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Formation of the First Organometallic Catenane

Gert-Jan M. Gruter, Frans J. J. de Kanter, Peter R. Markies,
Tateo Nomoto, Otto S. Akkerman, and
Friedrich Bickelhaupt*

Department of Chemistry, Vrije Universiteit
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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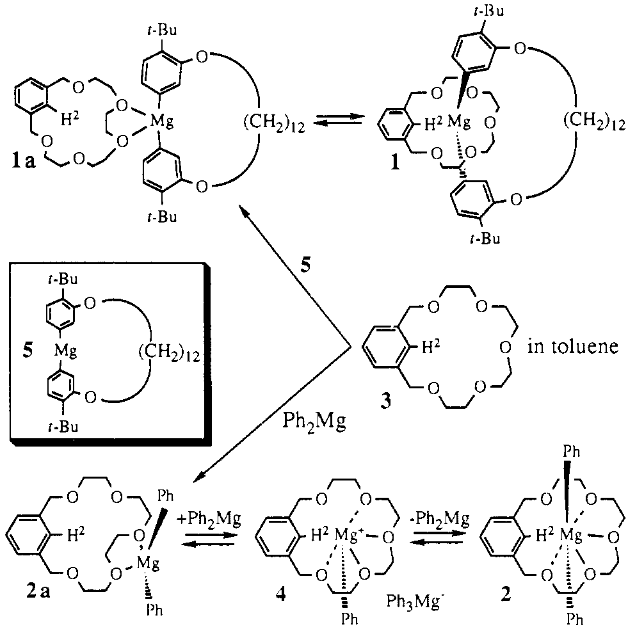
Recently, the synthesis of extended, supramolecular structures has received considerable attention; self-organization, self-assembly, and molecular recognition are expected to play a major role in the ultimate goal of synthesizing nanometer-scale devices like molecular machines.[1] Catenanes (consisting of two or more interlocking rings) and rotaxanes (consisting of a linear molecule which is threaded through a cyclic molecule, often with bulky end groups to prevent extrusion) are not only of topological interest, but they have been considered as important building blocks for molecular assemblies.[2]

Catenanes have often been prepared by statistical threading of a linear chain through a ring, followed by closure of the chain.[3] In this approach, randomness is a highly limiting factor. It may, however, become less detrimental when the threading process is favored by an attractive interaction between the linear thread and the cycle. This concept was the basis of the synthesis of the organometallic catenane **1**, the first member of a new class of catenanes in which a metal atom is incorporated into one of the rings.

Our starting point was the formation of rotaxane **2** (Scheme I), which was obtained from 1,3-xylylene-18-crown-5 (**3**) and diphenylmagnesium; from the NMR data in toluene solution and from an X-ray crystal structure of **2**, it became clear that in solution a "side-on" complex **2a** and rotaxane **2** were in equilibrium.[4] This equilibrium is temperature dependent and shifts to the rotaxane side upon lowering of the temperature. Other crystal structures of organometallics threaded through crown ethers have been obtained for diethylthallium(III) cations,[5] dimethylaluminum cations,[6] diethylzinc,[7] and diethylmagnesium.[7]

The mechanism of this equilibrium was intriguing, because the cavity of the crown ether ring is too small for a phenyl group of diphenylmagnesium to penetrate. We therefore proposed dissociation of a magnesium–carbon bond in the initially formed **2a** to form a phenyl "anion", stabilized by coordination to a second molecule of diphenylmagnesium as a magnesiate anion. The formation of magnesiate species from diorganylmagnesium compounds and crown ethers has been observed spectroscopically and confirmed by a crystal structure.[8,9] However, the magnesiate species must be present in a very low steady-state concentration, as Richey *et al.* have observed that, unlike cryptands, crown ethers have a lesser tendency to generate solvation-separated ion pairs from dialkylmagnesium compounds.[8] In our case, it is suggested that the phenylmagnesium cation moves inside the crown ether cavity, where it is more efficiently coordinated, to form the cationic phenylmagnesium intermediate **4**. The rotaxane complex is formed upon recombination of both components by transfer of a phenyl anion by the magnesiate counterion from the other side.

Scheme I



To definitely prove that the mechanism of rotaxane formation was dissociative, we decided to synthesize a diarylmagnesium compound **5**, in which the two aryl groups are connected by a bridge. If combination of this cyclic molecule **5** with **3** would result in catenane **1**, the dissociative mechanism would be proven, and we would obtain the first organometallic catenane.

Compound **5** was prepared from the corresponding dibromide in a straightforward way. It was completely insoluble in toluene, but it slowly dissolved on shaking with a toluene solution of **3**. In the ^{1}H NMR spectrum, we observed an equilibrium $\mathbf{1a} \rightleftarrows \mathbf{1}$ (at room temperature in toluene-d_8, ratio 2:1), completely analogous to that of $\mathbf{2a} \rightleftarrows \mathbf{2}$ (ratio 1:1).

Almost all signals in the ^{1}H NMR spectrum were identified with the help of 2D 400-MHz NOESY and COSY NMR spectroscopy. The assignments were further corroborated by the ^{1}H NMR spectrum in *n*-pentane; in this solvent, only the pure side-on complex **1a** is present. The shift of the intraannular crown ether hydrogen atom (H^2) of the side-on complex **1a** (δ = 7.90 ppm; reference $C_6D_5CD_2H$ at 2.03 ppm) expectedly does not differ much from that of the free ligand **3** (δ = 7.87 ppm) or of **2a** (δ = 7.94 ppm). However, as in **2** (δ = 8.79 ppm), the signal of H^2 in **1** (δ = 8.93 ppm) is deshielded by about 1 ppm. The validity and diagnostic value of this chemical shift difference of the H^2 proton for the side-on and the rotaxane/catenane version of complexes of **3** were further substantiated by the observation that the zinc complexes **6** (=**3**·[Ph_2Zn]) show the same chemical shift behavior. The structure assignment of **6a** ($\delta(H^2)$ = 7.96

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ppm) has been based on an X-ray crystal structure determination[10] as the equilibrium lies so far to the side-on complex **6a** (at room temperature in toluene-d_8, ratio **6a**:**6** = 96:4) that, in this case, **6a** crystallized and in fact the rotaxane **6** ($\delta(H^2) = 8.82$ ppm) was originally not observed.

The benzylic crown ether protons, which were used to determine the ratio of **1a** and **1**, show a typical downfield shift of 0.17 ppm. As was the case with the rotaxanes **2** and **6**, the equilibrium **1a** ⇄ **1** is temperature dependent and shifts to the catenane side upon lowering of the temperature, from which $\Delta H = -28$ kJ mol^{-1} and $\Delta S = -98$ J K^{-1} mol^{-1} were determined. Unfortunately, in spite of extensive attempts, crystals of **1** have not been obtained so far, presumably because of the less favorable equilibrium position.

Higher aggregated [3]- or [4]-catenanes, which would involve 42-membered and higher organomagnesium cycles or oligomeric molecular "necklaces", are not very likely to be involved, as the solubility and the thermodynamic parameters of **1a** ⇄ **1** and **2a** ⇄ **2**[11] are of the same sign and order of magnitude.

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Supplementary Material Available: Scheme depicting the synthesis of **5**, an NMR spectrum, and NMR spectral data of **1** and **1a** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead-page for ordering information.

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