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A [2]Catenane Constructed around a Rhodium(III) Center Used as a Template

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Rhodium(III) has been used as a templating metal center for building a [2]catenane. In the first stage, a $Rh(phen)_2$ motif has been incorporated into a large ring. Subsequently, a 2,2′-bipyridine derivative has been threaded through the ring, this process being driven by coordination of the chelate to the Rh(III) center. The formation of the second ring has been performed using the ring-closing metathesis approach. Contrary to the other catenanes synthesized around transition metals, the second ring is formed *at the rear* of the coordination unit which it contains, by cyclizing two flexible end-functionalized fragments attached at the 4 and 4′ positions of the 2,2′-bipyridine chelate.

Introduction

An impressive variety of catenanes and rotaxanes have been elaborated in the course of the last 20 years,[1,2] following the pioneer work of Schill and co-workers.[3] A particularly promising extension is that of molecular systems which can be set in motion in a controlled way (molecular machines and motors).[4−8] On the basis of the transition-metal-templated synthesis of catenanes, many examples of interlocking ring systems could be made,[9−11] either still coordinated to the gathering metal used in their preparation or as free ligands after removal of the metal. For most of the systems made, the metal center used as a template was copper(I) and the ligands affording the entanglement after coordination to the center were derivatives of 2,9-diphenyl-1,10-phenanthroline.[12] Some time ago, we moved from tetrahedral coordination to octahedral systems containing a $Ru(terpy)_2^{2+}$ core[13] (terpy = 2,2′,6′,2″-terpyridine), but the difficulites encountered in trying to remove the metal template from its ligand set, after catenation, turned out to be a severe limitation. Leigh et al. recently reported spectacular results based on the template effect of first-row transition metals.[14] Octahedrally coordinated centers led to high-yield synthesis of a series of [2]catenanes in a few steps. Very recently, we proposed an approach based on $Ru(diimine)_3^{2+}$ complexes with one of the three bidentate chelates included in a ring and the two other ones being part of an axial component (to make rotaxanes)[15] or inscribed in a ring (for the synthesis of catenanes).[16] We now report that another second-row transition-metal center, rhodium(III), can also be used as a template. In addition, the strategy used with ruthenium(II) had to be modified so as to allow Rh(III) to be coordinated

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to three nonsterically hindering bidentate chelates, thus imposing that the cyclization reaction leading to the catenane be carried out in an unusual way. In this case, the terminal functions leading to the catenane are located *beyond the noncoordinating fragment of the other ring* and not beyond the metal, so as to avoid any destabilizing interaction due to steric repulsion between the various ligands.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker AVANCE 300 (300 MHz), Bruker AVANCE 400 (400 MHz), or Bruker AVANCE 500 (500 MHz) spectrometer, with the deuterated solvent as the lock and residual solvent as the internal reference. A VG BIOQ triple-quadrupole spectrometer was used for the electrospray mass spectrometry measurements (ES-MS), in the positive mode. FAB-MS spectra were obtained on a ZAB-HF (FAB) spectrometer. Absorption spectra were recorded with a Uvikon XS spectrometer.

Synthesis. Oxygen-sensitive reactions were conducted under a positive pressure of argon, by Schlenk techniques. All solvents and reagents were of the highest quality available and were used as received without further purification. Starting materials were from commercial sources. $RhCl_3 \cdot 3H_2O$ was purchased from Strem.

[Rh·1·Cl$_2$]PF$_6$. Macrocycle **1**[16] (37.8 mg, 4.31×10^{-5} mol) and $RhCl_3 \cdot 3H_2O$ (11.3 mg, 4.31×10^{-5} mol) were boiled in an ethanol−dichloroethane mixture (40 mL/40 mL) for 4 h. The solution turned from orange to yellow. After evaporation of the solvents, the residue was refluxed for 1 h in a mixture of 50 mL of acetonitrile and 20 mL of an aqueous saturated solution of KPF_6. Acetonitrile was then evaporated, and the resulting precipitate was filtered off and chromatographed on alumina (CH_2Cl_2 (95%)/MeOH (5%)). Pure [Rh·**1**·Cl$_2$]PF$_6$ (19 g) was recovered as a yellow solid (19 mg, yield 37%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.01 (d, 2H, ^4J = 1.5 Hz, H$_9$), 9,38 (d, 2H, ^4J = 1.5 Hz, H$_7$), 8.57 (d, 2H, ^3J = 9.2 Hz, H$_5$), 8.51 (d, 2H, ^3J = 9.2 Hz, H$_6$), 7.81 (d, 4H, ^3J = 8.8 Hz, H$_o$), 7.62 (d, 2H, ^3J = 5.6 Hz, H$_2$), 7.35 (d, 4H, ^3J = 9.2 Hz, H$_m$), 7.31 (d, 2H, ^3J = 5.6 Hz, H$_3$), 6.86 Hz (d, 2H, ^4J = 1.5 Hz, ^3J = 8 Hz, H$_{c'}$), 6.3 (d, 2H, ^4J = 1.5 Hz, ^3J = 8 Hz, H$_c$), 4.6 (complex, 2H, H$_\alpha$ or H$_{\alpha 1}$), 4.09 (complex, 2H, H$_\alpha$ or H$_{\alpha 1}$), 4 (complex, 2H, H$_{b'}$), 3.9−3 (complex, 14H, H$_{a,a',b}$, H$_{\beta,\gamma,\delta,\epsilon}$). FAB-MS: *m*/*z* found 1049.2 ([Rh·**1**·Cl$_2$]$^+$, calcd 1049.4).

[Rh·1·(4,4′-dmbp)](PF$_6$)$_3$. Macrocycle **1** (30 mg, 3.4×10^{-5} mol) and $RhCl_3 \cdot 3H_2O$ (10 mg, 3.8×10^{-5} mol) were boiled in a mixture of ethanol and dichloroethane (30 mL/30 mL) for 4 h. The solvents were evaporated, and the crude residue was boiled in acetonitrile (35 mL) with an excess of $AgBF_4$ (40 mg) for one night. The resulting solution was filtered on Celite and concentrated by partial evaporation of acetonitrile. 4,4′-Dimethylbipyridine (8 mg, 4.34×10^{-5} mol) and 20 mL of butanol were added, and the solution was heated at 120 °C for 4 h. The solvents were then evaporated, and the chloride ions were exchanged for PF_6^-. The crude was purified on silica (eluant acetonitrile/water/saturated aqueous KNO_3 (100:7:1)). A yellow solid (22 mg, yield 40%) was isolated. Yellow crystals were obtained by slow diffusion of diethyl ether into an acetonitrile solution. ^{1}H NMR (400 MHz, CD_3CN): δ = 9.13 (d, 2H, ^4J = 1.7 Hz, H$_7$), 8.72 (s, 2H, H$_{3b}$, H$_{3b'}$), 8.55 (d, 2H, ^3J = 9.2 Hz, H$_5$), 8.43 (d, 2H, ^3J = 9.2 Hz, H$_6$), 7.87 (d, 2H, ^3J = 5.9 Hz, H$_{6b}$, H$_{6b'}$), 7.56 (d, 2H, ^4J = 1.7 Hz, H$_9$), 7.50 (d, 2H, ^3J = 5.6 Hz, H$_2$), 7.44 (d, 2H, ^3J = 5.9 Hz, H$_{5b'}$, H$_{5b}$), 7.35 (2d, 6H, ^3J = 8.9 Hz, H$_m$, H$_3$), 7.12 (d, 4H, ^3J = 8.9 Hz, H$_o$), 6.85 (dd, 2H, ^4J = 1.7 Hz, ^3J = 8.1 Hz, H$_{c'}$), 6.44 (dd, 2H, ^4J = 1.7 Hz, ^3J = 8.1 Hz, H$_c$), 4.53 (m, 2H, H$_\alpha$ or H$_{\alpha'}$), 4.14 (m, 2H, H$_\alpha$ or H$_{\alpha'}$), 4.04 (m, 2H, H$_{a'}$), 3.8−3 (complex, 22H, m, H$_{a,b,b'}$, H$_{\alpha,\beta,\delta,\epsilon}$), 2.59 (s, 6H, CH_3). Assignment of the ^{1}H NMR spectrum was done using 2D ROESY. FAB-MS: *m*/*z* found 1453.3 ([Rh·**1**·(4,4′-dmbp)]-(PF$_6$)$_2^+$, calcd 1453.4), 1308.4 ([Rh·**1**·(4,4′-dmbp)](PF$_6$)$^{2+}$ + e, calcd 1308.5), 1163.4 ([Rh·**1**·(4,4′-dmbp)]$^{3+}$ + 2e, calcd 1163.5), 979.3 ([Rh·**1**]$^{3+}$ + 2e, calcd 979.3). Crystals were obtained by slow diffusion of diethyl ether to the solution of [Rh·**1**·(4,4′-dmbp)]-(PF$_6$)$_3$ in acetonitrile. The complex was further characterized by X-ray single-crystal analysis. For the X-ray experimental data see Table 1.

Table 1

empirical formula	$C_{158}H_{165}F_{36}N_{21}O_{13}P_6Rh_2$	color	yellow
fw	3641.81	D_{calcd} (g cm^{-3})	1.37
cryst syst	triclinic	μ (mm^{-1})	0.340
space group	*P*-1	temp (K)	173
a (Å)	11.2169(2)	wavelength (Å)	0.71073
b (Å)	17.3198(3)	no. of data meas.	20592
c (Å)	24.4733(4)	no. of data with $I > 3s(I)$	12593
α (deg)	76.478(5)	GOF	1.227
β (deg)	88.744(5)	largest peak in final	0.745
γ (deg)	73.413(5)	R[a]	0.070
V (Å^3)	4425.2(1)	R_w[b]	0.090
Z	1		

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$.

Ligand 3. A freshly prepared LDA solution (prepared by addition of 3.25 mL, 4.8 mmol, of a 1.5 mol L^{-1} ^{n}BuLi solution to 4.8 mmol of diisopropylamine in 10 mL of distilled THF) was added by cannula to a solution of 4,4′-dimethylbipyridine (0.375 g, 0.00203 mol) in 10 mL of THF (10 mL) kept at − 78 °C. The solution turned from white to orange. The mixture was stirred for 2 h at −78 °C. The temperature was raised to 20 °C for 2 min, and lowered to − 78 °C again, before addition of 1.465 g, 4.88 mmol, of 2-(2-iodoethoxy)ethoxy)ethyl allyl ether[17] dissolved in 10 mL of THF. After the dark green solution was stirred at room temperature overnight, 10 drops of ethanol was added, the THF evaporated, and the crude taken off with CH_2Cl_2, washed with water, and dried over $MgSO_4$. The product was purified by chromatography over an alumina column (ether). A yellow oil (350 mg) was recovered (yield 32%). ^{1}H NMR (300 MHz, CD_3Cl): δ = 8.49 (d, 2H, ^3J = 8.3 Hz, H$_{6b}$, H$_{6b'}$), 8.18 (d, 2H, ^4J = 0.9 Hz, H$_{3b}$, H$_{3b'}$), 7.09 (dd, 2H, ^3J = 8.3 Hz, ^4J = 0.9 Hz, H$_{5b}$, H$_{5b'}$), 5.80 (m, 2H, H$_l$), 5.10 (m, 4H, H$_m$ and H$_n$), 3.95 (m, 4H, H$_k$), 3.60−3.50 (complex, 16H, H$_{g,h,i,j}$), 3.42 (t, 4H, ^3J = 4.1 Hz, H$_f$), 2.72 (t, 4H, ^3J = 7.3 Hz, H$_d$), 1.90 (m, 4H, H$_e$). FAB-MS: *m*/*z* found 529.3 (**3** + H$^+$, calcd 529.3).

[Rh·1·3](PF$_6$)$_3$. A solution of macrocycle **1** (30 mg, 3.4×10^{-2} mmol) and $RhCl_3 \cdot 3H_2O$ (10 mg, 3.8×10^{-2} mmol) in ethanol−dichloroethane (30 mL/30 mL) was refluxed for 4 h. The solvents were evaporated. The crude material was suspended in a solution of **3** (27.2 mg) in ethylene glycol (10 mL), one drop of *N*-ethylmorpholine was added, and the mixture was kept at 140 °C overnight. A precipitate was formed, which was filtered off, copiously rinsed with water, and chromatographed on silica (eluant acetonitrile/water/saturated aqueous KNO_3 (100:10:1)). After ion exchange, a yellow solid was isolated (14%, 9 mg). ^{1}H NMR (300 MHz, CD_3CN): δ = 9.06 (br d, 2H, H$_7$), 8.69 (br d, 2H, H$_{3b}$ and H$_{3b'}$), 8.59 (d, 2H, ^3J = 9.1 Hz, H$_5$), 8.36 (d, 2H, ^3J = 9.1 Hz, H$_6$), 7.83 (d, 2H, ^3J = 6.1 Hz, H$_{6b'}$ and H$_{6b}$), 7.44 (complex, 6H, H$_2$, H$_{5b}$ and H$_{5b'}$, H$_9$), 7.28 (2d, 6H, ^3J = 5.7 Hz, ^3J = 8.8 Hz, H$_3$, H$_m$), 7.03 (d, 4H, ^3J = 8.8 Hz, H$_o$), 6.78 (d, 2H, ^3J = 7.1 Hz, H$_{c'}$), 6.37

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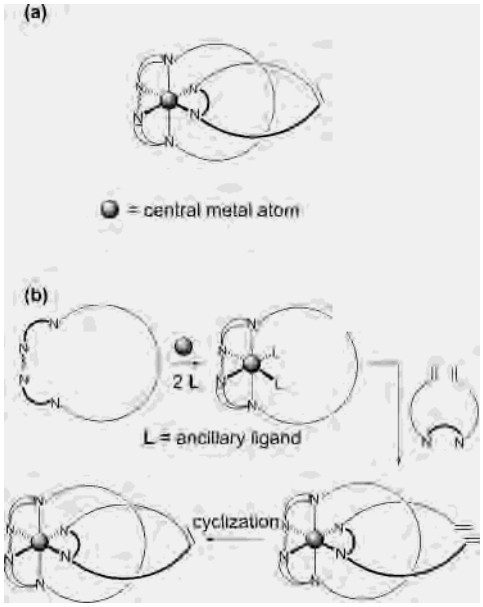


Figure 1. (a) Schematic representation of a transition-metal-complexed [2]catenane containing two different rings. One of the macrocyles incorporates a bidentate chelate, whereas the other contains two bidentate coordinating fragments with a cis arrangement. (b) Synthetic strategy.

(d, 2H, ^3J = 7.1 Hz, H_c), 5.75 (complex, 2H, H_l), 5.05 (complex, 4H, H_m and H_n), 4.6 (m, 2H, H_α or $H_{\alpha1}$), 4.2 (m, 2H, H_α or $H_{\alpha1}$), 4.10−3.2 (complex, 48H, $H_{a,a',b',b}$, $H_{e,f,g,h,i,j,k}$, $H_{\beta,\gamma,\epsilon}$), 2.9 (t, 4H, ^3J = 8,5 Hz, H_d). ES-MS: *m*/*z* found 826.5 ([Rh·**1**·**3**]$(PF_6)^{2+}$, calcd 826.8), 502.8 ([Rh·**1**·**3**]$^{3+}$, calcd 502.8).

[Rh·cat](PF$_6$)$_3$. The complex [Rh·**1**·**3**]$(PF_6)_3$ (9 mg, 4.6×10^{-3} mmol) and 1 mg of $[(PCy_3)_2Cl_2RuCHPh]$ were dissolved at room temperature in freshly distilled dichloromethane (2 mL). One day later, more ruthenium catalyst (1 mg) was added. The reaction was stopped after 3 days. The mixture was chromatographed on silica (eluant acetonitrile/water/saturated aqueous KNO_3 (100:10:1)) to give, after exchange of the chloride anions by hexafluorophosphate, 3 mg of a yellow solid. The catenane was obtained in a yield of 34%. ^{1}H NMR (500 MHz, CD_3CN): δ = 9.17 (br d, 2H, H_7), 8.82 (br d, 2H, $H_{3b'}$ and H_{3b}), 8.59 (d, 2H, ^3J = 9.2 Hz, H_5), 8.47 (d, 2H, ^3J = 9.2 Hz, H_6), 7.94 (d, 2H, ^3J = 5.9 Hz, $H_{6b'}$ and H_{6b}), 7.55−7.51 (complex, 6H, H_2, H_{5b} and $H_{5b'}$, H_9), 7.39 (2d, 6H, ^3J = 5.7 Hz, ^3J = 8.9 Hz, H_m, H_3), 7.14 (d, 4H, ^3J = 8.9 Hz, H_o), 6.9 (d, 2H, ^3J = 8.1 Hz, $H_{c'}$), 6.47 (d, 2H, ^3J = 8.1 Hz, H_c), 5.81 (m, 2H, H_l), 4.58 (m, 2H, $H_{\alpha1}$ or H_α), 4.2 (m, 2H, $H_{\alpha1}$ or H_α), 4.10 (complex, 48H, $H_{a,a',b,b'}$, $H_{e,g,h,i,j,k}$, $H_{\beta,\gamma,\epsilon}$), 2.95 (t, 4H, ^3J = 8.5 Hz, H_d). Assignment of the ^{1}H NMR spectrum was done using 2D ROESY. ES-MS: *m*/*z* found 1769.6 ([Rh·cat]$(PF_6)_2^+$, calcd 1770.5), 812.4 ([Rh·cat]$(PF_6)^{2+}$, calcd 812.9), 493.6 ([Rh·cat]$^{3+}$, calcd 493.6). UV−vis (CH_3CN) [λ_{max}, nm (log ϵ)]: 304 (4.25), 317 (4.18), 369 (3.9).

Results and Discussion

Strategy and Design of the System. The construction principle is represented in Figure 1. In the first step, the metal was coordinated to the two bidentate units of the macrocycle **1** (Figures 2 and 3). Macrocycle **1** is a 50-membered ring.[16] The coordinating units are both identical 4-methyl-8-phenoxy-1,10-phenanthroline derivatives, connected via a *p*-xylenyl bridge linked to the methyl groups. A pentaoxoethylene chain binds together the two phenoxy end positions

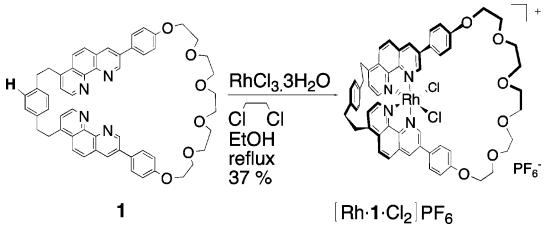


Figure 2. Reaction affording the complex [Rh·**1**·Cl_2]PF_6.

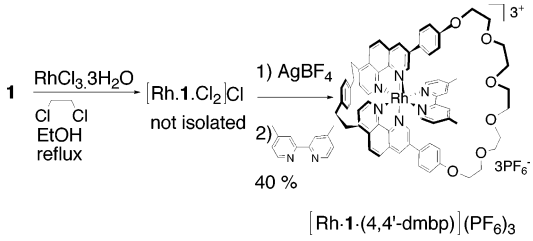


Figure 3. Sequence of reactions leading to [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$.

of the two phenanthrolines. In the resulting [Rh·**1**·Cl_2]Cl complex, two chloride anions are bound to the metal. In the second step a bidentate unit was threaded through the ring of the complexed macrocycle [Rh·**1**·Cl_2]Cl. This was done by substituting the ancillary chloride ligands by a bipyridine (bipy) derivative. The bipy bears two end-functionalized arms which will allow in the ultimate step the formation of the second macrocycle and, consequently, the catenane.

Preliminary attempts with bipy derivatives functionalized at the 6 and 6′ positions turned out to be negative. Complexation of rhodium being sensitive to steric congestion of the coordinating center, these arms were linked to positions 4 and 4′ of the bipyridine. Their length has to be long enough to allow the encircling of the polyoxoethylene chain of the macrocycle **1**. CPK models showed that tetra- or pentaoxoethylene fragments should have the appropriate length. These molecular fragments are ended by an olefinic functionality each. The last step then becomes obvious: A ring-closing metathesis (RCM) reaction was performed on the threaded rhodium complex and led to the corresponding rhodium catenane.

In all the metallocatenanes synthesized until now, the coordinating bis- or trischelates inscribed in the rings of the assemblies were in the endo position. It is noteworthy that, as a consequence of the strategy described here, one of the rings of the catenane will incorporate a bidentate moiety in an exo orientation. A crucial step in the synthesis of the Rh(III) catenane described here is the substitution of the chloride ancillary ligands of [Rh·**1**·Cl_2]Cl followed by the threading of the bipyridine derivative through the cavity of the rhodium macrocyclic complex. This ligand substitution reaction was first studied with an analogous but less elaborate bidentate unit. As a first model, the synthesis of a Rh(III) complex bearing a 4,4′-dimethyl-2,2′-bipyridine was undertaken.

Synthesis of a Rh(III) Macrocyclic Complex. $RhCl_3 \cdot 3H_2O$ and macrocyle **1** were refluxed for 4 h in a dichloroethane−ethanol mixture. The solution turned progessively from orange to yellow. The chloride counterion was ex-

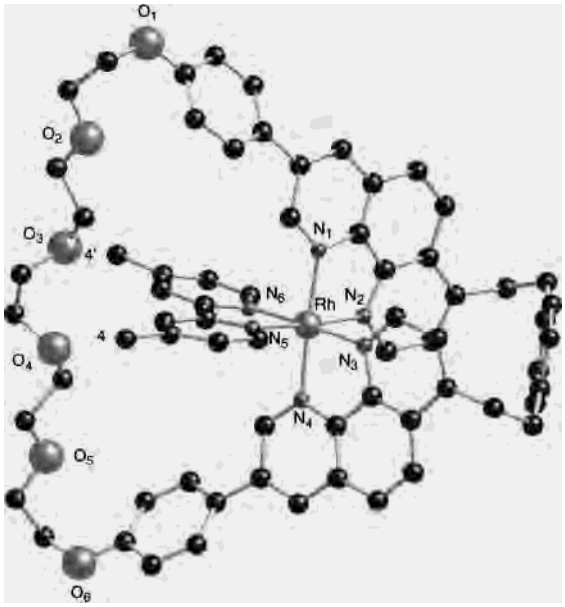


Figure 4. X-ray crystal structure of [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−N_1, 2.04; Rh−N_2, 2.04; Rh−N_3, 2.04; Rh−N_4, 2.03; Rh−N_5, 2.02; Rh−N_6, 2.03; N_1−Rh−N_2, 80.75; N_1−Rh−N_3, 96.53; N_1−Rh−N_4, 176.52; N_1−Rh−N_5, 94.87; N_1−Rh−N_6, 87.01; N_2−Rh−N_3, 83.02; N_2−Rh−N_4, 96.81; N_2−Rh−N_5, 175.61; N_2−Rh−N_6, 99.33; N_3−Rh−N_4, 80.65; N_3−Rh−N_5, 97.26; N_3−Rh−N_6, 176.04, N_4−Rh−N_5, 87.54; N_4−Rh−N_6, 96.86; N_5−Rh−N_6, 80.63.

changed by PF_6^- ion, and the resulting complex was purified by chromatography on alumina. The expected complex [Rh·**1**·Cl_2]PF_6 was isolated in 37% yield. [Rh·**1**·Cl_2]PF_6 is a yellow compound, poorly soluble in common solvents. Protons H (Figure 2) of the phenylene bridge in the free macrocycle **1** are homotopic. A splitting of the corresponding signals in the ^{1}H NMR spectrum of [Rh·**1**·Cl_2]PF_6 is observed which originates from the diastereotopic nature of these protons. The FAB-MS spectrum shows the peak of [Rh·**1**·Cl_2]$^+$ (*m*/*z* 1049.2).

Synthesis of a Rh(III) Macrocyclic Complex Bearing a 4,4′-Dimethyl-2,2′-bipyridine Unit as a Third Chelate. From a practical point of view, the manipulation of [Rh·**1**·Cl_2]PF_6 is not easy, due to its low solubility. For this reason, a method which would allow access to [Rh·**1**·(4,4′-dmbp)]-$(PF_6)_3$ (4,4′-dmbp = 4,4′-dimethyl-2,2′-bipyridine) without the isolation of the [Rh·**1**·Cl_2]PF_6 intermediate was developed in the following manner.

After the formation of crude [Rh·**1**·Cl_2]Cl (Figure 3, vide ante), the chloride anions were removed by treatment with $AgBF_4$ and the reaction mixture was subsequently heated in an acetonitrile−butanol mixture in the presence of a slight excess of 4,4′-dmbp. The resulting complex was precipitated as its hexafluorophosphate salt, [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$, and isolated as a yellow solid in a 40% yield based on macrocycle **1**.

The X-ray structure of [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$ (Figure 4) shows clearly that the bipy derivative is linked to the rhodium and is threaded through the cavity formed by the metal−macrocycle assembly. The coordination sphere of the metal is slightly distorted, the N_6−Rh−N_2 and N_2−Rh−N_3 angles being 97.33° and 83.02° respectively. Noteworthy is

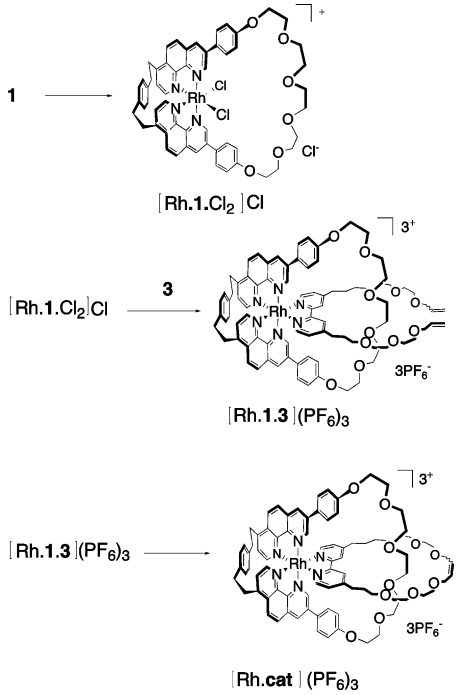


Figure 5. Synthesis of the rhodium(III)-complexed [2]catenane[Rh·cat]-$(PF_6)_3$.

the O_1–O_6 distance. The polyoxoethylene chain which connects O_1 to O_6 is made up of 5 C−C and 10 C−O bonds, and the 14.99 Å length observed for the O_1−O_6 distance indicates that the polyoxoethylene chain is almost fully extended. In other words, its size is just long enough to allow the coiling-up of the ring around the metal and subsequently the coordination of the two subunits of **1** to the metal. The two methyl groups of the dmbp are close to the polyoxoethylene chain. Oxygens O_3 and O_4 are as close as ∼4 Å from the hydrogens of the 4- and 4′-methyl groups, respectively. The C_4−Rh−$C_{4'}$ angle (72.90°) shows that these two arms are actually well oriented, being on either side of the polyoxoethylene segment. The formation of [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$ and the observation by X-ray analysis that the dmbp is really threaded through macrocycle **1** in [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$ encouraged us to apply the same strategy to prepare a rhodium catenane, based on the same ligand set.

Synthesis of the Rhodium Catenane. The reaction route is represented in Figure 5. The first step, i.e., the complexation of the metal with the macrocycle **1**, was described in the previous section. The third chelate **3** is a long molecular string—a 36 atom-membered one—in which the methyl groups of the dmbp core are each connected to an identical polyoxoethylene chain. The two chains bear an olefinic terminal function each. **3** was obtained by reaction of the dilithio derivative of the 4,4′-dmbp with (2-(2-iodoethoxy)-ethoxy)ethyl allyl ether (Figure 6).[17]

Threading of **3** through [Rh·**1**·Cl_2]Cl needed harsher reaction conditions by comparison with those used for the formation of [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$. A suspension of [Rh·**1**·Cl_2]Cl in ethylene glycol was heated for 14 h at 140 °C in the presence of a slight excess of **3** and a drop of

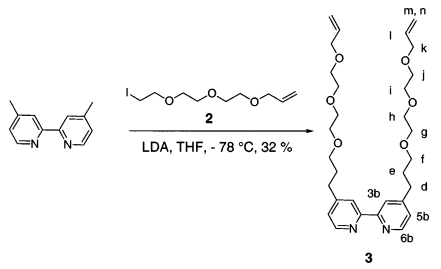
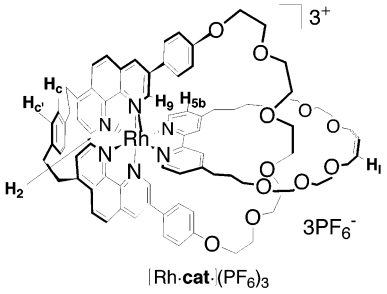


Figure 6. Preparation of the ligand **3**.

N-ethylmorpholine. The resulting complex was precipitated as its PF_6^- salt and purified. The rhodium catenane precursor [Rh·**1**·**3**]$(PF_6)_3$ was isolated in an overall yield of 14% based on free macrocycle **1**. The molecular peak of the complex was characterized by mass spectroscopy, and by using the electrospray technique, and the successive loss of two and three PF_6^- ions was observed: *m*/*z* 826.5 ([Rh·**1**·**3**]$(PF_6)^{2+}$, calcd 826.8), 502.8, ([Rh·**1**·**3**]$^{3+}$, calcd 502.8). The aromatic region of the ^{1}H NMR spectrum is similar to that observed for [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$. The vinylic protons of the olefinic functionalities of the threaded chelate **3** are located at $\delta = 5.75$ ppm (H_l) and 5.05 ppm (H_m and H_n).

An RCM reaction was undertaken to connect the two arms via the olefinic functions.[18] The complex [Rh·**1**·**3**]$(PF_6)_3$ was stirred for 3 days in dichloromethane in the presence of $[(PCy_3)_2Cl_2RuCHPh]$ (50% mol equiv). After a thorough purification of the raw product by chromatography, 3.0 mg of rhodium catenane [Rh·cat]$(PF_6)_3$ was isolated (34% yield). The structure was confirmed by one- and two-dimensional ^{1}H NMR spectroscopies and by mass spectrometry. The exo linking nature of the compound, whose general shape is very likely to be close to the drawing of Figure 5, is supported by CPK models and by the X-ray structure of its model [Rh·**1**·(4,4′-dmbp)]$(PF_6)_3$. On going from the precatenane [Rh·**1**·**3**]$(PF_6)_3$ to the catenane itself, the disappearance of the two signals corresponding to the olefinic H_m and H_n protons was observed, and simultaneously one new complex signal appeared centered at $\delta = 5.81$ ppm. This signal was assigned to the vinylic protons H_l linked to the C−C double bond formed by the RCM reaction, but a definitive assignment of the *Z* or *E* configuration of the double bound could not be made. The simplicity of the ^{1}H NMR spectrum is in accordance with the expected C_2 symmetry of the catenane. In particular, the protons of the *p*-phenylene bridge H_C and $H_{C'}$ resonate as two doublets of doublets, confirming their diastereotopic nature. The most relevant observations in the aromatic region, when the ^{1}H NMR spectra of [Rh·**1**·Cl_2]PF_6 and [Rh·cat]$(PF_6)_3$ are compared, is the strong upfield shift of the signal of protons H_9 of the bisphenanthroline core ($\Delta\delta = -2.5$ ppm), which could be explained (Figure 7) by the influence of the ring current effect of the bipyridine subunit on these two protons.

(18) a) Mohr, B.; Weck, M.; Sauvage, J.-P.; Grubbs, R. H. *Angew. Chem., Int. Ed, Engl.* **1997**, 1308−1310. (b) Dietrich-Buchecker, C. O.; Rapenne, G.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1999**, *121*, 994−1001.



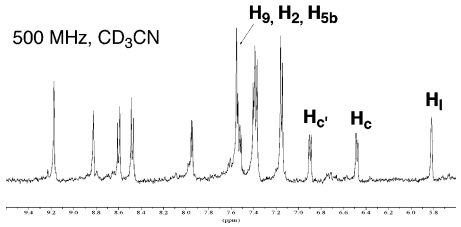


Figure 7. ^{1}H NMR (500 MHz) spectra (low-field region, CD_3CN) of [Rh·cat]$(PF_6)_3$.

For the rhodium catenane, the peaks corresponding to the successive loss of one, two, and three PF_6^- counterions were observed by electrospray mass spectroscopy: *m*/*z* 1769.6 ([Rh·cat]$(PF_6)_2^+$, calcd 1770.5), 812.4 ([Rh·cat]$(PF_6)^{2+}$, calcd 812.9), 493.6 ([Rh·cat]$^{3+}$, calcd 493.6).

Conclusion

Macrocycle **1,** in which two bidentate units connected through a well-adapted bridge are inscribed, displays remarkable coordination properties. By coordinating ruthenium[16] or rhodium, as described in this work, complexes of C_2 symmetry are formed. Despite the low reactivity of Rh(III), threading a third chelate, a bipyridine derivative, through the macrocyclic cavity and binding it to the metal appears possible. This bipyridinic chelate bears two arms which are connected to its 4 and 4′ positions instead of the 6 and 6′ positions in the case of ruthenium.[16] This minimizes steric hindrance effects in the vicinity of the binding site which could prevent or render more difficult the coordination to the metal. As a consequence, the rhodium catenane, formed by RCM, displays a novel geometry, the ancillary polyoxoethylene chain of the second ring of the catenane being far away from the coordination core.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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