

Unusual Metalation and Halogen-Metal Exchange Reactions between 1,3-Xylyl Crown Ethers and Organomagnesium Reagents. X-ray Structure of 2-[(*p*-*tert*-Butylphenyl)magnesio]-1,3-xylylene-18-crown-5

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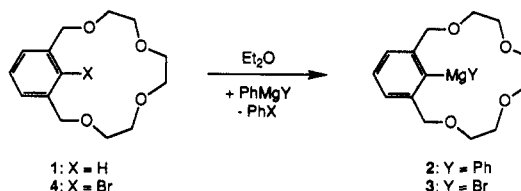
The scope of the surprising exchange reactions between 1,3-xylyl crown ethers and organomagnesium reagents was investigated. Halogen-metal exchange was found for both 2-bromo-1,3-xylylene-15-crown-4 (4) and 2-bromo-1,3-xylylene-18-crown-5 (14) as substrates, while metalation occurred with 1,3-xylylene-15-crown-4 (1). Attempts with other substrates failed, which demonstrates the highly specific structural requirements of these reactions. They are proposed to proceed after initial formation of a 1:1 complex of crown ether and organometallic reagent. Support was obtained by the metalation of 5-bromo-1,3-xylylene-15-crown-4 (17) at the intraannular 2-position. Product formation was investigated by ^1H NMR spectroscopy and by derivatization. An X-ray structure determination of the metalation product 2-[(*p*-*tert*-butylphenyl)magnesio]-1,3-xylylene-18-crown-5 (25) was carried out: space group $P\bar{1}$ (triclinic), $a = 10.297$ (1) Å, $b = 10.825$ (1) Å, $c = 12.476$ (2) Å, $\alpha = 109.27$ (1)°, $\beta = 94.43$ (1)°, $\gamma = 106.74$ (1)°, $V = 1234.0$ (3) Å³, $Z = 2$, $R = 0.052$. Reactions of 2-(phenylmagnesio)-1,3-xylylene-15-crown-4 (2) with 9-phenylfluorene or with diphenylzinc suggest the formation of a stable organomagnesium cation of the type RMg^+ (32, 33, 34; R = 1,3-xylylene-15-crown-4-2-yl). Metal-halogen exchange is not restricted to organomagnesiums as illustrated by the reaction of diphenylcalcium with 14, which gave 2-(phenylcalcio)-1,3-xylylene-18-crown-5 (35).

Introduction

In a preliminary communication,¹ we reported the reactions of 1,3-xylyl crown ethers with diphenylmagnesium and phenylmagnesium bromide. Upon heating of 1,3-xylylene-15-crown-4 (1) with these reagents in an apolar solvent, metalation occurred at the xylyl 2-position under the formation of 2-(phenylmagnesio)-1,3-xylylene-15-crown-4 (2) and 2-(bromomagnesio)-1,3-xylylene-15-crown-4 (3), respectively (Scheme I). Analogous halogen-metal exchange reactions were found to proceed even more easily with 2-bromo-1,3-xylylene-15-crown-5 (4). Upon mixing of 4 with diphenylmagnesium in diethyl ether at room temperature, 2 was formed in quantitative yield within a few minutes; phenylmagnesium bromide reacted somewhat slower. No chemical transformation occurred with the larger macrocycle 1,3-xylylene-18-crown-4 (5); instead, a 1:1 complex 6 was formed with diphenylmagnesium and characterized by a crystal structure determination.² Even after prolonged heating in an apolar solvent, metalation of 6 was not observed.

Exchange reactions between a nonactivated hydrogen or a halogen atom and a metal are well-known for organolithium compounds³ but are quite unusual for organomagnesiums. Normally, these reactions occur not at all or only with low yield under rather drastic conditions. Only with relatively "acidic" hydrocarbons, metalations

Scheme I



have been observed.^{3,4} High yields were obtained in the reaction of acetylene and cyclopentadiene derivatives with Grignard compounds. Cyclopropenes can also be metalated, but the addition of the organomagnesium reagent to the C=C double bond is usually the preferred reaction mode.⁵ Another example is the metalation of polyhalogenated substrates like polyfluorinated or polychlorinated aromatics,⁶ which can be explained by the electron-withdrawing effect of the halogens. A few examples are known of ortho-metalation by organomagnesiums induced by intramolecularly coordinating groups; this type of reaction is of great synthetic value in preparative or-

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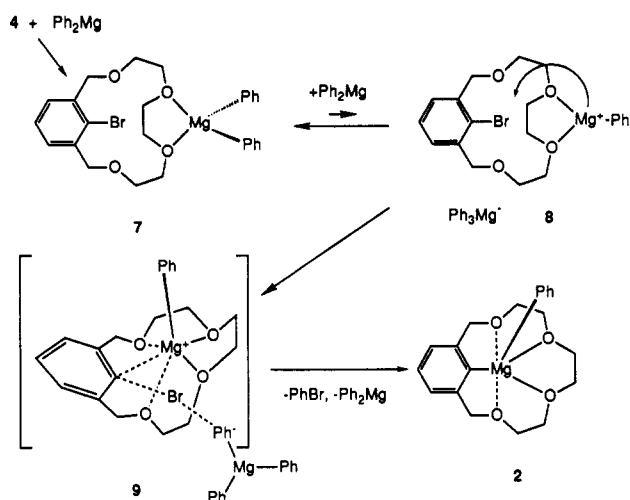
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Scheme II



ganolithium chemistry.⁷ Metalation of aryl ethers and aryl tertiary amines by organomagnesiums was feasible, though under vigorous conditions and in unsatisfactory yield.⁸ A specific case is the metalation of bis(trimethylsilyl)-*o*-pyridylmethane with *n*-butyl-*sec*-butylmagnesium,⁹ where both the acidity of the methyl hydrogen and the presence of an ortho-coordinating group play a role. Recently, ortho-magnesiation was reported using organomagnesium derivatives of 2,2,6,6-tetramethylpiperidine and diisopropylamine.¹⁰

Halogen-metal exchange reactions involving Grignard reagents and ordinary alkyl and aryl halides were extensively studied by Zakharkin et al.¹¹ Generally, the yield is low. The rate of exchange between an alkylmagnesium halide and alkyl or aryl halides appeared to depend on the solvating power of the solvent and on the polarizability of the halogen in the alkyl halide; the highest yields were found with the strongly coordinating solvent 1,2-dimethoxyethane and alkyl iodides as substrates. The extent of exchange is further influenced by the electronegativity of the organic group of the halide: electron-withdrawing groups facilitate the exchange reaction. This trend holds for both the metalation and the halogen-metal exchange reactions. Halogen derivatives of "acidic" hydrocarbons that are susceptible to a direct metalation are also suitable for a halogen-metal exchange reaction. Therefore, alkynyl halides, vinyl halides, and polyhalogenated substrates are candidates for a halogen-metal exchange.^{3,4,12} Similarly, an efficient exchange reaction was observed between halogenated pyridines and phenylmagnesium bromide.¹³

Of the exchange reactions discussed so far, none is comparable in ease and efficiency with those of 1,3-xylylene-15-crown-4 substrates.¹ In the present investigation, the scope of these reactions has been studied more ex-

tensively. Besides the crown ethers used earlier, other substrates were checked for exchange activity. The course of the (exchange) reactions was monitored with ^1H NMR spectroscopy to follow the progress of the reaction and the product formation. In some cases, the exchange product was isolated and used in consecutive reactions to investigate its reactivity. Supplementary to the structures of the crown-4 derivatives 2 and 3,^{1,14} the crystal structure of the crown-5 organomagnesium compound will be presented.

Our major goal was the confirmation of our earlier mechanistic proposals. Several factors responsible for the remarkable ease of the exchange reactions had been considered, as illustrated for the fastest of all reactions, the conversion of 4 with diphenylmagnesium to 2¹ (Scheme II). First, preorganization must be important: 4 as an ethylene glycol ether is predisposed to form an initial 1:1 complex 7 with the organometallic reagent. Subsequently, the reaction clearly has an "intramolecular" component. The coordinating power of the crown ether ring helps the heterolytic cleavage of one of the phenylmagnesium bonds by stabilizing the phenylmagnesium cation in 8, probably via all of the four crown ether oxygens (as indicated in the transition state 9). The heterolytic cleavage is further facilitated by a second molecule of diphenylmagnesium, which stabilizes the phenyl "anion" as a magnesate counterion. The formation of magnesate species from diorganomagnesium compounds and polyether ligands has been observed spectroscopically by Richey et al.^{15,16} Magnesate complexes from dialkylmagnesiums with cryptands were characterized by a crystal structure.¹⁵ The weaker chelating crown ethers did not generate solvation-separated ion pairs.¹⁶ Therefore, the magnesate species 8 must be present in a very low steady-state concentration only. The additional molecule of diphenylmagnesium needed for its formation may arise either directly from a second 7 or from the equilibrium between 7 and $\text{Ph}_2\text{Mg}(\text{Et}_2\text{O})_2$.

In the transition state 9, both an electrophilic and a nucleophilic component of the substitution reaction can be discerned; probably, both take place more or less simultaneously. The cationic magnesium is involved in an electrophilic attack on the aromatic xylyl 2-carbon; it is directed by the coordination with the crown ether ring. From the opposite side, the magnesate counterion attacks the bromine in a nucleophilic substitution process; a diarylbrominidane intermediate or transition state is postulated in analogy to the diphenyliodinidane anion observed by ^{13}C NMR spectroscopy by Reich et al. in the reaction of iodobenzene and phenyllithium in THF/HMPA.¹⁷ The postulate of the magnesate attack is necessitated by the fact that for steric reasons; it is impossible that both the magnesium and a phenyl group in 7 can reach the xylyl 2-carbon and the bromine simultaneously. Elimination of bromobenzene (and of diphenylmagnesium) rounds off the process leading to product 2. In the latter, magnesium presumably enjoys particularly favorable coordinative stabilization, which is undoubtedly one of the factors driving the reaction to completion.

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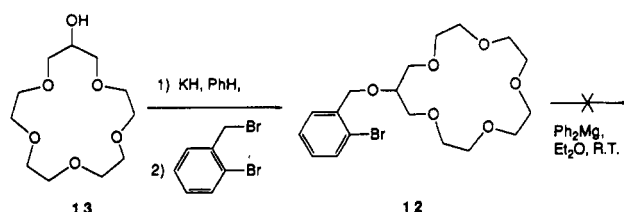
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Scheme III



Results and Discussion

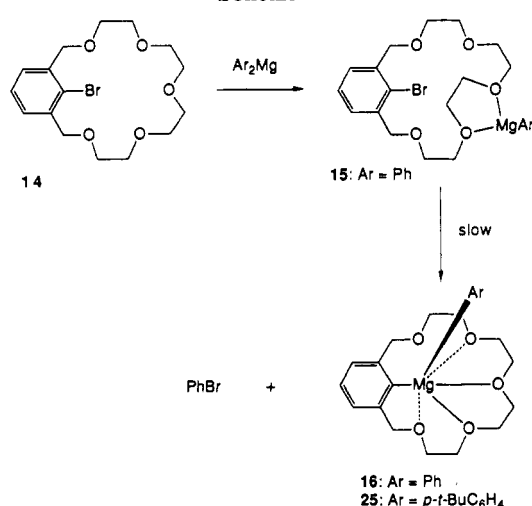
Scope of the Crown Ether Activation. From a mechanistic as well as preparative point of view, it was of interest to investigate the substrate selectivity of the newly found exchange reactions. Since especially the halogen-metal exchange between diphenylmagnesium and **4** occurred with remarkable ease, it seemed worthwhile to see if this reaction occurred also with other potentially activated substrates. However, halogen-metal exchange was found to be strictly limited to the 1,3-xylyl crown ether system; other aryl bromides failed to react. Thus, a mixture of diphenylmagnesium and the relatively simple substrates *p*-fluorobromobenzene (**10**) or 1,3-bis(methoxymethyl)benzene (**11**) remained unchanged during a period of several months at room temperature or on heating for several hours at 80 °C, as determined by ¹H NMR spectroscopy. The presence of a single electron-withdrawing fluorine group in **10** or of two coordinating and ortho-directing methoxymethyl groups in **11** is clearly not sufficient to induce the conversion.

Even a crown ether functionality incorporated into the substrate close to the site of reaction is not sufficient for the halogen-metal exchange to occur; this is illustrated by the behavior of **12**. Macrocycle **12** was obtained from **13**¹⁸ and *o*-bromobenzyl bromide with potassium hydride as a base (Scheme III). Substrate **12** gave no reaction with diphenylmagnesium. It is obvious that the activation of diphenylmagnesium by **12** must be as efficient, or more so, than that by **4**, but, apparently, this is as such not sufficient for the halogen-metal exchange to proceed; the ideal orientation of the polyether complex toward the carbon-bromine target as in **9** (Scheme II) seems to be at least equally important.

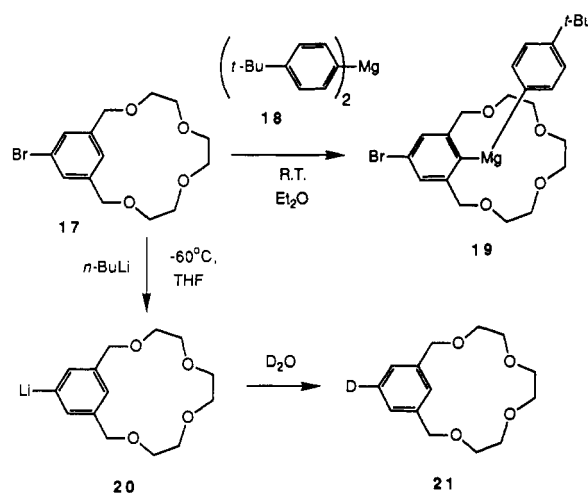
Additional evidence for an intramolecular reaction pathway was derived from the following experiments:

(1) The halogen-metal exchange reaction as observed between **4** and diphenylmagnesium also occurred with the larger crown ether 2-bromo-1,3-xylylene-18-crown-5 (**14**). Initially, the intermediate complex [**14**] $\cdot$ [Ph₂Mg] (**15**) precipitated after mixing the solutions of the two components; it was isolated as a colorless dry powder. When this precipitate was dissolved in benzene or toluene, a slow but quantitative conversion to 2-(phenylmagnesium)-1,3-xylylene-18-crown-5 (**16**) and bromobenzene (1:1) occurred as shown by ¹H NMR spectroscopy. A larger scale experiment yielded, in almost quantitative yield, crystalline **16**, the crown-5 homologue of **2**. The identity of **15** and **16** follows from their ¹H NMR spectral data (see Experimental Section). The halogen-metal exchange reaction with **14** probably proceeds by a mechanism analogous to that described for **4**, but in the case of **14**, the initially formed external complex **15** can be isolated due to its low solubility and slow conversion to the products. The slower

Scheme IV



Scheme V



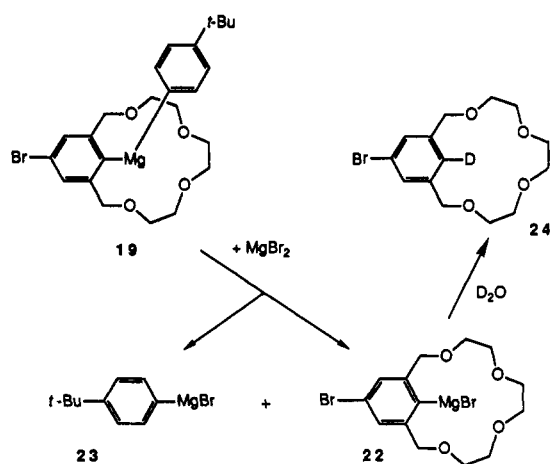
reaction rate is probably a consequence of the less ideal (=less symmetrical?) orientation in the complex corresponding to **9** (Scheme IV).

(2) No reaction occurred between diphenylmagnesium and either **4** or **14** in THF. The crown ethers cannot compete² with the more basic THF, which, moreover, is present in large excess. Consequently, the formation of the organomagnesium-crown ether complex **7** or **15**, respectively, as a necessary initial step, does not occur.

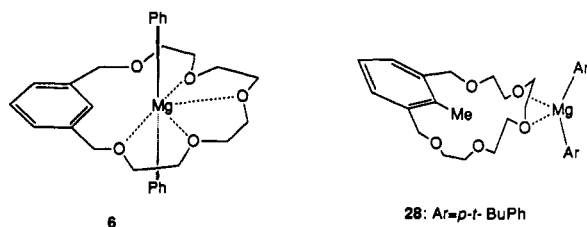
(3) A particular striking demonstration of the crown ether activation comes from the reaction between 5-bromo-1,3-xylylene-15-crown-4 (**17**) and bis(*p*-*tert*-butylphenyl)magnesium (**18**) in diethyl ether: it yielded 5-bromo-2-[(*p*-*tert*-butylphenyl)magnesium]-1,3-xylylene-15-crown-4 (**19**) as a colorless crystalline solid in nearly quantitative yield (Scheme V). Obviously, metalation at the 2-position of the crown ether is strongly preferred; halogen-metal exchange does not occur at all. Normally, e.g., in the couple **4**/1 or in organolithium chemistry, halogen-metal exchange proceeds under equal conditions much faster than metalation. Indeed, the reaction of **17** with *n*-butyllithium (at low temperature) in THF selectively yielded 5-lithio-1,3-xylylene-15-crown-4 (**20**) via halogen-metal exchange; after quenching with D₂O, the deuterated product 1,3-xylylene-15-crown-4-5-*d* (**21**) was obtained in quantitative yield. Not surprisingly, and contrary to the organomagnesium, the organolithium is not specifically complexed and activated by the crown ether and therefore follows the expected trend. The extreme

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Scheme VI



Scheme VII



reversal of the "natural" reactivity order for the combination 17/18 illustrates the dramatic effects of intramolecular coordination by a 1,3-xylylene-15-crown-4 ligand. It is all the more surprising in view of the relatively small energetic difference between "side on" and "rotaxane" structures and the complete displacement of the crown ethers in THF solution.²

The intraannular position of the arylmagnesium substituent in 19 was proved with ^1H NMR spectroscopy in $\text{THF}-d_8$ and toluene- d_8 , e.g., by comparison to typical chemical shifts with those of 2 and by the nonequivalence of the xylyl CH_2 protons; COSY and NOESY 2D spectra confirmed the assignments. By addition of a THF solution of magnesium bromide to a THF solution of 19, the latter was completely converted to the two Grignard compounds 5-bromo-2-(bromomagnesio)-1,3-xylylene-15-crown-4 (22) and (*p*-*tert*-butylphenyl)magnesium bromide (23) (Scheme VI). This process was possibly facilitated by the precipitation of 22, which occurred within several minutes, while 23 remained in solution. In spite of its low solubility, a ^1H NMR spectrum, by which 22 ($\text{THF}-d_8$) could be identified, was obtained. Reaction of 22 with D_2O gave the expected deuterio compound 5-bromo-1,3-xylylene-15-crown-4-2-*d* (24) in quantitative yield.

As reported previously,² the unsubstituted crown ether 5 shows a behavior quite different both from that of its 2-bromo derivative 14 and of its smaller homologue 1: instead of undergoing metalation at position 2, 5 forms a rotaxane complex 6 (Scheme VII). Two factors may be responsible. In the first place, the inherently lower rate of metalation versus halogen-metal exchange (vide supra) is undoubtedly important. We feel, however, that a second factor must be even more important, namely, the tendency of the organomagnesium species to attain a polycordinated state (=rotaxane structure) and the impossibility of achieving this in 1 or 14, because the cavity of these ligands is too small to accommodate a magnesium that is not covalently bonded to the 2-position of the xylyl group. Another important implication is the following: the rotaxane structure, plausible as it may seem in view of the

Table I. Schematic Representation of the Reaction of Substrates 2-X-1,3-xylylene-(3*n* + 3)-crown-*n* with Diphenylmagnesium and Phenylmagnesium Bromide

substrate	X	<i>n</i>	Ph_2Mg	PhMgBr
1	H	4	metalation (slow)	metalation (slow)
4	Br	4	Br-Mg exchange (fast)	Br-Mg exchange
5	H	5	rotaxane complex	(side on?) complex
14	Br	5	Br-Mg exchange	(side on?) complex (Br-Mg exchange very slow)

close vicinity of magnesium and C(2) of the xylyl unit, is not responsible for the metalation reaction; this indirectly supports the course of events depicted in Scheme II.

The exchange product 16 is of interest as one of the very few examples of a stable "unsymmetrical" diorganylmagnesium derivative, in which the magnesium atom is substituted by two different organic groups, such as *n*-butyl-*sec*-butylmagnesium⁹ and 3.¹ A crystal structure determination would therefore be highly desirable. The coordination of the central magnesium atom in 16 will certainly be different from those of the crown-4 organomagnesium derivatives 2 and 3.^{1,14} Unfortunately, only low-quality crystals of 16 were isolated from toluene or benzene. For that reason, the ^1H NMR spectrum of 16 in toluene- d_8 was subjected to a detailed analysis, even though it was rather complicated. The CH_2 signals were a broad, complex multiplet consisting of two ABCD systems (*two* different ethylene units) and an AB system (*one* aryl CH_2). This suggests that, in solution, the structure is symmetrical with respect to a plane through aryl C(2), aryl C(5), and the central oxygen atom but that the plane of the crown ether is not a plane of symmetry. The initial interpretation of the ^1H NMR spectrum was confirmed by COSY NMR spectroscopy; a spectrum simulation yielded values for the shifts and coupling constants. By means of NOESY spectroscopy, some additional through space couplings were found, which facilitated the assignment of the signals (see Experimental Section). The structure assignment is endorsed by the crystal structure of the related 25 (vide infra). The ^1H NMR spectrum of 16 in $\text{THF}-d_8$ showed relatively simple C_2H_4 multiplets and a singlet for the aryl CH_2 hydrogens. This is indicative of a more flexible or dynamic system; exchange of phenyl groups via magnesate anions may be involved.

When 14 was treated with phenylmagnesium bromide, halogen-metal exchange could hardly be observed. An amorphous insoluble adduct of 1:1 stoichiometry was isolated, even on heating this adduct in toluene to 100 °C, only a minute amount of halogen-metal exchange product could be detected by quenching with D_2O . In Table I, the results of the reactions between crown ethers 1, 4, 5, or 14 and diphenylmagnesium or phenylmagnesium bromide are summarized. Whenever a reaction did occur, complete conversion of the reactants was found. The reactions were monitored with ^1H NMR spectroscopy after dissolving the reactants in a deuterated solvent. The reaction rates differ widely; especially the metalation of 1 was very slow (several days). Precise kinetic investigations by NMR spectroscopy were not feasible, due to low solubilities and to the presence of diethyl ether originating from the phenylmagnesium reagents. Nevertheless, the following trends can be deduced:

(1) Halogen-metal exchange at the xylyl 2-position is faster than the analogous metalation (vide supra).

(2) The 1,3-xylylene-15-crown-4 derivatives react faster than their crown-5 analogues; the "catalysis" by the small crown ether is clearly more efficient. In a reaction pathway as depicted in Scheme II, a larger and more flexible crown

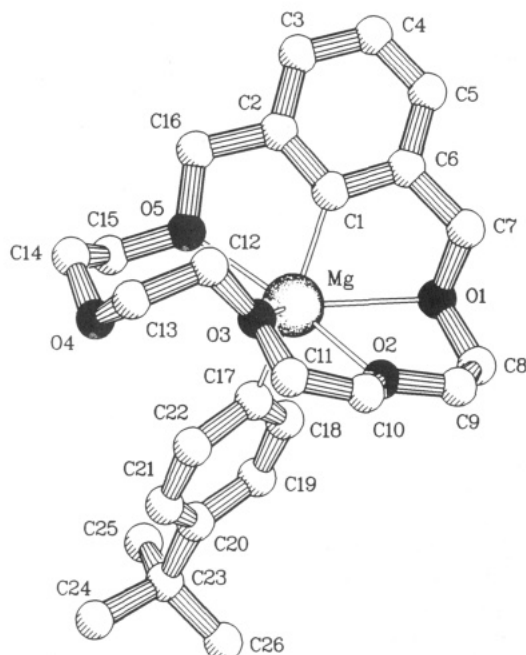


Figure 1. PLUTON drawing for compound **25**. Hydrogen atoms not shown.

ether ring is probably less effective in inducing the magnesium center to perform an electrophilic attack on the aryl C(2) carbon atom; this may in part be due to the nonsymmetrical coordination of magnesium to oxygens 2 and 3, as observed in the corresponding organozinc structures.¹⁹

(3) Reactions involving diphenylmagnesium are generally faster than those with phenylmagnesium bromide. This might be attributed to the formation of a less reactive, halide-containing magnesate species (Scheme II: $\text{Ar}_{3-n}\text{MgX}_n^-$ instead of Ar_3Mg^+), which is less reactive in attacking the substituent at the xyllyl 2-position (H or Br).

Crystal Structure of 25. Since a structure determination of **16** was not possible, its *tert*-butyl-substituted derivative 2-[(*p*-*tert*-butylphenyl)magnesium]-1,3-xylylene-18-crown-5 (**25**) was synthesized (Scheme IV). It is reasonable to assume that the *p*-*tert*-butyl group in the periphery of the molecule does hardly influence its chemical properties and (crystal) structure. From a dilute solution of equimolar amounts of **14** and **18** in diethyl ether, **25** precipitated as a finely divided crystalline solid. The reaction proceeded slowly but completely and without formation of any byproducts. Crystals suitable for an X-ray structure determination were obtained by crystallization from THF. Although characterization of **25** by ^1H NMR in THF- d_8 or toluene- d_8 was hampered by its low solubility, the absence of crystal solvent could be established. As expected, its ^1H NMR spectrum closely resembles that of **16**. An X-ray crystal structure determination confirmed that **25** is one of the few structurally characterized unsymmetrical diarylmagnesium compounds (Figure 1). The compound is completely saturated by intramolecular coordination, but only three of the five crown ether oxygen atoms are involved in the coordination process. The interaction of O(1) with magnesium is extremely weak (Mg–O(1) 2.713 (4) Å), while O(4) has no interaction at all (Mg–O(4) 3.946 (4) Å). The crown ether ring in **25** is folded around the metal atom and has a conformation that is completely different from that of the free crown ether²⁰

Table II. Bond Distances (Å) and Bond Angles (deg) for **25**

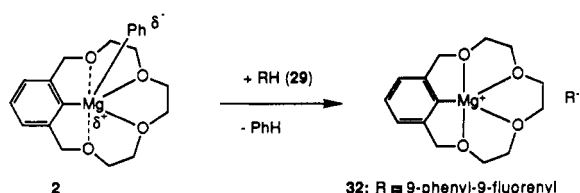
Mg–O(1)	2.713 (4)	O(4)–C(14)	1.412 (6)	C(12)–C(13)	1.507 (6)
Mg–O(2)	2.337 (4)	O(5)–C(15)	1.433 (5)	C(14)–C(15)	1.500 (6)
Mg–O(3)	2.146 (4)	O(5)–C(16)	1.427 (4)	C(17)–C(18)	1.402 (6)
Mg–O(5)	2.317 (3)	C(1)–C(2)	1.398 (5)	C(17)–C(22)	1.393 (7)
Mg–C(1)	2.128 (4)	C(1)–C(6)	1.405 (6)	C(18)–C(19)	1.379 (6)
Mg–C(17)	2.154 (4)	C(2)–C(3)	1.388 (6)	C(19)–C(20)	1.384 (7)
O(1)–C(7)	1.417 (6)	C(2)–C(16)	1.518 (6)	C(20)–C(21)	1.388 (6)
O(1)–C(8)	1.426 (6)	C(3)–C(4)	1.379 (8)	C(20)–C(23)	1.528 (7)
O(2)–C(9)	1.40 (2)	C(4)–C(5)	1.380 (7)	C(21)–C(22)	1.384 (6)
O(2)–C(10)	1.38 (2)	C(5)–C(6)	1.384 (7)	C(23)–C(24)	1.507 (8)
O(3)–C(11)	1.411 (6)	C(6)–C(7)	1.510 (7)	C(23)–C(25)	1.539 (8)
O(3)–C(12)	1.435 (5)	C(8)–C(9)	1.38 (2)	C(23)–C(26)	1.513 (8)
O(4)–C(13)	1.406 (6)	C(10)–C(11)	1.39 (2)		
O(1)–Mg–O(2)	62.9 (1)	C(3)–C(2)–C(16)	117.5 (4)		
O(1)–Mg–O(3)	126.3 (1)	C(2)–C(3)–C(4)	119.0 (4)		
O(1)–Mg–O(5)	135.9 (1)	C(3)–C(4)–C(5)	119.9 (4)		
O(1)–Mg–C(1)	67.7 (1)	C(4)–C(5)–C(6)	119.5 (5)		
O(1)–Mg–C(17)	99.7 (2)	C(1)–C(6)–C(5)	123.3 (4)		
O(2)–Mg–O(3)	71.0 (1)	C(1)–C(6)–C(7)	117.5 (4)		
O(2)–Mg–O(5)	156.8 (1)	C(5)–C(6)–C(7)	119.1 (4)		
O(2)–Mg–C(1)	111.7 (2)	O(1)–C(7)–C(6)	109.7 (4)		
O(2)–Mg–C(17)	93.7 (2)	O(1)–C(8)–C(9)	112.2 (9)		
O(3)–Mg–O(5)	85.7 (1)	O(2)–C(9)–C(8)	115 (1)		
O(3)–Mg–C(1)	108.6 (2)	O(2)–C(10)–C(11)	112 (1)		
O(3)–Mg–C(17)	109.7 (2)	O(3)–C(11)–C(10)	115.2 (9)		
O(5)–Mg–C(1)	74.0 (1)	O(3)–C(12)–C(13)	111.6 (3)		
O(5)–Mg–C(17)	95.3 (2)	O(4)–C(13)–C(12)	114.5 (4)		
C(1)–Mg–C(17)	139.3 (2)	O(4)–C(14)–C(15)	111.7 (4)		
Mg–O(1)–C(7)	105.0 (3)	O(5)–C(16)–C(2)	109.9 (3)		
Mg–O(1)–C(8)	109.8 (3)	O(5)–C(15)–C(14)	112.4 (4)		
C(7)–O(1)–C(8)	114.5 (4)	Mg–C(17)–C(18)	122.8 (3)		
Mg–O(2)–C(9)	126.6 (7)	Mg–C(17)–C(22)	124.8 (3)		
Mg–O(2)–C(10)	115.6 (9)	C(18)–C(17)–C(22)	112.3 (4)		
C(9)–O(2)–C(10)	113 (1)	C(17)–C(18)–C(19)	123.6 (4)		
Mg–O(3)–C(11)	117.5 (3)	C(18)–C(19)–C(20)	122.7 (4)		
Mg–O(3)–C(12)	126.2 (2)	C(19)–C(20)–C(21)	115.3 (4)		
C(11)–O(3)–C(12)	115.6 (4)	C(19)–C(20)–C(23)	120.7 (4)		
C(13)–O(4)–C(14)	115.5 (4)	C(21)–C(20)–C(23)	124.0 (5)		
Mg–O(5)–C(15)	129.4 (2)	C(20)–C(21)–C(22)	121.2 (5)		
Mg–O(5)–C(16)	117.2 (3)	C(17)–C(22)–C(21)	124.9 (4)		
C(15)–O(5)–C(16)	113.4 (3)	C(20)–C(23)–C(24)	112.9 (5)		
Mg–C(1)–C(2)	119.9 (3)	C(20)–C(23)–C(25)	109.6 (4)		
Mg–C(1)–C(6)	125.8 (3)	C(20)–C(23)–C(26)	110.7 (5)		
C(2)–C(1)–C(6)	114.2 (4)	C(24)–C(23)–C(25)	106.7 (5)		
C(1)–C(2)–C(3)	123.8 (4)	C(24)–C(23)–C(26)	109.7 (5)		
C(1)–C(2)–C(16)	118.7 (3)	C(25)–C(23)–C(26)	107.1 (5)		

or of the “rotaxane” complex.² Obviously, the cavity of the 1,3-xylylene-18-crown-5 ligand is too large for an efficient complexation of the intraannular organomagnesium group. The Mg–O coordinative bonds may also be weakened by conformational ring strain of the crown ether ligand. The crystal structures of 1,3-xylylene-15-crown-4 compounds **2** and **3** (described in previous communications^{1,14}) show that in these compounds, the organomagnesium unit fits nicely inside the crown ether cavity and is efficiently surrounded by the crown ether ring.

Bond distances and angles for **25** are given in Table II. The crown ring adopts two conformations in the crystal, mainly affecting the positions of C(9) and C(10). Only the major disorder form (site occupation factor = 0.55 (2)) is discussed here and shown in Figure 1. The geometry around the central magnesium atom is quite irregular; it might be described as intermediate between distorted pseudo trigonal bipyramidal (TBP) or octahedral, depending on whether or not one includes O(1). Undoubtedly, the conformational restrictions of the crown ether ring impose this irregular behavior. In the TBP description, the angle between the axial oxygens (O(2)–Mg–O(5) 156.8 (1)°) and those inside the five-membered coordinative rings (C(1)–Mg–O(5) 74.0 (1)°, O(2)–Mg–O(3) 71.0 (1)°), are much smaller than the ideal values. In the equatorial plane, the C–Mg–C angle is enlarged (139.3 (2)°) leading to smaller C–Mg–O angles (C(1)–Mg–O(3) 108.6 (2)°, C(17)–Mg–O(3) 109.7 (2)°). The Mg–C bond lengths are different, the xyllyl–Mg bond being shorter (Mg–C(1) 2.128 (4) Å) than the aryl–Mg bond (Mg–C(17) 2.154 (4) Å). The equatorial Mg–O(3) bond is much shorter (2.146

(19) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. J. *Organomet. Chem.*, in press.

Scheme VIII



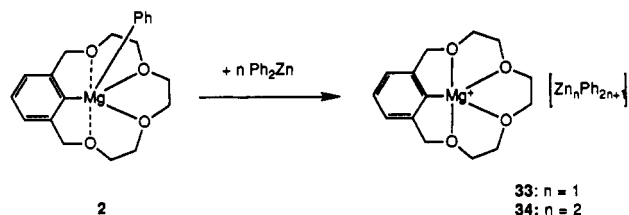
(4) Å) than the axial ones (Mg–O(2) 2.337 (4) Å, Mg–O(5) 2.317 (3) Å).

Miscellaneous Complexes. In order to investigate the reactivity of 1,3-xylyl crown ethers toward other organomagnesium reagents, the halogen-metal exchange reaction between the most reactive substrate 4 and diethylmagnesium was studied. After mixing the reagents in diethyl ether, 2-(ethylmagnesium)-1,3-xylylene-15-crown-4 (26) separated quantitatively as colorless crystals within 24 h; its identity was proven by ^1H NMR spectroscopy in THF-d_8 and a titration on "total base" and Mg^{2+} . Since a stable mixed alkyl-arylmagnesium has so far not been described, a crystal structure determination of 26 would be highly desirable. Unfortunately, the crystals pulverized after decantation and removal of the remaining solvent by pumping, and other solvents gave no success either.

Treatment of 2-methyl-1,3-xylylene-18-crown-5 (27) with the diarylmagnesium reagent 18 did not yield a metalation product, even at elevated temperatures. Instead, a complex $[\text{27}] \cdot [\text{18}] \cdot [\text{toluene}]_4$ (28) was isolated; it could be crystallized from toluene and characterized by ^1H NMR spectroscopy. The xylyl crown ether is clearly not capable of inducing attack on the intraannular methyl group, which would have led to an unsymmetrical aryl-benzylmagnesium compound. A structure determination of 28 was not possible because of easy loss of crystal solvent. Recrystallization from benzene yielded the derivative $[\text{27}] \cdot [\text{18}] \cdot [\text{benzene}]_4$ (28a), exhibiting analogous properties as 28. The cavity of 28 is relatively small and will probably be completely filled by the intraannular methyl group.²⁰ Therefore, 28 cannot assume a "rotaxane" structure and probably is a "side-on" complex as shown in Scheme VII.²

Reactions of 2. The reactivity of the crown ether diarylmagnesium 2 was investigated as due to the efficient encapsulation of the central magnesium by the crown ether oxygens, a relatively low reactivity was conceivable. On the other hand, one of the Mg–C bonds might be weakened and hence susceptible to dissociation. This tendency might be even more pronounced when the phenyl group in 2 is replaced by a stable, delocalized anion. Therefore, 2 was reacted with the "acidic hydrocarbons" 9-phenylfluorene (29), pentamethylcyclopentadiene (30), and triphenylmethane (31), but its reactivity was very low. Conversion was achieved with the most acidic substrate 29 only (in THF, at room temperature). With the others, no reactions took place even at elevated temperatures, although normally organomagnesium reagents are capable to metalate hydrocarbons such as 29 and 30.⁴ Thus, there is no indication for an increased reactivity of the Mg–phenyl bond in 2; this is in line with its normal Mg–phenyl bond length (2.154 (4) Å).¹ The orange-red crystalline product from the reaction of 2 and 29 is probably [2-magnesio-1,3-xylylene-15-crown-4 9-phenylfluorenyl] (32) (Scheme VIII); it was isolated in almost quantitative yield. Hydrolysis of 32 yielded a colorless oil, which by ^1H NMR spectroscopy was shown to be a 1:1 mixture of crown ether 1 and 29. In the ^1H NMR spectrum (THF-d_8) of 32, the signals

Scheme IX



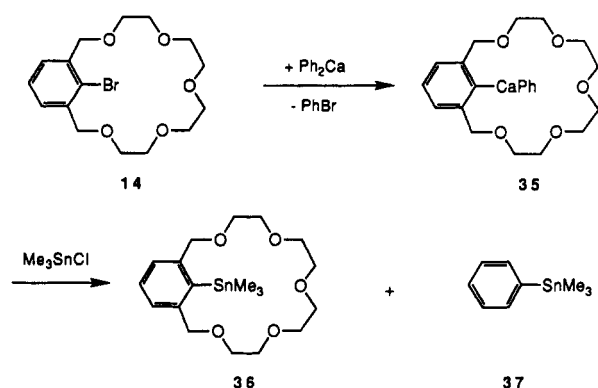
of the aromatic 9-phenylfluorenyl anion were considerably broadened. The signals of the crown ether ethylene groups were clearly identified; they showed large upfield shifts. In the ^{13}C NMR spectrum of 32 (THF-d_8 , 80 °C), most signals could not be observed due to signal broadening; only the xylyl C and xylyl CH_2 signals were identified. Significantly, the ^1H NMR spectrum of 32 showed the protons to give rise to singlets, which indicates C_{2v} symmetry of the crown ether moiety. This can be rationalized by assigning to 32 the structure of a solvent-separated ion pair (Scheme VIII), although rapid equilibria involving unsymmetrical contact ion pairs cannot be excluded. Unfortunately, in spite of several attempts, it was not possible to grow single crystals of 32 suitable for an X-ray structure determination.

In another attempt to obtain the solvent-separated cation 2-magnesio-1,3-xylylene-15-crown-4, we investigated the reaction of 2 with diphenylzinc. We envisaged the formation of an ate complex with triphenylzincate as counterion as shown in Scheme IX; comparable homometallic complex formation has been observed in organomagnesium chemistry.^{15,16} The reaction was performed by stirring a solution of diphenylzinc in THF with an excess of solid 2, which resulted in partial solution of the poorly soluble 2. Analysis of the resulting solution by ^1H NMR spectroscopy showed the formation of a complex 2-magnesio-1,3-xylylene-15-crown-4 triphenylzincate (33), besides the presence of some 2. The spectra of 2 and 33 are strongly different, both in the crown ether and in the phenyl signals. The three phenyl groups in 33 are equivalent; the phenyl/crown ether integral ratio was 3:1. The characteristic AB pattern for the xylyl CH_2 protons of 2 is transformed into a singlet in 33, suggesting that the phenyl group is removed from the magnesium, which, as a cation, occupies a (time-averaged?) symmetrical position in the crown ether cavity. In spite of several attempts, isolation of crystalline 33 was not possible. Upon addition of an excess of diphenylzinc, the signals of 2 in the ^1H NMR spectrum disappeared and the ratio phenyl/crown ether increased, while only minor changes were found in the shifts of the crown ether signals (<0.04 ppm). Probably, the additional amount of diphenylzinc is used in part for the formation of higher zincate anions such as Ph_5Zn_2^- . The formation of these species was also suggested by the isolation of solid [2-magnesio-1,3-xylylene-15-crown-4]· $[\text{Ph}_5\text{Zn}_2]$ (34), though this was not well reproducible. This adduct crystallized from a THF/diethyl ether solution and was characterized with ^1H NMR spectroscopy in THF-d_8 ; the spectrum was practically identical with that of 33 with the exception of more shielded ortho protons of the phenyl groups ($\Delta\delta = -0.11$ ppm) and the expected integral ratios.

An Organocalcium Complex (35). The halogen-metal exchange and metalation reactions may open an interesting synthetic access to a variety of intraannularly substituted derivatives of 1,3-xylyl crown ethers, as the organomagnesium function inside a 1,3-xylyl crown ether is easily converted to other substituents. Alternatively, the application of organometallic reagents of other electrophilic metals instead of magnesium should, in principle, allow

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Scheme X



the direct introduction of such organometallic functions inside the crown ether ring via an exchange reaction. To illustrate the feasibility of this approach, the halogen-metal exchange reaction between 14 and diphenylcalcium in diethyl ether was performed. The expected products 2-(phenylcalcio)-1,3-xylylene-18-crown-5 (35) and bromobenzene were obtained in almost quantitative yield (Scheme X). The identity of 35 follows from the reaction with trimethyltin chloride, which yielded 2-(trimethylstannyl)-1,3-xylylene-18-crown-5 (36)¹⁴ and phenyltrimethyltin (37). Unfortunately, crystallization of 35 for a X-ray crystal structure determination was unsuccessful: the solubility of 35 in diethyl ether was insufficient, and decomposition took place when THF-d_8 was tried. Analogous reactions with other organometallics are under investigation.

Experimental Section

All manipulations involving organomagnesium compounds were carried out in fully sealed glassware, using standard high-vacuum techniques. Solvents were dried by distillation from liquid Na/K alloy after predrying on NaOH. Amounts of "total base" and Mg^{2+} in organometallic compounds were determined after hydrolysis of a sample by titration with HCl and EDTA, respectively. NMR spectra were measured on a Bruker WH 90 (^1H NMR, 90 MHz), a Bruker WM 250 (^1H NMR, 250 MHz; ^{13}C NMR, 62.89 MHz), or a Bruker SML 400 (^1H NMR, 400 MHz, NOESY) spectrometer. GC/MS analyses were performed on a HP 5890 GC/5970 MS combination, operating at 70 eV and equipped with a Chrompack CP Sil 19CB 51 m/0.21 mm column. The starting materials 1-bromo-4-*tert*-butylbenzene (Aldrich), 3,5-dimethylaniline (Merck), 2,6-dimethylaniline (Janssen), 1,3-bis(bromomethyl)benzene (Janssen), triethylene glycol (Merck), tetraethylene glycol (Merck), sodium hydride (Janssen), potassium hydride (Janssen), mercuric bromide (Merck, z.a.), and diphenylmercury (Merck) were commercially available. Elemental analyses were carried out at the TNO Institute for Applied Chemistry and Elemental Analysis, Zeist, The Netherlands.

Synthesis of 1,3-Xylyl Crown Ethers. The 1,3-xylyl crown ethers 1, 4, 5, and 14 were known; they were synthesized from the appropriate oligoethylene glycol and (substituted) bis(bromomethyl)benzenes in the presence of potassium hydride in THF.^{21,22} A typical experimental procedure for the case of 1 is given below. 2-Bromo-1,3-bis(bromomethyl)benzene was obtained from 2,6-dimethylaniline via a Gattermann reaction, followed by direct photolytic bromination.²³⁻²⁵ Since 2-bromo-1,3-xylylene-

15-crown-4 (4) and 2-bromo-1,3-xylylene-18-crown-5 (14) are crystalline solids, their purification was easily achieved by repeated crystallization from diethyl ether at -20°C (4, mp 44°C ; 14, mp 42°C). All purified products were characterized by ^1H and ^{13}C NMR and GC/MS; the obtained spectral data were in accordance with those reported.^{26,27}

5-Bromo-1,3-xylylene-15-crown-4 (17). Crown ether 17 was obtained in a three-step procedure in analogy to its structural isomer 4,^{14,22} starting from 3,5-dimethylaniline. Crude 17 (brown oil) was purified by column chromatography (Al_2O_3 , activity II-III), to separate the crown ether from polymeric material. During the elution, the eluent was gradually changed in 10% increments from pure petroleum ether $40-60^\circ\text{C}$ to pure THF. The fractions containing 17 were combined and after removal of the solvent, the residue was recrystallized several times from Et_2O /pentane at -20°C to give colorless crystals, mp 52°C (30% yield relative to 1-bromo-3,5-bis(bromomethyl)benzene).

17: ^1H NMR spectrum (CDCl_3 , 250 MHz, ref $\text{CHCl}_3 = 7.27$ ppm) δ 3.71–3.72 (m, 12 H, C_2H_4), 4.596, 4.598 (m, AB, 4 H, xylyl CH_2), 7.20 (s, br, 2 H, xylyl $\text{H}(4,6)$), 7.96 (s, br, 1 H, xylyl $\text{H}(2)$); ^{13}C NMR spectrum (CDCl_3 , 62.89 MHz, ref $\text{CDCl}_3 = 77.0$ ppm) δ 69.7 (t, $^1J(\text{C-H}) = 141$ Hz, 2 C, C_2H_4), 70.1 (t, $^1J(\text{C-H}) = 141$ Hz, 2 C, C_2H_4), 70.5 (t, $^1J(\text{C-H}) = 141$ Hz, 2 C, C_2H_4), 71.3 (t, $^1J(\text{C-H}) = 142$ Hz, 2 C, xylyl CH_2), 121.2 (s, 1 C, xylyl C(5)), 124.7 (d, $^1J(\text{C-H}) = 164$ Hz, 1 C, xylyl C(2)), 128.3 (d, $^1J(\text{C-H}) = 165$ Hz, 2 C, xylyl C(4,6)), 141.5 (s, 2 C, xylyl C(1,3)); GC/MS, m/z (rel intensity) 330 (M^+ , 2), 182 (27, $\text{C}_6\text{H}_7\text{Br}$), 133 (32, $\text{C}_6\text{H}_{13}\text{O}_3$), 103 (29), 89 (53), 77 (25), 45 (100).

Synthesis of Diarylmagnesium Compounds. Diphenylmagnesium and bis(*p*-*tert*-butylphenyl)magnesium (18) were prepared from diphenylmercury and bis(*p*-*tert*-butylphenyl)mercury, respectively. In a fully sealed glass apparatus, the diarylmercury (20 mmol) was stirred with magnesium (2.4 g, 100 mmol) in diethyl ether (200 mL) for 2–3 weeks. After settling of the magnesium amalgam, the clear solution was decanted into a second vessel and, after hydrolysis, titrated to verify complete conversion of the starting material (total base: $\text{Mg}^{2+} = 2:1$). In some cases of incomplete reaction, stirring was continued with a fresh portion of magnesium metal (2.4 g, 100 mmol) for another 1–2 weeks.

Preparation of Magnesium Bromide. In a fully sealed glass apparatus, mercuric bromide (18 mmol, 6.49 g) was stirred with an excess of magnesium metal (100 mmol, 2.4 g) in THF (180 mL). A white suspension (possibly Hg_2Br_2) was formed within 24 h, which gradually disappeared during another 2 weeks of stirring. After settling of the magnesium amalgam, the almost colorless solution was decanted into a second vessel. Complete exchange was checked by titration of a hydrolyzed aliquot on Mg^{2+} ; the expected magnesium bromide concentration (0.1 M) was found.

Metalation of 1,3-Xylylene-15-crown-4 (1). Solutions of 1 (1 mmol, 0.25 g, in 2 mL of Et_2O) and diphenylmagnesium (1 mmol, in 8 mL of Et_2O) were mixed. A slightly cloudy solution was obtained; probably, some impurities precipitated upon combination of the reagents. The solution was filtered over a glass filter to remove the small amount of solid material. Upon storage of the clear solution at room temperature a finely divided solid was slowly formed. This indicated the formation of the metalation product 2-(phenylmagnesium)-1,3-xylylene-15-crown-4 (2), which has a very low solubility in diethyl ether. After a period of 2.5 weeks, the reaction mixture was quenched with D_2O (2 mL, during 0.5 h). The diethyl ether was distilled off, water and NH_4Cl were added, and all organic material was extracted with CH_2Cl_2 . The organic layer was dried (MgSO_4), filtered, and evaporated to dryness. The residue (colorless oil, 0.26 g) was analyzed by ^1H NMR spectroscopy (CDCl_3 , 90 MHz) and GC/MS; a mixture of starting material 1 (52%) and deuterated material 1-2-*d* (48%) had been formed. Apparently, the metalation reaction of 1 with

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diphenylmagnesium is very slow.

In another experiment, the metalation reaction was monitored with ^1H NMR spectroscopy (250 MHz). A toluene- d_8 solution containing diphenylmagnesium, 1, and Et_2O in a stoichiometry of 1:1.23:3.03 was prepared. In this sample, metalation proceeded much faster than in pure diethyl ether; 85% conversion of the diphenylmagnesium was found after 24 h. Apparently, the absence of a bulk of diethyl ether molecules facilitates the formation of the weak $[1]\cdot[\text{Ph}_2\text{Mg}]$ complex, which is necessary for a further reaction. Due to fast exchange processes, separate signals for the phenyl groups in 2 and diphenylmagnesium or free and Ph_2Mg -associated crown ether were not discernible. Complete conversion of diphenylmagnesium was reached after 6 days. The spectral data of the final product mixture are presented below.

2: ^1H NMR (250 MHz, toluene- d_8 , ref toluene $\text{CD}_2\text{H} = 2.32$ ppm) δ 2.88–3.00 (m, $1/2\text{A}_2\text{B}_2$, 4 H, C_2H_4), 3.33–3.39 (m, $1/2\text{A}_2\text{B}_2$, 4 H, C_2H_4), 3.45–3.59 (m, 4 H, C_2H_4), 4.72 (m, AB, $\Delta\delta = 0.48$ ppm, $^2J = 13$ Hz, 4 H, xylyl CH_2), 7.11 (d, $^3J = 7$ Hz, 2 H, xylyl H(4,6)), 7.46 (t, $^3J = 7$ Hz, 1 H, xylyl H(5)), 7.54 (tt, $^3J = 7$ Hz, $^4J = 2$ Hz, 1 H, phenyl H(4)), 7.65 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 2 H, phenyl H(3)), 8.26 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 2 H, phenyl H(2)); benzene (1 equiv) δ 7.36 (s, 6 H, aryl H). The signals of the residual free crown ether 1 (0.23 equiv), as far as discernible in the spectrum, corresponded to those in a reference spectrum of pure 1: ^1H NMR (250 MHz, toluene- d_8 , ref toluene $\text{CD}_2\text{H} = 2.32$ ppm) δ 3.65 (s, 8 H, C_2H_4), 3.69 (s, 4 H, C_2H_4), 4.661 and 4.663 (m, AB, 4 H, xylyl CH_2), 7.09 (d, $^3J = 7$ Hz, 2 H, xylyl H(4,6)), 7.32 (t, $^3J = 7$ Hz, 1 H, xylyl H(5)), 8.45 (s, 1 H, xylyl H(2)).

Reaction of 2-Bromo-1,3-xylylene-15-crown-4 (4) with Diphenylmagnesium. In a fully sealed glass apparatus, solutions of 4 (1 mmol, 0.33 g, in 2 mL of Et_2O) and diphenylmagnesium (1 mmol, in 8 mL of Et_2O) were mixed. Within a few seconds, a finely crystalline precipitate was formed. The clear supernatant was carefully decanted, and some diethyl ether was distilled back to wash the precipitate. By cooling with liquid nitrogen, the solvent was completely distilled off from the solid reaction product. The diethyl ether fraction was quenched with D_2O (0.5 mL), dried (MgSO_4), filtered, and evaporated to dryness. By GC/MS, the residue (about 0.2 g of a colorless liquid) was identified as bromobenzene containing a trace of 1- d ; no 4 was present. The experiment was repeated in order to demonstrate the completeness of the reaction. Now, the diethyl ether mother liquor was titrated on total base and Mg^{2+} after hydrolysis. Less than 0.05 mmol of basic material was found, indicating a yield of 2 in the precipitate of >95%.

The solid product (a colorless powder) was characterized with its ^1H NMR spectrum (250 MHz, toluene- d_8 , vide supra) as pure 2-(phenylmagnesium)-1,3-xylylene-15-crown-4 (2). Recrystallization of 2 was performed from toluene; the isolated crystals are unexpectedly stable toward air. A 1-mmol sample stored in a normal stoppered flask for 24 h and subsequently quenched with D_2O still showed a deuterium incorporation of about 50% (GC/MS).

The reaction between 4 (1 mmol, 0.33 g) and diphenylmagnesium (1 mmol) was also attempted in THF (10 mL). A clear solution was obtained after mixing of the reagents, which did not change during a period of 4 days. The reaction mixture was quenched with D_2O (0.1 mL), water (100 mL) was added, and all organic material was collected by extraction with CH_2Cl_2 . The organic phase was dried (MgSO_4), filtered, and evaporated to dryness: the starting material 4 was recovered quantitatively (0.33 g; identified by ^1H NMR).

Reaction of 4 with Phenylmagnesium Bromide. In a fully sealed glass apparatus, solutions of 4 (1 mmol, in 2 mL of Et_2O) and phenylmagnesium bromide (1 mmol, in 8 mL of Et_2O) were combined to give a clear solution. Within 1 min, a finely divided white powder started to precipitate. After 1 h, the solvent was decanted, quenched with D_2O (0.1 mL), dried (MgSO_4), and filtered. The diethyl ether was distilled off, giving a colorless liquid (0.13 g), which was identified by ^1H NMR spectroscopy (CDCl_3 , 90 MHz) as bromobenzene. No 1- d or 4 could be detected.

An aliquot of the solid white powder (vide supra) was dissolved in THF- d_6 ; the ^1H NMR spectrum showed the presence of 4 and of 2-(bromomagnesium)-1,3-xylylene-15-crown-4 (3, ^1H NMR in accordance with the known data²) in a ratio of about 3:1; this ratio is not representative for the composition of the solid because of

the limited solubility of 3 in THF. Therefore, the nondissolved material was quenched with D_2O (0.5 mL); water and NH_4Cl were added, and the organic material was collected by extraction with CH_2Cl_2 . The organic layer was dried (MgSO_4), filtered, and evaporated to dryness. The residue (colorless oil) was identified as a mixture of 1- d and 4 (ratio 3:1) with GC/MS and a ^1H NMR spectrum (CDCl_3 , 90 MHz), indicating a 75% conversion of 4 to 3. The incompleteness of the reaction may be caused by the heterogeneous character and slowness of the reaction; possibly, another factor could be the Schlenk equilibrium leading to the unreactive $[4]\cdot[\text{MgBr}_2]$ complex, which, on hydrolysis, would yield 4.

Reaction of 2-Bromo-1,3-xylylene-18-crown-5 (14) with Diphenylmagnesium. A solution of 14 (1 mmol, 375 mg, in 2 mL of Et_2O) was mixed with that of diphenylmagnesium (1 mmol, in 8 mL of Et_2O) to give a white precipitate. The solvent was decanted, and the last traces of solvent were removed by high-vacuum pumping. According to a ^1H NMR spectrum of the solid in C_6D_6 , an initial adduct $14\cdot\text{Ph}_2\text{Mg}$ (15) was formed. A slow conversion of 15 took place in several days to the exchange products 2-(phenylmagnesium)-1,3-xylylene-18-crown-5 (16) and bromobenzene (ratio 1:1), as monitored by ^1H NMR spectroscopy.

Half of the remaining solid material (~ 0.4 mmol) was heated in toluene (10 mL) until a clear solution was obtained. Compound 16 crystallized upon slowly cooling to room temperature. The quality of the crystals was not sufficient for a X-ray structure determination. A subsequent recrystallization from THF gave no improvement. According to ^1H NMR spectra in THF- d_6 , 16 crystallized solvent free both from toluene and THF. The identity of 16 follows from the ^1H NMR spectrum, which was quite similar to that of 25; the latter was identified by its crystal structure (vide infra).

16: ^1H NMR (250 MHz, THF- d_6 , ref THF $\text{D}_2\text{H} = 1.75$ ppm) δ 3.57–3.73 (m, 4 H, C_2H_4), 3.83–4.01 (m, 12 H, C_2H_4), 4.69 (s, 4 H, xylyl CH_2), 6.77 (d, 2 H, xylyl H(4,6)), 6.82 (t, $^3J = 7$ Hz, 1 H, phenyl H(4)), 6.88 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 2 H, phenyl H(3,5)), 7.65 (d, $^3J = 7$ Hz, 2 H, phenyl H(2,6)). The xylyl H(5) triplet is possibly hidden under the other signals.

The rather complicated ^1H NMR spectrum of 16 in C_6D_6 was analyzed with the additional help of 2D COSY and NOESY spectra. In a benzene solution, 16 has an (averaged) symmetry with respect to the plane perpendicular to the crown ether plane through xylyl C(2) and the central oxygen atom. Since the phenylmagnesium substituent resides at one side of the crown ether plane, endo (close to the PhMg substituent) and exo CH_2 hydrogen atoms can be discerned.

^1H NMR (400 MHz, C_6D_6 , ref $\text{C}_6\text{D}_5\text{H} = 7.30$ ppm) δ 2.797 (ddd, ABCD, $^2J = -11.37$ Hz, $^3J = 4.66$ Hz, $^3J = 3.23$ Hz, 2 H, CH_2 (7 exo)), 2.940 (ddd, ABCD', $^2J = -11.25$ Hz, $^3J = 6.29$ Hz, $^3J = 2.72$ Hz, 2 H, CH_2 (9 exo)), 3.035 (ddd, ABCD, $^2J = -11.31$ Hz, $^3J = 4.66$ Hz, $^3J = 3.12$ Hz, 2 H, CH_2 (6 exo)), 3.102 (ddd, ABCD', $^2J = -11.83$ Hz, $^3J = 6.44$ Hz, $^3J = 2.72$ Hz, 2 H, CH_2 (10 exo)), 3.172 (ddd, ABCD, $^2J = -11.31$ Hz, $^3J = 8.04$ Hz, $^3J = 3.23$ Hz, 2 H, CH_2 (6 endo)), 3.316 (ddd, ABCD, $^2J = -11.37$ Hz, $^3J = 8.04$ Hz, $^3J = 3.12$ Hz, 2 H, CH_2 (7 endo)), 3.424 (ddd, ABCD', $^2J = -11.25$ Hz, $^3J = 6.44$ Hz, $^3J = 2.76$ Hz, 2 H, CH_2 (9 endo)), 3.659 (ddd, ABCD', $^2J = -11.83$ Hz, $^3J = 6.29$ Hz, $^3J = 2.76$ Hz, 2 H, CH_2 (10 endo)), 4.545 (d, AB, $^2J = 11.6$ Hz, 4 H, xylyl CH_2 (exo)), 4.666 (d, AB, $^2J = 11.6$ Hz, 4 H, xylyl CH_2 (endo)), 7.118 (d, $^3J = 7$ Hz, 2 H, xylyl H(4,6)), 7.359 (t, $^3J = 7$ Hz, 1 H, xylyl H(5)), 7.409 (t, $^3J = 7$ Hz, 1 H, phenyl H(4)), 7.54 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 2 H, phenyl H(3)), 8.163 (d, $^3J = 7$ Hz, 2 H, phenyl H(2)). The ABCD and ABCD' systems were easily identified in the COSY spectrum, since all expected COSY couplings between their components were observed. Coupling constants of the ABCD systems were refined by spectrum simulation and yielded accurate (absolute) values for all coupling constants. A consistent assignment of the CH_2 proton signals was facilitated by some through-space couplings derived from the NOESY spectrum: CH_2 (10 endo)–phenyl(2), CH_2 (9 endo)–phenyl(2), CH_2 (7 endo)–phenyl(2), CH_2 (6 endo)–phenyl(2), CH_2 (9 exo)– CH_2 (7 exo), CH_2 (6 endo)–xylyl CH_2 (endo).

2-[(*p*-tert-Butylphenyl)magnesium]-1,3-xylylene-18-crown-5 (25). A solution of 14 (1 mmol, 375 mg, in 50 mL of Et_2O) was mixed with a solution of 18 (1 mmol, in 10 mL of Et_2O) to give a clear solution. After several days, finely divided crystalline 25

started to separate from the reaction mixture. The solvent was decanted after 3 weeks, and some diethyl ether was distilled back to wash the remaining solid. The last traces of solvent were removed by high-vacuum pumping. About one-half of the solid was dissolved in THF (10 mL) under heating (80 °C) and subsequently slowly cooled to give well-shaped colorless crystals. The crystals were analyzed with ^1H NMR spectroscopy and proved to be suitable for an X-ray structure determination. The solubility of **25** in toluene or THF was low.

25: ^1H NMR (250 MHz, THF- d_8 , ref THF $D_7\text{H}$ = 1.75 ppm) δ 1.26 (s, 9 H, t -Bu), 3.62–3.75 (m, 8 H, C_2H_4), 3.87–3.99 (m, 8 H, C_2H_4), 4.69 (s, 4 H, xylyl CH_2), 6.76 (d, 3J = 7 Hz, 2 H, xylyl H(4,6)), 6.88 (t, 3J = 7 Hz, 1 H, xylyl H(5)), 6.97 (d, AB, 3J = 8 Hz, 2 H, aryl H(3)), 7.59 (d, AB, 3J = 8 Hz, 2 H, aryl H(2)); ^1H NMR (250 MHz, toluene- d_6 , ref toluene $\text{C}_6\text{D}_6\text{CD}_2\text{H}$ = 2.32 ppm) δ 1.67 (s, 9 H, t -Bu), 3.01–3.09 (m, 2 H, C_2H_4), 3.14–3.21 (m, 2 H, C_2H_4), 3.25–3.71 (m, 10 H, C_2H_4), 3.86–3.94 (m, 2 H, C_2H_4), 4.79 (m, AB, Δ = 0.11 ppm, 3J = 12 Hz, 4 H, xylyl CH_2), 7.10 (d, 3J = 8 Hz, 2 H, xylyl H(4,6)), 7.50 (t, 3J = 8 Hz, 1 H, xylyl H(5)), 7.69 (d, AB, 3J = 8 Hz, 2 H, aryl H(3)), 8.22 (d, AB, 3J = 8 Hz, 2 H, aryl H(2)). The crystals of **25** were free of crystal solvent. The mass spectrum of **25** was measured via a specially developed inlet system (EI, Varian CH5 DF): m/z (rel intensity) 319 (M^+ – Ar, 6), 296 (5 $^+$, 10), 231 (13), 177 (7), 134 (26), 119 (100), 104 (57), 91 (57), 57 (24), 44 (98). HRMS calcd for $\text{C}_{16}\text{H}_{23}\text{MgO}_5$ 319.140, found 319.145 (0.006).

Reaction of 14 with Phenylmagnesium Bromide. A solution of **14** (1 mmol, 0.38 g, in 2 mL of Et_2O) was mixed with phenylmagnesium bromide (1 mmol, in 8 mL of Et_2O). Immediately, a white precipitate was formed. The solvent was decanted, and the solid reaction product was further dried by pumping in high vacuum. Characterization of the white solid with ^1H NMR spectroscopy in THF- d_8 and C_6D_6 revealed the formation of [14]·[PhMgBr], which also contained some residual diethyl ether (0.42 equiv). In spite of several attempts, recrystallization of the complex from benzene or toluene was not successful. From the NMR spectra, the formation of the halogen-metal exchange product (**16**) at room temperature can be excluded.

[14]·[PhMgBr]: ^1H NMR (250 MHz, C_6D_6 , ref $\text{C}_6\text{D}_5\text{H}$ = 7.30 ppm) δ 3.50 (s, br, 8 H, C_2H_4), 3.56 (s, br, 4 H, C_2H_4), 3.70 (s, br, 4 H, C_2H_4), 4.68 (s, br, 4 H, C_2H_4), 4.68 (s, br, 4 H, xylyl CH_2), 7.06 (d, 3J = 7 Hz, 2 H, xylyl H(4,6)), 7.24 (t, 3J = 7 Hz, 1 H, xylyl H(5)). In THF, a complete dissociation into the components occurs: ^1H NMR (250 MHz, THF- d_8 , ref THF $D_7\text{H}$ = 1.75 ppm) **14**, δ 3.47–3.71 (m, 16 H, C_2H_4), 4.66 (s, 4 H, xylyl CH_2), 7.29 (t, 3J = 7 Hz, 1 H, xylyl H(5)), 7.39 (d, 3J = 7 Hz, 2 H, xylyl H(4,6)); phenylmagnesium bromide, δ 6.89 (t, 3J = 7 Hz, 1 H, phenyl H(4)), 6.98 (dd, 3J = 7 Hz, 3J = 6 Hz, 2 H, phenyl H(3)), 7.69 (d, 3J = 6 Hz, 2 H, phenyl H(2)).

Even at elevated temperature, the exchange reaction between phenylmagnesium bromide and **14** was slow and incomplete. A sample of the complex (about 0.5 mmol) was heated in toluene (10 mL) for 11 h at 95–100 °C. After cooling to room temperature, the reaction mixture was quenched with D_2O (0.1 mL). The organic phase was dried (MgSO_4), filtered, and analyzed with GC/MS. The resulting solution contained **14** and 1,3-xylyl-18-crown-5-2-*d* in a ratio of 2:1.

Stability of the "Rotaxane" Complex 6. Crystalline **6** was prepared from **5** and diphenylmagnesium as described earlier.² A solution of **6** in toluene- d_8 was heated for a prolonged time (90 °C, 10 h), and the changes in the ^1H NMR spectrum were monitored. Partial hydrolysis was observed to give **5**, benzene, and some finely divided precipitate. Due to a fast dynamic exchange on the NMR time scale between free **5** and the side-on complex,² these species give one single set of signals.

Reaction of 1-Bromo-4-fluorobenzene (10) with Diphenylmagnesium. In a fully sealed glass apparatus, a solution of diphenylmagnesium (0.2 mmol) in diethyl ether (2 mL) was concentrated by removal of the free solvent by cooling with ice. The residue (a yellowish brown oil) was redissolved in benzene- d_6 (2 mL). A portion of this solution (500 μL) was mixed with pure **10** (about 20 μL , 3 equiv) and analyzed with ^1H NMR spectroscopy. No bromine/magnesium exchange occurred, even at elevated temperatures (80 °C, several hours).

10: ^1H NMR (C_6D_6 , 250 MHz, ref $\text{C}_6\text{D}_5\text{H}$ = 7.30 ppm) δ 6.52 (dd, ABX, $^3J(\text{H-H})$ = 9 Hz, $^3J(\text{H-F})$ = 8 Hz, 2 H, aryl H(3,5)),

7.08 (dd, ABX, $^3J(\text{H-H})$ = 9 Hz, $^4J(\text{H-F})$ = 5 Hz, 2 H, aryl H(2,6)).

Reaction of 2-Bromo-1,3-bis(methoxymethyl)benzene (11) with Diphenylmagnesium. A solution of diphenylmagnesium (0.05 mmol, in 500 μL of C_6D_6) was mixed with solid **11** (about 25 mg, 2 equiv). The resulting clear solution was analyzed by ^1H NMR spectroscopy. Even at elevated temperatures (several hours at 80 °C), bromine/magnesium exchange reaction was not observed.

11: ^1H NMR (C_6D_6 , 250 MHz, ref $\text{C}_6\text{D}_5\text{H}$ = 7.30 ppm) δ 3.27 (s, 6 H, OMe), 4.56 (s, 4 H, CH_2), 6.72 (t, 3J = 7 Hz, 1 H, H(5)), 7.05 (d, 1J = 7 Hz, 2 H, H(4,6)).

Synthesis of 3-[(2-Bromobenzyl)oxy]-5,8,1,14,17-pentaoxacyclohexadecane (12). The reaction was performed in a three-necked flask with magnetic stirring under nitrogen. In dry benzene (50 mL), potassium hydride (18 mmol, in 2.3 mL of liquid paraffin, three times washed with benzene) was suspended, and a solution of 3-hydroxy-5,8,1,14,17-pentaoxacyclohexadecane (**13**,¹⁸ 12 mmol, 3.0 g, in 25 mL of benzene) was added. After the hydrogen evolution had ceased (1 h), a solution of *o*-bromobenzyl bromide (12 mmol, 3.0 g) was added and the reaction mixture was stirred overnight. Water was added (100 mL) and the organic layer isolated. The aqueous phase was extracted with benzene. The combined organic layers were dried (MgSO_4), filtered, and evaporated to dryness. The crude product (yellowish oil) was purified by fractional column chromatography (Al_2O_3 , Merck 90, activity II-III, 2.5 $\times$ 30 cm, 100 mL fractions, eluents Et_2O /THF). The elution was started with pure diethyl ether, and the THF concentration was increased in steps of 10%. The fractions containing pure **12** were identified by ^1H NMR spectroscopy (CDCl_3 , 90 MHz) and combined (yield 2.7 g colorless oil, 54%).

12: ^1H NMR (CDCl_3 , 250 MHz, ref CHCl_3 = 7.27 ppm) δ 3.66 (s, 8 H, C_2H_4), 3.68 (s, 8 H, C_2H_4), 3.64–3.84 (m, 5 H, CH_2 (2,4)), 4.74 (s, 2 H, aryl CH_2), 7.12 (t, 3J = 7 Hz, 1 H, aryl H), 7.29 (t, 3J = 7 Hz, 1 H, aryl H), 7.54–7.59 (m, 2 H, aryl H); ^{13}C NMR (CDCl_3 , 62.89 MHz, ref CDCl_3 = 77.0 ppm) δ 70.0 (t, $^1J(\text{C-H})$ = 141 Hz, 2 C, CH_2), 70.2 (t, $^1J(\text{C-H})$ = 140 Hz, 2 C, CH_2), 70.3 (t, $^1J(\text{C-H})$ = 140 Hz, 2 C, CH_2), 70.7 (t, $^1J(\text{C-H})$ = 141 Hz, 4 C, CH_2), 71.0 (t, $^1J(\text{C-H})$ = 144 Hz, 1 C, aryl CH_2), 77.6 (d, $^1J(\text{C-H})$ = 139 Hz, 1 C, CH_2 (3)), 122.1 (s, 1 C, aryl C(2)), 126.9 (d, $^1J(\text{C-H})$ = 163 Hz, 1 C, aryl C), 128.3 (d, $^1J(\text{C-H})$ = 161 Hz, 1 C, aryl C), 128.9 (d, $^1J(\text{C-H})$ = 164 Hz, 1 C, aryl C), 131.9 (d, $^1J(\text{C-H})$ = 165 Hz, 1 C, aryl C), 137.8 (s, 1 C, aryl C(1)). MS (DCI, NH_3 , Finnigan MAT 90), m/z (rel intensity) 436 (M-NH_4^+ , 11), 358 (ArH-NH_4^+ , 100), 266 (36). Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{BrO}_6$: C, 51.56; H, 6.49. Found: C, 51.09; H, 6.43.

Reaction of 12 with Diphenylmagnesium. Upon mixing of a solution of diphenylmagnesium (1 mmol) in diethyl ether (10 mL) with pure **12** (1 mmol, 420 μL in a fully sealed glass apparatus), a sticky oily precipitate was formed. The diethyl ether was decanted and cooled with liquid nitrogen to remove the last trace of solvent from the remaining solid. The solvent fraction was quenched with water (<0.1 mL), dried (MgSO_4), filtered, and evaporated to dryness. According to a ^1H NMR spectrum, the residual oil (0.29 g) contained only starting bromide **12** (about 70%). No magnesium/bromine exchange had occurred, as could be derived from the absence of bromobenzene.

The analysis of an aliquot of the residue by ^1H NMR spectroscopy in THF- d_8 showed that nothing but **12**, diphenylmagnesium, and diethyl ether were present in the solution, confirming the nonoccurrence of an exchange reaction. The remaining solid was dissolved in toluene (10 mL) under heating in a water bath (80 °C). From the resulting almost clear solution, no material crystallized upon cooling; the solution was quenched with D_2O (0.5 mL). After addition of water and NH_4Cl , the organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried (MgSO_4), filtered, and evaporated to dryness. The residue (0.20 g of yellowish oil) was characterized by ^1H NMR spectroscopy (CDCl_3 , 90 MHz): a complete degradation of the starting crown ether, possibly by ether cleavage, had taken place.

Lithiation of 5-Bromo-1,3-xylylene-15-crown-4 (17). The reaction was performed under argon in THF, dried by distillation from LiAlH_4 . A solution of **17** (0.23 g, 0.69 mmol) in THF (25 mL) was cooled to –60 °C. The addition of an equivalent amount of *n*-butyllithium (0.46 mL of hexane solution) immediately converted **17** to 5-lithio-1,3-xylylene-15-crown-4 (**20**). Within 1

min, ethanol-*O-d* (200 μ L) was added, and the reaction mixture was quickly warmed up to room temperature. After removal of all THF by distillation and addition of water, all organic material was collected by extraction with dichloromethane. The combined organic layers were dried (MgSO_4), filtered, and evaporated to dryness. The remaining colorless oil (0.20 g) was identified by ^1H and ^{13}C NMR spectroscopy and GC/MS as pure 1,3-xylylene-15-crown-4-5-*d* (21).

21: ^1H NMR (CDCl_3 , 250 MHz, ref $\text{CHCl}_3 = 7.27$ ppm) δ 3.71 (s, 8 H, C_2H_4), 3.72 (s, 4 H, C_2H_4), 4.641 and 4.643 (m, AB, 4 H, xylyl CH_2), 7.07 (s, br, 2 H, xylyl H(4,6)), 7.99–8.00 (m, 1 H, xylyl H(2)); ^{13}C NMR (CDCl_3 , 62.89 MHz, ref $\text{CDCl}_3 = 77.0$ ppm) δ 69.6 (t, $^1\text{J}(\text{C}-\text{H}) = 141$ Hz, 2 C, CH_2), 70.3 (t, $^1\text{J}(\text{C}-\text{H}) = 141$ Hz, 2 C, CH_2), 70.6 (t, $^1\text{J}(\text{C}-\text{H}) = 141$ Hz, 2 C, CH_2), 72.1 (t, $^1\text{J}(\text{C}-\text{H}) = 141$ Hz, 2 C, xylyl CH_2), 125.6 (d, $^1\text{J}(\text{C}-\text{H}) = 157$ Hz, 2 C, xylyl C(4,6)), 126.3 (d, $^1\text{J}(\text{C}-\text{H}) = 157$ Hz, 1 C, xylyl C(2)), 127.2 (t, low intensity, $^1\text{J}(\text{C}-\text{D}) = 24.3$ Hz, 1 C, xylyl C(5)), 139.1 (s, 1 C, xylyl C(1,3)); GC/MS, m/z (rel intensity) 253 (M^+ , 11), 133 (68), 118 (15), 105 (75), 89 (59), 79 (32), 45 (100).

5-Bromo-2-[(*p*-*tert*-butylphenyl)magnesium]-1,3-xylylene-15-crown-4 (19). Solutions of 17 (1 mmol, 331 mg, in 2 mL of Et_2O) and di(*p*-*tert*-butylphenyl)magnesium (18, 1 mmol, in 8 mL of Et_2O) were mixed to give a clear solution. Colorless crystals of 19 started to form within 1 day. After 4 days, the solvent was decanted and the crystalline product was washed by distilling back some diethyl ether. Titration of the decanted and hydrolyzed solution (total base and Mg^{2+}) indicated a 63% yield of crystalline 19. The crystalline solid was pumped under high vacuum to remove the last traces of solvent and characterized by ^1H NMR spectroscopy.

19: ^1H NMR (250 MHz, toluene- d_8 , ref toluene $\text{CD}_2\text{H} = 2.32$ ppm) δ 1.67 (s, 9 H, *t*-Bu), 2.86–2.95 (m, 4 H, C_2H_4), 3.31–3.4 (m, 4 H, C_2H_4), 3.45–3.63 (m, 4 H, C_2H_4), 4.51 (m, AB, $\Delta\delta = 0.49$ ppm, $^3J = 13$ Hz, 4 H, xylyl CH_2), 7.23 (s, 2 H, xylyl H(4,6)), 7.68 (d, AB, $^3J = 8$ Hz, 2 H, aryl H(3)), 8.15 (d, AB, $^3J = 8$ Hz, 2 H, aryl H(2)); ^1H NMR (250 MHz, THF- d_8 , ref THF $\text{D}_7\text{H} = 1.75$ ppm) δ 1.26 (s, 9 H, *t*-Bu), 3.70–4.02 (m, 12 H, C_2H_4), 4.62 (m, AB, $\Delta\delta = 0.28$ ppm, $^3J = 13$ Hz, 4 H, xylyl CH_2), 6.85 (s, 2 H, xylyl H(4,6)), 6.96 (d, AB, $^3J = 8$ Hz, 2 H, aryl H(3)), 7.56 (d, AB, $^3J = 8$ Hz, 2 H, aryl H(2)). Signals of crystal solvent were not observed.

5-Bromo-2-(bromomagnesium)-1,3-xylylene-15-crown-4 (22). Compound 19 (vide supra, about 0.5 mmol) was dissolved in THF (11.2 mL) to a clear solution, to which a solution of magnesium bromide (0.87 mmol, 4.9 mL of THF) was added. Within 1 h, a voluminous solid was formed, which was isolated by decanting the solvent. The solid material was washed several times by distilling back some diethyl ether and dried by high-vacuum pumping. An aliquot was hydrolyzed and titrated; total base and Mg^{2+} were both 0.065 mmol, which shows that a Grignard compound had been obtained. A ^1H NMR spectrum in THF- d_8 identified the isolated product as 22.

22: ^1H NMR (250 MHz, THF- d_8 , ref THF $\text{D}_7\text{H} = 1.75$ ppm) δ 3.91–3.96 and 4.01–4.06 (m, A_2B_2 , 8 H, C_2H_4), 4.04 (s, 4 H, C_2H_4), 4.62 (s, 4 H, xylyl CH_2), 6.85 (s, 2 H, xylyl H(4,6)). Since 22 has a very low solubility in THF, an appreciable amount of hydrolysis product 17 was discernible in the spectrum.

About 0.2 mmol of the solid material was quenched with D_2O (0.5 mL). After the addition of water and NH_4Cl , the organic material was extracted with CH_2Cl_2 . The organic layer was dried (MgSO_4), filtered, and evaporated to dryness. A colorless, slowly crystallizing residue (0.06 g) was obtained, identified as pure 5-bromo-1,3-xylylene-15-crown-4-2-*d* (24) by ^1H and ^{13}C NMR spectroscopy and GC/MS. The spectral data of 24 are closely related to those of 17.

24: ^1H NMR (250 MHz, CDCl_3 , ref $\text{CHCl}_3 = 7.27$ ppm) δ 3.71–3.72 (m, 12 H, C_2H_4), 4.60 (s, 4 H, xylyl CH_2), 7.20 (s, 2 H, xylyl H(4,6)); ^{13}C NMR (62.89 MHz, CDCl_3 , ref $\text{CDCl}_3 = 77.0$ ppm) δ 69.8 (t, $^1\text{J}(\text{C}-\text{H}) = 141$ Hz, 2 C, C_2H_4), 70.2 (t, $^1\text{J}(\text{C}-\text{H}) = 141$ Hz, 2 C, C_2H_4), 70.6 (t, $^1\text{J}(\text{C}-\text{H}) = 141$ Hz, 2 C, C_2H_4), 71.3 (t, $^1\text{J}(\text{C}-\text{H}) = 139$ Hz, 2 C, xylyl CH_2), 121.2 (s, 1 C, xylyl(5)), 124.5 (t, $^1\text{J}(\text{C}-\text{D}) = 25$ Hz, 1 C, xylyl(2)), 128.3 (d, $^1\text{J}(\text{C}-\text{H}) = 163$ Hz, 2 C, xylyl(4,6)), 141.5 (s, 2 C, xylyl(1,3)); GC/MS, m/z (rel intensity) 331 (M^+ , 5), 183 (48), 133 (41), 104 (41), 89 (51), 78 (24), 45 (100).

2-(Ethylmagnesium)-1,3-xylylene-15-crown-4 (26). Solid 4 (0.75 mmol, 248 mg) was shaken with a solution of diethyl-

magnesium (1.75 mmol) in diethyl ether (15 mL) to give an initially clear solution. After standing for 24 h, colorless crystals formed, which were isolated by decanting the supernatant. The solvent fraction was titrated to find amounts of 2.02 mmol of total base and 1.01 mmol of Mg^{2+} , suggesting that an exchange reaction had occurred. The crystalline material was further dried by pumping off the solvent; during this operation the crystals pulverize probably due to the loss of crystal solvent. Some crystals were dissolved in THF- d_8 and characterized by ^1H NMR spectroscopy as 2-(ethylmagnesium)-1,3-xylylene-15-crown-4 (26). The remaining material was recrystallized from toluene and THF, but no crystals suitable for an X-ray structure determination could be obtained.

26: ^1H NMR (THF- d_8 , 250 MHz, ref THF $\text{D}_7\text{H} = 1.75$ ppm) δ -0.78 (q, $^3J = 8$ Hz, 3 H, CH_2CH_3), 1.20 (t, $^3J = 8$ Hz, 2 H, CH_2CH_3), 3.71–4.02 (m, 12 H, C_2H_4), 4.61 (d, AB, $\Delta = 0.29$, $^2J = 13$ Hz, 4 H, xylyl CH_2), 6.63 (d, $^3J = 7$ Hz, 2 H, xylyl H(4,6)), 6.83 (t, $^3J = 7$ Hz, 1 H, xylyl H(5)).

2-Methyl-1,3-xylylene-18-crown-5 (27). A solution of 14 (2 mmol, 0.75 g) in THF (50 mL, dried by distillation from LiAlH_4) was prepared under argon. After the solution was cooled to -60 $^\circ\text{C}$, 1 equiv of *n*-butyllithium (2 mmol, in *n*-hexane, 1.36 mL) was added within 1 min. To the resulting solution of 2-lithio-1,3-xylylene-18-crown-5, methyl iodide (10 mmol, 623 μL) was added with a syringe. After stirring for another 4 h at -60 $^\circ\text{C}$, the solution was warmed to room temperature. The reaction mixture was evaporated to dryness, water added, and the organic material isolated by extraction with dichloromethane. Sodium bisulfite was added. The organic phase was dried (MgSO_4), filtered, and evaporated to dryness to yield a yellowish oil (0.62 g), which crystallized slowly. A ^1H NMR spectrum of the crude product revealed the formation of almost pure (>95%) 27 in quantitative yield; it was crystallized from diethyl ether/*n*-pentane at -20 $^\circ\text{C}$ (mp 45–48 $^\circ\text{C}$). The colorless crystalline solid was pure according to GC/MS.

27: ^1H NMR (250 MHz, CDCl_3 , ref $\text{CHCl}_3 = 7.27$ ppm) δ 2.52 (s, 3 H, Me), 3.54–3.65 (m, 16 H, C_2H_4), 4.61 (s, 4 H, xylyl CH_2), 7.08 (t, $^3J = 7$ Hz, 1 H, xylyl H(5)), 7.19 (d, $^3J = 7$ Hz, 2 H, xylyl H(4,6)); ^{13}C NMR (62.89 ppm, CDCl_3 , ref $\text{CDCl}_3 = 77.0$ ppm) δ 14.8 (q, $^1\text{J}(\text{C}-\text{H}) = 127$ Hz, 1 C, Me), 68.8 (t, $^1\text{J}(\text{C}-\text{H}) = 140$ Hz, 2 C, C_2H_4), 70.3 (t, $^1\text{J}(\text{C}-\text{H}) = 140$ Hz, 2 C, C_2H_4), 70.5 (t, $^1\text{J}(\text{C}-\text{H}) = 140$ Hz, 4 C, C_2H_4), 72.7 (t, $^1\text{J}(\text{C}-\text{H}) = 139$ Hz, 2 C, xylyl CH_2), 124.4 (d, $^1\text{J}(\text{C}-\text{H}) = 161$ Hz, 1 C, xylyl(5)), 130.1 (d, $^1\text{J}(\text{C}-\text{H}) = 152$ Hz, 2 C, xylyl(4,6)), 136.6 (s, 2 C, xylyl(1,3)), 139.3 (s, 1 C, xylyl(2)); GC/MS, m/z (rel intensity) 310 (M^+ , 3), 177 (7), 133 (8), 118 (55), 115 (12), 103 (7), 91 (14), 89 (34), 45 (100).

Complexation of 27 with 18. A solution of 18 (0.5 mmol) in diethyl ether (5 mL) was mixed with an equivalent amount of 27 (0.5 mmol, 0.155 g). The crystalline crown ether dissolved and then a white amorphous precipitate was formed. The reaction product was isolated as a dry powder by removal of all volatile products with liquid nitrogen. The solvent fraction was analyzed after evaporation of the diethyl ether at atmospheric pressure using a warm water bath. Almost no residue (<0.02 g) was left, indicating the absence of *tert*-butylbenzene (an amount of 0.5 mmol = 67 mg would be formed in a metalation reaction). The solid product was identified with ^1H NMR spectroscopy (toluene- d_8 , 90 MHz) as the adduct [27]·[18] (28). No metalation occurred at elevated temperatures, the NMR spectrum remained unchanged after heating of the sample (100 $^\circ\text{C}$, 3 h). Recrystallization of 28 was possible from toluene or benzene; the isolated crystals were unstable due to the easy loss of crystal solvent.

28: ^1H NMR (toluene- d_8 , 250 MHz, ref toluene $\text{CD}_2\text{H} = 2.32$ ppm) δ 1.66 (s, 18 H, *t*-Bu), 2.63 (s, 3 H, Me), 3.35–3.38 and 3.48–3.51 (m, A_2B_2 , 8 H, C_2H_4), 3.40–3.44 and 3.69–3.73 (m, A_2B_2 , 8 H, C_2H_4), 4.57 (s, 4 H, xylyl CH_2), 7.24 (d, $^3J = 7$ Hz, 1 H, xylyl H(5)), 7.36 (t, $^3J = 7$ Hz, 2 H, xylyl H(4,6)), 7.57 (d, AB, $^3J = 8$ Hz, 4 H, aryl H(3,5)), 7.89 (d, AB, $^3J = 8$ Hz, 4 H, aryl H(2,6)).

Reaction of 2 with 9-Phenylfluorene (29). A solution of 9-phenylfluorene (1 mmol, 0.24 g) in THF (10 mL) was shaken with crystalline 2 (0.95 mmol). At room temperature, the crystalline starting material partially dissolved and a deep orange color developed, indicating the formation of the 9-phenylfluorenyl anion. Heating of the reaction ampule in a water bath (80 $^\circ\text{C}$) was necessary to complete the reaction. The dark orange clear solution gave upon cooling to room temperature fine needles of 2-magnesium-1,3-xylylene-15-crown-4 9-phenylfluorene (32), which

were isolated by decantation of the solvent. Titration of the solvent fraction (total base, 1.07 mmol; Mg^{2+} , 0.55 mmol) indicated a 42% yield of crystalline **32**. The crystalline fraction was pumped under high vacuum to remove the last traces of solvent and dissolved in $\text{THF}-d_8$ for ^1H and ^{13}C NMR spectroscopy.

Part of compound **32** was recovered from the NMR solution and hydrolyzed in aqueous hydrochloric acid (2 N); the orange color immediately disappeared. All organic hydrolysis products were collected by extraction with dichloromethane. The organic phase was dried (MgSO_4), filtered, and evaporated to dryness. The residue (colorless oil, with traces of solid material) was characterized with ^1H NMR spectroscopy; a mixture of **1** and **29** (stoichiometry 1:1.14) was found. The small excess of **29** can be explained by the relatively high solubility of **1** in $\text{H}_2\text{O}/\text{HCl}$, which makes the extraction with CH_2Cl_2 incomplete. The remaining **32** was subjected to recrystallization tests (THF, toluene, and 2-methyltetrahydrofuran), but no crystals suitable for a X-ray structure determination could be obtained.

32: ^1H NMR ($\text{THF}-d_8$, 250 MHz, ref $\text{THF H}_8 = 1.80$ ppm) δ 2.66 (s, 4 H, C_2H_4), 2.92 (t, A_2B_2 , $^3J = 5$ Hz, 4 H, C_2H_4), 3.32 (t, A_2B_2 , $^3J = 5$ Hz, 4 H, C_2H_4), 4.34 (s, 4 H, xylyl CH_2), 6.54 (d, $^3J = 7$ Hz, 2 H, xylyl H(4,6)), 6.75 (t, $^3J = 7$ Hz, 1 H, xylyl H(5)), 6.5–8.2 (m, v br, aryl H (9-phenylfluorenyl anion)); ^{13}C NMR ($\text{THF}-d_8$, 62.89 MHz, ref $\text{THF}-d_8 = 67.4$ ppm, only BB) δ 69.7 (2 C, C_2H_4), 74.9 (2 C, xylyl CH_2), 119.6 (2 C, xylyl C(4,6)), 124.5 (1 C, xylyl C(5)), 145.1 (2 C, xylyl C(1,3)), 167.7 (1 C, xylyl C(2)). Because of the low solubility of **32**, this spectrum was measured at 80 °C. The 9-phenylfluorenyl anion signals (118–130 ppm) are almost invisible due to signal broadening. Two C_2H_4 signals are missing, possibly masked by a high THF solvent signal (67.4 ppm).

Reaction of 2 with Pentamethylcyclopentadiene (30). A solution of **30** (1 mmol, 157 μL , vacuum distilled and dried on molecular sieve 4 Å) in THF (10 mL) was heated with solid **2** (1 mmol). At 80 °C (water bath), a colorless clear solution was obtained. Crystals were formed upon cooling to room temperature, which were identified as the starting material **2** with ^1H NMR spectroscopy. According to a titration of the mother liquor (total base; 0.43 mmol; Mg^{2+} , 0.22 mmol), the recovery of **2** was high (78%).

Reaction of 2 with Triphenylmethane (31). The reaction between **2** and **31** gave the analogous (negative) results as with **30**. The experimental procedure was completely identical.

Reaction of 2 with Diphenylzinc. A solution of diphenylzinc (0.1 mmol) in THF (10 mL) was shaken with crystalline **2** (1 mmol, large excess) at room temperature. Part of the yellowish suspension obtained (0.5 mL) was evaporated to dryness, pumped, and washed with $\text{THF}-d_8$ (500 μL) in order to identify the THF-soluble reaction products with ^1H NMR spectroscopy. Apart from **2** and **1** (hydrolysis product), signals of the diphenylzinc adduct 2-magnesio-1,3-xylylene-15-crown-4 triphenylzincate (**33**) were observed. The remaining THF suspension (0.95 mmol of **2** and 0.095 mmol of Ph_2Zn in 9.5 mL of THF) was shaken with an additional amount of diphenylzinc (0.5 mmol) in diethyl ether (5 mL); more of **2** dissolved. After settling of the solid material (the excess of **2**), the clear solution containing **33** was decanted. Complete evaporation of the solvent yielded a highly viscous brown oil. In spite of several attempts, the isolation of crystalline **33** from this crude mixture proved to be impossible.

In a separate reaction, **2** (1 mmol, solid material) was reacted with an excess of diphenylzinc (2 mmol, in 20 mL of diethyl ether). A brown oil precipitated, which solidified after evaporation of the solvent with liquid nitrogen. The diethyl ether was poured back to wash the solid residue and carefully decanted. Hydrolysis and titration of the decanted solution revealed the presence of 1.70 mmol of total base and 0.88 mmol of Zn^{2+} , which was a little less than the excess of diphenylzinc used. Attempts to recrystallize the solid residue almost invariably yielded a viscous oil. However, in some cases a small amount of a crystalline product, presumably 2-magnesio-1,3-xylylene-15-crown-4 pentaphenylzincate (**34**) was obtained; it was characterized by ^1H NMR spectroscopy.

2: ^1H NMR ($\text{THF}-d_8$, 250 MHz, ref $\text{THF D}_8\text{H} = 1.75$ ppm) δ 3.60–4.08 (m, 12 H, C_2H_4), 4.68 (m, AB, $^2J = 13$ Hz, 4 H, xylyl CH_2), 6.66 (d, $^3J = 7$ Hz, xylyl H(4,6)), 6.78 (t m, $^3J = 7$ Hz, phenyl H(4)), 6.86 (d, $^3J = 7$ Hz, 2 H, phenyl H(3)), 7.65 (d m, $^3J = 7$ Hz, 2 H, phenyl H(2)). The xylyl H(5) signal was probably masked by the other signals.

33: ^1H NMR ($\text{THF}-d_8$, 400 MHz, ref $\text{THF D}_8\text{H} = 1.75$ ppm) δ 3.416 (s, 4H, C_2H_4), 3.517–3.543 and 3.649–3.675 (m, A_2B_2 , 8 H, C_2H_4), 4.494 (s, 4 H, xylyl CH_2), 6.619 (d, $^3J = 7$ Hz, 2 H, xylyl H(4,6)), 6.841 (t, $^3J = 7$ Hz, 1 H, xylyl H(5)), 6.931 (t, $^3J = 7$ Hz, 3 H, phenyl H(4)), 7.056 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 6 H, phenyl H(3)), 7.933 (d, $^3J = 7$ Hz, 6 H, phenyl H(2)). The crown ether to phenyl group stoichiometry in this spectrum was exactly 1:3. The phenyl groups in **33** were identical, both at room temperature and at 210 K (low-temperature spectrum); this is in agreement with the formation of a triphenylzincate anion.

34: The ^1H NMR spectrum ($\text{THF}-d_8$, 250 MHz) of **34** is almost identical with that of **33** except for a small high-field shift (0.11 ppm) of the phenyl H(2) signals. The ratio of the crown ether to phenyl group signals, as determined from their integrals, is 1.5:1.9.

2-(Phenylcalcio)-1,3-xylylene-18-crown-5 (35). At –20 °C, a solution of iodobenzene (10 mmol, 1.11 mL, dried on molecular sieve 4 Å) in THF (50 mL) was reacted with calcium metal (12 mmol, 0.5 g). After 24 h of stirring, THF was completely removed by distillation while the crude reaction product mixture was kept at –20 °C. Before warming up to room temperature, the last traces of free THF were removed by high-vacuum pumping. The remaining solid was washed with diethyl ether (178 mL) to give a light-brown solution, which slowly turned red. This solution contained, according to a titration of an 6.5-mL aliquot (total base and Ca^{2+}), about 0.009 mmol/mL diphenylcalcium. The symmetrization is possibly induced by the tendency of phenylcalcium iodide to give relatively insoluble $[\text{PhCaI}]\cdot[\text{CaI}_2]_n$ adducts.²⁷

The diethyl ether solution, containing about 1.5 mmol of diphenylcalcium, was divided into two equal portions. One of them was stored at room temperature over a period of several days; it gradually turned dark red–brown and a brown precipitate was formed, indicating the limited stability of diphenylcalcium in THF. Therefore, the other fraction was immediately reacted with an equimolar amount of **14** (0.75 mmol, 281 mg). The solution became almost colorless, and a grey-brown solid precipitated. The solvent was decanted, and some diethyl ether was distilled back to wash the insoluble reaction product. The solvent fraction was carefully concentrated by distillation at atmospheric pressure. According to a ^1H NMR spectroscopic analysis, the residue (0.36 g of colorless liquid) contained the expected amount (0.75 mmol, 0.12 g) of bromobenzene (also identified by GC/MS). This result is consistent with the formation of 2-(phenylcalcio)-1,3-xylylene-18-crown-5 (**35**) in a bromine/calcium exchange reaction, in analogy with the reaction between **14** and a diarylmagnesium compound.

The solid reaction product was high-vacuum pumped to remove the last traces of solvent. Due to its low solubility, identification by ^1H NMR spectroscopy in C_6D_6 or $\text{Et}_2\text{O}-d_{10}$ was not possible. In $\text{THF}-d_8$, a decomposition reaction (possibly proton abstraction from the solvent) took place, yielding a dark brown solution. Therefore, **35** was positively identified by reaction with trimethyltin chloride, to give 2-(trimethylstannyl)-1,3-xylylene-18-crown-5 (**36**) and phenyl(trimethylstannyl)benzene (**37**) in a 1:1 ratio. To this end, solid **35** (about 0.7 mmol) was stirred with an excess of trimethyltin chloride (2 mmol) in diethyl ether (10 mL) for 24 h. The suspension slowly decolorized during the reaction, indicating the conversion of **35** into insoluble calcium halide. Water was added to the reaction mixture and the organic products were collected by extraction with dichloromethane. The organic layer was dried (MgSO_4), filtered, and concentrated to about 1 mL of colorless liquid. Analysis by ^1H NMR spectroscopy showed the presence of only two reaction products, **36** and **37**, in a 1:0.93 ratio. The 7% loss of **37** can be attributed to the volatility of this compound (bp about 200 °C).²⁹ The identity of the stannylated products was further confirmed by GC/MS. Isolation of pure **36**¹⁴ was achieved by evaporation most of **37** in a rotavapor and subsequent crystallization from diethyl ether (mp 43–44 °C).

37: GC/MS, m/z (rel intensity) 227 ($\text{M}^+ - \text{Me}$, 100), 212 ($\text{M}^+ - 2\text{Me}$, 6), 197 (46), 150 (7), 135 (43), 120 (74), 91 (28), 77 (50), 65 (21), 51 (86). The ^1H NMR spectrum (CDCl_3 , 250 MHz) was in accordance with published data.²⁸

(29) In *Zinn-Organische Verbindungen*; Gmelins Reihe; Bnd 2, 1.1.2.1, p 120.

Table III. Crystal Data and Details of the Structure Determination

Crystal Data	
formula	C ₂₆ H ₃₆ O ₅ Mg
molec wt	452.87
cryst syst	triclinic
space group	P $\bar{1}$ (No. 2)
a, b, c, Å	10.297 (1), 10.825 (1), 12.476 (2)
α , β , γ , deg	109.27 (1), 94.43 (1), 106.74 (1)
V, Å ³	1234.0 (3)
Z	2
D _{calc} , g cm ⁻³	1.219
F(000)	488
μ cm ⁻¹	1.0
cryst size, mm	0.25 × 0.30 × 0.18
Data Collection	
temp, K	295
$\theta_{\min}$, $\theta_{\max}$, deg	1.76, 25.17
radiatn	Mo K α (Zr filtered), 0.71073 Å
scan type	$\omega/2\theta$
$\Delta\omega$, deg	0.60 + 0.35 tan θ
hor and vert aperture, mm	3.0, 6.0
dist cryst to detector, mm	173
ref reflns	0, -3, 2, 1, -1, 1, -2, 2
data set	h 0:12; k -12:12; l -14:14
total data	4677
total unique data	4407
obsd data	2139 [$I > 2.5\sigma(I)$]
Refinement	
no. of refined params	318
weighting scheme	$w = 1.0/\sigma^2(F)$
final, R, R _w , S	0.052, 0.051, 0.76
(Δ/σ) _{av} in final cycle	0.0046
min and max resd dens, e/Å ³	-0.22, 0.30

Structure Determination and Refinement of 25. A colorless block-shaped crystal was mounted under nitrogen in a Lindemann capillary and transferred to an Enraf-Nonius CAD4F diffractometer for data collection. The unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $6.6 < \theta < 13.4^\circ$. The unit cell parameters were checked for the presence of higher lattice symmetry.³⁰ Data were corrected for Lp and for a small linear decay (<0.2%) of the intensity control reflections during the 66 h of X-ray exposure time but not for absorption. Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma_{\text{CS}}^2(I) + (0.039I)^2$.³¹ The structure was solved with direct methods (SHELXS86);³² the solution with the best figure of merit showed all non-hydrogen atoms. Refinement on F was carried out by full-matrix least-squares techniques. C(9) and C(10) are disordered over two positions. H atoms were introduced on calculated positions (C-H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; H atoms were refined with one common isotropic thermal parameter ($U = 0.080$ (3) Å²). Weights were introduced in the final refinement cycles; convergence was reached at $R = 0.052$.

Final atomic coordinates and equivalent isotropic parameters are listed in Table IV. Crystal data and numerical details of the structure determination are given in Table III. Neutral atom scattering factors were taken from Cromer and Mann and cor-

Table IV. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their ESD's in Parentheses for 25

atom	x	y	z	U(eq), Å ²
Mg	0.0007 (2)	0.6901 (1)	0.3231 (1)	0.0464 (5)
O(1)	0.2560 (3)	0.7471 (3)	0.2690 (3)	0.072 (1)
O(2)	0.0518 (3)	0.5055 (3)	0.1946 (3)	0.063 (1)
O(3)	-0.1183 (3)	0.5006 (3)	0.3389 (2)	0.051 (1)
O(4)	-0.3683 (3)	0.5575 (3)	0.3957 (3)	0.060 (1)
O(5)	-0.1024 (3)	0.7984 (3)	0.4676 (2)	0.044 (1)
C(1)	0.1600 (4)	0.8049 (4)	0.4723 (3)	0.040 (2)
C(2)	0.1284 (4)	0.8756 (4)	0.5773 (3)	0.043 (2)
C(3)	0.2254 (5)	0.9524 (4)	0.6789 (4)	0.052 (2)
C(4)	0.3621 (5)	0.9638 (4)	0.6774 (4)	0.058 (2)
C(5)	0.4010 (5)	0.9019 (4)	0.5752 (4)	0.054 (2)
C(6)	0.3014 (4)	0.8246 (4)	0.4757 (4)	0.044 (2)
C(7)	0.3446 (5)	0.7540 (5)	0.3651 (4)	0.059 (2)
C(8)	0.2543 (6)	0.6440 (7)	0.1619 (4)	0.093 (3)
C(9) ^b	0.175 (2)	0.512 (1)	0.152 (2)	0.079 (6)
C(10) ^b	-0.017 (2)	0.376 (1)	0.195 (2)	0.080 (6)
C(11)	-0.1312 (6)	0.3749 (5)	0.2491 (5)	0.085 (2)
C(12)	-0.1708 (4)	0.4872 (4)	0.4392 (3)	0.052 (2)
C(13)	-0.3247 (4)	0.4578 (5)	0.4228 (4)	0.059 (2)
C(14)	-0.3366 (4)	0.6868 (4)	0.4873 (4)	0.055 (2)
C(15)	-0.2407 (4)	0.8022 (4)	0.4612 (4)	0.052 (2)
C(16)	-0.0195 (4)	0.8730 (4)	0.5807 (3)	0.052 (2)
C(17)	-0.1094 (5)	0.7244 (4)	0.1876 (3)	0.045 (1)
C(18)	-0.0448 (4)	0.8152 (4)	0.1346 (3)	0.047 (2)
C(19)	-0.1148 (5)	0.8451 (4)	0.0530 (3)	0.047 (2)
C(20)	-0.2566 (5)	0.7876 (4)	0.0159 (3)	0.045 (2)
C(21)	-0.3235 (5)	0.6941 (4)	0.0642 (3)	0.053 (2)
C(22)	-0.2516 (5)	0.6663 (4)	0.1468 (3)	0.051 (2)
C(23)	-0.3305 (5)	0.8300 (5)	-0.0699 (4)	0.065 (2)
C(24)	-0.4853 (5)	0.7640 (7)	-0.0934 (5)	0.108 (3)
C(25)	-0.2996 (6)	0.9881 (5)	-0.0203 (5)	0.089 (2)
C(26)	-0.2781 (8)	0.7959 (8)	-0.1825 (4)	0.122 (4)
Minor Disorder Atoms [sof = 0.45 (2)]				
C(9)'	0.116 (2)	0.540 (2)	0.106 (1)	0.060 (5)
C(10)'	-0.076 (2)	0.396 (2)	0.155 (1)	0.061 (6)

^a U_{eq} = one-third of the trace of the orthogonalized U matrix.

^b Major disorder atoms [sof = 0.55 (2)].

rected for anomalous dispersion.^{33,34} All calculations were performed with SHELX76 and the EUCLID package (geometrical calculations and illustrations) on a MicroVAX cluster.^{35,36} The data for the minor conformer are included in the supplementary material.

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Supplementary Material Available: Tables of anisotropic thermal parameters, all H-atom parameters, bond lengths, bond angles, and torsion angles and a thermal motion ellipsoid plot (8 pages); a listing of observed and calculated structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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