

A rotaxane with two Ru(terpy)₂ derivatives as stoppers

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Starting from organic fragments, a [2]-rotaxane is constructed using pure coordination chemistry; threading of a string into a ring is directed by Cu^I complexation and the blocking reaction involves coordination of Ru^{II} to terminal chelates.

Rotaxanes are molecular systems consisting of a string threaded through one or more rings, the two ends of the string bearing bulky groups acting as stoppers and preventing the molecular string from dethreading.¹

In the course of the last few years, *functional* rotaxanes have been synthesized, whose stoppers and threaded fragment display specific chemical properties such as electro- and photo-activity, ability to complex metals or to form donor-acceptor π complexes, *etc.*²⁻⁴ Porphyrins have been used as stoppers, in relation with electron-transfer studies and models of the photosynthetic reaction centre.⁵ Cyclodextrin-based rotaxanes have been elaborated 15 years ago by Ogino and Ohata,⁶ the blocking reaction being formation of cobalt(III) complexes at both ends of the thread. Very few related systems, consisting of transition-metal complexes as stoppers, have been proposed, although a few interesting examples of transition-metal incorporating catenanes have been reported.^{7,8} We would now like to describe a new type of rotaxane containing two types of transition metals: the template, Cu^I, and the stopper Ru^{II}. The construction principle is indicated in Scheme 1.

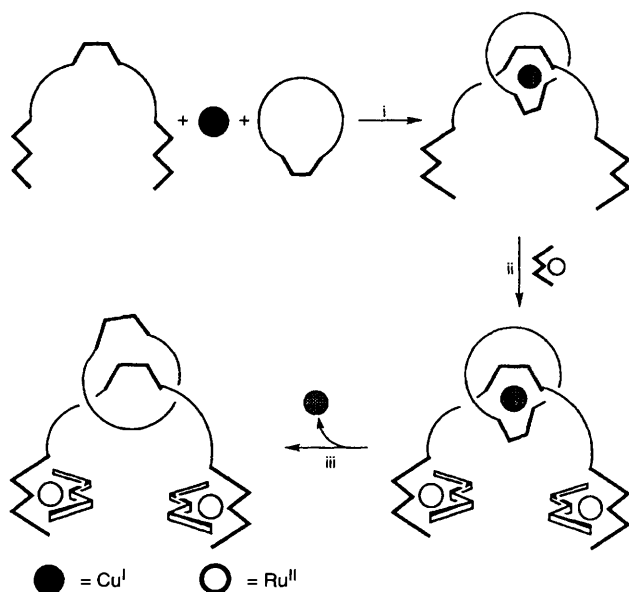
The threading step (i) is similar to previous work from our group to make various rotaxanes and catenanes,⁹ except that the string to be threaded into the ring contains two terminal coordinating fragments (terpy derivatives; terpy = 2,2':6',2''-terpyridine, symbolized by a stylized W) in addition to the central chelate (substituted dpp; dpp = 2,9-diphenyl-1,10-phenanthroline, represented by an inverted U) used in the metal-

assisted gathering and threading step. Due to the greater stability of four-coordinate bis-phenanthroline copper(I) complexes as compared to five- or six-coordinated ones, a high selectivity in the coordination is expected. The blocking reaction (ii) is performed by coordinating a Ru(terpy) moiety to the free ends of the thread.

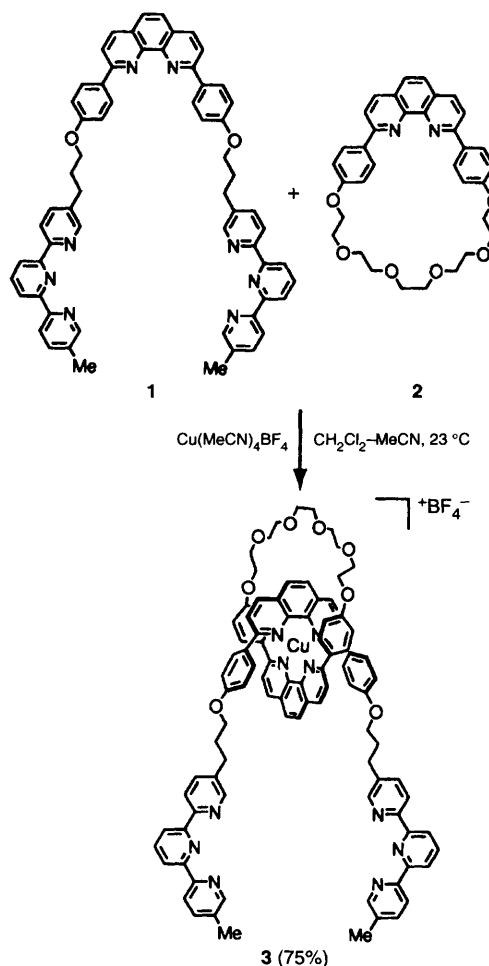
The system obtained will thus consist of two different types of complexes, the Ru(terpy)₂²⁺ stoppers being also of interest for electron and energy transfer, possibly involving the central complex. It should be noted that the chemical stability of the terminal complex subunits is expected to be sufficient to allow selective demetallation of the central complex without affecting the blocking groups [see Scheme 1, (iii)].

The molecules used and the actual threading, clipping and demetallation reactions are depicted in Schemes 2 and 3.

Compound **1**[†] was chosen as the key ambidentate ligand and the dpp-containing macrocycle **2**¹⁰ as its partner for Cu^I coordination (Scheme 2). The reaction between **2** and [Cu(MeCN)₄]BF₄ followed by addition of **1** was performed in



Scheme 1



Scheme 2

MeCN-CH₂Cl₂ at 23 °C to give the desired threaded complex **3** in 75% yield after column chromatography. Spectroscopic and electrochemical data confirm its structure.† As expected, once the complex had been formed, no competition of the terpy ligands for Cu^I was observed. The presence of Cu^{II} in the starting complex led to lower yields probably due to interaction with the terpy moieties. The complex [Ru(terpy)(Me₂CO)₃][BF₄]₂, used to build the stoppers, was prepared in the usual way and used without isolation.¹¹ The reaction between **3** and this ruthenium complex in EtOH-1,2-dichloroethane at 70 °C gave the trimetallic complex **4** in 33% yield after column chromatography (twice). This complex was characterized by spectroscopic methods (¹H NMR, UV-VIS), FABMS [calc. for **4** - PF₆⁻: *m/z* 2817.9, found: 2818.4) and cyclic voltammetry (CV). The voltammogram shows three reversible waves: two two-electron waves for the ruthenium complex subunits (Ru^{III}-Ru^{II}: *E*^o = 1.23 V vs. SCE in MeCN and Ru^{II}-Ru^I: *E*^o = -1.30 V) and a one-electron wave for the central copper complex Cu^{II}-Cu^I: *E*^o = +0.59 V), as expected for the observed stoichiometry.

Reaction of complex **4** with KCN (MeCN-H₂O, 23 °C) gave the desired rotaxane **5** in 59% yield after column chromatography

(Scheme 3). As expected, the high stability of the Ru(terpy)₂ complexes allowed for the selective demetallation. The ¹H NMR spectrum of **5** shows a downfield shift of the signals corresponding to the hydrogens of the phenoxy moieties as compared to **4**. This indicates that these hydrogens are no longer undergoing ring-current effects from the other phenanthroline nucleus and, thus, that the entwined topography of the complex has been destroyed.¹⁰ The rotaxane structure was confirmed by FABMS. The spectrum shows no signal between the molecular ion peaks and the peaks corresponding to the loss of macrocycle **2**. The UV-VIS spectrum and CV data are in accordance with this structure. Ru^{II} oxidation and reduction potentials for both **4** and **5** are the same and within the range usually observed for Ru(terpy)₂ complexes.

In summary, Ru(terpy)₂ complexes can be used as stoppers for the preparation of rotaxanes. The high stability of these fragments makes them compatible with our templated synthesis and the Cu^I decomplexation procedure. This approach opens a new way for the preparation of multicomponent species with promising photochemical properties.

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Footnotes

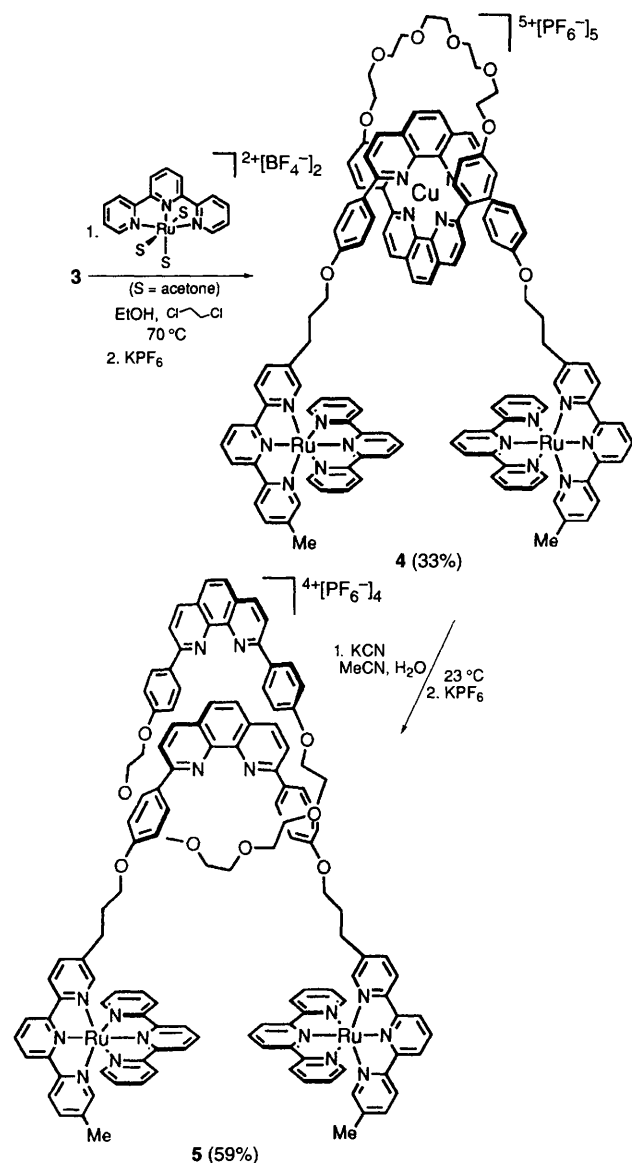
† Compound **1** was prepared in 85% yield by double alkylation of 2,9-di(4-hydroxyphenyl)-1,10-phenanthroline with 5-(3-methanesulfonyl-1-propyl)-5'-methyl-2,2':6',2''-terpyridine under the usual conditions (DMF, K₂CO₃, 70 °C). This terpyridine derivative was prepared by alkylation of 2,2':6',2''-terpyridine with Br(CH₂)₂OTHP followed by hydrolysis and metallation.

‡ ¹H NMR spectrum and redox potential (*E* = +0.60 V) of **3** are typical of a Cu(dpp)₂⁺-type complex.¹⁰

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Scheme 3