

A [2]Catenane Constructed around a Ru(Diimine)₃²⁺ Complex Used as a Template

Pierre Mobian, Jean-Marc Kern,* and Jean-Pierre Sauvage*

Laboratoire de Chimie Organo-Minérale, UMR 7513 du CNRS, Université Louis Pasteur, Faculté de Chimie, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France

Received July 8, 2002; E-mail: mobian@chimie.u-strasbg.fr, jmk@chimie.u-strasbg.fr, sauvage@chimie.u-strasbg.fr

Octahedral transition metal centers have only been scarcely used as templates for synthesizing topologically nontrivial molecules such as catenanes and knots. An early example is dealing with the use of a bis-terpy complex (terpy = 2,2',6',2''-terpyridine).¹ A spectacular synthetic achievement was recently reported that was based on two terdentate ligands entwined around a first-row transition metal.² Knots have been made using two octahedral iron centers, each metal being coordinated to two terpy derivatives.³ 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.⁴

Until now, tris-bidentate chelate complexes have not been utilized for making [2]catenanes. This is understandable in view of the success of the tetrahedral copper(I) center for promoting interlocking or knotting of various molecular stringlike fragments.⁵ It may also be explained by the difficulty of entwining *two* threads using *three* chelates gathered around a transition metal center. We now report such an example based on a Ru(diimine)₃²⁺ derivative.

The design of the system and the synthetic strategy are depicted in Figure 1. The main point of the design is the observation that it should be possible to incorporate two bidentate chelates of the octahedron in a ring and subsequently to thread a fragment containing the third chelate through the ring. This second process would of course be driven by coordination to the central metal.

Tetradentate ligands consisting of two separate bidentate ligands connected by an appropriate spacer and leading to C₂-symmetric complexes have already been reported. A particular interesting example is that of von Zelewsky's chiragens,⁶ consisting of two chiral bipy derivatives (bipy = 2,2'-bipyridine). Our group has also proposed a bis-phen molecule leading to a Ru(phen)₃²⁺-derivative with a clearly identified axis bearing chemical functions.^{7,8} In the present work, the substitution positions on the phen nuclei attached to the functions to be used for further derivatization are different than those corresponding to the previous axis-containing complex, as shown in Figure 2. They seem to be appropriate to the formation of cyclic complexes.

The synthetic procedure starts with the preparation of a large ring incorporating two phen units. The choice of the ring was dictated by CPK models and by synthesis considerations.

The precursors and the open-chain and cyclic compounds incorporating two phen fragments are represented in Figure 3.

1 was prepared in four steps from 3-bromo-8-amino-1,10-phenanthroline (see Supporting Information). It is a 50-membered ring which, on CPK models, looks adapted to the formation of octahedral bis-phen complexes, the two phen fragments being disposed cis to one another in the metal coordination sphere. Interestingly, the substitution positions of the *p*-alkoxyphenyl groups (8 and 8' in **1**) are determining. By contrast, if *p*-anisyl groups are introduced para to the N-atoms of the phen nuclei (positions 7 and 7'), wrapping the corresponding ligand around an octahedron leads

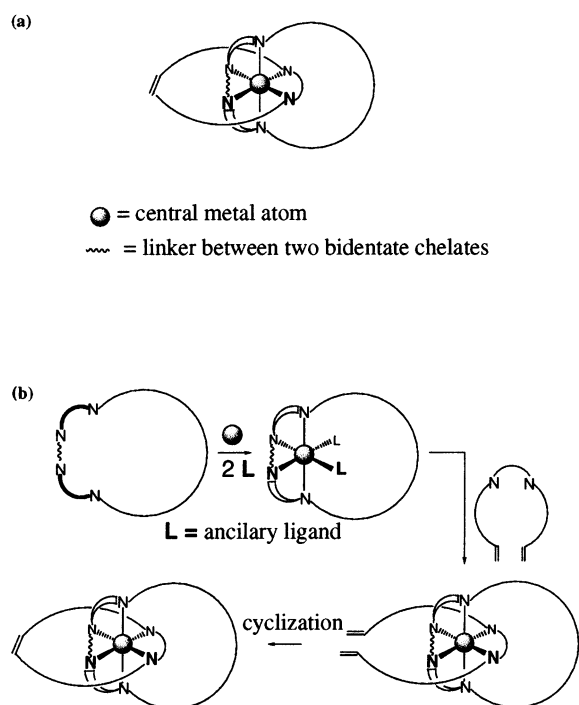


Figure 1. (a) Schematic representation of a transition metal-complexed [2]catenane containing two different rings. One of the macrocycles incorporates a bidentate chelate, whereas the other contains two bidentate-coordinating fragments with a cis arrangement. (b) Synthetic strategy.

to a system with a clearly identified axis.^{7,8} The key step of the present work is the coordination reaction, supposed to lead to the cyclic complex (Figure 2b). Several first-row transition metals were tested (Zn²⁺ and Fe²⁺ in particular), leading to limited success. However, ruthenium(II) afforded the desired complex.

Complex **2**²⁺ was formed by reacting **1** and Ru(DMSO)₄Cl₂⁹ in refluxing 1,2-dichloroethane under high dilution conditions. The bis-chloro intermediate complex was not isolated. The crude mixture from the reaction between **1** and Ru(DMSO)₄Cl₂ was heated under reflux in CH₃CN–H₂O (80:20 v/v) to afford [2²⁺]+2PF₆⁻ as an orange solid in 21% yield after anion exchange. It is noteworthy that **2**²⁺ is a rare example of a bis-phen or, more generally, a bis-bidentate octahedral complex with a cis-arrangement, inscribed in a ring.

The next step was carried using **3**, a 2,2'-bipyridine derivative analogous to a previously described example,¹⁰ and the macrocyclic complex **2**²⁺. Threading does take place under relatively harsh conditions (ethylene glycol: 140 °C) and the catenane precursor **4**²⁺ was obtained with a surprisingly good yield of 56%. This step, which is identical to passing a long thread (44 atoms) through the eye of a needle, represents also a key reaction whose success was

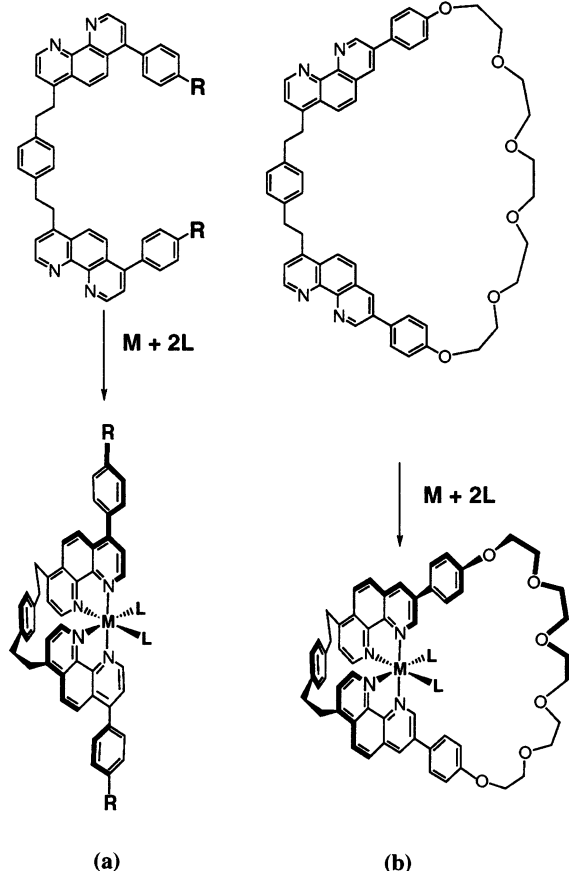


Figure 2. Formation of an axial (a) or a macrocyclic (b) complex. In both cases, connection of two positions para to the N atoms of the phen nuclei by the $-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-$ bridge leads to a cis arrangement.^{7,8} Introduction of aromatic groups ($-\text{C}_6\text{H}_4-\text{R}$) on the other para positions leads to the axial complex (a), whereas the macrocycle complex (b) can be obtained by utilizing the meta positions (C8) to attach the $-\text{C}_6\text{H}_4-\text{R}$ aromatic groups.

not guaranteed, especially if one considers that it requires brutal conditions.

The final compound, catenane 5^{2+} , was prepared from 4^{2+} in 68% yield by ring-closing metathesis (RCM). This preparative yield is in the same range as that obtained for making other transition-metal containing catenanes and knots using a similar RCM-based approach.^{2,3,11} $[5^{2+}]\cdot 2\text{PF}_6^-$ is a red-orange solid which has been fully characterized by various spectroscopic techniques (see Supporting Information). The ES-MS and ^1H NMR spectra afford clear evidence for the structure of 5^{2+} .

This catenane is with no doubt the first example of an interlocking ring system built on a tris-bidentate chelate transition-metal complex used as template. Its photochemical properties, in relation to light-driven molecular machines,¹² are presently investigated. Preliminary studies show that the bipy-incorporating ring is cleanly decoordinates under the action of light, in the presence of Et_4NCl , leading to a catenane for which the two rings are only mechanically linked.

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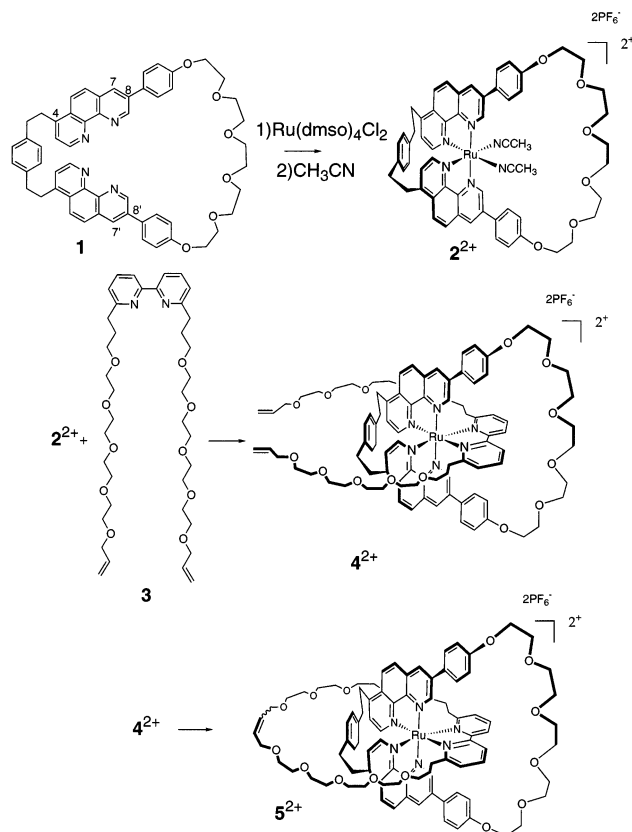


Figure 3. Sequence of reactions affording the ruthenium (II)-complexed [2]catenane 5^{2+} .

Supporting Information Available: Experimental details and additional Figure (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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