A Ruthenium(II)-Complexed Rotaxane Whose Ring Incorporates a 6,6′-Diphenyl-2,2′-bipyridine: Synthesis and Light-Driven Motions

Jean-Paul Collin,[a] Damien Jouvenot,[a] Masatoshi Koizumi,[b] and Jean-Pierre Sauvage*[a]

Keywords: Rotaxanes / Ruthenium / Light-driven motions

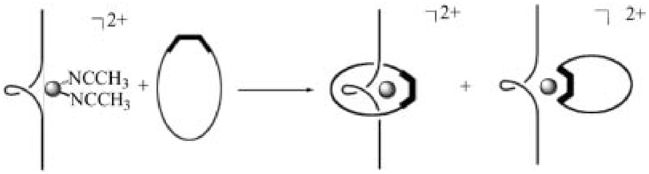
By incorporating a 6,6′-diphenyl-2,2′-bipyridine (dpbipy) fragment in a ring, *endo* coordination of a ruthenium(II) center is performed selectively and almost quantitatively. The threaded system, containing a helical fragment, could be fully characterized. When the terminal functions of the rod-shaped helical complex threaded through the macrocycle are phenol groups, the complete rotaxane is prepared by the classical Williamson stoppering reaction in moderate yield. Light-induced motions of the unstoppered system (pseudo-rotaxane) and the real rotaxane have been studied. Under visible light irradiation, quantitative decoordination of the dpbipy-containing ring is observed, leading to the separate fragments (ring and helical thread) or to a new rotaxane (uncoordinated ring threaded by the dumbbell).

Introduction

The use of transition metals as templates to construct various interlocking and knotted topologies has been exploited by various groups in the course of the last few decades.[1–5] On the basis of related strategies, rotaxanes have also been prepared efficiently.[6,7] In the field of molecular machines and motors[8] light-driven machines are particularly promising.[9] In addition, several systems have been proposed which contain an electroactive transition-metal complex as the key component.[10] A related class of molecules is based on photoinduced electron transfer from the metal-to-ligand charge transfer excited state of a transition-metal complex [copper(I) or ruthenium(II)] to afford a new redox state, which will subsequently rearrange.[11] A very distinct family of dynamic molecular systems takes advantage of the dissociative character of ligand-field states in $Ru(diimine)_3^{2+}$ complexes.[12] In these compounds, one part of the system is set in motion by photochemically expelling a given chelate, the reverse motion being performed simply by heating the product of the photochemical reaction so as to regenerate the original state.

Results and Discussion

We have recently reported the synthesis of a [2]rotaxane constructed around a $Ru(diimine)_3^{2+}$ core.[13] The ring was a derivative of 6,6′-dimethyl-2,2′-bipyridine (dmbipy), and, in the course of the threading reaction, we noticed that both *exo-* and *endo*-coordination to the ruthenium(II) center of the rod-like fragment take place, as schematically represented in Scheme 1.



Scheme 1.

In order to circumvent this synthetic difficulty, we replaced the dmbipy motif by a 6,6′-diphenyl-2,2′-bipyridine chelate (dpbipy), which provides the system with greatly improved geometrical control. According to CPK models, exo coordination of a dpbipy-incorporating ring is virtually impossible, except with very large rings. As reported in this paper, this approach proved successful, and the desired rotaxane could be prepared in good yield, without formation of *exo*-coordinated species. In addition, the photochemical behavior of the compound and of its nonstoppered analogue has been investigated. In particular, it was shown that the ring is efficiently decoordinated from the ruthenium(II) center under visible light irradiation.

Synthesis of a Pseudo-Rotaxane

Preliminarily, we investigated the threading reaction leading to a pseudo-rotaxane, both ends of the helical rod-shaped fragment bearing inert $-OCH_3$ groups. As depicted in Figure 1, the starting ruthenium(II) complex $\mathbf{1}^{2+}$ [13] and

---

[a] Laboratoire de Chimie Organo-Minérale, UMR 7513 du CNRS, Université Louis Pasteur, Faculté de Chimie,
4, rue Blaise Pascal, 67070 Strasbourg Cedex, France
E-mail: sauvage@chimie.u-strasbg.fr
[b] Present address: Graduate School of Pharmaceutical Sciences, The University of Tokyo, ERATO, Japan Science and Technology Agency (JST),
Hongo, Bunkyo-ku, Tokyo 113–0033, Japan

DOI: 10.1002/ejic.200401008

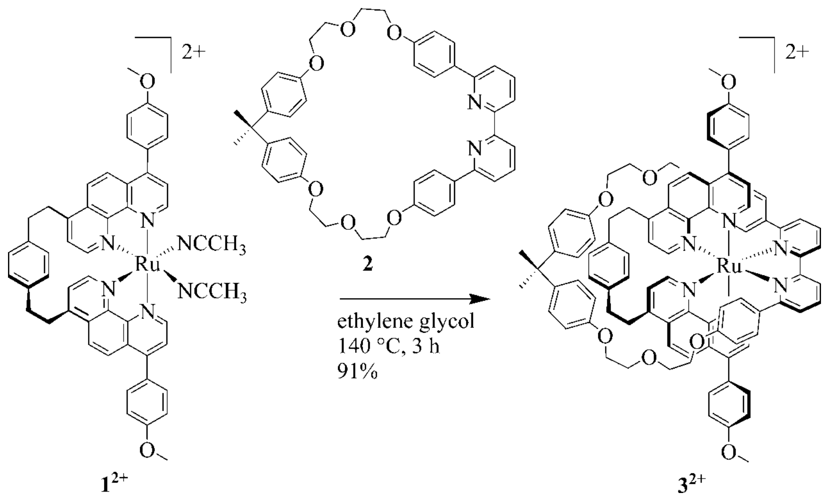


Figure 1. Synthesis of the threaded complex 3^{2+}.

ring 2[14] reacted under relatively harsh conditions to afford the threaded complex 3^{2+} in good yield (91%) after chromatography (silica). Compound 2 is a 37-membered ring whose synthesis was recently described.[13] The presence of a dpbipy chelate and a bis(phenol) A unit ensures a certain rigidity to the ring, prohibiting swinging of the bis(phenol) A fragment "behind" the bipy chelate. Complex 1^{2+} is a ruthenium(II) complex that contains a helical bis(phenanthroline) organic fragment[13] (Figure 1).

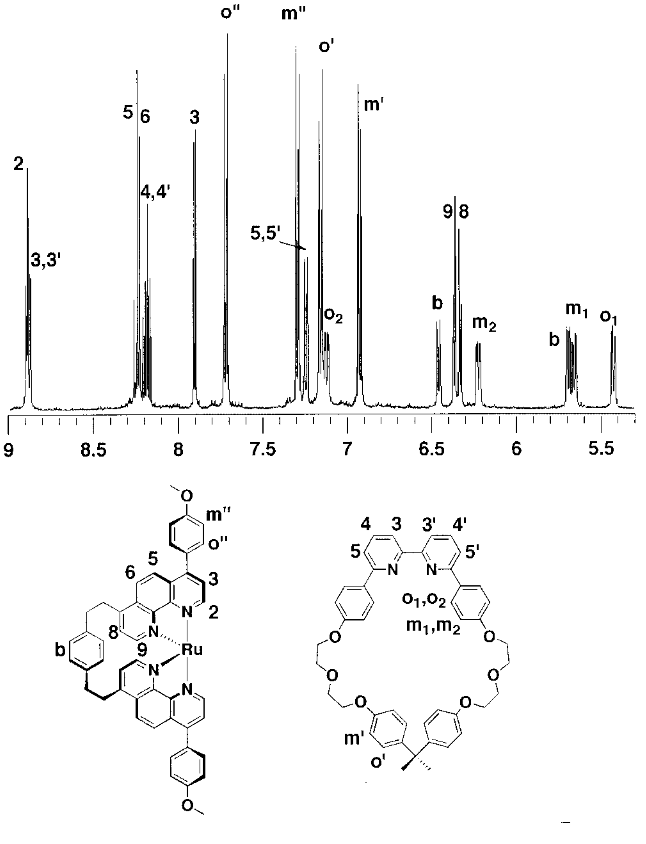


Figure 2. Aromatic region of the ^{1}H NMR spectrum of 3^{2+} in CD_3COCD_3, and proton indexation of the two parts of the molecule (thread and ring).

Complex $3[PF_6]_2$ is a red complex, which can be recrystallized from an acetone/diethyl ether mixture. As expected, 3^{2+} is the *endo*-coordinated compound, with no contamination by a hypothetical *exo* isomer. ^{1}H NMR spectroscopy turned out to be particularly informative in this respect. The ^{1}H NMR spectrum of 3^{2+} is represented in Figure 2.

The assignment of the various H atoms (indicated on the drawing of the molecular fragments of 3^{2+}) could be done easily by analogy with related systems.[13,14] The most remarkable features of the spectrum are:

(i) The number of signals corresponding exactly to the expected number for a single and *symmetrical* complex ("upper" and "lower" parts of the screwlike fragment identical) and their sharpness.

(ii) The presence of four very well resolved signals for the protons of the two phenyl rings borne by the 2,2′-bipyridine fragment of the ring (o_1, o_2, m_1, m_2). Clearly, the "upper" part and the "lower" part of these phenyl rings are different and they do not interchange, at least at room temperature, as represented in a schematic fashion in the drawing of Figure 2.

Preparation of the Rotaxane

The complete rotaxane was prepared from 2 and 4^{2+}, the phenolic analogue of 1^{2+}, whose synthesis was previously reported.[13] The reaction is represented in Figure 3.

The "threading" step of 4^{2+} through ring 2 afforded the pre-rotaxane 5^{2+} in 82% yield. It was carried out in ethylene glycol at 140 °C. A high-purity sample was obtained by crystallization in acetone/diethyl ether. The "stoppering" reaction was performed using large tetraaryl-methane derivatives of the Gibbson type.[15] The precursor 6 was prepared as previously reported.[16] It reacted with $5[PF_6]_2$ in DMF, at 60 °C, in the presence of a large excess of K_2CO_3 under argon. After work up and chromatography on silica the real rotaxane 7^{2+} was obtained as a red solid, in 56% yield. The compound can be crystallized in acetone/hexane.

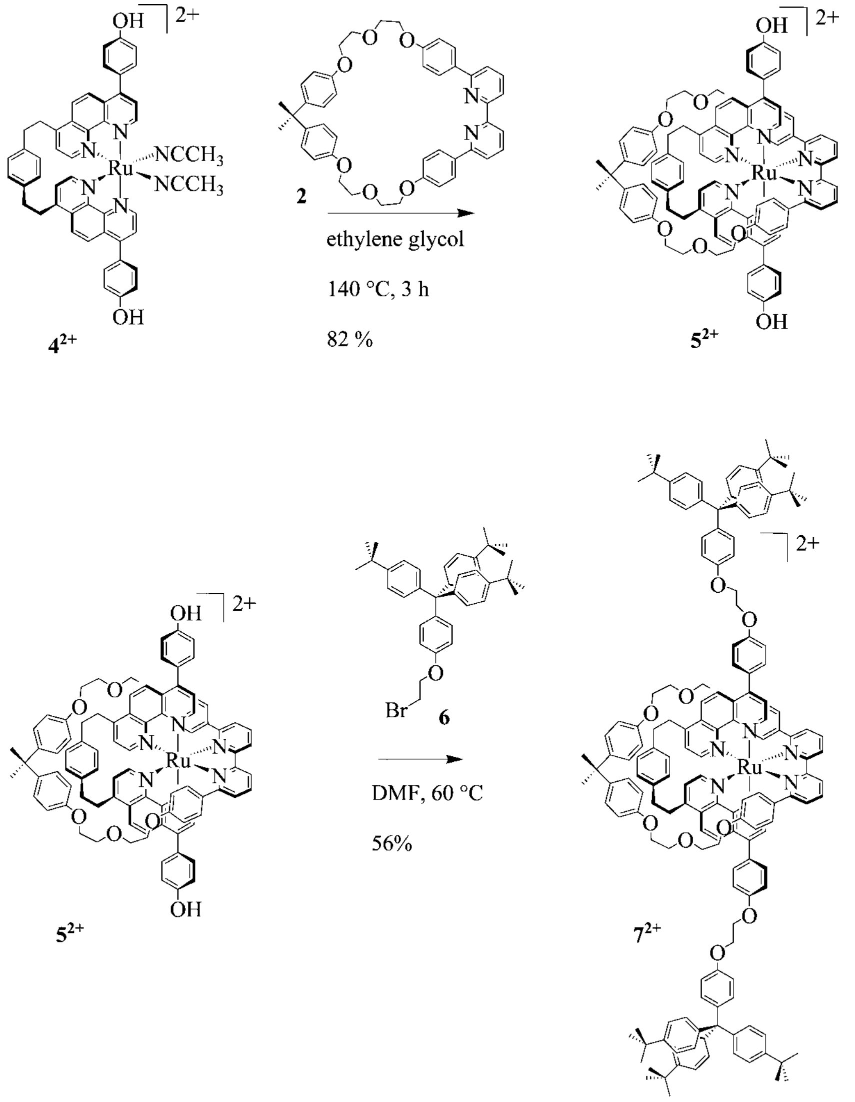


Figure 3. Sequence of reactions leading to the rotaxane 7^{2+}.

In the aromatic region, the ^{1}H NMR spectrum of $\mathbf{7^{2+}}$ is more or less identical to the superimposition of the spectra of $\mathbf{3^{2+}}$ and **6**. The "rope jump" phenomenon observed for pseudo-rotaxanes containing a larger and more flexible ring than in the present case, as already observed,[13,16] is not operative in $\mathbf{7^{2+}}$.

Light-Driven Molecular Motions in the Pseudo-Rotaxane $\mathbf{3^{2+}}$ and in the Rotaxane $\mathbf{7^{2+}}$

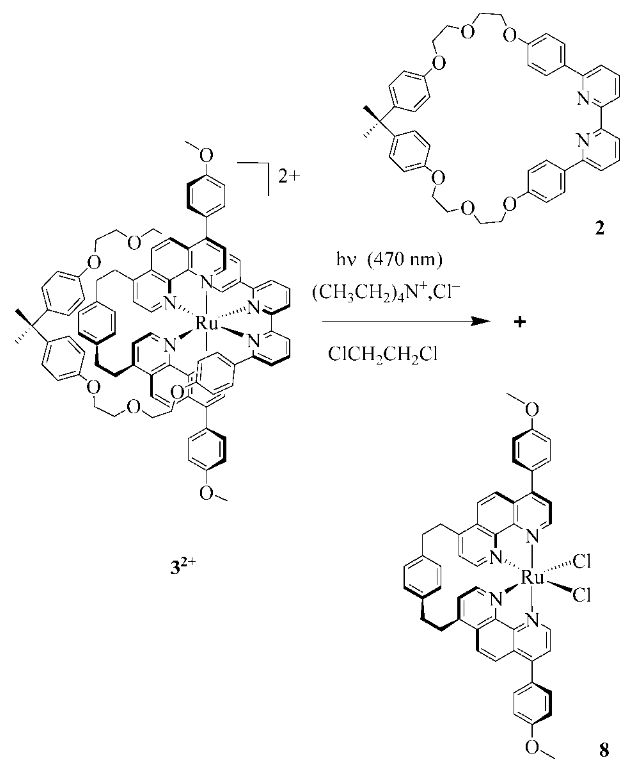
In a first step, the photochemical behavior of complex $\mathbf{3^{2+}}$ was studied. By irradiating a solution of $\mathbf{3[PF_6]_2}$ in 1,2-dichloroethane, using a pass band filter centered around 470 nm and in the presence of a large excess of Cl^-, a clean photochemical reaction takes place. The reaction is schematically represented in Figure 4.

The photoinduced "unthreading" reaction was monitored by UV/Vis spectroscopy. The series of visible spectra, characteristic of metal-to-ligand charge transfer (MLCT) bands, is given in Figure 5.

From a band centered at 465 nm, typical of a Ru(diimine)$_3{}^{2+}$ complex,[17] a new spectrum is obtained by irradiation, which corresponds to a $RuCl_2$(diimine)$_2$ complex (λ_{max} = 562 nm). As expected, the MLCT band for the photochemical product is strongly bathochromically shifted from that of the tris(diimine) complex. The presence of a clean isosbectic point at 485 nm tends to indicate that the photochemical reaction is selective and quantitative. This has been confirmed by ^{1}H NMR spectroscopy and by thin-layer chromatography (silica; eluent: $CH_3CN/H_2O/KNO_3$, 100:10:1). Complex **8** is the only photochemical product detected and the starting complex $\mathbf{7^{2+}}$ has completely disappeared.

Similar experiments have been performed with the rotaxane. The reaction is represented in a schematic fashion in Figure 6.

The photochemical decoordination of the ring in $\mathbf{7^{2+}}$ is also selective and clean. Here again, in an analogous way as with $\mathbf{3^{2+}}$, an isosbectic point is observed at 486 nm. Thin-layer chromatography turned out to be particularly useful



2

$\mathbf{3}^{2+}$

8

Figure 4. Photochemical expulsion of the macrocycle **2** from the threaded ruthenium complex $\mathbf{3}^{2+}$ in the presence of chloride anions.

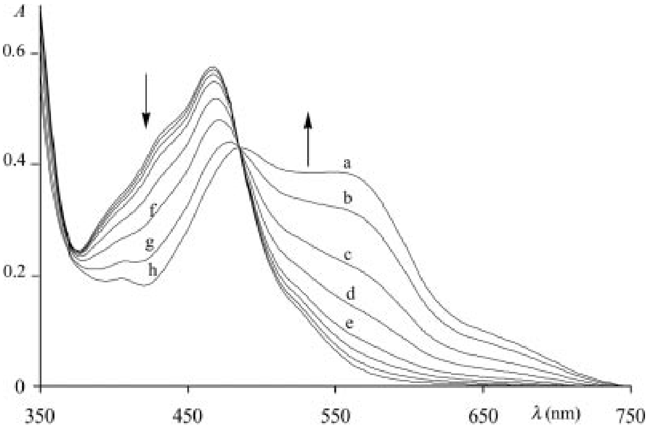
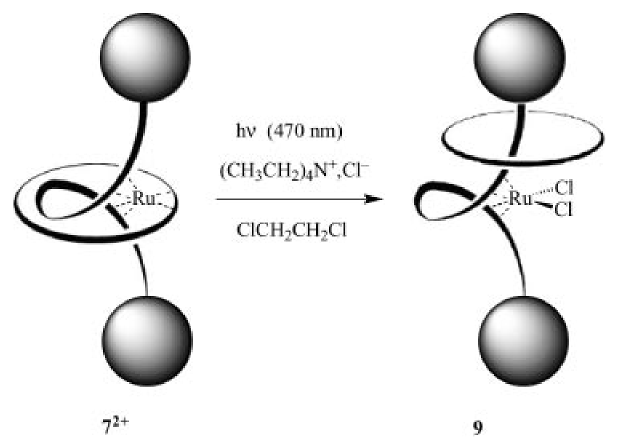


Figure 5. Absorption spectra (visible region) of a solution containing $\mathbf{7}^{2+}$ and $NEt_4^+Cl^-$ in $ClCH_2CH_2Cl$ before, during, and after irradiation. Spectra were recorded at t = 0 s (a), 15 s (b), 40 s (c), 90 s (d), 200 s (e), 400 s (f), 900 s (g), 2400 s (h).

to monitor the reaction. It showed that **7[PF$_6$]$_2$** is gradually converted to a single purple complex, **9**, under irradiation (470 nm). Importantly, traces of the free ring **2** could not be detected, demonstrating that both forms of the rotaxane, $\mathbf{7}^{2+}$ and **9**, do not undergo unthreading, even to a minor extent; The thermal recoordination reaction of **8**, leading back to $\mathbf{7}^{2+}$, is presently under investigation. Unfortunately, preliminary data seem to indicate that this reaction is not as clean and selective as in the case of a related catenane[10] nor as the presently described threading reaction of $\mathbf{1}^{2+}$ through **2**.



$\mathbf{7}^{2+}$

9

Figure 6. Schematic representation of the photochemical reaction leading to the disconnected rotaxane **9**.

Conclusions

The present report shows that a rotaxane and its non-stoppered analogue could be selectively prepared, the formation of *exo*-coordinated species being completely avoided. The size of the ring is important in controlling the course of the coordination reaction. In the present case, the 37-membered ring is large enough to accommodate the thick helical fragment by which it is threaded. However, it is neither so large nor flexible as to permit unthreading of the rotaxane dumbbell from the ring, once a decoordinated compound such as **9** has been formed.

Preliminary photochemical experiments demonstrated that clean and selective light-induced motions take place, the ring being decomplexed from the ruthenium(II) center. The thermal backward reaction is presently under investigation.

Experimental Section

General Methods: Oxygen- or moisture-sensitive reactions were performed in oven-dried glassware attached to a vacuum line with Schlenk techniques. Dry solvents were distilled from suitable desiccants under argon. Compounds **2** and **6** as well as complex **5[PF$_6$]$_2$** were prepared according to literature procedures.[13,16] All other chemicals were purchased from commercial sources and used without further purification. Column chromatography was carried out on silica gel 60 [Merck, 40–63 (fine) or 63–200 mesh]. Thin-layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F254 (Merck). ^{1}H NMR spectra were recorded with either Bruker AVANCE 300 (300 MHz) or Bruker AVANCE 400 (400 MHz) spectrometers with the deuterated solvent as the lock and residual solvent as the internal reference. Electron-spray ionization mass spectra (ESI-MS) were recorded with a Bruker MicroTOF instrument. UV/Vis spectra (absorption spectroscopy) were recorded with a Kontron Instruments UVIKON 860 spectrometer at room temperature. All solutions were degassed and then saturated with oxygen-free argon. Light irradiation experiments: 3 mL of a sample solution of the complex (c = 10–5 M) were put in a closed UV-visible glass cell. The sample was irradiated with the beam of a 250 W slide projector, filtered by a water filter and focused on the cell. The evolution of the absorption spectrum of the solution was followed with respect to irradiation time.

3[PF$_6$]$_2$: A suspension of **2** (15.0 mg, 0.0212 mmol) and **1[PF$_6$]$_2$** (16.0 mg, 0.0135 mmol) in degassed ethylene glycol (5 mL) was heated at 140 °C for 2 h under argon. The orange suspension turned into a red solution. After cooling to room temperature, a saturated aqueous solution of KPF_6 (10 mL) was added. The orange precipitate was then filtered and washed with water. The crude product was purified by column chromatography on silica gel [eluent: acetone/H_2O/saturated aqueous KNO_3 (100:0:0 to 100:5:0.5)] affording **3[PF$_6$]$_2$** (22.2 mg, 0.0123 mmol) in 91% yield. Crystallization from acetone/diethyl ether afforded a highly pure sample of **3[PF$_6$]$_2$** (8.9 mg, 0.0051 mmol) in 38% yield. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 25 °C): δ = 5.43 (d, 2 H, ^3J = 8.6 Hz, H^{o1}), 5.66 (d, 2 H, ^3J = 8.6 Hz, H^{m1}), 5.69 (d, 2 H, ^3J = 9.8 Hz, H^{b}), 6.23 (d, 2 H, ^3J = 8.5 Hz, H^{m2}), 6.33 (d, 2 H, ^3J = 5.8 Hz, H^{8}), 6.37 (d, 2 H, ^3J = 5.6 Hz, H^{9}), 6.46 (d, 2 H, ^3J = 8.6 Hz, H^{b}), 6.93 (d, 4 H, ^3J = 8.9 Hz, H$^{m'}$), 7.13 (d, 2 H, ^3J = 8.6 Hz, H^{o2}), 7.16 (d, 4 H, ^3J = 9.0 Hz, H$^{o'}$), 7.25 (d, 2 H, ^3J = 7.6 Hz, H$^{5,5'}$), 7.30 (d, 4 H, ^3J = 8.8 Hz, H$^{m''}$), 7.73 (d, 4 H, ^3J = 8.8 Hz, H$^{o''}$), 7.91 (d, 2 H, ^3J = 5.6 Hz, H^{3}), 8.19 (dd, 2 H, J = 7.6 and 7.9 Hz, H$^{4,4'}$), 8.23 (d, 2 H, ^3J = 9.5 Hz, H^{6}), 8.26 (d, 2 H, ^3J = 9.4 Hz, H^{5}), 8.89 (d, 2 H, ^3J = 6.8 Hz, H$^{3,3'}$), 8.90 (d, 2 H, ^3J = 5.2 Hz, H^{2}) ppm. ESI-MS: m/z = 829.08 ([M – 2 PF$_6$]/2); calcd. for $C_{93}H_{82}F_6N_6O_8PRu/2$ 829.24.

5[PF$_6$]$_2$: A suspension of **2** (39.4 mg, 0.056 mmol) and **4[PF$_6$]$_2$** (42.5 mg, 0.037 mmol) in degassed ethylene glycol (10 mL) was heated at 140 °C for 2 h under argon. The orange suspension turned into a red solution. After cooling to room temperature, a saturated aqueous solution of KPF_6 (30 mL) was added. The orange precipitate was then filtered and washed with water. The crude product was purified 3 times by column chromatography on silica gel [eluent: acetone/H_2O/saturated aqueous KNO_3 (100:0:0 to 100:10:1)] affording **5[PF$_6$]$_2$** (54.0 mg, 0.03 mmol) in 82% yield. Crystallization from acetone/diethyl ether afforded pure **5[PF$_6$]$_2$** (7.7 mg, 0.0044 mmol) in 12% yield. ^{1}H NMR (300 MHz, (CD_3) $_2CO$, 25 °C): δ = 5.45 (d, 2 H, ^3J = 8.3 Hz, H^{o1}), 5.72 (m, 4 H, H^{m1}, H^{b}), 6.25 (d, 2 H, ^3J = 8.5 Hz, H^{m2}), 6.36 (d, 2 H, ^3J = 5.6 Hz, H^{8}), 6.40 (d, 2 H, ^3J = 5.5 Hz, H^{9}), 6.48 (d, 2 H, ^3J = 7.9 Hz, H^{b}), 6.96 (d, 4 H, ^3J = 8.8 Hz, H$^{m'}$), 7.22 (m, 12 H, H^{o2}, H$^{o'}$, H$^{5,5'}$, H$^{m''}$), 7.66 (d, 4 H, ^3J = 8.6 Hz, H$^{o''}$), 7.92 (d, 2 H, ^3J = 5.6 Hz, H^{3}), 8.3 (m, 6 H, H$^{4,4'}$, H^{6}, H^{5}), 8.92 (m, 4 H, H$^{3,3'}$, H^{2}) ppm. ESI-MS: m/z = 1483.65 ([M– 2 PF_6^- – H + e^-]); calcd. for $C_{91}H_{77}N_6O_8Ru$ 1483.48.

7[PF$_6$]$_2$: 5[PF$_6$]$_2$ (54.0 mg, 0.03 mmol) and **6** (183.5 mg, 0.3 mmol) were added to a vigorously stirred suspension of K_2CO_3 (42 mg, 0.3 mmol) in DMF (30 mL) under a stream of argon. The mixture was heated to 60 °C and stirred for 42 h. DMF was removed in vacuo and a saturated aqueous solution of KPF_6 (30 mL) was added. The orange precipitate was then filtered and washed with water. The crude product was purified by column chromatography on silica gel [eluent: acetone/H_2O/saturated aqueous KNO_3 (100:0:0 to 100:5:0.5)] affording **7[PF$_6$]$_2$** (39.8 mg, 0.017 mmol) in 56% yield. Crystallization from acetone/*n*-hexane afforded pure **7[PF$_6$]$_2$** (30.7 mg, 0.011 mmol) in 36% yield. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 25 °C): δ = 5.44 (d, 2 H, ^3J = 8.6 Hz, H^{o1}), 5.67 (d, 2 H, ^3J = 8.3 Hz, H^{m1}), 5.70 (d, ^3J = 8 Hz, 2 H, 6 Hz, H^{b}), 6.24 (d, 2 H, ^3J = 8.6 Hz, H^{m2}), 6.35 (d, 2 H, ^3J = 5.4 Hz, H^{8}), 6.38 (d, 2 H, ^3J = 5.4 Hz, H^{9}), 6.47 (d, 2 H, ^3J = 8.3 Hz, H^{b}), 6.93 (m, 6 H, H$^{m'}$, H^{w}), 7.16 (m, 22 H, H^{o2}, H$^{o'}$, H^{x}, H^{y}), 7.26 (d, 2 H, ^3J = 7.9 Hz, H$^{5,5'}$), 7.36 (d, 16 H, Hz, H$^{m''}$), 7.74 (d, 4 H, ^3J = 8.6 Hz, H$^{o''}$), 7.93 (d, 2 H, ^3J = 5.4 Hz, H^{3}), 8.20 (t, 2 H, ^3J = 7.9 Hz, H$^{4,4'}$), 8.23 (d, 2 H, ^3J = 9.4 Hz, H^{6}), 8.28 (d, 2 H, ^3J = 9.4 Hz, H^{5}), 8.9 (m, 4 H, H$^{3,3'}$, H^{2}) ppm. ESI-MS: m/z = 1272.81 ([M – 2 PF$_6$]/2); calcd. for $C_{169}H_{1706}N_6O_{10}Ru/2$ 1273.1.

Acknowledgments

We thank the CNRS and the European Commission for financial support. We are also grateful to the French Ministry of Education for a fellowship (D. J.). M. K. thanks the JSPS Postdoctoral Fellowship for Research Abroad. We thank also Johnson Matthey Inc. for a loan of $RuCl_3$.

---

[1] a) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron Lett.* **1983**, *24*, 5095; b) J.-P. Collin, C. Dietrich-Buchecker, C. Hamann, D. Jouvenot, J.-M. Kern, P. Mobian, J.-P. Sauvage, in *From the molecular to the Nanoscale: Synthesis and Structure,* Comprehensive Coordination Chemistry II, vol. 6 (Eds.: M. Fujita, A. Powell), Elsevier, **2003**.

[2] a) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 189; b) C. O. Dietrich-Buchecker, J. Guilhem, C. Pascard, J.-P. Sauvage, *Angew. Chem. Int. Ed. Engl.* **1990**, *98*, 1154.

[3] a) D. A. Leigh, P. J. Lusby, S. J. Teat, A. J. Wilson, J. K. Y. Wong, *Angew. Chem.* **2001**, *113,* 1586; *Angew. Chem. Int. Ed.* **2001**, *40,* 1538; b) C. A. Hunter, P. C. Mayers, *Nature* **2001**, *411*, 763; c) L. Hogg, D. A. Leigh, P. J. Lusby, A. Morelli, S. Parsons, J. K. Y. Wong, *Angew. Chem. Int. Ed.* **2004**, *43,* 1217; d) A.-M. Fuller, D. A. Leigh, P. J. Lusby, I. D. H. Oswald, S. Parsons, D. B. Walker, *Angew. Chem. Int. Ed.* **2004**, *43,* 3914.

[4] C. Hamann, J.-M. Kern, J.-P. Sauvage, *Inorg. Chem.* **2003**, *42*, 1877–1883.

[5] K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308.

[6] a) J.-C. Chambron, A. Harriman, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1993**, *115*, 6109; b) J.-C. Chambron, A. Harriman, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1993**, *115*, 7419; c) J.-C. Chambron, V. Heitz, J.-P. Sauvage, *Bull. Soc. Chim. Fr.* **1995**, *132*, 340; d) M.-J. Blanco, J.-C. Chambron, V. Heitz, J.-P. Sauvage, *Org. Lett.* **2000**, *2*, 3051.

[7] T. J. Kidd, T. J. A. Loontjens, D. A. Leigh, *Angew. Chem. Int. Ed.* **2003**, *42,* 3379.

[8] a) V. Balzani, M. Gimez-Lipez, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405; b) J.-P. Collin, C. Dietrich-Buchecker, P. Gaviña, M. C. Jimenez-Molero, J.-P. Sauvage, *Acc. Chem. Res.* **2001**, *34*, 477 (special issue on molecular machines); c) V. Balzani, M. Venturi, A. Credi, *Molecular Devices and Machines: A Journey into the Nanoworld*, Wiley-VCH, Weinheim, **2003**; d) *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**; e) Molecular Machines and Motors (Ed.: J.-P. Sauvage), Structure and Bonding, vol. 99, Springer, New York, **2001**; f) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2000**, *112,* 3484.

[9] a) R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philp, H. G. Ricketts, J. F. Stoddart, *Angew. Chem. Int. Ed.* **1993**, *32*, 1301; b) A. M. Brower, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G. W. H. Wurpel, *Science* **2001**, *291*, 2124; c) D. A. Leigh, J. K. Y. Wong, F. Dehez, F. Zerbetto, *Nature* **2003**, *424*, 174.

[10] a) A. Livoreil, C. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 9399; b) D. J. Cardenas, A. Livoreil, J.-P. Sauvage, *J. Am. Chem. Soc.* **1996**, *118*, 11980; c) L. Raehm, J.-M. Kern, J.-P. Sauvage, *Chem. Eur. J.* 1999, 5, 3310; d) I. Poleschak, J.-M. Kern, J.-P. Sauvage, *Chem. Commun.* **2004**, 474.

[11] a) A. Livoreil, J.-P. Sauvage, N. Armaroli, L. Balzani, V. Flamigni, B. Ventura, *J. Am. Chem. Soc.* **1997**, *119*, 12114; b) N. Armaroli, V. Balzani, J.-P. Collin, P. Gavina, J.-P. Sauvage, B. Ventura, *J. Am. Chem. Soc.* **1999**, *121*, 4397; c) P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, K. R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi, S. Wenger, *Chem. Eur. J.* **2000**, *6*, 3558.

[12] a) A.-C. Laemmel, J.-P. Collin, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **1999**, 383; b) E. Baranoff, J.-P. Collin, J. Furusho, Y.

Furusho, A.-C. Laemmel, J.-P. Sauvage, *Inorg. Chem.* **2002**, *41*, 1215; c) P. Mobian, J.-M. Kern, J.-P. Sauvage, *Angew. Chem. Int. Ed.* **2004**, *43*, 2392; d) R. Schofield, J.-P. Collin, N. Gruber, J.-P. Sauvage, *Chem. Commun.* **2003**, 188.

[13] D. Pomeranc, D. Jouvenot, J.-C. Chambron, J.-P. Collin, V. Heitz, J.-P. Sauvage, *Chem. Eur. J.* **2003**, *9*, 4247.

[14] J.-P. Collin, D. Jouvenot, M. Koizumi, J.-P. Sauvage, *Inorg. Chem.* Submitted.

[15] H. W. Gibson, S.-H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bhela, *J. Org. Chem.* **1999**, *5*, 3310.

[16] Damien Jouvenot, PhD Thesis, Université Louis Pasteur, Strasbourg, June **2004**.

[17] V. Balzani, A. Credi, M. Venturi, *Coord. Chem. Rev.* **1998**, *171*, 3.

Received: December 08, 2004