[1] a) "Chemosensors for Ion and Molecular Recognition": J. P. Desvergne, A. W. Czarnik, *NATO ASI Ser. Ser. C* **1997**, *492*; b) A. Bianchi, K. Bowman-James, E. García-España, *Supramolecular Chemistry of Anions*, Wiley-VCH, New-York, **1997**.

[2] See for example: a) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566; b) C. Bargossi, M. C. Fiorini, M. Montalti, L. Prodi, N. Zaccheroni, *Coord. Chem. Rev.* **2000**, *208*, 17–32; c) A. B. Descalzo, D. Jimenez, M. D. Marcos, R. Martínez-Máñez, J. Soto, J. El Haskouri, C. Guillem, D. Beltrán, P. Amorós, M. V. Borrachero, *Adv. Mater.* **2002**, *14*, 966–969.

[3] a) H. G. Löhr, F. Vögtle, *Acc. Chem. Res.* **1985**, *18*, 65–72; b) M. Inouye, *Color. Non-Text. Appl.* **2000**, 238–274; c) S. L. Wiskur, H. Aït-Haddou, J. J. Lavigne, E. V. Anslyn, *Acc. Chem. Res.* **2001**, *34*, 963–972.

[4] a) O. Brümmer, J. J. La Clair, K. D. Janda, *Bioorg. Med. Chem.* **2001**, *9*, 1067–1071; b) B. Valeur, I. Leray, *Coord. Chem. Rev.* **2000**, *205*, 3–40; c) K. Fuji, K. Tsubaki, K. Tanaka, N. Hayashi, T. Otsubo, T. Kinoshita, *J. Am. Chem. Soc.* **1999**, *121*, 3807–3808.

[5] V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, A. Poggi, A. Taglietti, *Coord. Chem. Rev.* **2001**, *219*–221, 821–837;b) P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502–532; *Angew. Chem. Int. Ed.* **2001**, *40*, 486–516; c) H. Miyaji, J. L. Sessler, *Angew. Chem.* **2001**, *113*, 158–161; *Angew. Chem. Int. Ed.* **2001**, *40*, 154–157.

[6] a) D. H. Lee, H. Y. Lee, K. H. Lee, J. I. Hong, *Chem. Commun.* **2001**, 1188–1189; b) P. Anzenbacher, Jr., A. C. Try, H. Miyaji, K. Jursíková, V. M. Lynch, M. Marquez, J. L. Sessler, *J. Am. Chem. Soc.* **2000**, *122*, 10268–10272; c) H. Miyaji, W. Sato, J. L. Sessler, *Angew. Chem.* **2000**, *112*, 1847–1850; *Angew. Chem. Int. Ed.* **2000**, *39*, 1777–1780; d) F. Sancenón, R. Martínez-Máñez, J. Soto, *Angew. Chem.* **2002**, *114*, 1474–1477; *Angew. Chem. Int. Ed.* **2002**, *41*, 1416–1419; e) D. Jiménez, R. Martínez-Máñez, F. Sancenón, J. Soto, *Tetrahedron Lett.* **2002**, *43*, 2823–2825.

[7] a) K. Niikura, A. Metzger, E. V. Anslyn, *J. Am. Chem. Soc.* **1998**, *120*, 8533–8534; b) L. A. Cabell, M. K. Monahan, E. V. Anslyn, *Tetrahedron Lett.* **1999**, *40*, 7753–7756; c) H. Aït-Haddou, S. L. Wiskur, V. M. Lynch, E. V. Anslyn, *J. Am. Chem. Soc.* **2001**, *123*, 11296–11297; d) R. Kato, S. Nishizawa, T. Hayashita, N. Teramae, *Tetrahedron Lett.* **2001**, *42*, 5053–5056.

[8] When the color change is coupled to an irreversible chemical reaction the term "sensor" should not be applied, and should instead be replaced by terms such as "chromogenic reagent" or "chromogenic dosimeter" (or "chemodosimeter").

[9] F. Sancenón, A. B. Descalzo, R. Martínez-Máñez, M. A. Miranda, J. Soto, *Angew. Chem.* **2001**, *113*, 2710–2713; *Angew. Chem. Int. Ed.* **2001**, *40*, 2640–2643.

[10] M. S. Goodman, A. D. Hamilton, J. Weiss, *J. Am. Chem. Soc.* **1995**, *117*, 8447–8455.

[11] a) A. Metzger, E. V. Anslyn, *Angew. Chem.* **1998**, *110*, 862–865; *Angew. Chem. Int. Ed.* **1998**, *37*, 649–652; b) J. J. Lavigne, E. V. Anslyn, *Angew. Chem.* **1999**, *111*, 3903–3906; *Angew. Chem. Int. Ed.* **1999**, *38*, 3666–3669.

[12] a) C. Seel, A. Galan, J. De Mendoza, *Top. Curr. Chem.* **1995**, *175*, 102–132; b) R. Fitzmaurice, G. M. Kyne, D. Douheret, J. D. Kilburn, *J. Chem. Soc. Perkin Trans. 1* **2002**, 841–864.

[13] Hyperchem 6.0. Molecular Modeling System, Hypercube, Inc.

Porphyrin-Containing [3]Rotaxanes

Synthesis of Porphyrin-Containing [3]Rotaxanes by Olefin Metathesis[**]

Ruud G. E. Coumans, Johannes A. A. W. Elemans, Pall Thordarson, Roeland J. M. Nolte, and Alan E. Rowan[*]

Rotaxanes are fascinating examples of interlocked molecules. Their synthesis is now well-established, and a large variety of interesting rotaxane-based architectures have been reported.[1,2] Our interest in rotaxanes partly arises from the reports by others on the synthesis of these molecules and their application in molecular devices, but predominantly by the impressive way nature makes use of catalytically efficient (pseudo)rotaxane structures in processes such as DNA replication and degradation.[3] In these structures the enzyme (for example, DNA polymerase III)[3] completely encircles the DNA strand and performs numerous rounds of catalysis (for example, template polymerization or hydrolysis) on the macromolecular substrate before dissociating from it. These so-called processive enzymes are therefore very efficient. Inspired by this concept, we have initiated a research project to construct synthetic analogues of these processive enzymes. For this purpose we have designed porphyrin host **1** (see Scheme 1), which can form very stable 1:1 host–guest complexes with viologen derivatives ($K_{\mathrm{ass}} > 10^{6}\,\mathrm{M}^{-1}$),[4] and have synthesized simple porphyrin-containing [2]rotaxanes.[5] It was also shown that the manganese derivative of **1** is a very active epoxidation catalyst.[6] A polymeric rotaxane with double bonds in the polymeric thread and host **1** as the circular component is needed to be able to construct a processive mimic. The latter molecule can then slide over the thread and epoxidize the double bonds (Figure 1). Herein we report the synthesis of such a rotaxane molecule by using olefin metathesis protocols.

Grubbs and co-workers have developed an elegant and efficient route to synthesize end-functionalized polybutadienes. They showed that an acyclic olefin can act as a chain transfer agent (CTA) in the ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD), using ruthenium carbenes **2** and **3** (Scheme 1) as initiators.[7] The CTA is incorporated at both ends of the polymer, with the average number of end groups per polymer chain (F_n) being close to 2. We decided to apply this protocol to synthesize the desired

---

[*] Dr. A. E. Rowan, R. G. E. Coumans, Dr. J. A. A. W. Elemans,
Dr. P. Thordarson, Prof. R. J. M. Nolte
Department of Organic Chemistry, NSRIM
University of Nijmegen
Toernooiveld, 6525 ED Nijmegen (The Netherlands)
Fax: (+31) 24-3652929
E-mail: rowan@sci.kun.nl

[**] National Research School Combination Catalysis (NRSCC) is acknowledged for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

0044-8249/03/11506-0674 $ 20.00+.50/0

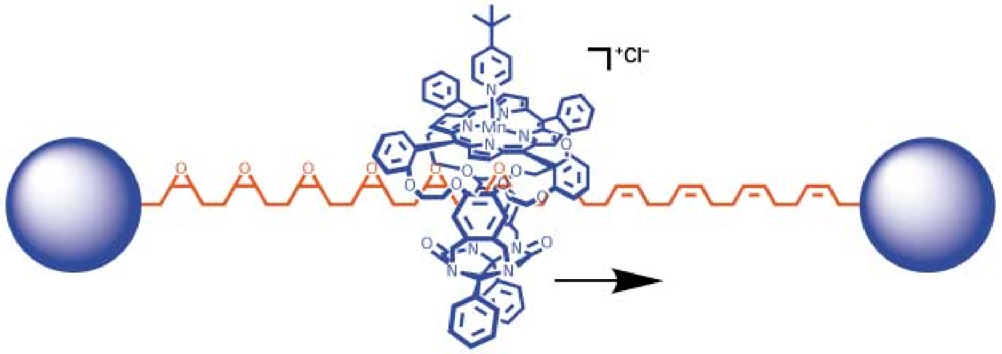
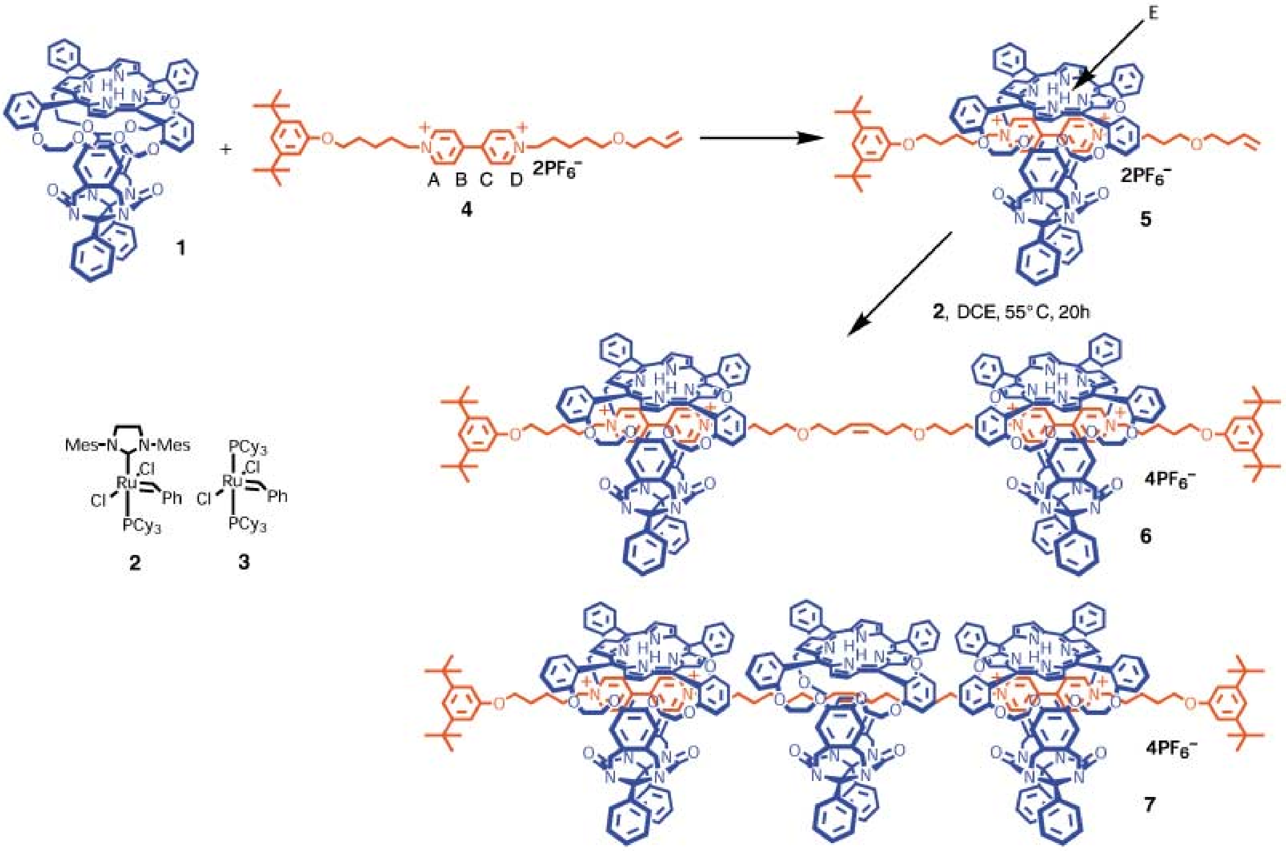


Figure 1. Schematic representation of an oxidative processive enzyme mimic, which involves a synthetic porphyrin threaded on a polymeric chain containing double bonds. The manganese porphyrin catalyst is shielded on the outside by a bulky 4-(*tert*-butyl)pyridine group and converts the double bonds into epoxides on the inside.



Scheme 1. Synthesis of [3]rotaxane **6** and [4]rotaxane **7**.

rotaxane by using a [3]rotaxane which contains a double bond as the CTA. The latter compound is synthesized by olefin self-metathesis. To the best of our knowledge there is only one example in the literature where olefin metathesis has been used to synthesize [2]rotaxanes, one in which the double bond is in the macrocyclic part.[8,9]

As a first step in the synthesis, viologen derivative **4** was synthesized which contains a blocking group on one end and a terminal alkene on the other end (Scheme 1). As expected, complexation of this guest molecule with host **1** afforded [2]pseudorotaxane **5**, which was soluble in solvents such as dichloromethane and 1,2-dichloroethane (DCE). The formation of **5** was evidenced by the large upfield complexation-induced shifts (CIS) of the bipyridinium protons A–D in the ^{1}H NMR spectra (Table 1) and by the presence of NOE contacts between these protons and the pyrrole NH protons E of the porphyrin.

It was envisioned that the addition of the second generation Grubbs' catalyst **2** (20 mol%) to a solution of **5** in DCE at 55°C would give rise to a homodimerization

Table 1: Complexation-induced shifts for viologen protons A–D of [2]pseudorotaxane **5**.[a]

Proton	**4** (δ [ppm])	**5** ($\Delta\delta$ [ppm])
A	8.97	−2.48
B	8.44	−4.04
C	8.44	−4.30
D	8.94	−2.81

[a] 500 MHz, 298 K, $CDCl_3$/MeCN (1/1, v/v), 4×10^{-3} M.

reaction and yield [3]rotaxane **6** (Scheme 1). MALDI-TOF analysis of the reaction mixture after 20 h indeed showed peaks at m/z 4243.6, 4097.1, 3952.4, and 3807.2, which correspond to $[M^+-n\,PF_6]$ ($n=1,2,3,4$; Figure 2a). However, only a 25% conversion to **6** was observed (as judged by ^1H NMR spectroscopy). Therefore, an excess (five equivalents) of host **1** was used to drive the equilibrium more to the direction of **6** to improve the conversion of the reaction. Disappointingly, the conversion did not increase, but to our surprise MALDI-TOF analysis now clearly showed the presence of [4]rotaxane **7** ($[M^+-n\,PF_6]$ ($n=1,2,3,4$) at m/z 5588.1, 5443.2, 5298.2, and 5153.2) in addition to the [3]rotaxane (Scheme 1), which were inseparable (Figure 2a). This result suggests that viologen **4** is capable of forming a 2:1 host–guest complex with **1**.[10]

Interestingly, MALDI-TOF analysis showed, in addition to the expected masses for the rotaxanes **6** and **7**, peaks with values m/z 14 lower than the expected masses (Figure 2a). We believe that these peaks arise from a product that is formed from an initial isomerization reaction of a terminal alkene to an internal alkene, which can react with a second terminal olefin (with liberation of propene) to yield a [3]rotaxane with one methylene group less than in the expected product. Previous reports have demonstrated that catalyst **2** indeed is active in isomerization reactions of terminal alkenes to internal alkenes and leads to similar results.[11] Moreover, the isomerization of homoallyl ethers by **2** to yield vinyl ether species has been described in a recent report.[12] This observation can explain the rather low yield in the rotaxane synthesis, since the generated vinyl ether species can react with the metathesis catalyst to yield a Fisher carbene, which has already been shown to be inactive in cross-metathesis.[13] A signal at $\delta=13.74$ ppm arising from Ru=CHOR was observed in the ^1H NMR spectrum, which definitively supports the presence of this Fisher-carbene species.[13]

It was decided to use catalyst **3** instead of **2** to induce a metathesis reaction between the [2]pseudorotaxanes because of this interfering isomerization side-reaction. However, in a recent report by Grubbs and co-workers on cross-metathesis

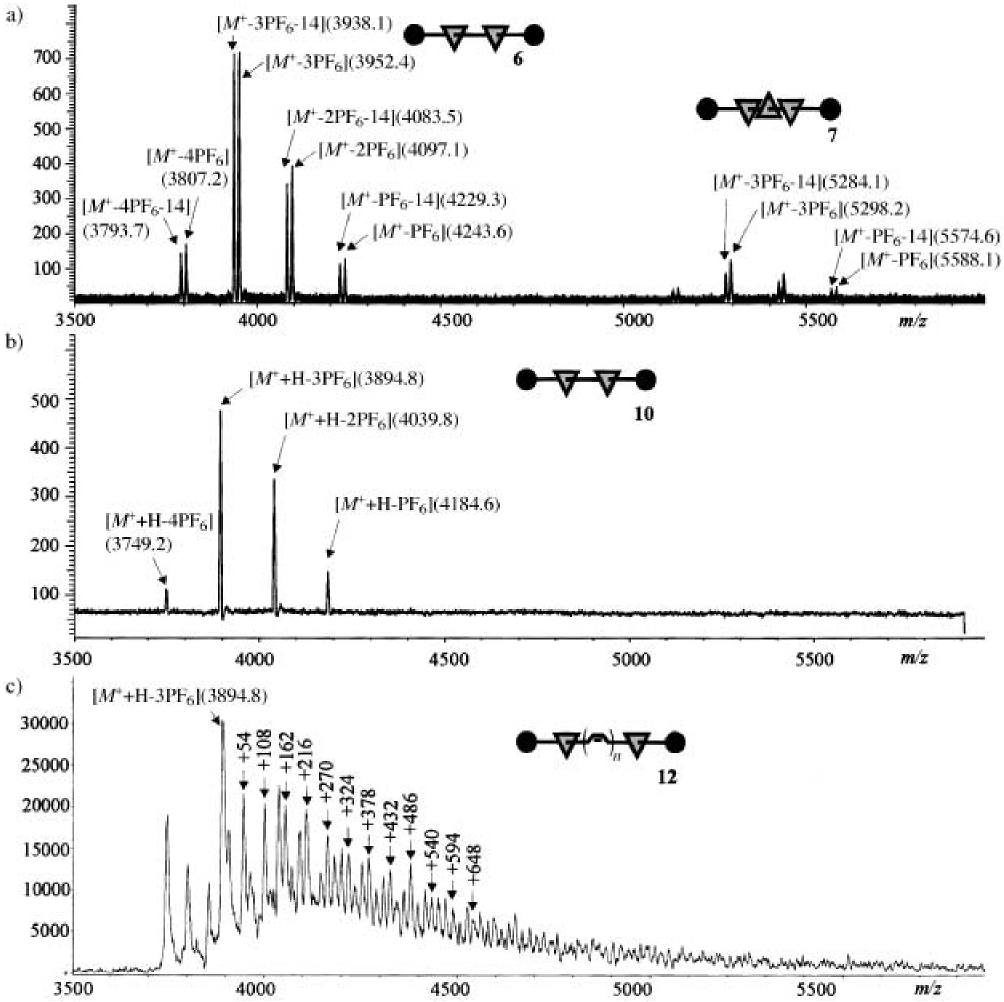
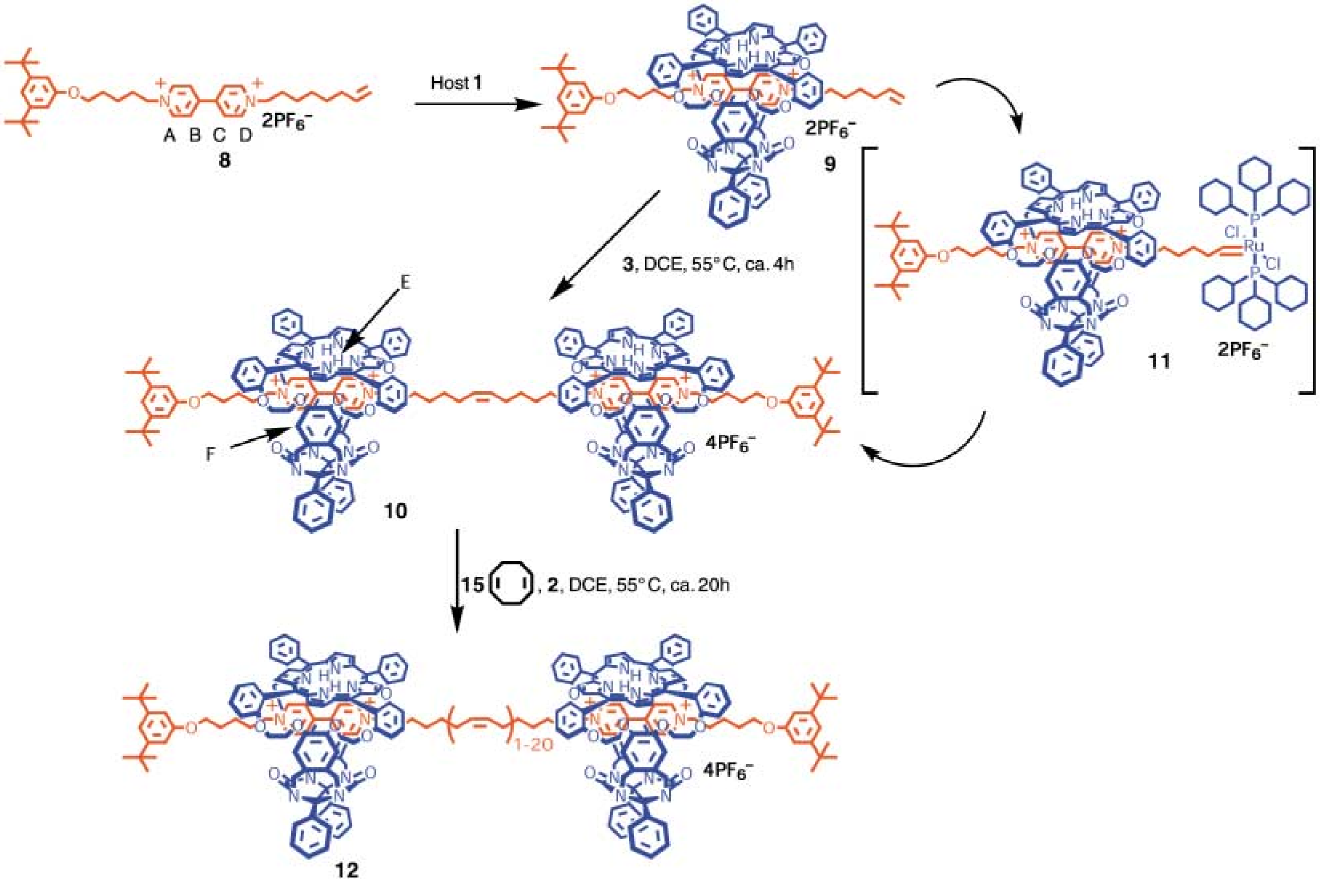


Figure 2. MALDI-TOF spectra of: a) [3]rotaxane **6** and [4]rotaxane **7**, b) [3]rotaxane **10**, and c) polymeric [3]rotaxane **12**.

0044-8249/03/11506-0676 $ 20.00+.50/0



Scheme 2. Synthesis of [3]rotaxanes **10** and **12**.

using catalyst **3**, it was demonstrated that 4,4-diethoxy-1-butene is not very active in self-metathesis.[14] We, therefore, switched to using viologen **8**, in which the oxygen atom is omitted from the alkene part of the molecule (Scheme 2).

A solution of [2]pseudorotaxane **9** was treated with 16 mol % of **3** in DCE at 55 °C for approximately 4 h to reach a conversion of approximately 60 % into [3]rotaxane **10** (as judged by ^{1}H NMR spectroscopy; Scheme 2). Small amounts of [2]rotaxane, styrene-cross coupled [2]pseudorotaxane, and **9** were observed as side-products. MALDI-TOF analysis revealed peaks at m/z 4184.6, 4039.8, 3894.8, and 3749.2, which correspond to $[M^+ + \mathrm{H} - n\,\mathrm{PF}_6]$ ($n = 1, 2, 3, 4$; Figure 2b). No peaks for any isomerized product were visible, which probably accounts for the increase in the conversion relative to that in the previous reaction using **2**. Purification of the product was possible by chromatography: firstly on silica gel and and then on a size-exclusion column, and afforded [3]rotaxane **10** in 40 % yield as a mixture of *cis* and *trans* isomers in a 2:3 ratio. The accepted mechanism for olefin self-metathesis is that catalyst **3** reacts with a terminal alkene to give an intermediate alkylidene complex.[15] This complex further reacts with another terminal alkene to give the homodimer and a propagating methylidene complex. In our case, the intermediate alkylidene complex is **11**, which is already a [2]rotaxane since the bulky PCy$_3$ groups bound to the ruthenium center prevent porphyrin host **1** from sliding off the thread. This intermediate could be oberved by ^{1}H NMR spectroscopy, namely, by the presence of a characteristic triplet at 19.26 ppm (Ru=CHR).

^{1}H NMR spectroscopic analysis showed that the resonances of protons A–D in **10** were dramatically shifted relative to those in [2]pseudorotaxane **9** (Table 2). The data suggest that the porphyrin beads in [3]rotaxane **10** are pulled towards each other, which results in downfield shifts for resonances A and B and upfield shifts for resonances C and D relative to those in the spectrum of the [2]pseudorotaxane **9**. Furthermore, NOE contacts of viologen protons A–D with porphyrin protons E and side-wall protons F are indicative of a rotaxane geometry.[5] The *cis* or *trans* geometry at the double bond is

Table 2: Comparison of chemical shifts of viologen protons A–D in [2]pseudorotaxane **9** and [3]rotaxane **10**.[a]

Proton	**9** (δ [ppm])	*cis*-**10** ($\Delta\delta$ [ppm])	*trans*-**10** ($\Delta\delta$ [ppm])	Δ(*cis* − *trans*) [ppm]
A	6.46	+0.90	+0.71	+0.19
B	5.08	+0.44	+0.35	+0.09
C	4.73	−0.76	−0.68	−0.08
D	5.91	−0.98	−0.79	−0.19

[a] 500 MHz, 298 K, CDCl$_3$, 4×10^{-3} M.

reflected in the differences in the chemical shift of the resonances arising from the viologen protons A–D in the ^{1}H NMR spectrum of **10** (Table 2). These differences can be explained from the fact that the porphyrin beads are slightly more shifted towards the central double bond in the *cis* isomer than in the *trans* isomer, which results in downfield shifts for resonances A and B, and upfield shifts for resonances C and D.

Compound **10** was used as a chain transfer agent in the polymerization of cyclooctadiene catalyzed by **2** to synthesize a [3]rotaxane containing a polymeric thread (Scheme 2). Initial studies using 15 equivalents of COD showed that up to 10 units of COD are inserted (Figure 2c). This observation means that [3]rotaxane **10** can successfully be extended to [3]rotaxane **12**. Since **2** is a very active catalyst, chain transfer results in a stepwise increase in mass of *m/z* 54 (Figure 2c).

In conclusion, we have presented a novel procedure to synthesize porphyrin-containing [3]rotaxanes starting from [2]pseudorotaxanes through a self-metathesis reaction using Grubbs' catalyst **3**. These [3]rotaxanes can be extended to [3]rotaxanes containing a polymeric thread by using them as a CTA in the polymerization of COD by **2**. Further studies will be focused on the catalytic epoxidation of the double bonds in the manganese porphyrin derivative of [3]rotaxane **12**, with the intention of mimicking a natural processive enzyme.

Received: September 10, 2002 [Z50137]

---

[1] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828.

[2] A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier, J. R. Heath, *Acc. Chem. Res.* **2001**, *34*, 433–444.

[3] a) W. A. Breyer, B. W. Matthews, *Protein Sci.* **2001**, *10*, 1699–1711; b) S. J. Benkovic, A. M. Valentine, F. Salinas, *Annu. Rev. Biochem.* **2001**, *70*, 181–208; c) E. T. Kool, J. C. Morales, K. M. Guckian, *Angew. Chem.* **2000**, *112*, 1026–1044; *Angew. Chem. Int. Ed.* **2000**, *39*, 990–1009.

[4] J. A. A. W. Elemans, M. B. Claase, P. P. M. Aarts, A. E. Rowan, A. P. H. J. Schenning, R. J. M. Nolte, *J. Org. Chem.* **1999**, *64*, 7009–7016.

[5] A. E. Rowan, P. P. M. Aarts, K. W. M. Koutstaal, *Chem. Commun.* **1998**, 611–612.

[6] J. A. A. W. Elemans, E. J. A. Bijsterveld, A. E. Rowan, R. J. M. Nolte, *Chem. Commun.* **2000**, 2443–2444.

[7] a) M. A. Hillmyer, S. T. Nguyen, R. H. Grubbs, *Macromolecules* **1997**, *30*, 718–721; b) C. W. Bielwaski, O. A. Sherman, R. H. Grubbs, *Polymer* **2001**, *42*, 4939–4945.

[8] D. A. Leigh, A. J. Wilson, T. J. Kidd in *Abstracts (Part 2) of the 218th American Chemical Society National Meeting* (New Orleans), **1999**, ORGN 0243.

[9] Olefin metathesis has been used in the synthesis of [2]catenanes and knots; see a) B. Mohr, M. Weck, J.-P. Sauvage, R. H. Grubbs, *Angew. Chem.* **1997**, *109*, 1365–1367; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1308–1310; b) T. J. Kidd, D. A. Leigh, A. J. Wilson, *J. Am. Chem. Soc.* **1999**, *121*, 1599–1600; c) D. G. Hamilton, N. Feeder, S. J. Teat, J. K. M. Sanders, *New J. Chem.* **1998**, *22*, 1019–1021; d) D. A. Leigh, P. J. Lusby, S. J. Teat, A. J. Wilson, J. K. Y. Wong, *Angew. Chem.* **2001**, *113*, 1586–1591; *Angew. Chem. Int. Ed.* **2001**, *40*, 1538–1543; e) C. O. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, *Chem. Commun.* **1997**, 2053–2054.

[10] Detailed investigations concerning this novel binding mode are under investigation and will be reported elsewhere.

[11] a) A. Furstner, O. R. Thiel, L. Ackermann, H. J. Schanz, S. P. Nolan, *J. Org. Chem.* **2000**, *65*, 2204–2207; b) D. Bourgeois, A. Pancrazi, S. P. Nolan, J. Prunet, *J. Organomet. Chem.* **2002**, *643–644*, 247–252; c) S. S. Kinderman, J. H. van Maarseveen, H. E. Schoemaker, H. Hiemstra, F. P. J. T. Rutjes, *Org. Lett.* **2001**, *3*, 2045–2048.

[12] C. Cadet, P. I. Dalko, J. Cossy, *Tetrahedron Lett.* **2002**, *43*, 1839–1841.

[13] A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 3783–3784.

[14] H. E. Blackwell, D. J. O'Leary, A. K. Chatterjee, R. A. Washenfelder, D. A. Bussmann, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 58–71.

[15] M. S. Sanford, J. F. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.

Crown-Shaped Ln Polyoxometalates

Alkali-Metal-Controlled Self-Assembly of Crown-Shaped Ring Complexes of Lanthanide/ $[\alpha\text{-}AsW_9O_{33}]^{9-}$: $[K\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_6]^{35-}$ and $[Cs\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_4]^{23-}$[**]

Keisuke Fukaya and Toshihiro Yamase[*]

Polyoxometalates that are formed by self-assembly combine their nanoscopic size with the electronic, magnetic, or optical properties of the metal atoms, which should lead to interesting new materials.[1] The incorporation of the lanthanide ions Ln^{3+} in such polyoxometalates is of interest in supramolecular chemistry because of their luminescent and magnetic properties.[1c,2] With the aim of producing large clusters, much attention has focused on developing Ln^{3+}-incorporated polyoxometalates (polyoxometallolanthanoates), in which the Ln^{3+} ions are used as linkers in the self-assembled structure. Recently it was demonstrated that nano-sized polyoxometallolanthanoates, such as $\{Pr_6Mo_{120}\}$,[3] $\{Eu_4Mo_{128}\}$,[4] and

---

[*] Prof. Dr. T. Yamase, K. Fukaya
Chemical Resources Laboratory
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 226-8503 (Japan)
Fax: (+81) 45-924-5260
E-mail: tyamase@res.titech.ac.jp

[**] This work was supported by Grants-in-Aid for Scientific Research, No. 10304055 and 14204067 from the Ministry of Education, Science, Sports, and Culture and No. 99P01201 from RFTF/JSPS, and by Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Corporation. Approximately 50% of this work was presented at the Conference of "Metal-assembled Complexes, Grant-in-Aid for Scientific Research on Priority Area" in Sendai, on December 11–13, 2001 and written up in the proceedings (P117) of that meeting.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.