ethane (33.3 mol%) and nitrogen, with or without any additive (higher alkanes or olefins), as the feed at a space velocity of $6100 \pm 100\,cm^3\,g^{-1}\,h^{-1}$ with a square-pulse technique described earlier [21]. The space velocity was measured at 0 °C and 1 atm. Conversion X in %, S_{Ar} in %, and yield of arene based on ethane conversion ($Y_{Ar(C_2H_6)}$ in %) were determined as follows: X = [{(wt% of reactant in the feed hydrocarbons) − (wt% of reactant in the product hydrocarbons)}/(wt% of reactant in the feed hydrocarbons)] × 100; S_{Ar} = [(wt% of arenes in the hydrocarbon products)/{100 − wt% of reactant(s) in the hydrocarbon products}] × 100; $Y_{Ar(C_2H_6)} = (X S_{Ar})/100$.

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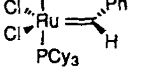
High-Yield Synthesis of [2]Catenanes by Intramolecular Ring-Closing Metathesis[**]

Bernhard Mohr, Marcus Weck, Jean-Pierre Sauvage,* and Robert H. Grubbs*

The development of effective approaches to interlocked molecular rings, catenanes, constitutes a great challenge in preparative chemistry,[1] especially in light of their role in DNA structure and related molecules of biological relevance.[2] Following the pioneering work of Schill and Wasserman,[3] template-directed strategies that used transition metal complexation,[4, 5] π-donor–acceptor interactions,[6] and hydrogen bonding[7] have not only made the synthesis of interlocking rings more accessible but have also allowed the introduction of various functional groups. In most cases, the cyclization reaction is restricted to the formation of ether and amide bonds or quaternary ammonium salts by an intermolecular pathway.

Ring-closing metathesis (RCM) has been established as an efficient approach to macrocyclic systems with intramolecular formation of carbon–carbon double bonds.[8, 9] The ruthenium benzylidene catalyst **1** (Cy = cyclohexyl) is particularly attractive in these reactions, due to its high activity and tolerance to an array of functional groups.[8, 10] Although RCM was initially applied in the synthesis of small five- to eight-membered rings,[11] this methodology has recently been extended to larger ring systems incorporating up to 38 atoms.[12]



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The approach presented here utilizes a combination of a transition metal based template strategy and RCM to provide access to [2]catenanes (Figure 1). The building blocks are the 30-membered macrocycle **2**, bearing a 2,9-diphenyl-1,10-phenanthroline (dpp) bidentate chelate in its backbone, and the acyclic ligands **3** and **4**, in which the dpp moiety is symmetrically substituted with ethylene oxide groups with a terminal olefin (Scheme 1a).[13] The threaded complexes **5** and **6** were formed quantitatively by the reaction of **2** with a stoichiometric amount of $[Cu(MeCN)_4]PF_6$ in CH_2Cl_2/MeCN followed by addition of diolefins **3** and **4**, respectively. Analogously, the intertwined

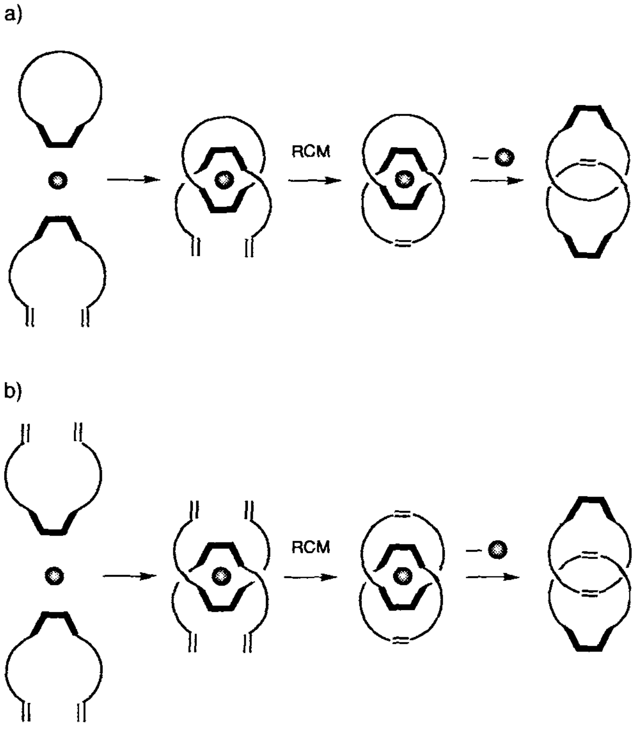

Figure 1. Schematic drawing of the approach utilizing a combination of a transition metal based template strategy and RCM to provide access to [2]catenanes: a) formation of a threaded complex followed by RCM and decomplexation; b) formation of an intertwined complex followed by twofold RCM and decomplexation. The black circle represents the transition metal ion.

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[*] Dr. J.-P. Sauvage, Dr. B. Mohr
Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS
Faculté de Chimie
Université Louis Pasteur
4, rue Blaise Pascal, F-67070 Strasbourg (France)
Fax: Int. code +(388)607-312
e-mail: sauvage@chimie.u-strasbg.fr
Prof. R. H. Grubbs, M. Weck
Arnold and Mabel Beckman Laboratories of Chemical Synthesis
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125 (USA)
Fax: Int. code +(818)564-9297
e-mail: rhg@starbase1.caltech.edu

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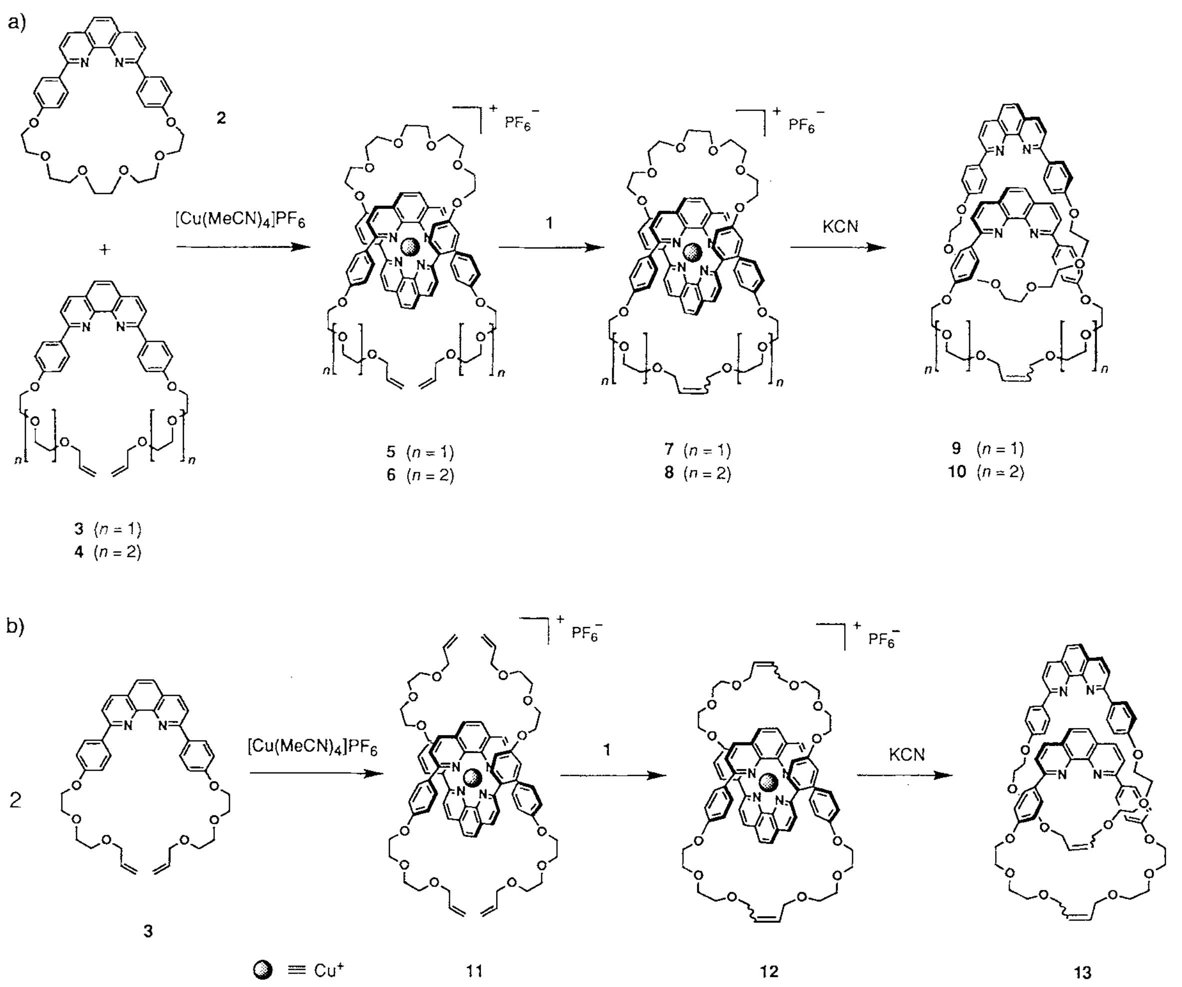

Scheme 1. Synthesis of the [2]catenanes **9**, **10**, and **13**. a) RCM of the threaded complexes **5** and **6** resulting in a 32- and 38-membered ring, respectively. b) RCM of the intertwined complex **11** resulting in two 32-membered rings.

complex **11** was obtained in quantitative yields by complexation of two equivalents of **3** with $[Cu(MeCN)_4]PF_6$ (Scheme 1b). Complexes **5**, **6**, and **11** were then subjected to intramolecular RCM with catalyst **1** to yield the corresponding catenates **7**, **8**, and **12** by formation of 32- (**7**, **12**) and 38-membered (**8**) rings. Twofold RCM of **11** led exclusively to the system with two interlocked rings; the twisted product (formed by the intramolecular reaction between the olefins of different ligands) did not form, as unequivocally concluded by ^1H NMR spectroscopy, FAB-MS (FAB = Fast Atom Bombardment), and the topology of the demetalated species. The yields obtained in these cyclization reactions (Table 1) exceed those for most other medium or even large rings, where hydrogen bonding,[8, 12] the presence of conformational constraints, or template effects[14] are present to facilitate RCM. We believe that the remarkable efficiency of this RCM reaction stems, at least in part, from a preorganization of the olefins due to electrostatic interactions between the oxygen atoms and the phenanthroline system,[15] in combination with a locked conformation of the phenyl rings (π donor) and phenanthroline system (π acceptor).[16] This is supported by the exclusive formation of the interlocked species in the RCM of **11** and the observation that RCM of the free ligands **3** and **4** proceeds in lower yields (73%). For all catenates, the energetically favored *trans* configuration at the double bond prevails.

Table 1. Results of the ring-closing metathesis and demetalation reaction.

Catenate	Yield [%] [a]	*trans*/*cis* [b]	Catenand	Yield [%] [a]
7	92	97/3	**9**	92
8	88	95/5	**10**	93
12	92	98/2	**13**	90

[a] Yield of isolated product. [b] Determined by integration of the ^1H NMR signals of the isomeric olefin protons.

Demetalation of the catenates **7**, **8**, and **12** with potassium cyanide in aqueous MeCN afforded the [2]catenands **9**, **10**, and **13** in almost quantitative yields (Scheme 1, Table 1). Their composition was confirmed by FAB-MS (see Figure 2 for **13**). All spectra display the characteristic pattern for catenated species, in particular the absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles.[17] The FAB-MS of **13** provides further proof for the exclusive formation of the interlocked species **12** in the RCM step.

In conclusion, RCM has been established as a highly efficient protocol for the synthesis of [2]catenanes by intramolecular cyclization. This methodology provides a versatile approach for the efficient synthesis of [*n*]catenanes, knots, and topologically related species.

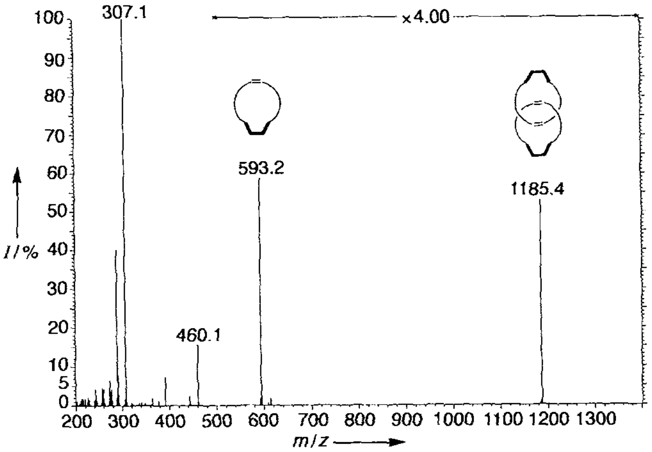

Figure 2. Positive FAB-MS spectrum of catenane **13** in a *p*-nitrobenzyl alcohol matrix (display from $m/z = 200$ to 1400; peaks at $m/z = 307.1$ and 460.1 result from the alcohol matrix). The peak at $m/z = 1185.4$ corresponds to [catenane $-$ H$^+$], and at $m/z = 593.2$ to [macrocycle $-$ H$^+$]. The absence of peaks between the molecular ion peak and the the peak corresponding to the individual macrocycle is characteristic for catenated species [16].

Experimental Section

General procedure for ruthenium benzylidene catalyzed RCM: Under exclusion from air and moisture, **1** (5 mol%) in CH_2Cl_2 was added to a 0.01 M solution of the diolefin (typically 200 to 900 mg) in CH_2Cl_2. After the mixture was stirred for 6 h at room temperature, additional catalyst (5 mol%) was added, and stirring continued for 6 h. The solvent was then removed under reduced pressure, and the crude reaction mixture purified by repeated column chromatography (silica gel, CH_2Cl_2/MeOH 96/4 v/v) to yield the [2]catenates as burgundy solids. All compounds were characterized by NMR spectrscopy, FAB-MS, and elemental analysis.

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Azo-Dye Rotaxanes

Sally Anderson,* Tim D. W. Claridge, and
Harry L. Anderson*

Azo dyes are the largest and most commercially important class of synthetic colorants.[1] Their interaction with cyclodextrins (CDs) has been investigated as a method of controlling their stability, solubility, and aggregation.[2] Rotaxane formation offers a way of converting these labile inclusion complexes into robust encapsulated chromophores, with the dye permanently protected inside the cavity of the CD. There seem to be no previous reports of rotaxanes of this type.[3] We have synthesized a range of water-soluble azo-dye rotaxanes using the hydrophobic effect to direct rotaxane formation (Scheme 1).[4]

When azobenzene diazonium salt **1a** is added to an aqueous solution of β-naphthol **2** in the presence of either α-CD **3a** or β-CD **3b** at 0–5 °C, the solution immediately turns deep purple. Paper chromatography reveals the formation of the fast-running rotaxanes **4a** ⊂ **3a** or **4a** ⊂ **3b**, respectively, as well as the less mobile non-rotaxanated dye **4a**, which is rather insoluble in water and can be separated from the rotaxanes by centrifugation. Rotaxanes **4a** ⊂ **3a** and **4a** ⊂ **3b** were purified by paper chromatography and recrystallization, and isolated in 12 and 15% yields, respectively. The tolidine diazonium salt **1b** also gave a

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[*] Dr. S. Anderson, Dr. H. L. Anderson, Dr. T. D. W. Claridge
University of Oxford
Dyson Perrins Laboratory
South Parks Road, Oxford OX1 3QY (UK)
Fax: Int. code +(1865)275-674
e-mail: harry.anderson@dyson.ox.ac.uk

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