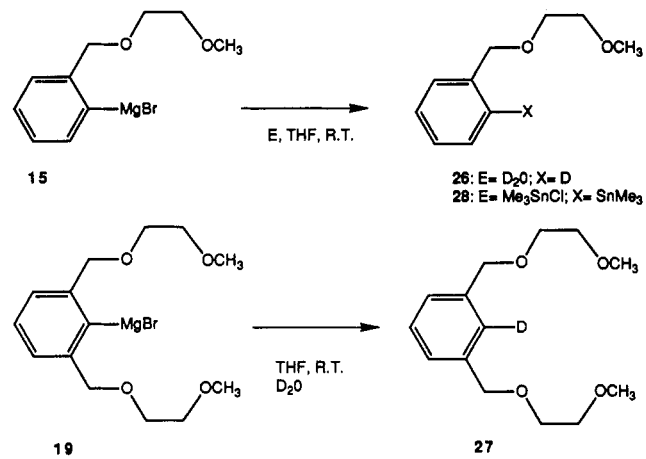
Scheme II



Scheme III



Scheme IV



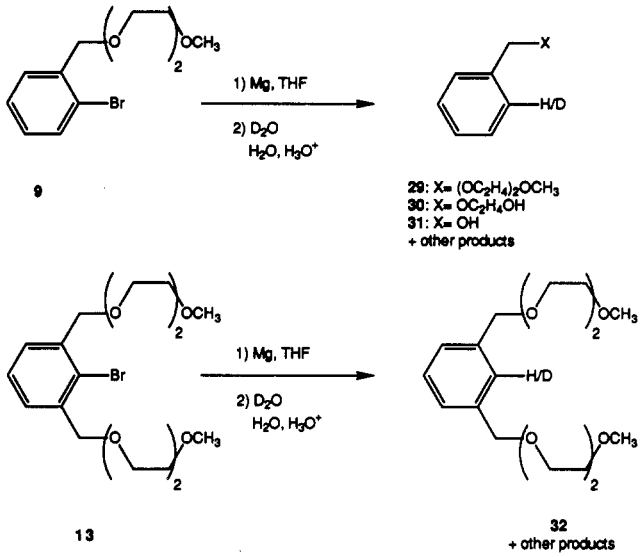
were discernible in the ^1H NMR spectrum, including the characteristic vinyl ether patterns, indicating the presence of many ether cleavage products. Based on the ether cleavage mechanism as suggested for **2** and **3**,[5] the formation of the open polyether-substituted Grignards must be accompanied by the formation of **22**, **24**, and **25** in a 1:1:1 stoichiometry (Scheme III). The reactive carbanion intermediate **21** from the Grignard formation reaction will be converted into hydrolysis product **22**, while the attacked Grignard molecule (**23**) decomposes into an alcoholate fragment (**24**) and a vinyl ether fragment (**25**). In a nonselective reaction, the number of possible fragments will increase rapidly with increasing substituent length, each additional ethylenoxy unit introducing two additional cleavage sites. This large number of homologous cleavage products give a ^1H NMR spectrum with many overlapping multiplets in the aryl–H and $(C_2H_4O)_n$ regions and several singlets for different benzylic CH_2 and OMe groups.

Ether Cleavage Reactions Analyzed by Quench Reactions. Larger scale Grignard reactions of aryl bromides **8**, **9**, **12**, and **13** gave complete conversion of the bromide, as shown by titration after H_2O quench.

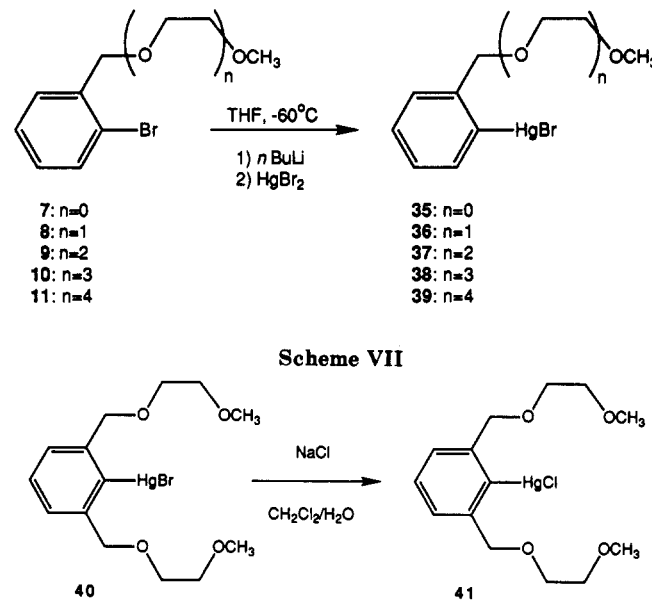
The purity of the Grignards **15** and **19** was confirmed by quench reactions with D_2O (Scheme IV). Spectroscopic analysis (^1H NMR spectroscopy and GCMS) revealed the formation of the pure aryl–D products **26** and **27**. In the case of **15**, the Grignard solution was also quenched with a 2-fold excess of Me_3SnCl, yielding **28** (characterized spectroscopically) quantitatively.

The crude Grignard solutions originating from bromides **9** and **13** were quenched with D_2O to confirm the occurrence of ether cleavage reactions (Scheme V). The organic products were isolated by extraction after addition of dilute hydrochloric acid and were characterized by GCMS. Under these workup conditions, vinyl ether groups are hydrolyzed to alcohols and acetaldehyde. In the case of **9**, three partially deuterated products were found: diethylene glycol benzyl methyl ether (**29**, 77%; about 50% D), ethylene glycol benzyl ether (**30**, 12%; about 90% D), and benzyl alcohol (**31**, 11%; about 60% D). The complementary fragments formed together with **29–31** were not found, as the volatile (acetaldehyde) or highly water soluble (ethylene glycol monomethyl ether) reaction products were lost during the workup procedure. Bromide

Scheme V



Scheme VI



Scheme VII

13 gave mainly 1,3-bis(2,5,8-trioxanonyl)benzene (**32**, 67%), which was partially deuterated (28% D), together with some unidentified side products.

The reaction of **9**, the smallest member of the polyether-substituted aryl bromides showing ether cleavage in the Grignard reagent formation reaction, was studied in more details; the volatile products were distilled from the crude reaction mixture into the NMR tube and were analyzed by ^1H NMR spectroscopy. Methyl vinyl ether (**33**, 32%) and ethylene glycol methyl vinyl ether (**34**, 68%) were found, the percentages in parentheses giving their *relative* yields. These products are important, being complementary to the ether cleavage fragments **30** and **31**. According to ^1H NMR analysis, the nonvolatile residue still contained some vinyl ether compounds, indicating the presence of compounds in which the hydroxy groups of **30** and **31** are (partially) replaced by a vinyloxy group; in the workup procedure, these are cleaved by hydrolysis with the acid.

The experimental data indicate that all *o*-CH_2-$(OC_2H_4)_nOCH_3$-substituted aryl bromides with $n \geq 2$ undergo ether cleavage reactions during the Grignard formation. The nonselectivity of this cleavage must be related to the increased flexibilities of the coordinating substituents, as compared to those of **2** and **3**. In solution, probably all oxygen atoms of the polyether substituent can take part in the coordination process when the Grignard molecule optimizes its conformation. In addition, exchange is possible in solution between several enthalpically comparable conformations. As a consequence, *all* polyether methylene groups can be activated for anionic attack during the formation of the Grignard reagents and selectivity[5] will not be found in the ether cleavage process. Therefore, the crystal structures of **14–20** cannot give an unequivocal answer at which position in the chain ether cleavage will be preferred; this was possible in the case of crown ether Grignard **2**. While in solution several other conformations may occur; only one favorable conformation will be found in the crystalline state.

Grignard Reagents via Arylmercury Compounds. To obtain the pure Grignard compounds **16–18**, an alternative synthetic route was developed. The aryl bromides were reacted with *n*-butyllithium at low temperature, giving the corresponding aryllithium compounds, which were subsequently converted into the Grignard reagents either by direct reaction with magnesium bromide at low temperature or in a two-step procedure involving the arylmercury bromides as intermediates. The second option was advantageous because the air-stable arylmercury compounds can be purified and the subsequent exchange reaction with magnesium proceeds without side products (Scheme VI). [*o*-(Methoxymethyl)phenyl]mercury bromide (**35**), was available in our laboratory.[7] Arylmercury compounds **36** and **40** were synthesized to compare the results of their magnesium-exchange reactions with the direct Grignard formation by reaction of **8** and **12** with magnesium, which occurs without ether cleavage (vide supra), by ^1H NMR spectroscopy.

The two-step conversion of the aryl bromides into the arylmercury bromides (Scheme VI) gave best results when performed rapidly and at low temperature[11-13] (contrary to literature procedures[14-16]); this procedure avoids ether cleavage or coupling of the aryllithium compound with *n*-butyl bromide. The arylmercury bromides were thoroughly purified in order to obtain pure, crystallizable Grignard reagents in the subsequent step. ^{199}Hg NMR spectroscopy was used to check the purity; only trace impurities were detectable.

Due to the complexing power of glymes toward mercury(II) halides,[17-20] $HgBr_2$ adducts were sometimes isolated; e.g. in the synthesis of **39** the 1:1 adduct **39a** with $HgBr_2$ was obtained in 28% yield. The use of NaCl of NH_4Cl solutions must be avoided in the workup, as the bromine in **35–40** was easily exchanged with chlorine. This was independently demonstrated for **40**: shaking its CH_2Cl_2 solution with aqueous NaCl for 24 h at room temperature gave complete conversion to **41** (Scheme VII). The relatively high rate of this exchange probably stems from the

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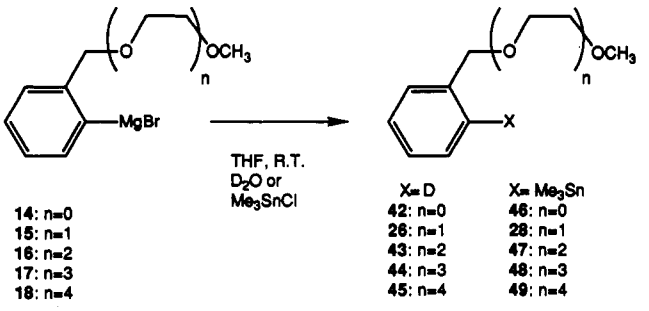
(20) Weber, G. *Acta Crystallogr. B* **1980**, *36*, 2779.

Scheme VIII



stabilization of intermediate $ArHg^+$ species by the polyether side chains.

The exchange reactions of **36–40** with (triply sublimed) magnesium metal were performed initially on a NMR scale in [D_8]THF and gave pure Grignard solutions, containing less than 5% hydrolysis product aryl–H according to ^1H NMR spectroscopy (250 and 400 MHz). Although the ^1H NMR spectra of the aryl bromides show a broadened singlet at a nearly constant δ value for the polyether substituent, the almost *chemically* equivalent methylene protons of the polyether substituents of the Grignards **15–18** showed a wide variation in chemical shifts ($\Delta\delta$ = 0.7 ppm), which must result from specific interactions of the ether oxygens with the magnesium. In each ^1H NMR spectrum, a number of A_2B_2 systems equal to the number of C_2H_4O units was identified. A complete analysis of the spectra was not possible. For **17** and **18**, NOESY spectra were measured (^1H NMR, [D_8]THF) at room temperature and at −50 °C. For **18** these spectra could not be analyzed due to the very weak cross peaks; in the case of **17**, the spectra were analyzed in part (see Experimental Section). As the NOESY spectra were measured in [D_8]THF, rapid coordination equilibria between intramolecular and solvent coordination will occur and hinders complete interpretation of the spectra; C_6D_6 or [D_8]toluene could not be used due to the insolubility of the solvent free Grignards in these solvents.

For the crystallization experiments, Grignards **14–18** were also synthesized on a larger scale (5 mmol). Reaction times of at least 2 weeks were necessary for a complete conversion of the starting material, as deduced from titrations ("total base" and Mg^{2+}, see Experimental Section). The purity of the Grignards was confirmed by D_2O and Me_3SnCl quench reactions (Scheme VIII); the deuterated products **42–45** and the tin derivatives **46–49** were characterized spectroscopically, indicating a purity >98%. The quench products **26** and **28** of **15**, which had been prepared both via a normal Grignard reaction and via the arylmercury bromide route, were identical.

Crystal Structures of Grignard Reagents 14–17. It could initially not be excluded that a shift in the Schlenk equilibrium might occur during the crystallization of the Grignard compounds, giving the symmetrical diorganomagnesium compound and magnesium bromide; the latter tends to crystallize from THF solutions as the bis- or tetrakis(tetrahydrofuranate) complex.[21,22] Crystals of the Grignards containing extra magnesium bromide might give additional problems in the structure elucidation. Therefore, each crystal sample of the Grignards **14–18** was checked by titration to verify its 1:1 ratio of total base versus Mg^{2+}. It was gratifying to find that the compounds

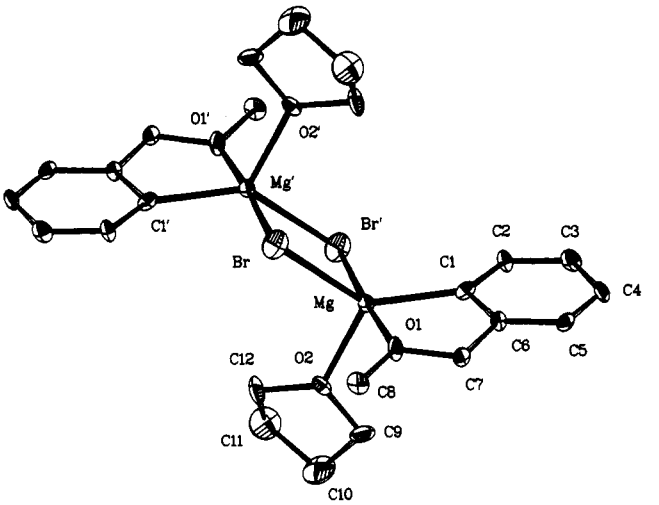


Figure 1. ORTEP drawing (50% probability level) of dimeric 1-bromomagnesio-2-methoxymethylbenzene (**14**). Hydrogen atoms are omitted for clarity.

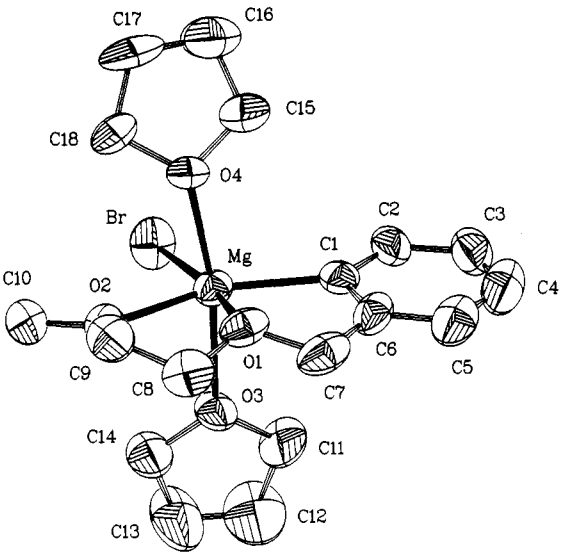


Figure 2. ORTEP drawing (40% probability level) of 1-bromomagnesio-2-(2,5-dioxahexyl)benzene (**15**). Hydrogen atoms are omitted for clarity.

crystallized as pure Grignards, probably because the Grignards are particularly favored by intramolecular coordination; the intramolecular coordination in the diarylmagnesium compounds may be less efficient because of steric crowding and coordination saturation.

The crystallizations were performed by using stock solutions of **14–18** in THF (0.1 M). For compounds **15–17**, the technique of dilution with an apolar solvent (*n*-hexane), concentration to the saturation point at room temperature, and subsequent cooling proved to give best results. Under these conditions, the crystallization takes place from a solution that contains a large excess of free THF. The formation of crystalline monomeric complexes is favored, because in THF solutions organomagnesium compounds tend to be monomeric.[23] Crystals of **14** were grown from a concentrated residue left after evaporation of almost all of the solvent; lack of sufficient THF is probably the reason for its dimeric, halogen-bridged structure (vide infra).

The crystal structures of **14–17** are shown in Figures 1–4. The complexes are depicted from similar viewpoints, in

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Table I. Crystal Data and Details of the Structure Determination of 14–17

	14	15	16	17
		(a) Crystal Data		
formula	$C_{24}H_{34}O_4Mg_2Br_2$	$C_{18}H_{29}O_4MgBr$	$C_{16}H_{25}O_4MgBr$	$C_{14}H_{21}O_4MgBr$
mol wt	549.95	413.63	385.58	357.53
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/a$ (no. 14)	$Pbca$ (No. 61)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
$a/b/c$, Å	7.804 (4)/18.224 (8)/ 9.152 (5)	14.975 (2)/13.490 (2)/ 20.712 (3)	8.555 (1)/13.221 (2)/ 17.292 (2)	11.817 (2)/7.861 (2)/ 18.111 (3)
β, deg	94.51 (2)		101.86 (1)	105.23 (2)
V, Å^3	1298 (1)	4184 (1)	1914.0 (4)	1623.3 (6)
Z	2	8	4	4
D_{calc}, g cm^{-3}	1.523	1.313	1.338	1.463
$F(000)$	608	1728	800	736
μ, cm^{-1}	31.7	19.9	21.7	25.5
cryst size, mm	0.75 × 0.37 × 0.12	0.80 × 0.40 × 0.15	0.76 × 0.25 × 0.23	0.55 × 0.30 × 0.08
		(b) Data Collection		
T, K	100	295	295	295
$\theta_{min}/\theta_{max}$, deg	1.12/26.4	0.98/27.5	1.20/27.5	1.16/27.5
Mo Kα radiation (Zr-filtered), Å	0.71073	0.71073	0.71073	0.71073
$\Delta\omega$, deg	0.65 + 0.35 tan θ	0.55 + 0.35 tan θ	0.65 + 0.35 tan θ	0.65 + 0.35 tan θ
hor and vert aperture, mm	3.0, 3.0	3.0, 6.0	3.0, 6.0	3.0, 6.0
X-ray exposure time, h	34	105	69	58
linear decay, %		9.3	3.0	19
ref reflns	−2,0,3, −2,3,0, 0,3,−2	−5,1,4, −5,1,−4	2,0,−2, 130, 041	3,0,−5, −2,−2,−4
data set	h −9 to 0; k −22 to 21; l −10 to 11	h −19 to 9; k 0 to 17; l −26 to 0	h 0 to 11; k 0 to 17; l −22 to 21	h 0 to 15; k −10 to 0; l −23 to 22
tot no. of data	5149	8256	5298	4198
tot no. of unique data	2390 (R_{int} = 6.9%)	4794 (R_{int} = 3.4%)	4382	3730
no. of obsd data	1635 [$I > 2.5\sigma(I)$]	1495 [$I > 2.5\sigma(I)$]	1785 [$I > 2.5\sigma(I)$]	1409 [$I > 2.5\sigma(I)$]
DIFABS corrn range		0.66–1.39		0.36–1.96
		(c) Refinement		
no. of reflns	1635	1494	1785	1409
no. of refined params	146	218	200	182
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.00544F^2]$	$w = 1.0/[\sigma^2(F) + 0.000486F^2]$	$w = 1.0/[\sigma^2(F) + 0.00176F^2]$	$w = 1.0/\sigma^2(F)$
final R, R_w, S	0.073, 0.111, 3.10	0.067, 0.067, 2.88	0.055, 0.069, 1.62	0.065, 0.056, 1.79
isotrop therm param H atoms, Å^2	0.034 (2)	0.152 (7)	0.121 (7)	0.084 (6)
$(\Delta/\sigma)_{av}$ in final cycle	0.072	0.057	0.026	0.0006
min and max residual dens, e/Å^3	−1.65, 1.14 (near Br)	−0.43, 0.66	−0.41, 0.41	−0.92, 0.88

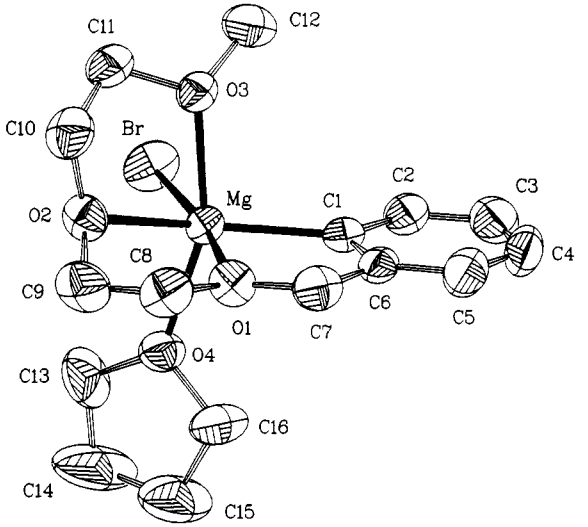

Figure 3. ORTEP drawing (40% probability level) of 1-bromomagnesio-2-(2,5,8-trioxanonyl)benzene (**16**). Hydrogen atoms are omitted for clarity.

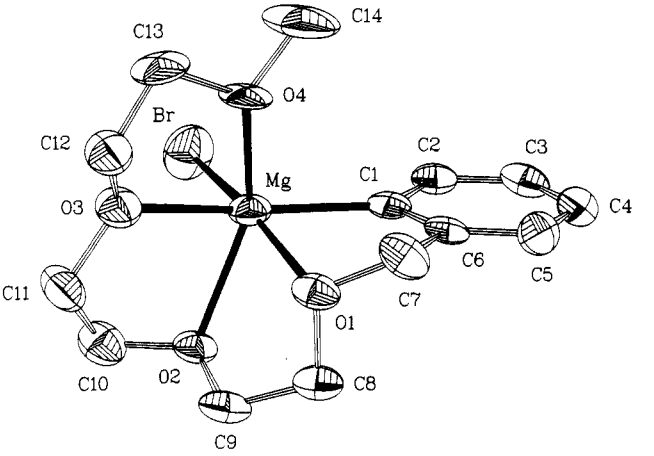

Figure 4. ORTEP drawing (40% probability level) of 1-bromomagnesio-2-(tetraoxadodecyl)benzene (**17**). Hydrogen atoms are omitted for clarity.

order to facilitate their comparison. Hydrogen atoms are omitted for clarity. The experimental data for the X-ray structure determinations are given in Tables I–V. Grignard **14**, the smallest member of the series, was the only one that crystallized in a dimeric form; this may be related to its crystallization conditions (vide supra). Its pentacoordinated state, however, is already different from that of "normal" organomagnesium compounds, where tetrahedral complexes are the rule. The structure can be regarded as intermediate between the unsubstituted parent compound phenylmagnesium bromide (PhMgBr·$[THF]_2$,[8] PhMgBr·$[Et_2O]_2$[9]) and Grignards **15–17**. From **15** on, monomeric structures with a pseudooctahedral coordination of the central magnesium atom were found. Additional THF molecules serve to complete the coordination sphere where necessary: **15** has two molecules of THF and **16** one molecule of THF. The octahedral coordination state is quite unusual for a Grignard compound and must be induced by the intramolecular polyether ligand. The small intraannular angles within the connected five-membered rings (about 75°) formed in the complexation process

Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for 14

atom	x	y	z	U(eq),[a] Å²
Br	0.3956 (2)	0.07600 (6)	0.0914 (1)	0.0297 (3)
Mg	0.4406 (3)	−0.0569 (2)	0.1555 (3)	0.0116 (7)
O(1)	0.3218 (7)	−0.0502 (3)	0.3538 (7)	0.019 (1)
O(2)	0.2235 (7)	−0.1017 (3)	0.0544 (6)	0.015 (1)
C(1)	0.616 (1)	−0.1173 (4)	0.2955 (9)	0.013 (1)
C(2)	0.768 (1)	−0.1531 (5)	0.2742 (9)	0.014 (1)
C(3)	0.864 (1)	−0.1950 (5)	0.3770 (9)	0.018 (1)
C(4)	0.803 (1)	−0.2025 (5)	0.5167 (9)	0.020 (1)
C(5)	0.651 (1)	−0.1675 (5)	0.5470 (9)	0.014 (1)
C(6)	0.559 (1)	−0.1254 (4)	0.4394 (8)	0.011 (1)
C(7)	0.391 (1)	−0.0914 (5)	0.4766 (9)	0.015 (1)
C(8)	0.159 (1)	−0.0177 (5)	0.3816 (9)	0.020 (1)
C(9)	0.203 (1)	−0.1807 (5)	0.075 (1)	0.024 (1)
C(10)	0.098 (1)	−0.2068 (6)	−0.063 (1)	0.042 (1)
C(11)	0.130 (1)	−0.1486 (6)	−0.175 (1)	0.043 (1)
C(12)	0.140 (1)	−0.0792 (5)	−0.0864 (9)	0.025 (1)

[a] U(eq) = one-third of the trace of the orthogonalized U matrix.

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for 15

atom	x	y	z	U(eq),[a] Å²
Br	0.20105 (8)	0.22578 (8)	0.18529 (5)	0.0836 (4)
Mg	0.1523 (2)	0.3570 (2)	0.1025 (1)	0.056 (1)
O(1)	0.1078 (4)	0.4823 (5)	0.0470 (3)	0.072 (3)
O(2)	0.1416 (4)	0.4812 (5)	0.1704 (3)	0.064 (2)
O(3)	0.2895 (4)	0.4114 (5)	0.0925 (3)	0.070 (2)
O(4)	0.0121 (4)	0.3296 (5)	0.1269 (3)	0.074 (2)
C(1)	0.1500 (6)	0.2969 (8)	0.0056 (5)	0.061 (3)
C(2)	0.1621 (6)	0.2021 (9)	−0.0190 (5)	0.076 (4)
C(3)	0.1651 (7)	0.181 (1)	−0.0849 (6)	0.097 (4)
C(4)	0.1527 (7)	0.256 (1)	−0.1285 (6)	0.112 (4)
C(5)	0.1411 (7)	0.353 (1)	−0.1080 (5)	0.094 (4)
C(6)	0.1388 (6)	0.3705 (9)	−0.0404 (5)	0.073 (4)
C(7)	0.1294 (7)	0.4778 (9)	−0.0204 (5)	0.086 (4)
C(8)	0.1178 (8)	0.5769 (8)	0.0759 (5)	0.086 (4)
C(9)	0.0949 (7)	0.5663 (8)	0.1456 (5)	0.086 (4)
C(10)	0.1538 (7)	0.4845 (7)	0.2384 (5)	0.086 (4)
C(11)	0.3464 (7)	0.374 (1)	0.0439 (6)	0.107 (4)
C(12)	0.4350 (9)	0.402 (1)	0.0646 (7)	0.190 (5)
C(13)	0.4350 (9)	0.439 (1)	0.1249 (7)	0.162 (5)
C(14)	0.3426 (7)	0.4477 (9)	0.1443 (6)	0.097 (4)
C(15)	−0.0329 (8)	0.2546 (9)	0.0918 (6)	0.108 (4)
C(16)	−0.0960 (9)	0.204 (1)	0.1304 (7)	0.146 (5)
C(17)	−0.095 (1)	0.260 (2)	0.1880 (8)	0.242 (6)
C(18)	−0.0294 (7)	0.334 (1)	0.1892 (5)	0.106 (4)

[a] U(eq) = one-third of the trace of the orthogonalized U matrix.

accord better with higher coordination states; the octahedral geometry (ideal angles 90°) is much more favorable than a tetrahedral coordination (angles of 100–110°) or a trigonal-pyramidal geometry (angles 90°/120°). In addition, intramolecular coordination diminishes the steric crowding that normally is a consequence of higher coordination numbers; moreover, it may be favored entropically over bonding of independent solvent molecules, in which case the number of particles decreases.

From **15** on, the THF molecules that serve to complete the pseudooctahedral coordination sphere are substituted one by one by intramolecular ether oxygen atoms, until, with **17**, an intramolecularly saturated, solvent-free complex is obtained. The difficulties met in the crystallization of **18** also fit this picture. If **17** presents the coordinative saturation point of the series, the surplus of one oxygen atom in **18** may prevent the formation of a *single* complex with a well-defined structure, as several pseudooctahedral complexes can be imagined and probably are present in solution. In any case, suitable crystals of **18** were not obtained.

In **15–17**, the Mg–Br bonds are slightly elongated [**15**, 2.570 (3) Å; **16**, 2.590 (2) Å; **17**, 2.569 (3) Å], as compared

Table IV. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for 16

atom	x	y	z	U(eq),[a] Å²
Br	0.0034 (1)	0.19881 (6)	0.23147 (6)	0.0750 (3)
Mg	−0.0593 (3)	0.3656 (2)	0.2975 (1)	0.0449 (8)
O(1)	−0.1108 (6)	0.5139 (3)	0.3365 (3)	0.060 (2)
O(2)	0.0912 (6)	0.4748 (3)	0.2477 (3)	0.063 (2)
O(3)	0.1794 (5)	0.3578 (3)	0.3715 (3)	0.059 (2)
O(4)	−0.2390 (6)	0.3977 (4)	0.1957 (3)	0.066 (2)
C(1)	−0.1889 (8)	0.3355 (5)	0.3890 (4)	0.052 (3)
C(2)	−0.2395 (8)	0.2456 (7)	0.4181 (5)	0.068 (3)
C(3)	−0.315 (1)	0.2405 (9)	0.4817 (6)	0.087 (4)
C(4)	−0.348 (1)	0.328 (1)	0.5177 (5)	0.091 (4)
C(5)	−0.3021 (9)	0.4180 (8)	0.4913 (5)	0.080 (4)
C(6)	−0.2250 (8)	0.4231 (6)	0.4292 (4)	0.056 (3)
C(7)	−0.1740 (9)	0.5253 (6)	0.4043 (5)	0.068 (3)
C(8)	−0.038 (1)	0.6024 (6)	0.3109 (6)	0.076 (3)
C(9)	0.017 (1)	0.5730 (6)	0.2387 (6)	0.086 (4)
C(10)	0.2549 (9)	0.4798 (6)	0.2908 (5)	0.078 (4)
C(11)	0.2981 (9)	0.3795 (6)	0.3270 (5)	0.072 (3)
C(12)	0.220 (1)	0.2739 (7)	0.4234 (5)	0.087 (4)
C(13)	−0.242 (1)	0.3788 (8)	0.1130 (5)	0.097 (4)
C(14)	−0.397 (2)	0.401 (1)	0.0719 (7)	0.186 (8)
C(15)	−0.498 (1)	0.428 (1)	0.1247 (7)	0.136 (6)
C(16)	−0.3982 (9)	0.4221 (7)	0.2037 (5)	0.084 (4)

[a] U(eq) = one-third of the trace of the orthogonalized U matrix.

Table V. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for 17

atom	x	y	z	U(eq),[a] Å²
Br	0.21445 (9)	0.2582 (1)	0.00907 (6)	0.0778 (4)
Mg	0.3148 (2)	−0.0038 (3)	0.0829 (2)	0.047 (1)
O(1)	0.4420 (5)	−0.2239 (6)	0.1368 (3)	0.052 (2)
O(2)	0.3719 (5)	−0.1211 (7)	−0.0114 (3)	0.048 (2)
O(3)	0.1739 (5)	−0.1728 (7)	0.0224 (4)	0.061 (3)
O(4)	0.2117 (5)	−0.0700 (8)	0.1604 (4)	0.067 (3)
C(1)	0.4559 (7)	0.123 (1)	0.1633 (5)	0.042 (3)
C(2)	0.4859 (7)	0.2978 (9)	0.1733 (5)	0.045 (3)
C(3)	0.5806 (8)	0.357 (1)	0.2283 (5)	0.055 (4)
C(4)	0.6515 (7)	0.249 (1)	0.2782 (5)	0.063 (3)
C(5)	0.6284 (8)	0.075 (1)	0.2725 (5)	0.056 (3)
C(6)	0.5312 (7)	0.019 (1)	0.2172 (5)	0.041 (3)
C(7)	0.5030 (8)	−0.170 (1)	0.2127 (5)	0.063 (4)
C(8)	0.5211 (7)	−0.238 (1)	0.0889 (5)	0.056 (3)
C(9)	0.4471 (7)	−0.268 (1)	0.0107 (5)	0.063 (4)
C(10)	0.2738 (8)	−0.153 (1)	−0.0734 (5)	0.063 (4)
C(11)	0.1838 (8)	−0.255 (1)	−0.0480 (5)	0.068 (4)
C(12)	0.1143 (8)	−0.264 (1)	0.0674 (5)	0.071 (4)
C(13)	0.0989 (8)	−0.143 (1)	0.1279 (6)	0.077 (5)
C(14)	0.209 (1)	0.043 (1)	0.2204 (7)	0.130 (7)

[a] U(eq) = one-third of the trace of the orthogonalized U matrix.

with those of normal tetrahedral organomagnesium complexes (2.48–2.51 Å). This bond elongation may be accompanied by a slight additional polarization of these bonds. Dissociation of the Mg–Br bond resulting in a "saltlike" structure with coordination-stabilized arylMg$^+$ cations and Br$^-$ counterions was not observed. A detailed description of the structures of Grignards **14–17** is given below.

Complex 14. The smallest member of the series, **14**, crystallizes as a centrosymmetric dimer (Figure 1). Relevant bond distances and angles are summarized in Table VI. The structure has some remarkable features, as compared with structures of some "simple" dimeric Grignard reagents like $[EtMgBr\cdot Et_3N]_2$[24] or $[EtMgBr\cdot i\text{-}Pr_2O]_2$.[25]

(1) The association in the dimer is relatively weak, resulting in short [2.509 (3) Å] and long [2.705 (3) Å] Mg–Br distances, allowing in the dimeric structure the distinction

(24) Toney, J.; Stucky, G. D. *J. Chem. Soc., Chem. Commun.* **1967**, 1169.
(25) Spek, A. L.; Voorbergen, P.; Schat, G.; Blomberg, C.; Bickelhaupt, F. *J. Organomet. Chem.* **1974**, *77*, 147.

Table VI. Bond Distances (Å) and Bond Angles (deg) for 14[a]

Br–Mg	2.509 (3)	O(2)–C(9)	1.46 (1)	C(5)–C(6)	1.40 (1)
Br–Mg′	2.705 (3)	O(2)–C(12)	1.46 (1)	C(6)–C(7)	1.52 (1)
Mg–O(1)	2.105 (7)	C(1)–C(2)	1.38 (1)	C(9)–C(10)	1.52 (1)
Mg–O(2)	2.037 (6)	C(1)–C(6)	1.43 (1)	C(10)–C(11)	1.51 (1)
Mg–C(1)	2.110 (8)	C(2)–C(3)	1.38 (1)	C(11)–C(12)	1.50 (1)
O(1)–C(7)	1.42 (1)	C(3)–C(4)	1.41 (1)		
O(1)–C(8)	1.44 (1)	C(4)–C(5)	1.39 (1)		

Mg–Br–Mg′	90.24 (9)	C(9)–O(2)–C(12)	110.2 (6)
Br–Mg–Br′	89.76 (9)	Mg–C(1)–C(2)	133.2 (6)
Br–Mg–O(1)	94.8 (2)	Mg–C(1)–C(6)	112.4 (5)
Br–Mg–O(2)	100.7 (2)	C(2)–C(1)–C(6)	114.3 (7)
Br–Mg–C(1)	135.9 (2)	C(1)–C(2)–C(3)	125.9 (8)
Br′–Mg–O(1)	175.3 (2)	C(2)–C(3)–C(4)	118.0 (7)
Br′–Mg–O(2)	90.0 (2)	C(3)–C(4)–C(5)	119.4 (8)
Br′–Mg–C(1)	96.5 (2)	C(4)–C(5)–C(6)	120.4 (7)
O(1)–Mg–O(2)	90.4 (2)	C(1)–C(6)–C(5)	121.9 (7)
O(1)–Mg–C(1)	79.3 (3)	C(1)–C(6)–C(7)	120.0 (7)
O(2)–Mg–C(1)	122.9 (3)	C(5)–C(6)–C(7)	118.0 (7)
Mg–O(1)–C(7)	119.0 (5)	O(1)–C(7)–C(6)	108.7 (6)
Mg–O(1)–C(8)	129.0 (5)	O(2)–C(9)–C(10)	104.9 (7)
C(7)–O(1)–C(8)	111.2 (6)	C(9)–C(10)–C(11)	103.8 (8)
Mg–O(2)–C(9)	115.6 (5)	C(10)–C(11)–C(12)	103.4 (8)
Mg–O(2)–C(12)	126.0 (5)	O(2)–C(12)–C(11)	103.8 (7)

[a] Prime indicates symmetry operation $1 - x, -y, -z$.

of two weakly associated monomeric units. The central four-membered Mg_2Br_2 ring in **14** is planar (centrosymmetric) and rectangular [Br–Mg–Br′, 89.76 (9)°; Mg–Br–Mg′, 90.24 (9)°]. In the dimeric ethylmagnesium bromide structures, the Mg–Br distances are almost equal (2.57–2.58 Å).

(2) Compared with the dimeric ethylmagnesium bromide structures, the coordination number in **14** is increased to 5. Each magnesium atom has not only two μ-Mg–Br bonds, one Mg–C bond [2.110 (8) Å], and a coordinating THF [Mg–O(2), 2.037 (6) Å] but also interaction with the intramolecular ether group [Mg–O(1), 2.105 (7) Å]. It is remarkable that, in spite of the higher coordination number of magnesium, this latter bond is only slightly elongated. This must be attributed to ring strain involved in the formation of the five-membered chelate ring with an unfavorably small bite angle C(1)–Mg–O(1) of 79.3 (3)° at magnesium. The length of the Mg–C bond is normal and not affected by the unusual coordination geometry.

(3) The coordination of the magnesium atoms can be described as distorted trigonal-bipyramidal (TBP). This coordination geometry is rare in organomagnesium compounds; just one TBP example, $MeMgBr·[THF]_3$, is known so far.[2] The weakly bonded ligands O(1) and Br′ occupy the axial positions [Br′–Mg–O(1), 175.3 (2)°]. The largest deviations from the ideal TBP geometry are found in the equatorial plane [Br–Mg–C(1), 135.9 (2)°; O(2)–Mg–C(1), 122.9 (3)°; Br–Mg–O(2), 100.7 (2)°]. The remaining angles are close to 90° [Br′–Mg–O(2), 90.0 (2)°; Br′–Mg–C(1), 96.5 (2)°; Br–Mg–O(1), 94.8 (2)°; O(1)–Mg–O(2), 90.4 (2)°; O(1)–Mg–C(1), 79.3 (3)°].

Complex 15. This complex as well as the remaining members of the series, **16** and **17**, are monomeric, with a remarkable pseudooctahedral coordination geometry; only one crystal structure of a Grignard compound with this geometry is known (**1**, Chart I).[3] In **15–17**, the central magnesium atom is coordinated by four ether oxygen atoms; the aryl and bromine ligands are always cis. In **15**, two extra THF molecules serve to complete the coordination sphere (Figure 2 and Table VII). The angles necessarily deviate from those of an ideal octahedral geometry. Inside the five-membered rings, the angles are forced to be smaller by geometric constraints [O(1)–Mg–C(1), 78.1 (3)°; O(1)–Mg–O(2), 73.7 (3)°], whereas in the same plane, the Br–Mg–C(1) angle is enlarged [111.4 (3)°], which seems to be a general tendency in Grignard reagents.

Table VII. Bond Distances (Å) and Bond Angles (deg) for 15

Br–Mg	2.570 (3)	O(3)–C(11)	1.41 (1)	C(6)–C(7)	1.51 (2)
Mg–O(1)	2.150 (7)	O(3)–C(14)	1.42 (1)	C(8)–C(9)	1.49 (1)
Mg–O(2)	2.193 (7)	O(4)–C(15)	1.42 (1)	C(11)–C(12)	1.45 (2)
Mg–O(3)	2.192 (7)	O(4)–C(18)	1.43 (1)	C(12)–C(13)	1.35 (2)
Mg–O(4)	2.191 (7)	C(1)–C(2)	1.39 (2)	C(13)–C(14)	1.45 (2)
Mg–C(1)	2.16 (1)	C(1)–C(6)	1.39 (1)	C(15)–C(16)	1.41 (2)
O(1)–C(7)	1.43 (1)	C(2)–C(3)	1.39 (2)	C(16)–C(17)	1.41 (2)
O(1)–C(8)	1.42 (1)	C(3)–C(4)	1.37 (2)	C(17)–C(18)	1.41 (2)
O(2)–C(9)	1.44 (1)	C(4)–C(5)	1.39 (2)		
O(2)–C(10)	1.42 (1)	C(5)–C(6)	1.42 (1)		

Br–Mg–O(1)	170.4 (2)	Mg–O(4)–C(15)	117.3 (6)
Br–Mg–O(2)	96.8 (2)	Mg–O(4)–C(18)	128.0 (6)
Br–Mg–O(3)	91.6 (2)	C(15)–O(4)–C(18)	106.7 (8)
Br–Mg–O(4)	90.1 (2)	Mg–C(1)–C(2)	133.1 (8)
Br–Mg–C(1)	111.4 (3)	Mg–C(1)–C(6)	111.8 (8)
O(1)–Mg–O(2)	73.7 (3)	C(2)–C(1)–C(6)	115 (1)
O(1)–Mg–O(3)	88.7 (3)	C(1)–C(2)–C(3)	123 (1)
O(1)–Mg–O(4)	87.6 (3)	C(2)–C(3)–C(4)	120 (1)
O(1)–Mg–C(1)	78.1 (3)	C(3)–C(4)–C(5)	121 (1)
O(2)–Mg–O(3)	82.7 (3)	C(4)–C(5)–C(6)	117 (1)
O(2)–Mg–O(4)	84.9 (3)	C(1)–C(6)–C(5)	124 (1)
O(2)–Mg–C(1)	151.6 (4)	C(1)–C(6)–C(7)	120 (9)
O(3)–Mg–O(4)	167.6 (3)	C(5)–C(6)–C(7)	115 (1)
O(3)–Mg–C(1)	93.0 (3)	O(1)–C(7)–C(6)	109.2 (9)
O(4)–Mg–C(1)	97.8 (3)	O(1)–C(8)–C(9)	107.4 (8)
Mg–O(1)–C(7)	114.7 (6)	O(2)–C(9)–C(8)	108.1 (8)
Mg–O(1)–C(8)	116.7 (6)	O(3)–C(11)–C(12)	104 (1)
C(7)–O(1)–C(8)	115.2 (8)	C(11)–C(12)–C(13)	112 (1)
Mg–O(2)–C(9)	114.6 (5)	C(12)–C(13)–C(14)	107 (1)
Mg–O(2)–C(10)	130.5 (6)	O(3)–C(14)–C(13)	107 (1)
C(9)–O(2)–C(10)	113.0 (7)	O(4)–C(15)–C(16)	112 (1)
Mg–O(3)–C(11)	120.8 (6)	C(15)–C(16)–C(17)	103 (1)
Mg–O(3)–C(14)	124.6 (6)	C(16)–C(17)–C(18)	113 (1)
C(11)–O(3)–C(14)	108.9 (8)	O(4)–C(18)–C(17)	105 (1)

The central magnesium atom and its intramolecular "ligands" C(1), Br, O(1), and O(2) are nearly coplanar [within 0.10 (2) Å]; the two bonds to THF, opposite to each other [O(3)–Mg–O(4), 167.6 (3)°] are nearly perpendicular to this plane. A second plane is formed by the atoms O(2), O(3), O(4), and Mg [within 0.00 (2) Å], perpendicular [89.4 (3)°] to the first one. In this plane, the angles O(2)–Mg–O(3) and O(2)–Mg–O(4) are 82.7 (3) and 84.9 (3)°, respectively. Compared with "normal" Grignard reagents, all bond lengths are somewhat elongated as a result of the higher coordination number [intramolecular bonds: Mg–C(1) 2.16 (1) Å; Br–Mg, 2.570 (3) Å; Mg–O(1), 2.150 (7) Å; Mg–O(2), 2.193 (7) Å]; the THF molecules [Mg–O(3), 2.192 (7) Å; Mg–O(4), 2.191 (7) Å] are bound relatively weakly. When the crystalline complex is dissolved in an apolar solvent ([D_8]toluene), dissociation occurs and a solvent-free complex precipitates; free THF can be observed by ^1H NMR spectroscopy. Possibly, an insoluble dimeric complex analogous to **14** is formed.

Complex 16. The structure of this complex (Figure 3 and Table VIII) has much in common with that of **15**. In **16**, one of the THF molecules present in **15** is replaced by an intramolecular ether oxygen of the (longer) chain of the polyether substituent. Because of the conformational restrictions imposed by the presence of three five-membered chelate rings, the polyether chain coordinates its three adjacent oxygen atoms in a facial arrangement; angles inside the five-membered rings are small [O(1)–Mg–C(1), 76.6 (2)°; O(1)–Mg–O(2), 72.6 (2)°; O(2)–Mg–O(3), 73.2 (2)°]; as a consequence, other angles are relatively large [Br–Mg–C(1), 110.6 (2)°; O(4)–Mg–C(1), 104.6 (3)°]. Bond lengths are comparable to those in **15** [Mg–C(1), 2.147 (7) Å; Br–Mg, 2.590 (2) Å; Mg–O(1), 2.148 (5) Å; Mg–O(2), 2.222 (5) Å; Mg–O(3), 2.178 (5) Å], the only remarkable difference being the short bond to the THF molecule [Mg–O(4), 2.129 (6) Å]. The complex is unstable in apolar solvent: attempts to dissolve crystals in [D_8]toluene resulted in pulverization to a white powder which, even upon

Table VIII. Bond Distances (Å) and Bond Angles (deg) for 16

Br-Mg	2.590 (2)	O(2)-C(10)	1.45 (1)	C(4)-C(5)	1.36 (2)
Mg-O(1)	2.148 (5)	O(3)-C(11)	1.424 (9)	C(5)-C(6)	1.37 (1)
Mg-O(2)	2.222 (5)	O(3)-C(12)	1.42 (1)	C(6)-C(7)	1.51 (1)
Mg-O(3)	2.178 (5)	O(4)-C(13)	1.45 (1)	C(8)-C(9)	1.47 (1)
Mg-O(4)	2.129 (6)	O(4)-C(16)	1.43 (1)	C(10)-C(11)	1.48 (1)
Mg-C(1)	2.147 (7)	C(1)-C(2)	1.39 (1)	C(13)-C(14)	1.40 (2)
O(1)-C(7)	1.40 (1)	C(1)-C(6)	1.42 (1)	C(14)-C(15)	1.42 (2)
O(1)-C(8)	1.437 (9)	C(2)-C(3)	1.38 (1)	C(15)-C(16)	1.46 (1)
O(2)-C(9)	1.441 (9)	C(3)-C(4)	1.38 (2)		

Br-Mg-O(1)	171.9 (2)	C(11)-O(3)-C(12)	112.9 (6)
Br-Mg-O(2)	101.1 (2)	Mg-O(4)-C(13)	130.2 (5)
Br-Mg-O(3)	87.9 (1)	Mg-O(4)-C(16)	120.3 (5)
Br-Mg-O(4)	89.1 (2)	C(13)-O(4)-C(16)	108.1 (6)
Br-Mg-C(1)	110.6 (2)	Mg-C(1)-C(2)	132.1 (5)
O(1)-Mg-O(2)	72.6 (2)	Mg-C(1)-C(6)	114.0 (5)
O(1)-Mg-O(3)	95.0 (2)	C(2)-C(1)-C(6)	113.9 (7)
O(1)-Mg-O(4)	85.3 (2)	C(1)-C(2)-C(3)	123.9 (9)
O(1)-Mg-C(1)	76.6 (2)	C(2)-C(3)-C(4)	120 (1)
O(2)-Mg-O(3)	73.2 (2)	C(3)-C(4)-C(5)	118.9 (8)
O(2)-Mg-O(4)	85.8 (2)	C(4)-C(5)-C(6)	121.7 (9)
O(2)-Mg-C(1)	146.5 (2)	C(1)-C(6)-C(5)	122.1 (8)
O(3)-Mg-O(4)	157.8 (2)	C(1)-C(6)-C(7)	119.1 (6)
O(3)-Mg-C(1)	97.0 (2)	C(5)-C(6)-C(7)	118.7 (8)
O(4)-Mg-C(1)	104.6 (3)	O(1)-C(7)-C(6)	109.1 (6)
Mg-O(1)-C(7)	120.1 (4)	O(1)-C(8)-C(9)	106.2 (6)
Mg-O(1)-C(8)	121.1 (5)	O(2)-C(9)-C(8)	110.9 (7)
C(7)-O(1)-C(8)	115.9 (6)	O(2)-C(10)-C(11)	107.9 (6)
Mg-O(2)-C(9)	110.4 (5)	O(3)-C(11)-C(10)	105.4 (6)
Mg-O(2)-C(10)	114.0 (4)	O(4)-C(13)-C(14)	106.6 (9)
C(9)-O(2)-C(10)	112.0 (6)	C(13)-C(14)-C(15)	111 (1)
Mg-O(3)-C(11)	111.1 (4)	C(14)-C(15)-C(16)	106 (1)
Mg-O(3)-C(12)	119.0 (4)	O(4)-C(16)-C(15)	107.9 (7)

heating to 80 °C, was completely insoluble.

Complex 17. This compound crystallizes as a monomeric, pseudooctahedral complex analogous to **15** and **16**. Its polyether substituent contains four ether oxygen atoms and extra THF molecules are not needed to complete the coordination sphere: the crystalline complex is solvent-free (Figure 4 and Table IX). The formation of four condensed five-membered chelate rings in the coordination process imposes large constraints on the conformation of the polyether chain. Therefore, many bond angles deviate from the ideal octahedral angle of 90°. As expected, the smallest angles are found inside the five-membered rings [O(1)-Mg-C(1), 76.2 (3)°; O(1)-Mg-O(2), 73.6 (2)°; O(2)-Mg-O(3), 72.8 (2)°; O(3)-Mg-O(4), 72.1 (3)°]. Other bond angles vary between 88° [O(1)-Mg-O(4), 87.7 (2)°] and 112° [O(2)-Mg-C(1), 112.3 (3)°]. The Br-Mg-C angle is relatively small [98.6 (2)°] but still larger than 90° as a reflection of the "natural" tendency of Grignard reagents to have angles in the range 110-125°. Some bond lengths in **17** [Mg-C(1), 2.151 (9) Å, Mg-Br, 2.569 (3) Å] are comparable to those in **15** and **16**. The Mg-O distances in **17** show an obvious trend as they decrease toward the end of the polyether substituent [Mg-O(1), 2.331 (6) Å; Mg-O(2), 2.197 (6) Å; Mg-O(3), 2.186 (7) Å; Mg-O(4), 2.151 (7) Å]. This can be attributed to the accumulation of conformational strain originating from the formation of the many chelate rings, which prevents oxygen atoms close to the aryl group from optimizing their positions with respect to the magnesium atom. Complex **17** is also remarkable in that it deviates from **15** and **16** in the arrangement of the polyether oxygens O(1) and O(2). In **15** and **16**, O(1) and O(2) lie in one plane with the carbon-magnesium bond, whereas in **17**, the plane O(1)-Mg-O(2) is perpendicular to C(1)-Mg-O(1). It is not obvious why **16** and **17** behave so differently in this regard. Once it has crystallized, the solubility of **17** in THF is very low, just like that of crown ether Grignard **2**.[5] This might be related to the solvent-free nature of the complex, possibly in combination with a highly polar nature of the Mg-Br bond. Efficient coordination of the central magnesium atom by the polyether oxygen atoms may change the character of a Grignard and make it more saltlike, even though this is not clearly expressed in the Mg-Br distance.

Table IX. Bond Distances (Å) and Bond Angles (deg) for 17

Br-Mg	2.569 (3)	O(2)-C(9)	1.45 (1)	C(2)-C(3)	1.37 (1)
Mg-O(1)	2.331 (6)	O(2)-C(10)	1.41 (1)	C(3)-C(4)	1.36 (1)
Mg-O(2)	2.197 (6)	O(3)-C(11)	1.46 (1)	C(4)-C(5)	1.39 (1)
Mg-O(3)	2.186 (7)	O(3)-C(12)	1.41 (1)	C(5)-C(6)	1.38 (1)
Mg-O(4)	2.151 (7)	O(4)-C(13)	1.43 (1)	C(6)-C(7)	1.52 (1)
Mg-C(1)	2.151 (9)	O(4)-C(14)	1.41 (1)	C(8)-C(9)	1.48 (1)
O(1)-C(7)	1.44 (1)	C(1)-C(2)	1.42 (1)	C(10)-C(11)	1.50 (1)
O(1)-C(8)	1.44 (1)	C(1)-C(6)	1.40 (1)	C(12)-C(13)	1.50 (1)

Br-Mg-O(1)	166.3 (2)	Mg-O(3)-C(12)	116.9 (6)
Br-Mg-O(2)	97.2 (2)	C(11)-O(3)-C(12)	116.4 (7)
Br-Mg-O(3)	92.3 (2)	Mg-O(4)-C(13)	117.1 (6)
Br-Mg-O(4)	105.7 (2)	Mg-O(4)-C(14)	119.0 (6)
Br-Mg-C(1)	98.6 (2)	C(13)-O(4)-C(14)	111.1 (8)
O(1)-Mg-O(2)	73.6 (2)	Mg-C(1)-C(2)	131.3 (6)
O(1)-Mg-O(3)	94.7 (2)	Mg-C(1)-C(6)	115.9 (6)
O(1)-Mg-O(4)	87.7 (2)	C(2)-C(1)-C(6)	112.7 (8)
O(1)-Mg-C(1)	76.2 (3)	C(1)-C(2)-C(3)	123.4 (8)
O(2)-Mg-O(3)	72.8 (2)	C(2)-C(3)-C(4)	121.0 (8)
O(2)-Mg-O(4)	138.4 (3)	C(3)-C(4)-C(5)	119.4 (8)
O(2)-Mg-C(1)	112.3 (3)	C(4)-C(5)-C(6)	118.6 (8)
O(3)-Mg-O(4)	72.1 (3)	C(1)-C(6)-C(5)	124.9 (8)
O(3)-Mg-C(1)	167.1 (3)	C(1)-C(6)-C(7)	116.4 (7)
O(4)-Mg-C(1)	98.2 (3)	C(5)-C(6)-C(7)	118.7 (8)
Mg-O(1)-C(7)	106.8 (4)	O(1)-C(7)-C(6)	112.7 (7)
Mg-O(1)-C(8)	104.9 (4)	O(1)-C(8)-C(9)	106.1 (7)
C(7)-O(1)-C(8)	111.0 (7)	O(2)-C(9)-C(8)	107.7 (7)
Mg-O(2)-C(9)	114.3 (5)	O(2)-C(10)-C(11)	110.7 (7)
Mg-O(2)-C(10)	109.8 (5)	O(3)-C(11)-C(10)	104.9 (7)
C(9)-O(2)-C(10)	113.1 (6)	O(3)-C(12)-C(13)	105.8 (8)
Mg-O(3)-C(11)	118.8 (5)	O(4)-C(13)-C(12)	106.1 (8)

The conformations of the polyether ligands in the crystal structures of **14-17** show no regular trend. Their torsion angles, starting with C(aryl)-C(benzyl) (e = eclipsed, g = gauche, and t = trans) are as follows: **14**, e-t; **15**, e-t-t-g-t; **16**, e-t-t-g-g-t-g-t; **17**, e-g-t-g-t-g-g-t-t-g-t. Sequences of t-t-g, characteristic for the complexation of glymes, occur in **15-17**.

Experimental Section

Bromides **8-11** were synthesized by using standard glassware with ground joints under a nitrogen atmosphere. Conversion of the bromides into the analogous arylmercury bromides **36-39** was carried out under argon by using Schlenk techniques. Toluene was dried on molecular sieves (4 Å). THF was predried on NaOH and distilled from $LiAlH_4$. Reactions and crystallizations involving organomagnesium compounds were carried out in fully sealed glassware by using high-vacuum techniques. In the same fashion, extremely dry solvents were prepared by distillation from liquid Na/K alloy after predrying on NaOH. Yields of the organomagnesium compounds were determined by titration with HCl for total base and EDTA for total Mg^{2+} after hydrolysis. The starting materials *n*-butyllithium (Merck), potassium hydride (Janssen, 40% in liquid paraffin), chlorotrimethylstannane (Janssen), *o*-bromotoluene (Merck), 2,6-dimethylaniline (Janssen), ethylene glycol monomethyl ether (Merck), diethylene glycol monomethyl ether (Merck), triethylene glycol monomethyl ether (Fluka), and mercuric bromide (Merck) were commercially available. Column chromatography was performed with Al_2O_3 (Merck, activity II-III). For all organomagnesium reactions, triply sublimed magnesium was used (particle size 0.5-1 cm for 1-10-mmol scale preparations, 1-2 mm for NMR scale reactions). *o*-Bromobenzyl bromide was prepared by direct bromination of *o*-bromotoluene according to literature procedures.[10] 1-Bromo-2,6-bis(bromomethyl)benzene was prepared by conversion of 2,6-dimethylaniline into 1-bromo-2,6-dimethylbenzene via a Sandmeyer reaction, followed by a photochemical bromination.[6] Tetraethylene glycol monomethyl ether was available in our laboratory. The purity of the organic starting materials was checked by gas chromatography (Intersmat GC 120, katharometer detection, 10% OV 101 column, 1.5 m × 4 mm i.d., glass) at appropriate oven temperatures. NMR spectra were measured on a Bruker WH90 (^1H NMR, 90 MHz) or a Bruker WH 250

instrument (^{1}H NMR, 250 MHz; ^{13}C NMR, 62.89 MHz; ^{199}Hg NMR, 44.77 MHz). GCMS 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. In some cases, special techniques were used to characterize nonvolatile compounds by their mass spectrum (Finnigan MAT 90, DCI using NH_3 or isobutane, FAB). Elemental analyses were carried out at the TNO Institute for Applied Chemistry and Elemental Analysis (Zeist, The Netherlands).

1-Bromo-2-(methoxymethyl)benzene (7). Compound **7** was obtained from *o*-bromobenzyl bromide and sodium methoxide;[6,7] its purity was checked with ^{1}H NMR spectroscopy and GCMS. ^{1}H NMR (90 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.50 (s, 3 H, OMe), 4.54 (s, 2 H, aryl CH_2), 7.00–7.67 (m, 4 H, aryl H). MS (70 eV), *m/z* (relative intensity): 200 (M^+, 21), 169 (M^+ – OMe, 39), 121 (M^+ – Br, 100), 91 (26), 89 (25), 77 (32), 63 (21).

Preparation of Bromides 8–11. The reactions were performed in a three-necked flask (1 L) equipped with a dropping funnel (250 mL) and magnetical stirring under nitrogen. By use of a disposable syringe, the KH suspension (75 mmol) was introduced into the reaction vessel. The paraffin was removed by washing three times with toluene (50 mL). The KH was suspended in toluene (250 mL), and the appropriate oligoethylene glycol monomethyl ether (50 mmol) was added as a solution in toluene (125 mL) in 10 min. When the formation of the alcoholate was complete (after about 0.5 h, the hydrogen development ceased), a solution of *o*-bromobenzyl bromide (50 mmol, 12.7 g) in toluene (125 mL) was added within several minutes. The reaction was left stirring overnight; a white suspension indicated the formation of potassium bromide. The excess of KH was quenched by adding a few milliliters of water, and the reaction mixture was transferred into a separatory funnel. More water was added and the organic phase separated. The aqueous phase was further extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$), filtered, and evaporated to dryness. Characterization of the crude product (a yellow to brown oil) by ^{1}H NMR spectroscopy ($CDCl_3$, 90 Mz) indicated in all cases >90% formation of the desired product. Further purification was performed by high-vacuum distillation (**8**, at 68 °C/4.5 × 10^{-5} mbar) or filtration over an Al_2O_3 column (2.5 × 30 cm) using diethyl ether as the eluent (**9–11**). The pure bromides are colorless oils, which did not crystallize.

Preparation of Bromides 12 and 13. These reactions were performed analogously to the preparation of **8–11**, by using 1-bromo-2,6-bis(bromomethyl)benzene (25 mmol) instead of *o*-bromobenzyl bromide. Analysis of the crude product (yellowish oil) by ^{1}H NMR spectroscopy (90 MHz, $CDCl_3$) revealed a >80% purity. Further purification was achieved by column chromatography (Al_2O_3, 2.5 × 40 cm, eluent PE 40–60 °C/Et_2O, 200 mL fractions). Starting with 10% diethyl ether, the polarity of the eluents was increased gradually (10% increments). The fractions containing the pure compound (colorless oil) were identified by ^{1}H NMR (90 MHz, $CDCl_3$) spectroscopy and combined. The pure product (60–80% yield) was characterized by ^{1}H and ^{13}C NMR spectroscopy.

1-Bromo-2-(2,5-dioxahexyl)benzene (8). ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.41 (s, 3 H, OMe), 3.63–3.59 (m, 2 H, OCH_2), 3.73–3.69 (m, 2 H, OCH_2), 4.63 (s, 2 H, aryl CH_2), 7.13 (dd, ^3J = 7.8 and 7.5 Hz, 1 H, aryl H), 7.30 (dd, ^3J = 7.6 and 7.5 Hz, 1 H, aryl H), 7.50 (d, ^3J = 7.6 Hz, 1 H, aryl H), 7.52 (d, ^3J = 7.8 Hz, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$ = 77 ppm): δ 59.03 (qt, ^1J = 140 Hz, ^3J = 3.2 Hz, OMe), 69.97 (t, ^1J = 141 Hz, CH_2), 71.88 (t, ^1J = 141 Hz, CH_2), 72.42 (t, ^1J = 144 Hz, CH_2), 122.55 [bs, aryl C(1)], 127.29 [dd, ^1J = 162 Hz, ^3J = 8 Hz, aryl C(4) or C(5)], 128.75 [dd, ^1J = 166 Hz, ^3J = 9 Hz, aryl C(5) or C(4)], 128.99 [ddt, ^1J = 162 Hz, ^3J = 8 and 4 Hz, aryl C(3)], 132.37 [dd, ^1J = 166 Hz, ^3J = 7 Hz, aryl C(6)].[7] A GCMS analysis confirmed the purity of the product. MS (70 eV), *m/z* (relative intensity): 244 (M^+, 4), 165 (M^+ – Br, 6), 187 (19), 171 (44), 90 (22), 89 (22), 59 (10), 45 (100). Anal. Calcd for $C_{10}H_{13}O_2Br$: C, 49.00; H, 5.35; Br, 32.60. Found: C, 48.84; H, 5.42; Br, 32.63.

1-Bromo-2,6-bis(2,5-dioxahexyl)benzene (12). ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.41 (s, 6 H, OMe), 3.65–3.60 (m, 4 H, CH_2), 3.76–3.69 (m, 4 H, CH_2), 4.65 (s, 4 H, aryl CH_2), 7.31 [t, ^3J = 7.5 Hz, aryl H(4)], 7.43 [d, ^3J = 7.5 Hz, 2 H, aryl H(3,5)]. ^{13}C NMR (62.89 MHz, $CDCl_3$ = 77 ppm): δ 58.95 (qt, ^1J = 141 Hz, ^3J = 3 Hz, OMe), 62.92 (t, ^1J = 141 Hz, CH_2), 71.80 (t, ^1J = 141 Hz, CH_2), 71.80 (t, ^1J = 141 Hz, CH_2), 72.64 (t, ^1J = 144 Hz, CH_2), 122.59 [bs, aryl C(1)], 127.02 [dd, ^1J = 162 Hz, aryl C(4)], 127.81 (ddt, ^1J = 163 Hz, ^3J = 8.2 and 4.1 Hz, aryl C(3,5)], 137.73 [bs, aryl C(2)].[7] A GCMS analysis confirmed the purity of the product. MS (70 eV), *m/z* (relative intensity): 332 (M^+, $C_{14}H_{21}O_4Br$, 0.6), 253 (M^+ – Br, 58), 199 (19), 185 (62), 104 (36), 103 (38), 91 (8), 89 (10), 77 (22), 59 (77), 45 (100). Anal. Calcd for $C_{14}H_{21}O_4Br$: C, 50.46; H, 6.35; Br, 23.98. Found: C, 50.12; H, 6.44; Br, 24.12.

1-Bromo-2-(2,5,8-trioxanonyl)benzene (9). ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.39 (s, 3 H, OMe), 3.60–3.55 (m, 2 H, CH_2), 3.65–3.70 (m, 2 H, CH_2), 4.63 (s, 2 H, aryl CH_2), 7.13 (dd, ^3J = 7 and 8 Hz, 1 H, aryl H), 7.30 (dd, ^3J = 7 and 8 Hz, aryl H), 7.49–7.54 (m, 2 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$ = 77 ppm): δ 59.97 (qt, ^1J = 141 Hz, ^3J = 3 Hz, OMe), 71.11 (t, ^1J = 142 Hz, CH_2), 71.58 (t, ^1J = 141 Hz, CH_2), 72.94 (t, ^1J = 141 Hz, aryl CH_2), 73.39 (t, ^1J = 144 Hz, CH_2), 123.49 [bs, C(1)], 128.96 [ddd, ^1J = 162 Hz, ^3J = 4 and 8 Hz, aryl C(3)], 129.70 [dd, ^1J = 161 Hz, ^3J = 8 Hz, aryl C(4) or C(5)], 129.96 [ddt, ^1J = 163 Hz, ^3J = 4 and 8 Hz, aryl C(3)], 133.34 [dd, ^1J = 166 Hz, ^3J = 7 Hz, aryl C(6)].[7] A GCMS analysis confirmed the purity of the product. MS (70 eV), *m/z* (relative intensity): 209 (M^+ – Br, 22), 187 (17), 171 (100), 133 (57), 103 (43), 90 (25), 89 (27), 59 (100), 45 (43). Anal. Calcd for $C_{12}H_{17}O_3Br$: C, 49.84; H, 5.93; Br, 27.63. Found: C, 50.31; H, 6.06; Br, 26.55.

1-Bromo-2,6-bis(2,5,8-trioxanonyl)benzene (13). ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.39 (s, 6 H, OMe), 3.55–3.59 (m, 4 H, CH_2), 3.65–3.70 (m, 4 H, CH_2), 3.73 (s, 8 H, CH_2), 4.64 (s, 4 H, aryl CH_2), 7.31 [t, ^3J = 8 Hz, 1 H, aryl H(4)], 7.43 [d, ^3J = 8 Hz, 2 H, aryl H(3,5)]. ^{13}C NMR (62.89 MHz, $CDCl_3$ = 77 ppm): δ 60.01 (qt, ^1J = 141 Hz, ^3J = 3 Hz, OMe), 71.16 (t, ^1J = 141 Hz, CH_2), 71.60 (t, ^1J = 141 Hz, 2 CH_2), 72.97 (t, ^1J = 141 Hz, aryl CH_2), 73.71 (t, ^1J = 144 Hz, CH_2), 123.61 [bs, aryl C(1)], 128.08 [d, ^1J = 162 Hz, aryl C(4)], 128.85 [ddt, ^1J = 163 Hz, ^3J = 4 and 8 Hz, aryl C(3)].[7] A GCMS analysis confirmed the purity of the product. Anal. Calcd for $C_{18}H_{29}O_6Br$: C, 51.31; H, 6.94; Br, 18.97. Found: C, 50.75; H, 6.94; Br, 19.06.

1-Bromo-2-(2,5,8,11-tetraoxadodecyl)benzene (10). ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.38 (s, 3 H, OMe), 3.53–3.58 [m, $^1/_2$ A_2B_2, 2 H, CH_2(10)], 3.63–3.71 [m, 6 H, CH_2(6,7,9)], 3.72 [s, 4 H, CH_2(3,4)], 4.63 (s, 2 H, aryl CH_2), 7.11–7.17 (m, 1 H, aryl H), 7.27–7.34 (m, 1 H, aryl H), 7.40–7.54 (m, 2 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$ = 77 ppm): δ 58.62 (q, ^1J = 141 Hz, 1 C, OMe), 69.81 (t, ^1J = 141 Hz, 1 C, CH_2), 70.21 (t, ^1J = 139 Hz, 1 C, CH_2), 70.26 (t, ^1J = 139 Hz, 1 C, CH_2), 70.31 (t, ^1J = 139 Hz, 1 C, CH_2), 70.35 (t, ^1J = 139 Hz, 1 C, CH_2), 71.60 (t, ^1J = 140 Hz, 1 C, CH_2), 72.05 (t, ^1J = 142 Hz, 1 C, aryl CH_2), 122.13 [s, 1 C, aryl C(1)], 126.98 (d, ^1J = 163 Hz, 1 C, aryl C), 128.43 (d, ^1J = 162 Hz, 1 C, aryl C), 128.63 (d, ^1J = 162 Hz, 1 C, aryl C), 132.02 [d, ^1J = 165 Hz, 1 C, aryl C(6)], 137.34 [s, 1 C, aryl C(2)]. MS (70 eV), *m/z* (relative intensity): 253 (M^+ – Br, 10), 186 (7), 171 (77), 147 (39), 133 (6), 103 (15), 90 (25), 59 (100), 45 (29). MS (DCI, NH_3), *m/z* (relative intensity): 350 (M·NH_4^+, $C_{14}H_{25}NO_4Br$, 100), 333 (M·H, 6), 272 (M^+ – Br·NH_4, 6). Anal. Calcd for $C_{14}H_{21}O_4Br$: C, 50.46; H, 6.35. Found: C, 51.66; H, 6.50.

1-Bromo-2-(2,5,8,11,14-pentaoxapentadecyl)benzene (11). ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.37 (s, 3 H, OMe), 3.52–3.56 [m, $^1/_2$ A_2B_2, 2 H, CH_2(13)], 3.62–3.71 [m, 10 H, CH_2(6,7,9,10,12)], 3.72 [s, 4 H, CH_2(3,4)], 4.63 (s, 2 H, aryl CH_2), 7.11–7.17 (m, 1 H, aryl H), 7.27–7.34 (m, 1 H, aryl H), 7.48–7.54 (m, 2 H, aryl H). ^{13}C NMR (62.89 MHz, reference $CDCl_3$ = 77 ppm): δ 58.42 (q, ^1J = 142 Hz, 1 C, OMe), 69.67 (t, ^1J = 140 Hz, 1 C, CH_2), 69.97 (t, ^1J = 141 Hz, 1 C, CH_2), 70.10 (t, ^1J = 141 Hz, 3 C, CH_2), 70.18 (t, ^1J = 141 Hz, 1 C, CH_2), 71.42 (t, ^1J = 139 Hz, 1 C, CH_2), 71.86 (t, ^1J = 142 Hz, 1 C, aryl CH_2), 121.93 [s, 1 C, aryl, C(1)], 126.83 (d, ^1J = 163 Hz, 1 C, aryl C), 128.28 (d, ^1J = 162 Hz, 1 C, aryl C), 128.48 (d, ^1J = 165 Hz, 1 C, aryl C), 131.83 [d, ^1J = 165 Hz, 1 C, aryl C(6)], 137.19 [s, 1 C, aryl C(2)]. MS (70 eV), *m/z* (relative intensity): 297 (M^+ – Br, 3), 186 (3), 171 (45), 147 (3), 133 (6), 103 (33), 89 (20), 59 (100), 45 (46). MS (DCI, NH_3), *m/z* (relative intensity): 394 (M·NH_4^+, $C_{16}H_{29}NO_5Br$, 100). Anal. Calcd for $C_{16}H_{25}O_5Br$: C, 50.94; H, 6.68. Found: C, 47.02; H, 6.03. According to the elemental analysis, **13** possibly contained salts, lowering its C and H contents by about 8–10%. The impurities were not visible by the spectroscopic methods used.

Reactions of 8–12 with Magnesium in [D_8]THF. The bromides 8–12 were reacted on a ^1H NMR scale (about 5 mg) with magnesium (excess, 50 mg) in [D_8]THF (500 μL) by stirring for 3–5 days. After 1 additional day for the magnesium dust to settle, the reaction mixture was decanted into an NMR tube (5 mm), which was sealed off from the glass assembly. The products were analyzed by ^1H NMR spectroscopy (250 MHz, reference (THF)D_7H = 1.75 ppm) to determine the yields of the expected Grignard product. In the case of 8 and 12, Grignard formation was quite good (about 90%), with hydrolyzed material (aryl H) as the only side product. This can be regarded as normal in these small scale experiments (<100 μmol), due to residual moisture (or OH groups) in the starting compound and the glassware. The bromides 9–11 showed much lower yields of Grignard product (around 50% in all cases); besides the signals of the hydrolysis products, a variety of signals of other byproducts was visible in the ^1H NMR spectrum. In contrast to the selective ether cleavage reactions of Grignards 2 and 3, side product formation appeared to be nonselective. Characteristic multiplets indicated the formation of several ether cleavage products containing a vinyl group (three dd clusters at δ 3.9, 4.2, and 6.5 ppm). The conversion of 9 was investigated more thoroughly. After the reaction in [D_8]THF, the solvent together with all volatile products were distilled into the NMR tube. The ^1H NMR spectrum showed the presence of methyl vinyl ether (**33**) and ethylene glycol methyl vinyl ether (**34**) in relative yields of 32% and 68%, respectively, ^1H NMR (250 MHz, [D_8]THF, reference (THF)D_7H = 1.75 ppm): **33** δ 3.51 (s, 3 H, OMe), 3.92–3.93 and 3.95–3.96 [m, 1 H, CH_2(trans)], 4.15 [dd, ^3J(trans) = 14 Hz, ^2J(*gem*) = 2 Hz, 1 H, CH_2(cis)], 6.52 [dd, ^3J(trans) = 14 Hz, ^3J(cis) = 7 Hz, 1 H, CH]; **34** δ 3.33 (s, 3 H, OMe), 3.55–3.58 and 3.78–3.84 (m, A_2B_2, 4 H, C_2H_4), 3.93 [dd, ^3J(cis) = 7 Hz, ^2J(*gem*) = 2 Hz, 1 H, CH_2(trans)], 4.16 [dd, ^3J(trans) = 14 Hz, ^2J(*gem*) = 2 Hz, 1 H, CH_2(cis)], 6.48 [dd, ^3J(trans) = 14 Hz, ^3J(cis) = 7 Hz, 1 H, CH].

Reactions of 8, 9, 12, and 13 with Magnesium in THF. The (larger scale) reactions were carried out in THF (100 mL) by stirring the bromide (5 mmol) with magnesium (1.0 g = 42 mmol) for 1 week.[7] The reaction of 13 only took place at 50 °C, the other bromides reacted at room temperature. After settling of the magnesium dust, the crude Grignard solutions were decanted into a second vessel. Titration of samples of these solutions (total base and Mg^{2+}) revealed the complete conversion of the starting bromide.

D_2O Quench of the Crude Grignards 15 and 19. An aliquot of a Grignard solution (1 mmol) was quenched with an excess of D_2O (0.5 mL), dilute HCl (1 N) and CH_2Cl_2 were added, and the organic material was isolated by extraction with CH_2Cl_2. The organic phase was dried ($MgSO_4$), filtered, and evaporated to dryness. The residue (colorless oil) was characterized by ^1H NMR (250 MHz, $CDCl_3$) and GCMS, revealing the formation of deuterated hydrolysis products **26** and **27**, respectively (about 95% purity).

[2-D]-1-(2,5-Dioxahexyl)benzene (26). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.41 (s, 3 H, OMe), 3.56–3.66 (m, 4 H, C_2H_4), 4.59 (s, 2 H, aryl CH_2), 7.27–7.37 (m, 4 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.96 (q, ^1J = 141 Hz, 1 C, OMe), 69.26 (t, ^1J = 141 Hz, 1 C, CH_2), 71.97 (t, ^3J = 140 Hz, 1 C, CH_2), 73.20 (t, ^1J = 141 Hz, 1 C, aryl CH_2), 127.35 [t, low intensity, ^1J(C–D) = 24 Hz, 1 C, aryl C(1)], 127.48 (d, ^1J = 159 Hz, 1 C, aryl C), 127.64 (d, ^1J = 158 Hz, 1 C, aryl C), 128.15 (d, ^1J = 160 Hz, 1 C, aryl C), 128.25 (d, ^1J = 159 Hz, 1 C, aryl C), 138.07 [s, 1 C, aryl C(2)]. MS (70 eV), m/z (relative intensity): 167 (M^+, 12), 134 (3), 108 (39), 106 (12), 92 (100), 78 (10), 66 (24), 59 (9), 45 (100).

[2-D]-1,3-Bis(2,5-Dioxahexyl)benzene (27). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.40 (s, 6 H, OMe), 3.58–3.63 (m, 8 H, C_2H_4), 4.58 (s, 4 H, aryl CH_2), 7.27–7.31 (m, 3 H, aryl H). The mass spectrum (GCMS) was in accordance with the published data.[5]

Me_3SnCl Quench of Crude Grignard 15. The remaining Grignard solution (vide supra) was divided into four 1-mmol samples. Several quench reactions with Me_3SnCl (solid, about 2 mmol) were performed by mixing the reagents in a fully sealed glass apparatus, giving a clear solution. After opening of the reaction ampule, the solution was transferred to a sepratory funnel and the excess of Me_3SnCl was hydrolyzed with 5 mL of NaOH (1 N). After addition of aqueous NH_4Cl, the organic material was isolated by extraction with CH_2Cl_2. The organic phase was dried ($MgSO_4$), filtered, and evaporated to dryness. The residue (colorless oil) was characterized by ^1H NMR (90 MHz, $CDCl_3$) spectroscopy to check the formation of **28**. A reaction time of <10 min between **5** and Me_3SnCl appeared to be essential to isolate pure **28**, as longer reaction times resulted in the formation of byproducts from methyl–chlorine exchange between **28** and the excess of Me_3SnCl. These byproducts were identified by GCMS as (aryl)$SnMe_2X$ (X = Cl or Br, both with the same retention time on the GC column) but not isolated and further characterized.

1-(2,5-Dioxahexyl)-2-(trimethylstannyl)benzene (28). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 0.31 [s, ^2J(Sn–H) = 55 and 53 Hz, 9 H, Sn–Me], 3.40 (s, 3 H, OMe), 3.57–3.60 and 3.62–3.66 (m, A_2B_2, 4 H, C_2H_4), 4.57 [s, ^4J(Sn–H) = 4 Hz, 2 H, aryl CH_2], 7.29–7.37 [m, 3 H, aryl H(4–6)], 7.51–7.54 [m, dm, ^3J = 7 Hz, 1 H, aryl H(3)]. ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ −8.14 [q, ^1J = 128 Hz, ^1J(Sn–C) = 354 and 339 Hz, 1 C, SnMe], 58.89 (q, ^1J = 142 Hz, 1 C, OMe), 69.37 (t, ^1J = 141 Hz, 1 C, CH_2), 71.79 (t, ^1J = 141 Hz, 1 C, CH_2), 75.26 [t, ^1J = 142 Hz, ^4J(Sn–C) = 22 Hz, 1 C, aryl CH_2], 127.04 [d, ^1J = 160 Hz, ^3J(Sn–C) = 47 Hz, 1 C, aryl C(6)], 127.95 [d, ^1J = 155 Hz, ^3J(Sn–C) = 38 Hz, 1 C, aryl C(4)], 128.22 [d, ^1J = 160 Hz, ^4J(Sn – C) = 10 Hz, 1 C, aryl C(5)], 136.30 [d, 1J = 159 Hz, ^3J(Sn–C) = 35 Hz, 1 C, aryl C(3)], 141.52 [s 1 C, aryl C(2)], 144.41 [s, 1 C, aryl C(1)]. MS (70 eV), m/z (relative intensity): 315 (M^+ – Me, $C_{12}H_{19}O_2Sn$, 100), 255 (8), 241 ($C_9H_{13}Sn$, 66), 225 (14), 209 (17), 151 (16), 135 (15), 120 (16), 91 (13), 59 (27), 45 (33).

D_2O Quench of Crude Grignard 16. The Grignard solution was quenched with an excess of D_2O (1 mL). After concentration in vacuo, aqueous HCl (1 N) and CH_2Cl_2 were added and the organic material was isolated by extraction with CH_2Cl_2. The organic phase was dried ($MgSO_4$), filtered, and evaporated to dryness. Characterization of the residue by GCMS revealed the formation of three products, **31** (11%; 60% D), **30** (12%; 90% D), and the expected hydrolysis product **29** (77%; 50% D). The deuterium content of these products at the aryl 2-position was estimated from M^+ in the case of **31** and from the benzyl cation signals (C_7H_7, 91; C_7H_6D, 92) in the case of **30** and **29**. MS of **31** (70 eV), m/z (relative intensity): 109 (M^+, C_7H_7OD, 81), 92 (C_7H_6D, 13), 80 (100), 78 (50), 66 (6), 63 (6), 51 (33). **30** MS (70 eV), m/z (relative intensity): 153 (M^+, $C_9H_{11}O_2D$, 15), 108 (25), 92 (100), 80 (7), 78 (6), 66 (14). In the ^1H NMR spectrum (250 MHz, $CDCl_3$), the presence of side products (>20%) was derived from their aryl CH_2 singlets and the integral ratios of these signals.

D_2O Quench of Crude Grignard 20. The Grignard solution was quenched with D_2O (1 ML), worked up, and analyzed by GCMS and ^1H NMR (250 MHz, $CDCl_3$) spectroscopy, in a procedure analogous to that described for **16**. GCMS analysis of the residue (colorless oil) revealed the formation of mainly three products; one of them was identified as the expected hydrolysis **32** (67%, 28% D). The mass spectrum of this compound is in accordance with the published data.[5] The other components are probably ether cleavage products and were not further identified. In the ^1H NMR spectrum (250 MHz, $CDCl_3$), the presence of side products (>25%) was detected from the different aryl CH_2 singlets and the integral ratios between the signals. The presence of only one OMe signal indicates that the polyether fragments, originating from the cleavage reaction, were lost during the workup procedure.

[2-D]-1,3-Bis(2,5,8-trioxanonyl)benzene (32). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.39 (s, 6 H, OMe), 3.55–3.59 (m, $^1/_2$ A_2B_2, 4 H, C_2H_4), 3.63–3.71 (m, 12 H, C_2H_4), 7.27–7.32 (m, about 3.3 H, aryl H).

Synthesis of Arylmercury Bromides 36–40. These compounds were synthesized by lithiation of the appropriate aryl bromides 8–12 with 1 equiv of *n*-BuLi, followed by reaction with 1 equiv of $HgBr_2$. The reactions were performed under argon in a magnetically stirred three-necked flask (250 mL) equipped with a septum. The bromide (oil, 10 mmol) was degassed by evacuation in the reaction vessel and dissolved in dry THF (100 mL) under an argon atmosphere. The resulting colorless solution was cooled to −60 °C, and by means of a syringe, *n*-BuLi (10 mmol, 6.25 mL of *n*-hexane solution) was added within several minutes; the formation of the aryllithium compound was deduced from brown coloring. Immediately afterwards, a solution of $HgBr_2$ (10 mmol,

3.60 g, in 10 mL of THF) was added analogously. During the second reaction, a viscous white precipitate (probably lithium salts) was formed. While being stirred, the reaction mixture was allowed to warm to room temperature, during which the precipitate dissolved almost completely. The reaction mixture was evaporated to dryness, and the residue was transferred to a separatory funnel with CH_2Cl_2 and water. The organic products were collected by extraction with CH_2Cl_2; to improve the separation of the phases, some NH_4Br was added. Chlorides like NaCl or NH_4Cl could not be used, due to conversion of the arylmercury bromide to the corresponding chloride by halogen-exchange reactions. The organic phase was dried ($MgSO_4$), filtered, and evaporated to dryness yielding a slightly colored oil. After weighing, the crude product was characterized by ^1H NMR spectroscopy (90 MHz, $CDCl_3$). In the crude product, a broad variety of contaminations was observed such as aryl-H, aryl-Br, aryl-*n*-Bu, $(aryl)_2Hg$, *n*-BuHg-containing compounds and adducts of $HgBr_2$ with aryl-H, aryl-Br (cf. **38** for **10a**), aryl-*n*-Bu, or aryl-HgBr. The analytical yield of the desired product varied between 70 and 90%; isolated yields were in some cases much lower due to the difficult purification and crystallization of the arylmercury bromides.

1-(Bromomercurio)-2-(methoxymethyl)benzene (35). In contrast to the other arylmercury bromides, **35** was synthesized via the corresponding Grignard **14** due to the absence of ether cleavage reactions. A solution of **7** (80 mmol, in 100 mL of anhydrous THF) was slowly added to magnesium (100 mmol, initially covered with 20 mL of THF). The excess magnesium was filtered off, and titration revealed a complete formation of **14**. To the Grignard reagent, a solution of mercuric bromide (31.7 g, 88 mmol, in 100 mL of THF) was added dropwise. The mixture was heated under reflux for 1 h. After cooling and addition of water/THF (v/v, 50 mL), followed by brine (50 mL), the organic layer was separated, washed twice with brine, and dried ($MgSO_4$). Evaporation of the solvent yielded the crude product, which was recrystallized from acetone. ^1H NMR (90 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.52 (s, 3 H, OMe), 4.51 [s + d, ^4J(Hg–H) = 18 Hz, 2 H, aryl CH_2], 7.25–7.46 [m, 3 H, aryl H(3–5)], 7.10 [d + dd, ^3J = 7 Hz, ^3J(Hg–H) = 201 Hz, 1 H, aryl H(6)].

Toxification Hazard. Although the arylmercury compounds are nonvolatile, they must be handled with care due to their high toxicity. Precautions must be taken to prevent contamination of the laboratory.

1-(Bromomercurio)-2-(2,5-dioxahexyl)benzene (36). The crude product was crystallized from acetone (–20 °C): colorless crystals, mp 81–82 °C, yield 83%. ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.40 (s, 3 H, OMe), 3.62–3.66 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.68–3.72 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 4.57 [s, ^4J(Hg–H) = 17 Hz, 2 H, aryl CH_2], 7.22–7.41 (m, 4 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.59 (q, ^1J = 141 Hz, 1 C, OMe), 69.37 (t, ^1J = 142 Hz, 1 C, CH_2), 71.30 (t, ^1J = 141 Hz, 1 C, CH_2), 73.42 [t, ^1J = 139 Hz, ^3J(Hg–C) = 92 Hz, 1 C, aryl CH_2], 127.59 [d, ^1J = 161 Hz, ^3J(Hg–C) = 203 Hz, 1 C, aryl C(3)], 128.03 [d, ^1J = 156 Hz, ^3J(Hg–C) = 173 Hz, 1 C, aryl C(5)], 128.27 [d, ^1J = 161 Hz, ^4J(Hg–C) = 32 Hz, 1 C, aryl C(4)], 136.71 [d, ^1J = 161 Hz, ^2J(Hg–C) = 117 Hz, 1 C, aryl C(6)], 142.73 [s, ^2J(Hg–C) = 74 Hz, 1 C, aryl C(2)], 151.90 [s, ^1J(Hg–C) = 2396 Hz, 1 C, aryl C(1)]. MS (DCI, NH_3), *m/z* (relative intensity): 464 ($M{\cdot}NH_4^+$, $C_{10}H_{17}NO_2BrHg$, 100), 447 ($M{\cdot}H^+$, 26), 367 ($aryl{-}Hg^+$, 11), 331 ($(aryl)_2{\cdot}H^+$, 17). Anal. Calcd for $C_{10}H_{13}O_2HgBr$: C, 26.95; H, 2.94; Hg, 45.00. Found: C, 27.28; H, 2.99; Hg, 44.93.

1-(Bromomercurio)-2,6-bis(2,5-dioxahexyl)benzene (40). The compound was crystallized from diethyl ether/*n*-pentane 1:1 (–20 °C): colorless solid, mp 42–43 °C. ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.41 (s, 6 H, OMe), 3.64–3.70 (m, A_2B_2, 8 H, C_2H_4), 4.55 [s, ^4J(Hg–H) = 16 Hz, 4 H, aryl CH_2], 7.18–7.22 (m, 3 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.70 (q, ^1J = 141 Hz, 2 C, OMe), 69.42 (t, ^1J = 140 Hz, 2 C, C_2H_4), 71.49 (t, ^1J = 141 Hz, 2 C, C_2H_4), 74.37 [t, ^1J = 141 Hz, ^3J(Hg–C) = 104 Hz, 2 C, aryl CH_2], 127.42 [d, ^1J = 160 Hz, ^3J(Hg–C) = 174 Hz, 2 C, aryl C(3,5)], 128.09 [d, ^1J = 161 Hz, ^4J(Hg–C) = 26 Hz, 1 C, aryl C(4)], 143.62 [s, ^2J(Hg–C) = 73 Hz, 2 C, aryl C(2,6)], 149 [s, very broad, 1 C, aryl C(1)]. ^{199}Hg NMR (44.77 MHz, $CDCl_3$, reference Ph_2Hg = 0 ppm, BB): δ 447. MS (DCI, NH_3), *m/z* (relative intensity): 552 ($M{\cdot}NH_4^+$, $C_{14}H_{25}O_4NBrHg$, 100), 535 ($M{\cdot}H^+$, 37), 272 ($aryl{-}H{\cdot}NH_4^+$, 55). Anal. Calcd for $C_{14}H_{21}O_4HgBr$: C, 31.50; H, 3.97; Hg, 37.58. Found: C, 31.58; H, 4.00; Hg, 37.75.

Reaction of 40 with Chloride. A solution of **40** (0.53 g, 1.0 mmol) in CH_2Cl_2 (25 mL) was stirred (room temperature) with a saturated NaCl solution (50 mL H_2O). After 5 h, the NaCl solution was refreshed, and stirring was continued for another 19 h. After this period, the organic material was isolated by extraction with CH_2Cl_2, and the organic layer was dried ($MgSO_4$), filtered, and evaporated to dryness. The crude prodct (colorless oil, 0.48 g) was characterized by ^1H NMR spectroscopy (90 MHz, $CDCl_3$) as a single product (**41**), with a spectrum only slightly different from that of the starting material. Crystallization was achieved from diethyl ether/*n*-pentane 1:1 at –20 °C (mp 45 °C).

1-(Chloromercurio)-2,6-bis(2,5-dioxahexyl)benzene (41). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.41 (s, 6 H, OMe), 3.63–3.66 and 3.68–3.72 (m, A_2B_2, 8 H, C_2H_4), 4.55 [s, ^4J(Hg–H) = 16 Hz, 4 H, aryl CH_2], 7.15–7.24 (m, 3 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.76 (q, ^1J = 141 Hz, 2 C, OMe), 69.47 (t, ^1J = 142 Hz, 2 C, C_2H_4), 71.53 (t, ^1J = 141 Hz, 2 C, C_2H_4), 74.41 [t, ^1J = 142 Hz, ^3J(Hg–C) = 105 Hz, 2 C, aryl CH_2], 127.48 [d, ^1J = 159 Hz, ^3J(Hg–C) = 175 Hz, 2 C, aryl C(3,5)], 128.17 [d, ^1J = 161 Hz, ^4J(Hg–C) = 25 Hz, 1 C, aryl C(4)], 143.67 [s, ^2J(Hg–C) = 73 Hz, 2 C, aryl C(2,6)], 148.10 [s, low intensity, 1 C, aryl C(1)]. ^{199}Hg NMR (44.77 MHz, $CDCl_3$, reference Ph_2Hg = 0 ppm): δ 332 [tm, ^4J(Hg–H) = 68 Hz, 1 Hg]. MS (DCI, NH_3), *m/z* (relative intensity): 998 ($M_2{\cdot}NH_4^+$, 1), 508 ($M{\cdot}NH_4^+$, $C_{14}H_{25}O_4NClHg$, 100), 455 ($M{\cdot}H^+$, 12), 272 ($M - H{\cdot}NH_4^+$, 50). Anal. Calcd for $C_{14}H_{21}O_4HgCl$: C, 34.36; H, 4.33; Hg, 41.99. Found: C, 34.42; H, 4.22; Hg, 40.00.

1-(Bromomercurio)-2-(2,5,8-trioxanonyl)benzene (37). The crude product was crystallized from acetone (–20 °C): colorless crystals, mp 79–80 °C. Due to several crystallizations necessary for a complete purification, the final yield was rather low (40%). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.39 (s, 3 H, OMe), 3.56–3.60 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.64–3.68 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.73 (s, 4 H, C_2H_4), 4.58 [s, ^4J(Hg–H) = 16 Hz, 2 H, aryl CH_2], 7.21–7.40 (m, 4 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.72 (q, ^1J = 141 Hz, 1 C, OMe), 69.69 (t, ^1J = 144 Hz, 1 C, CH_2), 69.96 (t, ^1J = 142 Hz, 1 C, CH_2), 70.02 (t, ^1J = 141 Hz, 1 C, CH_2), 71.66 (t, ^1J = 134 Hz, 1 C, CH_2), 73.57 [t, ^1J = 136 Hz, ^3J(Hg–C) = 92 Hz, 1 C, aryl CH_2], 127.59 [d, ^1J = 161 Hz, ^3J(Hg–C) = 202 Hz, 1 C, aryl C(3)], 127.96 [d, ^1J = 156 Hz, ^3J(Hg–C) = 175 Hz, 1 C, aryl C(5)], 128.27 [d, ^1J = 161 Hz, ^4J(Hg–C) = 31 Hz, 1 C, aryl C(4)], 136.69 [d, ^1J = 163 Hz, ^2J(Hg–C) = 116 Hz, 1 C, aryl C(6)], 142.97 [s, ^2J(Hg C) = 74 Hz, 1 C, aryl C(2)], 152.09 [s, ^1J(Hg–C) = 2404 Hz, 1 C, aryl C(1)]. MS (DCI, NH_3), *m/z* (relative intensity): 508 ($M{\cdot}NH_4^+$, $C_{12}H_{21}O_3NBrHg$, 100), 491 ($M{\cdot}H^+$, 2), 428 ($aryl{-}Hg^+$, 5), 228 ($aryl{-}H{\cdot}NH_4^+$, 84). Anal. Calcd for $C_{12}H_{17}O_3HgBr$: C, 29.43; H, 3.50; Hg, 40.96. Found: C, 29.72; H, 3.54; Hg, 41.18.

1-(Bromomercurio)-2-(2,5,8,11-tetraoxadodecyl)benzene (38). A fractionated column separation (Al_2O_3 column, 2.5 × 30 cm, eluent petroleum ether 40–60 °C/THF mixtures, 80-mL fractions) was used for purification. Fractions were collected containing 0, 5, 15 (2×), 25, 35 (2×), 40 (2×), 45, 50, and 60% THF; those containing the desired product (35 and 40% THF) were combined. Pure **38** (colorless, mp 39 °C) was obtained by subsequent crystallization (–20 °C) from a 1:1 diethyl ether/*n*-pentane mixture. Due to the rather tedious purification procedure, the isolated yield was 36%. ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.40 (s, 3 H, OMe), 3.56–3.78 (m, 12 H, CH_2), 4.56 [s, ^4J(Hg–H) = 16 Hz, 2 H, aryl CH_2], 7.19–7.32 [m, 3 H, aryl H(3–5)], 7.42–7.46 [m, 1 H, aryl H(6)]. ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.56 (q, ^1J = 141 Hz, 1 C, OMe), 67.59 (t, ^1J = 141 Hz, 1 C, CH_2), 69.32 (t, ^1J = 141 Hz, 1 C, CH_2), 69.85 (t, ^1J = 141 Hz, 1 C, CH_2), 69.93 (t, ^1J = 141 Hz, 1 C, CH_2), 70.06 (t, ^1J = 141 Hz, 1 C, CH_2), 70.20 (t, ^1J = 141 Hz, 1 C, CH_2), 71.57 (t, ^1J = 142 Hz, 1 C, CH_2), 73.48 [t, ^1J = 143 Hz, ^3J(Hg–C) = 92 Hz, 1 C, aryl CH_2], 127.44 [d, ^1J = 160 Hz, ^3J(Hg–C) = 203 Hz, 1 C, aryl C(3)], 127.87 [d, ^1J = 152 Hz, ^3J(Hg–C) = 175 Hz, 1 C, aryl C(5)], 127.99 [d, ^1J = 160 Hz, ^4J(Hg–C) = 31 Hz, 1 C, aryl C(4)], 136.60 [d, ^1J = 161 Hz, ^2J(Hg–C) = 112 Hz, 1 C, aryl C(6)], 142.95 [s, ^2J(Hg–C) = 77 Hz, 1 C, aryl C(2)], 152.23 [s, ^1J(Hg–C) = 2430 Hz, 1 C, aryl C(1)]. ^{199}Hg NMR (44.77 MHz, $CDCl_3$, reference Ph_2Hg = 0 ppm): δ 487 [dm, ^3J(H–Hg) = 201 Hz, 1 Hg]. Anal. Calcd for

$C_{14}H_{21}O_4HgBr$: C, 31.50; H, 3.97; Hg, 37.58. Found: C, 31.67; H, 4.24; Hg, 38.28.

1-Bromo-2-(2,5,8,11-tetraoxadodecyl)benzene·$(HgBr_2)_n$ (10a). This byproduct from the synthesis of **38** was easily isolated from the crude reaction product mixture by crystallization from acetone (-20 °C) as a colorless solid (mp 72-75 °C). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.37 (s, 3 H, OMe), 3.57-3.61 and 3.65-3.69 (m, A_2B_2, 4 H, C_2H_2), 3.70-3.73 (m, $A'_2B'_2$, 4 H, C_2H_4), 3.76 (s, broad, 4 H, C_2H_4), 4.67 (s, 2 H, aryl CH_2), 7.15 (ddd, ^3J = 7 and 7 Hz, ^4J = 2 Hz, 1 H, aryl H), 7.33 (ddd, ^3J = 7 and 7 Hz, ^4J = 1 Hz, 1 H, aryl H), 7.54 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, aryl H), 7.58 (dm, ^3J = 7 Hz, 1 H, aryl H). ^{199}Hg NMR (44.77 MHz, $CDCl_3$, reference Ph_2Hg = 0 ppm): δ 1497 (s, broad). The number of n was not determined.

1-(Bromomercurio)-2-(2,5,8,11,14-pentaoxapentadecyl)benzene (39). A column filtration (Al_2O_3 column, 2.5 × 20 cm, Et_2O eluent) was necessary to remove polar impurities. Repeated crystallizations (Et_2O/n-pentane mixture, 1:1, -20 °C) gave a 62% yield of pure **39** (colorless solid, mp 32-34 °C). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm) δ 3.35 (s, 3 H, OMe), 3.55-3.61 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.63-3.64 (m, $A'_2B'_2$, 4 H, CH_2), 3.65-3.70 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.68-3.69 (m, 8 H, CH_2), 4.55 [s, ^4J(Hg-H) = 16 Hz, 2 H, aryl CH_2], 7.20-7.32 [m, 3 H, aryl H(3-5)], 7.45-7.49 [m, 1 H, aryl H(6)]. In a 90-MHz ^1H NMR spectrum, additional Hg-H couplings become visible: δ 7.47 [d, ^3J(Hg-H) = 205 Hz, ^3J(H-H) = 7 Hz, 1 H, aryl H(6)]. The aryl H(3-5) multiplet also has Hg satellites [^4J(Hg-H) = 77 Hz], which could not be identified. ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.76 (q, ^1J = 141 Hz, 1 C, OMe), 69.42 (t, ^1J = 144 Hz, 1 C, CH_2), 69.98 (t, ^1J = 141 Hz, 1 C, CH_2), 70.07 (t, ^1J = 141 Hz, 1 C, CH_2), 70.26 (t, ^1J = 140 Hz, 1 C, CH_2), 70.35 (t, ^1J = 140 Hz, 2 C, CH_2), 70.43 (t, ^1J = 140 Hz, 1 C, CH_2), 71.74 (t, ^1J = 141 Hz, 1 C, CH_2), 73.62 [t, ^1J = 142 Hz, ^3J(Hg-C) = 93 Hz, 1 C, aryl CH_2], 127.55 [d, ^1J = 160 Hz, ^3J(Hg-C) = 202 Hz, 1 C, aryl C(3)], 127.97 [d, ^1J = 160 Hz, ^3J(Hg-C) = 175 Hz, 1 C, aryl C(5)], 128.08 [d, ^1J = 160 Hz, ^4J(Hg-C) = 32 Hz, 1 C, aryl C(4)], 136.80 [d, ^1J = 163 Hz, ^2J(Hg-C) = 112 Hz, 1 C, aryl C(6)], 143.13 [s, ^2J(Hg-C) = 77 Hz, 1 C, aryl C(2)], 152.46 [s, ^1J(Hg-C) = 2440 Hz, 1 C, aryl C(1)]. MS (DCI, NH_3), m/z (relative intensity): 596 ($M·NH_4^+$, 29, 499 (M^+ - Br, 2), 316 [(aryl-H)·NH_4^+, 100]. MS (FAB, Xe), m/z (relative intensity): 499 (M^+ - Br, 100). MS (FD), m/z (relative intensity): 1076 (M_2^+ - Br, 10), 499 (M^+ - Br, 66), 297 (M^+ - HgBr, 100). Anal. Calcd for $C_{16}H_{25}O_5HgBr$: C, 33.26; H, 4.36; Hg, 34.71. Found: C, 33.23; H, 4.31; Hg, 35.22.

1-(Bromomercurio)-2-(2,5,8,11,14-pentaoxapentadecyl)benzene·$HgBr_2$ (39a). This compound was isolated from a synthesis of **39** in 28% yield. It readily crystallized from the crude reaction mixture in acetone (at -20 °C, colorless crystals, mp 102 °C). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 2.99 (s, 3 H, OMe), 3.44-3.49 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.54-3.58 (m, A_2B_2, 4 H, CH_2), 3.61-3.72 (m, 8 H, C_2H_4), 3.83 (s, 4 H, C_2H_4), 4.59 [s, ^4J(Hg-H) = 16 Hz, 2 H, aryl CH_2], 7.23-7.31 [m, 3 H, aryl H(3-5)], 7.42-7.46 [m, 1 H, aryl H(6)]. In [D_8]THF, the ^1H NMR (250 MHz, reference (THF)D_7H = 1.75 ppm) spectra of **39** and its $HgBr_2$ adduct **39a** were identical due to dissociation into the components upon dissolution: δ 3.27 (s, 3 H, OMe), 3.27-3.29 (m, $^1/_2$ A_2B_2, 2 H, C_2H_4), 3.46-3.60 (m, 10 H, C_2H_4), 3.64 (s, 4 H, C_2H_4), 4.52 [s, ^4J(Hg-H) = 16 Hz, 2 H, aryl CH_2], 7.19-7.27 [m, 3 H, aryl H(3-5)], 7.52 [dm, ^3J = 7 Hz, 1 H, aryl H(6)]. ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.42 (q, ^1J = 141 Hz, 1 C, OMe), 69.89 (t, ^1J = 140 Hz, 1 C, CH_2), 70.00 (t, ^1J = 140 Hz, 1 C, CH_2), 70.07 (t, ^1J = 140 Hz, 1 C, CH_2), 70.11 (t, ^1J = 140 Hz, 1 C, CH_2), 70.19 (t, ^1J = 140 Hz, 2 C, CH_2), 70.30 (t, ^1J = 140 Hz, 1 C, CH_2), 71.38 (t, ^1J = 143 Hz, 1 C, CH_2), 73.84 (t, ^1J = 148 Hz, 1 C, aryl CH_2), 127.86 [d, ^1J = 154 Hz, 1 C, aryl C(3)], 128.38 [d, ^1J = 160 Hz, 1 C, aryl C(5)], 128.63 [d, ^1J = 159 Hz, 1 C, aryl C(4)], 136.84 [d, ^1J = 169 Hz, 1 C, aryl C(6)], 142.49 [s, 1 C, aryl C(2)], 153.38 [s, 1 C, ary C(1)]. Due to a low number of scans, J(Hg-C) couplings could not be observed. ^{199}Hg NMR (44.77 MHz, $CDCl_3$, reference Ph_2Hg = 0 ppm): δ 461 (dt, ^3J = 192 Hz, ^4J = 62 Hz, 1 Hg, aryl Hg), 1530 (s, broad, 1 Hg, $HgBr_2$). MS (DCl, NH_3) data are identical with that of **39**. Anal. Calcd for $C_{16}H_{25}O_5Hg_2Br_3$: C, 20.48; H, 2.69; Hg, 42.76. Found: C, 21.01; H, 2.73; Hg, 42.85.

Small-Scale Reactions of 35-40 with Magnesium in [D_8]THF. The arylmercury bromides **35-40** were reacted on a ^1H NMR scale (about 5 mg) with magnesium (excess, 50 mg) in [D_8]THF (500 μL) by stirring for 1-2 weeks. After settling of the magnesium amalgam (1 day), the reaction mixture was decanted into a NMR tube (5 mm), which was sealed off from the glass assembly. The Grignard products were analyzed by ^1H NMR spectroscopy (250 MHz, reference (THF)D_7H = 1.75 ppm). Their purity was high (>95%), with the hydrolysis product (oligoethylene glycol benzyl methyl ether) as the only byproduct, which is normal in these small scale (<100 μmol) experiments and is due to residual moisture in the starting material and the glassware.

1-(Bromomagnesio)-2-(methoxymethyl)benzene (14). ^1H NMR (250 MHz, [D_8]THF, reference (THF)D_7H = 1.75 ppm): δ 3.76 (s, 3 H, OMe), 4.66 (s, 2 H, aryl CH_2), 6.73-6.78 (m, 1 H, aryl H), 6.82-6.87 (m, 2 H, aryl H), 7.60-7.63 [m, 1 H, aryl H(6)].

1-(Bromomagnesio)-2-(2,5-dioxahexyl)benzene (15). ^1H NMR (250 MHz, [D_8]THF, reference (THF)D_7H = 1.75 ppm): δ 3.79 (s, 3 H, OMe), 3.85 (t, A_2B_2, ^3J = 5 Hz, 2 H, C_2H_4), 3.95 (t, A_2B_2, ^3J = 5 Hz, 2 H, C_2H_4), 4.67 (s, 2 H, aryl CH_2), 6.70 [d, ^3J = 7 Hz, 1 H, aryl H(3)], 6.78-6.85 [m, 2 H, aryl H(4,5)], 7.75 [d, ^3J = 6 Hz, 1 H, aryl H(6)]. The spectrum was identical with that of **15** from the reaction of **8** with magnesium in [D_8]THF. ^{13}C NMR (62.89 MHz, [D_8]THF, reference [D_8]THF = 24.0 ppm) δ 59.26 (q, ^1J = 144 Hz, 1 C, OMe), 70.29 (t, ^1J = 146 Hz, 1 C, CH_2), 75.82 (t, ^1J = 142 Hz, 1 C, aryl CH_2), 119.83 [d, ^1J = 147 Hz, 1 C, aryl C(3)], 122.25 (d, ^1J = 154 Hz, 1 C, aryl, C), 123.73 (d, ^1J = 162 Hz, 1 C, aryl C), 139.16 [d, ^1J = 153 Hz, 1 C, aryl C(6)], 144.42 [s, 1 C, aryl C(2)], 171.19 [s, 1 C, aryl C(1)] (one CH_2 signal was not found).

1-(Bromomagnesio)-2,6-bis(2,5-dioxahexyl)benzene (19). ^1H NMR (250 MHz, [D_8]THF, reference (THF)D_7H = 1.75 ppm): δ 3.65 (s, 6 H, OMe), 3.72-3.77 and 3.82-3.86 (m, A_2B_2, 8 H, C_2H_4), 4.81 (s, 4 H, aryl CH_2), 6.89 (s, 3 H, aryl H). The spectrum was identical with that of **19** from the reaction of **12** with magnesium in [D_8]THF.

1-(Bromomagnesio)-2-(2,5,8-trioxanonyl)benzene (16). ^1H NMR (400 MHz, [D_8]THF, reference (THF)D_7H = 1.75 ppm): δ 3.31 (s, 3 H, OMe), 3.58-3.61 and 3.71-4.02 (m, A_2B_2, 4 H, C_2H_4), 3.97 (s, broad, 4 H, C_2H_4), 4.72 (s, 2 H, aryl CH_2), 6.72 [d, ^3J = 7 Hz, 1 H, aryl H(3)], 6.80-6.86 [m, 2 H, aryl H(4,5)], 7.74 [d, ^3J = 6 Hz, 1 H, aryl C(6)]. ^{13}C NMR (62.89 MHz, [D_8]THF, reference [D_8]THF = 24.0 ppm): δ 57.83 (q, ^1J = 142 Hz, 1 C, OMe), 66.70 (t, ^1J = 141 Hz, 1 C, CH_2), 68.75 (t, ^1J = 143 Hz, 1 C, CH_2), 68.82 (t, ^1J = 143 Hz, 1 C, CH_2), 69.54 (t, ^1J = 140 Hz, 1 C, CH_2), 75.54 (t, ^1J = 140 Hz, 1 C, aryl CH_2), 119.93 [d, ^1J = 160 Hz, 1 C, aryl C(3)], 122.50 (d, ^1J = 156 Hz, 1 C, aryl C), 123.65 (d, ^1J = 152 Hz, 1 C, aryl C), 139.49 [d, ^1J = 152 Hz, 1 C, aryl C(6)], 144.97 [s, 1 C, aryl C(2)], 169.02 [s, 1 C, aryl C(1)].

1-(Bromomagnesio)-2-(2,5,8,11-tetraoxadodecyl)benzene (17). ^1H NMR (400 MHz, [D_8]THF, reference (THF)D_7H = 1.75 ppm): δ 3.25 (s, 3 H, OMe), 3.46 [t, A_2B_2, ^3J = 5 Hz, 2 H, CH_2(10)], 3.65 [t, A_2B_2, ^3J = 5 Hz, 2 H, CH_2(9)], 3.84 [t, $A'_2B'_2$, ^3J = 5 Hz, 2 H, CH_2(7)], 3.95-3.98 [m, $A''_2B''_2$, 2 H, CH_2(C)], 3.98-4.03 [m, $A''_2B''_2$, 2 H, CH_2(4)], 4.10 [t, $A'_2B'_2$, ^3J = 5 Hz, 2 H, CH_2(6)], 4.71 (s, 2 H, aryl CH_2), 6.72 [d, ^3J = 7 Hz, 1 H, aryl H(3)], 6.79-6.86 [m, 2 H, aryl H(4,5)], 7.74 [dm, ^3J = 6 Hz, 1 H, aryl H(6)]. ^1H NMR (250 MHz, [D_8]THF, room temperature): NOESY interactions aryl H(6)-aryl H(5); aryl H(5)-aryl H(4), aryl H(4)-aryl H(3); aryl H(3)-aryl CH_2; aryl CH_2-CH_2(3); CH_2(3)-CH_2(4); CH_2(4)-CH_2(6); CH_2(6)-CH_2(7); CH_2(7)-CH_2(9); CH_2(9)-CH_2(10); CH_2(10)-OMe. ^{13}C NMR (62.89 MHz, [D_8]THF, reference [D_8]THF = 24.0 ppm): δ 57.58 (q, ^1J = 140 Hz, 1 C, OMe), 67.04 (t, ^1J = 141 Hz, 1 C, CH_2), 68.92 (t, ^1J = 141 Hz, 1 C, CH_2), 68.89 (t, ^1J = 141 Hz, 1 C, CH_2), 69.35 (t, ^1J = 145 Hz, 1 C, CH_2), 69.62 (t, ^1J = 145 Hz, 1 C, CH_2), 71.03 (t, ^1J = 144 Hz, 1 C, CH_2), 75.55 (t, ^1J = 142 Hz, 1 C, aryl CH_2), 120.07 [d, ^1J = 145 Hz, 1 C, aryl C(3)], 122.53 (d, ^1J = 148 Hz, 1 C, aryl C), 123.71 (d, ^1J = 152 Hz, 1 C, aryl C), 139.47 [d, ^1J = 153 Hz, 1 C, aryl C(6)], 145.03 [s, 1 C, aryl C(2)], 169.23 [s, 1 C, aryl C(1)].

1-(Bromomagnesio)-2-(2,5,8,11,14-pentaoxapentadecyl)benzene (18). ^1H NMR (250 MHz, [D_8]THF, reference (THF)D_7H = 1.75 ppm): δ 3.32 (s, 3 H, OMe), 3.43-3.47 and 3.52-3.56 (m, A_2B_2, 4 H, CH_2), 3.58-3.62 and 3.69-3.73 (m, $A'_2B'_2$, 4 H, CH_2), 3.84-3.89 and 3.98-4.02 (m, $A'''_2B'''_2$, 4 H, CH_2), 4.71 (s, 2 H, aryl CH_2), 6.71 [d, ^3J = 7 Hz, 1 H, aryl H(3)], 6.77-6.86 [m, 2 H, aryl H(4,5)], 7.72-7.75 [m, 1 H, aryl H(6)]. ^1H NMR (250 MHz, [D_8]THF, room temperature) NOESY interactions (aliphatic

region): signal intensities are weak, which makes it difficult to distinguish real signals from artifacts. The NOESY spectrum does not allow a further interpretation of the ^1H NMR spectrum. A spectrum measured at lower temperature (−50 °C) was almost identical with the NOESY spectrum. ^{13}C NMR (62.89 MHz, [D_8]THF, reference [D_8]THF = 24.0 ppm): δ 57.82 (q, ^1J = 141 Hz, 1 C, OMe), 67.84 (t, ^1J = 145 Hz, 1 C, CH_2), 68.79 (t, ^1J = 141 Hz, 1 C, CH_2), 68.97 (t, ^1J = 141 Hz, 1 C, CH_2), 69.17 (t, ^1J = 141 Hz, 1 C, CH_2), 69.37 (t, ^1J = 141 Hz, 1 C, CH_2), 69.43 (t, ^1J = 141 Hz, 1 C, CH_2), 69.63 (t, ^1J = 141 Hz, 1 C, CH_2), 71.26 (t, ^1J = 140 Hz, 1 C, CH_2), 75.95 (t, ^1J = 139 Hz, 1 C, aryl CH_2), 119.83 [d, ^1J = 153 Hz, 1 C, aryl C(3)], 122.33 (d, ^1J = 159 Hz, 1 C, aryl C), 123.62 (d, ^1J = 151 Hz, 1 C, aryl C), 139.35 [d, ^1J = 154 Hz, 1 C, aryl C(6)], 145.36 [s, 1 C, aryl C(2)], 169.92 [s, 1 C, aryl C(1)].

1-(Bromomagnesio)-2,6-bis(2,5,8-trioxanonyl)benzene (20). Analogous to the synthesis of Grignards **15–19**, the synthesis of the larger homologue of **19** was also attempted via the arylmercury bromide route. Unfortunately, pure arylmercury bromide 1-(bromomercurio)-2,6-bis(2,5,8-trioxanonyl)benzene could not be obtained, since crystallization was impossible. With column chromatography (Al_2O_3, activity III, eluents Et_2O/THF), small fractions with a maximum purity of about 90% were obtained. ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.38 (s, 6 H, OMe), 3.56–3.60 and 3.65–3.69 (m, A_2B_2, 8 H, C_2H_4), 3.73–3.74 (m, 8 H, C_2H_4), 4.55 [sd, ^4J(Hg) = 16 Hz, 4 H, aryl CH_2], 7.17–7.22 (m, 3 H, aryl H). Reaction of these samples with magnesium metal in [D_8]THF on a ^1H NMR scale, analogous to **36–40**, gave a mixture of unidentified products.

In analogy to **39**, a crystalline $HgBr_2$ adduct (mp 114–116 °C, from acetone) was isolated. Elemental analysis showed the inclusion of (about) 2 equiv of mercuric bromide. Upon dissolution in chloroform, the complexed mercuric bromide partially precipitates from solution ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.34 (s, 6 H, OMe), 3.57–3.61 and 3.67–3.71 (m, A_2B_2, 8 H, C_2H_4), 3.83–3.84 (m, 8 H, C_2H_4), 4.58 [sd, ^4J(Hg) = 15 Hz, 4 H, aryl CH_2], 7.25–7.27 (m, 3 H, aryl H). ^{199}Hg NMR (44.77 MHz, only BB, $CDCl_3$, reference Ph_2Hg = 0 ppm): δ 446 (1 Hg, aryl Hg), 1487 (1 Hg, $HgBr_2$). Anal. Calcd for $C_{18}H_{28}O_6HgBr\cdot[HgBr_2]_2$: C, 16.10; H, 2.18; Hg, 44.82. Found: C, 16.12; H, 2.21; Hg, 43.81.

Large-Scale Reaction of 35–39 with Mg. Pure Grignards **14–18** were obtained by the exchange reactions of the arylmercury bromides **35–39** with magnesium metal. In a typical reaction, the arylmercury bromide (5 mmol) was stirred with magnesium (1.15 g, 50 mmol) in THF (50 mL) for 2 weeks at room temperature. During the period, the arylmercury bromide is first symmetrized (reduction), under formation of $MgBr_2$, and subsequently, mercury is exchanged to give the desired Grignard reagent. After settling of the magnesium amalgam, the solution was decanted into a second vessel, and an aliquot was titrated on total base and Mg^{2+} to check complete conversion of the starting material. In the case of incomplete reaction, the solution was further stirred with fresh magnesium metal (1.15 g, 50 mmol). The solution was divided into several samples (about 1 mmol, in 10 mL of THF) for quench reactions and crystallization experiments. Quench reactions with D_2O and Me_3SnCl were performed analogous to the procedure described for **15** (vide supra). All aryl-D and aryl-$SnMe_3$ products were colorless oils. Their purity was checked by ^1H NMR and ^{13}C NMR spectroscopy and GCMS. The formation of the expected quench products was quantitative; side reactions were not detected. The exchange reaction of **40** was not performed, because it had already been established that crystallization of Grignard **19** was not possible.

Reaction of 37 with Mg in Et_2O. When **37** (200 mg) was stirred with magnesium (100 mg) in diethyl ether (10 mL), the solid slowly dissolved. After a reaction period of 3 weeks and subsquennt settling of the magnesium dust, the colorless solution was decanted and the solvent distilled back. The crystalline residue was characterized by ^1H NMR spectroscopy ($CDCl_3$, 90 MHz) to be pure **37**; no reaction had taken place.

[2-D]Benzyl Methyl Ether (42). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.41 (s, 3 H, OMe), 4.48 (s, 2 H, aryl CH_2), 7.29–7.38 (m, 4 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 57.47 (q, ^1J = 141 Hz, 1 C, OMe), 73.97 (t, ^1J = 141 Hz, 1 C, aryl CH_2), 126.0 [t, very low intensity, ^1J(C–D) = 24 Hz, 1 C, aryl C(2)], 126.30 [d, ^1J = 159 Hz, 2 C, aryl C(4,6)], 127.85 (d, ^1J = 159 Hz, 2 C, aryl C(3,5)], 137.94 (s, 1 C, aryl C(1)]. MS (70 eV), *m/z* (relative intensity): 123 (M^+, 50), 122 (M^+ − H, 47), 92 (Bz^+, 100), 78 (30), 66 (16), 51 (16).

Reactions of 15 with D_2O and Me_3SnCl. When **15** was prepared via the arylmercury bromide route, its D_2O and Me_3SnCl quench products were identical with those obtained earlier from a Grignard solution prepared via the reaction of **10** with magnesium metal (vide supra).

[2-D]-(2,5,8-Trioxanonyl)benzene (43). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.40 (s, 3 H, OMe), 3.55–3.60 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.64–3.70 (m, 6 H, CH_2), 4.58 (s, 2 H, aryl CH_2), 7.28–7.37 (m, 4 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.91 (q, ^1J = 141 Hz, 1 C, OMe), 69.40 (t, ^1J = 140 Hz, 1 C, CH_2), 70.47 (t, ^1J = 141 Hz, 1 C, CH_2), 70.59 (t, ^1J = 141 Hz, 1 C, CH_2), 71.89 (t, ^1J = 141 Hz, 1 C, CH_2), 73.11 (t, ^1J = 141 Hz, 1 C, aryl CH_2), 127.29 [t, very low intensity, ^1J(C–D) = 24 Hz, 1 C, aryl C(2)], 127.43 (d, ^1J = 158 Hz, 1 C, aryl C), 127.58 (d, ^1J = 158 Hz, 1 C, aryl C), 128.10 (d, ^1J = 153 Hz, 1 C, aryl C), 128.21 (d, ^1J = 153 Hz, 1 C, aryl C), 138.12 [s, 1 C, aryl, C(1)]. MS (70 eV), *m/z* (relative intensity): 211 (M^+, $C_{12}H_{17}O_3D$, 10), 135 (11), 108 (12), 106 (20), 92 (100), 76 (24), 66 (20), 59 (84), 45 (79).

[2-D]-(2,5,8,11-Tetraoxadodecyl)benzene (44). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.39 (s, 3 H, OMe), 3.52–3.58 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.62–3.72 (m, 10 H, CH_2), 4.58 (s, 2 H, aryl CH_2), 7.28–7.36 (m, 4 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.97 (q, ^1J = 141 Hz, 1 C, OMe), 69.42 (t, ^1J = 141 Hz, 1 C, CH_2), 70.50 (t, ^1J = 141 Hz, 1 C, CH_2), 70.62 (t, ^1J = 141 Hz, 3 C, CH_2), 71.92 (t, ^1J = 142 Hz, 1 C, CH_2), 73.17 (t, ^1J = 141 Hz, 1 C, aryl CH_2), 127.34 [t, very low intensity, ^1J(C–D) = 24 Hz, 1 C, aryl C(2)], 127.50 (d, ^1J = 162 Hz, 1 C, aryl C), 127.66 (d, ^1J = 162 Hz, 1 C, aryl C), 128.17 (d, ^1J = 160 Hz, 1 C, aryl C), 128.28 (d, ^1J = 159 Hz, 1 C, aryl C), 138.17 [s, 1 C, aryl C(1)]. MS (70 eV), *m/z* (relative intensity): 255 (M^+, $C_{14}H_{21}O_4D$, 0.1), 196 (0.4), 148 (3), 135 (2), 120 (3), 106 (12), 92 (100), 66 (12), 59 (98), 45 (47).

[2-D]-(2,5,8,11,14-Pentaoxapentadecyl)benzene (45). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 3.38 (s, 3 H, OMe), 3.53–3.57 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.61–3.71 (m, 14 H, CH_2), 4.58 (s, 2 H, aryl CH_2), 7.29–7.36 (m, 4 H, aryl H). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 58.87 (q, ^1J = 141 Hz, 1 C, OMe), 69.38 (t, ^1J = 141 Hz, 1 C, CH_2), 70.41 (t, ^1J = 141 Hz, 1 C, CH_2), 70.52 (t, ^1J = 141 Hz, 3 C, CH_2), 70.55 (t, ^1J = 142 Hz, 2 C, CH_2), 71.85 (t, ^1J = 140 Hz, 1 C, CH_2), 73.08 (t, ^1J = 141 Hz, 1 C, aryl CH_2), 127.26 [t, very low intensity, ^1J(C–D) = 24 Hz, 1 C, aryl C(2)], 127.40 (d, ^1J = 158 Hz, 1 C, aryl C), 127.55 (d, ^1J = 152 Hz, 1 C, aryl C), 128.08 (d, ^1J = 153 Hz, 1 C, aryl C), 128.19 (d, ^1J = 167 Hz, 1 C, aryl C), 138.12 [s, 1 C, aryl C(1)]. MS (70 eV), *m/z* (relative intensity): 299 ($M^{+\cdot}$, $C_{16}H_{25}O_5D$, 0.06), 240 (0.2), 196 (0.6), 150 (2), 133 (5), 103 (12), 92 (100), 59 (94), 45 (41).

1-(Methoxymethyl)-2-(trimethylstannyl)benzene (46). ^1H NMR (90 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 0.28 [s, ^2J(Sn–H) = 55 and 52 Hz, 9 H, Sn–Me], 3.36 (s, 3 H, OMe), 4.47 [s, ^4J(Sn–H) = 5 Hz, 2 H, aryl CH_2), 7.27–7.35 [m, 3 H, aryl H(4–6)], 7.58–7.65 [m, 1 H, aryl H(3)]. ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ −8.10 [q, ^1J = 128 Hz, ^1J(Sn–C) = 354 and 339 Hz, 1 C, SnMe], 57.77 (q, ^1J = 141 Hz, 1 C, OMe), 76.28 [t, ^1J = 141 Hz, ^4J(Sn–C) = 18 Hz, 1 C, aryl CH_2], 127.07 [d, ^1J = 161 Hz, ^3J(Sn–C) = 48 Hz, 1 C, aryl C(6)], 127.63 [d, ^1J = 156 Hz, ^3J(Sn–C) = 39 Hz, 1 C, aryl C(4)], 128.14 [d, ^1J = 160 Hz, ^4J(Sn–C) = 10 Hz, 1 C, aryl C(5)], 136.51 [d, ^1J = 160 Hz, ^3J(Sn–C) = 36 Hz, 1 C, aryl C(3)], 141.44 [s, 1 C, aryl C(2)], 144.46 [s, 1 C, aryl C(1)]. MS (70 eV), *m/z* (relative intensity): 286 (M^+, $C_{11}H_{18}OSn$, 88), 241 (M^+ − $(CH_3)_3$, 100), 211 (37), 151 (18), 135 (17), 120 (22), 91 (22).

1-(2,5,8-Trioxanonyl)-2-(trimethylstannyl)benzene (47). ^1H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 0.30 [s, ^2J(Sn–H) = 55 and 53 Hz, 9 H, Sn–Me], 3.40 (s, 3 H, OMe), 3.54–3.58 and 3.64–3.68 [m, A_2B_2, 4 H, CH_2(3,4)], 3.67–3.68 [m, A_2B_2, 4 H, CH_2(6,7)], 4.56 [s, ^4J(sn–H) = 5 Hz, 2 H, aryl CH_2], 7.28–7.35 [m, 3 H, aryl H(4–6)], 7.52 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1 H, ary H(3)]. ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ −8.08 [q, ^1J = 128 Hz, ^1J(Sn–C) = 354 and 339 Hz,

1 C, SnMe], 59.02 (q, ^1J = 141 Hz, 1 C, OMe), 69.55 (t, ^1J = 141 Hz, 1 C, CH_2), 70.51 (t, ^1J = 140 Hz, 1 C, CH_2), 70.56 (t, ^1J = 141 Hz, 1 C, CH_2), 71.97 (t, ^1J = 141 Hz, 1 C, CH_2), 75.30 [t, ^1J = 140 Hz, ^4J(Sn–C) = 22 Hz, 1 C, aryl CH_2], 127.08 [d, ^1J = 159 Hz, ^3J(Sn–C) = 47 Hz, 1 C, aryl C(6)], 127.99 (d, ^1J = 161 Hz, ^3J(Sn–C) = 37 Hz, 1 C, aryl C(4)], 128.28 [d, ^1J = 160 Hz, ^4J(Sn–C) = 10 Hz, 1 C, aryl C(5)], 136.36 [d, ^1J = 159 Hz, ^3J(Sn–C) = 35 Hz, 1 C, aryl C(3)], 141.60 [s, 1 C, aryl C(2)], 144.53 [s, 1 C, aryl C(1)]. MS (70 eV), m/z (relative intensity): 359 (M^+ – Me, $C_{14}H_{23}O_3Sn$, 100), 257 (10), 241 (55), 225 (14), 209 (11), 165 (7), 151 (7), 135 (12), 120 (11), 91 (18), 59 (53), 45 (49).

1-(2,5,8,11-Tetraoxadodecyl)-2-(trimethylstannyl)benzene (48). ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 0.30 [s, ^2J(Sn–H) = 55 and 52 Hz, 9 H, Sn–Me], 3.39 (s, 3 H, OMe), 3.52–3.58 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.62–3.71 (m, 10 H, CH_2), 4.56 [s, ^4J(Sn–H) = 5 Hz, 2 H, aryl CH_2], 7.25–7.34 [m, 3 H, aryl H(4–6)], 7.50–7.53 [dm, ^3J = 7 Hz, 1 H, aryl H(3)]. ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ –8.07 [q, ^1J = 128 Hz, ^1J(Sn–C) = 354 and 339 Hz, 1 C, SnMe], 57.77 (q, ^1J = 140 Hz, 1 C, OMe), 69.56 (t, ^1J = 140 Hz, 1 C, CH_2), 70.49 (t, ^1J = 141 Hz, 1 C, CH_2), 70.55 (t, ^1J = 141 Hz, 2 C, CH_2), 70.65 (t, ^1J = 141 Hz, 1 C, CH_2), 71.97 (t, ^1J = 141 Hz, 1 C, CH_2), 75.28 [t, ^1J = 140 Hz, ^4J(Sn–C) = 22 Hz, 1 C, aryl CH_2], 127.06 [d, ^1J = 159 Hz, ^3J(Sn–C) = 47 Hz, 1 C, aryl C(6)], 127.97 [d, ^1J = 160 Hz, ^3J(Sn–C) = 38 Hz, 1 C, aryl C(4)[, 128.25 [d, ^1J = 160 Hz, ^4J(Sn–C) = 10 Hz, 1 C, aryl C(5)], 136.34 [d, ^1J = 158 Hz, ^3J(Sn–C) = 35 Hz, 1 C, aryl C(3)], 141.58 [s, 1 C, aryl C(2)], 144.55 [s, 1 C, aryl C(1)]. MS (70 eV), m/z (relative intensity): 403 (M^+ – Me, $C_{16}H_{27}O_4Sn$, 100), 255 (16), 241 (58), 225 (15), 209 (8), 195 (6), 165 (8), 151 (6), 135 (12), 120 (10), 103 (12), 91 (16), 59 (95), 45 (50).

1-(2,5,8,11,14-Pentaoxapentadecyl)-2-(trimethylstannyl)-benzene (49). ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 0.30 [s, ^2J(Sn–H) = 55 and 52 Hz, 9 H, Sn–Me], 3.39 (s, 3 H, OMe), 3.53–3.57 (m, $^1/_2$ A_2B_2, 2 H, CH_2), 3.61–3.73 (m, 14 H, CH_2), 4.56 [s, ^4J(Sn–H) = 5 Hz, 2 H, aryl CH_2], 7.25–7.34 (m, 3 H, aryl H(4–6)], 7.50–7.53 [m, 1 H, aryl H(3)]. ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ –8.13 [q, ^1J – 128 Hz, ^1J(Sn–C) = 354 and 339 Hz, 1 C, SnMe], 58.89 (q, ^1J = 141 Hz, 1 C, OMe), 69.48 (t, ^1J = 144 Hz, 1 C, CH_2), 70.40 (t, ^1J = 141 Hz, 1 C, CH_2), 70.43 (t, ^1J = 141 Hz, 1 C, CH_2), 70.54 (t, ^1J = 141 Hz, 4 C, CH_2), 71.84 (t, ^1J = 142 Hz, 1 C, CH_2), 75.19 [t, ^1J = 141 Hz, ^4J(Sn–C) = 22 Hz, 1 C, aryl CH_2], 126.99 [d, ^1J = 162 Hz, ^3J(Sn–C) = 46 Hz, 1 C, aryl C(6)], 127.89 [d, ^1J = 155 Hz, ^3J(Sn–C) = 38 Hz, 1 C, aryl C(4)], 128.18 [d, ^1J = 160 Hz, ^4J(Sn–C) = 10 Hz, 1 C, aryl C(5)], 136.26 [d, ^1J = 158 Hz, ^3J(Sn–C) = 35 Hz, 1 C, aryl C(3)], 141.47 [s, ^1J(Sn–C) = 469 and 449 Hz, 1 C, aryl C(2)], 144.46 [s, ^2J(Sn–C) = 28 Hz, 1 C, aryl C(1)]. MS (70 eV), m/z (relative intensity): 447 (M^+ – Me, $C_{18}H_{31}O_5Sn$, 100), 417 (3), 255 (21), 241 (48), 225 (12), 209 (6), 165 (6), 151 (3), 135 (6), 120 (6), 103 (20), 91 (17), 59 (77), 45 (22).

Crystallization of 1-(Bromomagnesio)-2-(methoxymethyl)benzene (14). A solution of 14 (0.95 mmol, in 10 mL THF) was mixed with n-hexane (10 mL), and the clear solution was concentrated to a colorless oil (<1 mL). After 1 week, the crystals which had grown in this oil were separated by quickly washing them with toluene (10 mL). The crystals were isolated by decanting the solvent and pumping and divided into two samples. The toluene solution, which became a suspension within several minutes due to the precipitation of more 14, was titrated and a total base to Mg^{2+} ratio of 1.01:1 determined, indicating that symmetrization had not occurred. The crystals were characterized by their ^{1}H NMR spectrum (90 MHz, [D_8]THF, reference THF = 1.81 ppm): δ 1.74–1.88 [m, 4 H, THF(3,4)], 3.59–3.73 [m, 4 H, THF(2,5)], 3.77 (s, broad, 3 H, OMe), 4.68 (s, broad, 2 H, aryl CH_2), 6.76–6.88 [m, 3 H, aryl H(3–5)], 6.88–6.97 [m, broad, 1 H, aryl H(6)]. An excess of THF (>3 equiv) was present, relative to the amount of 14. This must be caused by insufficient drying (high-vacuum pumping) of the crystals before dissolving them in [D_8]THF.

Crystallization of 1-(Bromomagnesio)-2-(2,5-dioxahexyl)benzene (15). A solution of 15 (1 mmol, in 8 mL of THF) was mixed with n-hexane (10 mL). The clear solution was slowly concentrated until the saturation point at room temperature was reached (total volume 14 mL). Upon cooling to 5 °C, 15 crystallized in long colorless needles. The mother liquor was decanted and titrated (total base, 0.54 mmol; Mg^{2+}, 0.53 mmol). The crystalline solid was dried (short pumping, 10^{-2} mbar) and divided into three samples. One of them was introduced into the nitrogen-filled glovebox to select crystals suitable for a structure determination. A ^{1}H NMR spectrum (250 MHz, vide supra) of the crystals in [D_8]THF (concentrated solution) showed the presence of THF crystal solvent (>2 equiv). A solution in [D_8]toluene proved to be unstable: a white crystalline solid (dimeric, solvent-free 15?) was formed, and THF remained in solution. After 4 months, a 10.4:1 stoichiometry of THF to 15 was found in solution. The intensity of the THF signals relative to the [D_7H]toluene was unchanged, indicating that the precipitate was free of THF. In spite of several attempts, the isolation of THF-free crystals of 15 suitable for structure determination from a toluene solution proved to be impossible. Analysis of the microcrystalline solids by ^{1}H NMR spectroscopy ([D_8]THF, 90 MHz) proved the absence of THF crystal solvent.

Crystallization of 1-(Bromomagnesio)-2-(2,5,8-trioxanonyl)benzene (16). A solution of 16 (0.58 mmol, in 10 mL of THF) was mixed with n-hexane (10 mL). The solution was decanted to remove some finely divided dark material (possibly Mg dust). The clear solution was concentrated to an oversaturated solution (total volume of 10 mL). Colorless crystals formed on standing for 1 week at room temperature and were isolated by decanting the mother liquid and removing the remainig solvent by high-vacuum pumping. They were divided into three samples; one of them was introduced into the glovebox in order to select crystals suitable for an X-ray structure determination. The mother liquor was titrated to check that symmetrization had not occurred (total base and Mg^{2+} were both 0.16 mmol). The crystals were characterized by ^{1}H NMR spectroscopy (250 MHz, [D_8]THF, vide supra), to find an arylmagnesium bromide to THF stoichiometry of about 1:0.9. From toluene/THF (10:1), 16 precipitated as an amorphous white powder which did not redissolve upon heating. This solid was identified by ^{1}H NMR spectroscopy (250 MHz, [D_8]THF, vide supra) as the pure, solvent-free Grignard reagent, but it could not be crystallized.

Crystallization of 1-(Bromomagnesio)-2-(2,5,8,11-tetraoxadodecyl)benzene (17). A solution of 17 (0.41 mmol) in THF (12.5 mL) was diluted with toluene (10 mL). Upon mixing, the Grignard reagent precipitated as a colorless oil. After 1 week, well-shaped crystals sticking to the glass wall were formed. They were washed by the addition of extra THF (0.5 mL) and isolated by decanting the solution. Titration of the solution indicated an almost complete crystallization (total base and Mg^{2+}, <0.03 mmol). Some crystals were analyzed by ^{1}H NMR spectroscopy (250 MHz, [D_8]THF, vide supra) and identified as pure 17, free of crystal solvent. The solubility of the crystals in THF was remarkably low; heating was necessary to dissolve them.

Crystallization of 1-(Bromomagnesio)-2-(2,5,8,11,14-pentaoxapentadecyl)benzene (18). A solution of 18 (0.80 mmol) in THF (10 mL) was diluted with n-hexane (10 mL) to give a clear solution. After standing at room temperature for several days, a microcrystalline precipitate was formed, which dissolved only partially upon heating (water bath). The mother liquor was decanted and analyzed by titration (total base and Mg^{2+}, 0.05 mmol); symmetrization had not occurred. The solid was dried by pumping (high vacuum) and analyzed by ^{1}H NMR spectroscopy (250 MHz, [D_8]THF, vide supra); THF was found not to be included in 18.

Crystallization of 1-(Bromomagnesio)-2,6-bis(2,5-dioxahexyl)benzene (19). Crystallization was tried from THF/n-hexane (1:1) and THF/toluene (1:10) at several concentrations and temperatures, but in all cases an oil precipitated.

Structure Determination and Refinement of 14–17. Crystal data and numerical details of the structure determinations are given in Table I. The crystals were mounted under nitrogen in a Lindemann glass capillary an transferred to an Enraf-Nonius CAD4F diffractometer for data collection. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections and were checked for the presence of higher lattice symmetry.[26] All crystals reflected rather poorly, the crystals of 14 showed broad reflection profiles, indicating a

(26) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

poor quality of these crystals. All data were collected with $\omega/2\theta$ scan mode. Data were corrected for Lp and for the observed linear decay of the reference reflections. Absorption correction was applied for 15 and 17 by using the DIFABS method;[27] redundant data were merged into a unique data set. The structures were solved with either standard Patterson methods (15, 16), or with direct methods (14, 17) (SHELXS86)[28] and subsequent difference Fourier syntheses. Refinement on F was carried out by full-matrix least-squares techniques. H atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carried atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, H atoms were refined with one common isotropic thermal parameter. Weights were introduced in the final refinement cycles. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables II–V.

Neutral-atom scattering factors were taken from Cromer and Mann[29] and corrected for anomalous dispersion.[30] All calculations were performed with SHELX76[31] and the EUCLID package (geometrical calculations and illustrations)[32] on a MicroVAX cluster.

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Supplementary Material Available: Tables of anisotropic thermal parameters, torsion angles, all H atom parameters, bond lengths, and bond angles (13 pages); listings of observed and calculated structure factor amplitudes (95 pages). Ordering information is given on any current masthead page.

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Synthesis and Study of Imidoalkyl Complexes of Tungsten(VI): Application of ^{14}N NMR Spectroscopy

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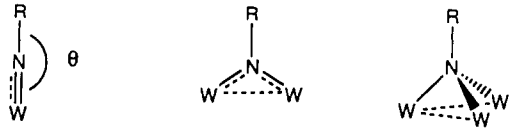
Complexes of the type $W(NR)(CH_2Bu^t)_3X$ have been synthetised by reaction of $WOCl_4$ with RNCO, followed by alkylation with dineopentylmagnesium. The structures of these complexes and their adducts with Lewis acids are proposed. In particular, the use of ^{14}N NMR spectroscopy indicates that the imido–tungsten linkage is linear in both the parent complexes and the adducts, where the binding of the Lewis acid is to the halide and not to the imido ligand.

Introduction

The imido ligand, RN, is proving to be of continuing interest in the chemistry of transition metals in high oxidation states.[1] It possesses properties similar in bonding and reactivity to those of the isoelectronic oxo ligand, but variations in the R group can allow control of the electronic and steric properties that are not available to the oxo group.

The bonding mode of the imido ligand to transition metals is generally one of three types:[1a]



Further, in the monodentate mode, linear coordination ($\theta \approx 180°$) is generally found although bent forms ($\theta \neq 180°$) have also been shown to exist.[2] One difficulty in trying to establish the detailed structures of imido complexes is the lack of a simple physical method to distinguish between these bonding forms. For example, the use of infrared spectroscopy to identify the metal–nitrogen mode and thereby the type of structure has not proved unambiguous.

Some time ago, we were drawn to this problem during our studies on catalysts for the metathesis of olefins. It was observed that oxo–alkyl complexes of W(VI), e.g. $WO(CH_2Bu^t)_3X$ (X = halide), were active for the metathesis of olefins only when strong Lewis acids such as AlX_3 were added.[3] We showed that the initial species formed was the adduct $W(OAlX_3)(CH_2Bu^t)_3X$ where the Lewis acid is bound via the oxo ligand.[4] This research was extended to the synthesis and study of the corresponding imido complexes $W(NR)(CH_2Bu^t)_3X$ (R = Me, Pr^i, Bu^t, 2,6-$(Pr^i)_2C_6H_3$), which we found were active also in the

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