

# Construction of Interlocking and Threaded Rings Using Two Different Transition Metals as Templating and Connecting Centers: Catenanes and Rotaxanes Incorporating Ru(terpy)<sub>2</sub>-Units in Their Framework

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**Abstract:** This work describes a new method for the preparation of metal-containing catenanes and rotaxanes, using pure coordination chemistry, by stepwise reaction of organic fragments with two different transition metals. The key organic compound contains two terpyridine (terpy) ligands and one diphenylphenanthroline (dpp) moiety and was prepared in high yield by alkylation of 2,9-bis(hydroxyphenyl)-1,10-phenanthroline with 5-(3-methanesulfonyl-1-propyl)-5''-methyl-2,2':6',2''-terpyridine. Reaction of this polyfunctional ligand with 1 equiv of a dpp-containing 30-membered macrocycle and Cu(I) as a template led to a threaded Cu(dpp)<sub>2</sub><sup>+</sup>-type precursor complex (**P**). Due to the high affinity of Cu(I) for the dpp ligands, the reaction is selective, and no competition of the terpy units for the metal takes place. Thus, this threaded complex contains two free terpy moieties suitable for a further coordination reaction. Ru(II) was used to build the stoppers or to clip the free ligands due to the high stability of Ru(terpy)<sub>2</sub><sup>2+</sup> complexes. Compound **P** reacts with Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> in 1,2-dichloroethane–EtOH at 70 °C under high dilution conditions to give the desired catenate in 43% yield. A Cu coordinated rotaxane was obtained by stoppering the free ends of precursor **P** with 2 equiv of Ru(terpy)(acetone)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>. In both cases the intertwined geometry of the dpp units is maintained after Ru(II) coordination. The complexes were characterized by spectroscopic methods, FAB-MS, and cyclic voltammetry. The high stability of the Ru complexes allows for the selective removal of Cu(I). Thus, reaction of the Cu-complexed rotaxane or the catenate with KCN in MeCN–H<sub>2</sub>O led to the corresponding rotaxane or catenane, respectively, in which the intertwined topography has been destroyed upon liberation of the dpp ligands. This approach opens a new way for the preparation of multicomponent species with promising photochemical properties.

## Introduction

Catenanes and rotaxanes have attracted considerable attention in the 1960s and the 1970s, representing a real synthetic challenge. They also appeared as promising chemical objects, with novel physical properties, and as precursors to new molecular materials. Particularly significant are the pioneering contributions by Schill,<sup>1</sup> Wasserman,<sup>2</sup> and their co-workers, in the field of chemical topology and interlocking rings. Somewhat surprisingly, although their structure looks simpler than that of interlocking rings and their topology is clearly less noble, rotaxanes were not reported in a fully convincing way before catenanes.<sup>1–3</sup> Schill and co-workers have described an elegant directed route to rotaxanes, based on the stepwise construction of the molecule.<sup>1</sup> An alternative attractive approach is based on the threading reaction of an acyclic fragment bearing two bulky groups at both extremities and forcing it to thread inside a presynthesized ring by heating.<sup>3</sup> After cooling down to room temperature, the system is frozen, the bulky groups playing the role of stoppers and thus preventing the acyclic string from dethreading from the ring, provided the latter is small enough to block the unthreading process.<sup>3</sup>

In the course of the last 15 years, the field has undergone some kind of renaissance due to the introduction of template strategies, making the preparation of threaded and interlocking systems much more accessible. These developments as well as the early works above mentioned have been surveyed and discussed in several reviews.<sup>4–10</sup>

In modern approaches, more and more functionality is introduced into the catenanes and rotaxanes made, so that the compounds are able to fulfill more and more complex chemical and physical functions, and they display interesting and sophisticated properties, such as photoinduced intramolecular electron transfer,<sup>11</sup> electrochemically triggered molecular motions,<sup>12,13</sup> photochemical dethreading processes,<sup>14</sup> etc. Some of

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the multicomponent molecular systems, able to perform some kind of chemical action, have been named "molecular machines".<sup>15</sup>

Due to their potential electro- and photochemical properties, transition metal complexes are appealing units to incorporate into the target structures. In fact, the use of the transition metal-to-ligand bond as a structural element is not very common, also for the reason that this type of bonding is less considered as a "normal" covalent bond by the organic chemists who have tried to make catenanes and rotaxanes in the past. A remarkable achievement was reported in 1981 by Ogino, whose strategy was based on both a template effect (cyclodextrin threaded by a hydrocarbon fragment) and the use of transition metals to stopper the threaded unit.<sup>16</sup> The strategy was in part related to previous unsuccessful attempts published long ago by German chemists in a historical paper<sup>17</sup> and aimed at making a catenane after threading of a cyclodextrin by a doubly end-functionalized polymethylene chain. Since then, several metal incorporating rotaxanes and catenanes have been described,<sup>18–20</sup> including a structurally characterized catenane constructed via the templating effect of two different transition metal centers.<sup>21</sup> A wide family of fascinating catenanes containing Pd(II) centers has also been recently described by Fujita *et al.*<sup>22</sup> Noteworthy, macrocycles containing transition metal atoms as constitutive elements are numerous and known for many years,<sup>23–27</sup> including essential natural products such as vitamin B<sub>12</sub>.<sup>28</sup>

We would now like to describe our strategy for making rotaxanes and catenanes, using *two* different types of transition metals, both acting as assembling and templating species but utilizing different coordinating fragments of the organic backbone precursors:<sup>29</sup> (i) the first metal center will gather and orient two ligands, leading to the "intertwined" situation which has been used extensively in the past for building interlocking rings.<sup>4–6,30</sup> (ii) The second metal will effect a clipping reaction on the intertwined precursor and thus freeze the interweaving or the interlocking situation. This step will afford a rotaxane or a catenane. Subsequently, removal of the first templating metal will be allowed without destruction of the complete structure. Obviously, this last step requires demetalation selectivity since the complexes formed in the blocking or closing reaction with the second metal (leading to rotaxanes or catenanes, respectively) will have to resist the decomplexation conditions necessary to remove the first metal.

## Results and Discussion

**Strategy.** The strategy leading to rotaxanes or catenanes using a complexation reaction with a transition metal as stopper-forming or cyclization reaction from a threaded precursor is represented in a schematic way in Figure 1.

Clearly, the two metal centers to be used along the strategy of Figure 1 must have very different properties. In fact Cu(I) and Ru(II) are ideally suited to the synthetic approach since (i) Cu(I) is preferentially low-coordinate, with a strong tendency to form tetrahedral complexes (bis-bidentate complexes of the type Cu(dpp)<sub>2</sub><sup>+</sup>; dpp = 2,9-diphenyl-1,10-phenanthroline) and (ii) Ru(II) is invariably six-coordinate when complexed to aromatic imine-based ligands. Furthermore, whereas Cu(I) complexes are substitutionally labile, Ru(II) forms very stable and kinetically inert complexes, as required for the selective demetalation step of copper, leading to rotaxanes or catenanes with a free coordination site (reaction (iii) of Figure 1).

**Ligands.** The organic compounds used in the present study are indicated in Figure 2. The starting 5,5''-dimethyl-2,2':6',2''-terpyridine (**1**) was prepared by the Stille cross-coupling reaction as previously reported.<sup>31</sup> Alkylation of **1** was performed in THF by deprotonation with LDA (1 equiv) followed by reaction with Br(CH<sub>2</sub>)<sub>2</sub>OTHP to give the desired monosubstituted derivative **2** in 44% yield after chromatographic purification. Hydrolysis of the acetal in refluxing EtOH in the presence of a catalytic amount of HCl afforded the free alcohol **3** (85%, isolated yield), which was transformed into the mesylate **4** by reaction with MsCl in the usual conditions (CH<sub>2</sub>Cl<sub>2</sub>, NEt<sub>3</sub>; 95%). On the other hand, the phenanthroline containing building block (2,9-di(4-hydroxyphenyl)-1,10-phenanthroline, **5**) was prepared as

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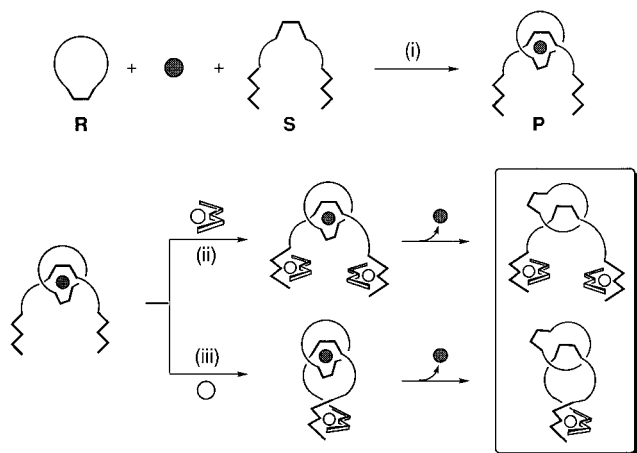
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**Figure 1.** Principle of the two-metal approach leading to rotaxanes or catenanes from organic fragments, using coordination reactions. Noteworthy, the strategy does not involve organic reactions once the two building blocks have been made (the ring **R** and the string **S**). The two chelates used are a 2,9-diphenyl-1,10-phenanthroline unit (dpp, bidentate ligand symbolized by a U) and a 2,2':6',2''-terpyridine motif (terpy, terdentate ligand represented by a stylized W). The metal center with a preferred tetrahedral geometry is indicated by a dotted disk, whereas the six coordinate (octahedral) metal is represented by a white circle. (i) *The gathering and threading step:* The tetrahedral metal (Cu(I) in the present case) is first reacted with the ring. It will first coordinate to the dpp fragment. After the string **S** has been added, due to the great stability of four-coordinate complexes, it will thread inside the ring in order to also bind to the metal already coordinated to the dpp unit of the macrocyclic ring, **R**. By analogy with similar Cu(I)-governed threading reactions,<sup>4–6,29</sup> formation of the precursor **P** is expected to be quantitative. (ii) *The stopper-forming reaction:* By adding a second metal (Ru(II) in the present work) already complexed to a terpy chelate, with its three remaining coordination sites being occupied by labile ligands. These ancillary ligands are substituted by the appended terpys of the precursor **P** to give a trimetallic complex. Selective removal of the first assembling metal in the Cu-complexed rotaxane (Cu(I), black dot) will afford a rotaxane containing a free coordination site and whose blocking groups are two Ru(terpy)<sub>2</sub>-derivatives. (iii) *The cyclization reaction:* Upon addition of an octahedral metal, the two dangling terpy chelates will gather and complex to this second metal (white circle). In this case, a starting complex with a fully exchangeable coordination sphere is used. Similarly as for (ii), selective demetalation of the tetrahedral center of the catenane will lead to a “free” catenane (a catenand).

previously reported.<sup>32</sup> Alkylation of diphenol **5** with mesylate **4** in DMF at 80 °C in the presence of K<sub>2</sub>CO<sub>3</sub> gave the target bifunctional ligand (**6**). The compound can be easily recrystallized from CHCl<sub>3</sub>–EtOH to give a high yield (88%) of analytically pure white product. Compound **6** contains both terpy and dpp-derived binding sites suitable for Ru(II) and Cu(I) coordination, respectively. The spacers joining the coordinating units are long enough to permit ring closure after templated threading of a macrocycle (see Figure 1). On the other hand, 30-membered macrocycle **7** (Figure 2), which has been extensively used in previous syntheses of catenanes and catenands,<sup>32,33</sup> was chosen as the ring partner for Cu(I) coordination. It contains the dpp unit necessary to furnish a stable Cu(I) complex, and it has the suitable ring size to thread ligand **6** through it.

**Synthesis of a Catenane and a Rotaxane.** The reaction between **7** and Cu(MeCN)<sub>4</sub>BF<sub>4</sub> in MeCN at 23 °C for some minutes gave a yellow solution of complex Cu(**7**)(MeCN)<sub>2</sub>(BF<sub>4</sub>). Treatment of this complex with a CH<sub>2</sub>Cl<sub>2</sub> solution of **6** proceeded regioselectively on the ambidentate ligand to give the desired threaded bis(dpp) complex **8** in 75% yield after column chromatography (Figure 3). <sup>1</sup>H-NMR spectrum of **8** shows the usual high field shifted signals corresponding to the H of phenyl rings of both ligands, due to the phenanthroline (phen) ring current effect in the intertwined structure (6.05 and 5.97 ppm, for the H meta to the phen moiety; and 7.49 and 7.29 ppm for the ortho H). The absorption at 440 nm in the visible spectrum and the redox potential (+0.60 V vs SCE in MeCN) are typical of these bis(dpp) complexes.<sup>34</sup> Reactions leading to Cu(dpp)<sub>2</sub><sup>+</sup> species usually proceed with quantitative yields. The presence of small amounts of Cu(II) in the starting Cu complex, which may interact with the terpy moieties, leads to lower yields in this case. As expected, once the complex had been formed, no competition of the terpy ligands versus dpp for Cu(I) was observed. This is in agreement with the results previously obtained in the electrochemically triggered ring gliding motion in catenanes containing the same coordinating units,<sup>12</sup> and it is a consequence of the preferred tetrahedral coordination for Cu(I).

As shown in Figure 1, threaded complex (**P** of Figure 1 or **8** of Figure 3) is the common intermediate in the preparation of rotaxanes and catenanes. A rotaxane could be prepared by stoppering the ends with a suitable metal complex already containing a terpy ligand, whereas a catenane should be synthesized by clipping both free terpy ligands with a metal in a macrocyclization coordination reaction. As it has been indicated before, Ru(II) was chosen as the most suitable metal, since it forms highly kinetically stable bis(terpy) complexes. In addition, it permits the stepwise introduction of two terpy ligands, a necessary condition for the preparation of rotaxanes following the strategy shown above.

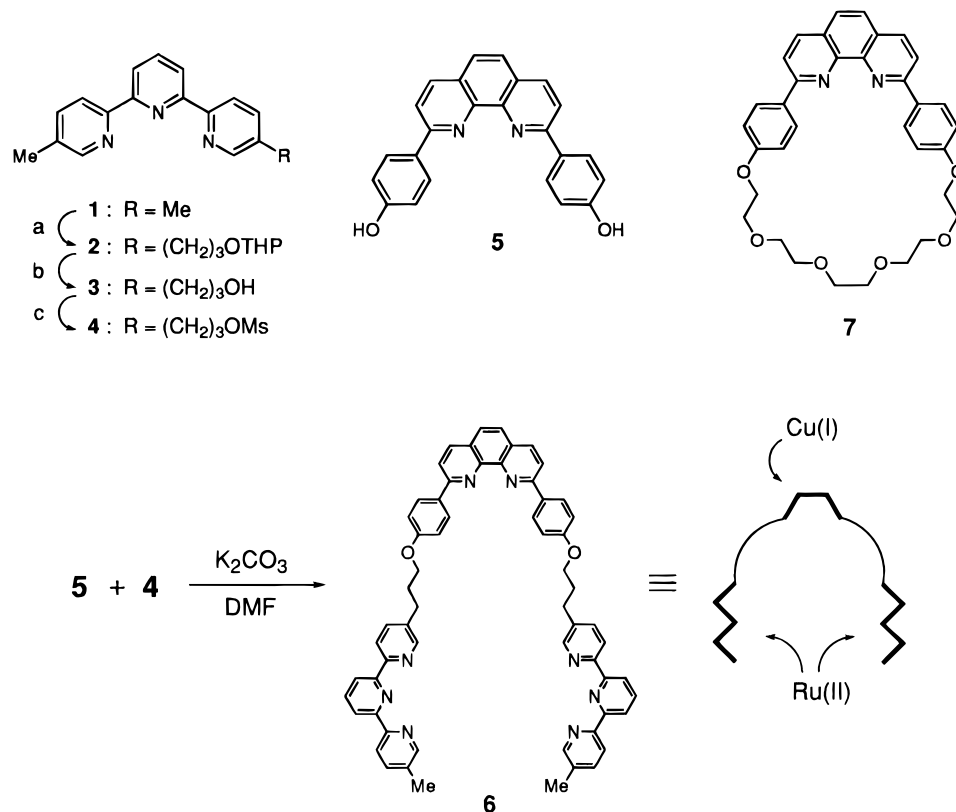
The complex Ru(terpy)(acetone)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub> was used to build the stoppers. This species was prepared as previously reported from Ru(terpy)Cl<sub>3</sub>, by removal of the chloro ligands with AgBF<sub>4</sub> in acetone,<sup>35</sup> which affords a more reactive species toward a second terpy ligand. Reaction between this Ru complex and the threaded species **8** in EtOH–1,2-dichloroethane at 70 °C for 5 h gave the trimetallic Cu-coordinated rotaxane **9** (Figure 4, top). After two column chromatographies and recrystallization, the product was isolated in 33% yield as a deep red solid. This complex was characterized by spectroscopic methods, FAB-MS (calc. for [9-(PF<sub>6</sub>)]<sup>+</sup>: 2817.9, found: 2818.4) and cyclic voltammetry (CV). Its <sup>1</sup>H-NMR spectrum presents the same features as in **8** for the phenyl hydrogens, indicating that the intertwined structure remains after Ru complexation. The UV–vis spectrum shows an absorption at 475 nm (ε = 24 200 L·mol<sup>-1</sup>·cm<sup>-1</sup>) typical of Ru(terpy)<sub>2</sub><sup>2+</sup> moieties,<sup>35b</sup> the ε value corresponding to two Ru complexes. Its cyclic voltammogram (Figure 6a) exhibits three reversible waves: one for the central Cu complex (Cu(II)/Cu(I):E° = +0.59 V vs. SCE in CH<sub>3</sub>CN) and two waves for the Ru(terpy)<sub>2</sub> subunits (Ru(III)/Ru(II):E° = 1.23 V and Ru(II)/Ru(I):E° = –1.30 V) having both double the intensity of the Cu couple signal, as expected for the observed stoichiometry.

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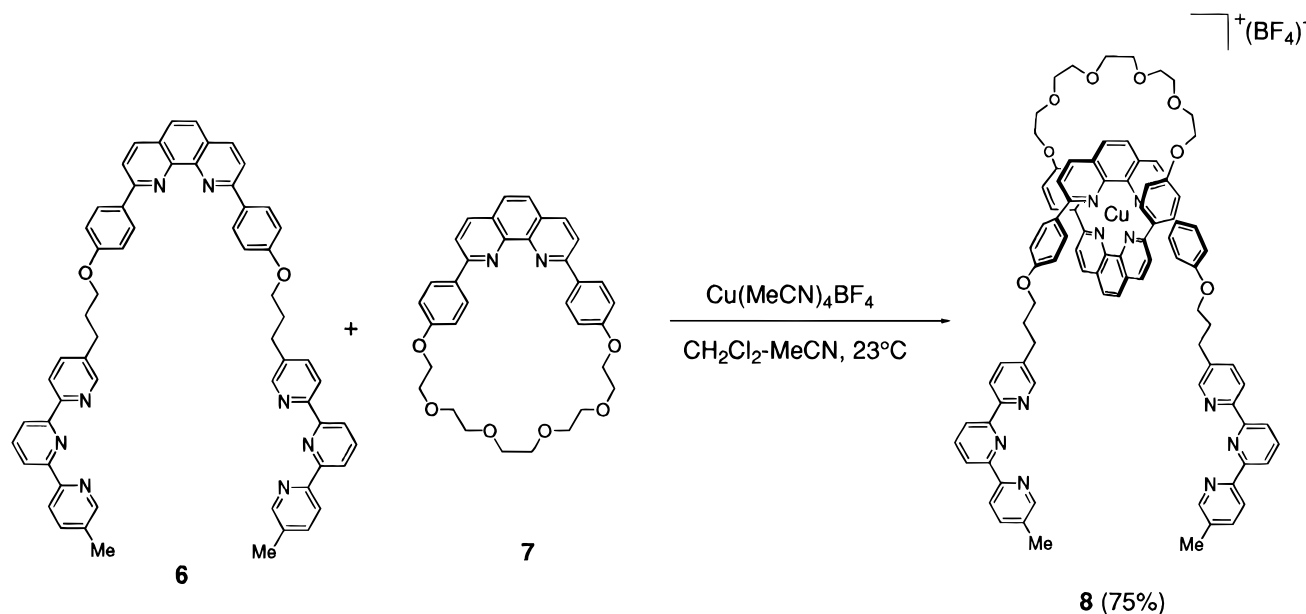
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**Figure 2.** Synthesis of polyfunctional ligand **6**. (a) LDA, THF,  $-78^\circ\text{C}$ ; then  $\text{Br}(\text{CH}_2)_2\text{OTHP}$ ; 44%. (b) EtOH, HCl (catalyst); reflux; 85%. (c)  $\text{MsCl}$ ,  $\text{NEt}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-5^\circ\text{C}$ ; 95%.



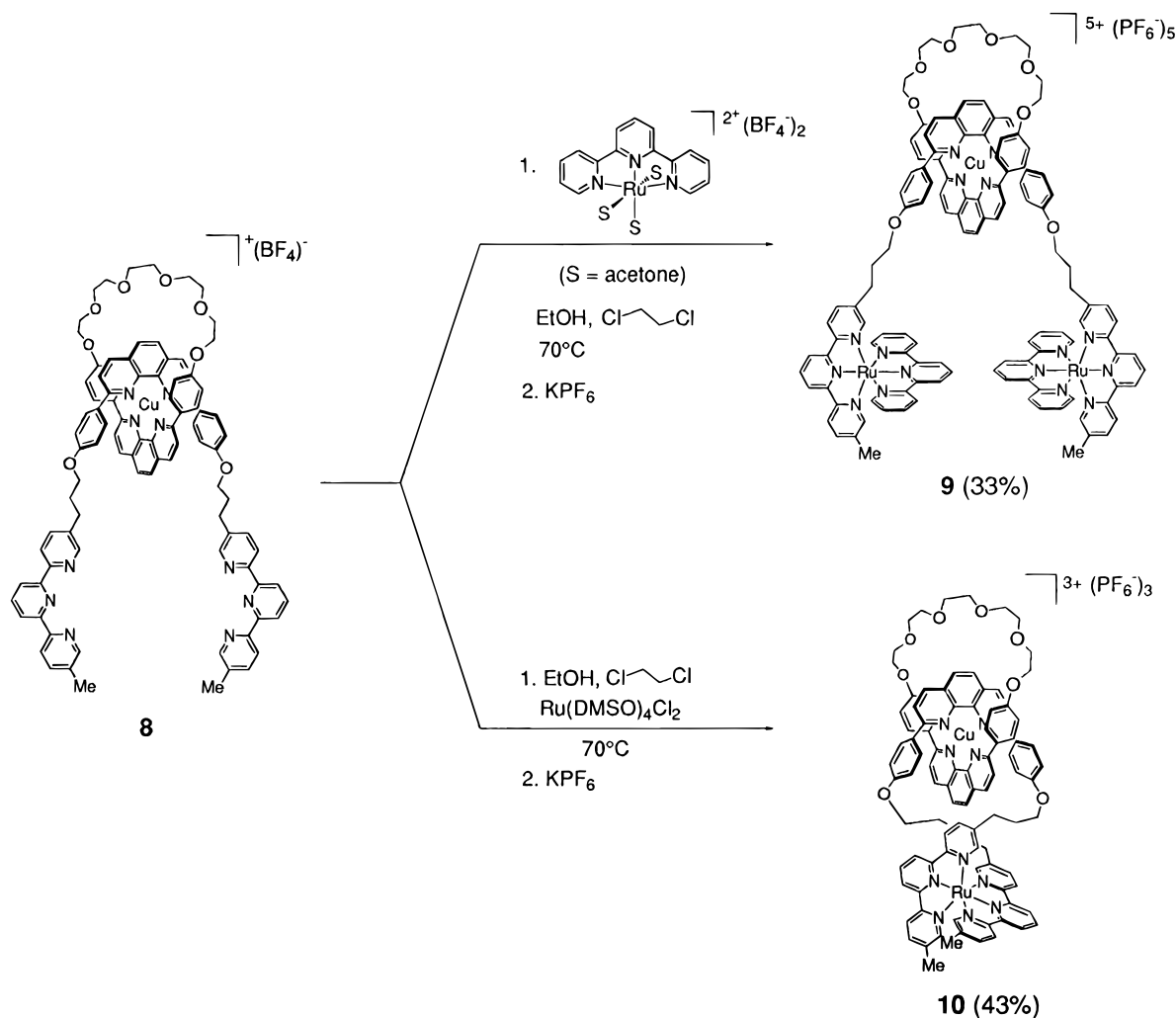
**Figure 3.** The regioselective threading step.

The related catenate **10** (Figure 4, bottom) was prepared by reaction of **8** with  $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ .<sup>36</sup> This starting Ru complex presents the advantage of requiring less drastic conditions than  $\text{RuCl}_3$  for the formation of a  $\text{Ru}(\text{terpy})_2$  complex. Since preparation of **10** requires the formation of a 29-membered ring (*i.e.*, a macrocycle), the Ru atom being a part of the cyclic structure, relatively high dilution of the reactants is expected to be favorable.<sup>37</sup> The reaction was thus performed by slow

addition of a solution of  $\text{Ru}(\text{DMSO})_4\text{Cl}_2$  in EtOH ( $4 \times 10^{-4}$  M) to a solution of precatenate **8** in EtOH-1,2-dichloroethane (1:1;  $1.2 \times 10^{-4}$  M) at  $70^\circ\text{C}$ . The desired catenate **10** was isolated in 43% yield after column chromatography. Its  $^1\text{H-NMR}$  spectrum (Figure 7a) shows the expected high field signals for the H atoms of the phenyl rings (6.05 and 5.98 ppm, for the H meta to the phen moiety; and 7.43 and 7.38 ppm for the ortho H). Besides, there is another signal (singlet) appearing at high field (6.27, 2H), corresponding to the H atoms of the phenanthroline central ring of macrocycle **7** ( $\text{H}_{5',6'}$ ; Figure 7a), as shown by  $^1\text{H}$  COSY and ROESY experiments. This chemical shift is a consequence of the effect of the  $\text{Ru}(\text{terpy})_2$  unit, since it has

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**Figure 4.** Clipping and stoppering coordination reactions leading to a Cu-complexed rotaxane (**9**) and to a catenate (**10**), respectively.

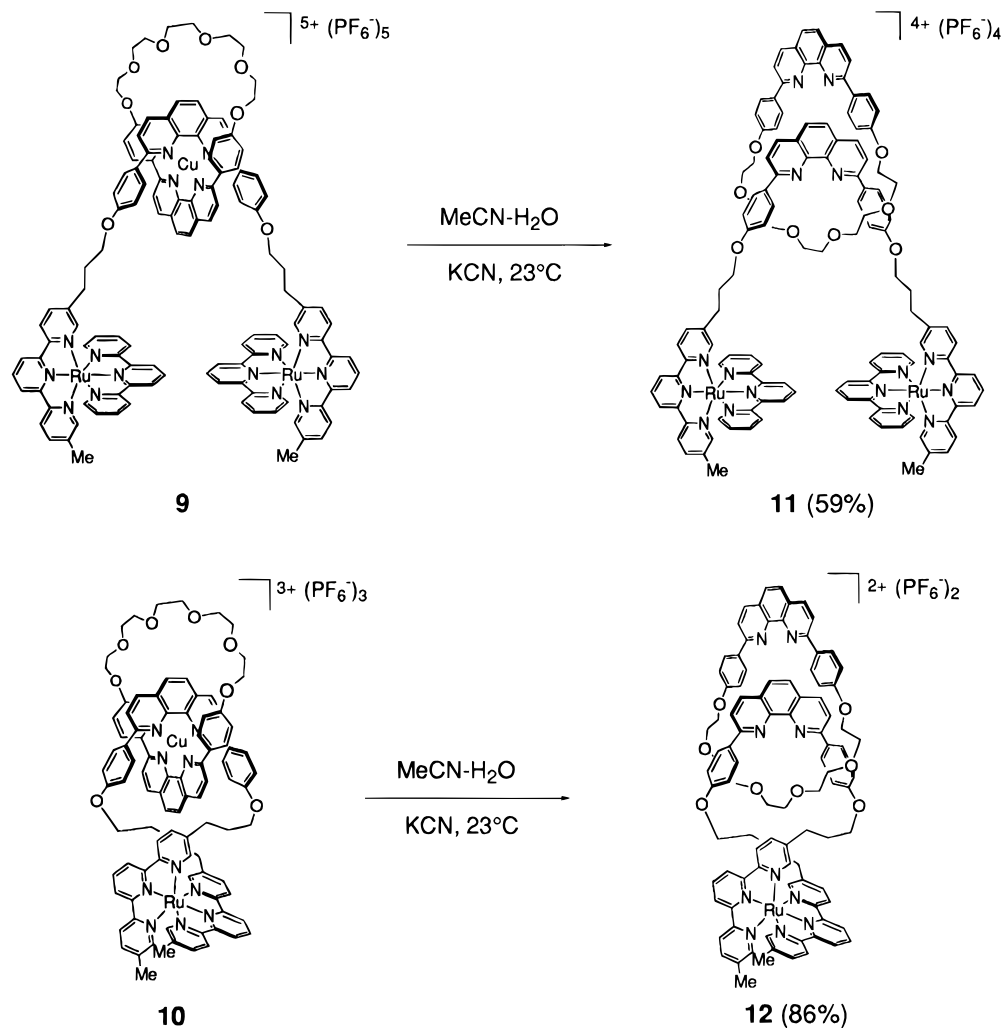
not been previously found for these hydrogens in non-Ru-containing catenates.<sup>32</sup> The  $\epsilon$  value for the absorption at 474 nm ( $\epsilon = 14\,900$ ) is the result of the addition of the absorptivities of both metal complexes. The CV shows three reversible waves (Ru(III)/Ru(II): $E^\circ = 1.24$  V; Ru(II)/Ru(I): $E^\circ = -1.32$  V and Cu(II)/Cu(I): $E^\circ = 0.58$  V), as observed for complex **9**, but, in the case of the catenate, the intensity for the Cu couple wave is the same as for the Ru ones, in accordance with the stoichiometry.

**Demetalation Reactions.** As it has been previously reported, Cu catenates and Cu-coordinated rotaxanes can be easily demetalated by reaction with cyanide.<sup>4,32,33</sup> Our aim was to selectively remove the templating metal (Cu) from compounds **9** and **10** without affecting the Ru complexes, so that the stoppers or the clipping units remained unaltered. This would, of course, preserve the topological properties of the compounds and lead to a rotaxane and a catenane, respectively.

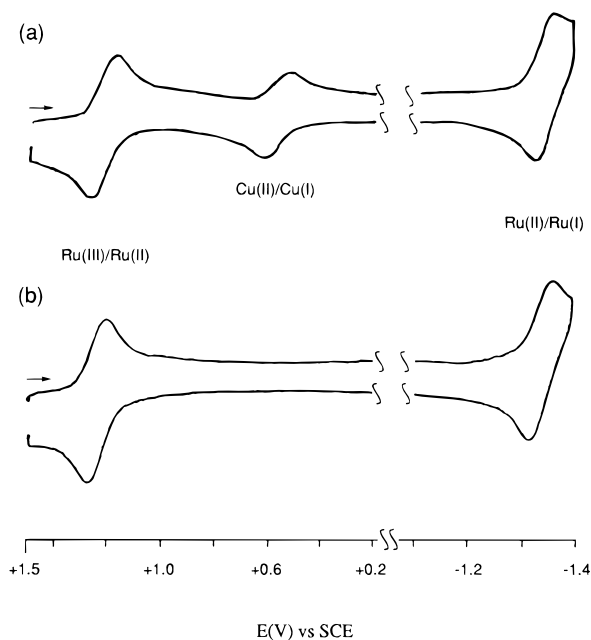
The reaction between the trimetallic complex **9** and KCN in MeCN–H<sub>2</sub>O at room temperature led to the rotaxane **11** (Figure 5, top) in 59% yield after column chromatography. The UV–vis spectrum and the CV clearly indicate the absence of Cu. Figure 6 shows the CV of complexes **9** and **11**. Ru(II) oxidation and reduction potentials for both **9** and **11** are the same and within the range usually observed for Ru(terpy)<sub>2</sub> complexes. The rotaxane structure was confirmed by FAB–MS spectrometry. No peaks are observed in the region lying between the signals of the molecular ions resulting from the loss of  $PF_6^-$  anions and the peaks corresponding to the loss of the macrocyclic

fragment, as usually observed for interlocked or threaded systems. A dramatic downfield shift of the <sup>1</sup>H-NMR phenyl signals takes place upon demetalation, as it has been observed for other catenands. 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 dpp units has been destroyed. Similar features are observed in the <sup>1</sup>H-NMR spectrum of catenane **12** (Figure 7b), analogously obtained by reaction of **10** with KCN in 86% yield after column chromatography (Figure 5, bottom). In this case, the downfield shift of the meta hydrogens corresponding to macrocycle **7** is not so large ( $H_m$ ; Figure 7), indicating that they are under the influence of the metal-containing ring. The previously mentioned singlet signal ( $H_{5',6'}$ ; Figure 7) exhibits the highest downfield shift (*ca.* 1.6 ppm). Demetalation also affects some of the terpy hydrogens ( $H_{3t}$ ,  $H_{9t}$ , and  $H_{11t}$ ), which appear at higher field. The structure of this catenane was also confirmed by the absence of peaks between the ones for the molecular ions and those corresponding to the macrocycles in the FAB–MS spectrum. CV and UV–vis data are also in accordance with this structure.

Thus, the high stability of Ru(terpy)<sub>2</sub><sup>2+</sup> moieties allows for the selective demetalation of Cu(I), giving rise to multicomponent species with interlocked and threaded structures containing Ru complexes within the skeleton and free coordination sites, ready to be remetalated at will to afford new multimetallic complexes.



**Figure 5.** Selective demetalation gives Ru-containing rotaxane **11** and catenane **12**.

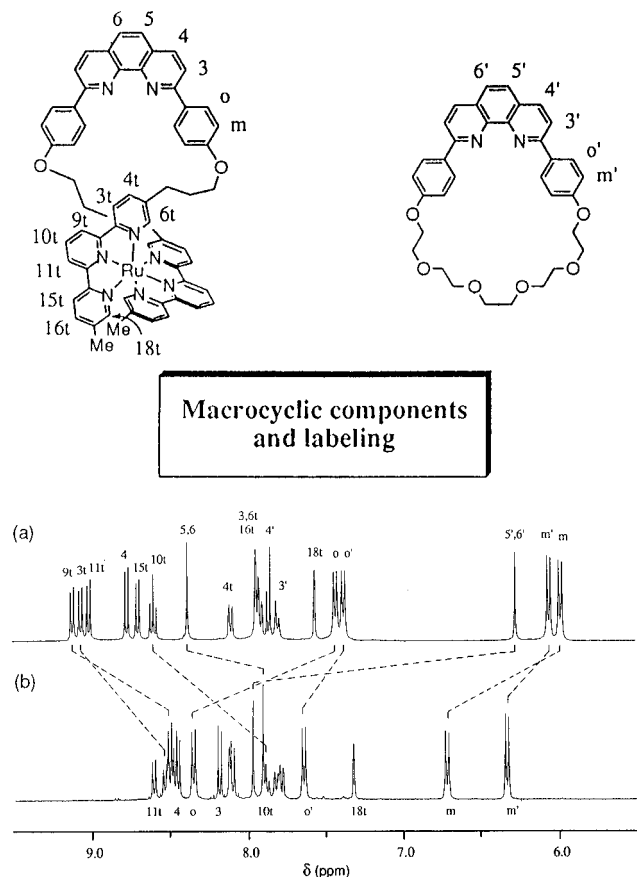


**Figure 6.** Cyclic voltammograms of (a) trimetallic complex **9**, showing the waves of both Ru and Cu complexes, and (b) rotaxane **11**, containing free dpp moieties (vs. SCE; MeCN,  $\text{Bu}_4\text{NBF}_4$ , 0.1 M; 200  $\text{mV s}^{-1}$ ).

### Conclusion

A new way for the preparation of metal-containing rotaxanes and catenanes is presented in this work. Several concepts on

coordination chemistry are illustrated. A bifunctional ligand and two different metals participate in the construction of multicomponent complexes using *pure coordination chemistry*, by taking advantage of the different stereoelectronic requirements of both metals. The ambidentate ligand **6** containing one diphenylphenanthroline (dpp) and two terpyridine (terpy) units reacts with a preformed  $\text{Cu}(\text{dpp})_2^+$  macrocyclic complex to give *regioselectively* a  $\text{Cu}(\text{dpp})_2^+$  species. This fact is in accordance with the preferred tetrahedral coordination for Cu(I) complexes, especially in the case of dpp ligands, since a highly stable intertwined structure is obtained. This threaded Cu complex presenting two free terpy moieties has been used for the preparation of a catenane and a Cu complexed rotaxane. Thus, a macrocyclization coordination reaction with a suitable Ru(II) source afforded a catenane containing a Cu atom as a template and a  $\text{Ru}(\text{terpy})_2$  complex as a lock. Ru(II) is also suitable for the preparation of a rotaxane, since it permits the formation of appropriate stoppers from mono(terpy) complexes containing ancillary labile ligands which can be replaced by the free terpy units of the precatenane. Both the catenane and the Cu-complexed rotaxane can be selectively demetalated to give a catenane and a rotaxane containing Ru complexes in their structure. The high stability of these fragments makes them compatible with our templated synthesis and with the Cu(I) decomplexation procedure. It will also allow to incorporate back into the free coordination site, formed by the two dpp motifs, a large variety of tetrahedrally coordinated metal centers or



**Figure 7.**  $^1\text{H-NMR}$  spectra of (a) catenane **10** and (b) catenand **12** (acetone- $d_6$ , 400 MHz).

protons. This approach opens a new way for the preparation of multicomponent species with promising photochemical properties.<sup>38</sup>

## Experimental Section

**Materials and General Procedures.** The following chemicals were prepared according to literature procedures:  $\text{Cu}(\text{MeCN})_4\text{BF}_4$ ,<sup>39</sup>  $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ ,<sup>36</sup> and 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline **5**.<sup>32</sup> All other chemicals were of the best commercially available grade and were used without further purification. Dry solvents were distilled from suitable desiccants (DMF from  $\text{CaH}_2$  under reduced pressure,  $\text{CH}_2\text{Cl}_2$  from  $\text{P}_2\text{O}_5$  or  $\text{CaH}_2$ , and THF from Na and benzophenone). 1,2-Dichloroethane (SDS, synthesis grade) and EtOH (Normapur, analytical reagent) were used as received. UV-vis spectra were recorded on a Kontron Instruments UVIKON 860 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on either Bruker WP 200SY (200 MHz) or WP 400SY (400 MHz) spectrometers (using the deuterated solvent as the lock and residual solvent as the internal reference). Fast atom bombardment mass spectra (FABMS) were recorded in the positive ion mode with either a krypton primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a Kratos MS80RF mass spectrometer coupled to a DS90 system or a xenon primary atom beam with the same matrix and a ZAB-HF mass spectrometer. Melting points were measured with a Büchi SMP20 apparatus. Electrochemical measurements were performed with a three-electrode system consisting of a platinum working electrode, a platinum-wire counter-electrode, and a standard reference calomel electrode (SCE), versus which all potentials are reported. All measurements were carried out under Ar, in degassed spectroscopic grade solvents, using 0.1 M  $n\text{-Bu}_4\text{NBF}_4$  solutions as supporting electrolyte. A potentiostat EG&G Princeton

Applied Research Model 273A connected to a computer was used (software: Programme Research Electrochemistry Software) as well as a potentiostat Bruker E130M, connected to a printing table.

**5,5''-Dimethyl-2,2':6',2''-terpyridine (1).** This compound was prepared by Stille cross coupling reaction as previously reported:<sup>31</sup> white needles (EtOH), mp 303–304 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.52 (br s, 2H), 8.50 (d,  $J = 8.1$  Hz, 2H), 8.38 (d,  $J = 7.8$  Hz, 2H), 7.92 (t,  $J = 7.5$  Hz, 1H), 7.65 (ddd,  $J = 8.1, 2.4, 0.7$  Hz, 2H), 2.41 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 50 MHz, DEPT)  $\delta$  155.45 (C), 153.87 (C), 149.58 (CH), 137.76 (CH), 137.36 (C), 133.38 (CH), 120.71 (CH), 120.38 (CH), 18.42 ( $\text{CH}_3$ ); EIMS  $m/z$  (rel intensity, %): 261 ( $\text{M}^+$ , 100), 233 (11), 219 (12), 169 (11), 149 (15). Anal. Calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3$ : C, 78.13; H, 5.79; N, 16.08. Found: C, 78.20; H, 5.79; N, 16.18.

**5''-Methyl-5-{3-[(tetrahydro-2H-pyran-2-yl)oxy]-1-propyl}-2,2':6',2''-terpyridine (2).** A titrated commercial solution of LDA in THF (ca. 1.5 M, 20.2 mL, 30.3 mmol) was slowly added dropwise to a degassed solution of 5,5''-dimethyl-2,2':6',2''-terpyridine **1** (7.15 g, 27.4 mmol) in anhydrous THF (275 mL) at  $-78$  °C. The resulting deep purple solution was stirred under Ar at  $-78$  °C for 2 h and then at 0 °C for 0.5 h. After cooling back to  $-78$  °C, a degassed solution of 2-(2-bromoethoxy)tetrahydro-2H-pyran (5.72 g, 27.4 mmol) in anhydrous THF (270 mL) at 0 °C was added by means of a double-ended needle. The resulting mixture was left at 0 °C and slowly allowed to reach room temperature with stirring for 16 h. Then, it was hydrolyzed at 0 °C with 100 mL of  $\text{H}_2\text{O}$ . THF was evaporated, and the residue was taken in  $\text{CH}_2\text{Cl}_2$ , washed with  $\text{H}_2\text{O}$ , dried over  $\text{MgSO}_4$ , and filtered. Solvent was evaporated, and the residue was subjected to column chromatography on alumina (eluent: hexane-Et $_2\text{O}$ ) yielding **2** (4.66 g, 44%) as a white solid: mp 67–69 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.55–8.49 (m, 4H), 8.39 (d,  $J = 7.8$  Hz, 2H), 7.93 (t,  $J = 7.9$  Hz, 1H), 7.72–7.64 (m, 2H), 4.60 (t,  $J = 3.0$  Hz, 1H), 3.95–3.77 (m, 2H), 3.58–3.39 (m, 2H), 2.82 (t,  $J = 7.3$  Hz, 2H), 2.42 (s, 3H), 1.99 (qt,  $J = 7.4$  Hz, 2H), 1.91–1.50 (m, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 50 MHz, DEPT):  $\delta$  155.48 (2C), 154.29 (C), 153.89 (C), 149.60 (CH), 149.36 (CH), 137.79 (CH), 137.52 (C), 137.38 (CH), 136.79 (CH), 133.40 (C), 120.86 (CH), 120.72 (CH), 120.44 (2CH), 99.10 (CH), 66.51 ( $\text{CH}_2$ ), 62.54 ( $\text{CH}_2$ ), 31.09 ( $\text{CH}_2$ ), 30.83 ( $\text{CH}_2$ ), 29.58 ( $\text{CH}_2$ ), 25.53 ( $\text{CH}_2$ ), 19.77 ( $\text{CH}_2$ ), 18.43 ( $\text{CH}_3$ ); EIMS  $m/z$  (rel intensity, %): 389 ( $\text{M}^+$ , 10), 360 (11), 334 (8), 287 (69), 274 (73), 261 (100).

**5-(3-Hydroxy-1-propyl)-5''-methyl-2,2':6',2''-terpyridine (3).** A solution of **2** (5.11 g, 13.1 mmol) in EtOH (300 mL) was heated to reflux. Concentrated HCl (0.5 mL) was added, and the mixture was refluxed for 3 h. After cooling to 23 °C, the solution was neutralized with concentrated NaOH (ca. 30%). EtOH was evaporated, and the residue was treated with  $\text{CH}_2\text{Cl}_2$  and washed with brine. The organic phase was dried over  $\text{Na}_2\text{SO}_4$  and filtered. Evaporation of the solvent led to a yellow solid (3.78 g) which was purified by column chromatography on alumina (eluent:  $\text{CH}_2\text{Cl}_2$  containing 0–1% MeOH) to give pure alcohol **3** (3.40 g, 85%) as a white powder: mp 111–112 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.53–8.47 (m, 4H), 8.37 (d,  $J = 7.8$  Hz, 2H), 7.92 (t,  $J = 7.8$  Hz, 1H), 7.70–7.62 (m, 2H), 3.70 (t,  $J = 6.3$  Hz, 2H), 2.79 (t,  $J = 7.7$  Hz, 2H), 2.40 (s, 3H), 2.10 (br s, 1H), 1.99–1.85 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 50 MHz, DEPT):  $\delta$  155.40 (C), 155.31 (C), 154.15 (C), 153.74 (C), 149.48 (CH), 149.18 (CH), 137.82 (CH), 137.57 (C), 137.50 (CH), 136.89 (CH), 133.50 (C), 121.02 (CH), 120.86 (CH), 120.48 (2 CH), 61.46 ( $\text{CH}_2$ ), 33.80 ( $\text{CH}_2$ ), 29.12 ( $\text{CH}_2$ ), 18.39 ( $\text{CH}_3$ ); EIMS  $m/z$  (rel intensity, %): 305 (100,  $\text{M}^+$ ), 287 (18), 286 (38), 275 (35), 274 (45), 260 (65), 143 (20). Anal. Calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}$ : C, 74.73; H, 6.27; N, 13.76. Found: C, 74.63; H, 6.19; N, 13.61%.

**5-(3-Methanesulfonyl-1-propyl)-5''-methyl-2,2':6',2''-terpyridine (4).** A solution of **3** (3.38 g, 11.1 mmol) and freshly distilled  $\text{NEt}_3$  (9.3 mL, 66.6 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (300 mL) was cooled to  $-3$  °C. Mesyl chloride (3.5 mL, 44.4 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (85 mL) was added dropwise ( $-5$  °C  $< T < -2$  °C) and the resulting mixture was stirred under Ar for 4 h at  $-3$  °C. The reaction mixture was washed with cold  $\text{H}_2\text{O}$  and dried over  $\text{Na}_2\text{SO}_4$ . The organic phase was filtered and concentrated to furnish a white solid which was purified through a short alumina column ( $\text{CH}_2\text{Cl}_2$ ) to give **4** as a white powder (4.05 g, 95%): mp 92–94 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.58–8.48 (m, 4H), 8.40 (d,  $J = 7.8$  Hz, 2H), 7.93 (t,  $J = 7.8$  Hz, 1H), 7.72–7.64 (m, 2H), 4.29 (t,  $J = 6.2$  Hz, 2H), 3.03 (s, 3H), 2.86 (t,  $J$

(38) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelli, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.

(39) Meerwein, H.; Hederick, V.; Wunsderlich, K. *Arkiv. Pharm.* **1958**, *291*, 541.

=7.6 Hz, 2H), 2.42 (s, 3H), 2.22–2.08 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ , 50 MHz, DEPT):  $\delta$  155.41 (C), 155.15 (C), 154.72 (C), 153.66 (C), 149.54 (CH), 149.19 (CH), 137.91 (CH), 137.58 (CH), 136.95 (CH), 135.94 (C), 133.61 (C), 121.11 (CH), 120.79 (CH), 120.66 (CH), 120.57 (CH), 68.72 ( $\text{CH}_2$ ), 37.50 ( $\text{CH}_3$ ), 30.47 ( $\text{CH}_2$ ), 28.73 ( $\text{CH}_2$ ), 18.46 ( $\text{CH}_3$ ); EIMS  $m/z$  (rel intensity, %): 383 (45,  $\text{M}^+$ ), 287 (49), 286 (52), 274 (100), 260 (38).

**Ligand 6.** A mixture of mesylate **4** (1.58 g, 4.12 mmol), 2,9-bis-(4-hydroxyphenyl)-1,10-phenanthroline<sup>32</sup> (**5**) (792 mg, 2.16 mmol), and  $\text{K}_2\text{CO}_3$  (854 mg, 6.18 mmol) in DMF (90 mL) was heated at 80 °C for 16 h. After cooling to 23 °C, the suspension was diluted with  $\text{CHCl}_3$  (600 mL) and washed with  $\text{H}_2\text{O}$ . The organic phase was evaporated to dryness, the residue was dissolved in boiling  $\text{CHCl}_3$  (80 mL), and the resulting solution was concentrated to 40 mL by heating at atmospheric pressure. EtOH (240 mL) was added to precipitate the desired product as a white solid which was filtered and washed with EtOH and  $\text{Et}_2\text{O}$  (1.70 g, 88%): mp 209–211 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.59 (m, 2H), 8.51 (m, 8H), 8.40 (m, 6H), 8.28 (d,  $J$  = 8.5 Hz, 2H), 8.10 (d,  $J$  = 8.5 Hz, 2H), 7.93 (t,  $J$  = 7.8 Hz, 2H), 7.76 (br s, 2H), 7.73 (dd,  $J$  = 8.2, 5.9 Hz, 2H), 7.63 (br d,  $J$  = 8.2 Hz, 2H), 7.13 (d, 8.9 Hz, 4H), 4.12 (t,  $J$  = 6.1 Hz, 4H), 2.96 (t,  $J$  = 7.5 Hz, 4H), 2.40 (s, 6H), 2.22 (m, 4H);  $^{13}\text{C}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ , 100 MHz, DEPT):  $\delta$  160.21 (C), 156.39 (C), 155.47 (C), 155.33 (C), 154.45 (C), 153.79 (C), 149.53 (CH), 149.34 (CH), 146.07 (C), 137.79 (CH), 137.38 (CH), 136.95 (CH), 136.77 (CH), 133.37 (C), 132.32 (C), 129.06 (CH), 127.55 (C), 125.63 (CH), 120.94 (CH), 120.70 (CH), 120.44 (CH), 119.36 (CH), 114.79 (CH), 66.56 ( $\text{CH}_2$ ), 30.59 ( $\text{CH}_2$ ), 29.25 ( $\text{CH}_2$ ), 18.38 ( $\text{CH}_3$ ); there is one C signal left; a CH signal either overlaps or does not appear; FABMS:  $m/z$  939 ( $\text{M}^+$ ), 652, 518, 470, 261. Anal. Calcd for  $\text{C}_{62}\text{H}_{50}\text{N}_8\text{O}_2$ : C, 79.29; H, 5.37; N, 11.93. Found: C, 79.22; H, 5.55; N, 12.07.

**Threaded Complex 8.** A solution of  $\text{Cu}(\text{MeCN})_4\text{BF}_4$  (25.8 mg, 0.082 mmol) in degassed MeCN (5 mL) was transferred via a cannula to a stirred solution of macrocycle **7** (47 mg, 0.084 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) under Ar. The resulting orange solution was stirred at 23 °C for 30 min. Then, a degassed solution of ligand **6** (82 mg, 0.087 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was transferred via a cannula into it, resulting in the immediate formation of a brown-red solution which was stirred under Ar at 23 °C for 3 h. After evaporation of the solvent, the residue was chromatographed (alumina column;  $\text{CH}_2\text{Cl}_2$ –MeOH, 99.5:0.5) to give the desired complex **8** as a brown solid (102 mg, 75%):  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 200 MHz):  $\delta$  8.63 (br d,  $J$  = 8.1 Hz, 2H), 8.61 (d,  $J$  = 8.4 Hz, 2H), 8.52 (d,  $J$  = 7.8 Hz, 4H), 8.50 (m, 2H), 8.48–8.39 (m, 4H), 8.37 (d,  $J$  = 8.4 Hz, 2H), 8.23 (s, 2H), 7.94 (t,  $J$  = 7.8 Hz, 2H), 7.87 (d,  $J$  = 8.4 Hz, 2H), 7.86 (s, 2H), 7.81 (d,  $J$  = 8.4 Hz, 2H), 7.75 (dd,  $J$  = 8.2, 2.2 Hz, 2H), 7.67 (br d,  $J$  = 8.1 Hz, 2H), 7.49 (d,  $J$  = 8.7 Hz, 4H), 7.29 (d,  $J$  = 8.7 Hz, 4H), 6.05 (d,  $J$  = 8.7 Hz, 4H), 5.97 (d,  $J$  = 8.7 Hz, 4H), 3.83 (br s, 4H), 3.72 (m, 4H), 3.65–3.45 (m, 16H), 2.84 (t,  $J$  = 7.3 Hz, 4H), 2.40 (s, 6H), 2.04 (m, 4H); FABMS:  $m/z$  1569 ( $[\text{M}-\text{BF}_4]^-$ ), 1001, 939, 785 ( $[\text{M}-\text{BF}_4]^{2-}$ ), 629; UV–vis (MeCN– $\text{CH}_2\text{Cl}_2$ , 1:1)  $\lambda$  (nm) ( $\epsilon$ ,  $\text{mol}^{-1}\text{L cm}^{-1}$ ): 440 (2200), 283 (103 000), 246 (100 000), 224 (111 500); electrochemical data:  $E_{\text{Cu(II)/Cu(I)}} = +0.60\text{ V}$  ( $\Delta E = 90\text{ mV}$ ).

**Complex 9.**  $\text{Ru}(\text{terpy})(\text{Me}_2\text{CO})_3(\text{BF}_4)_2$  was prepared without isolation immediately before use from  $\text{Ru}(\text{terpy})\text{Cl}_3$  and  $\text{AgBF}_4$  in refluxing acetone.<sup>35</sup> A degassed solution of the threaded precursor **8** (80 mg, 0.046 mmol) in 1,2-dichloroethane (8 mL) was added to a degassed solution of freshly prepared  $\text{Ru}(\text{terpy})(\text{Me}_2\text{CO})_3(\text{BF}_4)_2$  (2.15 equiv) in refluxing EtOH (40 mL), and the mixture was stirred under Ar at 70 °C for 5 h. Solvent was evaporated, and the residue was purified by two successive column chromatographies ( $\text{SiO}_2$ ; eluent: MeCN– $\text{H}_2\text{O}$  9:1, containing 0.5–1% saturated aqueous  $\text{KNO}_3$ ). The product was isolated as the  $\text{PF}_6^-$  salt by anion exchange with  $\text{KPF}_6$ . A solution of the eluted nitrate in the minimum amount of MeCN was treated with excess of a  $\text{KPF}_6$  saturated solution in MeCN. The complex was precipitated as a brown-red solid by addition of  $\text{H}_2\text{O}$ , filtered, washed with  $\text{H}_2\text{O}$ , and dried under vacuum. It was recrystallized from MeCN– $\text{Et}_2\text{O}$  (45 mg, 33%):  $^1\text{H}$  NMR (acetone- $d_6$ , 400 MHz):  $\delta$  8.98 (d,  $J$  = 8.2 Hz, 2H), 8.96 (d,  $J$  = 8.9 Hz, 2H), 8.94 (d,  $J$  = 8.2 Hz, 4H), 8.80 (d,  $J$  = 8.5 Hz, 2H), 8.72 (d,  $J$  = 8.5 Hz, 2H), 8.67 (m, 6H), 8.59 (d,  $J$  = 8.5 Hz, 2H), 8.52 (t,  $J$  = 8.1 Hz, 2H), 8.49 (t,  $J$  = 8.1 Hz, 2H), 8.36 (s, 2H), 8.06 (d,  $J$  = 8.2 Hz, 2H), 8.05 (s, 2H), 7.99 (m, 6H),

7.91 (d,  $J$  = 8.5 Hz, 2H), 7.86 (br d,  $J$  = 8.5 Hz, 2H), 7.67 (br d,  $J$  = 4.7 Hz, 4H), 7.56 (d,  $J$  = 8.7 Hz, 4H), 7.52 (d,  $J$  = 1.5 Hz, 2H), 7.49 (br s, 2H), 7.38 (d,  $J$  = 8.7 Hz, 4H), 7.28 (m, 4H), 6.08 (d,  $J$  = 8.7 Hz, 4H), 5.98 (d,  $J$  = 8.7 Hz, 4H), 3.84 (s, 4H), 3.71 (m, 4H), 3.65 (m, 4H), 3.61 (m, 4H), 3.49 (m, 4H), 3.40 (t,  $J$  = 6.2 Hz, 4H), 2.50 (m, 4H), 2.01 (s, 6H), 1.68 (m, 4H); FABMS:  $m/z$  2818.4 ( $[\text{M} - \text{PF}_6]^-$ , calcd 2817.9), 2672.0 ( $[\text{M}-2\text{PF}_6]^-$ , calcd 2672.9), 2527.5 ( $[\text{M} - 3\text{PF}_6]^-$ , calcd 2527.9); UV–vis. (MeCN)  $\lambda$  (nm) ( $\epsilon$ ,  $\text{mol}^{-1}\text{L cm}^{-1}$ ): 475 (24 200), 311 (127 800), 274 (96 000), 248 (83 400); electrochemical data:  $E_{\text{Ru(III)/Ru(II)}} = +1.23\text{ V}$  ( $\Delta E = 65\text{ mV}$ );  $E_{\text{Cu(II)/Cu(I)}} = 0.59\text{ V}$  ( $\Delta E = 70\text{ mV}$ );  $E_{\text{Ru(I)/Ru(0)}} = -1.30\text{ V}$  ( $\Delta E = 65\text{ mV}$ ) (ligand-centered reduction).

**Rotaxane 11.** A red-brown solution of **9** (33 mg, 0.011 mmol) in MeCN (8 mL) was reacted with an aqueous KCN solution (36 mg, 0.55 mmol, in 1 mL). The mixture turned bright red. After having been stirred at 23 °C for 1.5 h, the solution was evaporated to 4 mL and treated successively with an excess of solid  $\text{KPF}_6$  and  $\text{H}_2\text{O}$  (50 mL). The resulting red precipitate was filtered and washed with  $\text{H}_2\text{O}$ . It was purified by column chromatography ( $\text{SiO}_2$ ; MeCN– $\text{H}_2\text{O}$ , 9:1, containing 0.1–1.5% saturated aqueous  $\text{KNO}_3$ ) and isolated as the  $\text{PF}_6^-$  salt (18 mg, 59%):  $^1\text{H}$  NMR (acetone- $d_6$ , 400 MHz):  $\delta$  8.88 (d,  $J$  = 8.0 Hz, 2H), 8.76 (d,  $J$  = 8.2 Hz, 2H), 8.57 (d,  $J$  = 8.2 Hz, 4H), 8.53 (m, 6H), 8.49 (d,  $J$  = 8.5 Hz, 2H), 8.42 (d,  $J$  = 8.0 Hz, 4H), 8.34 (m, 6H), 8.23 (d,  $J$  = 8.5 Hz, 2H), 8.10 (d,  $J$  = 8.5 Hz, 2H), 8.07 (t,  $J$  = 8.1 Hz, 2H), 8.02 (s, 2H), 7.98 (m, 6H), 7.94 (s, 2H), 7.82 (d,  $J$  = 8.7 Hz, 4H), 7.74 (br d,  $J$  = 8.2 Hz, 2H), 7.63 (s, 2H), 7.55 (d,  $J$  = 5.6 Hz, 2H), 7.24 (m, 6H), 7.21 (br s, 2H), 6.77 (d,  $J$  = 8.7 Hz, 4H), 6.42 (d,  $J$  = 8.7 Hz, 4H), 3.73 (t,  $J$  = 5.6 Hz, 4H), 3.67 (t,  $J$  = 5.8 Hz, 4H), 3.63 (s, 4H), 3.49 (m, 4H), 3.37 (m, 8H), 2.62 (m, 4H), 1.86 (s, 6H), 1.83 (m, 4H); FABMS:  $m/z$  2610.2 ( $[\text{M}-\text{PF}_6]^-$ , calcd 2609.3), 2464.5 ( $[\text{M}-2\text{PF}_6]^-$ , calcd 2464.3), 2318.9 ( $[\text{M}-3\text{PF}_6]^-$ , calcd 2319.3), 2043.1 ( $[\text{M}-7 - \text{PF}_6]^-$ ), 1897.6 ( $[\text{M}-7 - 2\text{PF}_6]^-$ ), 1752.6 ( $[\text{M}-7 - 3\text{PF}_6]^-$ ); UV–vis (MeCN)  $\lambda$  (nm) ( $\epsilon$ ,  $\text{mol}^{-1}\text{L cm}^{-1}$ ): 476 (22 100), 311 (123 300), 276 (111 200), 233 (77 000); electrochemical data:  $E_{\text{Ru(III)/Ru(II)}} = +1.26\text{ V}$  ( $\Delta E = 60\text{ mV}$ );  $E_{\text{Ru(I)/Ru(0)}} = -1.29\text{ V}$  ( $\Delta E = 50\text{ mV}$ ) (ligand-centered reduction).

**Catenate 10.** A degassed solution of  $\text{Ru}(\text{DMSO})_4\text{Cl}_2^{36}$  (33.5 mg, 0.069 mmol) in EtOH (250 mL) was added dropwise during 24 h, under efficient stirring, to an argon-flushed solution of the threaded complex **8** (115 mg, 0.069 mmol) in 1,2-dichloroethane–EtOH (1:1, 500 mL) kept at 70 °C. Once the addition was complete, the solution was stirred under Ar at 70 °C for 12 more hours. Solvent was evaporated, and the brown-red crude mixture was purified by column chromatography on silica gel (eluent: MeCN– $\text{H}_2\text{O}$ , 9:1, containing 0.1–0.5% saturated aqueous  $\text{KNO}_3$ ). Catenate **10** was isolated as the  $\text{PF}_6^-$  salt after treatment of the solid with a large excess of  $\text{KPF}_6$  in the minimum amount of MeCN, addition of excess of  $\text{H}_2\text{O}$ , filtration and washing with  $\text{H}_2\text{O}$  (brown solid, 63 mg, 43%):  $^1\text{H}$  NMR (acetone- $d_6$ , 400 MHz):  $\delta$  9.12 (d,  $J$  = 8.1 Hz, 2H), 9.06 (d,  $J$  = 8.4 Hz, 2H), 9.01 (d,  $J$  = 8.3 Hz, 2H), 8.77 (d,  $J$  = 8.3 Hz, 2H), 8.70 (d,  $J$  = 8.3 Hz, 2H), 8.60 (t,  $J$  = 8.2 Hz, 2H), 8.38 (s, 2H), 8.10 (dd,  $J$  = 8.3 and 1.6 Hz, 2H), 7.94–7.90 (m, 6H), 7.86 (d,  $J$  = 8.4 Hz, 2H), 7.80 (d,  $J$  = 8.4 Hz, 2H), 7.56 (s, 2H), 7.43 (d,  $J$  = 8.5 Hz, 4H), 7.38 (d,  $J$  = 8.5 Hz, 4H), 6.27 (s, 2H), 6.05 (d,  $J$  = 8.5 Hz, 4H), 5.98 (d,  $J$  = 8.5 Hz, 4H), 3.82 (s, 4H), 3.70–3.40 (m, 20H), 2.42–2.22 (m, 4H), 2.07 (s, 6H), 1.40–1.29 (m, 4H); FABMS:  $m/z$  1959.3 ( $[\text{M}-\text{PF}_6]^-$ , calcd 1959.4), 1815.4 ( $[\text{M} - 2\text{PF}_6]^-$ , calcd 1815.4), 1669.4 ( $[\text{M}-3\text{PF}_6]^-$ , calcd 1669.5); UV–vis (MeCN):  $\lambda_{\text{max}}$  (nm) 474 ( $\epsilon = 14\ 900$ ); electrochemical data:  $E_{\text{Ru(III)/Ru(II)}} = +1.24\text{ V}$  ( $\Delta E = 60\text{ mV}$ );  $E_{\text{Cu(II)/Cu(I)}} = +0.58\text{ V}$  ( $\Delta E = 70\text{ mV}$ );  $E_{\text{Ru(I)/Ru(0)}} = -1.32\text{ V}$  ( $\Delta E = 60\text{ mV}$ ) (ligand-centered reduction).

**Catenand 12.** A solution of KCN (50 mg, 0.77 mmol) in  $\text{H}_2\text{O}$  (1 mL) was added to a stirred solution of catenate **10** (27 mg, 0.0128 mmol) in MeCN (5 mL), and the mixture was stirred at 23 °C for 1.5 h. An excess of  $\text{KPF}_6$  was added to the resulting bright red solution. Addition of  $\text{H}_2\text{O}$  triggered the precipitation of a red solid which was purified by column chromatography ( $\text{SiO}_2$ ; MeCN– $\text{H}_2\text{O}$ , 9:1, containing 0–0.1% saturated aqueous  $\text{KNO}_3$ ) and isolated as the  $\text{PF}_6^-$  salt as described above (21 mg, 86%).  $^1\text{H}$  NMR (acetone- $d_6$ , 400 MHz):  $\delta$  8.61 (d,  $J$  = 8.1 Hz, 2H), 8.54 (d,  $J$  = 8.4 Hz, 2H), 8.51 (d,  $J$  = 8.3 Hz, 4H), 8.47 (d,  $J$  = 7.4 Hz, 2H), 8.45 (d,  $J$  = 8.5 Hz, 2H), 8.35 (d,  $J$  = 8.7 Hz, 4H), 8.19 (d,  $J$  = 8.5 Hz, 2H), 8.12 (s, 2H), 8.10 (d,  $J$  =



8.3 Hz, 2H), 7.97 (s, 2H), 7.91 (s, 2H), 7.91–7.87 (m, 2H), 7.83 (d,  $J = 8.4$  Hz, 2H), 7.79 (d,  $J = 7.4$  Hz, 2H), 7.65 (d,  $J = 8.8$  Hz, 4H), 7.33 (s, 2H), 6.72 (d,  $J = 8.7$  Hz, 4H), 6.34 (d,  $J = 8.8$  Hz, 4H), 3.87–3.80 (m, 4H), 3.69–3.63 (m, 4H), 3.66 (s, 4H), 3.54–3.49 (m, 2H), 3.44–3.28 (m, 10H), 2.63–2.54 (m, 2H), 2.46–2.38 (m, 2H), 1.99 (s, 6H), 1.95–1.87 (m, 2H), 1.80–1.72 (m, 2H); FABMS:  $m/z$  1751.6 ( $[M-PF_6]^+$ , calcd 1751.5), 1606.6 ( $[M-2PF_6]^+$ , calcd 1606.6), 1185.3 ( $[M-7 - PF_6]^+$ ), 1039.4 ( $[M-7 - 2PF_6]^+$ ); UV-vis (MeCN):

$\lambda$  (nm) ( $\epsilon$ ,  $\text{mol}^{-1} \text{L cm}^{-1}$ ) 474 (12 300), 314 (94 500), 278 (95 500); electrochemical data:  $E_{\text{Ru(III)/Ru(II)}} = +1.24 \text{ V}$  ( $\Delta E = 60 \text{ mV}$ );  $E_{\text{Ru(II)/Ru(I)}} = -1.34 \text{ V}$  ( $\Delta E = 60 \text{ mV}$ ).

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