

crown-6)⁺,¹⁵ an isoelectronic species, and for MgCl₂(18-crown-6).¹⁶ The O's in the cation surround Al in an equatorial fashion, but distances range from 1.93 to 3.80 Å. In the MgCl₂ species, five O's lie approximately in a plane around the Mg at distances of 2.22-2.33 Å, but the sixth O is far out of that plane and beyond bonding distance. In AlCl₂(benzo-15-crown-5)⁺¹⁷ and Mg-(NCS)₂(benzo-15-crown-5),¹⁸ with a smaller though unsymmetrical crown ether, the Al-O (2.03-2.30 Å) and Mg-O distances (2.17-2.20 Å) are considerably shorter and more nearly equal.

Addition of hexane solutions of Et₂Zn to benzene solutions of 18-crown-6 led to slow formation of precipitates. Dissolving a precipitate in CH₂Cl₂-benzene and layering hexane over the solution resulted in slow formation of plate-shaped crystals.¹⁹

An ORTEP drawing of the structure determined for the Et₂Zn(18-crown-6) units in a crystal is shown in Figure 2.²⁰ The general geometrical features are identical with those of the Mg metallomer, but the metal-oxygen distances of 2.837 (3), 2.890 (3), and 2.873 (3) Å are even longer, and the metal-carbon distance of 1.957 (5) Å is considerably shorter. The Zn-C distance is essentially identical with that of 1.950 (2) Å in gaseous Et₂Zn, in which the C-Zn-C angle also is 180°. By using the Cambridge Crystallographic Database,¹¹ a search for Zn-O distances up to 3.20 Å found none longer than 2.71 Å.

¹H NMR observations of solutions of (Tol)₂Zn and 18-crown-6 indicate the presence, among other components, of a Tol₂Zn-(18-crown-6) species that probably has a threaded structure.²² Particularly for diorganomagnesium and diorganozinc compounds with alkyl groups, however, establishing conclusively when threaded species exist in solution has been complicated by several problems, including the presence of several species in solution, equilibria that are rapid on the NMR time scale, separation of second liquid phases, and formation of solids.^{22,23} We hope to report on this subject later.

The work of Bickelhaupt and his co-workers¹⁴ and this work demonstrate the existence in solids of diorganomagnesium- and diorganozinc-crown ether species with threaded or rotaxane structures. The differences between the structures of Zn and Mg metallomers reflect the much greater propensity of organomagnesium compounds to form bonds to neutral O's.

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Registry No. Et₂Mg(18-crown-6), 114692-56-7; Et₂Zn(18-crown-6), 114692-57-8; Et₂Mg, 557-18-6; Et₂Zn, 557-20-0.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for both structures (7 pages); tables of observed and calculated structure factor amplitudes for both structures (19 pages). Ordering information is given on any current masthead page.

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(19) Their ¹H NMR spectrum (benzene) shows an ethyl group to crown ether ratio of 2.

(20) Et₂Zn(18-crown-6), C₁₆H₃₄O₆Zn: triclinic, space group P $\bar{1}$; *a* = 8.503 (6) Å, *b* = 8.719 (8) Å, *c* = 8.296 (7) Å, α = 111.8 (1)°, β = 114.8 (1)°, γ = 97.9 (1)°; *V* = 486 (2) Å³, *Z* = 1, *D*_{calc} = 1.33 g cm⁻³; *R* = 0.056 and *R*_w = 0.062 for 792 reflections with *I* > 3 σ (*I*) (1820 unique reflections measured).

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X-ray Structure of (1,3-Xylyl-18-crown-5)diphenylmagnesium: An Organometallic Rotaxane

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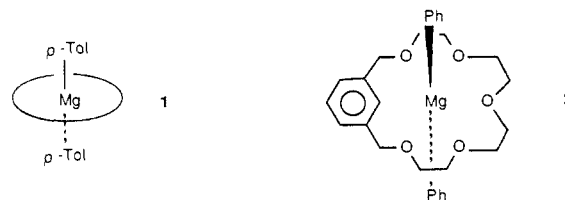
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Crown ethers and related compounds play an increasingly important role in many areas of chemistry. Their application in main group organometallic chemistry has so far received less attention.^{1,2} An interesting example is the complexation of *p*-tolylmagnesium with 18-crown-6 and 15-crown-5, for which Richey and Kushlan observed equivalence of the ligand protons in the ¹H NMR spectrum in C₆D₆ solution; they concluded that the 1:1 complex has the "threaded" structure **1**.^{1d} We wish to present the X-ray crystal structure of the related crown ether complex **2** which indeed reveals such a "threaded" or rotaxane³ structure.



In the course of our investigations of intramolecular coordination in organomagnesium compounds,^{4,5} we required **2** as an intermolecular analogue for comparison purposes. When solid 1,3-xylyl-18-crown-5 (**3**)⁶ was added to the solution of diphenylmagnesium in diethyl ether, a white precipitate of **2** was obtained. Crystals of **2** were grown by gradually cooling a saturated solution of **2** in toluene to -20 °C.⁷ The most conspicuous aspect of the

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(7) Crystal data for **2** (C₂₈H₃₄O₅Mg): monoclinic, space group P2₁/n, with *a* = 10.277 (2) Å, *b* = 13.837 (1) Å, *c* = 18.242 (3) Å, β = 93.89 (1)°, *V* = 2587.8 (7) Å³, *Z* = 4, *D*_c = 1.219 g cm⁻³, *F*(000) = 1016, μ (Cu K α) = 8.5 cm⁻¹, 4943 reflections with 3.2° < θ < 70.0° were collected on an Enraf-Nonius CAD4F diffractometer with Ni filtered Cu K α radiation (λ = 1.54184 Å). The structure was solved by direct methods (SHELXS86) and difference Fourier techniques and refined by full-matrix least-squares (SHELX76) to an *R* value of 0.054 *R*_w = 0.059, *w*² = $\sigma^2(F)$ for 1979 reflections with *I* > 2.5 σ (*I*). In the final stages of the refinement, hydrogen atoms were introduced on calculated positions; all non-hydrogen atoms were refined with anisotropic thermal parameters.

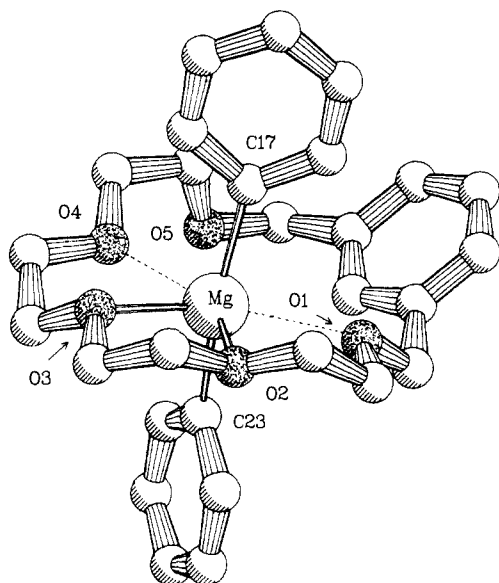
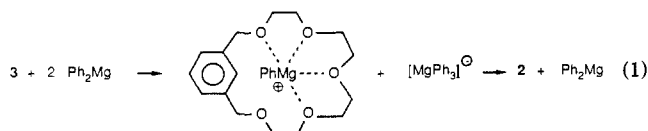


Figure 1. PLUTON drawing of **2**. Selected bond distances (Å) and angles (deg): Mg–C(17), 2.189 (5); Mg–C(23), 2.190 (5); Mg–O(2), 2.204 (3); Mg–O(3), 2.222 (4); Mg–O(1) 2.516 (4); Mg–O(4), 2.520 (4); C(17)–Mg–C(23), 163.8 (2); C(17)–Mg–O(2), 96.9 (2); C(17)–Mg–O(3), 96.9 (2); C(23)–Mg–O(2), 96.1 (2); C(23)–Mg–O(3), 95.9 (2); O(2)–Mg–O(3), 74.6 (1).

X-ray structure of **2** (Figure 1) is its rotaxane character: the diphenylmagnesium is almost linear and rod-shaped with bulky end groups and sticks through the cavity of the coordinating crown ether ring of ligand **3**.

The magnesium shows an unusual type of hexacoordination: besides to the two apical carbons in the nearly sp -hybridized,⁸ covalent Ph–Mg–Ph unit (angle C(17)–Mg–C(23) = 163.8 (2)°; dihedral angle between the two phenyl rings: 66.2 (2)°) magnesium is rather tightly bound to O(2) and O(3), and less so to O(1) and O(4); O(1)–O(4) and magnesium form, within 0.037 (7) Å, a quasi-equatorial plane, and O(5) is clearly not participating in the coordination ($d(\text{Mg}–\text{O}(5)) = 4.038$ (3) Å). The aromatic ring of the ligand makes an oblique angle with the equatorial plane. As in the $[\text{AlMe}_2 \cdot 18\text{-crown-6}]^+$ cation,² the folding of the C–M–C unit is directed away from the coordinating oxygens.

Another interesting feature of **2** concerns the presumable mode of its formation. The cavity of the ligand **3** is too small to permit direct penetration of a phenyl ring of diphenylmagnesium. Complex formation must therefore occur by dissociation of a phenyl anion, complexation of the PhMg^+ cation, and recombination with the phenyl anion from the other side. In view of known analogous dissociation processes,^{1,2} the phenyl anion is probably incorporated into an ate complex, and the course of events may be depicted as in eq 1. Dissolved in toluene- d_8 , **2** gives rise to



two clearly distinguishable complexes (**4a**: **4b** = 3:1), while uncomplexed diphenylmagnesium and **3** (cf. ref 2d) are absent.⁹ We assume that **4a** has the rotaxane structure of **2**, because the resonance of H(2) ($\delta = 9.02$ ppm) is strongly shifted downfield relative to the corresponding signal of **3** ($\delta = 8.16$ ppm) or of **4b** ($\delta = 8.24$ ppm), presumably due to steric congestion.¹⁰ The close

(8) The normal hybridization of magnesium in monomeric uncoordinated R_2Mg seems to be sp ; cf. bis(neopentyl)magnesium: Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Scott Smith, R. *Acta Chem. Scand.* **1980**, A34, 213.

similarity between the resonances of **3** and **4b** suggests that in **4b** diphenylmagnesium is externally coordinated to some of the oxygens of **3**. It is remarkable that the two complexes differ so little in stability; in THF- d_8 solution, **2** is completely dissociated into its components.⁹

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Registry No. **2**, 114691-81-5; **3**, 53914-83-3; Ph_2Mg , 555-54-4.

Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, all bond distances and angles and Figure 2 (ORTEP drawing of **2**) (6 pages); listings of observed and calculated structure factors of **2** (22 pages). Ordering information is given on any current masthead page.

(9) ^1H NMR of a solution of pure **2** in toluene- d_8 (250 MHz, $\text{C}_6\text{D}_6/\text{CHD}_2$ (δ (^1H) 2.32 ppm) as internal standard): **4a** δ 2.89–2.93 and 2.96–3.00 (m, A_2B_2 , 8 H, C_2H_4), 3.03–3.07 and 3.18–3.27 (m, A_2B_2 , 8 H, C_2H_4), 4.44 (s, 4 H, xylyl- CH_2), 7.15 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 2 H, xylyl-H(4,6)), 7.47 (tt, $^3J = 7$ Hz, $^2J = 2$ Hz, 2 H, phenyl-H(4)), 7.59 (dd, $^3J = 8$ Hz, $^3J = 7$ Hz, 4 H, phenyl-H(3,5)), 8.09 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 4 H, phenyl-H(2,6)), 9.02 (m, 1 H, xylyl-H(2)). **4b** δ 3.11–3.15 (m, A_2B_2 , 8 H, C_2H_4), 3.18–3.22 and 3.34–3.38 (m, A_2B_2 , 8 H, C_2H_4), 4.54 (s, 4 H, xylyl- CH_2), 6.96 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 2 H, xylyl-H(4,6)), 7.47 (tt, 2 H, phenyl-H(4)), coinciding with those of **4a**), 7.66 (dd, $^3J = 8$ Hz, $^3J = 7$ Hz, 4 H, phenyl-H(3,5)), 8.44 (dd, $^3J = 8$ Hz, $^4J = 2$ Hz, 4 H, phenyl-H(2,6)), 8.24 (m, 1 H, xylyl-H(2)). The resonances of the protons xylyl-H(5) of **4a** and **4b** could not be assigned; probably, they coincide with other signals of **4a**, **4b** or toluene- d_8 (δ 7.2, 7.25, 7.33). The relative amounts of **4a** and **4b** and the position of phenyl-H(4) of **4b** were determined from the integral ratios. ^1H NMR of a solution of pure **2** in THF- d_8 (250 MHz, β -H of THF- d_8 (δ 1.75 ppm) as internal standard): diphenylmagnesium δ 6.90 (tt, $^3J = 7.2$ Hz, $^4J = 1.5$ Hz, 2 H, H(4)), 6.99 (dd, $^3J = 7.3$ Hz, $^3J = 7.2$ Hz, 4 H, H(3,5)), 7.72 (dd, $^3J = 7.3$ Hz, $^4J = 1.5$ Hz, H(2,6)). **3**: δ 3.57–3.66 (m, A_2B_2 , 16 H, C_2H_4), 4.57 (s, 4 H, xylyl- CH_2), 7.09 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 2 H, xylyl-H(4,6)), 7.21 (t, $^3J = 7$ Hz, 1 H, xylyl-H(5)), 7.70 (m, 1 H, xylyl-H(2)).

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Bis(2,3,4,6,7- η^5 -bicyclo[3.2.2]nona-2,6,8-trien-4-yl)iron, a Ferrocene Analogue with Separated Allyl and Olefin Systems

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It is a long-standing question in organic chemistry whether carbanions like bicyclo[3.2.2]nona-2,6,8-trien-4-yl (BCNT) anion **2** or the congener **5** (cf. Scheme I) experience some extra stabilization by homoaromatic interaction of the allyl and the olefin part(s) of the molecule. It dates back to early studies¹ and even the most recent calculations² and experiments³ find arguments

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