Rotaxanes and Catenanes Built Around Octahedral Transition Metals

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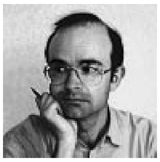
Transition metals are extremely useful tools for the preparation of rotaxanes and catenanes. Traditionally, copper(I) has played an important role in this field, but recently octahedrally coordinated metal centres such as ruthenium(II), have allowed the preparation of highly functional interlocking ring systems. The present review article will discuss this new approach, which gives access to novel rotaxanes and catenanes. Besides the purely synthetic work described, the potential of the prepared compounds to be used as light-driven molecular machines will be mentioned.

I. Introduction

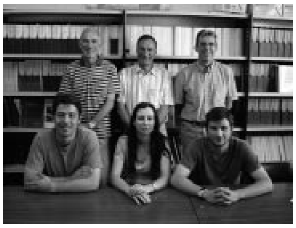
Interlocking rings (catenanes) and rings threaded by string-like fragments (rotaxanes) have experienced spectacular development over the last two decades.[1−3] While they once presented primarily a synthetic challenge, the interest in these compounds has recently moved towards their potential applications, in particular as molecular machines.[4−8]

Interlocking or threaded rings based on transition metals, either used as temporary templates[9] or incorporated in their backbone,[10,11] represent a special class of such molecules. Conceptually, it is easy to design a synthetic strategy



Jean-Claude Chambron (left) gained his Ph.D. in 1986 at Louis Pasteur University (Strasbourg, France) with Jean-Pierre Sauvage. After a postdoctoral stay at UC Berkeley with Kenneth N. Raymond, he took up a CNRS research position in the group of J.-P. Sauvage, where he was appointed as research director in 1999. In 2001 he established a new research group at the University of Burgundy (Dijon) in the laboratory headed by Roger Guilard. His past and present research interests concern topological stereochemistry, porphyrin-based catenanes and rotaxanes, and synthetic models of metalloenzymes.

Didier Pomeranc (right) was born in 1974 in Belfort and studied Chemistry at the Université Louis Pasteur in Strasbourg. After a brief period spent in Cambridge working under the supervision of Jeremy K. M. Sanders, in 1998 he joined the group of J.-P. Sauvage in Strasbourg, where he obtained his Ph.D. in 2002. He is now working at the University of California in Berkeley as a postdoctoral fellow in the group of Kenneth N. Raymond.



First row, left to right: Jean-Marc Kern, Jean-Paul Collin, Jean-Pierre Sauvage
Second row, left to right: Damien Jouvenot, Valérie Heitz, Pierre Mobian

Jean-Paul Collin was born in 1945 in Metz. After working for his Ph.D. in electrochemistry with Prof. J.-P. Schwing at Strasbourg University, he did postdoctoral work with Prof. Jean-Marie Lehn on water photolysis. He is now a CNRS research director. He joined J.-P. Sauvage's group in 1983, and his present research interests concern photoinduced charge separation in multicomponent molecular systems and molecular machines.

Valérie Heitz received her Ph.D. in 1992 for work done with Dr. J.-P. Sauvage on multiporphyrin systems performing photoinduced electron transfer. She did postdoctoral work with Dr. A. Harriman at the Universty of Texas at Austin. She obtained a position as "maître de conférences" at the University of Strasbourg in 1993 and carries out research in the group led by J.-P. Sauvage. Her current interests concern the synthesis of functional models of the photosynthetic reaction centre and of rotaxanes and catenanes.

Damien Jouvenot was born in Maracaibo (Venezuela) in 1977. After studying at the University of Grenoble, he worked for a few of months on biomimetic homogeneous catalysis with Stéphane Ménage in Grenoble (CEA) (2000). Then he moved to Strasbourg where he is currently working on the field of light-driven molecular machines towards his Ph.D. under the supervision of J.-P. Collin and J.-P. Sauvage.

Jean-Marc Kern was born in Alsace. He received his Ph.D. (1976) at the University Louis Pasteur in Strasbourg with Prof. P. Federlin. He spent two periods of post-doctoral research in Prof. H. Schäfer's group (organic electrochemistry) in Münster (1978, 1979). He occupied a "maître de conferences" position at the Université Louis Pasteur until 1992, and since then has been Professor at the same university. The first publication with Prof. Sauvage dates from 1984. He joined Prof. Sauvage's group in 1989. His present research fields include the synthesis of molecular machines and motors and electronic conducting polymers including transition metal complexes.

Pierre Mobian was born in 1976 in Strasbourg and studied Chemistry at the Université Louis Pasteur in Strasbourg. After a brief period spent in Cambridge working under the supervision of Jeremy K. M. Sanders, in 1999 he joined the group led by J.-P. Sauvage in Strasbourg, where he obtained his Ph.D. in 2003, working on the field of light-driven molecular machines.

Jean-Pierre Sauvage is a CNRS director of research. His current interests range from models of the photosynthetic reaction centre, using transition metal complexes and porphyrins, to topology (catenanes and knots) and molecular machines and motors. He is a member of the French Academy of Sciences.

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based on the entwining of two molecular threads around a transition metal centre. Many examples of such an approach have been reported, consisting of coordinating 1,10-phenanthroline-incorporating organic fragments perpendicularly to one another around a tetrahedral copper(I) centre before cyclizing to afford the desired catenane.[12] An alternative but related approach is based on the copper(I)-directed threading of an acyclic coordinating fragment through a presynthesized ring containing a complexing unit pointing towards the inside of the ring. This strategy allows the preparation of rotaxanes and has been extensively utilized to construct porphyrin-stoppered rotaxanes.[13]

Recently, five-coordinate geometries, based on Zn^{2+} associated to a pair of ligands containing a 2,2′,6′,2′′-terpyridine fragment and a 1,10-phenanthroline unit, have been exploited to prepare catenanes containing a five-coordinate complexation site.[14]

Octahedral transition metal centres have rarely been used as templates for synthesizing topologically nontrivial molecules such as catenanes and knots. An early example uses a bis(terpy) complex (terpy = 2,2′,6′,2"-terpyridine),[15] and more recently a spectacular synthetic achievement was reported based on two terdentate ligands entwined around a first-row transition metal atom[16] (Figure 1). Knots have been prepared by using two octahedral iron centres with each metal atom coordinated to two terpy derivatives.[17] An "open" knot was also described whose synthesis was made possible by knotting a long molecular thread incorporating three bidentate chelates around a zinc(II) atom[18] (Figure 2).

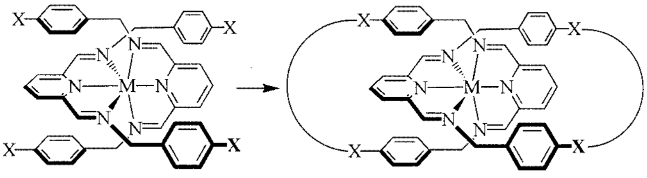


Figure 1. Synthesis of catenanes by orthogonalization of coordinated ligands about metal templates with octahedral preference

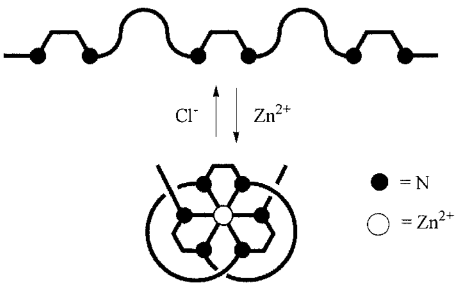
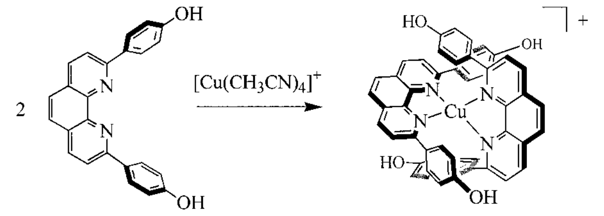


Figure 2. A synthetic oligomer that folds into a knot in the presence of zinc ions: reversible folding of the knot complex

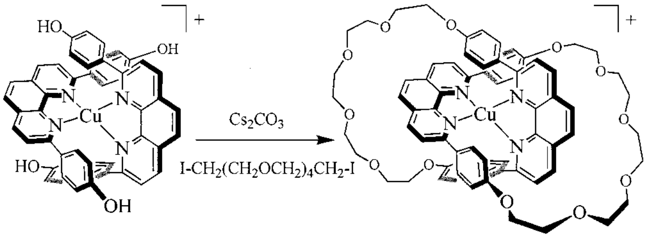
II. Design of the Compounds and Synthesis Strategy

As mentioned above, tetrahedral transition metals, such as copper(I), have been used for a relatively long time as templates to construct interlocking rings in an efficient way, following very short strategies.[12] The success of the approach relies on a three-dimensional template effect around a metal centre, as represented in Figures 3 and 4. In the synthesis of $Cu(\mathbf{1})^+$ the coordinating core is based on 2,9-diphenyl-1,10-phenanthroline (dpp). Combining Cu(I) ions and dpp fragments has proven to be an ideal approach to the templated synthesis of catenanes.



2 $[Cu(\mathbf{2})_2]^+$ (100%)

Figure 3. Template synthesis of the (pre-catenane)copper cation $Cu(\mathbf{2})_2{}^+$



$[Cu(\mathbf{2})_2]^+$ $[Cu(\mathbf{1})]^+$ (27%)

Figure 4. Synthesis of the ([2]catenane)copper cation $[Cu(\mathbf{1})]^+$

An octahedral metal atom coordinated to three bidentate chelates is an attractive template for preparimg catenanes and rotaxanes because of the synthetic challenge that such syntheses represent as well as the interesting electro- and photochemical properties that compounds based on $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) display. However, the use of a metal centre of this type as the template is less straightforward than using a tetrahedral metal centre such as copper(I). Indeed, it is conceptually difficult to induce an entwining process of two threads using three chelates gathered around a transition metal centre. In the present review article, we discuss our recent work related to the use of $[Ru(phen)_3]^{2+}$ derivatives (phen = 1,10-phenanthroline) as gathering and templating complex cores in the synthesis of various catenanes and rotaxanes.

In addition, preliminary studies of photochemical properties will be mentioned, which suggest that such compounds represent promising prototypes of light-driven molecular machines and motors.

The design of the systems and the synthetic strategy are depicted in Figures 5 and 6. For preparimg a rotaxane, an attractive strategy consists of "threading" an axial component through a ring, followed by a "stoppering" reaction (attaching bulky substituents at the extremities of the axis). This appears to be a viable approach, as it has recently been reported that an $[Ru(diimine)_3]^{2+}$ moiety can be inscribed in an axial compound through appropriate substitution of the diimine chelates. For the synthesis of catenanes it should be possible to incorporate two bidentate chelates of the octahedron in a ring and subsequently thread a fragment containing the third chelate through the ring. This second process would be driven by coordination to the metal core, analogous to the threading step of the rotaxane synthesis. The catenane synthesis would then be completed by cyclizing the bidentate-containing fragment, with ring-closing metathesis reactions being particularly attractive.

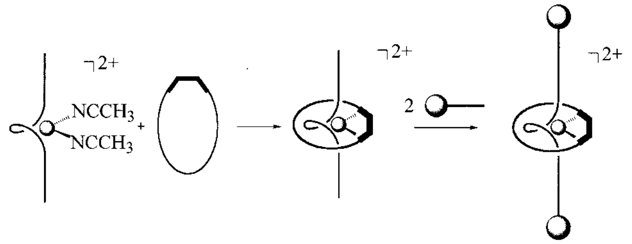


Figure 5. Synthesis of a rotaxane around an octahedral metal atom: principle; the helical fragment is a tetradentate ligand wrapped around the metal atom by coordination to it; it is threaded through the coordinating ring or complexed to it in an exotopic fashion

It should be noted that for a bis(bidentate) organic compound three different situations can be obtained, having markedly different symmetries, as represented in Figure 7.

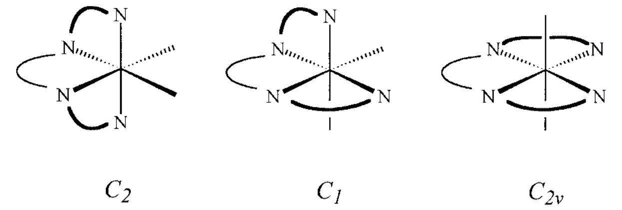


Figure 7. The three different situations corresponding to the complexation of a metal centre by a tetradentate ligand [in fact, a bis(bidentate) coordinating unit]

Tetradentate ligands consisting of two separate bidentate ligands connected by an appropriate spacer and leading to C_2-symmetric complexes have already been reported. A particularly interesting example is that of von Zelewsky's chiragens,[19] consisting of two chiral bipy derivatives. A representative complex of this family is depicted in Figure 8.

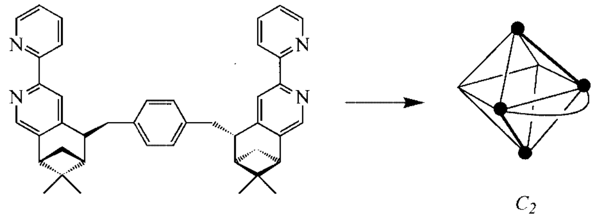


Figure 8. A particularly representative example of a chiragen, prepared and utilized in Fribourg (Switzerland) by von Zelewsky et al.[19]

Our group has also proposed a bis(phen) molecule leading to an $[Ru(phen)_3]^{2+}$ derivative with a clearly identified axis bearing chemical functions.[20,21] The substitution positions of the functions on the phen nuclei, attached to be

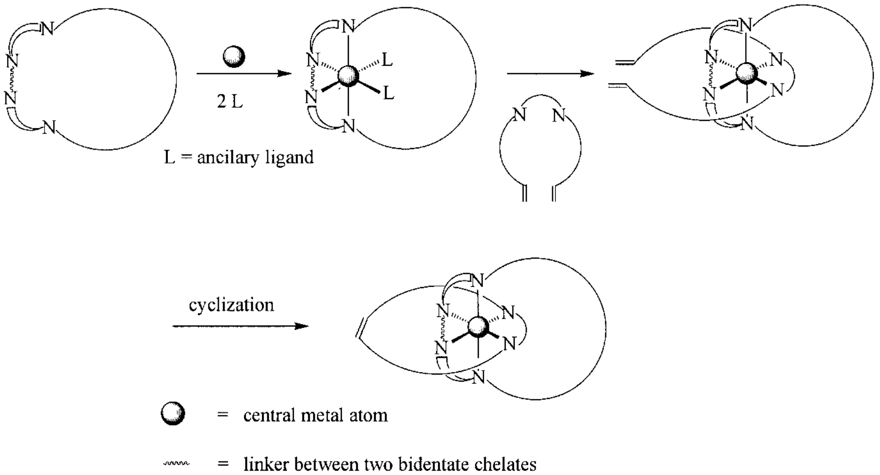
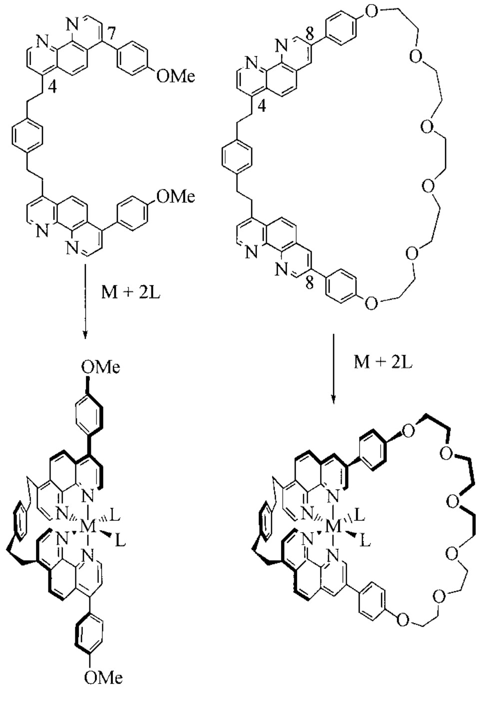


Figure 6. Synthesis of a catenane using an octahedral metal atom and three bidentate chelates: construction principle; the tetradentate ligand is inscribed in a ring in such a way that the local symmetry around the metal atom is C_2; the third bidentate unit is threaded through the ring, the driving force of the process being the coordination of the chelate to the metal centre; from the threaded precursor to the final catenane, cyclization is carried out by performing ring-closing metathesis of terminal olefins

used for further derivatization, are of the utmost importance and will determine whether the tetradentate ligand can easily be incorporated in an axial fragment or in a cycle (Figure 9).



(a) (b)

Figure 9. Formation of an axial (a) or a macrocyclic (b) complex; in both cases, connection of two positions *para* to the N atoms of the phen nuclei by the $-CH_2CH_2-C_6H_4-CH_2CH_2-$ bridge leads to a *cis* arrangement; introduction of aromatic groups ($-C_6H_4-OMe$) on the other *para* positions leads to the axial complex (a) whereas the macrocyclic complex (b) can be obtained by utilizing the *meta* positions (C8) to attach the $-C_6H_4-OMe$ aromatic groups

III. Synthesis of Rotaxanes and Catenanes Based on a Ru(phen)$_3^{2+}$ Derivative

1. Rotaxanes Synthesis

In order to clearly identify an axis in a rotaxane based on an $[Ru(phen)_3]^{2+}$ derivative, an appropriate bis(phen) ligand $\mathbf{L_1}$ was designed which is substituted on both 7-positions of phen with an anisyl group. Ligand $\mathbf{L_1}$ was obtained by coupling two 4,7-disubstituted phenanthrolines **6** (Figure 10). This precursor was prepared using Skraup reactions, which have been extremely useful in the past for preparing various substituted 1,10-phenanthrolines.[22] First, quinoline **3** was obtained in 55% yield by reaction of *o*-nitroaniline (**2**) with but-3-en-2-one (**1**) in sulfuric acid in the presence of arsenic pentoxide. Reduction of **3** with tin(II) chloride gave the amino derivative **4** in 95% yield. Compund **4** was finally treated with **5** in orthophosphoric acid in the presence of arsenic pentoxide to afford the desired phenanthroline **6** in 52% yield after recrystallization.[23] Coupling of the two phenanthroline derivatives **6** was achieved by deprotonation of 1 equiv. of **6** with a solution of LDA followed by reaction with 0.5 equiv. of α,α′-dibromo-*p*-xylene. Ligand $\mathbf{L_1}$ was obtained in 88% yield after purification.

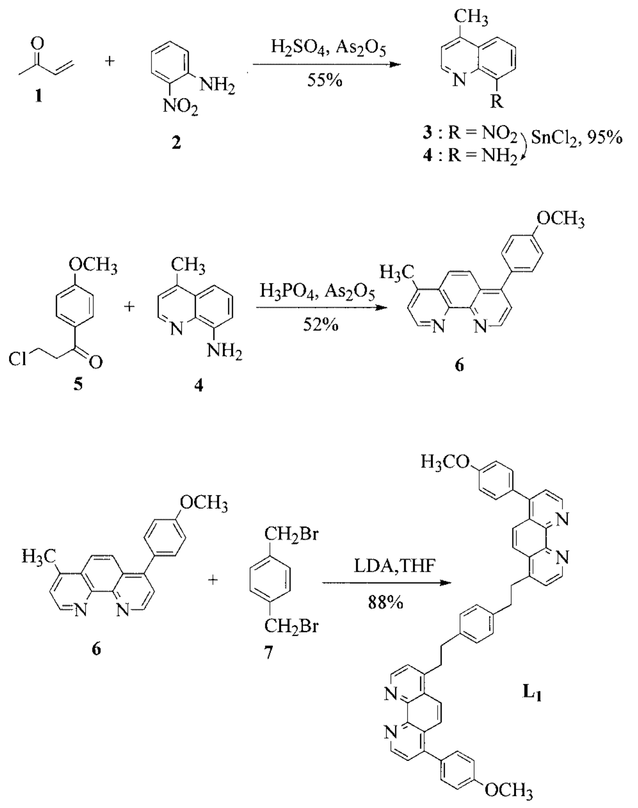


Figure 10. Precursors and synthetic route to the bis(chelate) $\mathbf{L_1}$

The chelating properties of ligand $\mathbf{L_1}$ were tested on Ru^{II} and Fe^{II} (Figure 11). $[Ru(\mathbf{L_1})(4,4'\text{-dmbp})](PF_6)_2$ (4,4′-dmbp = 4,4′-dimethyl-2,2′-bipyridine) was prepared in two steps. First, the reaction of freshly prepared $[Ru(CH_3CN)_4(Cl)_2]$ with stoichiometric amounts of $\mathbf{L_1}$ in refluxing 1,2-dichloroethane under high-dilution conditions as described by von Zelewsky and co-workers,[24] afforded the intermediate $[Ru(\mathbf{L_1})(Cl)_2]$ complex in 65% yield. $[Ru(\mathbf{L_1})(Cl)_2]$ was then treated with 1.6 equiv. of 4,4′-dmbp in a 2:1 mixture of ethanol/water. $[Ru(\mathbf{L_1})(4,4'\text{-dmbp})](PF_6)_2$ was obtained in 80% yield as an orange solid after anion exchange and chromatographic separation. The Fe^{II} complex was prepared by taking advantage of the lability of the 4,4′-dmbp ligands in the $[Fe(4,4'\text{-dmbp})_3]^{2+}$ complex as well as the stronger chelating properties of the tetradentate ligand $\mathbf{L_1}$ compared with two bidentate 4,4′-dmbp ligands. Thus, $[Fe(4,4'\text{-dmbp})_3](PF_6)_2$ was treated with 1 equiv. of $\mathbf{L_1}$ in refluxing 1,2-dichloroethane for 24 h. After anion exchange, chromatographic separation afforded $[Fe(\mathbf{L_1})(4,4'\text{-dmbp})](PF_6)_2$ in 75% yield.

The structures of $[Ru(\mathbf{L_1})(4,4'\text{-dmbp})](PF_6)_2$ and $[Fe(\mathbf{L_1})(4,4'\text{-dmbp})](PF_6)_2$ were solved by single-crystal X-ray analysis. They show that in the two octahedral complexes ligand $\mathbf{L_1}$ coils around the metal atom by coordi-

$$(1)\ [Ru(CH_3CN)_4(Cl)_2] + \mathbf{L_1} \xrightarrow[\text{high dilution}]{CH_2ClCH_2Cl,\ 83^\circ C} [Ru(\mathbf{L_1})(Cl)_2] + 4\ CH_3CN$$

$$(2)\ [Ru(\mathbf{L_1})(Cl)_2] + 4,4'\text{-dmbp} \xrightarrow{EtOH / H_2O,\ \text{reflux}} [Ru(\mathbf{L_1})(4,4'\text{-dmbp})]^{2+} + 2\ Cl^-$$

$$(3)\ [Fe(4,4'\text{-dmbp})_3]^{2+} + \mathbf{L_1} \xrightarrow{CH_2ClCH_2Cl,\ 83^\circ C} [Fe(\mathbf{L_1})(4,4'\text{-dmbp})]^{2+} + 2\ (4,4'\text{-dmbp})$$

Figure 11. Preparation of the Ru^{II} and Fe^{II} complexes of $\mathbf{L_1}$

nation to the axial and two equatorial positions providing C_2-symmetric complexes. The remaining equatorial positions are occupied by the 4,4′-dmbp ligand. As an example, the X-ray crystal structure of the cation $[Ru(\mathbf{L_1})(4,4'\text{-dmbp})]^{2+}$ is represented in Figure 12.

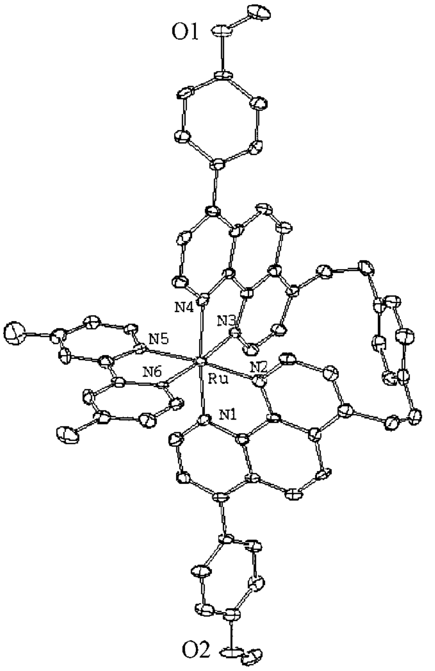


Figure 12. X-ray molecular structure of complex $[Ru(\mathbf{L_1})(4,4'\text{-dmbp})]^{2+}$

The nitrogen atoms of the ligands occupy the vertices of a slightly distorted octahedral coordination sphere around Ru^{II} with an average Ru−N distance of 2.07 Å. All three N−Ru−N angles show some deviation from linearity, the largest effect being observed in the case of the N1−Ru−N4 axis (172.5 vs. 174.4° for the others). This could be a consequence of the strain imposed by the *p*-phenylene bridge. The methoxy groups of the anisyl substituents form the extremities of the axis based on the N1−Ru−N4 approximately straight line. The O1−Ru−O2 distance is 21.04 Å.

The bis(phenanthroline) ligand $\mathbf{L_1}$ is such that its ruthenium(II) complexes possess a clearly identified axis (Figure 12) making such compounds ideal components of rotaxanes constructed around an octahedral ruthenium(II) centre used as a template. The synthetic strategy used to obtain the rotaxane consists of a "threading" step (the axial component is threaded through the ring) followed by a "stoppering" reaction (bulky substituents are attached at the ends of the axis). The threading reaction was first tested on a model whose axis is end-functionalized by two unreactive chemical groups (methyl ethers). The reaction is depicted in Figure 13.

The complex $[Ru(\mathbf{L_1})(CH_3CN)_2](PF_6)_2$ is a yellow solid, formed quantitatively from its dichloro precursor (purple complex) by replacing the Cl^- ligands by CH_3CN in H_2O/CH_3CN.[21] The macrocyclic compound **m35** incorporates a bipy ligand substituted at its 6- and 6′-positions by alkyl groups, and a bis(*p*-alkoxyphenyl)dimethylmethane fragment derived from "bis(phenol) A" (4,4′-isopropylidenediphenol). It has been obtained by reaction of the appropriate dibromo precursor {6,6′-bis[2-(2-bromoethoxy)ethoxypropyl]-2,2′-bipyridine} with "bis(phenol) A" in 45% yield.[25] Compound **m35** is a 35-membered ring and CPK models suggest that its size should be sufficient to allow the threading reaction shown in Figure 13, although the rotaxane-like molecule obtained should be congested, with contacts between the "bis(phenol) A" motif of the ring and the $-CH_2-CH_2-C_6H_4-CH_2-CH_2-$ fragment of the axial component. This steric hindrance may in part explain the poor yield of the reaction: $[Ru(\mathbf{L_1})(CH_3CN)_2](PF_6)_2$ and **m35** were allowed to react in ethylene glycol (140 °C, 4 h; stoichiometric proportion; concentration of the reactants: 0.01 $mol\cdot L^{-1}$) to afford a 20−25% yield of a mixture of complexes containing the pseudorotaxane *endo*-$[Ru(\mathbf{L_1})(\mathbf{m35})](PF_6)_2$ and the nonthreaded isomer *exo*-$[Ru(\mathbf{L_1})(\mathbf{m35})](PF_6)_2$ after chromatography (Figure 13). This mixture gives only one round spot on a thin-layer chromatograph, making the separation of these two complexes extremely difficult. By comparison, $[Ru(\mathbf{L_1})(CH_3CN)_2]^{2+}$ reacts with the acyclic ligand 6,6′-dmbp (6,6′-dmbp = 6,6′-dimethyl-2,2′-bipyridine) to afford the corresponding complex in quantitative yield, under reaction conditions similar to those used for preparing $[Ru(\mathbf{L_1})(\mathbf{m35})]^{2+}$. The formation of *endo*-$[Ru(\mathbf{L_1})(\mathbf{m35})]^{2+}$ and *exo*-$[Ru(\mathbf{L_1})(\mathbf{m35})]^{2+}$ was supported by ES-MS and ^1H NMR studies.[25]

Single crystals of the pseudorotaxane *endo*-$[Ru(\mathbf{L_1})(\mathbf{m35})](PF_6)_2$ could be obtained by slow diffusion of hexane into an acetone solution of the mixture of complexes, and an X-ray structure has been obtained.[25] As shown in Figure 14, *endo*-$[Ru(\mathbf{L_1})(\mathbf{m35})]^{2+}$ is indeed a threaded species with a helical axis, the bis(phen) ligand being wrapped around the metal atom in a way similar to that recently observed with nonrotaxane-like species.[20,21] The metal atom is octahedrally coordinated, with little distortion. The Ru−N distances and N−Ru−N angles have the expected values (Ru−N 2.055−2.068 Å for the phen ligands and 2.12−2.13 Å for the bipy part). The most striking feature of the structure is the distortion of the ring from planarity. Clearly, the ring is too small to accommodate the relatively thick axle and it cannot run around the $-CH_2-CH_2-C_6H_4-CH_2-CH_2-$ part of the helical axis. The folded conformation of the macrocyclic component of *endo*-$[Ru(\mathbf{L_1})(\mathbf{m35})]^{2+}$ results in a nonsymmetrical situation

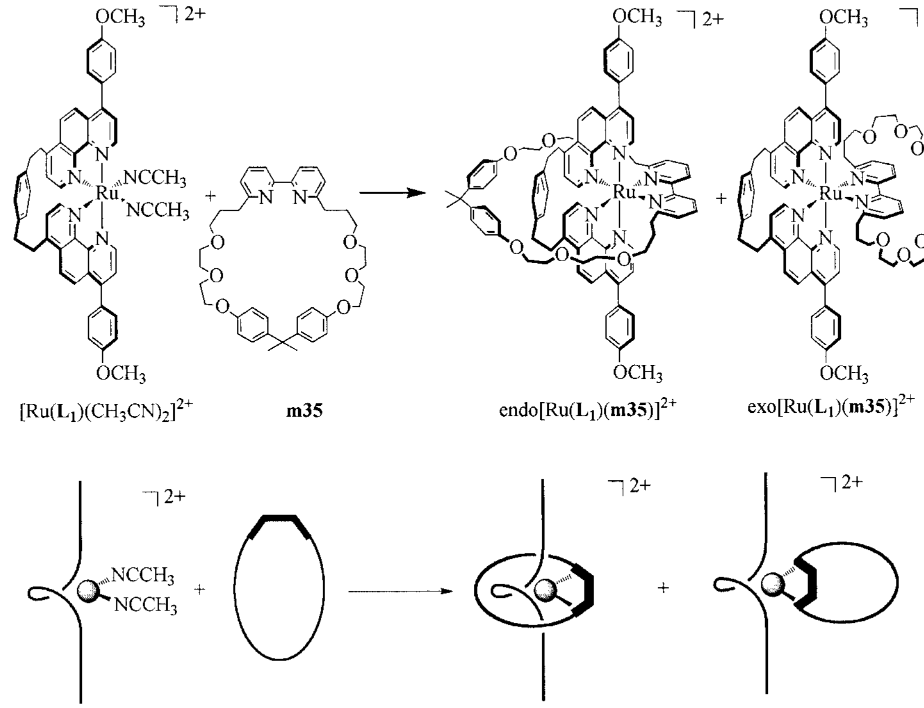


Figure 13. Synthesis of the pseudorotaxane *endo*-[Ru(**L**$_1$)(**m35**)]$^{2+}$ and of the *exo* isomer *exo*-[Ru(**L**$_1$)(**m35**)]$^{2+}$

for which the "upper" and the "lower" parts of the rotaxane become nonequivalent in the solid state.

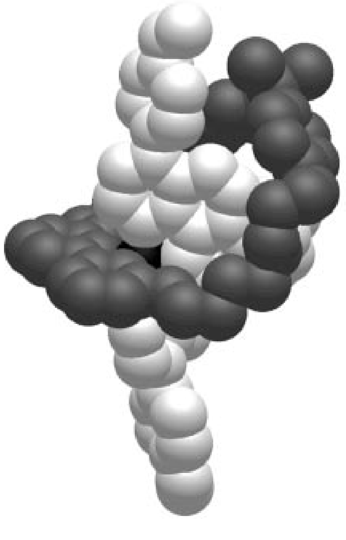


Figure 14. X-ray structure of the pseudorotaxane *endo*-[Ru(**L**$_1$)(**m35**)]$^{2+}$; H atoms have been omitted for clarity

The very congested situation in *endo*-[Ru(**L**$_1$)(**m35**)]$^{2+}$, as evidenced by the X-ray structure, tends to explain why the preparative yield is poor. The presence of a certain proportion of the nonthreaded species (Figure 13) can also be understood: the "unnatural" conformation of the ring in this species may be unfavourable but this destabilization energy is compensated by the energy introduced by the steric repulsion between the ring and the thread in the pseudorotaxane *endo*-[Ru(**L**$_1$)(**m35**)]$^{2+}$.

Finally, the real rotaxane derived from *endo*-[Ru(**L**$_1$)(**m35**)]$^{2+}$ was synthesized. Among the various routes tested in our group, only the one indicated in Figure 15 turned out to be successful.

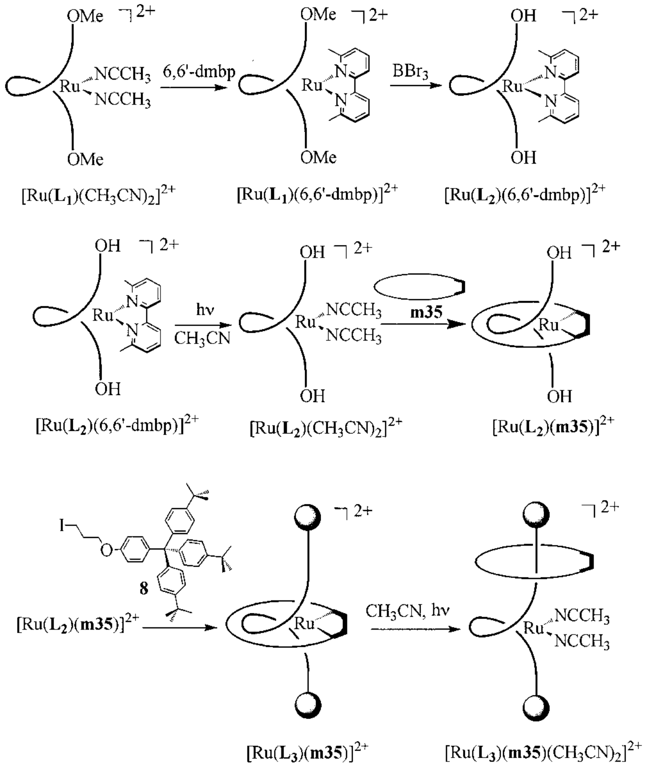


Figure 15. Synthesis of the rotaxane [Ru(**L**$_3$)(**m35**)(CH$_3$CN)$_2$]$^{2+}$

Since the demethylation reaction of the anisyl groups of $[\mathrm{Ru}(\mathbf{L_1})(\mathrm{CH_3CN})_2]^{2+}$ failed, probably because of the relative lability of the CH_3CN ligands, this same reaction was carried out on $[\mathrm{Ru}(\mathbf{L_1})(6{,}6'\text{-dmbp})]^{2+}$, which can be regarded as a protected version of $[\mathrm{Ru}(\mathbf{L_1})(\mathrm{CH_3CN})_2]^{2+}$. In the dark, the 6,6′-dmbp chelate is sufficiently coordinated and chemically robust for the complex to resist the aggressive conditions required to cleave the methyl ethers (BBr_3). $[\mathrm{Ru}(\mathbf{L_2})(6{,}6'\text{-dmbp})]^{2+}$ was subsequently deprotected by photochemically expelling 6,6′-dmbp from the complex to afford $[\mathrm{Ru}(\mathbf{L_2})(\mathrm{CH_3CN})_2]^{2+}$ {100% from $[\mathrm{Ru}(\mathbf{L_1})(6{,}6'\text{-dmbp})]^{2+}$}. The threading reaction of **m35** by $[\mathrm{Ru}(\mathbf{L_2})(\mathrm{CH_3CN})_2]^{2+}$ (ethylene glycol; 140 °C; 2 h) led to $[\mathrm{Ru}(\mathbf{L_2})(\mathbf{m35})]^{2+}$ with a 27% yield. The stoppering step was performed on $[\mathrm{Ru}(\mathbf{L_2})(\mathbf{m35})]^{2+}$ following classical conditions (DMF/K_2CO_3) using **8**[26] in stoichiometric proportion. The (rotaxane)$\mathrm{Ru^{II}}$ compound $[\mathrm{Ru}(\mathbf{L_3})(\mathbf{m35})](\mathrm{PF_6})_2$ was isolated in 74% yield. After Vis irradiation it was possible to identify the real rotaxane, $[\mathrm{Ru}(\mathbf{L_2})(\mathbf{m35})(\mathrm{CH_3CN})_2](\mathrm{PF_6})_2$, by ES-MS.

2. Catenane Synthesis

As already mentioned, the substitution positions on the phen nuclei in the bis(phen) core are of the utmost importance and determine whether the tetradentate ligand can be incorporated in an axial fragment (Figure 9, a), as discussed in the previous section, or in a ring (Figure 9, b). In this section, we shall show how a slight structural modification of the design of the bis(phenanthroline) core, i.e. the connection of the anisyl moiety to position 8 of the phenanthroline instead of 7 as in $\mathbf{L_1}$, allow the construction of a large macrocycle from the bis(phen) moiety and subsequently the synthesis of a catenane complexed to an octahedral ruthenium(II) centre.[27] The strategy is depicted in Figure 16. The bis(phen)-containing macrocycle is a 50-membered ring, **R50**, prepared in five steps from the quinoline **9** (Figure 16).

Compound **R50** looks well adapted to the formation of octahedral bis(phen) complexes, on CPK models with the two phen fragments being disposed *cis* to one another in the metal coordination sphere. The substitution positions of the *p*-alkoxyphenyl groups (8 and 8′ in **R50**) determine the final structure, but the key step of the present work is the coordination reaction leading to the cyclic complex (Figure 6). Several first-row transition metals were tested (Zn^{2+} and Fe^{2+} in particular) with limited success. However, ruthenium(II) afforded the desired complex (Figure 17).

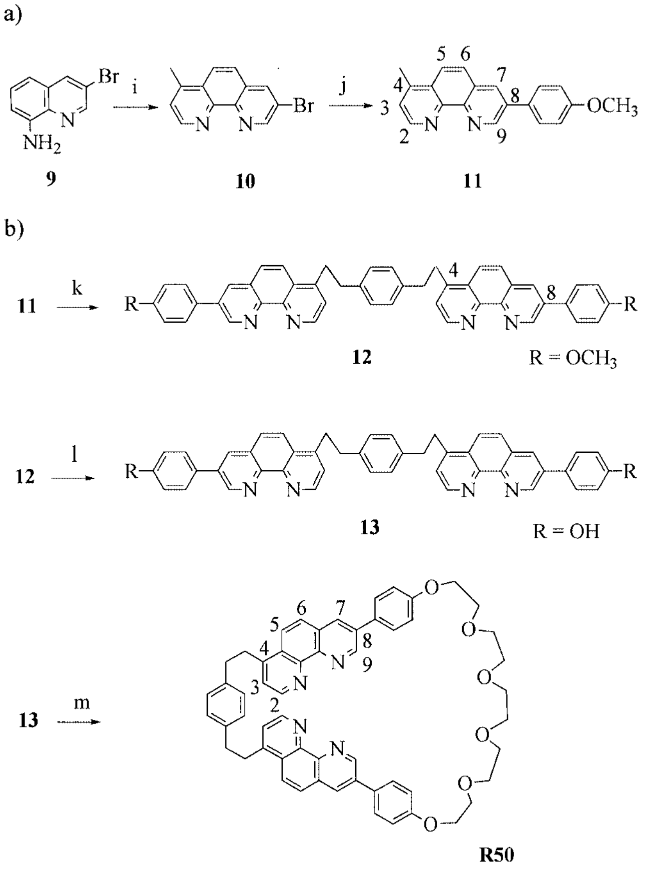


Figure 16. (a) Synthetic path leading from 8-amino-3-bromoquinoline **9** to 3-(*p*-anisyl)-7-methyl-1,10-phenanthroline **11**; (b) synthetic path leading from **11** to macrocycle **R50**: i) methyl vinyl ketone, NaI, H_2SO_4 (70% in water), 110 °C, 67%, j) (*p*-methoxyphenyl)boronic ester, $\mathrm{Pd[P(Ph)_3]_4}$, mixture toluene/aqueous solution of NaOH (2 $\mathrm{mol{\cdot}L^{-1}}$), 50 °C, 80%, k) α,α′-dibromo-*p*-xylene, LDA, THF, 0 °C, 53%, l) anhydrous pyridinium chloride, 220 °C, 97%, m) diiodopentaethylene glycol, Cs_2CO_3, DMSO/DMF, 60 °C, 23%

Complex $[\mathrm{Ru}(\mathbf{R50})(\mathrm{CH_3CN})_2]^{2+}$ was formed by allowing **R50** and $\mathrm{Ru(DMSO)_4Cl_2}$ [28] to react in refluxing 1,2-dichloroethane under high-dilution conditions. The dichloro intermediate complex was not isolated. The crude mixture from the reaction between **R50** and $\mathrm{[Ru(DMSO)_4]Cl_2}$ was heated under reflux in a mixture of CH_3CN/H_2O (80:20, v/v) to afford $[\mathrm{Ru}(\mathbf{R50})(\mathrm{CH_3CN})_2](\mathrm{PF_6})_2$ as an orange solid in 21% yield after anion exchange. It is noteworthy that $[\mathrm{Ru}(\mathbf{R50})(\mathrm{CH_3CN})_2]^{2+}$ is a rare example of a bis(phen), or more generally a bis(bidentate), octahedral complex with a *cis* arrangement embedded in a ring.

The next step was carried out using **14**, a 2,2′-bipyridine derivative analogous to a previously described example,[21] and the macrocyclic complex $[\mathrm{Ru}(\mathbf{R50})(\mathrm{CH_3CN})_2]^{2+}$. Threading takes place under relatively harsh conditions (ethylene glycol, 140 °C) and the catenane precursor $[\mathrm{Ru}(\mathbf{R50})(\mathbf{14})]^{2+}$ was obtained in a surprisingly good yield of 56%. This step represents another key reaction whose success was not guaranteed, especially considering that it requires such harsh conditions.

The final compound, catenane $[\mathrm{Ru}(\mathbf{15})]^{2+}$, was prepared from $[\mathrm{Ru}(\mathbf{R50})(\mathbf{14})]^{2+}$ in 68% yield by ring-closing metathesis (RCM). This preparative yield is in the same range as that obtained for preparing other transition metal containing catenanes and knots using a similar RCM-based approach.[2,16,17,29] $[\mathrm{Ru}(\mathbf{15})](\mathrm{PF_6})_2$ is a red-orange solid, which has been fully characterized by various spectroscopic techniques. This catenane is the first example of an interlocking ring system built on a tris(bidentate) chelate transition metal complex used as template.

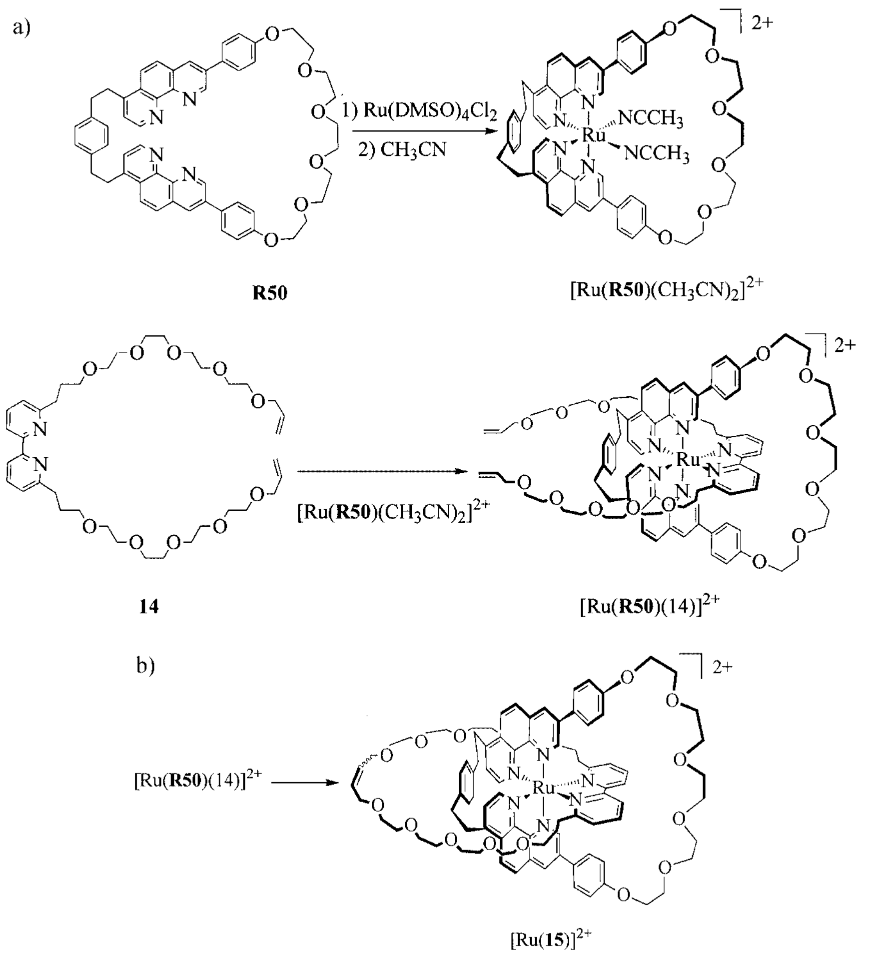


Figure 17. (a) Wrapping of the macrocycle **R50** around a ruthenium(II) atom and threading of the bipyridine derivative **14** through the coordinated macrocycle [Ru(**R50**)$(CH_3CN)_2]^{2+}$; (b) ring-closing metathesis (RCM) sequence affording the ([2]catenane)ruthenium(II) cation [Ru(**15**)]$^{2+}$

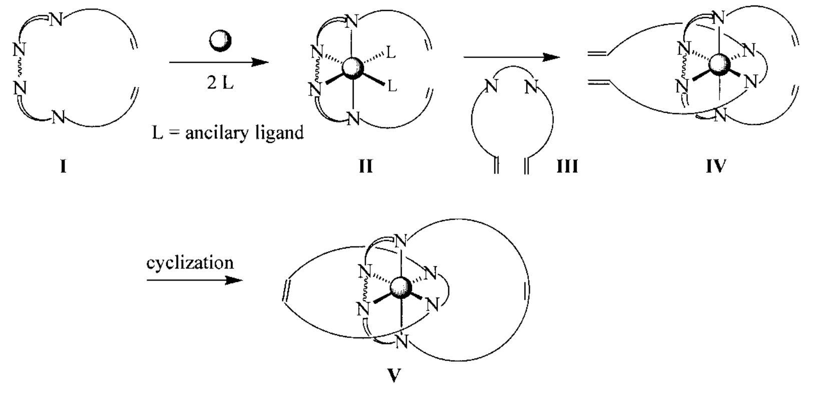


Figure 18. RCM-based synthesis of a catenane with a tris(bidentate) chelate transition metal complex as scaffold; the bidentate chelates are represented as arcs of a circle (bold); the tetradentate ligand **I** is able to wrap around the metal atom (black disc) so as to dispose the two bidentate chelates *cis* to one another and to allow relative proximity between the two terminal olefins of the ligand; the precursor complex **II** can react with a third bidentate chelate **III**, so as to form the catenane precursor **IV**; this complex contains two entwined fragments (**I** and **III**), arranged roughly orthogonal to one another; the double RCM reaction between the appropriate end functions is expected to afford catenane **V**

The success of these sequential-assembling/ring-closure reactions prompted us to adopt a more direct way of synthesizing an analogous octahedral ruthenium catenane.[30]

Figures 18 and 19 illustrate the concept of this more straightforward process and the synthetic route, respectively. A bis(phenanthroline) fragment, **16**, and the 6,6′-

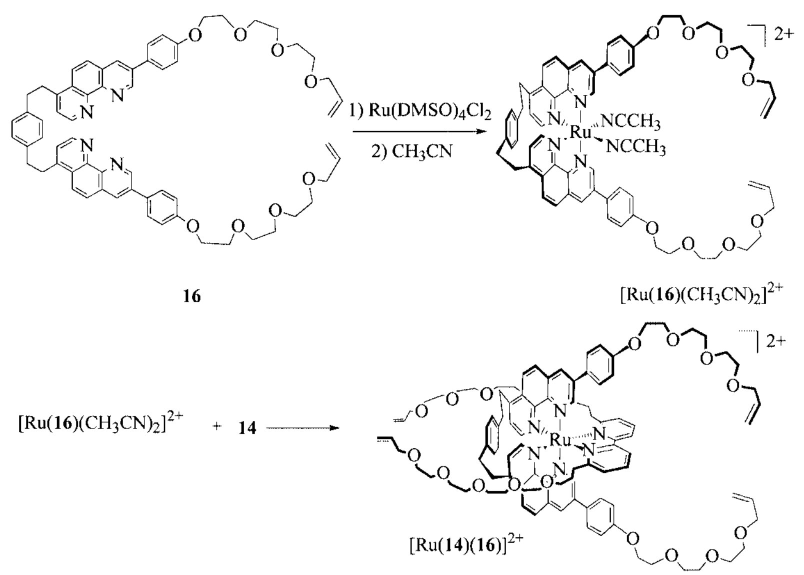


Figure 19. Synthesis of the complex [Ru(**16**)(CH$_3$CN)$_2$]$^{2+}$ and of the catenane precursor [Ru(**14**)(**16**)]$^{2+}$

dmbp derivative **14** are coordinated in two sequential steps to Ru^{II} acting as a three-dimensional templating agent. Each end position of these two ligands bears an alkene group. A double RCM reaction leads to the expected (catenane)Ru compound.

The acyclic ligand **16** was obtained by reaction of the diphenolic precursor **13** with {2-[2-(2-iodoethoxy)ethoxy]-ethoxy}allyl ether in basic medium (72% yield). The catenane precursor [Ru(**14**)(**16**)]$^{2+}$ was prepared by sequentially coordinating ligand **16** and the substituted 2,2′-bipyridine **14** to the metal atom (Figure 19). In the first step, coordination of **16** to Ru^{II} was performed by treating [Ru(DMSO)$_4$]Cl$_2$ with **16** under high-dilution conditions. When the reaction was complete, the crude material was refluxed in acetonitrile/water (80:20) for 4 h, in order to substitute the auxiliary chloride ligands with acetonitrile. The expected complex [Ru(**16**)(CH$_3$CN)$_2$]$^{2+}$ was isolated in a surprising 91% yield. The protons of the phenylene bridge are homotopic in the free ligand **16**. A splitting of the corresponding signal in the ^{1}H NMR spectrum of [Ru(**16**)(CH$_3$CN)$_2$]$^{2+}$ is observed, indicating the diastereotopic nature of these protons. In a second step, the 2,2′-bipyridine derivative **14** was coordinated to [Ru(**16**)(CH$_3$CN)$_2$]$^{2+}$ by substitution of the acetonitrile auxiliary ligands. The reaction requires relatively harsh conditions (ethylene glycol, 140 °C, 2 h). The final step of the catenane synthesis is described in Figure 20.

The complex [Ru(**14**)(**16**)](PF$_6$)$_2$ was subjected to two intramolecular ring closing metathesis reactions using the Grubbs carbene [(PCy)$_3$(Cl)$_2$Ru=CHPh] as catalyst. A dichloromethane solution of complex [Ru(**14**)(**16**)](PF$_6$)$_2$ and "catalyst" (100 mol%) was stirred under argon for one week. The catenane [Ru(**17**)](PF$_6$)$_2$ was obtained in 46% yield. Two interlocked rings around the ruthenium centre were formed, a 58-membered one and a 42-membered one. The spectroscopic results, the assignment of the ^{1}H NMR signals, and the FAB MS *m*/*z* values are in full accordance with the expected catenane structure of [Ru(**17**)](PF$_6$)$_2$.

The two strategies discussed here and the success of their application to synthesize octahedral (catenane)ruthenium compounds are based on the design and utilization of bis(phenanthroline) moieties, capable of coordinating the metal atom in a *cis* geometry, and consequently to form complexes displaying a C_2 symmetry. Despite the differences in the choice of the templating metal and the chemical reactions involved, these strategies are reminiscent of those de-

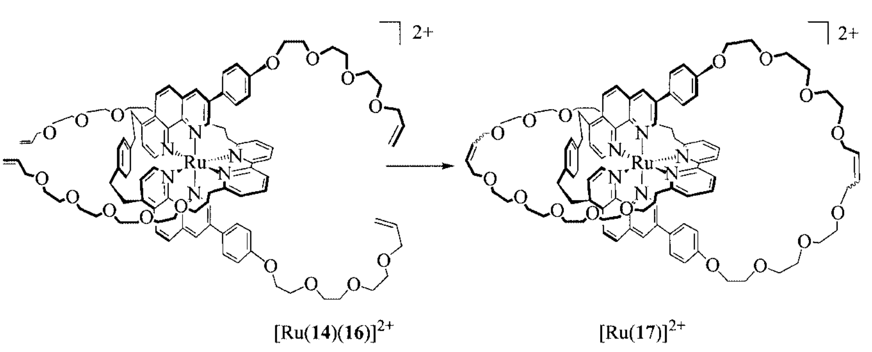


Figure 20. Double RCM leading to the (catenane)ruthenium cation [Ru(**17**)]$^{2+}$

veloped about twenty years ago to synthesize the two first metallocatenanes.[12]

IV. Towards Light-Driven Molecular Machines

Multicomponent systems can be set in motion by sending a signal, causing one of the components to change its position in space while the other positions are considered motionless. Most of the artificial systems proposed up to now rely on an electrochemical signal. In this case, an electroactive component is reduced or oxidized to lead to a new and unstable species whose relaxation to a thermodynamically more stable situation implies a motion.[31−33] A few molecular machines have also been described which operate under the action of a chemical signal (pH change,[34] metal exchange,[35] or a series of organic reactions[36]). Light irradiation has also been reported to produce molecular motions, either alone or in conjunction with a redox chemical reaction.[37,38] In this respect, the rotary motor proposed by Ferringa and Harada is a remarkable example since the rotation motion is realized by a sequence of photochemical or thermal steps, without consuming any chemical reagent.[39,40] Transition metal based light-driven machines are particularly promising. Ru^{II} complexes of the [Ru(diimine)$_3$]$^{2+}$ family (diimine = bidentate ligand) are interesting building blocks for the construction of light-driven machines since the use of a sterically hindered chelate (e.g. a 6,6′-disubstituted bipy ligand) associated to an [Ru(phen)$_2$]$^{2+}$ core leads to the specific and quantitative photolabilization of the chelate.[41] Excitation into the absorption bands of (polyimine)Ru^{II} complexes corresponding to the singlet metal-to-ligand charge-transfer (^{1}MLCT) transition, is followed by intersystem crossing to the lowest-lying triplet level (^{3}MLCT), which, by thermal redistribution, may populate upper-lying dissociative d−d metal-centred (MC) states.[42] The MC/MLCT energy gap is small and the thermal deactivation of the ^{3}MLCT state to the ^{3}MC is particularly effective when the ligand field is weakened by distortions due to the sterically hindering ligands (Figure 21).

We have recently taken advantage of this property to design and elaborate new ruthenium(II) complexes for which chelate exchange (expulsion or recoordination) can be performed either under light irradiation or thermally. For instance, an Ru(phen)$_2$ fragment hosted in a macrocyclic receptor can be photochemically expelled[43,44] with recoordination being induced by a thermal process (Figure 22).

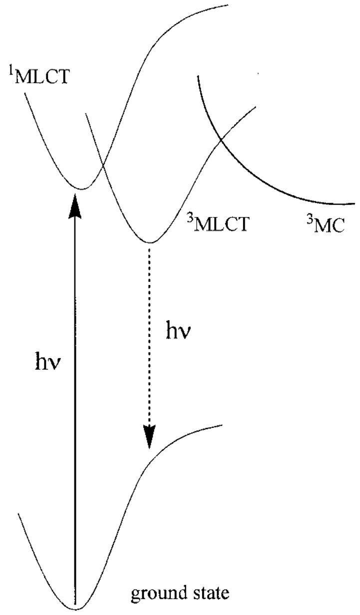


Figure 21. Main energy levels in the [Ru(bipy)$_3$]$^{2+}$ family

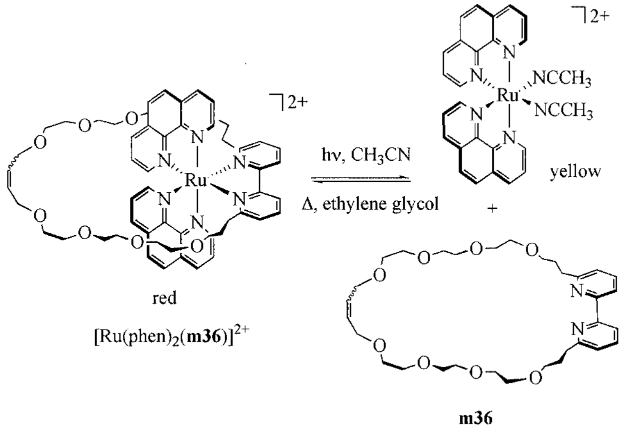


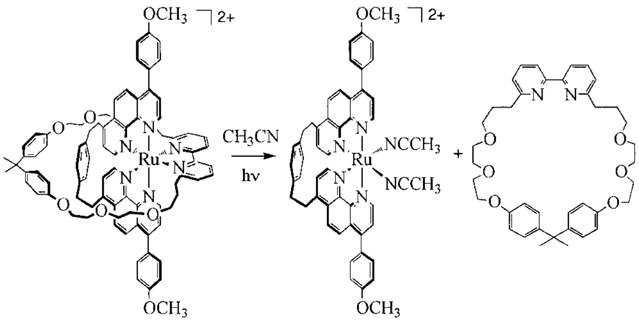
Figure 22. Principle of the photochemically driven and thermal backward reaction for [Ru(phen)$_2$(**m36**)]$^{2+}$

Under light irradiation ($\lambda > 300$ nm), [Ru(phen)$_2$(**m36**)]$^{2+}$ undergoes an efficient and quantitative photolabilization of the macrocycle **m36**. This process has been demonstrated by recording the electronic spectra during the course of the reaction as well as using ^{1}H NMR spectroscopy with direct light irradiation of the NMR tube. The characteristic spectrum of [Ru(phen)$_2$(**m36**)]$^{2+}$ is gradually replaced by the sum of [Ru(phen)$_2$(CD$_3$CN)$_2$]$^{2+}$ and free macrocyclic **m36** spectra. The thermal back reaction was also proven to be quantitative. An equimolecular mixture of [Ru(phen)$_2$(CH$_3$CN)$_2$]$^{2+}$ and **m36** leads back to the starting complex [Ru(phen)$_2$(**m36**)]$^{2+}$ in quantitative yield.

In the same manner,[25] the complex [Ru(**L$_1$**)(**m35**)]$^{2+}$, which contains a real axle and is thus closer to molecular machines of the rotaxane and catenane family, undergoes a selective and quantitative dethreading process (Figure 23).

V. Conclusion

The use of an octahedral metal centre such as ruthenium(II) as template turned out to be particularly convenient for preparing rotaxanes and catenanes, as discussed in the present review article. By applying the RCM strategy proposed by Grubbs in the course of the last decade, catenanes were prepared in good yields. This synthetic work



$[Ru(L_1)(m35)]^{2+}$ $[Ru(L_1)(CH_3CN)_2]^{2+}$ **m35**

Figure 23. Photochemical expulsion of the macrocycle **m35** and its substitution by CH_3CN in a precursor of a real rotaxane

combines the archetypical second-row transition metal complex $Ru(diimine)_3^{2+}$ and chemical topology (catenanes and related species). Naturally, the new compounds obtained should display interesting photochemical properties originating from the ruthenium(II)-containing fragment that they incorporate, as well as novel dynamic properties typical of interlocking ring systems. Preliminary experiments show that photochemical substitution reactions can take place, followed by backward thermal reaction.

The various rotaxanes and catenanes build around a ruthenium(II) octahedral centre that have been recently obtained in our group are now under study. They will lead to new light-driven molecular machines based on dissociative MC excited states.

Acknowledgments

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