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Article

Irreversible but Noncovalent Ru(II)–Pyridine Bond: Its Use for the Formation of [2]-Catenanes

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The reaction between ligand **1**, which consists of two terminal pyridines attached to a central 1,10-phenanthroline (phen), and the complex $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ has been studied. A new ruthenium containing metallamacrocycle has been obtained and fully characterized. Despite the relatively poor yield for the cyclization process involving the ruthenium center (20%), this strategy led to the synthesis of two different kinds of [2]-catenane. The first example reported in this article is a bimetallic Cu(I)/Ru(II) catenane $\mathbf{5}^{3+}$ consisting of a purely organic ring interlocked with the ruthenium(II)-incorporating metallacycle. Complex $\mathbf{5}^{3+}$ was selectively demetalated at the Cu(I) center to lead to the free Ru(II)-containing catenane. A trimetallic Ru(II)/Cu(I)/Ru(II) catenane $\mathbf{8}^{5+}$ was also synthesized showing that this approach is reliable and promising for the elaboration of photoactive multicomponent systems.

Introduction

The field of catenanes has experienced an impressive development in the course of the past two decades.[1−3] One particularly active branch is that of molecular machines and motors.[4−8] Interlocking rings incorporating transition metals, either in their coordination sites[9] or as components of their backbones,[10,11] represent a special class of such compounds.

Since the pioneering work of Fujita and co-workers on the preparation of catenanes containing coordinative bonds such as a Pd(II)−N bond,[12] several other systems have been reported which incorporate transition metals.[13] Magnesium has even been used as a constitutive atom to generate catenanes from Grignard reagents and crown ethers.[14]

A few years ago, our group has reported that catenanes can be constructed by coordination chemistry alone using a three-coordination site fragment consisting of a central phen chelate attached to two peripheral terpy units (phen = 1,10-phenanthroline; terpy = 2,2′:6′,2″-terpyridine).[15]

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(1) For early work, see: Schill, G. *Catenanes, Rotaxanes and Knots*; Academic Press: New York, 1971.

(2) *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, 1999.

(3) For recent review articles, see: Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725−2828. Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. In *Templating Self-Assembly, and Self-Organisation*; Sauvage, J.-P., Hosseini, M. W., Eds.; Comprehensive Supramolecular Chemistry 9; Pergamon: New York, 1996, pp 43−83. Breault, G. A.; Hunter, C. A.; Mayers, P. C. *Tetrahedron* **1999**, *55*, 5265−5293. Vögtle, F.; Dünnwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451−460.

(4) (a) Collin, J.-P.; Dietrich-Buchecker, C.; Gaviña, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res*., **2001**, *34*, 477−487 (special issue on molecular machines). (b) Balzani, V.; Credi, A.; Raymo, F.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391.

(5) Sauvage, J.-P. *Molecular Machines and Motors, Structure & Bonding*; Springer: Berlin, 2001; Vol. 99.

(6) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, 2001.

(7) Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G. W. H. *Science* **2001**, *291*, 2124−2128.

(8) Shigekawa, H.; Miyake, K.; Sumaoka, J.; Harada, A.; Komiyama, M. *J. Am. Chem. Soc*. **2000**, *122*, 5411−5412.

(9) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J.-P. *Tetrahedron Lett*. **1983**, *24*, 5091−5094; **1983**, *32*, 53−61.

(10) Fujita, M. *Acc. Chem. Res*. **1999**, *32*, 53−61.

(11) Park, K. M.; Kim, S. Y.; Heo, J.; Whang, D.; Sakamoto, S.; Yamaguchi, K.; Him, K. *J. Am. Chem. Soc*. **2002**, *124*, 2140−2147.

(12) (a) Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720. (b) Hori, A.; Kumazawa, K.; Kusukawa, T.; Chand, D. K.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *Chem. Eur. J*. **2001**, *7*, 4142 and references therein.

(13) (a) Beer, P. D.; Rothin, A. S. *Polyhedron* **1989**, *9*, 1251. (b) Piguet, C.; Bernardinelli, G.; Williams, A. F.; Bosquet, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 582. (c) Padilla-Tosta, M. E.; Fox, O. D.; Drew, M. G. B.; Beer, P. D. *Angew. Chem., Int. Ed.* **2001**, 40, 4235. (d) Mingos, D. M. P.; Yau, J.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1894. (e) Wiseman, M. R.; Marsh, P. A.; Bishop, P. T.; Brisdon, B. J.; Mahon, M. F. *J. Am. Chem. Soc.* **2000**, *122*, 12598. (f) McArdle, C. P.; Irwin, M. J.; Jennings, M. C.; Vittal, J. J.; Puddephatt, R. J. *Chem. Eur. J.* **2002**, *8*, 723.

(14) Gruter, G.-J. M.; de Kanter, F. J. J.; Markes, P. R.; Nomot, T.; Akkerman, O. S.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1993**, *115*, 12179.

10.1021/ic0302478 CCC: $27.50

We would now like to describe the use of ruthenium(II) centers in conjunction with simple monodentate ligands such as the pyridyl group, to synthesize symmetrical (two identical rings) or asymmetrical (two different rings) catenanes.

Experimental Section

^{1}H NMR spectra were recorded on either a Bruker AVANCE 300 (300 MHz) or a 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. Absorption spectra were recorded with an Uvikon XS spectrometer.

Synthesis. Oxygen-sensitive reactions were conducted under a positive pressure of argon, by Schlenk techniques. Light-sensitive reactions and purifications were performed in the dark. All solvents and reagents were of the highest quality available and were used as received without further purification. Ligands **1**[16] and **2**,[17] and the complexes $Cu(CH_3CN)_4(PF_6)$[18] and $Ru(phen)_2(CH_3CN)_2(PF_6)_2$,[19] were prepared as already reported in the literature.

$3^{2+}.(PF_6^-)_2$. Ligand **1** (101.9 mg, 0,124 mmol) and $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ (103.3 mg, 0.124 mmol) were suspended in 2-(2-ethoxyethoxy)ethanol (30 mL). The solution was stirred and heated at 140°C under argon for 3 h and then allowed to cool to room temperature. A saturated aqueous solution of KPF_6 was then added. The precipitate was filtered on a sintered glass funnel, dissolved in acetone, and purified by a short column (silica, acetone as eluent). This yielded 40 mg (20% yield) of **3**$^{2+}(PF_6^-)_2$ as an orange solid.

^{1}H NMR (500 MHz, CD_3CN): δ 9.44 (d, 2H, $H_{2''}$, $J = 5.5$ Hz); 8.77 (d, 2H, $H_{4''}$, $J = 7.1$ Hz); 8.58 (d, 4H, H_{m1}, $J = 8.6$ Hz); 8.47 (d, 2H, H_{4-7}, $J = 8.4$ Hz); 8.44 (d, 2H, $H_{7''}$, $J = 8.2$ Hz); 8.33 (m, 6H, $H_{3-8,m4}$); 8.20 (m, 4H, $H_{3'',5''}$); 8.11 (m, 4H, $H_{6'',9''}$); 7.92 (s, 2H, H_{5-6}); 7.85 (d, 4H, H_{m1}, $J = 8.8$ Hz); 7.75 (d, 8H, H_{o2-m3}); 7.55 (m, 6H, $H_{8'',o4}$); 7.15 (d, 4H, H_{m2}, $J = 8.8$ Hz); 7.07 (d, 4H, H_{o3}, $J = 8.8$ Hz). ES-MS: *m/z* 1429.3 $[M - PF_6]^+$, 642.3 $[M - 2PF_6]^{2+}$ (found); 1574.4 [M] (calcd). UV−vis: $\lambda_{max} = 419$ nm ($\epsilon = 14000$ L·mol^{-1}·cm^{-1}), $\lambda_{max} = 453$ nm ($\epsilon = 11700$ L·mol^{-1}·cm^{-1}).

$4^+.(PF_6^-)$. Ligand **1** (213.0 mg, 0.26 mmol), **2** (146.7 mg, 0.26 mmol), and $Cu(CH_3CN)_4PF_6$ (96.4 mg, 0.26 mmol) were combined in $CH_3CN/CHCl_3$ (30 mL) at room temperature under argon. The solution was stirred for 1 day. The solvent was then removed to afford a red solid (418 mg) in quantitative yield.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.72 (d, 2H, H_{4-7}, $J = 8.2$ Hz); 8.37 (d, 2H, $H_{4'-7'}$, $J = 8.3$ Hz), 8.33 (s, 2H, H_{5-6}); 8.00 (d, 2H, H_{3-8}, $J = 8.2$ Hz); 7.86 (s, 2H, $H_{5'-6'}$); 7.82 (d, 2H, $H_{3'-8'}$, $J = 8.3$ Hz); 7.72 (d, 4H, H_{m3}, $J = 8.7$ Hz); 7.65 (d, 4H, H_{o1}, $J = 8.4$ Hz); 7.35 (d, 4H, $H_{o'}$, $J = 8.7$ Hz); 7.18 (m, 8H, H_{o2-o3}); 7.10 (d, 4H, H_{m2}, $J = 8.7$ Hz); 6.81 (d, 4H, H_{m1}, $J = 8.4$ Hz); 6.03 (d, 4H, $H_{m'}$, $J = 8.7$ Hz); 3.86 (s, 4H, H_ϵ); 3.75−3.50 (brs, 16H, $H_{\alpha,\beta,\gamma,\delta}$). ES-MS: *m/z* 726.9 $[M - PF_6 + H]^{2+}$ (found); 1598.1 [M] (calcd). UV−vis: $\lambda_{max} = 438$ nm ($\epsilon = 4000$ L·mol^{-1}·cm^{-1}).

$5^{3+}\cdot(PF_6^-)_3$. The same procedure as for compound **3**$^{2+}$ was used, starting with **$4^+\cdot(PF_6^-)$** (197.4 mg, 0.124 mmol) and $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ (103.3 mg, 0.124 mmol). Purification was performed by column chromatography (silica using CH_2Cl_2/MeOH as eluents). The product **$5^{3+}\cdot(PF_6^-)_3$** was obtained as a red solid (50 mg, 20% yield).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.68 (d, 2H, $H_{2''}$, $J = 5.5$ Hz); 8.74 (d, 2H, $H_{4''}$, $J = 7.1$ Hz); 8.68 (d, 2H, H_{4-7}, $J = 8.3$ Hz); 8.42−8.37 (m, 6H, $H_{3'',7'',9''}$); 8.36 (d, 2H, $H_{4'-7'}$, $J = 8.3$ Hz); 8.32 (s, 2H, H_{5-6}); 8.19 (d, 2H, $H_{5''}$, $J = 8.9$ Hz); 8.14 (d, 4H, H_{m4}, $J = 1.2$ Hz); 8.08 (d, 2H, $H_{6''}$, $J = 8.9$ Hz); 7.99 (d, 2H, H_{3-8}, $J = 8.3$ Hz); 7.78 (d, 4H, H_{m3}, $J = 8.8$ Hz); 7.76 (d, 2H, $H_{3'-8'}$, $J = 8.3$ Hz); 7.75 (s, 2H, $H_{5'-6'}$); 7.66 (m, 10H, $H_{o1,o4,8''}$); 7.32 (d, 4H, $H_{o'}$, $J = 8.7$ Hz); 7.15 (d, 4H, H_{o3}, $J = 8.8$ Hz); 7.03 (d, 4H, H_{o2}, $J = 8.8$ Hz); 6.94 (d, 4H, H_{m2}, $J = 8.8$ Hz); 6.70 (d, 4H, H_{m1}, $J = 8.3$ Hz); 5.99 (d, 4H, $H_{m'}$, $J = 8.7$ Hz); 3.86 (s, 4H, H_ϵ); 3.75−3.50 (brs, 16H, $H_{\alpha,\beta,\gamma,\delta,}$). ES-MS: *m/z* 1029.9 $[M - 2PF_6]^{2+}$, 638.2 $[M - 3PF_6]^{3+}$ (found); 2349.5 [M] (calcd). UV−vis: $\lambda_{max} = 418$ nm ($\epsilon = 13300$ L·mol^{-1}·cm^{-1}), $\lambda_{max} = 452$ nm ($\epsilon = 11300$ L·mol^{-1}·cm^{-1}).

$6^{2+}\cdot(PF_6^-)_2$. Compound **$5^{3+}\cdot(PF_6^-)_3$** (10.7 mg) was dissolved in CH_2Cl_2. KCN (50 mg) in H_2O was added, and the solution was stirred for 48 h in the dark. The two layers were separated, and the solvent was removed to afford an orange solid.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.25 (d, 2H, $J = 5.5$ Hz); 8.59 (d, 2H, $J = 7.9$ Hz); 8.51 (m, 6H); 8.42 (m, 6H); 8.34 (d, 2H, $J = 8.0$ Hz); 8.23 (d, 2H, $J = 8.6$ Hz); 8.17 (d, 2H, $J = 8.0$ Hz); 8.06 (m, 8H); 7.90 (m, 6H); 7.77 (m, 10H); 7.60 (m, 4H); 7.19 (m, 4H); 7.07 (d, 4H, $J = 8.7$ Hz); 6.97 (d, 4H, $J = 8.8$ Hz); 6.27 (d, 4H, $J = 8.7$ Hz); 3.86 (s, 4H, H_ϵ); 3.75−3.50 (brs, 16H, $H_{\alpha,\beta,\gamma,\delta,}$). ES-MS: *m/z* 925.5 $[M - 2PF_6]^{2+}$ (found); 2141.0 [M] (calcd).

$7^{3+}\cdot(PF_6^-)_3$. The same procedure as for compound **$4^+\cdot(PF_6^-)$** was used, starting with **$3^{2+}\cdot(PF_6^-)_2$** (33.1 mg, 0,021 mmol), **1** (17.3 mg, 0.021 mmol), and $Cu(CH_3CN)_4PF_6$ (7.8 mg, 0.021 mmol). A 52 mg portion of **7**$^{3+}(PF_6^-)_3$ was obtained as a red solid (100% yield).

^{1}H NMR (500 MHz, CD_3CN): δ 9.54 (d, 2H, $H_{2''}$, $J = 5.5$ Hz); 8.82 (d, 2H, $H_{4''}$, $J = 8.4$ Hz); 8.63 (brs, 4H, H_{m4}); 8.51 (d, 2H, $H_{4'-7'}$, $J = 8.4$ Hz); 8.48 (d, 2H, $H_{7''}$, $J = 7.2$ Hz); 8.45 (d, 2H, H_{4-7}, $J = 8.4$ Hz); 8.41 (d, 4H, $H_{m4'}$, $J = 6.0$ Hz); 8.26 (m, 4H, $H_{3'',5''}$); 8.16 (m, 4H, $H_{6'',9''}$); 7.98 (d, 2H, $H_{3'-8'}$, $J = 8.40$ Hz); 7.96 (s, 2H, $H_{5'-6'}$); 7.95 (d, 2H, H_{3-8}, $J = 8.4$ Hz); 7.84 (d, 4H, $H_{m3'}$, $J = 8.6$ Hz); 7.83 (s, 2H, H_{5-6}); 7.80 (d, 4H, H_{m3}, $J = 8.1$ Hz); 7.67−7.60 (m, 18H, $H_{o1',o4,o1,o4',8''}$); 7.20−7.13 (m, 20H, $H_{o3',o3,o2,o2',m2'}$); 7.00 (d, 4H, H_{m2}, $J = 8.7$ Hz); 6.80 (d, 4H, H_{m1}, $J = 8.4$ Hz); 6.76 (d, 4H, $H_{m2'}$, $J = 8.4$ Hz). ES-MS: *m/z* 1158.0 $[M - 2PF_6]^{2+}$ (found); 2606.0 [M] (calcd). UV−vis: $\lambda_{max} = 419$ nm ($\epsilon = 11300$ L·mol^{-1}·cm^{-1}), $\lambda_{max} = 452$ nm ($\epsilon = 8900$ L·mol^{-1}·cm^{-1}).

$8^{5+}\cdot(PF_6^-)_5$. The same procedure as for compound **$3^{2+}\cdot(PF_6^-)_2$** was used, starting with **$7^{3+}\cdot(PF_6^-)_3$** (20.2 mg, 0.0077 mmol) and $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ (6.4 mg, 0.0077 mmol). The crude materials were dissolved in acetone. The precipitate was filtered, and the solvent was evaporated to afford 5 mg (19% yield) of an orange solid.

^{1}H NMR (500 MHz, CD_3CN): δ 9.92 (d, 4H, $H_{2''}$, $J = 5.5$ Hz); 9.01 (d, 4H, $H_{4''}$, $J = 8.4$ Hz); 8.78 (m, 14H); 8.56 (d, 4H); 8.42 (m, 8H); 8.32 (d, 4H); 8.11 (m, 8H); 7.92 (m, 12H); 7.76 (m, 18H); 7.25 (m, 16H); 7.05 (d, 8H); 6.87 (m, 8H). ES-MS: *m/z* 525.0 $[M - 5PF_6]^{5+}$; 694.4 $[M - 4PF_6^-]^{4+}$; 973.9 $[M - 3\ PF_6^-]^{3+}$ (found); 3357.4 [M] (calcd). UV−vis: $\lambda_{max} = 420$ nm ($\epsilon = 19200$ L·mol^{-1}·cm^{-1}), $\lambda_{max} = 454$ nm ($\epsilon = 15600$ L·mol^{-1}·cm^{-1}).

X-ray Structural Study. Orange single crystals suitable for X-ray analysis could be obtained for complex **$3^{2+}\cdot(PF_6^-)_2$** by slow

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[15] Cárdenas, D. J.; Sauvage, J.-P. *Inorg. Chem.* **1997**, *36*, 2777. (b) Cárdenas, D. J.; Gaviña, P.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1997**, *119*, 2656.

[16] Dietrich-Buchecker, C.; Colasson, B.; Fujita, M.; Hori, A.; Geum, N.; Sakamoto, S.; Yamaguchi, K.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2003**, *125*, 5717.

[17] Dietrich-Buchecker, C.; Sauvage, J.-P. *Tetrahedron* **1990**, *46*, 503.

[18] Kubas, G. J. *Inorg. Synth.* **1990**, *28*, 68.

[19] Sullivan, B. P.; Salman, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

Table 1. Crystallographic Data for $\mathbf{3^{2+}}$

formula	$C_{88}H_{67}F_{12}N_{11}O_4P_2Ru$
mol wt	1733.59
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	12.4176(3)
b (Å)	14.3068(5)
c (Å)	26.672(1)
α (deg)	78.491(5)
β (deg)	87.152(5)
γ (deg)	84.293(5)
V (Å^3)	4617.9(3)
Z	2
color	orange
D_{calcd} (g cm^{-3})	1.25
μ (mm^{-1})	0.281
temp (K)	173
wavelength (Å)	0.71073
R^a	0.096
$R_w{}^b$	0.129

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

evaporation of a CH_3CN solution of $\mathbf{3^{2+}\cdot(PF_6^-)_2}$. Crystal data and details of data collection are provided in Table 1.

Results and Discussion

Strategy. The strategy leading to a Ru(II) containing metallamacrocycle and two different catenanes is represented schematically in Figure 1.

The synthesis of ligand **1** and its coordination properties with Cu(I) and Pd(II) have been previously reported.[16,20] The sequential use of these two metals allowed the quantitative synthesis of two different catenanes following a strategy similar to that shown in Figure 1. We then wanted to investigate the possibility of making Ru(II) analogues of the Pd(II)-catenanes.

Ru(II) and Pd(II) display very different properties in the context of coordination chemistry using **1** and related ligands. Whereas Pd(II) is clearly a labile metal center, leading to the thermodynamically most stable complexes, Ru(II) is notoriously substitutionally inert. In addition, the presence of metal-to-ligand charge transfer (MLCT) states with Ru(II)

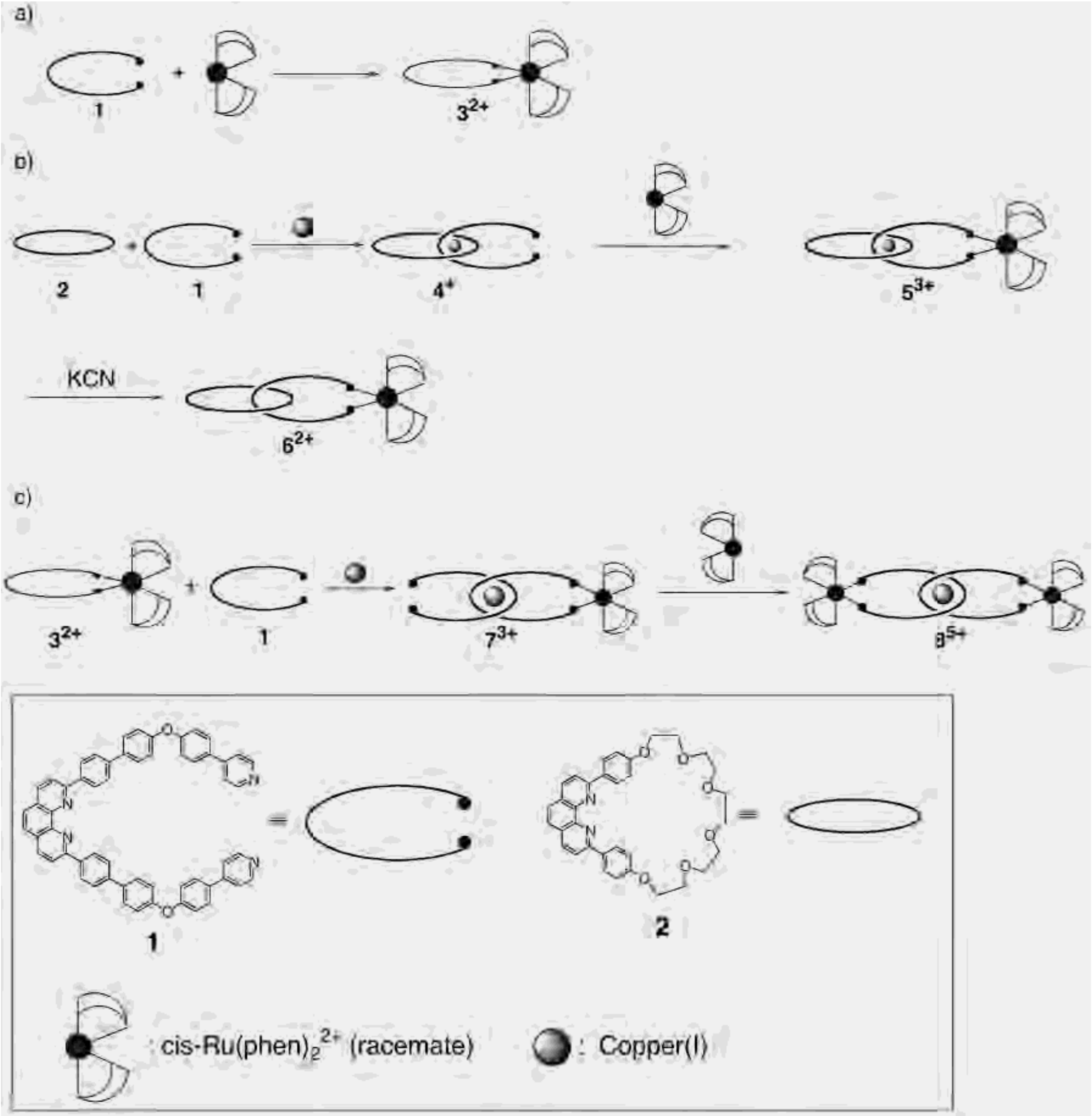
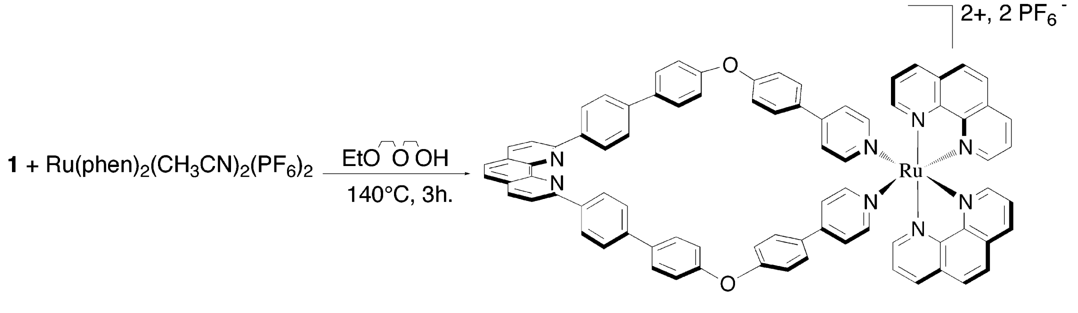


Figure 1. Strategies for the synthesis of (a) a ruthenium-containing macrocycle, (b) a Cu/Ru catenane using a covalent chelate-containing macrocycle and the correlated demetalated ruthenium-containing catenane, and (c) a Ru−Cu−Ru symmetrical catenane. The Ru(II) center is protected by two inert bidentate ligands (1,10-phenanthroline) so that only two *cis* positions are involved in the coordination process. $Ru(phen)_2{}^{2+}$ was used as a racemate whereas, for clarity, only the Δ enantiomer is represented.

Scheme 1. Synthesis of Macrocycle **3**$^{2+}$



3^{2+} (rac.)

can potentially lead to novel photochemical properties related to energy and electron transfer process or light-driven dynamics.

The phen/bis-pyridine ligand **1** has shown its great ability, under thermodynamic control, to coordinate, via the two pyridyl units, two *cis* positions of a metal to form a metallamacrocycle. The pincer-like shape of ligand **1** led us to believe that the formation of a metallamacrocycle could also be favored in a kinetic process. For this purpose, we chose Ru(II) which is known to form stable and kinetically inert complexes when it is coordinated to aromatic imine-based ligands. The appropriate Ru(II) precursor should be protected so that only two *cis* positions can be involved in the complexation process. *cis*-$Ru(phen)_2(CH_3CN)_2(PF_6)_2$ was chosen as the two acetonitrile ligands can easily be substituted by two pyridines.

Figure 1a presents the one-to-one coordination reaction between **1** and $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ which should lead to the macrocycle. Ru(II) is not expected to complex to the phen chelate of **1** since the pyridines are much more accessible, although Ru(II) complexes of 2,9-diaryl-1,10-phen can certainly be obtained.[21] Figure 1b represents the strategy used to make a catenane with two different rings. Ligand **1** is first threaded inside the phen-containing macrocycle **2** using the classical template effect of copper(I) leading to a $Cu^I(dpp)_2^+$-type complex (dpp is a 2,9-diphenyl-1,10-phenanthroline). Considering the great stability of four-coordinate $Cu^I(dpp)_2^+$ complexes, no side reactions involving the two pyridines should occur. Next, the cyclization reaction which consists of a 1:1 complexation reaction between the two dangling pyridines of **1** and the Ru(II) precursor should lead to the hetero [2]-catenane. The final approach presented in Figure 1c is the sum of the previous two strategies: formation of the Ru-macrocycle, threading process using copper(I) coordination, and cyclization step with the ruthenium precursor. This strategy was preferred to the double cyclization approach which should obviously proceed with a lower yield.

Synthesis of Macrocycle 3^{2+}. The reaction between **1** and $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ was examined. We first tried high-dilution conditions, which is a classical procedure for the formation of large macrocycles.[22] For unknown reasons, these conditions did not lead to **3**$^{2+}$. We then found that reacting **1** and $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ in 2-(2-ethoxyethoxy)-ethanol (the concentration of both reactants is 4×10^{-3} M) at 140 °C for 3 h provided the best conditions to obtain **3**$^{2+}$ (Scheme 1). Compound **3**$^{2+}$ was isolated after column chromatography in 20% yield as its PF_6 salt. Most of the crude product was recovered as an orange insoluble product which is likely to contain oligomeric coordination species. Moreover, no evidence for complexation occurring on the phen chelate was found. The 20% yield clearly indicates that the chelate effect of the two pyridines of **1** is very weak. It appears that Ru(II) first binds the most accessible coordination site, which is a pyridine, and subsequently another one (either intramolecularly or intermolecularly), without any possibility of equilibration in favor of the macrocycle, even at high temperature (some attempts were carried out at 160 °C).

The ES-MS spectrum shows two major peaks at *m*/*z* 1429.3 (monocharged species) and *m*/*z* 642.3 (dicharged species) indicating that the product of the complexation has a 1:1 (**1**:$Ru(phen)_2$) stoichiometry.

^1H NMR of the product provides some important features concerning the structure of the desired Ru-macrocycle (Figure 2). The signal corresponding to $H_{2'}$ appears at high field due to the presence of the two pyridyl units coordinated

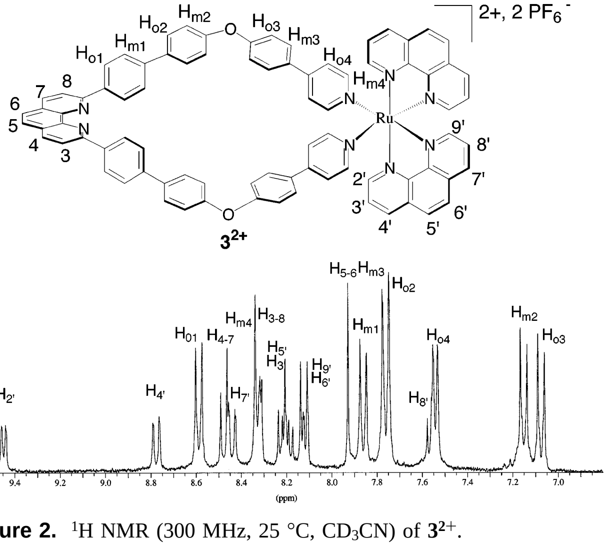


Figure 2. ^1H NMR (300 MHz, 25 °C, CD_3CN) of **3**$^{2+}$.

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(20) Dietrich-Buchecker, C. O.; Geum, N.; Hori, A.; Fujita, M.; Sakamoto, S.; Yamaguchi, K.; Sauvage, J.-P. *Chem. Commun.* **2001**, 1182.

(21) Laemmel, A.-C.; Collin, J.-P.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **1999**, *3*, 383 and unpublished results.

(22) Mürner, H.; Belser, P.; von Zelewsky, A. *J. Am. Chem. Soc.* **1996**, *118*, 7989.

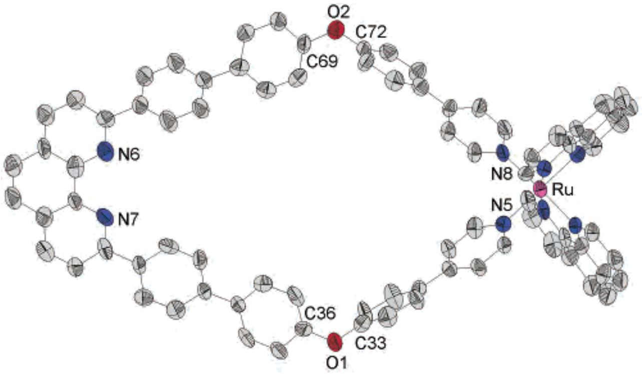


Figure 3. X-ray structure of **3**$^{2+}$. Wire frames representation (hydrogens are omitted for clarity). The compound represented in Figure 3 is the Δ enantiomer.

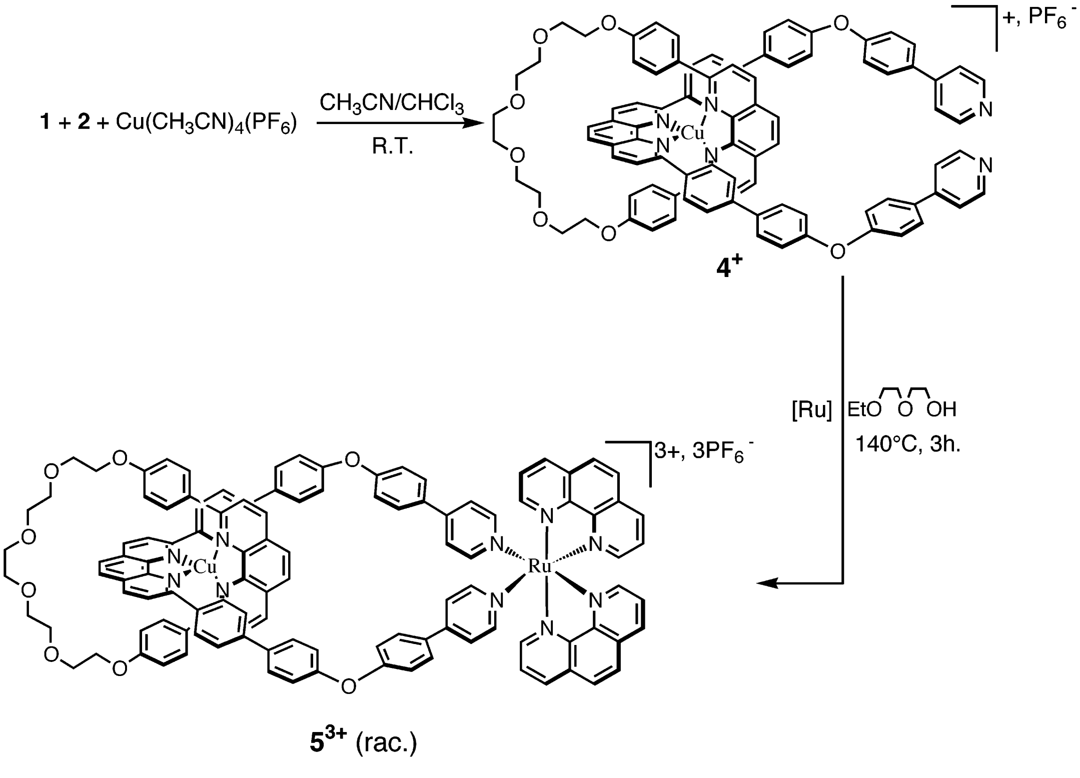
to the ruthenium. The ^{1}H ROESY experiment clearly displays spatial interaction between $H_{2'}$ and H_{m4} but shows no interaction between the ruthenium part and the phen core, indicating that the complexation occurred on the pyridines. Furthermore, H_{m2} and H_{o3}, which have the same chemical shift in **1** because of the conformational freedom around the oxygen, are differentiated once the macrocycle is formed.

We were able to grow orange single crystals by slow evaporation of a CH_3CN solution of $\mathbf{3^{2+}\cdot(PF_6^-)_2}$. The two enantiomers of **3**$^{2+}$ are present in the unit cell but only the Δ enantiomer is represented in Figure 3. Structural determination by single crystal X-ray diffraction confirms the macrocyclic structure of **3**$^{2+}$. Analysis of the structure proves that the ligand is well adapted to the formation of a cyclic complex such as **3**$^{2+}$, since almost no distortion from ideal geometry is observed. The N(5)−Ru−N(8) angle of the pyridine−Ru−pyridine coordination fragment is 90.0°. The geometry around the oxygens is close to ideal since the C(69)−O(1)−C(72) and C(36)−O(2)−C(33) angles of the diphenyl ether links are about 117°.[23] The size of the cavity can be described with three lengths: the O(1)−O(2) distance is 13.4 Å, and the N(6)(phen)−Ru and N(7)(phen)−Ru distances are both 17.3 Å.

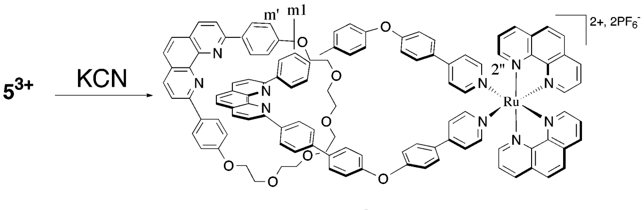
Synthesis of the Bimetallic Catenane $\mathbf{5^{3+}}$. Catenane **5**$^{3+}$ was obtained after two complexation steps (Scheme 2). The first reaction consisted of the threading of **1** into **2** by coordination of the two phen chelates on Cu(I). The copper salt was added to a solution (CH_3CN/ $CHCl_3$) of **2**. The orange solution of $\mathbf{Cu(2)(CH_3CN)_2}^+$ (not represented in Scheme 2) was stirred during 30 min after which a solution of **1** was added. The color turned immediately red, and the solution was allowed to stir another 24 h. After evaporation of the solvents, compound **4**$^+$ (PF_6 salt) could be obtained as a red powder in quantitative yield. Eventhough side reactions are possible due to the presence of the pyridines, the stability of the threaded complex **4**$^+$ shifts the equilibrium toward this single species. The cyclization step was then performed using the same conditions as for **3**$^{2+}$ (Ru(II) precursor, solvent, concentrations, temperature, reaction time), and compound $\mathbf{5^{3+}\cdot(PF_6^-)_3}$ was isolated after chromatography column in 20% yield, i.e., with approximately the same efficiency as for the preparation of the simple ring **3**$^{2+}$.

Compound **5**$^{3+}$ was characterized by ES-MS spectrometry and 2D ^{1}H NMR analysis. The mass spectrum exhibits two peaks corresponding to the product at *m*/*z* 1029.9 (for [**5**$^{3+}$ + PF_6^-]$^{2+}$) and *m*/*z* 638.2 (for [**5**$^{3+}$]$^{3+}$). The two coordination steps yielding **5**$^{3+}$ could be followed by ^{1}H NMR (Figure 4). The threaded precursor complex **4**$^+$ has the usual high

Scheme 2. Synthesis of Catenane **5**$^{3+}$ and Its Precursor **4**$^+$



Scheme 3. Demetalation of 5^{3+} Using KCN



6^{2+} (rac.)

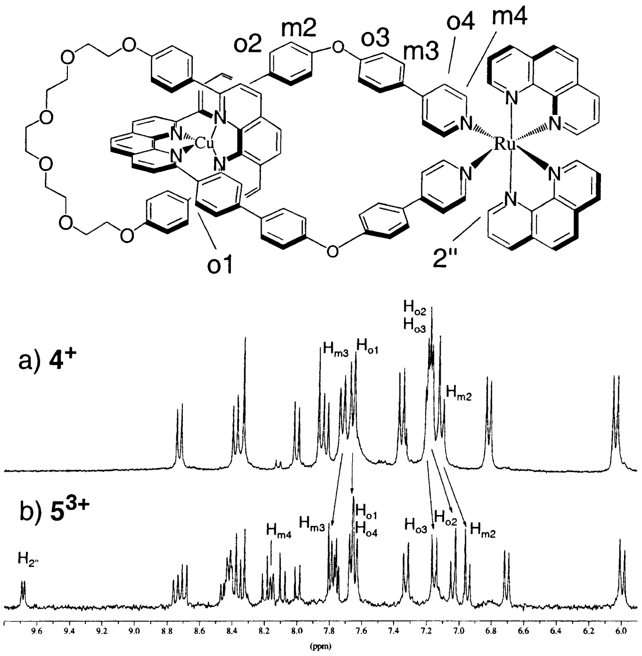


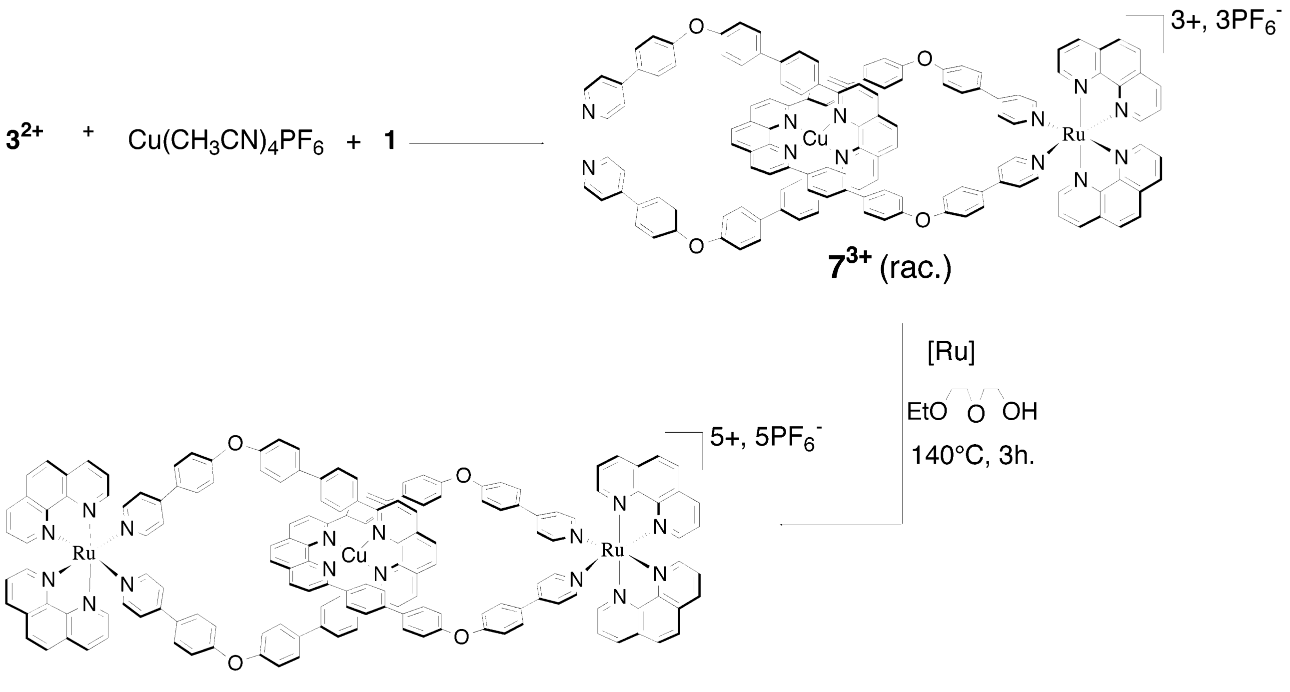
Figure 4. ^{1}H NMR monitoring for the preparation of catenane 5^{3+} (aromatic region, 300 MHz, 25 °C): (a) pre-catenane 4^+ in CD_2Cl_2; (b) catenane 5^{3+} in CD_2Cl_2.

field shifted signals corresponding to the protons of the phenyl rings directly attached to the phen of both **1** and **2**. This is due to the phen ring current effect. Surprisingly, the protons of the pyridines do not appear in the spectrum of 4^+. After cyclization, the characteristic shift of $H_{2''}$ appears at $\delta = 9.68$ ppm. We can also observe a slight difference for protons H_{m2} and H_{o3} again due to the restriction of conformational freedom in the macrocycle. When coordinated to ruthenium, the protons of the pyridines appear at approximately the same δ as in 3^{2+} (8.14 for H_{m4} and 7.66 for H_{o4}). ^{1}H ROESY experiments prove the spatial proximity of $H_{2''}$ and H_{m4}.

Demetalation of 5^{3+}. As it has been previously reported, Cu catenanes can be easily demetalated by reaction with cyanide.[17−24] Our aim was to selectively remove the templating metal (Cu) from compound 5^{3+} without affecting the Ru complex and, thus, the topological properties of the catenane. The reaction was performed in dichloromethane (5^{3+})/water (excess of KCN) in the dark and monitored by ^{1}H NMR (Scheme 3).

After 48 h, the signal of $H_{2''}$ at 9.68 ppm had completely disappeared and a doublet emerged at 9.25 ppm. This was correlated with the downfield shift of the protons H_{m1} ($\Delta\delta = +0.27$ ppm) and $H_{m'}$ ($\Delta\delta = +0.28$ ppm) (see Scheme 3). These downfield shifts are not as large as those observed in the case of classical covalent catenanes but are comparable to the demetalation of a Ru(terpy)$_2$ containing catenane.[15] The ES-MS spectrum of the product confirmed the demetalated structure of 6^{2+}. The predominant peak at *m*/*z* 925.5 corresponds to [6^{2+}]. A smaller one at *m*/*z* 642.3 corresponds to the fragment [3^{2+}] of 6^{2+}. This peak becomes more intense as the cone voltage increases (until the peak at *m*/*z* 925.5

Scheme 4. Synthesis of Catenane 8^{5+} and Its Precursor 7^{3+}



7^{3+} (rac.)

8^{5+} (diastereoisomeric mixture)

completely disappears). This indicates that we could selectively remove the copper(I) cation without affecting the ruthenium complex.

Synthesis of the Trimetallic Catenane 8^{5+}. We followed the final strategy (part c in Figure 1) to synthesize the symmetrical trimetallic catenane $\mathbf{8^{5+}}$. We repeated the sequence used for catenane $\mathbf{5^{3+}}$, threading reaction using Cu(I) and cyclization reaction with the Ru(II) precursor, but the phen containing macrocycle involved in this sequence was $\mathbf{3^{2+}}$ instead of **2** (Scheme 4).

The threaded complex $\mathbf{7^{3+}}$ was formed quantitatively after (1) addition of the copper salt to a CH_3CN/CH_3Cl solution of $\mathbf{3^{2+}}$ and (2) addition of ligand **1**. Complex $\mathbf{7^{3+}}$ (PF_6 salt) was isolated and fully characterized by 1D and 2D ^1H NMR and ES-MS. Reaction of $\mathbf{7^{3+}}$ with $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ in 2-(2-ethoxyethoxy)ethanol gave an orange solid. The solid was then dissolved in acetone, and insoluble species were filtered off. ^1H NMR of the soluble orange solid shows a well-resolved doublet at $\delta = 9.92$ ppm. Two kinds of signals can be distinguished: sharp and broad ones. We assume that the sharp signals belong to the protons of the phenanthrolines coordinated on the Ru and the broad signals are the superposition of the spectra of the two diastereoisomers (racemic mixture $\Delta-\Delta$ and $\Lambda-\Lambda$ and meso compound $\Delta-\Lambda$). ES-MS spectrum of the product indicated that the desired product has been made: three major peaks corresponding to $\mathbf{8^{5+}\cdot(PF_6^-)_5}$ with the loss of 3, 4, and 5 PF_6^- anions (respectively, *m/z* 973.9, 694.4, and 525.0). As only 5 mg of product $\mathbf{8^{5+}}$ (PF_6 salt, 19% yield) could be obtained, no further experiment (demetalation, separation of the two diastereoisomers) could be performed.

Conclusion

We have investigated the coordination properties of the phen/bis-pyridine ligand **1** with Ru(II). A metallamacrocycle constructed around a $Ru(II)(phen)_2(pyridine)_2$ fragment could be obtained. The cyclization step appeared to have a low yield because of the weak chelate effect of ligand **1**. Nevertheless, this cyclization based on the coordination reaction between $Ru(phen)_2(CH_3CN)_2(PF_6)_2$ and the two dangling pyridines of **1** was reliable since the yield was constant (20%) for the three different systems studied (metallamacrocycle and two catenanes). We were able to incorporate a $Ru(phen)_2$ fragment in a rigid structure. The large cavity of macrocycle $\mathbf{3^{2+}}$ with its aromatic walls could provide interesting behavior in host−guest chemistry. In addition, the different strategies used should enable us to construct related systems in which we can take advantage of both this rigidity and the photophysical properties of the metals. In this respect, we are now working on the synthesis of hetero-trimetallic systems with a catenane structure.

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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(23) Horn, E.; Zhang, S.-Z.; Furukawa, N. *New Cryst. Struct.* **2000**, 215, 557.

(24) Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795.