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# Synthesis of a [2]Catenane around a Ru(diimine)$_3^{2+}$ Scaffold by Ring-Closing Metathesis of Olefins

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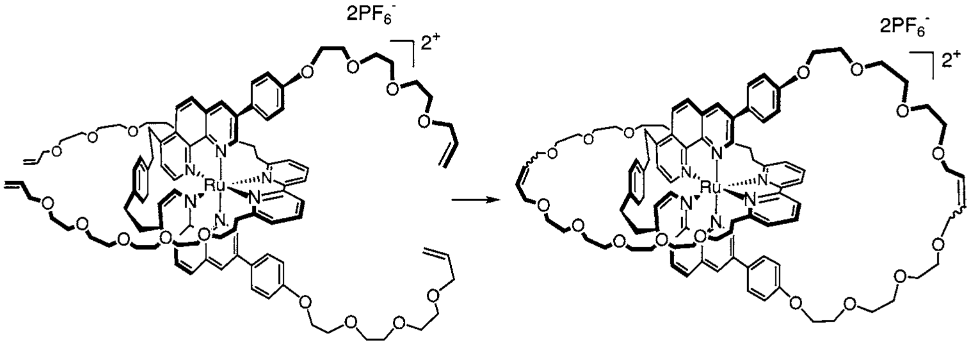
## ABSTRACT



**The synthesis of a ruthenium[2]catenane is described. One ring includes two 1,10-phenanthroline moieties, the other a bipyridinic unit. The interlocking ring system was formed by using a double ring closing metathesis reaction. Under irradiation, a rapid and selective decoordination of the bipyridinic fragment was observed, leading to a new catenane in which the metal is only coordinated to the bis-phenanthroline moiety.**

Among the numerous catenanes and rotaxanes elaborated in the course of the last two decades,[1−6] those synthesized with use of transition metals as templates represent a special family, with particularly interesting properties originating from the electro- and photochemical reactivity of the central metal complex.[7]

Copper(I) has been used extensively as a gathering and templating center in the past for preparing various catenanes. Very recently, our group has also proposed using a Ru(diimine)$_3^{2+}$ complex as a scaffold to construct rotaxanes and catenanes[8,9] with, in particular, the aim of making light-driven molecular machines.

Since the ring-closing metathesis (RCM) reaction of olefins turned out to be extremely efficient for preparing copper(I)-based catenanes and knots,[10] we applied the same methodology to Ru(diimine)$_3^{2+}$-based systems. The

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[1] For the early work on catenanes and related species carried out in Freiburg (Germany), see: Schill, G. *Catenanes, Rotaxanes and Knots*; Academic Press: New York, 1971. Some particularly representative more recent contributions are listed in refs 2−6.

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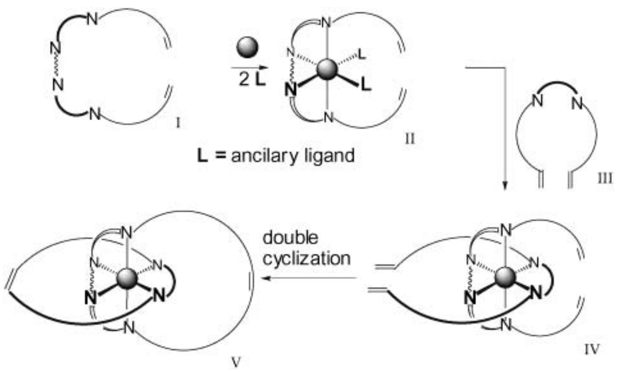

**Figure 1.** RCM-based synthesis of a catenane with a tris-bidentate chelate transition metal complex as scaffold. The bidentate chelates are represented as arcs of a circle (bold). The tetradentate ligand **I** is able to wrap around the metal (black disk) so as to dispose of the two bidentate chelates cis to one another and to allow relative proximity between the two terminal olefins that it bears. 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**), roughly arranged orthogonal to one another. The double RCM reaction between the appropriate end functions is expected to afford catenane **V**.

principle of the synthesis is depicted in Figure 1.

Ru(II) polyimine complexes are kinetically inert, which allows the use of two different fragments bearing two terminal olefins without the risk of ligand scrambling. This approach would of course not be possible with a labile metal center such as copper(I). In the present case, one of the components of the precursor complex is built on a tetradentate ligand containing two bidentate chelates derived from 1,10-phenanthroline (phen). The other component incorporates the third bidentate unit, namely a derivative of 2,2′-bipyridine (bipy).

These two organic fragments are entwined around the central metal center.

The various organic precursors are represented in Figure 2.

The allyl ether **4** was prepared from triethyleneglycol in 3 steps, as described in Figure 2. The acyclic ligand **6** was obtained by reaction of the diphenolic precursor **5**[9] with (2-(2-iodoethoxy)ethoxy)ethyl allyl ether **4** in basic medium (72% yield).

Ligand **7**[11] is a derivative of the previously reported 6,6′-dimethyl-2,2′-bipyridine (6-6′-dmbp). In **7**, two allyl functionalities are linked to the methyl group of a 6,6′-dimethyl-2,2′-bipyridine via a long and flexible spacer. The catenane precursor [Ru.**6**.**7**]$^{2+}$ was prepared by coordinating ligands **6** and **7** to the metal in two steps (Figure 3).

In the first step, coordination of **6** to Ru(II) was performed by reacting Ru(dmso)$_4$Cl$_2$ with **6** in high dilution conditions (80 °C, 1,2-dichloroethane). After evaporation of the solvent, the residue was dissolved and refluxed for 4 h in a mixture of acetonitrile and water (80/20), to substitute the auxiliary chloride ligands by acetonitrile. The expected complex [Ru.**6**.(CH$_3$CN)$_2$]$^{2+}$ was isolated in a surprising 91% yield. Protons H$_a$ of the phenylene bridge (Figure 2) in free ligand **6** are homotopic. A splitting of the corresponding signal in the $^1$H NMR spectrum of [Ru.**6**.(CH$_3$CN)$_2$]$^{2+}$ is observed, indicating in that case the diastereotopic nature of these protons. The ES-MS spectrum of [Ru.**6**.(CH$_3$CN)$_2$](PF$_6$)$_2$ is in accordance with its structure: *m*/*z* 1347.5 ([Ru.**6**.(CH$_3$CN)$_2$](PF$_6$)$^+$, calcd 1347.2), 601.3 ([Ru.**6**.(CH$_3$CN)$_2$]$^{2+}$, calcd 601.2), and 560.3 ([Ru.**6**]$^{2+}$, calcd 560.1).

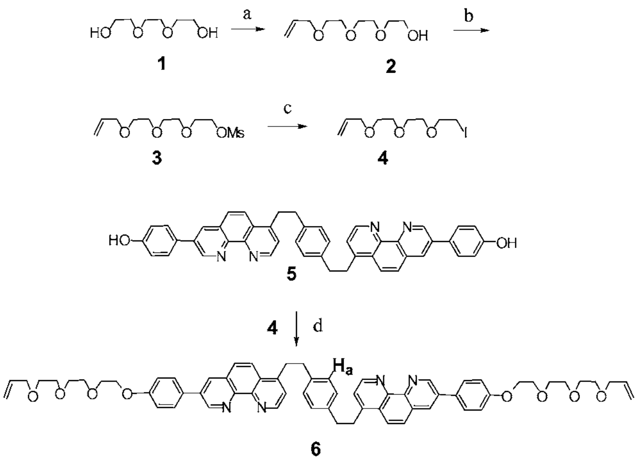

**Figure 2.** Synthetic route leading to the ligand **6**: (a) allylbromide, KOH, 60 °C; (b) MsCl, Et$_3$N, CH$_2$Cl$_2$, −7 °C; (c) NaI, acetone reflux; (d) Cs$_2$CO$_3$, DMF, 60 °C.

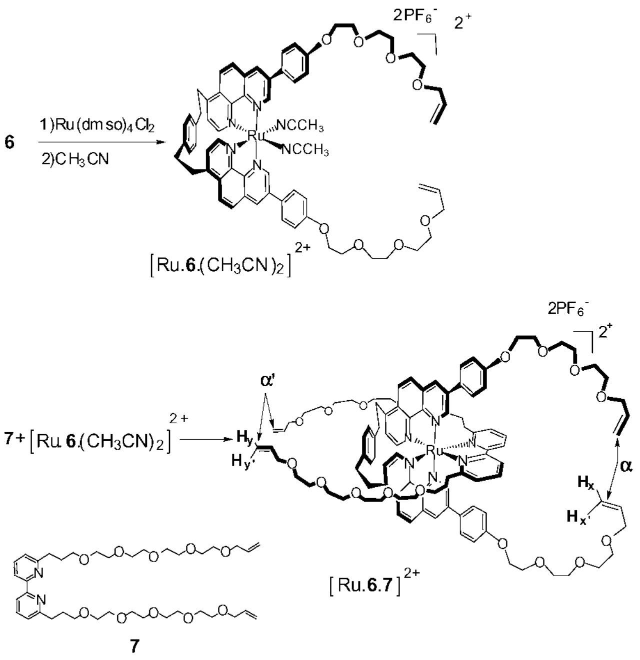

**Figure 3.** Synthesis of the complex [Ru.**6**.(CH$_3$CN)$_2$]$^{2+}$ and of the catenane precursor [Ru.**6**.**7**]$^{2+}$.

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In the second step, the 2,2′-bipyridine derivative **7** was coordinated to [Ru.**6**.(CH$_3$CN)$_2$]$^{2+}$ by substitution of the acetonitrile auxiliary ligands. The reactions required relatively harsh conditions (ethylene glycol, 140 °C, 2 h). The catenane precursor [Ru.**6**.**7**]$^{2+}$ was isolated in 53% yield and fully characterized by $^1$H NMR and ES-MS.

The final step of the catenane synthesis is described in Figure 4.

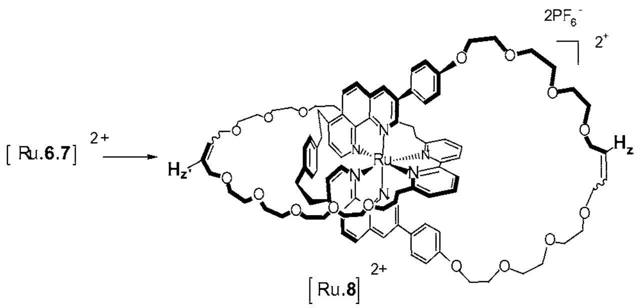

**Figure 4.** Double RCM leading to the catenane [Ru.**8**]$^{2+}$.

The complex [Ru.**6**.**7**]$^{2+}$ was subjected in a one- pot batch to two intramolecular ring-closing metathesis reactions with Grubbs carbene [(PCy$_3$)$_2$(Cl)$_2$Ru═CHPh].[10] A dichloromethane solution of complex [Ru.**6**.**7**]$^{2+}$ and [(PCy$_3$)$_2$(Cl)$_2$Ru═CHPh] (100% mol) was stirred under argon for one week. From TLC data (one round-shaped spot on silica gel; acetonitrile/water/aqueous saturated KNO$_3$ (100:20:2) as eluent) and $^1$H NMR (very sharp signals), it was clear that only one compound was obtained after workup and purification. This compound, which was isolated in 46% yield, turned out to be [Ru.**8**]$^{2+}$. Two interlocking rings were formed around the ruthenium center: a 58-membered ring resulting from the closing of **6**, and a 42-membered ring resulting from **7**. By comparison with that of [Ru.**6**.**7**]$^{2+}$, the $^1$H NMR spectrum of [Ru.**8**]$^{2+}$ showed the disappearance of the signals corresponding to the vinylic protons $H_x$, $H_{x'}$ and $H_y$, $H_{y'}$ (Figure 3) and the appearance of new signals at 5.70 ppm which integrate for four protons and which were assigned to protons $H_z$ and $H_{z'}$ (Figure 4). The FAB mass spectrum displays the expected *m*/*z* signals: *m*/*z* 1913.8 ([Ru.**8**](PF$_6$)$^+$, calcd 1913.7) and 1767.8 ([[Ru.**8**]$^{2+}$ + é], calcd 1767.8). These spectroscopic results are in full accordance with the expected catenane structure of [Ru.**8**]$^{2+}$. Nevertheless, the formation of the isomer [Ru.**9**]$^{2+}$ (Figure 5) cannot be excluded a priori. This hypothetical compound would result from the connection of position $\alpha$ of **6** with position $\alpha'$ of **7** (Figure 3) leading to a ruthenium complex for which the ligand is a large macrocycle including a bipyridine unit and a bis-phenanthroline unit[12] as coordinating moieties. The spectroscopic data of this isomer are expected to be quite similar to those of [Ru.**8**]$^{2+}$.

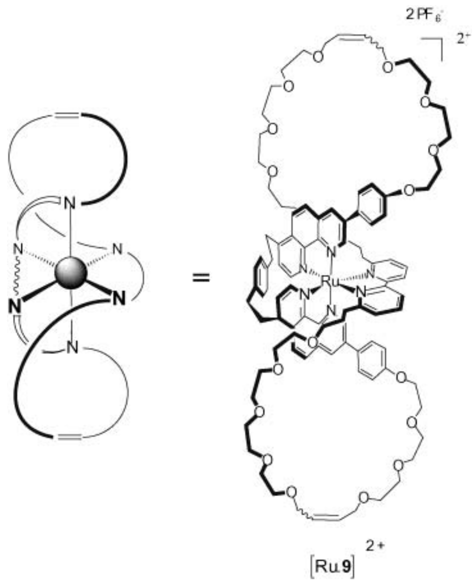

**Figure 5.** Possible isomer [Ru.**9**]$^{2+}$ that could be formed after the double RCM reaction.

Clear and unambiguous evidence for the expected catenane structure of [Ru.**8**]$^{2+}$ was obtained by studying its photochemical behavior.

In a previous work, it was demonstrated that irradiation of Ru(phen)$_2$(6,6′-dmbp)$^{2+}$ (phen = 1,10-phenanthroline) leads to selective photolabilization of the bipyridine-containing fragment.[11] Thus irradiation of [Ru.**8**]$^{2+}$ should lead to the decoordination of the bipyridinic macrocycle, i.e., to a real catenane, whose two interlocking rings are not connected anymore but are maintained together by a mechanical link. By contrast, irradiation of the loop [Ru.**9**]$^{2+}$ should lead to a large macrocycle in which the metal is only coordinated to the bis-phen site. Two sets of photochemical experiments described in Figure 6 have been run: (i) one in dichloromethane and in the presence of chloride ions, and (ii) the other in pure acetonitrile. (i) In the first case, a degassed solution of [Ru.**8**]$^{2+}$ in dichloromethane containing Et$_4$NCl (20% mol excess) was irradiated with visible light, and the visible absorption spectra were recorded at regular time intervals. A rapid transformation of the absorption spectrum occurred, and an isobestic point appeared at 480 nm. No further evolution of the spectrum was observed after 15 min. The color of the solution turned from yellow ($\lambda_{\max}$ 460 nm) to violet ($\lambda_{\max}$ 558 nm), which is the expected color for a dichloro bis-phen ruthenium complex.(ii) When the photochemical reaction was performed in acetonitrile, and without chloride anions, a rapid change of the visible spectrum also occurred, but this transformation led to a different compound than for the first experiment. In this case, substitution of the bipyridine moiety by acetonitrile was observed, as confirmed by mass spectroscopy.

The species resulting from these two different experiments were isolated and subjected to mass spectrometry analysis (Table 1).

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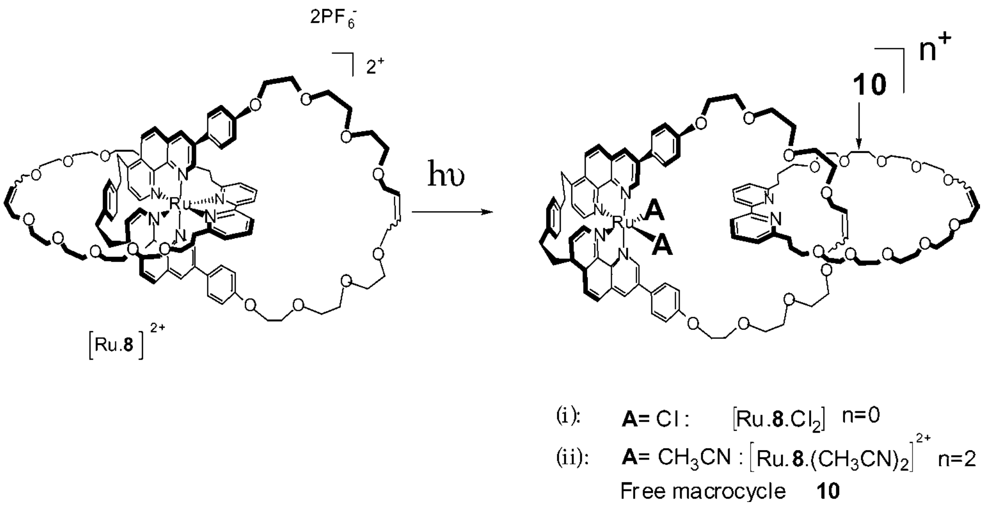

**Figure 6.** The two different irradiation experiments leading to $[Ru.\mathbf{8}.Cl_2]^{2+}$ and $[Ru.\mathbf{8}.(CH_3CN)_2]^{2+}$, respectively.

The observed fragmentations are in full accordance with the catenane nature assigned to $[Ru.\mathbf{8}]^{2+}$ and confirm that the double RCM reaction led to an interlocking ring system.

In conclusion, the synthesis of a [2]catenane constructed around a $Ru(diimine)_3^{2+}$ complex is described in this letter. A double RCM reaction was used in the final step. The original photochemical properties of the ruthenium(II) complex obtained were used to assess definitively the topological feature of this [2]catenane. Moreover, the conclusion of the preliminary photochemical studies presented here is very promising in the perspective of developing light-driven molecular machines based on ruthenium(II) catenanes or rotaxanes.[13,14]

**Table 1.** MS Analysis of the Products Resulting from the Irradiation of $[Ru.\mathbf{8}]^{2+}$ by Visible Light in Different Media[a]

| irradiation conditions[b] | *m/z* (formulas of the ions) |
|---|---|
| i | 1863.5 ($[Ru{\cdot}\mathbf{8}{\cdot}Cl_2] + Na^+$) |
| | 699 ($\mathbf{10} + Na^+$) |
| ii | 699 ($\mathbf{10} + Na^+$) |
| | 677 ($\mathbf{10} + H^+$) |
| | 715 ($\mathbf{10} + K^+$) |
| | 925.5 ($[Ru{\cdot}\mathbf{8}{\cdot}(CH_3CN)_2]^{2+}$) |
| | 884.5($[Ru{\cdot}\mathbf{8}{\cdot}(CH_3CN)_2]^{2+} - 2CH_3CN$) |

[a] Photoirradiation was performed in Pyrex with use of a Haminex slide projector (250 W halogen lamp). [b] i: $[Ru.\mathbf{8}]^{2+}$ in solution in dichloromethane in the presence of 20 equiv of $Et_4Cl$ analysis by FAB.MS. ii: $[Ru.\mathbf{8}]^{2+}$ in solution in acetonitrile, analysis by ES-MS.

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