2616 *Organometallics* 1994, *13*, 2616–2627

Complexation of Bis(*p*-*tert*-butylphenyl)magnesium with 1,3-Xylylene Crown Ethers and Glymes

Peter R. Markies, Otto S. Akkerman, and Friedrich Bickelhaupt*

Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083,
NL-1081 HV Amsterdam, The Netherlands

Wilberth J. J. Smeets and Anthony L. Spek†

Bijvoet Center for Biomolecular Research, Vakgroep Kristal- en Structuurchemie,
University of Utrecht, Padualaan 8, NL-3584 CH Utrecht, The Netherlands

Received February 22, 1994®

The complexation of bis(*p*-*tert*-butylphenyl)magnesium (**9**) with a series of polyether ligands was studied. Crystal structures of **9**·[1,3-xylylene-18-crown-5] (**8**), 2 **9**·[1,3,16,18-dixylylene-30-crown-8] (**11**), **9**·[diglyme] (**12**), and **9**·[tetraglyme] (**13**) were determined. Complex **8** has a "rotaxane" structure (**8a**) with hexacoordinated magnesium, analogous to that found previously for Ph_2Mg·[1,3-xylylene-18-crown-5] (**1a**); this provides additional evidence for the dissociative mechanism proposed earlier for rotaxane formation, as does an NMR investigation of **1** and **8** in solution. The thermodynamic parameters for the equilibrium **8b** ⇄ **8a** were determined by temperature dependent ^1H NMR spectroscopy as $\Delta H_{eq} = -5$ kJ mol^{-1} and $\Delta S_{eq} = -17$ mol^{-1} K^{-1}. It was anticipated that in **11**, two diarylmagnesium moieties could be accommodated within the large crown ether. However, in the 2:1 complex, the two magnesiums are not located inside the crown ether cavity, but each interacts at the outside of the crown ether with three adjacent oxygen atoms of a polyether chain and becomes pentacoordinated; the large crown ether ring is folded "inside out", thus facilitating this "side-on" bonding of the two Ar_2Mg units. In **12**, magnesium is also pentacoordinated, while in **13**, the magnesium is pentacoordinated to three adjacent oxygens of the five available, including the one of the methoxy group; apparently, in both **12** and **13** coordinative saturation has been reached within the limits of steric restraints. Complex **8**: space group $P\bar{1}$, $a = 11.949(1)$ Å, $b = 11.999(1)$ Å, $c = 15.302(1)$ Å, $\alpha = 73.20(1)°$, $\beta = 88.00(2)°$, $\gamma = 77.57(1)°$, $R = 0.066$. Complex **11**: space group $P\bar{1}$, $a = 11.453(1)$ Å, $b = 13.696(1)$ Å, $c = 14.217(1)$ Å, $\alpha = 111.40(1)°$, $\beta = 102.97(1)°$, $\gamma = 101.77(1)°$, $R = 0.067$. Complex **12**: space group $C2/c$, $a = 23.530(3)$ Å, $b = 8.821(1)$ Å, $c = 12.731(2)$ Å, $\beta = 97.26(1)°$, $R = 0.062$. Complex **13**: space group $P\bar{1}$, $a = 12.727(1)$ Å, $b = 15.268(1)$ Å, $c = 24.194(2)$ Å, $\alpha = 98.52(1)°$, $\beta = 93.49(1)°$, $\gamma = 99.75(1)°$, $R = 0.057$.

Introduction

In 1988, we presented the remarkable rotaxane structure of complex **1a**, formed by the interaction of diphenylmagnesium and 1,3-xylylene-18-crown-5 (**2**).(1) The monomeric 1:1 complex contained an almost linear diphenylmagnesium unit (C–Mg–C angle 163.8(2)°) piercing through the cavity of the crown ether ring (Scheme 1).

Structures with similar features had been found in complexes of trivalent metals, containing the cation $[MX_2\cdot crown]^+$ (X = Me or Cl; M = Al,(2–5) Yb,(6) and Tl(7)). The crown ether induces dissociation into ionic species; it encloses the positively charged and almost linear MX_2^+ unit in its cavity. As in **1a**, the metal atom is equatorially surrounded by crown ether oxygen atoms, while the M–X bonds are almost perpendicular to the plane of the crown ether. Adducts of R_nAlCl_{3-n} (n = 0–3) with crown ethers have been extensively investigated; a heptacoordinated, symmetrically surrounded AlX_2^+ unit was found in $[AlCl_2\cdot$(benzo-15-crown-5)$][AlCl_3Et]$,(2) $[AlMe_2\cdot$(15-crown-5)$][AlMe_2Cl_2]$,(3) and $[AlCl_2\cdot$(15-crown-5)$][AlCl_4]$.(4) The aluminum atom in $[AlMe_2\cdot$(18-crown-6)$][AlMe_2Cl_2]$(3) interacts with only three of the six available oxygen atoms; the geometry of the crown ether ring remains almost undistorted. Trialkylaluminum compounds gave [crown]·$n[R_3Al]$ complexes, each R_3Al unit being bonded to only one heteroatom of the crown ether ring.(8)

In contrast to the methyl or chlorine ligands in the $[MX_2\cdot crown]^+$ complexes, the phenyl group of **1a** is too large to pierce the rather small crown ether cavity. The stability of its rotaxane structure therefore results both from the bonding of magnesium to the crown ether oxygens

---

† Author to whom correspondence concerning the crystallography should be addressed.

® Abstract published in *Advance ACS Abstracts,* May 15, 1994.

(1) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 4845.

(2) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796.

(3) Bott, S. G.; Alvanipour, A.; Morley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem.* **1987**, *99*, 476.

(4) Strel'tsova, N. R.; Bel'skii, V. K.; Ivakina, L. V.; Storozhenko, P. A.; Bulyshev, B. M. *Koord. Khim.* **1987**, *13*, 1101.

(5) Richey, H. G., Jr.; Bergstresser, G. L. *Organometallics* **1988**, *7*, 1459.

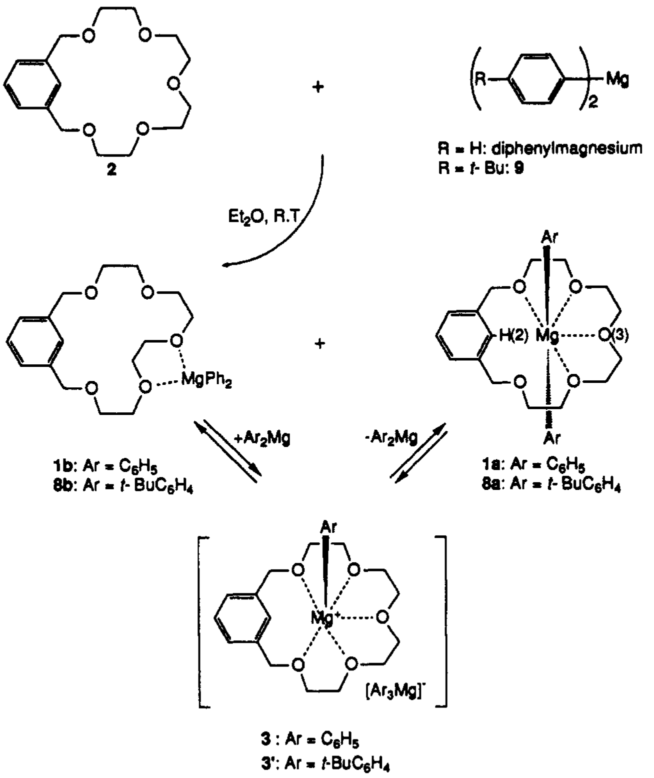
(6) Atwood, D. A.; Bott, S. G.; Atwood, J. L. *J. Coord. Chem.* **1987**, *17*, 93.

(7) Kobiro, K.; Takada, S.; Odaira, Y.; Kawasaki, Y. *J. Chem. Soc., Dalton Trans.* **1986**, 1767, 2613.

(8) (a) Atwood, J. L.; Priester, R. D.; Rogers, R. D.; Canada, L. G. *J. Inclusion Phenom.* **1983**, *1*, 61. (b) Robinson, G. H.; Bott, S. G.; Elgamal, H.; Hunter, W. E.; Atwood, J. L. *J. Inclusion Phenom.* **1985**, *3*, 65. (c) Robinson, G. H.; Hunter, W. E.; Bott, S. G.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *326*, 9. (d) Robinson, G. H.; Zhang, H.; Atwood, J. L. *Organometallics* **1987**, *6*, 887. (e) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 1494.

0276-7333/94/2313-2616$04.50/0

Scheme 1



and from the *mechanical* impossibility of removing the enclosed species as an *intact* entity.

As direct passage of the benzene rings of diphenylmagnesium through the crown ether cavity of **2** appears to be impossible for geometrical reasons, we proposed a stepwise dissociation process for the formation of **1a** instead. After formation of the initial "side-on" complex **1b**, a second molecule of diphenylmagnesium induces the dissociation of a magnesium–phenyl bond to give the intermediate complex **3** in which the phenylmagnesium cation is more efficiently coordinated (Scheme 1); rotaxane **1a** is formed by the transfer of a phenyl anion from Ph$_3$Mg$^-$ to the **2**·[PhMg]$^+$ cation from the opposite side.

The solution of crystallized **1a** in [^{2}H$_8$]toluene exhibited an equilibrium between rotaxane **1a** and side-one complex **1b**, in which the diphenylmagnesium unit is peripherally bonded to **2**. According to the proposed mechanism, conversion of **1a** to **1b** and vice versa can only proceed via intermediate **3**, the steady state concentration of which is probably too low and/or its lifetime too short for direct observation by ^{1}H NMR spectroscopy.[1] Organomagnesium rotaxane structures similar to **1a** have been observed by Richey et al., who studied the complexation of bis(*p*-tolyl)magnesium with 18-crown-6 and 15-crown-5.[9] Complexation of bis(*p*-tolyl)magnesium with the much stronger ligand [2,2,1]-cryptand gave rise to the formation of a magnesium cation/magnesiate species analogous to intermediate **3**. The crystal structure of the diethylmagnesium complex Et$_2$Mg·[18-crown-6] (**4**)[10] also revealed a rotaxane structure with linear magnesium (Chart 1); cf. the linear structures of unsolvated bis(2,2-dimethylpropyl)magnesium[11a] and bis((trimethylsilyl)methyl)magnesium.[11b] The rather long Mg–O bond lengths in **4** (2.767–2.792 Å) suggest an "inclusion compound" character. In the complex of 18-crown-6 with MgCl$_2$ (**5**),[12] however, the symmetry is strongly reduced, which is probably caused by contraction of the crown ether ring to facilitate the formation of five relatively short Mg–O bonds (2.220–2.263 Å); the Mg–O bond length in simple organomagnesium complexes containing two ethers per magnesium is about 2.05–2.10 Å.[13]

The cavity of a 15-crown-5 ligand matches the size of the smaller magnesium cation perfectly, as is illustrated by the crystal structure of the rotaxane complex Mg(NCS)$_2$·[benzo-15-crown-5] (**6**).[14] The Mg–O bonds in **6** (2.171–2.205 Å) are slightly shorter than those in **5**. The crystal structure of the Me$_2$Mg adduct with the smaller crown ether 15-crown-5, 3Me$_2$Mg·[15-crown-5] (**7**), revealed that the dissociation of the diorganylmagnesium into separate MeMg$^+$·crown and [Me$_5$Mg$_2$]$^-$ ions, the magnesiate anions forming a polymeric chain via μ-bridging methyl groups.[15] The solvation by the crown ether separates both ions almost completely, with a shortest Mg(cation)–Me(anion) contact distance of 3.28 Å. The crystal structure of **7** confirmed the results of earlier ^{1}H NMR studies of the 15-crown-5/diethylmagnesium system in THF;[16] even in this strongly coordinating solvent, the 15-crown-5 is able to form activated dialkylmagnesium/crown ether species; this must be caused by the optimal fit of magnesium into the crown ether cavity.

In this paper, the interaction of **2** with diarylmagnesium species is further investigated. In addition to **1**, the new complex **8** has been prepared from bis(*p-tert*-butylphenyl)magnesium (**9**) and **2**: both **1** and **8** are 1:1 adducts. Complex **8** crystallized more easily than **1**, while the remote *tert*-butyl groups do not influence the coordinational behavior of magnesium in an essential way.

By the presence of the *tert*-butyl groups in **9**, its complexes generally crystallized more easily, while the interpretation of the NMR spectra of the complexes was facilitated. Therefore, complexes were included in our studies of **9** with the ligands 1,3,16,18-dixylylene-30-crown-8 (**10**), diglyme, and tetraglyme which have a higher flexibility than **2**; these complexes have the compositions **2 9·10** (**11**), **9**·[diglyme] (**12**), and **9**·[tetraglyme] (**13**). (Scheme 2).

Initially, it was anticipated that in **11** a "double axled" rotaxane could be formed in which two molecules of **9** were threaded through the large crown ether cavity. However, the crystal structure of **11** revealed that both molecules of **9** are complexed to the crown ether in a "side-on" manner, each magnesium being coordinated to three adjacent oxygens of one polyether string in a pentacoordinated manner. Such pentacoordination of magnesium was also found in the crystal structures of **12** and **13** in which the magnesium is bonded to three adjacent oxygens of the polyether chain.

---

[9] Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510.

[10] Pajerski, A. D.; Bergstresser, G. L.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4844.

[11] (a) Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Scott Smith, R. *Acta Chim. Scand. A* **1980**, *34*, 213. (b) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Mc Geary, C. A.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1989**, 273.

[12] Strel'tsova, N. R.; Ivakina, L. V.; Storozhenko, P. A.; Bulychev, B.; Bel'skii, V. K. *Sov. Phys. Dokl.* (*Engl. Transl.*) **1986**, *31*, 943.

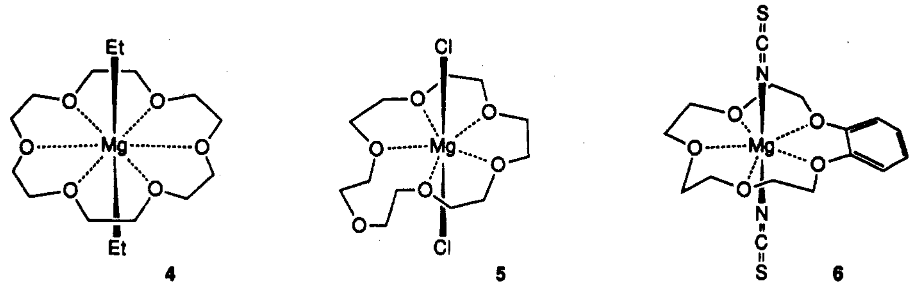
[13] (a) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K. 1982; Vol. I, p 155. (b) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Adv. Organomet. Chem.* **1991**, *32*, 147.

[14] Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1418.

[15] Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660.

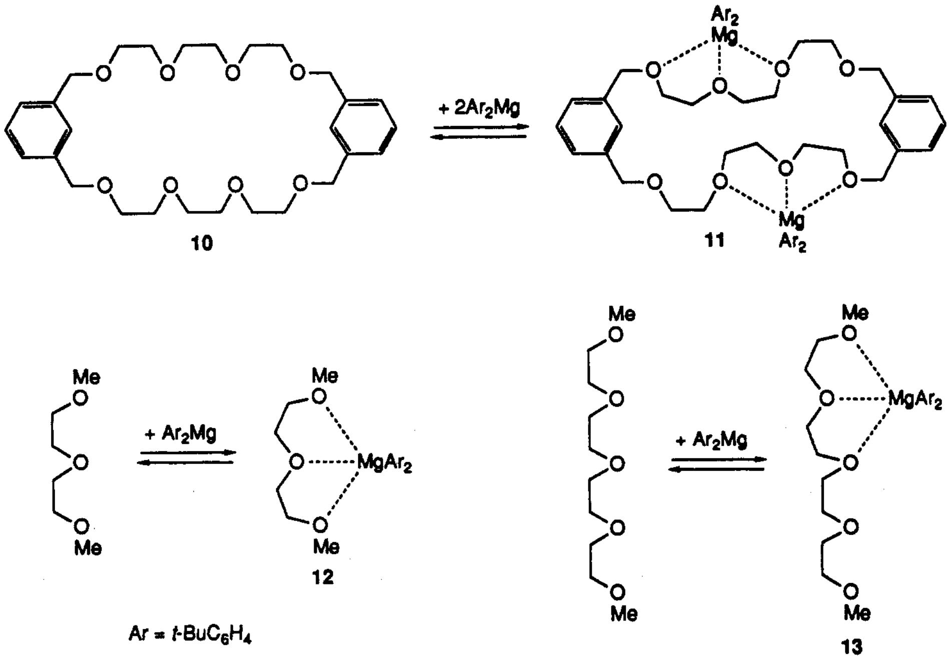
[16] Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672.

Chart 1



4 5 6

Scheme 2



10 11 12 13

Ar = *t*-BuC$_6$H$_4$

Results and Discussion

The starting materials diphenylmagnesium and 9 were prepared from the corresponding diarylmercury compounds in order to obtain pure, halogen free diorganylmagnesium solutions. Complexes with the glymes were prepared by mixing the appropriate components in an apolar solvent (see Experimental Section). The crown ether complexes were obtained by the interaction of the appropriate diarylmagnesium with 2 or 10 in diethyl ether; a precipitate formed that was recrystallized from toluene.

Studies of 1 and 8 in Solution. The crown ether complexes were studied by ^{1}H NMR spectroscopy in [^{2}H$_8$]-toluene solution. For 1, the influence of the addition of diphenylmagnesium or crown ether to the equilibrium mixture was investigated. Addition of an excess of 2 changed the signals of the "side-on" complex **1b**: due to a fast exchange between **1b** and free crown ether 2, the signals of these species coalesced, giving rise to an averaged set of signals. The chemical shifts were found at the weighted average positions between those of the pure components 2 and **1b**. The signals of rotaxane **1a** remained unchanged. This result indicates that a facile and rapid equilibrium is established between 2 and **1b** in accordance with Scheme 1; the kinetic barrier to **1a** is obviously higher (Scheme 3).

Addition of an excess of diphenylmagnesium etherate gave completely different results. Now the signals of both **1a** and **1b** broadened. This proves that diphenylmagnesium serves as a catalyst for the interconversion of **1a** and **1b**, and is supporting evidence for the postulated mechanism shown in Scheme 1, which needs external diphenylmagnesium for the formation of the magnesiate intermediate 3.

Scheme 3

$$2 + \mathrm{Ph_2Mg} \overset{\text{fast}}{\rightleftharpoons} \mathbf{1b} \underset{[\mathrm{Ph_2Mg}]}{\overset{\text{slow}}{\rightleftharpoons}} \mathbf{1a}$$

When crystalline 8 (=rotaxane **8a**; vide infra) was dissolved in [^{2}H$_8$]toluene, again an equilibrium mixture of **8a** and **8b** was formed. The unusually strong deshielding of the xylyl H(2) singlet of **8a** (δ = 9.08 ppm), similar to that in **1a**, indicates a rotaxane structure, in which this proton is located in the vicinity of the magnesium.[1] Compound 8 could be subjected to a detailed ^{1}H NMR spectroscopic analysis, as the *p-tert*-butylphenyl groups in 8 gave a simple signal pattern (quasi AB system (aryl H) plus a singulet (*t*-Bu)); in the 400-MHz ^{1}H NMR spectrum, all signals of both isomers were identified. With the help of 2D NOESY ^{1}H NMR spectroscopy (400 MHz) of the mixture of the rotaxane and side-on complex, the assignment of each signal as belonging to either **8a** or **8b** was confirmed. All protons of the crown ether rings were assigned to the AA′BB′ multiplets of the ethylene groups. Both **8a** and **8b** were found to be symmetrical with respect to the plane through xylyl H(2) and O(3), perpendicular to the aryl and crown ether planes. The higher symmetry of **8a** in solution (C_{2v}), as compared to that of its crystal structure (C_1, vide infra), must be the result of fast dynamic processes in solution. Exchange of the signals of the aryl

H(2) and of the xylyl CH_2 protons between **8a** and **8b** was observed. The NOESY interactions between the diarylmagnesium unit (especially its aryl H(2,6) signals) and ligand **2** were found to be stronger for **8a** than for **8b**. This is in agreement with the remote and rather weak complexation in **8b**.

The thermodynamic parameters ΔH_{eq} and ΔS_{eq} of the "rotaxane"/"side-on complex" equilibrium **8a**/**8b** were determined by variable temperature ^{1}H NMR spectroscopy ([$^2H_8$]toluene, 250 MHz). Upon raising the temperature, the amount of **8a** steadily decreased. At 355 K, the signals of both **8a** and **8b** became very broad due to the increased rate of interconversion. Moreover, at this temperature slow decomposition occurred, leading to the formation of the "hydrolysis products" *tert*-butylbenzene and free crown ether, but indications for a metalation reaction, which would yield the known 2-(arylmagnesio)-1,3-xylylene-18-crown-5,[17] were not obtained; other decomposition products were not identified. Values of ΔH_{eq} = -5 kJ mol^{-1} and ΔS_{eq} = -17 J mol^{-1} K^{-1} were found for the conversion of **8b** to **8a**. The negative values for ΔS_{eq} (an indication for the loss of degrees of freedom in **8a**) and for ΔH_{eq} (suggesting a more efficient complexation of the magnesium in **8a**) are in agreement with the structure assignments of Scheme 1. The accuracy of the values is limited due to the low solubility of **8** in toluene and to the presence of small amounts of impurities; the correlation coefficient for the applied linear regression is R = 0.98. The rather small difference in thermodynamic stability ΔH_{eq} was surprising, as we had expected that the polycoordination in **8a** would be more favorable. On the other hand, it explains why rotaxane formation does not occur at all in the strongly coordinating solvent THF.[1]

Crystal Structure of Crown Ether Complex 8a. Crystallization of **8** from toluene yielded crystals suitable for an X-ray structure determination; according to the ^{1}H NMR spectrum in [$^2H_8$]toluene, the crystals contained 2 equiv of toluene as crystal solvent.

A structure determination of **8** was of interest for two reasons. In the first place, it is not a priori predictable which of the components from an equilibrium such as **1a**/**1b** or **8a**/**8b** will crystallize; it turned out in both cases to be the rotaxane (**1a** and **8a**, respectively). Secondly, the unequivocal demonstration of the rotaxane structure for **8a** would be an even more compelling piece of evidence for the dissociation mechanism of Scheme 1, because for the bulky *tert*-butyl group it is even less feasible to penetrate the crown ether cavity of **2** than for the phenyl group, unlikely as it is for the latter! Very recently we obtained additional proof for this dissociative mechanism: an *organometallic catenane* was formed from 1,3-xylylene-18-crown-5 and a diphenylmagnesium in which the 3 and 3′ positions of the aryl groups were connected by a 1,12-dioxydodecane bridge.[17e]

The structure of **8a** is practically identical with that of **1a** (Figure 1). Even the conformations of the crown ether rings are analogous. Evidently, the influence of the *p-tert*-butylphenyl groups on the molecular structure is of minor importance. As compared to the highly symmetrical structure of **4**,[10] the structures of **1a** and **8a** are clearly irregular. In **1a** and **8a**, the presence of a 1,3-xylylene unit prevents all five crown ether oxygens from taking part equally in the coordination process; thus, not surprisingly, **2** is a less efficient ligand for the coordination of an organomagnesium than 1,3-xylylene-15-crown-4 (**14**).

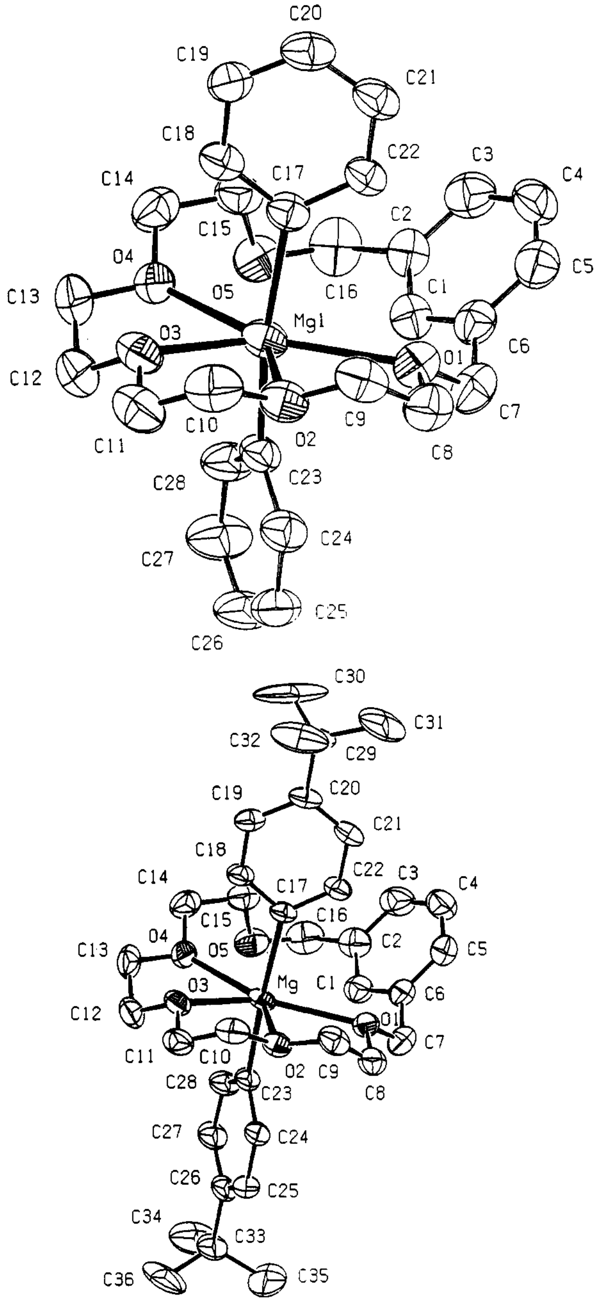


Figure 1. ORTEP drawing for the isostructural complexes **1a** (top) (40% probability) and **8a** (bottom) (30% probability), as seen from a similar viewpoint. Hydrogen atoms have been omitted for clarity.

Relevant data on the structure of **8a** are given in Table 1 (note that the numbering of the crystal structures is that given in the figures; it differs from the IUPAC numbering used in the rest of the text). As in **1a**, the magnesium atom is mainly bonded to O(2) (2.214(3) Å) and O(3) (2.211(3) Å); the coordination to O(1) (2.520(3) Å) and O(4) (2.550(3) Å) is significantly weaker. A coordinative plane is formed by magnesium and O(1–4) within 0.06(2) Å; one oxygen is not involved in the coordination process (Mg–O(5) 4.095(3) Å, distance to the O(1–4) plane 0.555(2) Å). Like in **1a**, the plane of the xylyl group in **8a** is not parallel

---

(17) (a) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Angew. Chem.* **1988**, *100*, 1143. (b) Gruter, G. J. M.; van Klink, G. P. M.; Akkerman, O. S.; Bickelhaupt, F. *Organometallics* **1993**, *12*, 1180. (c) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *Organometallics* **1985**, *4*, 1154. (d) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672. (e) Gruter, G. J. M.; de Kanter, F. J. J.; Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1993**, *115*, 12179.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 1a and 8a

param[a]	1a[b]	8a	param	1a	8a
Mg–C(17)	2.189(5)	2.187(4)	C(17)–Mg–C(23)	163.8 (2)	166.79(13)
Mg–C(23)	2.190(5)	2.188(4)	C(17)–Mg–O(2)	96.9 (2)	96.86(12)
Mg–O(1)	2.516(4)	2.520(3)	C(17)–Mg–O(3)	96.3 (2)	94.96(11)
Mg–O(2)	2.204(3)	2.214(3)	C(23)–Mg–O(2)	96.1 (2)	94.62(12)
Mg–O(3)	2.222(4)	2.211(3)	C(23)–Mg–O(3)	95.9 (2)	94.40(11)
Mg–O(4)	2.520(4)	2.550(3)	O(2)–Mg–O(3)	74.6 (1)	74.43(10)

[a] The labeling of the atoms in 1a and 8a is the same. [b] See ref 1.

to the O(1–4) plane; the angle between both planes is 49.2(2)°, creating a relatively long distance between magnesium and the xylylene group (Mg–H(1) 3.205(5) Å, Mg–C(1) 3.542(5) Å); the resulting steric compression of the C(1)–H(1) bond may be responsible for the deshielding observed in the ^1H NMR spectrum of H(1) (=xylylene H(2), see Scheme 1) although anisotropy effects due to the proximity of the diarylmagnesium moiety may also play a role.[18] The diarylmagnesium unit in 8a is slightly more linear (166.8(1)°) than that in 1a (163.8(2)°); in both complexes the aryl groups are folded slightly away from the coordinating oxygen atoms. The Mg–C bonds are slightly elongated (Mg–C(17) 2.189(5) and 2.187(4) Å, Mg–C(23), 2.190(5) and 2.188(4) Å for 1a and 8a, respectively), as compared with those found in the monomeric structures of [$Ph_2Mg\cdot 2THF$] and [$(p\text{-tolyl})_2Mg\cdot 2THF$] of 2.126(7)–2.132(8) Å.[19] This is probably a consequence of the higher coordination number of magnesium in the rotaxane complexes.

Crystal Structure of Crown Ether Complex 11. Our investigations of the metalation reaction[17] occurring when diphenylmagnesium was treated with 1,3-xylylene-15-crown-4 (14) had afforded, as byproducts from the synthesis of 14, minor quantities of the corresponding dimer 1,3,16,18-dixylylene-30-crown-8 (10). It was therefore tempting to investigate whether 10 was able to form a "double-axled rotaxane", as this polyether macrocycle is, in principle, large enough to accommodate two diarylmagnesium units in its cavity. Indeed, treatment of 1 equiv of 10 with 2 equiv of 9 yielded a crystalline adduct 11 having the composition 29·10·2[toluene], as derived from the ^1H NMR spectrum in [$^2H_8$]THF. In [$^2H_8$]toluene solution, the ^1H NMR spectrum showed broad signals, probably due to dynamic processes. The very low solubility of 11 in apolar solvents hampered further NMR spectroscopic studies. However, the high quality of the crystals obtained enabled us to perform an X-ray structure determination. A centrosymmetric structure was found, in which two molecules of 9 were coordinated to 10; surprisingly, it appeared to be a double side-on complex (see Figure 2). Apparently, there is, after all, not sufficient space in the cavity of 10 to accommodate the two diarylmagnesiums; thus, the diarylmagnesium units prefer coordination at the periphery of 10. Three oxygen atoms of the parallel triethylene glycol ether bridges connecting the 1,3-xylylene units are turned outward, each bonding one diarylmagnesium unit via three adjacent oxygens. Relevant structural parameters of 11 (bond distances and angles) are given in Table 2 (note that the numbering of the crystal structures is that given in the figures; it differs from the IUPAC numbering used in the rest of the text).

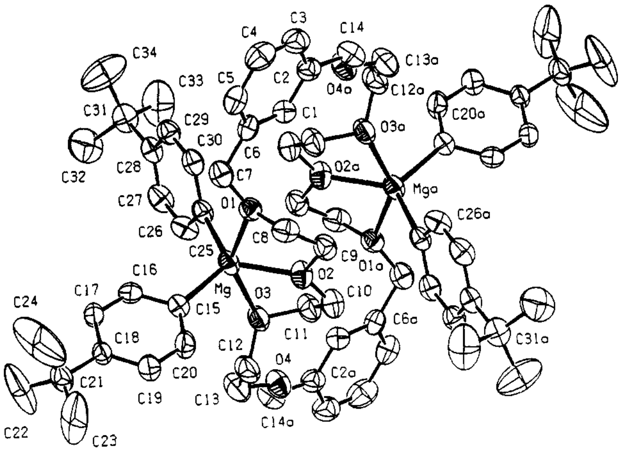


Figure 2. ORTEP drawing for complex 11 (30% probability). Hydrogen atoms have been omitted for clarity.

Each magnesium and its three coordinating oxygen atoms lie in a plane (A) within 0.142(3) Å. The Mg–O bonds are not equal, the central Mg–O(2) (2.119(4) Å) being shorter than the outer ones (Mg–O(1) 2.251(3) Å, Mg–O(3) 2.252(4) Å). A second plane B, nearly perpendicular to A (88.9(2)°), is formed by C(15), C(25), Mg, and O(2). Plane B is the equatorial plane of a distorted trigonal bipyramid (TBP), which explains the relative shortness of its bonds (see also the discussion of the structure of 13). The diarylmagnesium unit has normal structural features (Mg–C(15), 2.148(5) Å, Mg–C(25) 2.156(6) Å, C(15)–Mg–C(25) 119.9(2)°).

Because of disorder in the toluene solvent molecules, 11 was also crystallized from benzene, in order to determine a *duplo* crystal structure. Crystals of 11a with the composition 29·10·2[benzene] were isolated. The crystal structures of 11 and 11a proved to be almost identical. Unfortunately, in the case of 11a, the *tert*-butyl groups of the diarylmagnesium units were disordered, leading to less reliable structural data ($R = 0.097$).

When the crystal structure of pure 10[20] is compared with that of complex 11, it appears that significant conformational changes occur in the ligand when it complexes with the diphenylmagnesiums, clearly illustrating the flexibility of 10.

Crystal Structures of the Glyme Complexes 12 and 13. For comparison with the crown ether complexes 1a, 8a, and 11, adducts of 9 with a series of glymes $CH_3(OCH_2CH_2)_nOCH_3$ ($n = 2$, diglyme; $n = 3$, triglyme; $n = 4$, tetraglyme) were investigated. Unlike the "preorganized" crown ethers 2, 10, and 14, the more flexible glymes are expected to show a reduced complexing tendency, because the favorable enthalpy gain by (poly)coordination will be largely compensated for by an unfavorable loss of entropy.[21]

---

[18] Jenneskens, L. W.; de Kanter, F. J. J.; Turkenburg, L. A. M.; de Boer, H. J. R.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1984**, *40*, 4401 and references cited therein.

[19] Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Organomet. Chem.* **1990**, *393*, 315.

[20] Smeets, W. J. J.; Spek, A. L.; Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F. *Acta Crystallogr.*, to be published.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 11

Mg–C(15)	2.148(5)	C(15)–Mg–C(25)	119.87(19)	O(2)–Mg–O(3)	72.66(15)
Mg–C(25)	2.156(6)	O(1)–Mg–O(2)	70.75(14)	O(2)–Mg–C(15)	113.68(18)
Mg–O(1)	2.251(3)	O(1)–Mg–O(3)	142.79(15)	O(2)–Mg–C(25)	126.42(19)
Mg–O(2)	2.119(4)	O(1)–Mg–C(15)	98.87(15)	O(3)–Mg–C(15)	101.67(17)
Mg–O(3)	2.252(4)	O(1)–Mg–C(25)	98.60(17)	O(3)–Mg–C(25)	97.57(18)

Adduct **12** was obtained from **9** and diglyme by the same procedure as applied for **1** and **8**; due to its low solubility in diethyl ether, crystallization of **12** drives the reaction to completion. Recrystallization from toluene yielded crystals suitable for an X-ray structure determination. Characterization of **12** with ^{1}H NMR spectroscopy in [$^2H_8$]-toluene revealed the composition **9**·[diglyme].

A modified procedure was necessary for the isolation of the adducts of **9** with triglyme and tetraglyme. Because of the relatively high solubility of these adducts in diethyl ether, they did not precipitate on mixing the reagents; when the solution was cooled, **9**·$2Et_2O$ crystallized, while the free glyme stayed in solution. Apparently, there is a rather balanced competition between diethyl ether and the glyme, which illustrates the relatively low coordinative potential of these polyethers toward organomagnesiums. Evaporation of the diethyl ether solution yielded an oil, from which crystals were grown by addition of *n*-hexane and subsequent cooling. Characterization of the isolated crystals by ^{1}H NMR spectroscopy in [$^2H_8$]toluene revealed the formation of 1:1 adducts: **9**·[triglyme] (**15**) and **9**·[tetraglyme] (**13**). In these NMR spectra, the signals of the glymes (CH_2 and OMe) are shielded relative to those of the free ligands, indicating that in the noncoordinating [$^2H_8$]toluene, the 1:1 adducts remain intact. The multiplet patterns of the CH_2 groups showed that, in solution, the structures of **12**, **13**, and **15** are symmetrical (C_{2v}). A ^{13}C NMR spectrum of **15** in [$^2H_8$]toluene revealed C_{2v} symmetry, too.

For **12** and **13**, the quality of the crystals permitted a structure determination. The crystal structure for **12** is depicted in Figure 3; only half of it is crystallographically unique due to the presence of a C_2 rotation axis along the Mg–O(2) bond (note that the numbering of the crystal structures is that given in the figures; it differs from the IUPAC numbering used in the rest of the text). The diarylmagnesium unit is coordinated by the three oxygen atoms of the glyme ligand. Relevant data on the structure of **12** can be found in Table 3. The environments of the magnesium atom in **11** and **12** are closely similar, but in contrast to **11**, the Mg–O distances of **12** are almost equal (Mg–O(1) 2.158(2) Å, Mg–O(2) 2.153(3) Å). Probably due to the slightly stronger coordination of the magnesium atom, the C(1)–Mg–C(1a) angle is somewhat smaller (112.6(1)°).

Table 3. Selected Bond Distances (Å) and Angles (deg) of 12

Mg–C(1)	2.157(3)	O(1)–Mg–O(2)	70.99(6)
Mg–O(1)	2.158(2)	O(1)–Mg–C(1)	97.32(9)
Mg–O(2)	2.153(3)	O(1)–Mg–O(1a)[a]	141.97(9)
		O(2)–Mg–C(1a)	103.55(9)
		O(2)–Mg–C(1)	123.71(7)

[a] "a" indicates symmetry operation $-x, y, {}^1/_2 - z$.

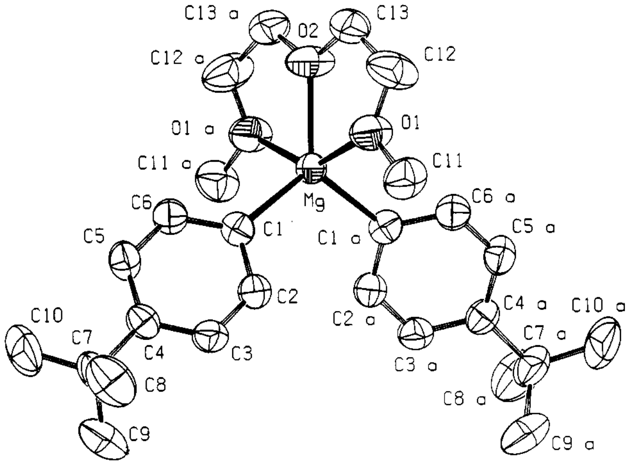


Figure 3. ORTEP drawing for complex **12** (50% probability). Hydrogen atoms have been omitted for clarity.

The crystal structure of **13** has two remarkable features. In the first place, three independent molecules were found in the unit cell in a 1:1:1 ratio; these residues (**13a**, **13b**, and **13c**) are chemically identical but different with respect to their structural details. In Figure 4, they are depicted from a similar point of view. Secondly, two adjacent oxygen atoms at one end of each glyme are not involved in the coordination process. We feel that this can be rationalized as follows. In **13** (and related structures with pentacoordinated magnesium), the metal has reached a state of coordinative saturation which is probably determined by steric factors more than by electronic saturation, because under favorable circumstances, organomagnesiums can exhibit hexacoordination and even higher coordination.[9,13b] It is probably also for steric reasons that one of the methoxy groups of the tetraglyme is used in the three-oxygen coordination, because the combination of a terminal methyl group with a dangling $CH_2CH_2OCH_2CH_2OMe$ residue is sterically less demanding (in the vicinity of magnesium) than two CH_2CH_2OMe residues. Moreover, as briefly pointed out above, the energy gain by additional oxygen coordination will be annihilated by a concomitant decrease in entropy. Finally, the cumulation of five-membered rings, occurring in the glyme structure when more than three oxygens participate in the coordination, may lead to either ring strain and/or unfavorable positions of the oxygens relative to the magnesium. The differences between residues **13a–c** can be derived from Table 4.

Rather small variations are found in the Mg–C bond distances (2.144(8) in **13a** to 2.167(8) Å in **13b**), and larger ones, in the Mg–O bond distances (2.106(6) in **13c** to 2.341(5) Å in **13c**); the C–Mg–C angles range from 119.9(3) in **13b** to 124.1(3)° in **13a**. While the coordinated parts of the tetraglyme have identical conformations (in underlined italics), the conformations of the noncoordinating parts are completely different: **13a**, *T-G-T-T-G′-T*-T-G′-T-T-G′-T; **13b**, *T-G-T-T-G′-T*-G-G′-G′-G-G-T; **13c**, *T-G′-T-T-G-T*-G′-G′-T-G′-G-G′. Obviously, this is caused by packing effects since residues **13a–c** have different environments in the unit cell. The structures of **11–13** can be compared by applying the scale from ideal TBP (0%) to ideal square pyramidal (SP, 100%) expressed in the

---

(21) Inoue, Y.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1985**, 935.

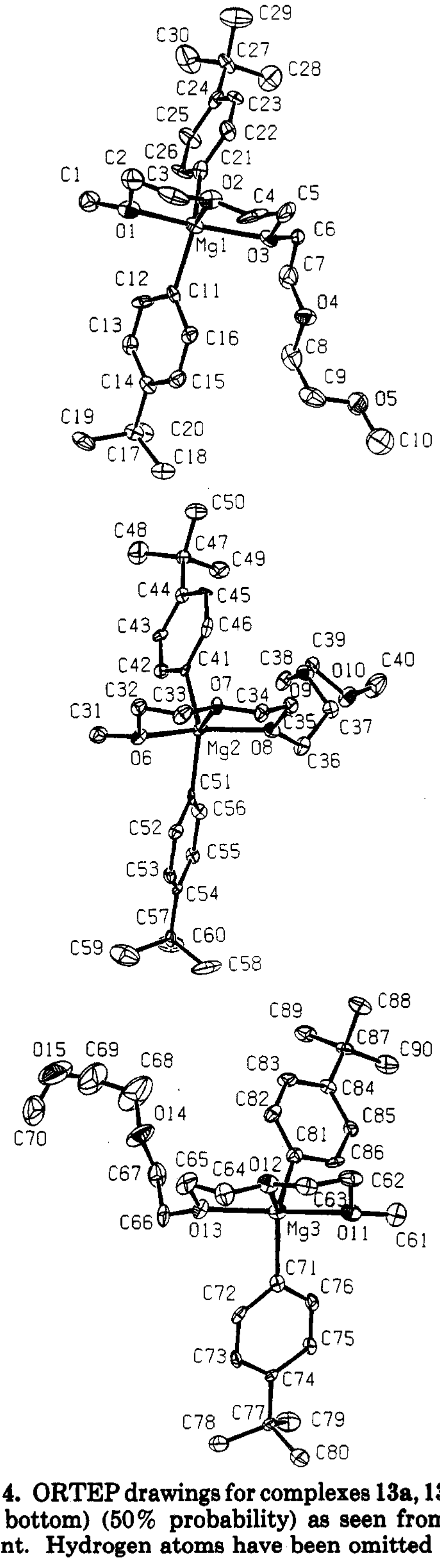


Figure 4. ORTEP drawings for complexes **13a**, **13b**, and **13c** (top to bottom) (50% probability) as seen from a similar viewpoint. Hydrogen atoms have been omitted for clarity.

percentage along the Berry pseudorotation coordinate.[22] In this way, the following values are found: **11**, 38.3%; **12**, 34.0%; **13a–c**; 41.2, 58.0, and 50.1%, respectively. These values indicate that **13b** has the highest tendency toward a SP surrounding, while **12** shows the smallest deviation from a distorted TBP surrounding; however, all structures are strongly distorted and the differences are not dramatic.

The closely related structures of **11**, **12**, and **13a–c** present a new coordination mode for organomagnesium compounds, which may be common among adducts of diorganylmagnesium reagents with flexible oligo(ethylene glycol) ligands. Although crystals were isolated of **15**, their quality was not sufficient to allow a structure determination. But, on the basis of the findings of **11–13**, a structure for **15** can be suggested in which one terminal oxygen atom is not involved in the coordination process. The symmetrical structures of **13** and **15** in solution, as derived from the NMR spectroscopic investigations, can be explained by a fast exchange at room temperature in which the diarylmagnesium unit moves along the glyme ligand. In principle, it should be possible to freeze this dynamic process at low temperature and to study it by variable temperature NMR spectroscopy. Due to fast exchange and low solubilities attempts to achieve this failed.

Conclusion

The results of this investigation again emphasize the importance of coordination for the structure of organomagnesium compounds. While simple ethers normally lead to a tetrahedrally coordinated magnesium,[13] as in $Ph_2Mg{\cdot}2THF$,[19] polyethers induce higher coordination states. This is of interest for two reasons.

In the first place, it underlines the importance of steric hindrance in the coordination chemistry of organomagnesium compounds: the magnesium is a sufficiently strong Lewis acidic center to demand coordination by three or four oxygen bases, but the electronically preferred high coordination number can only be achieved if the steric hindrance between the ligands is diminished through linking them by (intramolecular) bonds.

Secondly, it should be pointed out that the unusual, high coordination may lead to increased reactivity of the organomagnesium reagent.[17]

Experimental Section

Manipulations involving organomagnesium compounds were carried out in fully sealed glassware without ground joints or stopcocks using high vacuum techniques. Solvents were dried by distillation from liquid Na/K alloy after predrying on NaOH. The ligands diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) were dried by distillation from sodium in high vacuum. Amounts of "total base" and Mg^{2+} in organomagnesium samples were determined by titration with HCl and EDTA, respectively.[23] NMR spectra were measured on a Bruker WH 90 (^1H NMR, 90 MHz), Bruker WH 250 (^1H NMR, 250 MHz; ^{13}C NMR; 62.89 MHz; ^{199}Hg NMR, 44.77 MHz), or Bruker MSL 400 (^1H NMR, NOESY) spectrometer. 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. The starting materials 1-bromo-4-*tert*-butylbenzene (Aldrich), mercuric bromide (Merck, z.A.), diphenylmercury (Merck), aluminum oxide (Merck 90, activity II–III), diglyme (Merck), triglyme (Merck), and tetraglyme (Janssen) were commercially available. Elemental analyses were carried out at the Organic Chemical Institute TNO, Zeist, The Netherlands.

1,3-Xylylene-18-Crown-5 (2). Compound **2** was synthesized from 1,3-bis(bromomethyl)benzene and the tetraethylene glycol in THF using KH as a base. The crown ether was purified by gradual elution over an Al_2O_3 column using petroleum ether/THF as eluent, followed by repeated crystallization from diethyl ether at −20 °C (mp 41–43 °C, 59% yield). The purity of **2** was

---

[22] Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119.

[23] Blomberg, C.; Vreugdenhil, A. D.; Vink, P. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 662.

Table 4. Selected Bond Distances (Å) and Angles (deg) of 13a–c

residue **13a**		residue **13b**		residue **13c**	
Mg(1)–O(1)	2.194(5)	Mg(2)–O(6)	2.191(6)	Mg(3)–O(11)	2.341(5)
Mg(1)–O(2)	2.116(6)	Mg(2)–O(7)	2.176(5)	Mg(3)–O(12)	2.106(6)
Mg(1)–O(3)	2.230(6)	Mg(2)–O(8)	2.161(5)	Mg(3)–O(13)	2.224(5)
Mg(1)–C(11)	2.151(8)	Mg(2)–C(41)	2.158(7)	Mg(3)–C(71)	2.148(8)
Mg(1)–C(21)	2.144(8)	Mg(2)–C(51)	2.167(8)	Mg(3)–C(81)	2.145(8)
C(11)–Mg(1)–C(21)	124.1(3)	C(41)–Mg(2)–C(51)	123.4(3)	C(71)–Mg(3)–C(81)	119.9(3)
O(1)–Mg(1)–O(2)	72.9(2)	O(6)–Mg(2)–O(7)	73.5(2)	O(11)–Mg(3)–O(12)	73.5(2)
O(1)–Mg(1)–O(3)	146.2(2)	O(6)–Mg(2)–O(8)	140.6(2)	O(11)–Mg(3)–O(13)	144.3(2)
O(1)–Mg(1)–C(11)	93.4(3)	O(6)–Mg(2)–C(41)	103.0(2)	O(11)–Mg(3)–C(71)	97.2(2)
O(1)–Mg(1)–C(21)	102.2(3)	O(6)–Mg(2)–C(51)	90.4(3)	O(11)–Mg(3)–C(81)	95.1(2)
O(2)–Mg(1)–O(3)	74.8(2)	O(7)–Mg(2)–O(8)	72.0(2)	O(12)–Mg(3)–O(13)	73.2(2)
O(2)–Mg(1)–C(11)	126.9(3)	O(7)–Mg(2)–C(41)	106.7(2)	O(12)–Mg(3)–C(71)	130.6(3)
O(2)–Mg(1)–C(21)	109.0(3)	O(7)–Mg(2)–C(51)	129.7(3)	O(12)–Mg(3)–C(81)	109.4(3)
O(3)–Mg(1)–C(11)	98.0(3)	O(8)–Mg(2)–C(41)	104.7(3)	O(13)–Mg(3)–C(71)	94.7(3)
O(3)–Mg(1)–C(21)	97.5(3)	O(8)–Mg(2)–C(51)	97.0(3)	O(13)–Mg(3)–C(81)	107.7(3)

checked by ^{1}H and ^{13}C NMR spectroscopy and GCMS. The spectral data were in accordance with those in the literature.[25,26]

Bis(*p*-*tert*-butylphenyl)mercury was synthesized from 1-bromo-4-*tert*-butylbenzene according to literature procedures;[24] it was crystallized from acetone at −20 °C; yield 74%, mp 189 °C. ^{1}H NMR (250 MHz, $CDCl_3$ reference $CHCl_3$ = 7.27 ppm): δ 1.37 (s, 18 H, *t*-Bu), 7.40 (d, AB, ^3J = 8 Hz, 4 H, aryl H(3,5)), 7.52 (d, AB, ^3J = 8 Hz, aryl H(2,6)). ^{13}C NMR (62.89 MHz, $CDCl_3$, reference $CDCl_3$ = 77 ppm): δ 31.32 (qs, ^1J = 126 Hz, ^3J = 5 Hz, 6 C, Me), 34.44 (s, 2 C, C–Me_3), 125.4 (dd, ^1J = 155 Hz, ^3J = 6 Hz, ^3J(Hg–C) = 102 Hz, 4 C, aryl C(3,5)), 137.21 (dd, ^1J = 159 Hz, ^2J = 10 Hz, ^2J(Hg–C) = 86 Hz, 4 C, aryl C(2,6)), 150.81 (s, 2 C, aryl C(4)), 167.51 (s, 2 C, aryl C(1)). ^{199}Hg NMR (44.77 MHz, $CDCl_3$, reference Ph_2Hg = 0 ppm) δ 44.3 (pp, ^3J(H–Hg) = 103 Hz, ^4J(H–Hg) = 16 Hz, Hg). MS (Varian CH5 DF, direct inlet, EI, 70 eV): *m/z* (relative intensity) 468 (M^+, 37), 453 (M^+ − Me, 100), 219 (22), 133 (43), 117 (29), 105 (28), 91 (57), 77 (29), 57 (23). HRMS: calcd for $C_{20}H_{26}{}^{202}Hg$ 468.1741, found 468.1726.

Synthesis of Bis(*p*-*tert*-butylphenyl)magnesium (9). In a completely sealed high vacuum glass apparatus, bis(*p*-*tert*-butylphenyl)mercury (4.67 g, 10 mmol) was reacted with magnesium (triply sublimed, 2.4 g, 100 mmol) in diethyl ether (100 mL, dried by distillation from Na/K alloy). After stirring for 2 weeks and settling of the magnesium amalgam, the brownish solution was decanted into a second vessel. Completion of the reaction was checked by titration of an aliquot on "total base" and Mg^{2+}. To check the purity of **9**, a second aliquot (5.9 mL) was quenched with D_2O (0.5 mL), aqueous NH_4Cl was 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. Analysis of GCMS and ^{1}H NMR spectroscopy (90 MHz, $CDCl_3$) showed that monodeuterated *tert*-butylbenzene was the only product. The solution of **9** was divided into several samples containing about 1 mmol each.

(4-^{2}H)-*tert*-Butylbenzene. ^{1}H NMR (250 MHz, $CDCl_3$, reference $CHCl_3$ = 7.27 ppm): δ 1.35 (s, 9 H, *t*-Bu), 7.33 (m, AA′BB′, ^3J = 8 Hz, 4 H, aryl H(3,5)), 7.42 (m, AA′BB′, ^3J = 8 Hz, ^5J = 2 Hz, 4 H, aryl H(2,6)). MS (70 eV): *m/z* (relative intensity) 135 (M^+, $C_{10}H_{13}D$, 24), 120 (100), 92 (77), 78 (13).

Bis(*p*-*tert*-butylphenyl)magnesium·Bis(diethyl ether) (9a). Upon slow concentration or cooling (−20 °C) of a solution of **1** (0.1 M) in diethyl ether almost colorless, well shaped crystals were formed. The crystals, which measured up to several millimeters, were isolated by decanting and dried by cooling the mother liquor with liquid nitrogen. Some crystals were dissolved in [$^2H_8$]toluene for analysis by ^{1}H NMR (250 MHz, [$^2H_8$]toluene, reference $C_6D_5CD_2H$ = 2.32 ppm): δ 1.08 (m, very broad, 12 H, CH_3CH_2O), 1.59 (s, 18 H, *t*-Bu), 3.39 (m, very broad, 8 H, CH_3CH_2O), 7.63 (m, very broad, 4 H, aryl H(3,5)), 8.30 (m, very broad, 4 H, aryl H(2,6). Reference spectrum of diethyl ether under the same conditions: δ 1.25 (t, ^3J = 7 Hz, 6 H, Me), 3.40 (q, ^3J = 7 Hz, 4 H, CH_2). A stoichiometry of $Ar_2Mg{\cdot}1.96Et_2O$ was found from the ^{1}H integrals which suggests a monomeric, tetrahedrally coordinated diarylmagnesium complex. The NMR solution proved to be unstable; after several weeks, the diarylmagnesium compound started to precipitate, leaving diethyl ether in solution. In this process, which was accelerated upon heating, the diethyl ether signals sharpened and moved to the positions of free diethyl ether. Crystalline **9a** (0.3 mmol) was dissolved in [$^2H_8$]toluene (2.5 mL) in a 10-mm NMR tube; of the resulting clear solution a ^{13}C NMR spectrum was measured immediately (62.89 MHz, [$^2H_8$]toluene, reference $C_6D_5CD_2H$ = 2.32 ppm): δ 18.10 (q, ^1J = 127 Hz, 6 C, CMe_3), 34.96 (q, ^1J = 124 Hz, 2 C, CH_3CH_2O), 37.96 (s, 2 C, CMe_3), 69.02 (t, ^1J = 135 Hz, 2 C, CH_3CH_2O), 127.41 (d, ^1J = 150 Hz, 4 C, aryl C(3,5)), 147.2 (d, very broad, ^1J = 162 Hz, 4 C, aryl *C*(2,6)), 153.1 (s, very broad, 2 C, aryl *C*(4)), aryl *C*(1) was not discernible. The broadening of the aryl C signals indicates the formation of oligomers after dissociation of the relatively weakly bonded diethyl ether molecules.

1,3,16,18-Dixylylene-30-crown-8 (10). Compound **10** was formed as a side product (dimer) in the synthesis of 1,3-xylylene-15-crown-4 (**14**). The synthesis of **10**, together with its monomer 1,3-xylylene-15-crown-4 (**14**), has been reported by Gray et al. who isolated and characterized **10** as a crude oil.[24] We found that crystallization of **10** is essential to guarantee its identity, since the ^{1}H and ^{13}C NMR spectra of pure **10** and of the crude oligomeric material are nearly identical. Isolation and purification of **10** from the oligomeric fractions was achieved with a gradient column chromatography, followed by repeated crystallizations from ethanol (1% yield, mp 91 °C). ^{1}H NMR ($CDCl_3$, 250 MHz, $CHCl_3$ = 7.27 ppm): δ 3.61–3.64 and 3.66–3.72 (m, AA′BB′, 16H, C_2H_4), 3.68 (s, 8H, C_2H_4), 4.56 (s, 8H, aryl CH_2), 7.22–7.25 (m, 6H, aryl H(4–6)), 7.36 (s, 2H, aryl H(2)). ^{13}C NMR ($CDCl_3$, 62.89 MHz, $CDCl_3$ = 77 ppm): 69.2 (t, ^1J = 141 Hz, 4C, C_2H_4), 70.5 (t, ^1J = 141 Hz, 8C, C_2H_4), 72.8 (t, ^1J = 143 Hz, 4C, aryl CH_2), 126.5 (d, ^1J = 160 Hz, 4C, aryl C(4,6)), 126.6 (d, ^1J = 163 Hz, 2C, aryl C(2)), 128.0 (d, ^1J = 160 Hz, 2C, aryl C(5)), 138.2 (s, 4C, aryl C(1,3)). MS: *m/z* (relative intensity) 504 (4, M^+), 354 (5), 147 (9), 133 (20), 119 (17), 105 (87), 104 (85), 89 (40), 78 (81), 77 (27), 57 (21), 45 (100). Anal. Calcd for $C_{28}H_{40}O_8$: C, 66.65; H, 7.99. Found: C, 66.73; H, 7.87.

Effects of Stoichiometry on 1. The effects of changes of the crown ether:diarylmagnesium ratio on the ^{1}H NMR spectrum of **1a** were investigated. A ^{1}H NMR sample with a large excess of diphenylmagnesium was prepared by dissolving crystalline **1a** in a solution of Ph_2Mg etherate in C_6D_6. The ^{1}H NMR spectrum of this solution, with the composition $21.49Ph_2Mg4.02Et_2O$, showed very broad signals in which the separate components were no longer distinguishable. This effect is explained by a fast exchange between **1a**, **1b**, and the components of the dissociated

---

(24) Benkeser, R. A.; Crimmins, T. F.; Tong, W. *J. Am. Chem. Soc.* **1968**, *90*, 4366.

(25) Gray, R. T.; Reinhoudt, D. N.; Spaargaren, K.; de Bruijn, J. F. *J. Chem. Soc., Perkin Trans. 2* **1977**, 206.

(26) Gray, R. T.; Reinhoudt, D. N.; Smit, C. J.; Veenstra, I. *Recl. Trav. Chim. Pays-Bas.* **1976**, *95*, 258.

Table 5. Crystal Data and Details of the Structure Determination

	8	11	12	13
(a) Crystal Data				
formula	$C_{36}H_{50}MgO_5{\cdot}C_7H_8$	$C_{68}H_{92}Mg_2O_8{\cdot}2C_7H_8$	$C_{26}H_{40}MgO_3$	$C_{30}H_{48}MgO_5$
mol wt	679.23	1270.36	424.91	513.01
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a, b, c (Å)	11.949(1), 11.999(1), 15.302(1)	11.453(1), 13.696(1), 14.217(1)	23.530(3), 8.821(1), 12.731(2)	12.727(1), 15.268(1), 24.194(2)
α, β, γ (deg)	73.20(1), 88.00(2), 77.57(1)	111.40(1), 102.97(1), 101.77(1)	90, 97.26(1), 90	98.52(1), 93.49(1), 99.75(1)
V (Å^3)	2050.1(3)	1920.5(3)	2621.4(6)	4564.4(6)
Z	2	1	4	6
D_{calc} (g cm^{-3})	1.100	1.098	1.077	1.120
$F(000)$	736	688	928	1680
μ (cm^{-1})	6.6	6.9	7.2	0.9
cryst size (mm)	0.30 × 0.45 × 0.55	0.42 × 0.53 × 0.62	0.25 × 0.25 × 1.0	0.44 × 0.35 × 0.42
(b) Data Collection				
temp (K)	295	295	295	100
$\theta_{min}, \theta_{max}$	3.0, 70.3	3.5, 70.0	3.8, 69.9	0.9, 21.5
radiation λ (Å)	Cu Kα (Ni-filtered), 1.541 78	Cu Kα (Ni-filtered), 1.541 78	Cu Kα (Ni-filtered), 1.541 78	Mo Kα (Zr-filtered), 0.710 73
$\Delta\omega$ (deg)	0.55 + 0.35 tan θ	0.70 + 0.35 tan θ	0.45 + 0.35 tan θ	0.60 + 0.35 tan θ
hor and vert aperture (mm)	3.0, 4.0	3.0, 4.0	3.0, 4.0	3.0, 3.0
X-ray exposure time (h)	112	67	55	64
linear decay (%)	6.5	7.3	0.5	2.0
ref reflns	434, 3, −1, 0	202, 2, −3, 3	0,−2,3, −2,2,2, 312	230, 023
data set	h − 14 to +14; k −13 to +14; l 0–18	h 0–13; k −16 to 16; l −17 to +16	h −28 to +28; k − 10 to +10; l 0–15	h 0–12; k −14 to +14; l −24 to +23
total no. of data	8115	7685	5071	9547
total no. of unique data	7806	7293	2495 (R_{int} = 0.031)	9031
obsd data	4376 [$I > 3.0\sigma(I)$]	3257 [$I > 2.5\sigma(I)$]	1934 [$I > 2.5\sigma(I)$]	4590 [$I > 2.5\sigma(I)$]
(c) Refinement				
no. of reflns and params	4376, 457	3257, 361	1934, 150	4590, 976
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.00507F^2]$	$w = 1.0/[\sigma^2(F) + 0.000307F^2]$	$w = 1.0/[\sigma^2(F)]$	$w = 1.0/[\sigma^2(F) + 0.000232F^2]$
final R, wR, S	0.0660, 0.1028, 0.70	0.0669, 0.0799, 0.91	0.0623, 0.0627, 1.38	0.0566, 0.0485, 2.39
isotr therm param H-atoms (Å^2)	0.107(4), 0.101(3), 0.239(9) for CH, CH_2, CH_3 respectively	0.092(5), 0.121(5), 0.189(7) for CH, CH_2, CH_3 respectively	0.118(3)	0.014(4), 0.047(4), 0.058(3) for CH, CH_2, CH_3 respectively
$(\Delta/\sigma)_{av}$ in final cycle	0.041	0.031	0.047	0.024
min and max resd dens, (ϵ/Å^3)	−0.24, 0.56	−0.23, 0.39	−0.30, 0.30	−0.36, 0.32

complex. ^{1}H NMR (250 MHz, C_6D_6, reference C_6D_5H = 7.30 ppm): δ 1.19 (t, ^3J = 7 Hz, 6H, OCH_2CH_3), 3.40 (q, ^3J = 7 Hz, 4H, OCH_2CH_3), 3.1–3.4 (m, 16H, C_2H_4), 4.4 (s, broad, 4H, xylyl CH_2), 7.1–7.3 (m, 3H, xylyl H(4–6)), 7.5–7.7 (m, 6H, aryl H(3–5)), 8.1 (m, 4H, aryl H(2,6)), 8.3 (m, 4H, aryl H(2,6)), 8.3 (s, 1H, xylyl H(2)), 9.0 (s, 1H, xylyl H(2)). In contrast to the other signals, those of diethyl ether were sharp; relative to a reference spectrum of diethyl ether in C_6D_6, only minor upfield shifts were found ($\Delta\delta$ 0.06 ppm (CH_2); 0.00 ppm (CH_3)).

When a 3-fold excess of crown ether **2** was added to a solution of **1a** in C_6D_6, the signals of **1a** remained unchanged. The exchange reaction between **1b** and free **2** is apparently fast on the NMR time scale, giving rise to a single set of crown ether signals at averaged positions.

Bis(*p*-*tert*-butylphenyl)magnesium·1,3-Xylylene-18-crown-5] (8). Complex **8** was synthesized in analogy to its diphenylmagnesium derivative **1**.[1] A solution of **9** (1 mmol, in 8 mL of Et_2O) was mixed with solid 1,3-xylylene-18-crown-5 (1 mmol, in 2 mL of Et_2O). Immediately, a white precipitate formed, which was isolated from the reaction mixture by decantation as a white powder (90% yield). The last traces of diethyl ether were removed by high vacuum pumping. Crystals suitable for an X-ray structure determination were obtained by recrystallization from toluene; according to the ^{1}H NMR spectrum, they contained 1 equiv of toluene.

^{1}H NMR Spectrum of 8. Crystallized **8a** (rotaxane) was dissolved in [$^2H_8$]toluene, and the ^{1}H NMR spectrum (400 MHz) was analyzed by 2D NOESY techniques. Assignment of all signals was possible; a mixture of two complexes **8a** (rotaxane) and **8b** (side-on) was found with a ratio of 63:37. Both **8a** and **8b** showed a diarylmagnesium to crown ether ratio of 1:1. In diethyl ether, **8** was insoluble. Complete dissociation into the components takes place in [$^2H_8$]THF; the signals of **2** were identical to those of a reference spectrum of pure **2** reported earlier.[1]

^{1}H NMR (400 MHz, [$^2H_8$]toluene, reference $C_6D_5{\cdot}CD_2H$ = 2.32 ppm): (**8a**) δ 1.647 (s, 18 H, *t*-Bu), 3.202–3.225 and 3.281–3.315 (m, AA′BB′(1), 8H, CH_2(9,10,12,13)), 3.336–3.372 and 3.488–3.539 (m, AA′BB′(2), 8H, CH_2(6,7,15,16)), 4.447 (s, 4H, xylyl CH_2), 7.145 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 2H, xylyl H(4,6)), 7.347 (t, ^3J = 8 Hz, 1H, xylyl H(5)), 7.610 (d, AA′BB′, ^3J = 8 Hz, 4H, aryl H(3,5)), 8.054 (d, AA′BB′, ^3J = 8 Hz, 4H, aryl H(2,6)), 9.079 (bs, 1H, xylyl H(2)); (**8b**) δ 1.675 (s, 18H, *t*-Bu), 3.524–3.539 (m, A_2B_2(3), 8H, CH_2(6,7,15,16)), 3.538–3.607 and 3.679–3.725 (m, A_2B_2(4), 8H, CH_2(9,10,12,13)), 4.619 (s, 4H, xylyl CH_2), 7.073 (d, ^3J = 8 Hz, 2H, xylyl H(4,6)), 7.288 (t, ^3J = 8 Hz, 1H, xylyl H(5)), 7.68 (d, A part of AB, ^3J = 7 Hz, 4H, aryl H(3,5)), 8.225 (s, 1H, xylyl H(2)), 8.38 (d, B part of AB, ^3J = 7 Hz, 4H, aryl H(2,6)). NOESY interactions: (**8a**) xylyl(2)–aryl(2,6), xylyl(2)–xylyl CH_2, xylyl(4,6)–xylyl(5), xylyl(4,6)–xylyl CH_2, aryl(2,6)–aryl(3,5), aryl(2,6)–xylyl CH_2, aryl(2,6)–CH_2(7,9,10,12,13,15), aryl(3,5)–*t*-Bu, CH_2(6,16)–CH_2(7,15), CH_2(7,15)–CH_2(9,13), CH_2(9,13)–CH_2(10,12); (**8b**) xylyl(2)–aryl(2,6), xylyl(2)–xylyl CH_2, xylyl(2)–CH_2(6,7,15,16), xylyl(4,6)–xylyl(5), xylyl(6)–xylyl CH_2, aryl(2,6)–aryl(3,5), aryl(2,6)–xylyl CH_2, aryl(2,6)–CH_2(6,7,9,13,15,16), xylyl–CH_2–CH_2(6,7,15,16), CH_2(10,12)–CH_2(9,13). Dipolar interactions between **8a** and **8b** were observed for aryl(2,6) and for xylyl CH_2. The intramolecular NOESY interactions between the diarylmagnesium unit and the crown ether ligand are generally much weaker for **8b** than for **8a**.

Variable Temperature ^{1}H NMR Spectroscopy of 8. ^{1}H NMR spectra (250 MHz, [$^2H_8$]toluene, reference $C_6D_5{\cdot}CD_2H$ = 2.32 ppm) were measured from 305 to 220 K with an interval of

Table 6. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for 8

atom	*x*	*y*	*z*	*U*(eq)[a] (Å^2)
Mg	0.74794(9)	0.08889(10)	0.32270(8)	0.0595(4)
O(1)	0.8925(2)	–0.02982(19)	0.24195(17)	0.0670(9)
O(2)	0.8496(2)	–0.0720(2)	0.42087(16)	0.0666(8)
O(3)	0.6858(2)	0.0965(2)	0.45907(16)	0.0695(9)
O(4)	0.5860(2)	0.2704(2)	0.31077(18)	0.0716(9)
O(5)	0.5504(2)	0.3409(2)	0.1142(2)	0.0868(11)
C(1)	0.7356(4)	0.1499(4)	0.0821(3)	0.0776(16)
C(2)	0.7089(4)	0.2675(4)	0.0273(3)	0.0871(16)
C(3)	0.7952(6)	0.3130(5)	–0.0232(3)	0.103(2)
C(4)	0.9038(6)	0.2473(5)	–0.0184(3)	0.108(2)
C(5)	0.9303(4)	0.1312(4)	0.0387(3)	0.0926(17)
C(6)	0.8452(4)	0.0823(4)	0.0891(3)	0.0759(14)
C(7)	0.8719(4)	–0.0399(4)	0.1540(3)	0.0859(17)
C(8)	0.9424(3)	–0.1404(3)	0.3038(3)	0.0804(14)
C(9)	0.9597(3)	–0.1194(4)	0.3910(3)	0.0820(16)
C(10)	0.8485(4)	–0.0560(4)	0.5092(3)	0.0821(16)
C(11)	0.7265(4)	–0.0153(4)	0.5273(3)	0.0832(16)
C(12)	0.5647(3)	0.1417(5)	0.4576(3)	0.0898(19)
C(13)	0.5418(3)	0.2668(4)	0.4001(3)	0.0876(18)
C(14)	0.5718(3)	0.3890(3)	0.2530(3)	0.0864(16)
C(15)	0.6198(3)	0.3897(3)	0.1604(3)	0.0813(16)
C(16)	0.5903(5)	0.3415(5)	0.0261(4)	0.107(2)
C(17)	0.8690(3)	0.2041(3)	0.3159(2)	0.0550(10)
C(18)	0.8575(3)	0.2788(3)	0.3722(3)	0.0613(11)
C(19)	0.9334(3)	0.3496(3)	0.3771(3)	0.0687(13)
C(20)	1.0322(3)	0.3493(3)	0.3256(3)	0.0689(11)
C(21)	1.0474(3)	0.2760(3)	0.2689(3)	0.0721(12)
C(22)	0.9678(3)	0.2069(3)	0.2652(3)	0.0652(11)
C(23)	0.6167(3)	–0.0009(3)	0.2972(2)	0.0594(11)
C(24)	0.6289(3)	–0.1236(3)	0.3309(3)	0.0654(11)
C(25)	0.5456(3)	–0.1860(3)	0.3211(3)	0.0755(16)
C(26)	0.4421(3)	–0.1275(4)	0.2760(3)	0.0716(14)
C(27)	0.4254(3)	–0.0057(4)	0.2427(3)	0.0784(16)
C(28)	0.5095(3)	0.0548(3)	0.2523(3)	0.0731(14)
C(29)	1.1177(4)	0.4249(3)	0.3322(3)	0.0894(14)
C(30)	1.0643(6)	0.5497(5)	0.3041(9)	0.277(7)
C(31)	1.2225(6)	0.4045(8)	0.2692(6)	0.189(4)
C(32)	1.1746(6)	0.3824(7)	0.4230(5)	0.168(3)
C(33)	0.3523(4)	–0.1980(4)	0.2656(3)	0.094(2)
C(34)	0.2484(5)	–0.1154(6)	0.2025(5)	0.153(3)
C(35)	0.4025(5)	–0.2867(6)	0.2152(5)	0.151(3)
C(36)	0.3036(6)	–0.2479(7)	0.3543(4)	0.161(4)

[a] *U*(eq) is one-third of the trace of the orthogonalized U tensor.

Table 7. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for 11

atom	*x*	*y*	*z*	*U*(eq)[a] (Å^3)
Mg	0.72915(14)	0.35363(12)	0.45878(12)	0.0687(6)
O(1)	0.7408(3)	0.4521(2)	0.6285(2)	0.0684(11)
O(2)	0.8880(3)	0.3482(3)	0.5647(3)	0.0803(14)
O(3)	0.8374(3)	0.2685(3)	0.3592(3)	0.0799(12)
O(4)	0.9438(3)	0.1709(3)	0.1973(3)	0.0877(16)
C(1)	0.8388(5)	0.6745(4)	0.7838(4)	0.0665(19)
C(2)	0.8994(5)	0.7721(4)	0.8728(4)	0.0724(19)
C(3)	0.8369(7)	0.8092(5)	0.9463(5)	0.095(3)
C(4)	0.7198(7)	0.7484(6)	0.9300(5)	0.108(3)
C(5)	0.6577(5)	0.6478(5)	0.8385(5)	0.088(3)
C(6)	0.7195(5)	0.6114(4)	0.7646(4)	0.068(2)
C(7)	0.6533(5)	0.5048(4)	0.6670(4)	0.080(2)
C(8)	0.7942(5)	0.4058(4)	0.6964(4)	0.081(2)
C(9)	0.9158(5)	0.3997(4)	0.6798(4)	0.079(2)
C(10)	0.9836(5)	0.3109(4)	0.5300(4)	0.088(2)
C(11)	0.9698(5)	0.3148(4)	0.4231(4)	0.090(2)
C(12)	0.8000(5)	0.1533(4)	0.2904(5)	0.099(3)
C(13)	0.8163(6)	0.1333(5)	0.1845(5)	0.107(3)
C(14)	1.0331(6)	0.8362(4)	0.8955(4)	0.095(3)
C(15)	0.5603(4)	0.2203(3)	0.4119(3)	0.0616(17)
C(16)	0.4477(5)	0.2309(3)	0.3626(4)	0.069(2)
C(17)	0.3312(5)	0.1567(4)	0.3314(4)	0.0746(19)
C(18)	0.3151(4)	0.0620(3)	0.3482(3)	0.0625(17)
C(19)	0.4254(5)	0.0481(4)	0.3962(4)	0.082(2)
C(20)	0.5404(5)	0.1245(4)	0.4255(4)	0.082(2)
C(21)	0.1863(5)	–0.0212(4)	0.3133(5)	0.085(2)
C(22)	0.1094(7)	–0.0484(7)	0.2077(7)	0.225(5)
C(23)	0.1853(7)	–0.1153(7)	0.3271(10)	0.331(8)
C(24)	0.1093(9)	0.0321(9)	0.3753(10)	0.327(8)
C(25)	0.7237(4)	0.4792(4)	0.4020(4)	0.0665(17)
C(26)	0.7179(5)	0.4574(4)	0.2952(4)	0.086(2)
C(27)	0.6962(5)	0.5278(5)	0.2474(4)	0.082(2)
C(28)	0.6767(4)	0.6254(4)	0.3007(4)	0.0696(19)
C(29)	0.6815(4)	0.6505(4)	0.4052(4)	0.0711(19)
C(30)	0.7043(4)	0.5792(4)	0.4523(4)	0.0687(19)
C(31)	0.6508(6)	0.7006(5)	0.2480(4)	0.088(2)
C(32)	0.5698(8)	0.6359(6)	0.1322(5)	0.163(4)
C(33)	0.7706(7)	0.7640(7)	0.2461(7)	0.196(5)
C(34)	0.5862(9)	0.7791(7)	0.3033(7)	0.191(6)

[a] *U*(eq) is one-third of the trace of the orthogonalized U.

Table 8. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for 12

atom	*x*	*y*	*z*	*U*(eq)[a] (Å^2)
Mg	0	0.94032(12)	1 / 4	0.0400(4)
O(1)	0.05284(9)	1.0200(2)	0.38996(19)	0.0710(8)
O(2)	0	1.1844(3)	1 / 4	0.0741(11)
C(1)	0.06425(11)	0.8046(3)	0.1876(2)	0.0450(9)
C(2)	0.05008(11)	0.6614(3)	0.1438(3)	0.0536(10)
C(3)	0.08903(11)	0.5611(3)	0.1094(3)	0.0549(10)
C(4)	0.14745(11)	0.5967(3)	0.1176(2)	0.0488(10)
C(5)	0.16315(12)	0.7363(3)	0.1605(3)	0.0546(10)
C(6)	0.12318(11)	0.8355(3)	0.1935(2)	0.0517(10)
C(7)	0.18951(13)	0.4832(4)	0.0793(3)	0.0676(13)
C(8)	0.17555(17)	0.4621(5)	–0.0400(3)	0.0997(19)
C(9)	0.18320(17)	0.3292(4)	0.1335(3)	0.0966(18)
C(10)	0.25157(14)	0.5341(5)	0.1058(5)	0.118(2)
C(11)	0.08239(15)	0.9143(3)	0.4603(3)	0.0749(14)
C(12)	0.07193(17)	1.1620(4)	0.3937(3)	0.0919(16)
C(13)	0.03533(13)	1.2642(3)	0.3273(3)	0.0686(13)

[a] *U*(eq) is one-third of the trace of the orthogonalized U tensor.

5 K. From each spectrum, the ratio of **8a** and **8b** (vide infra) was determined from the integrals of the xylyl CH_2 signals; the peaks were cut out and weighed. The results were analyzed in a ln K versus $1/T$ plot, with K = **8a**/**8b**. For the conversion **8b** → **8a**, thermodynamic parameters $\Delta H_{eq} = -5$ kJ mol^{-1} and $\Delta S_{eq} = -17$ J mol^{-1} K^{-1} were obtained. Due to the low solubility of **8** in toluene, especially at low temperatures, these values have a limited accuracy (correlation coëfficient for linear regression $R = 0.98$).

Bis[bis(*p*-*tert*-butylphenyl)magnesium]·1,3,16,18-Dixylylene-30-crown-8 (11). Crown ether **10** (0.25 mmol, 126 mg, crystalline solid) was added to a solution of **9** (0.5 mmol, in 5 mL of Et_2O). After shaking and gentle heating (40 °C, water bath) for 15 min, a clear solution was obtained. Upon standing for 24 h at room temperature, a microcrystalline product precipitated. The solid was separated from the mother liquor and high vacuum pumped to remove the last traces of diethyl ether. The residual solution was titrated to yield "total base" (0.103 mmol) and Mg^{2+} (0.050 mmol), indicating a recovery of 90% of **9** in the precipitate. Recrystallization from toluene yielded crystals suitable for X-ray structure determination.

The crystals of **11** were analyzed by ^1H NMR spectroscopy in [$^2H_8$]THF; a stoichiometry of **2**9·**10**·2[toluene] was found. In THF solution, the complex dissociates completely; this is supported by the identity of the spectrum with those of the separate components. In [$^2H_8$]toluene, **11** remains intact but has a very low solubility. ^1H NMR (250 MHz, [$^2H_8$]THF, reference [$^2H_7$]THF = 1.75 ppm): δ 1.28 (s, 18H, *t*-Bu), 2.33 (s, 3H, toluene (CH_3)), 3.56–3.66 (m, A_2B_2, 16H, C_2H_4), 3.60 (s, 8H, C_2H_4), 4.52 (s, 8H, xylyl CH_2), 7.09 (d, AB, ^3J = 8 Hz, 4H, aryl H(3,5)), 7.15–7.21 (m, 6H, xylyl H(4–6)), 7.17–7.21 (m, 5H, toluene (aryl H)), 7.36 (s, broad, 2H, xylyl H(2)), 7.64 (d, AB, ^3J = 8 Hz, 4H, aryl H(2,6)). ^1H NMR (250 MHz, [$^2H_8$]toluene, reference C_6D_5·CD_2H = 2.32 ppm): δ 1.68 (s, 36H, *t*-Bu), 3.33 (m, broad, 8H, C_2H_4), 3.59 (m, broad, 8H, C_2H_4), 3.73 (s, 8H, C_2H_4), 4.58 (s, 8H, xylyl CH_2), 6.94 (d, ^3J = 7 Hz, 4H, xylyl H(4,6)), 7.59–7.68 (m, 10H, aryl H(3,5) and xylyl H(2)?), 8.33 (d, ^3J = 7 Hz, 8H, aryl H(2,6)), the xylyl H(5) signal was not localized.

Crystallization of 2 9·10·2[benzene] (11a). Since two disordered toluene molecules per complex were found in the unit

Table 9. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for 13

atom	*x*	*y*	*z*	*U*(eq)[a] (Å^2)	atom	*x*	*y*	*z*	*U*(eq)[a] (Å^2)
Mg(1)	0.8464(2)	0.68509(16)	0.18195(10)	0.0241(10)	C(13)	0.8627(6)	0.8725(5)	0.0578(3)	0.026(3)
O(1)	0.9681(4)	0.7809(3)	0.2389(2)	0.032(2)	C(14)	0.7676(7)	0.9076(5)	0.0567(3)	0.020(3)
O(2)	0.8072(5)	0.6741(4)	0.2647(2)	0.035(2)	C(15)	0.6967(6)	0.8823(5)	0.0958(3)	0.027(3)
O(3)	0.6836(4)	0.6000(3)	0.1723(2)	0.033(2)	C(16)	0.7189(6)	0.8229(5)	0.1314(3)	0.022(3)
O(4)	0.5461(4)	0.6086(3)	0.0741(2)	0.035(2)	C(17)	0.7470(6)	0.9700(5)	0.0144(3)	0.023(3)
O(5)	0.3504(5)	0.6254(3)	0.0041(2)	0.047(3)	C(18)	0.6319(6)	0.9875(5)	0.0126(3)	0.035(4)
C(1)	1.0708(7)	0.8113(5)	0.2200(3)	0.040(4)	C(19)	0.8253(7)	1.0595(5)	0.0300(3)	0.038(3)
C(2)	0.9754(7)	0.7644(5)	0.2945(3)	0.042(4)	C(20)	0.7645(6)	0.9265(5)	−0.0448(3)	0.035(3)
C(3)	0.8619(8)	0.7430(5)	0.3087(3)	0.045(4)	C(21)	0.9328(6)	0.5806(5)	0.1532(3)	0.025(3)
C(4)	0.6963(7)	0.6447(7)	0.2691(4)	0.055(4)	C(22)	0.9260(6)	0.4993(5)	0.1753(3)	0.028(3)
C(5)	0.6585(7)	0.5683(6)	0.2240(4)	0.055(4)	C(23)	0.9717(6)	0.4282(5)	0.1544(3)	0.020(3)
C(6)	0.6543(6)	0.5311(5)	0.1244(4)	0.044(4)	C(24)	1.0325(6)	0.4305(5)	0.1086(3)	0.023(3)
C(7)	0.6412(7)	0.5721(6)	0.0728(4)	0.043(4)	C(25)	1.0408(6)	0.5082(5)	0.0851(3)	0.032(3)
C(8)	0.5366(7)	0.6610(6)	0.0314(3)	0.042(4)	C(26)	0.9935(6)	0.5800(5)	0.1068(3)	0.030(3)
C(9)	0.4340(8)	0.6932(6)	0.0332(3)	0.047(4)	C(27)	1.0805(7)	0.3492(5)	0.0828(3)	0.026(3)
C(10)	0.2481(7)	0.6515(6)	0.0048(4)	0.064(5)	C(28)	0.9956(7)	0.2890(5)	0.0404(3)	0.049(4)
C(11)	0.8109(6)	0.7852(5)	0.1333(3)	0.020(3)	C(29)	1.1073(7)	0.2948(5)	0.1273(3)	0.057(4)
C(12)	0.8819(6)	0.8142(5)	0.0940(3)	0.028(3)	C(30)	1.1804(7)	0.3768(5)	0.0539(4)	0.066(4)
Mg(2)	0.0787(2)	0.11121(15)	0.29665(10)	0.0184(9)	C(43)	−0.0327(6)	0.3359(4)	0.4038(3)	0.015(3)
O(6)	0.2514(4)	0.1568(3)	0.29621(19)	0.0201(17)	C(44)	−0.0926(6)	0.3754(5)	0.3685(3)	0.015(3)
O(7)	0.1095(4)	0.1138(3)	0.20937(19)	0.0178(17)	C(45)	−0.0941(5)	0.3457(4)	0.3111(3)	0.016(3)
O(8)	−0.0554(4)	0.0269(3)	0.24457(19)	0.0208(19)	C(46)	−0.0386(6)	0.2777(5)	0.2917(3)	0.019(3)
O(9)	−0.2431(4)	0.1000(3)	0.2761(2)	0.0235(19)	C(47)	−0.1607(6)	0.4445(5)	0.3914(3)	0.019(3)
O(10)	−0.4122(4)	0.0323(3)	0.3451(2)	0.030(2)	C(48)	−0.1026(6)	0.5088(5)	0.4438(3)	0.041(3)
C(31)	0.3019(6)	0.2121(5)	0.3469(3)	0.027(3)	C(49)	−0.2642(6)	0.3923(5)	0.4089(3)	0.031(3)
C(32)	0.2775(6)	0.1969(5)	0.2477(3)	0.025(3)	C(50)	−0.1903(6)	0.5012(5)	0.3481(3)	0.032(3)
C(33)	0.2211(6)	0.1305(5)	0.1996(3)	0.030(3)	C(51)	0.1076(6)	0.0145(5)	0.3503(3)	0.016(3)
C(34)	0.0432(6)	0.0489(5)	0.1678(3)	0.023(3)	C(52)	0.1934(6)	−0.0327(5)	0.3433(3)	0.018(3)
C(35)	−0.0675(6)	0.0380(5)	0.1873(3)	0.024(3)	C(53)	0.2172(6)	−0.0950(5)	0.3751(3)	0.019(3)
C(36)	−0.1454(6)	−0.0264(5)	0.2642(3)	0.025(3)	C(54)	0.1593(6)	−0.1152(4)	0.4196(3)	0.014(3)
C(37)	−0.2506(6)	0.0071(5)	0.2552(3)	0.024(3)	C(55)	0.0732(6)	−0.0706(5)	0.4291(3)	0.018(3)
C(38)	−0.2435(6)	0.1211(5)	0.3352(3)	0.029(3)	C(56)	0.0493(6)	−0.0085(5)	0.3956(3)	0.018(3)
C(39)	−0.3554(6)	0.1221(5)	0.3534(3)	0.026(3)	C(57)	0.1868(6)	−0.1851(5)	0.4545(3)	0.019(3)
C(40)	−0.5185(6)	0.0286(5)	0.3613(4)	0.051(4)	C(58)	0.1567(8)	−0.2783(5)	0.4218(3)	0.071(5)
C(41)	0.0220(6)	0.2339(4)	0.3259(3)	0.016(3)	C(59)	0.3063(7)	−0.1653(6)	0.4737(3)	0.057(4)
C(42)	0.0225(6)	0.2684(5)	0.3834(3)	0.021(3)	C(60)	0.1304(7)	−0.1820(5)	0.5085(3)	0.043(4)
Mg(3)	0.3714(2)	0.51896(16)	0.30588(11)	0.0228(10)	C(73)	0.4596(6)	0.3212(5)	0.1685(3)	0.020(3)
O(11)	0.3286(4)	0.4463(3)	0.3824(2)	0.027(2)	C(74)	0.5432(6)	0.2872(4)	0.1917(3)	0.016(3)
O(12)	0.2119(4)	0.5301(3)	0.3193(2)	0.0279(19)	C(75)	0.5721(6)	0.3165(5)	0.2490(3)	0.016(3)
O(13)	0.3034(4)	0.5650(3)	0.2307(2)	0.025(2)	C(76)	0.5191(6)	0.3759(5)	0.2799(3)	0.020(3)
O(14)	0.3516(5)	0.7546(4)	0.2125(3)	0.061(3)	C(77)	0.6022(6)	0.2210(5)	0.1574(3)	0.021(3)
O(15)	0.3184(7)	0.9216(5)	0.1654(4)	0.093(4)	C(78)	0.5819(6)	0.2216(5)	0.0944(3)	0.035(3)
C(61)	0.4022(6)	0.4278(5)	0.4250(3)	0.036(3)	C(79)	0.7240(6)	0.2446(5)	0.1738(3)	0.037(3)
C(62)	0.2431(6)	0.4825(5)	0.4068(3)	0.034(3)	C(80)	0.5596(6)	0.1266(5)	0.1699(3)	0.031(3)
C(63)	0.1608(6)	0.4808(5)	0.3594(3)	0.031(3)	C(81)	0.4773(6)	0.6320(5)	0.3546(3)	0.021(3)
C(64)	0.1425(6)	0.5271(5)	0.2707(3)	0.036(3)	C(82)	0.4796(6)	0.7232(5)	0.3581(3)	0.025(3)
C(65)	0.2009(6)	0.5920(5)	0.2365(3)	0.037(3)	C(83)	0.5536(6)	0.7902(5)	0.3918(3)	0.025(3)
C(66)	0.3608(6)	0.5998(5)	0.1862(3)	0.030(3)	C(84)	0.6347(6)	0.7686(5)	0.4261(3)	0.016(3)
C(67)	0.4239(7)	0.6929(5)	0.2028(3)	0.038(3)	C(85)	0.6366(6)	0.6779(5)	0.4238(3)	0.020(3)
C(68)	0.4029(9)	0.8458(7)	0.2318(5)	0.107(6)	C(86)	0.5629(6)	0.6123(5)	0.3890(3)	0.019(3)
C(69)	0.4016(11)	0.9048(7)	0.1969(5)	0.104(7)	C(87)	0.7113(6)	0.8427(5)	0.4650(3)	0.020(3)
C(70)	0.2689(10)	0.8596(7)	0.1217(4)	0.093(6)	C(88)	0.6471(6)	0.8873(5)	0.5094(3)	0.035(3)
C(71)	0.4359(6)	0.4129(5)	0.2587(3)	0.019(3)	C(89)	0.7645(6)	0.9145(4)	0.4321(3)	0.030(3)
C(72)	0.4081(6)	0.3810(5)	0.2012(3)	0.020(3)	C(90)	0.8000(6)	0.8065(5)	0.4953(3)	0.033(3)

[a] U(eq) is one-third of the trace of the orthogonalized U tensor.

cell of 11, recrystallization from benzene (at 5 °C) was performed. Crystals of **11a** with benzene instead of toluene as crystal solvent were obtained; their quality permitted a second structure determination. The crystal structures of **11** and **11a** proved to be completely analogous. In **11a**, however, the *tert*-butyl groups appeared to be disordered, which resulted in a poor quality of the structure (*R* = 0.097).

Bis(*p*-*tert*-butylphenyl)magnesium·Diglyme (12). A solution of **9** (1 mmol, in 10 mL of diethyl ether) was mixed with pure diglyme (1 mmol, 0.14 mL). Immediately, a colorless precipitate formed which was isolated as a dry powder by decantation. Titration of the residual solution on "total base" and Mg^{2+} revealed that only 0.06 mmol of Ar_2Mg reagent was left. Part of the solid was characterized by ^1H NMR spectroscopy (C_6D_6, 90 MHz); a composition of **9**·1.09(diglyme)·0.38Et_2O was found. The solid (0.4 mmol) was dissolved in toluene (8 mL, 80 °C); good quality crystals were formed upon slow cooling to room temperature. The crystals were isolated from the mother liquor and pumped to high vacuum to remove the last traces of solvent. Their characterization with ^1H NMR spectroscopy revealed the isolation of the pure, solvent free 1:1 complex **12**. ^1H NMR (250 MHz, [$^2H_8$]toluene, reference $C_6D_5{\cdot}CD_2H$ = 2.32 ppm): δ 1.70 (s, 18 H, CMe_3), 3.09 (s, broad, 8H, C_2H_4), 3.21 (s, 6H, OMe), 7.73 (d, AB, ^3J = 8 Hz, 4H, aryl H(3,5)), 8.22 (d, AB, ^3J = 8 Hz, 4H, aryl H(2,6)). As a reference, the ^1H NMR spectrum of pure diglyme was measured under the same conditions: δ 3.35 (s, 6H, OMe), 3.52–3.57 (m, $^1/_2$AA'BB', 4H, C_2H_4), 3.65–3.69 (m, $^1/_2$AA'BB', 4H, C_2H_4).

Bis(*p*-*tert*-butylphenyl)magnesium·Tetraglyme (13). Tetraglyme (1 mmol, 0.22 mL), **9** (1 mmol, solid), and *n*-hexane (10 mL) were mixed in a sealed ampule to yield a system of two immiscible liquid phases. Crystallization was induced by fast cooling with liquid nitrogen, yielding finely divided material. The ampule was heated (80 °C) until almost all crystalline material had dissolved. Upon cooling to room temperature, again a two phase system formed in which large colorless crystals grew.

The crystals were separated from the mother liquor by decantation, pumped to high vacuum, and characterized by ^{1}H NMR spectroscopy as the pure 1:1 adduct **13**. ^{1}H NMR (250 MHz, toluene, reference $C_6D_5 \cdot CD_2H$ = 2.32 ppm): δ 1.70 (s, 18H, CMe$_3$), 3.22 (s, 6H, OMe), 3.23–3.27 and 3.31–3.35 (m, A_2B_2(1), 8H, C_2H_2), 3.39–3.43 and 3.61–3.65 (m, A_2B_2(2), 8H, C_2H_4), 7.71 (d, AB, ^3J = 8 Hz, 4H, aryl H(3,5)), 8.25 (d, AB, ^3J = 8 Hz, 4H, aryl H(2,6)). Reference spectrum of uncomplexed tetraglyme measured under the same conditions: δ 3.36 (s, 6H, OMe), 3.53–3.57 and 3.65–3.69 (m, A_2B_2, 8H, CH$_2$(3,4,12,13)), 3.67 (s, 8H, CH$_2$(6,7,9,10)).

Bis(*p-tert*-butylphenyl)magnesium·Triglyme (15). A solution of 1 mmol of **9** in diethyl ether was high vacuum pumped in order to remove most of the diethyl ether. The remaining amorphous solid was dissolved in a mixture of toluene (10 mL) and triglyme (1 mmol, 0.18 mL) to give a clear solution. Since crystallization from this solution was not possible, the toluene was removed and *n*-hexane (20 mL) added. After heating (70 °C) to dissolve all the material and slowly cooling to room temperature, large plate-shaped colorless crystals were formed. They were separated from the mother liquor (68% yield) and high vacuum pumped to remove all remaining solvent. Characterization with ^{1}H NMR spectroscopy revealed the formation of a pure, solvent free 1:1 complex **15**: ^{1}H NMR (250 MHz, [^{2}H$_8$]-toluene, reference $C_6D_5 \cdot CD_2H$ = 2.32 ppm): δ 1.69 (s, 18 H, CMe$_3$), 3.15 (s, 6H, OMe), 3.15–3.20 and 3.40–3.46 (m, A_2B_2, 8H, CH$_2$-(3,4,9,10)), 3.46 (s, 4H, CH$_2$(6,7)), 7.71 (d, AB, ^3J = 8 Hz, 4H, aryl H(3,5)), 8.23 (d, AB, ^3J = 8 Hz, 4H, aryl H(2,6)). A reference spectrum of uncomplexed triglyme was measured under the same conditions: δ 3.36 (s, 6H, OMe), 3.53–3.57 (m, AA′BB′, 8H, CH$_2$-(3,4,9,10)), 3.68 (s, 4H, CH$_2$(6,7)). ^{13}C NMR (62.89 MHz, [^{2}H$_8$]-toluene, reference $C_6D_5 \cdot CD_3$ = 21.3 ppm): δ 32.6 (q, ^1J(C–H) = 125 Hz, 6C, C*Me*$_3$), 34.9 (s, 2C, *C*Me$_3$), 59.1 (q, ^1J(C–H) = 142 Hz, 2C, OMe), 69.6 (t, ^1J(C–H) = 146 Hz, 2C, CH$_2$), 70.4 (t, ^1J(C–H) = 146 Hz, 2C, CH$_2$), 71.2 (t, ^1J(C–H) = 142 Hz, 2C, CH$_2$), 123.4 (d, ^1J(C–H) = 148 Hz, 4C, aryl C(3,5)), 141.7 (d, ^1J(C–H) = 150 Hz, 4C, aryl C(2,6)), 146.4 (s, 2C, aryl C(4)), 167.4 (s, 2C, aryl C(1)). Spectrum of uncomplexed triglyme under the same conditions: δ 59.1 (q, ^1J(C–H) = 140 Hz, 2C, OMe), 71.4 (t, ^1J(C–H) = 140 Hz, 2C, CH$_2$), 71.6 (t, ^1J(C–H) = 139 Hz, 2C, CH$_2$), 72.9 (t, ^1J(C–H) = 140 Hz, 2C, CH$_2$).

Structure Determination and Refinement of Complexes 8a and 11–13. Crystal data and numerical details of the structure determinations are given in Table 5. Crystals of **8**, **11**, and **12** were mounted under nitrogen in a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD-4 diffractometer for data collection. The crystal of **13** was brought directly into the cold nitrogen stream of the low-temperature unit of a CAD-4F diffractometer for data collection. Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 25 reflections (22 for **8**) and were checked for the presence of higher lattice symmetry.[27] All crystals reflected rather poorly; the crystals of **8** and **11** showed broad reflection profiles. All data were collected with the $\omega/2\theta$ scan mode and were corrected for *Lp* and for the observed linear decay of the intensity control reflections; redundant data were merged into a unique data set. An absorption correction was applied for **12** using the DIFABS[28] method (correction range: 0.795–2.125). The structures were solved with direct methods (SHELXS86[29]) and subsequent difference Fourier syntheses. Refinement on *F* was carried out by full matrix least squares techniques. A toluene solvate molecule in **11** which could not be located from difference Fourier maps unambiguously was taken into account in the structure factor and refinement calculations by direct Fourier transformation of the electron density in the cavity, following the BYPASS[30] procedure. A small cavity at $^1/_2$, $^1/_2$, $^1/_2$ of 93 Å^3 was found in the unit cell of **8**. However, no significant residual density could be detected in that area. H atoms were introduced on calculated positions [C–H = 0.98 Å] and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters, H atoms were refined with common isotropic thermal parameters. Weights were introduced in the final refinement cycles. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables 6–9. Neutral atom scattering factors were taken from ref 31 and corrected for anomalous dispersion.[32] All calculations were performed with SHELX76[33] and the PLATON package[34] (geometrical calculations and illustrations) on a MicroVAX cluster or a DEC-5000 cluster.

Acknowledgment. X-ray data were kindly collected by A. J. M. Duisenberg. This work was supported in part (P.R.M., W.J.J.S., A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO) which is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, all H-atom and non-H-atom parameters, bond lengths, and bond and torsion angles (51 pages). Ordering information is given on any current masthead page.

Author-Supplied Registry Nos.: 2, 53914-83-3; 10, 57624-54-1; 14, 57624-50-7.

OM940128N

---

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

(28) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(29) Sheldrick, G. M. SHELXS86. Program for crystal structure determination. University of Göttingen, Federal Republic of Germany, 1986.

(30) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

(31) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(32) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(33) Sheldrick, G. M. SHELX76. Crystal structure analysis package. University of Cambridge, England, 1976.

(34) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.