Building [2]Catenanes around a Tris(diimine)ruthenium(2+) ([Ru(diimine)$_3$]$^{2+}$) Complex Core Used as Template

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Dedicated to *Duilio Arigoni* on the occasion of his 75th birthday

In the course of the last two decades, the use of transition metals as templates for constructing catenanes has almost exclusively been restricted to tetrahedral copper(I). The present work is dealing with an octahedral metal, ruthenium(II), coordinated to three bidentate chelates. Incorporation of two chelates (1,10-phenanthroline) in a ring allows to prepare a C_2-symmetric ruthenium complex, the two chelates being disposed *cis* to one another (see **14**$^{2+}$ and **16**$^{2+}$ in *Scheme 5* and *6*, resp.). The ring is large enough to accomodate a third chelate, thus allowing the metal-directed threading of a long fragment containing the third chelate (2,2′-bipyridine derivative; see **23**$^{2+}$ and **24**$^{2+}$ in *Scheme 8*). The last step consists of a ring-closing metathesis reaction with two terminal olefins. The two ruthenium(II)-complexed catenanes **25**$^{2+}$ and **26**$^{2+}$ were prepared by using this strategy, each containing a 42-membered ring interlocked to a larger macrocycle (50- or 63-membered ring) incorporating the two 1,10-phenanthroline chelates. It is expected that these catenanes can be set in motion under light-irradiation, thus behaving as photochemically driven molecular machines.

Introduction. – Until now, octahedral transition-metal centers have been rarely used as templates to construct topologically non-trivial molecules such as catenanes and knots. The use of a bisterpy (terpy = 2,2′:6′,2″-terpyridine) to make a [2]catenane [1] is an early example [1]. More recently, it was shown that it is possible to form [2]catenanes based on two tridentate ligands entwined around a first-row octahedral transition metal in an extremely efficient way [2]. The synthesis of knots has been driven by the use of two octahedral iron(II) centers, each metal being coordinated to two terpy derivatives [3]. Another spectacular example is the formation of an 'open' knot by using a long molecular thread incorporating three didentate chelates embedded around a zinc(II) center [4].

Until now, there was no example of a [2]catenane constructed around a tris-didentate chelate complex [5]. This is not surprising when we consider that the use of a tetrahedral copper(I) centre as a template to promote the synthesis of interlocked molecules has been particularly successful [6]. It may also be explained by the difficulty to entwine *two* threads using *three* chelates gathered around an octahedral transition-metal center. A fundamental difference between tetrahedral and octahedral systems is also related to chirality. Whereas tetrahedral complexes consisting of two intertwined ligands are by nature achiral, tris-didentate octahedral complexes lead to interesting configurational properties (Λ and Δ enantiomers). This particular feature could be used to afford chiral catenanes, which makes the use of a three-chelate transition-metal

complex as templating core especially attractive. We would now like to report the synthesis of [2]catenanes constructed around a $[Ru(diimine)_3]^{2+}$ complex core[1]).

The design of the system and the synthetic strategy are depicted in *Fig. 1*. The main feature of this system is that it is possible to insert an octahedral metal center in a ring incorporating two didentate chelates and subsequently to thread a molecular fragment bearing the third chelate through the ring. This latter step is of course driven by the coordination of the thread to the metal. Finally, the catenane is obtained in a single cyclization step.

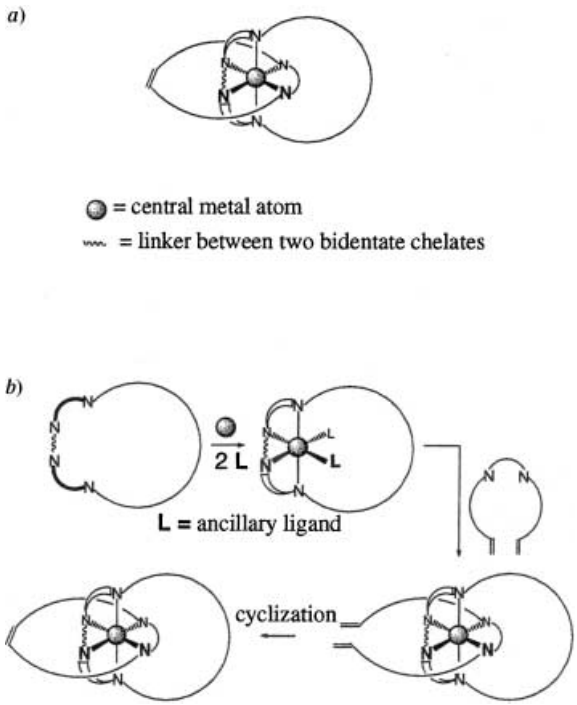


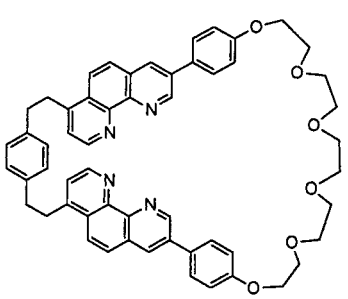
Fig. 1. a) *Schematic representation of a transition-metal-complexed [2]catenane containing two different rings* (one of the macrocycles incorporates a didentate chelate whereas the other contains two didentate coordinating fragments with a *cis* arrangement). b) *Synthetic strategy leading to the catenane* (complexation of the transition metal by the macrocycle incorporating two didentate moieties, threading of the didentate chelate through the cavity of the resulting complex, cyclization of the didentate fragment by using a ring-closing metathesis (RCM) reaction).

Tetradentate ligands consisting of two separate didentate ligands connected by an appropriate bridge and leading to C_2-symmetric complexes have already been described. Of particular interest are the chiragens, reported by *von Zelewsky* and co-workers [7] (a representative example of chiragen consists of two chiral bpy derivatives (bpy = 2,2′-bipyridine)) [7]. Our group has reported a related type of C_2-symmetric

[1]) A first preliminary communication has recently been published which describes one of the two catenanes described in the present work [5a]; the second one describes the synthesis of a catenane whose structure is close to that described in the present work, by using a double ring closing reaction in the last step [5b].

complexes, with a ligand specifically designed to afford helical complexes with strict control over the geometry of the compound. Interestingly, this ligand is able to form a $[Ru(phen)_3]^{2+}$-derivative complex (phen = 1,10-phenanthroline) with a clearly identified axis bearing chemical functions [8][9]. In the present work, the substitution positions on the bis-phen ligand are different from those of the previous axis-containing complex. From the CPK models, this new ligand seems to be more appropriate for the formation of cyclic complexes, as shown in *Scheme 1*.

The synthetic procedure starts with the preparation of two new large rings incorporating two phen units, *i.e.*, of **12** and **13**. The former consists of a 50-membered ring, whereas the latter, much larger, has a 63-membered ring. These two different macrocycles, on CPK models, look adapted to the formation of octahedral bis-phen complexes, the two phen fragments being disposed *cis* to one another in the metal-coordination sphere (see *Scheme 1*, **B**). Interestingly, the substitution positions of the 4-alkoxyphenyl group (at C(8) and C(8′) of the bis-phen moiety of these macrocycles) are determining. By contrast, if 4-methoxyphenyl groups are introduced *para* to the N-atoms of the phen moieties (at C(7) and C(7′)), wrapping the corresponding ligand around an octahedron leads to a system with a clearly identified axis, as shown in *Scheme 1* (see **A**). The choice of macrocycles **12** and **13** was dictated by CPK models and by synthesis considerations.



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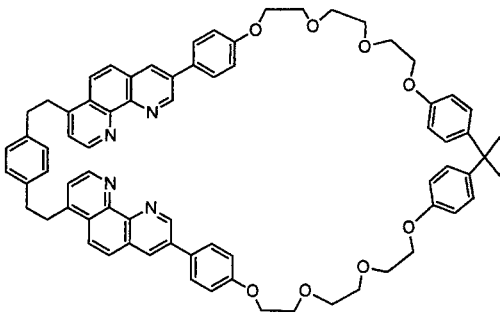

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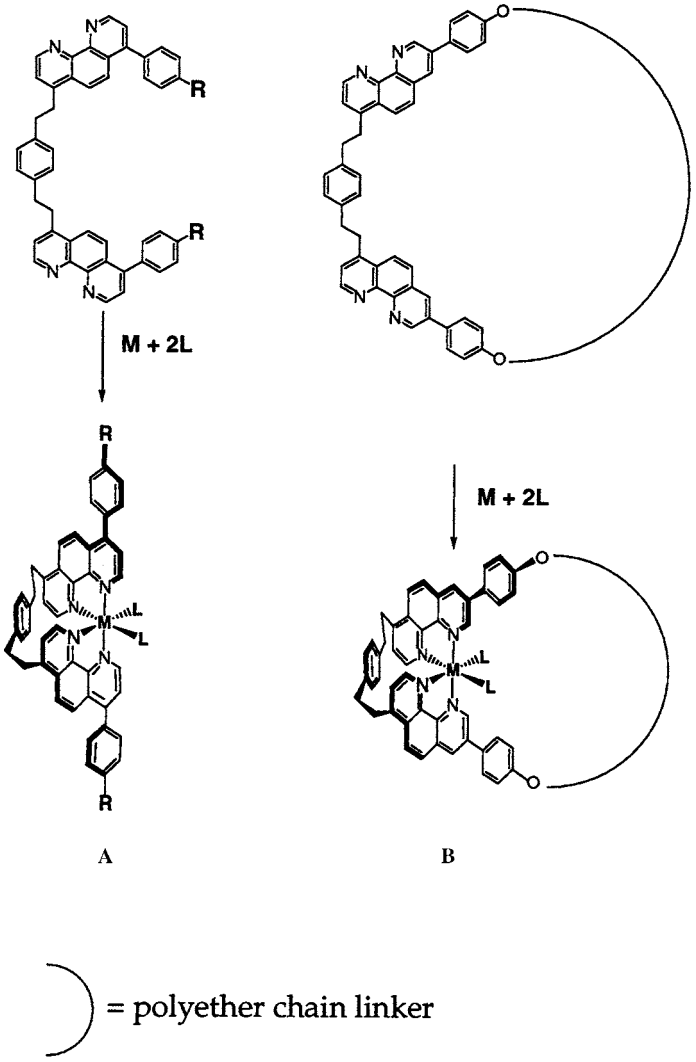
Macrocycles 12 and 13. – Macrocycles **12** and **13** were prepared in five steps from the 3-bromoquinolin-8-amine (**1**), which was itself synthetized according to the literature procedure from the commercially available 8-nitroquinoline [10][11]. The key intermediate, the bis-phenanthroline ligand **6**, bearing two terminal phenol functionalities, was obtained from **1** in four steps as shown in *Scheme 2*. Thus, **1** was transformed to **2** in 67% yield in the presence of methyl vinyl ketone and sulfuric acid. This procedure, described in the literature, is analogous to the classical *Skraup* reaction to make substituted 1,10-phenanthroline, but, in our case, the use of arsenic pentaoxide is unnecessary [12]. *Suzuki* coupling [13] between **2** and boronic ester **3** [14] yielded **4** in 80% yield after chromatography (alumina) and recrystallization. Ligand **5** was prepared by deprotonation of **4** with lithium diisopropylamide (LDA); the corresponding anion was then added to 0.5 equiv. of 1,4-bis(bromomethyl)benzene. The

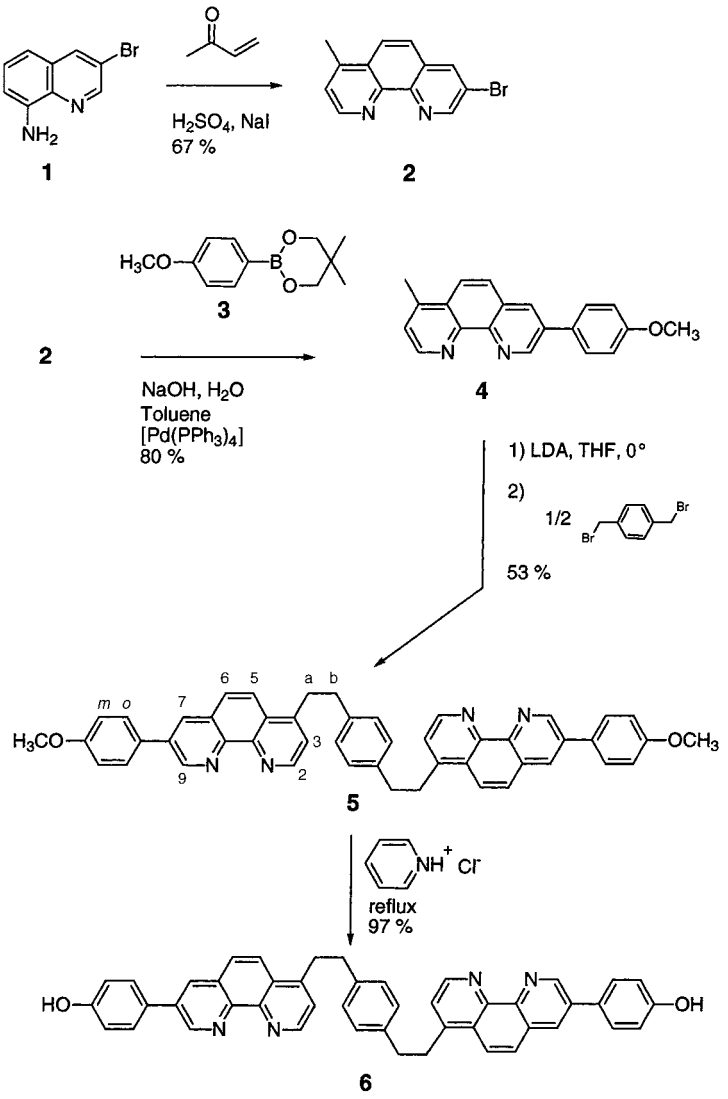
Scheme 1. *Formation of an Axial Complex* **A** *or a Macrocyclic Complex* **B**. In both cases, connection of two positions *para* to the N-atoms of the phen moieties by the $CH_2CH_2-C_6H_4-CH_2CH_2$ bridge leads to a *cis* arrangement. Introduction of aromatic groups RC_6H_4 at the other *para* positions leads to the axial complex **A**, whereas the macrocycle complex **B** can be obtained by utilizing the *meta* positions (C(8)) to attach the RC_6H_4 groups and, subsequently connecting these positions, the formation of a macrocyclic complex seems to be very favorable.



poorly soluble compound **5** was obtained in 53% yield after precipitation. By using a classical ether deprotection method [15], *i.e.*, treatment with pyridinium chloride in refluxing pyridine, **5** was converted to **6** in 97% yield.

The dihalogeno fragment needed for the synthesis of macrocycles **12** and **13** from **6** is either the diiodo derivative of pentaethylene glycol (for **12**) or the long-chain

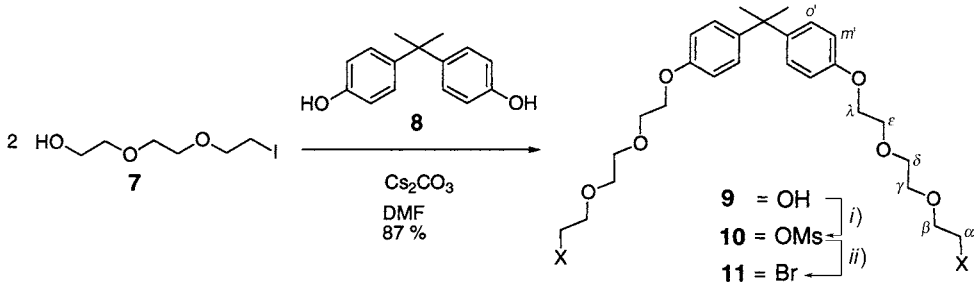
Scheme 2. *Synthesis of Key Intermediate* **6**



dibromide **11** bearing a 4,4′-isopropylidenebis[phenol]-derived moiety (for **13**). Dibromide **11** was easily synthesized starting from 4,4′-isopropylidenebis[phenol] (**8**) by connecting a long arm (from **7**) at each O-atom in basic medium (*Scheme 3*). The oily diol **9** obtained in 87% yield was then converted to the dimesylate derivative **10**, and finally to the dibromide **11**.

Macrocycles **12** and **13** were prepared in a similar manner by treating the bis-phenanthroline ligand **6** with the dihalogeno fragment under high-dilution conditions in basic medium (Cs_2CO_3) according to *Scheme 4* the products were isolated in 23 and

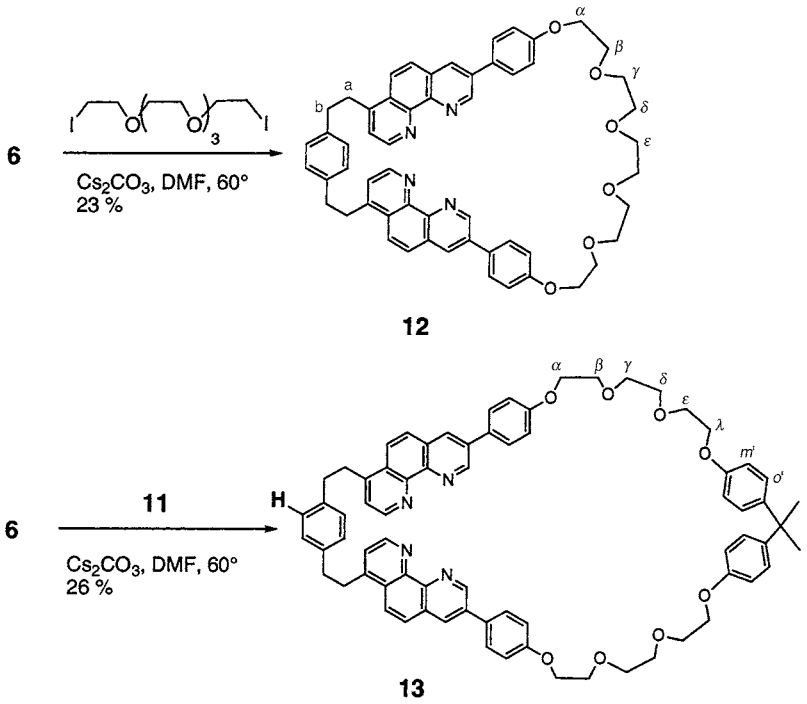
Scheme 3. *Synthesis of Dibromide* **11** *Containing the 4,4′-Isopropylidenebis[phenol]-Derived Moiety*



i) MsCl, Et_3N, CH_2Cl_2. *ii*) LiBr, acetone, reflux.

26% yield, respectively. These yields, although modest, are relatively satisfactory when we consider that neither ligand **6** nor the dihalogeno fragments, the diiodo derivative of pentaethylene glycol or **11**, contain in their backbone oriented groups able to favor the formation of macrocyclic species. Macrocycles **12** and **13** gave MS and NMR data in agreement with their structures (see *Exper. Part*).

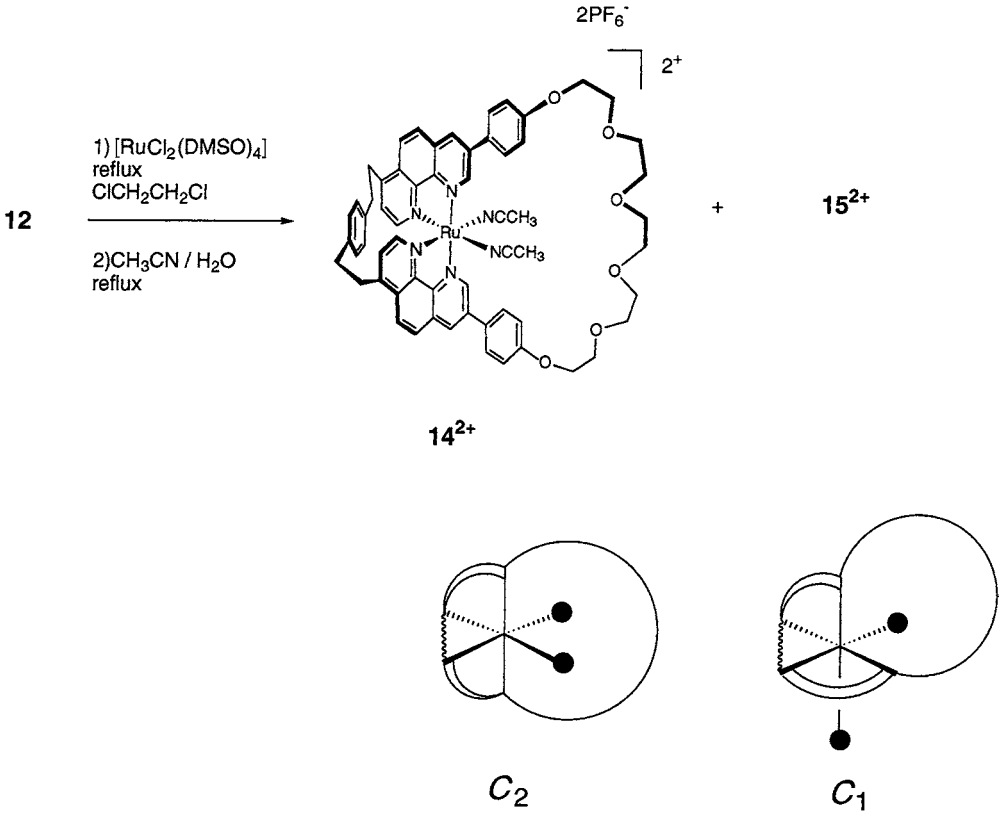
Scheme 4. *High-Dilution Reaction Leading to Macrocycles* **12** *and* **13**



Ruthenium(II) Complexes 14^{2+} and 16^{2+}. – Complex 14^{2+} was formed by reacting macrocycle **12** and $[RuCl_2(DMSO)_4]$ [16] in refluxing 1,2-dichloroethane under high-

dilution conditions (*Scheme 5*). The intermediate dichloro complex was not isolated; instead the crude reaction mixture was heated under reflux in MeCN/H_2O 80:12 (*v*/*v*) to replace the auxiliary chloro ligands by MeCN. On TLC of the obtained crude product, much to our surprise, two major spots were observed. The two corresponding products were isolated by chromatography, in 21% yield for the less-polar fraction, and in 26% yield for the more-polar fraction. Both products $\mathbf{14}^{2+}$ and $\mathbf{15}^{2+}$ (as PF_6^- salts) exhibited the same ES-MS with *m*/*z* 1205.3 ($[\mathbf{14}(PF_6)]^+$ or $[\mathbf{15}(PF_6)]^+$), 530.2 ($[\mathbf{14}]^{2+}$ or $[\mathbf{15}]^{2+}$), 489.1 ($[\mathbf{14} - 2\ MeCN]^{2+}$ or $[\mathbf{15} - 2\ MeCN]^{2+}$).

Scheme 5. *Complexation of* **12** *to Ruthenium(II) Giving Two Different Isomers* $\mathbf{14}^{2+}$ *and* $\mathbf{15}^{2+}$. The black dots represent the ancillary ligands (MeCN).



Single crystals suitable for X-ray crystallography were obtained for both ruthenium complex fractions by diffusion of a nonsolvent ($^iPr_2O$) into MeCN solution at room temperature. A view of the complex ion $\mathbf{14}^{2+}$ corresponding to the first fraction is shown in *Fig. 2*. It shows the coiling of the bis-chelate macrocycle around the Ru^{II} centre, to form a C_2-symmetric complex. The metal adopts a pseudo-octahedral geometry with Ru–N distances in the range 2.02–2.06 Å. The coordination sphere of the metal is slightly distorted, the N(6)–Ru–N(2) and N(2)–Ru–N(3) angles being 95.6 and 83.16°, respectively. Noteworthy is the O(1)–O(6) distance. The poly(oxyethane-1,2-

diyl) chain which connects O(1) to O(6) is made up of 5 C–C and 10 C–O bonds, and the 14.89 Å value observed for the O(1)–O(6) distance indicates that the polyoxyethane-1,2-diyl 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, but it will certainly not allow significant bending of the $CH_2(CH_2OCH_2)_4CH_2$ fragment.

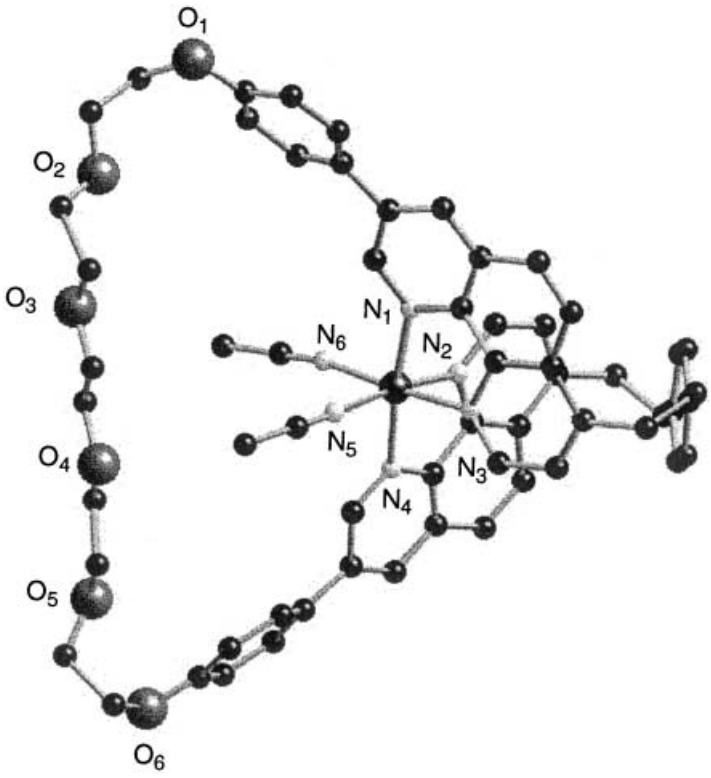


Fig. 2. *X-Ray crystal structure of* $\mathbf{14}^{2+}$. H-Atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Ru–N(1) 2.06, Ru–N(2) 2.04, Ru–N(3) 2.06, Ru–N(4) 2.05, Ru–N(5) 2.02, Ru–N(6) 2.05, N(1)–Ru–N(2) 96.84, N(1)–Ru–N(3) 79.02, N(1)–Ru–N(4) 173.77, N(1)–Ru–N(5) 90.02, N(1)–Ru–N(6) 98.19, N(2)–Ru–N(3) 83.16, N(2)–Ru–N(4) 79.07, N(2) Ru–N(5)172.73, N(2)–Ru–N(6) 95.60, N(3)–Ru–N(4) 95.74, N(3)–Ru–N(5) 95.81, N(3)–Ru–N(6) 176.81, N(4)–Ru–N(5) 93.90, N(4)–Ru–N(6) 86.94, N(5)–Ru–N(6) 85.66.

The structure of the complex ion $\mathbf{15}^{2+}$ corresponding to the second fraction was unexpected. Contrary to the C_2-symmetric complex $\mathbf{14}^{2+}$, in $\mathbf{15}^{2+}$, the macrocycle adopts a C_1 symmetry as shown in *Fig. 3*. The coordination sphere in $\mathbf{15}^{2+}$ is more distorted than in the C_2-symmetric analogue. The N(1)–Ru–N(4) angle is 159.95°, whereas the same angle in $\mathbf{14}^{2+}$ is 173.77°. It is also interesting to note that the polyether chain is less stretched in the case of $\mathbf{15}^{2+}$ (distance O(1)–O(6) 7.91 Å), by comparison with $\mathbf{14}^{2+}$ (distance O(1)–O(6) 14.89 Å).

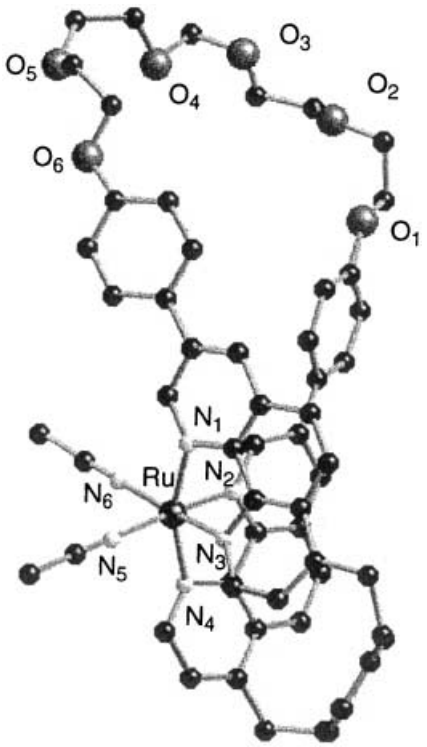
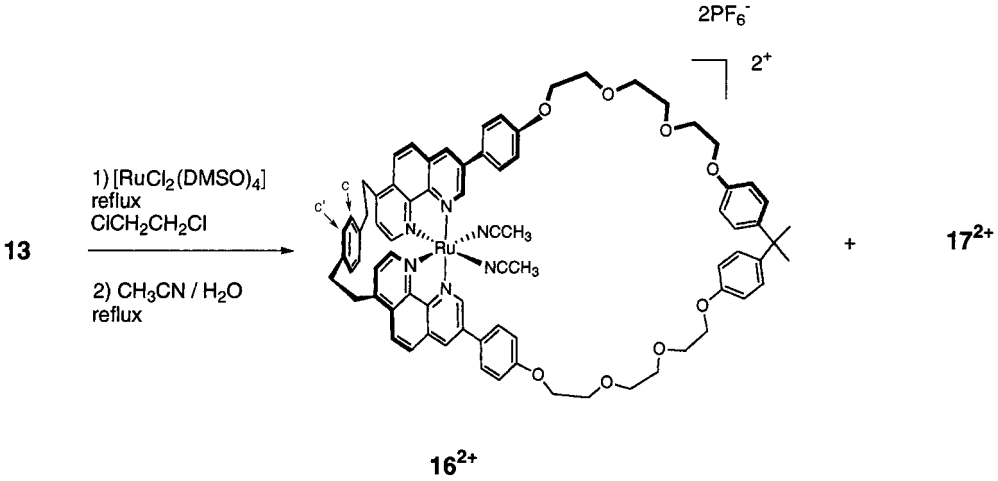


Fig. 3. *X-Ray crystal structure of* **15**$^{2+}$. H-Atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Ru–N(1) 2.07, Ru–N(2) 2.05, Ru–N(3) 2.03, Ru–N(4) 2.08, Ru–N(5) 2.03, Ru–N(6) 2.03, N(1)–Ru–N(2) 86.94, N(1)–Ru–N(3) 79.11, N(1)–Ru–N(4) 159.95, N(1)–Ru–N(5) 98.18, N(1)–Ru–N(6) 94.97, N(2)–Ru–N(3) 91.91, N(2)–Ru–N(4) 79.31, N(2)–Ru–N(5) 174.78, N(2)–Ru–N(6) 91.56, N(3)–Ru–N(4) 86.75, N(3)–Ru–N(5) 89.96, N(3)–Ru–N(6) 172.96, N(4)–Ru–N(5) 95.94, N(4)–Ru–N(6) 99.89, N(5)–Ru–N(6) 87.06.

In contrast to the formation of **14**$^{2+}$, coordination of **13** to Ru^{II} was performed without using high-dilution conditions. A solution of macrocycle **13** ($2.2 \cdot 10^{-4}$ M) and 1 equiv. of $[RuCl_2(DMSO)_4]$ in 1,2-dichloroethane was refluxed under Ar during 4 h (*Scheme 6*). After evaporation, the residue was dissolved and refluxed for 4 h in $MeCN/H_2O$ 80 : 20. Again, two compounds were isolated after column chromatography (silica gel). The less-polar one was obtained in 25% yield and attributed to the C_2-symmetric complex **16**$^{2+}$, due to the simplicity of his NMR spectra. The protons of the phenylene bridge in the free macrocycle **13** are homotopic (see *Scheme 4*). Splitting of the corresponding signal in the ^{1}H-NMR of **16**$^{2+}$ was observed, indicating in that case the diastereotopic nature of these protons. The more-polar compound **17**$^{2+}$ was isolated in 25% yield and its structure determined by comparing the very complicated aromatic zone of its ^{1}H-NMR spectrum with the corresponding aromatic zone of **15**$^{2+}$. These two regions were very similar, and this observation is in full accordance with the C_1 symmetry of the bis-acetonitrile complex **17**$^{2+}$.

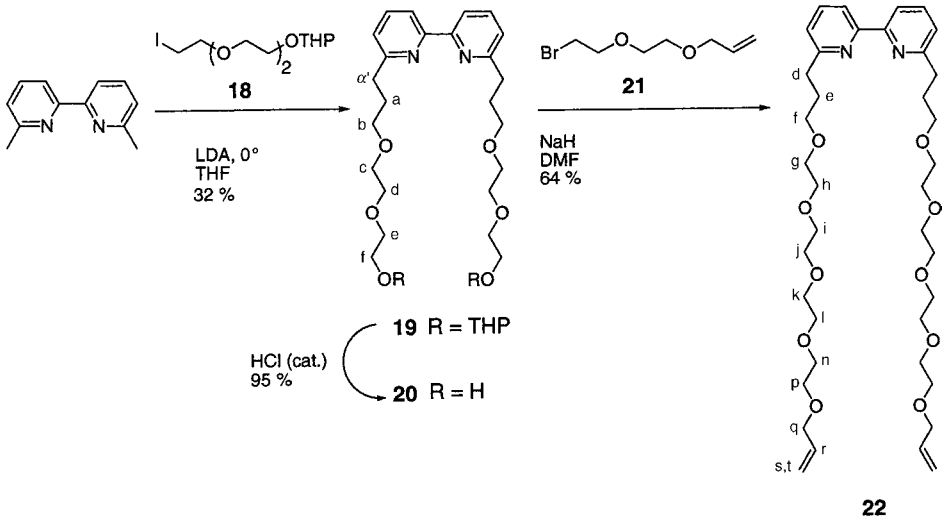
Scheme 6. *Complexation of* **13** *to Ruthenium(II) Giving Two Different Isomers* $\mathbf{16}^{2+}$ *and* $\mathbf{17}^{2+}$



It is noteworthy that the complexes $\mathbf{14}^{2+}$, and $\mathbf{16}^{2+}$ are rare examples of a bis-phen, or, more generally, a bis-didentate octahedral complex with a *cis*-arrangement, embedded in a ring.

Threading Reaction and Formation of Catenanes. – For the threading reaction, the 2,2′-bipyridine derivative **22** was used. This ligand, substituted at C(6) and C(6′) by two long chains terminated by olefinic groups, was prepared in three steps from 6,6′-dimethyl-2,2′-bipyridine (dmbp), as described in *Scheme 7*. By deprotonation of dmbp with LDA in THF, followed by addition of 2 equiv. of THP-protected 2-[2-(2-

Scheme 7. *Synthesis of the 'Thread Chelate', the Bipyridine Derivative* **22**

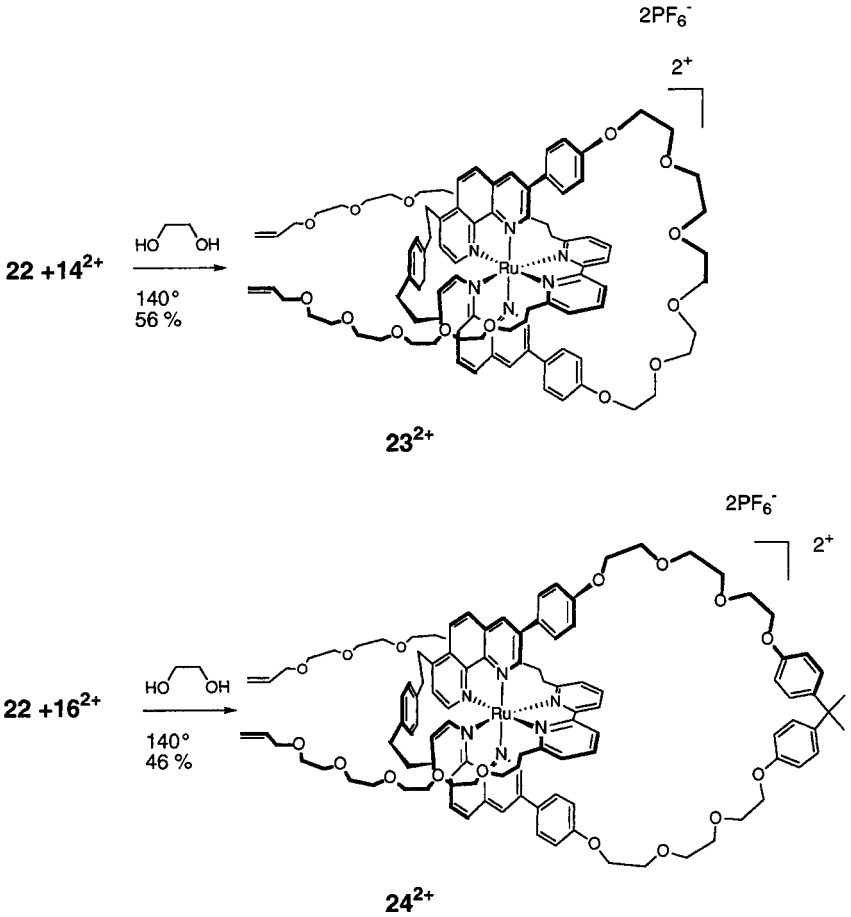


iodoethoxy)ethoxy]ethanol **18** (THP = tetrahydro-2*H*-pyran-2-yl), **19** was obtained in 32% yield. Deprotection of **19** afforded diol **20** in 95% yield. This diol was converted into **22** following the *Williamson* methodology (NaH, DMF) by reaction with 2 equiv. of the polyether chain **21** bearing a terminal olefin moiety (64% yield).

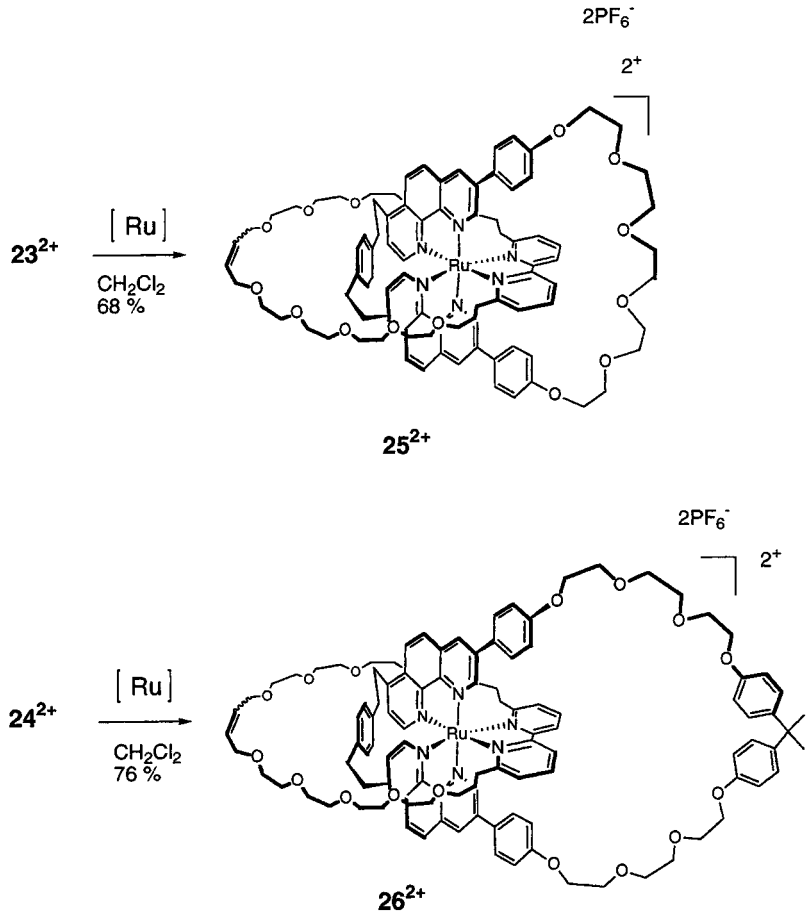
The reaction conditions for threading the third chelate **22** into $\mathbf{14}^{2+}$ or $\mathbf{16}^{2+}$ were the same for both complexes (*Scheme 8*). Threading took place under relatively harsh conditions (ethylene glycol; 140°), and the catenane precursors $\mathbf{23}^{2+}$ and $\mathbf{24}^{2+}$ were obtained in surprisingly good yield (56 and 46%, resp.). This step, which is identical to passing a long thread (44 atoms) through the eye of a needle, represents also a key reaction whose success was not guaranteed, especially when one considers that it requires severe conditions.

The final catenanes $\mathbf{25}^{2+}$ and $\mathbf{26}^{2+}$ were prepared from $\mathbf{23}^{2+}$ and $\mathbf{24}^{2+}$, respectively, by ring-closing metathesis (RCM) [17]. A CH_2Cl_2 solution of complex $\mathbf{23}^{2+}$ or $\mathbf{24}^{2+}$ and $[RuCl_2=CHPh(PCy_3)_2]$ (20 mol-%) were stirred under Ar for three days (*Scheme 9*).

Scheme 8. *Threading Reaction Leading to Precatenanes* $\mathbf{23}^{2+}$ *and* $\mathbf{24}^{2+}$



Scheme 9. *Ring Closing Methathesis Reactions Affording the Catenanes* $\mathbf{25}^{2+}$ *and* $\mathbf{26}^{2+}$



Catenanes $\mathbf{25}^{2+}$ and $\mathbf{26}^{2+}$ were isolated in 68 and 76% yield, respectively. These preparative yields are in the same range as those obtained for making other transition-metal-containing catenanes and knots by means of a similar RCM-based approach [18]. Catenanes $\mathbf{25}^{2+}$ and $\mathbf{26}^{2+}$, which are red-orange solids, were fully characterized by various spectroscopic techniques. The ES-MS and ^{1}H-NMR spectra afford clear evidence for their structure.

Another probe to confirm that the synthetic route afforded the expected catenanes is the comparison of the ^{1}H-NMR spectra of the complexes isolated during the synthesis. *Fig. 4* shows the ^{1}H-NMR signals of the aromatic protons of the complexions $\mathbf{14}^{2+}$, $\mathbf{23}^{2+}$, and $\mathbf{25}^{2+}$. A similar comparison can be done for catenane $\mathbf{26}^{2+}$ (not shown). The most-relevant change in going from $\mathbf{14}^{2+}$ to $\mathbf{23}^{2+}$ is the strong upfield shift of the signal of H–C(9,9′) of the bis-phenanthroline core ($\Delta\delta = 1.43$ ppm). This could be explained by the ring-current effect of the bipyridine unit on these two protons when the third chelate is threaded into the macrocyclic cavity. When going from the

precatenane $\mathbf{23}^{2+}$ to the catenane itself $\mathbf{25}^{2+}$, disappearance of the two signals of the olefinic protons is observed, and, simultaneously, one new signal, which appears as a *m* at δ 5.77, is assigned to the olefinic protons at the C=C bond formed by the RCM reaction; however, a definitive assignment of the (*Z*)- or (*E*)-configuration of the C=C bound can not be made. Moreover, the simplicity of the ^{1}H-NMR spectrum of $\mathbf{25}^{2+}$ is in accordance with the expected C_2 symmetry of the catenane.

Conclusions. – The two new [2]catenanes $\mathbf{25}^{2+}$ and $\mathbf{26}^{2+}$ were synthesized by using the three-dimensional-template effect of an octahedral transition metal (Ru^{II}). The

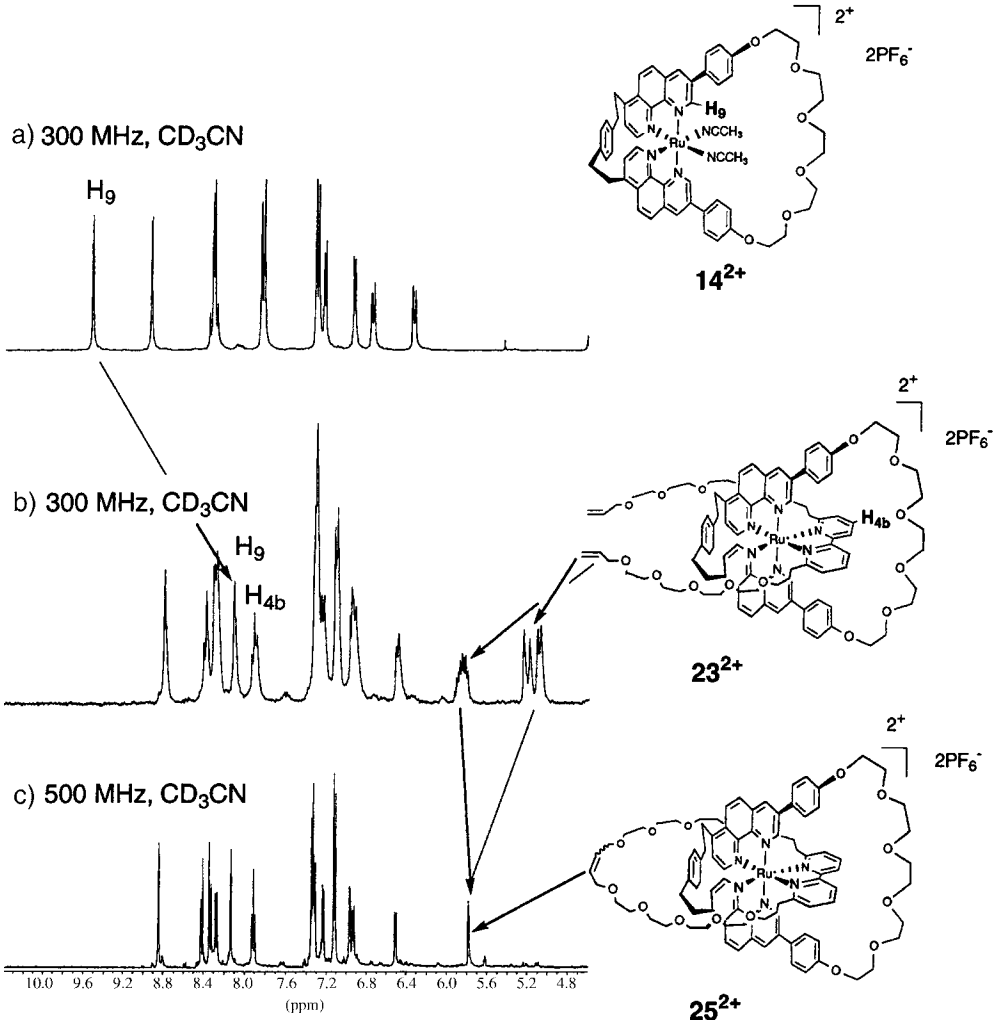


Fig. 4. *^{1}H-NMR Region of aromatic protons of* a) $\mathbf{14}^{2+}$, b) $\mathbf{23}^{2+}$, *and* c) $\mathbf{25}^{2+}$. H_9 = H−C(9,9′) of the bis-phenanthroline core; H_{4b} = H−C(4,4′) of the bipyridine moiety.

strategy is such that each catenane consists of two different rings: the smaller, 42-membered ring incorporates a bpy fragment, whereas the other, 50- or 63-membered ring contains the two other diimine chelates of the octahedral metal complex (1,10-phenanthroline). Interestingly, due to the chiral nature of a tris-chelate complex, both [2]catenanes are chiral, with a C_2 symmetry. These catenanes are with no doubt the first examples of an interlocking ring system built on a tris-didentate chelate transition-metal complex used as template. The photochemical properties of these two ruthenium(II)-complexed [2] catenanes are now under study, in relation to light-driven molecular machines [19]. They are expected to undergo large amplitude motions under the action of a photonic stimulus.

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Experimental Part

General. Oxygen-sensitive reactions were conducted under a positive pressure of Ar by *Schlenk* techniques. All solvents and reagents were of the highest quality available and were used as received without further purification. CC = Column chromatography. Absorption spectra: *Uvikon XS* spectrometer, λ_{max} (log ε) in nm. ^{1}H-NMR Spectra: *Bruker AVANCE-300* (300 MHz), *Bruker AVANCE-400* (400 MHz), or *Bruker AVANCE-500* (500 MHz) spectrometer; deuterated solvent as lock and residual solvent as internal reference; δ in ppm, J in Hz. MS (in m/z): *VG-BIOQ* triple-quadrupole spectrometer for electrospray ionization (ES) (positive mode); *ZAB-HF (FAB)* spectrometer for fast-atom bombardment (FAB).

3-Bromo-7-methyl-1,10-phenanthroline (**2**). But-3-en-2-one (1.7 ml, 21 mmol) was added dropwise to 70% sulfuric acid (8.5 ml) containing 3-bromoquinolin-8-amine (**1**; 2.90 g, 13 mmol) and a cat. amount of NaI (0.019 g, 0.13 mmol). The soln. became dark and viscous after heating at 110° for 1 h. After cooling, the pH of the soln. was raised to 8 by addition of 1M Na_2CO_3 (100 ml). The precipitate that appeared was extracted with CH_2Cl_2 (150 ml). The resulting org. phase was treated with charcoal, dried ($MgSO_4$), and evaporated, and the residual solid purified by CC (SiO_2, CH_2Cl_2/MeOH): **2** (2 g, 67%). White solid. M.p. 170°. ^{1}H-NMR (200 MHz, $CDCl_3$): 9.2 (*d*, ^4J = 2.2, H–C(2)); 9.06 (*d*, ^3J = 4.6, H–C(9)); 8.43 (*d*, ^4J = 2.2, H–C(4)); 8.08 (*d*, ^3J = 9.1, H–C(6), or H–C(5)); 7.77 (*d*, ^3J = 9.1, H–C(5) or H–C(6)); 7.51 (*d*, ^3J = 3.9, H–C(8)); 2.82 (*s*, Me). Anal. calc. for $C_{13}H_9BrN_2$: C 57.16, H 3.32, N 10.25; found: C 57.20, H 3.10, N 10.09.

3-(4-Methoxyphenyl)-7-methyl-1,10-phenanthroline (**4**). Under Ar, 2M aq. NaOH (200 ml) was transferred by canula to toluene (200 ml) containing **2** (8.29 g, 30.4 mmol) and tetrakis(triphenylphosphine)palladium (1.77 g, 1.52 mmol). After addition of a MeOH soln. (15 ml) of **3** (8.81 g, 45 mmol), the mixture was heated overnight at 50°. After cooling, the aq. phase was extracted with CH_2Cl_2 (3×). The combined org. phase was dried ($MgSO_4$) and evaporated. The residual solid was purified by CC (alumina, CH_2Cl_2/MeOH 99:1), and crystallized from toluene: **4** (7.35 g, 80%). Beige solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 9.39 (*d*, ^4J = 2.4, H–C(9)); 9.03 (*d*, ^4J = 4.4, H–C(2)); 8.35 (*d*, ^4J = 2.4, H–C(7)); 8.04 (*d*, ^3J = 9.1, H–C(5)); 7.85 (*d*, ^3J = 9.1, H–C(6)); 7.72 (*d*, ^3J = 8.8, 2 H_o); 7.48 (*d*, ^4J = 4.4, H–C(3)); 7.10 (*d*, ^3J = 8.8, 2 H_m); 2.82 (*s*, Me); 3.92 (*s*, MeO).

4,4′-(1,4-Phenylenediethane-2,1-diyl)bis[8-(4-methoxyphenyl)-1,10-phenanthroline] (**5**). Under Ar, 1.4M BuLi (1.7 ml) was added at 0° to freshly distilled ^{i}Pr$_2$NH (0.3 ml) in THF (7 ml). The mixture was stirred at 0° for 1 h. A soln. of **4** (700 mg, 2.33 mol) in THF (17.5 ml) was transferred *via* canula at 0° to this soln. (→ immediately dark-blue). After 20 min stirring at r.t., the soln. was cooled again to 0°, and 1,4-bis(bromomethyl)benzene (307 mg, 1.15 mmol) in THF (9 ml) was added. After stirring overnight at r.t., EtOH (30 drops) and H_2O (100 ml) were successively added. The precipitate that appeared was filtered off and washed with CH_2Cl_2: **5** (587 mg, 53%). Yellow solid. ^{1}H-NMR (200 MHz, $CDCl_3$)[2]: 9.42 (*d*, ^4J = 2.2, 2 H, H–C(9,9′)); 9.08 (*d*, ^3J = 4.4, 2 H, H–C(2,2′)); 8.33 (*d*, ^4J = 2.2, 2 H, H–C(7,7′)); 8.04 (*d*, ^3J = 9.1, 2 H, H–C(5,5′)); 7.83 (*d*, ^3J = 9.1, 2 H, H–C(6,6′)); 7.74 (*d*, ^3J = 8.6, 4 H_o); 7.40 (*d*, ^3J = 4.6, 2 H, H–C(3,3′)); 7.14 (*s*, C_6H_4); 7.12 (*d*, ^3J = 8.6, 4 H_m); 3.93 (*s*, 2 MeO); 3.45 (*m*, 4 H, H–C(a,a′)); 3.11 (*m*, 4 H, H–C(b,b′)). MALDI-TOF-MS: 703 ([**5** + H]$^+$; calc. 702.3).

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[2]) Arbitrary numbering; see *Schemes 2–4*, *6*, and *7*.

4,4′-[1,4-Phenylenebis(ethane-2,1-diyl[1,10]phenanthroline-7,3-diyl]bis[phenol] (**6**). Under stirring, 12M HCl (28 ml) was added to pyridine (26 ml). H_2O was distilled off from the mixture until its internal temp. rose to 220°. The anh. pyridinium chloride soln. was cooled to 150°. Then **5** (1.73 g, 2.4 mmol) was added as a solid under Ar flush, and the mixture was refluxed (220°) under Ar for 4 h. The mixture was cooled to 90°, hot H_2O was added, and the resulting suspension was poured into lukewarm H_2O (100 ml). The precipitate was filtered off, washed with H_2O, suspended in EtOH/H_2O 2:1 (300 ml), and neutralized with 0.1M NaOH. The suspension was filtered off and dried for three days under high vacuum: **6** (1.61 g, 97%). Green solid. ^{1}H-NMR (200 MHz, (D_6)DMSO)[2]): 9.86 (*s*, 2 OH); 9.40 (br. *d*, 2 H, H–C(8,8′)); 9.00 (*d*, ^3J = 4.4, 2 H, H–C(9,9′)); 8.71 (br. *d*, 2 H, H–C(4,4′)); 8.4 (*d*, ^3J = 8.4, 2 H, H–C(5,5′), or H–C(6,6′)); 8.0 (*d*, ^3J = 8.4, 2 H, H–C(5,5) or H–C(6,6′)); 7.83 (*d*, ^3J = 8.4, 4 H_o); 7.61 (*d*, ^3J = 4.5, 2 H, H–C(8,8′)); 7.23 (*s*, C_6H_4); 7.01 (*d*, ^3J = 8.4, 4 H_m); 3.05 (*m*, 4 H, CH_2CH_2). FAB-MS: 675.2 ([**6** + H]$^+$; calc. 674.2).

*15,16,18,19,21,22,24,25,27,28,43,44,49,50-Tetradecahydro-10,13:30,33:45,48-trietheno-9,4,7:34,36,39-bis(methenonitrilomethyno)[1,4,7,10,13,16]hexaoxacyclohexatetracontino[26,27-*c*:37,36-*c*′]dipyridine* (**12**). Compound **6** (1.5 g, 2.22 mmol) and 1,14-diiodo-3,6,9,12-tetraoxatetradecane (1.21 g, 2.66 mmol) were dissolved under Ar in DMSO (50 ml) and DMF (110 ml), and the soln. was added at a controlled rate (0.1 drop s^{-1}) *via* a dropping funnel to a suspension of Cs_2CO_3 (2.9 g, 8.88 mmol) in DMF (300 ml) maintained at 60°. Then the soln. was further stirred and heated for 4 h. DMF was evaporated, the residue dissolved in CH_2Cl_2, the soln. washed with H_2O (7×) to remove the remaining DMSO, the org. phase evaporated, and the residue purified by CC (alumina, CH_2Cl_2/MeOH 98:2): **12** (450 mg, 23%). White powder. ^{1}H-NMR (400 MHz, CD_2Cl_2)[2]): 9.36 (*d*, ^4J = 2.3, 2 H, H–C(9,9′)); 9.08 (*d*, ^3J = 4.5, 2 H, H–C(2,2′)); 8.12 (*d*, ^4J = 2.3, 2 H, H–C(7,7′)); 7.67 (*d*, ^3J = 6.6, 4 H_o); 7.59 (*d*, ^3J = 4.5, 2 H, H–C(3,3′)); 7.41 (*d*, ^3J = 9.1, 2 H, H–C(5,5′)); 7.34 (*d*, ^3J = 9.1, 2 H, H–C(6,6′)); 7.05 (*d*, ^3J = 6.6, 4 H_m); 6.82 (*s*, $CH_2C_6H_4CH_2$); 4.10 (*m*, 4 H, H_α); 3.81 (*m*, 4 H, H_β); 3.70 (*m*, 12 H, $H_{\gamma,\delta,\varepsilon}$); 3.33 (*t*, ^3J = 7.3, 4 H, H–C(a,a′)); 3.06 (*t*, ^3J = 7.3, 4 H, H–C(b,b′)). ES-MS: 877.6 ([**12** + H]$^+$; calc. 876.3).

2,2′-[(1-Methylethylidene)bis(4,1-phenyleneoxyethane-2,1-diyloxyethane-2,1-diyloxy]bis[ethanol] (**9**). A degassed soln. of 4,4′-(1-methylethylidene)bis[phenol] (1.22 g, 5.3 mmol) and Cs_2CO_3 (7 g, 21.5 mmol) in anh. DMF (50 ml) was heated at 60°. A soln. of 2-[2-(2-iodoethoxy)ethoxy]ethanol (**7**; 3.47 g, 13.4 mmol) in DMF (5 ml) was added to this degassed soln. The mixture was stirred under Ar at 60° during 24 h. After evaporation, the residue was extracted with CH_2Cl_2; the org. layer washed with H_2O, dried (Na_2CO_3), and evaporated, and the residue purified by CC (Al_2O_3, CH_2Cl_2/MeOH, 98:2): **9** (2.31 g, 87%). White oil. ^{1}H-NMR (300 MHz, $CDCl_3$)[2]): 7.1 (*d*, ^3J = 8.9, 4 $H_{m'}$); 6.8 (*d*, ^3J = 8.9, 4 $H_{o'}$); 4.09 (*t*, ^3J = 4.5, 4 H_λ); 3.83 (*t*, ^3J = 4.5, 4 H_ε); 3.68 (*m*, 12 H, $H_{\beta,\gamma,\delta}$); 3.58 (*t*, ^3J = 4.1, 4 H, H_α); 1.61 (*s*, 2 Me).

2,2′-[(1-Methylethylidene)bis(4,1-phenyleneoxyethane-2,1-diyloxyethane-2,1-diyloxy]bis[ethanol] Dimethanesulfonate (**10**). A soln. of **9** (2.32 g, 4.7 mmol) and freshly distilled Et_3N (4 ml, 28 mmol) in freshly distilled CH_2Cl_2 (50 ml) was cooled to −5° under Ar, and methanesulfonyl chloride (1.1 ml, 28 mmol) was added slowly. After 4 h at −5°, the mixture was brought to r.t., washed with H_2O, and dried (Na_2SO_4), and evaporated: **10** (2.855 g, 93%). Oil. ^{1}H-NMR (300 MHz, $CDCl_3$)[2]): 7.1 (*d*, ^3J = 8.9, 4 $H_{m'}$); 6.8 (*d*, ^3J = 8.9, 4 $H_{o'}$); 4.36 (*t*, ^3J = 2.8, 4 H_α); 4.08 (*t*, ^3J = 4.9, 4 H_λ); 3.82 (*t*, ^3J = 4.5, 4 H_ε); 3.77 (*t*, ^3J = 2.8, 4 H_β); 3.69 (*m*, 8 H, $H_{\gamma,\delta}$), 3.03 (*s*, 2 MeS); 1.62 (*s*, 2 Me).

1,1′-(1-Methylethylidene)bis[4-[2-[2-(2-iodoethoxy)ethoxy]ethoxy]benzene] (**11**). The soln. of **10** (2.85 g, 4 mmol) in acetone (80 ml) was refluxed for 4 h in the presence of a large excess of LiBr (3.8 g, 44 mmol). After evaporation, the crude mixture was taken up in CH_2Cl_2/H_2O, the org. phase dried (Na_2SO_4) and evaporated, and the residue purified CC (Al_2O_3, CH_2Cl_2): **11** (2.5 g, 92%). White oil. ^{1}H-NMR (300 MHz, $CDCl_3$)[2]): 7.1 (*d*, ^3J = 8.9, 4 $H_{m'}$); 6.8 (*d*, ^3J = 8.9, 4 $H_{o'}$); 4.12 (*t*, ^3J = 4.7, 4 H_λ); 3.8 (*m*, 8 H, $H_{\varepsilon,\alpha}$); 3.72 (*m*, 8 H, $H_{\gamma,\delta}$); 3.45 (*t*, ^3J = 6.3, 4 H_β); 1.61 (*s*, 2 Me).

*15,16,18,19,21,22,34,35,37,38,40,41,56,57,62,63-Hexadecahydro-28,28-dimethyl-10,13:24,27:29,32:43,46:58,61-pentaetheno-9,4,7:47,49,52-bis(methenonitrilomethyno)-28*H*-[1,4,7,10,20,23,26,29]octaoxacyclononapentacontino[39,40-*c*:50,49-*c*′]dipyridine* (**13**). As described for **12**, with **6** (0.4 g, 4 mmol), **11** (0.4 g, 6.5 mmol), DMSO (60 ml), DMF (40 ml), Cs_2CO_3 (2 g, 6 mmol), and DMF (200 ml). CC (alumina, CH_2Cl_2/MeOH 99:1) gave **13** (177 mg, 26%). Glassy solid. ^{1}H-NMR (300 MHz, $CDCl_3$)[2]): 9.36 (*d*, ^4J = 2.3, 2 H, H–C(9,9′)); 9.0 (*d*, ^3J = 4.5, 2 H, H–C(2,2′)); 8.20 (*d*, ^4J = 2.3, 2 H, H–C(7,7′)); 7.71 (*d*, ^3J = 9.1, 2 H, H–C(5,5′) or H–C(6,6′)); 7.61 (2*d*, 6 H, 4 H_o); 7.31 (*d*, ^3J = 4.5, 2 H, H–C(3,3′)); 7.11–6.99 (2*d*, 8 H, ^3J = 9.2, 4 $H_{m'}$, 4 $H_{o'}$); 6.80 (*d*, *s*, $CH_2C_6H_4CH_2$, 4 H_m); 4.15 (*m*, 8 H, $H_{\alpha,\lambda}$), 3.84 (*m*, 8 H, $H_{\beta,\varepsilon}$); 3.74 (*s*, 8 H, $H_{\gamma,\delta}$); 3.46 (*t*, ^3J = 6.9, 4 H, H–C(a,a′)); 3.00 (*t*, ^3J = 6.9, 4 H, H–C(b,b′)); 1.59 (*s*, 2 Me). FAB-MS: 1131.8 ([**13** + H]$^+$; calc. 1131.5).

*Bis(acetonitrile){15,16,18,19,21,22,24,25,27,28,43,44,49,50-tetradecahydro-10,13:30,33:45,48-trietheno-9,4,7:34,36,3 9-bis(methenonitrilomethyno)[1,4,7,10,13,16]hexaoxacyclohexatetracontino[26,27-*c*:37,36-*c*′]dipyri-*

dine-κN³,κN⁴⁰,κN⁵⁴,κN⁶¹]ruthenium(2+) Bis[hexafluorophosphate(1−)] ([**14**]$(PF_6)_2$ and [**15**]$(PF_6)_2$) Macrocycle **12** (126 mg, 0.143 mmol) was dissolved in 1,2-dichloroethane (70 ml) under Ar. $[RuCl_2(DMSO)_4]$ (0.143 mmol) was dissolved in 1,2-dichloroethane (70 ml) under Ar. The two solns. were simultaneously added within 3 days to refluxing 1,2-dichloroethane (650 ml) under Ar in a high-dilution device under vigourous magnetic stirring. The crude of the reaction was then dissolved in a MeCN/H_2O 80:20 (100 ml). After 3 h of heating, the purple mixture had turned to a yellow-orange soln. The reaction was stopped, and aq. sat. $K(PF_6)$ soln. (50 ml) was added. The MeCN was evaporated to afford a black precipitate which was isolated by filtration. This solid was purified by CC (silica gel, MeCN/H_2O/sat. aq. KNO_3 soln. 100:5:1). The first fraction yielded, after anion exchange (PF_6/NO_3), the C_2-isomer, [**14**]$(PF_6)_2$ (42 mg, 21%). Red-orange solid. Crystals for X-ray analysis were obtained by slow diffusion of $^iPr_2O$ into a soln. of [**14**]$(PF_6)_2$ in MeCN (see *Table*). ^{1}H-NMR (300 MHz, MeCN)[2]): 9.54 (*d*, ^4J = 1.8, 2 H, H−C(9,9′)); 8.95 (*d*, ^4J = 1.8, 2 H, H−C(7,7′)); 8.4–8.2 (2*d*, ^3J = 9.1, 4 H, H−C(5,5′), H−C(6,6′)); 7.86 (*d*, ^3J = 8.6, 4 H_o); 7.32 (*d*, ^3J = 8.6, 4 H_m); 7.24 (*d*, ^3J = 5.3, 2 H, H−C(2,2′)); 6.94 (*d*, ^3J = 5.3, 2 H, H−C(3,3′)); 6.76 (*d*, ^3J = 8.1, 2 H, H−C(c′)); 6.36 (*d*, ^3J = 8.1, 2 H, H−C(c)); 4.59 (*m*, 2 H, H_α or $H_{\alpha'}$); 4.31 (*m*, 2 H, H_α or $H_{\alpha'}$); 4–3 (*m*, 24 H, $H_{\beta,\gamma,\delta,\varepsilon}$, H−C(a,a′,b,b′)); 2.26 (*s*, 2 MeCN). ES-MS: 1205 ([**14**$(PF_6]^+$, calc. 1204), 530.2 ([**14**$]^{2+}$, calc. 529.5), 489.1 ([**14** − 2MeCN$]^{2+}$, calc. 488.5).

Table. *X-Ray Experimental Data for* [**14**] *$(PF_6)_2$ and* [**15**]$(PF_6)_2$

	[**14**]$(PF_6)_2$	[**15**]$(PF_6)_2$
Formula	$C_{124}H_{124}F_{24}N_{14}O_{14}P_4Ru_2$	$C_{62}H_{63}F_{12}N_7O_7P_2Ru$
	$C_{120}H_{116}N_{12}O_{12}Ru_2 \cdot 4PF_6 \cdot 2\,CH_3CN \cdot 2\,H_2O$	$C_{60}H_{58}N_6O_6Ru \cdot 2\,PF_6 \cdot CH_3CN \cdot H_2O$
M_r	2816.45	1409.23
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a [Å]	17.0461(2)	15.2790(1)
b [Å]	18.0355(2)	15.9553(2)
c [Å]	24.1003(3)	15.9775(2)
α [°]	102.988(5)	94.990(5)
β [°]	94.447(5)	117.763(5)
γ [°]	101.215(5)	109.815(5)
V [Å^3]	7024.7(1)	3099.1(3)
Z	2	2
Color	red	light red
Crystal dim. [mm]	0.12 × 0.10 × 0.10	0.10 × 0.10 × 0.06
D_{calc} [gcm^{-3}]	1.33	1.51
F(000)	2884	1444
μ [mm^{-1}]	0.353	0.400
Trans. min., max.	0.958, 0.965	0.9468, 1.0000
Temp. [K]	173	173
Wavelength [Å]	0.71073	0.71073
Radiation	MoK_α graphite monochromated	MoK_α graphite monochromated
Diffractometer	*KappaCCD*	*KappaCCD*
Scan mode	ϕ scans	ϕ scans
hkl limits	−23.3, −25.24, −26.33	0.21, −22.21, −22.19
θ limits [°]	2.5, 30.03	2.5, 30.07
Number of data measured	56477	18083
Number of data with $I > 3\sigma(I)$	18135	13474
Number of variables	1672	820
R	0.123	0.063
R_w	0.149	0.074
G.o.f.	1.224	1.013
Largest peak in final	1.199	

The second fraction yielded, after anion exchange, the C_1-isomer [**15**]$(PF_6)_2$ (51 mg, 26%). Red-orange solid. Crystals for X-ray analysis were obtained as for [**14**]$(PF_6)_2$: *Table.* ES-MS: 1205.3 ([**15**(PF_6)]$^+$; calc. 1204),530.2 ([**15**]$^{2+}$, calc. 529.5), 489.2 ([**15** $-$ 2CH_3CN]$^{2+}$; calc. 488.5).

*Bis(acetonitrile){15,16,18,19,21,22,34,35,37,38,40,41,56,57,62,63-hexadecahydro-28,28-dimethyl-10,13:24,27:29,32:43,46:58,61-pentaetheno-9,4,7:47,49,52-bis(methenonitrilomethyno)-28*H*-[1,4,7,10,20,23,26,29]octaoxacyclononapentacontino[39,40-*c*:50,49-*c*′]dipyridine-*κ*N^{53},*κ*N^{67},*κ*N^{78}]ruthenium(2+) Bis[hexafluorophosphate(1 −)]* ([**16**$(PF_6)_2$ and [**17**$(PF_6)_2$). Compound **13** (70 mg, $6.1 \cdot 10^{-5}$ mol) and [$RuCl_2(DMSO)_4$] (0.143 mmol) were dissolved in 1,2-dichloromethane (280 ml). The soln. was degassed and refluxed under Ar for 4 h (yellow → dark violet). The dark violet soln. was evaporated and this crude was dissolved in (100 ml) of MeCN/H_2O 80 : 20 (100 ml). After 2 h of heating, the purple mixture turned to a yellow-orange soln. The reaction was stopped, and aq. sat. K(PF_6) soln. (50 ml) was added. The MeCN was evaporated to afford a precipitate, which was isolated by filtration. This solid was purified by CC (silica gel, MeCN/H_2O/sat. aq. KNO_3 soln. 100 : 5 : 1). The first fraction, after anion exchange, gave [**16**$(PF_6)_2$ (25 mg, 25%). Red-orange solid. ^{1}H-NMR (300 MHz, MeCN)^2): δ 9.81 (*d*, ^4J = 1.7, 2 H, H−C(9,9′)); 9.03 (*d*, ^4J = 1.7, 2 H, H−C(7,7′)); 8.4–8.3 (2*d*, ^3J = 9.1, 4 H, H−C(5,5′), H−C(6,6′)); 8.06 (*d*, ^3J = 8.7, 4 H_o); 7.32 (*d*, ^3J = 8.6, 4 H_m); 7.24 (*d*, ^3J = 5.5, 2 H, H−C(2,2′)); 6.94 (*d*, ^3J = 5.3, H−C(3,3′)); 6.82 (*d*, ^3J = 8.8, 4 H_o); 6.66 (*d*, ^3J = 8.8, 6 H, 2 H−C(c′), 4 $H_{m'}$); 6.36 (*d*, ^3J = 8.1, 2 H, H−C(c)); 4.41 (*m*, 4 H_α); 4–3 (*m*, 28 H, $H_{\beta,\gamma,\delta,\varepsilon,\lambda}$, CCH_2CH_2C); 2.08 (*s*, MeCN); 1.31 (*s*, Me_3CN). ES-MS: 1459.6 ([**16**(PF_6)]$^+$; calc. 1459), 657.4 ([**16**]$^{2+}$; calc. 657), 636.8 ([**16**(PF_6) − CH_3CN]$^+$; calc. 636.5), 636.5 ([**16** − 2CH_3CN]$^+$; calc. 616).

Furthermore, the second fraction from the chromatography led to the C_1-isomer (25 mg, [**17**$(PF_6)_2$ 25%). Red-orange solid.

*6,6′-Bis{3-[2-[2-(tetrahydro-2*H*-pyran-2-yl)ethoxy]ethoxy}propyl]-2,2′-bipyridine* (**19**). Under Ar, 1.7M BuLi (5.75 ml, 9.76 mmol) was added dropwise to a soln. of ^{i}Pr$_2$NH (1.36 ml, 9.76 mmol) in distilled THF (20 ml). A degassed soln. of 6,6′-dimethyl-2,2′-bipyridine (0.75 g, 4.07 mmol) in distilled THF (20 ml) was cooled to −78°, and the freshly prepared LDA soln. was added *via* cannula (yellow → green). The mixture was stirred during 2 h at −78°, after which the mixture was stirred at r.t. during 2 min. The deep purple soln. was cooled to −78° again. Meanwhile, a soln. of tetrahydro-2-{2-[2-(2-iodoethoxy)ethoxy]ethoxy}-2*H*-pyran (**18**) (3.07 g, 8.95 mmol) in distilled THF (20 ml) was cooled to −78° and degassed. This soln. was then transferred under Ar onto the 6,6′-dimethyl-2,2′-bipyridine soln. at −78° (→ dark red). The soln. was stirred overnight. The final soln. was hydrolyzed with H_2O (80 ml). Some CH_2Cl_2 was added, the org. layer dried ($MgSO_4$), and evaporated, and the product purified by CC (alumina, Et_2O/MeOH 99 : 1): **19** (798 mg, 31.8%). Yellow oil. ^{1}H-NMR (200 MHz, $CDCl_3$)^2): 8.21 (*d*, ^3J = 7.6, 2 H, H−C(3,3′)); 7.65 (*t*, ^3J = 7.7, 2 H, H−C(4,4′)); 7.12 (*d*, ^3J = 7.5, 2 H, H−C(5,5′)); 4.60 (*t*, ^3J = 3.0, 2 H of THP); 3.85 (*m*, 4 H of THP); 3.70–3.30 (*m*, 20 H, H_{b-f}); 2.89 (*t*, ^3J = 8.0, 4 $H_{\alpha'}$); 2.05 (*m*, 4 H_a); 1.8–1.3 (*m*, 12 H of THP).

2,2′-[2,2′-Bipyridine-6,6′-diylbis(propane-3,1-diyloxyethane-2,1-diyloxy)]bis[ethanol] (**20**). A soln. of **19** (840 mg, 1.19 mmol) in EtOH (150 ml) was refluxed, and five drops of 37% HCl soln. were added. The reflux was maintained for 16 h. After evaporation, the residue was dissolved in CH_2Cl_2 and neutralized with an aq. $NaHCO_3$ soln. (100 ml). The org. layer was dried and evaporated: **20** (507 mg, 95.5%), which was used without further purification. ^{1}H-NMR (200 MHz, $CDCl_3$)^2): 8.22 (*d*, ^3J = 7.7, 2 H, H−C(3,3′)); 7.69 (*t*, ^3J = 7.7, 2 H, H−C(4,4′)); 7.14 (*d*, ^3J = 7.5, 2 H, H−C(5,5′)); 3.71–3.53 (*m*, 20 H, $H_{b,c,d,e,f}$); 2.92 (*t*, ^3J = 8.0, 4 $H_{\alpha'}$); 2.05 (*m*, 4 H_a).

6,6′-Bis(4,7,10,13,16-pentaoxanonadec-18-en-1-yl)-2,2′-bipyridine (**22**). A soln. (10 ml) of DMF containing NaH (120 mg, 0.234 mmol) and **20** (300 mg, 0.6 mmol) was stirred for 1 h at 60°. Then **21** (559 mg, 2.6 mmol) in DMF (5 ml) was added dropwise, and heating was continued overnight. DMF was evaporated, the crude taken up with CH_2Cl_2, the soln. washed with H_2O, dried ($MgSO_4$), and evaporated, and the oily residue purified by CC (silica gel, CH_2Cl_2/MeOH 97 : 3): **22** (304 mg, 64%). Pale oil. ^{1}H-NMR (300 MHz, $CDCl_3$)^2): 7.71 (*d*, ^3J = 7.7, 2 h, H−C(3,3′)); 7.66 (*t*, ^3J = 7.7, 2 H, H−C(4,4′)); 7.12 (*d*, ^3J = 7.7, 2 H, H−C(5,5′)); 5.89 (*m*, 2 H_r); 5.18 (*m*, 4 H, $H_{s,t}$); 3.98 (*m*, 2 H_q); 3.60 (*m*, 36 H, $H_{f,g,h,i,j,k,l,n,p}$); 2.92 (*t*, ^3J = 7.9, 4 H_d); 2.09 (*m*, 4 H_e).

*[6,6′-Bis(4,7,10,13,16-pentaoxanonadec-18-en-1-yl)-2,2′-bipyridine-*κ*N^{1},*κ*N$^{1'}$][15,16,18,19,21,22,24,25,27,28,43,44,49,50-tetradecahydro-10,13:30,33:45,48-trietheno-9,4,7:34,36,39-bis(methenonitrilomethyno)[1,4,7,10,13,16]hexaoxacyclohexatetracontino[26,27-*c*:37,36-*c*′]dipyridine-*κ*N^{3},*κ*N^{40},*κ*N^{54},*κ*N^{61}]ruthenium(2+) Bis[hexafluorophosphate(1 −)]* ([**23**$(PF_6)_2$). Complex [**14**$(PF_6)_2$ (38 mg, $2.7 \cdot 10^{-5}$ mol) and **22** (23 mg, $3.3 \cdot 10^{-5}$ mol) were heated together in a degassed soln. of ethylene glycol (5 ml) for 2 h at 140°. After cooling, aq. sat. K(PF_6) soln. (5 ml) was added. The formed precipitate was isolated by filtration, washed with H_2O, and purified by CC (silica gel, MeCN/H_2O/sat. aq. KNO_3 soln. 100 : 7 : 1). Anion exchange (NO_3/PF_6) yielded [**23**$(PF_6)_2$ (30 mg, 56%). Orange solid. ^{1}H-NMR (300 MHz, CD_3CN)^2): 8.80 (*d*, ^4J = 1.7, 2 H, H−C(7,7′)); 8.40 (*d*, ^3J = 9.0, 2 H,

H–C(5,5′)); 8.29 (*d*, 4 H, H–C(6,6′), H–C(3,3′)(bpy)); 8.11 (*d*, ^4J = 1.8, 2 H, H–C(9,9′)); 7.91 (*t*, ^3J = 8.2, 2 H, H–C(4,4′)(bpy)); 7.32 (*m*, 6 H, 4 H_o, H–C(2,2′)); 7.24 (*d*, ^3J = 7.0, 2 H, H–C(5,5′)(bpy)); 7.11 (*d*, ^3J = 8.8, 4 H_m); 6.94 (*m*, 4 H, H–C(3,3′), H–C(c′)); 6.50 (*d*, ^3J = 7.7, 2 H, H–C(c)); 5.85 (*m*, 2 H_r); 5.3–5.0 (*m*, 4 H, $H_{s,t}$); 4.5 (*m*, 2 H, H_α or $H_{\alpha1}$); 4.25 (*m*, 2 H, H_α or $H_{\alpha1}$); 3.96 (*m*, 6 H, H_q, $H_{b'}$); 3.7–3 (*m*, 54 H, $H_{\beta,\gamma,\delta,\varepsilon}$, $H_{g,h,i,j,k,l,n,p}$, $H_{a',b,a}$); 2.5 (*m*, 4 H_f); 1.3 (*m*, 6 H, H_d or $H_{d'}$, H_e); 1.0 (*m*, 2 H, H_d or $H_{d'}$). FAB-MS: 1827.7 ([**23**(PF_6)]$^+$; calc. 1827.7), 1682.7 ([**23**]; calc. 1682.7), 841.3 ([**23**]$^{2+}$; calc. 841.3).

[6,6′-Bis(4,7,10,13,16-pentaoxanonadec-18-en-1-yl)-2,2′-bipyridine-κN^{1},$\kappa N^{1'}$*][15,16,18,19,21,22,34,35,37,38,40,41,56,57,62,63-hexadecahydro-28,28-dimethyl-10,13:24,27:29,32:43,46:58,61-pentaetheno-9,4,7:47,49,52-bis(methenonitrilomethyno)-28*H*-[1,4,7,10,20,23,26,29]octaoxacyclononapentacontino[39,40-*c*:50,49-c′]dipyridine-*κN^{3},κN^{53},κN^{67},κN^{78}*]ruthenium(2+) Bis[hexafluorophosphate(1−)]* ([**24**$(PF_6)_2$). As described for [**23**$(PF_6)_2$, with [**16**]/$(PF_6)_2$ (25 mg, $1.5\cdot10^{-5}$ mol), **22** (17 mg, $2.4\cdot10^{-5}$ mol), ethylene glycol (3 ml), and aq. sat.K(PF_6) soln. (8 ml): [**24**$(PF_6)_2$ (16 mg, 46%). Orange solid. ^{1}H-NMR (300 MHz, $CD_3CN)^2$): 8.88 (*d*, ^4J = 1.4, 2 H, H–C(7,7′)); 8.43–8.29 (*d* and *s*, ^3J = 9.2, 6 H, H–C(5,5′), H–C(6,6′), H–C(9,9′)); 7.86 (*d*, ^3J = 7.86, 2 H, H–C(3,3′)(bpy)); 7.86 (*t*, ^4J = 7.86, 2 H, H–C(4,4′)(bpy)); 7.59 (*d*, ^3J = 8.8, 4 H_o); 7.21 (*m*, ^3J = 8, 2 H, H–C(5,5′)(bpy)); 7.16 (*d*, ^3J = 8.07, 4 H_m); 7.11–7.07 (2*d*, ^3J = 8.7, 6 H, 4 $H_{o'}$, H–C(2,2′)); 6.94 (*d*, ^3J = 5.6, 2 H, H–C(3,3′)); 6.8 (*d*, ^3J = 8.7, 6 H, 4 $H_{m'}$, H–C(c′)); 6.39 (*d*, ^3J = 7.8, 2 H, H–C(c)); 5.9 (*m*, 2 H_r); 5.3–5.0 (*m*, 4 H, $H_{s,t}$); 4.3 (*m*, 2 H, H_α or $H_{\alpha1}$); 4.25 (*m*, 2 H, H_α or $H_{\alpha1}$); 3.96 (*m*, 6 H, H_q, $H_{b'}$); 3.7–3.0 (*m*, 58 H, $H_{\beta,\gamma,\delta,\varepsilon,\lambda}$, $H_{g,h,i,j,k,l,n,p}$, $H_{a,a',b}$); 2.5 (*m*, 4 H_f); 1.45 (*s*, 2 Me); 1.3 (*m*, 6 H, H_d or $H_{d'}$, H_e); 1.2 (*m*, 2 H, H_d or $H_{d'}$). ES-MS: 2081.9 ([**24**(PF_6)]$^+$; calc. 2082.1), 968.5 ([**24**]$^{2+}$; calc. 968.5).

[24Z)-10,13,16,19,22,27,30,33,36,39-Decaoxa-47,48-diazatricyclo[41.3.1.1^{2,6}*]octatetraconta-1(47),2,4,6(48),24,43,45-heptaene-*κN^{47},κN^{48}*][15,16,18,19,21,22,24,25,27,28,43,44,49,50-tetradecahydro-10,13:30,33:45,48-trietheno-9,4,7:34,36,39-bis(methenonitrilomethyno)[1,4,7,10,13,16](hexaoxacyclohexatetracontino[26,27-*c*:37,36-c′]dipyridine-*κN^{3},κN^{40},κN^{54},κN^{61}*]ruthenium(2+) Bis[hexafluorophosphate(1−)]* ([**25**$(PF_6)_2$). Complex [**23**$(PF_6)_2$, (29 mg, $1.5\cdot10^{-5}$ mol) and $[Ru(=CHPh)]Cl_2(PCy_3)_2$] (1 mg) were dissolved in freshly distilled CH_2Cl_2 to yield a 0.01M soln. which was stirred at r.t. for several days. Each two days the reaction was stopped, the mixture analyzed by ^{1}H-NMR, and more ruthenium catalyst added. After one week, a total of 6 mg of the *Grubbs* catalyst was added, and the reaction was finished. The mixture was submitted to CC (silica gel, MeCN/H_2O/sat. aq. KNO_3 soln. 100:10:2) and then to anion exchange: [**25**$(PF_6)_2$ (20 mg, 68%). Orange crystalline solid. UV/VIS (MeCN): 341 (4.39), 455 (3.99). ^{1}H-NMR (500 MHz, $CD_3CN)^2$): 8.84 (*d*, ^4J = 1.8, 2 H, H–C(7,7′)); 8.41 (*d*, ^3J = 9.1, 2 H, H–C(5,5′)); 8.31 (*d*, ^3J = 9.1, 2 H, H–C(6,6′)); 8.27 (*d*, ^3J = 8.0, 2 H, H–C(3,3′)(bpy)); 8.13 (*d*, ^4J = 1.8, 2 H, H–C(9,9′)); 7.91 (*dd*, ^3J = 8.0, 2 H, H–C(4,4′)(bpy)); 7.34 (*d*, ^3J = 8.8, 4 H_o); 7.32 (*d*, ^3J = 5.6, 2 H, H–C(2,2′)); 7.24 (*d*, ^3J = 7.0, 2 H, H–C(5,5′)(bpy)); 7.12 (*d*, ^3J = 8.8, 4 H_m); 6.96 (*d*, ^3J = 5.6, 2 H, H–C(3,3′)); 6.94 (*d*, ^3J = 9.9, 2 H, H–C(c′)); 6.51 (*d*, ^3J = 9.9, 2 H, H–C(c)); 5.78 (*m*, H_r, 88% *cis*); 5.63 (*m*, H_r, 12% *trans*); 4.5 (*m*, 2 H, H_α or $H_{\alpha1}$); 4.2 (*m*, 2 H, H_α or $H_{\alpha1}$); 3.96 (*m*, 6 H, H_q and $H_{b'}$); 3.7–3.0 (*m*, 54 H, $H_{\beta,\gamma,\delta,\varepsilon}$, $H_{g,h,i,j,k,l,n,p}$, $H_{b,a,a'}$); 2.5 (*m*, 4 H_f); 1.3 (*m*, 6 H, H_d or $H_{d'}$, and H_e); 1.0 (*m*, H_d or $H_{d'}$). 2D-ROESY NMR. ES-MS: 1799.7 ([**25**(PF_6)]$^+$; calc. 1799.7), 827.4 ([**25**]$^{2+}$; calc. 827.8).

[(24Z)-10,13,16,19,22,27,30,33,36,39-Decaoxa-47,48-diazatricyclo[41.3.1.1^{2,6}*]octatetraconta-1(47),2,4,6,(48),24,43,45-heptaene-*κN^{47},κN^{48}*][15,16,18,19,21,22,34,35,37,38,40,41,56,57,62,63-hexadecahydro-28,28-dimethyl-10,13:24,27:29,32:43,46:58,61-pentaetheno-9,4,7:47,49,52-bis(methenonitrilomethyno)-28*H*-[1,4,7,10,20,23,26,29]-octaoxacyclononapentacontino[39,40-*c*:50,49-c′]dipyridine-*κN^{3},κN^{53},κN^{67},κN^{78}*]ruthenium(2+) Bis[hexafluorophosphate(1−)]* ([**26**$(PF_6)_2$). Complex [**24**$(PF_6)_2$, (16 mg, $7.2\cdot10^{-6}$ mol) and $[Ru(=CHPh)Cl_2(PCy_{3)2}]$ (1.2 mg, 20 mol-%) were dissolved at r.t. in freshly distilled CH_2Cl_2 to yield a 0.1M soln. which was stirred for several days. After one day, the reaction was stopped, and more catalyst was added (2 mg). After three days, a total of 4 mg of the *Grubbs* catalyst was added, and the reaction was finished. The mixture was submitted to CC (silica gel, MeCN/H_2O/sat. aq. KNO_3 soln. 100:7:1) and then to anion exchange [**26**$(PF_6)_2$ (12 mg, 76%). Orange crystalline solid. UV/VIS (MeCN): 460 (4.1). ^{1}H-NMR (400 MHz, CD_3CN): 8.88 (*d*, ^4J = 1.7, 2 H, H–C(7,7′)); 8.40–8.29 (*d*, ^3J = 9.2, 6 H, H–C(5,5′), H–C(6,6′), H–C(9,9′)); 8.12 (*d*, ^3J = 7.7, 2 H, H–C(3,3′)(bpy)); 7.73 (*t*, ^3J = 7.7, 2 H, H–C(4,4′)); 7.56 (*d*, ^3J = 8.7, 4 H_o); 7.15 (*d*, ^3J = 7.7, 2 H, H–C(5,5′)(bpy)); 7.13 (*d*, ^3J = 8.8, 4 H_m); 7.07–7.0 (2*d*, ^3J = 8.8, ^3J = 5.4, 6 H, H–C(2,2′), 4 $H_{o'}$); 7.99 (*d*, ^3J = 5.4, 2 H, H–C(3,3′)); 7.12 (2*d*, ^3J = 8.8, 6 H, 4 $H_{m'}$, 2 H–C(c′)); 6.36 (*d*, ^3J = 9.2, 2 H, H–C(c)); 5.78 (*m*, H_r); 4.25 (*m*, 4 H_α); 4.00 (*m*, 8 H, H_λ, H_q); 3.79 (*m*, 4 H_β); 3.7–3 (*m*, 32 H, $H_{\gamma,\delta,\varepsilon}$, $H_{j,k,l,n,p}$); 3.47 (*m*, 4 H_i); 3.28 (*m*, 4 H_h); 3.05 (*m*, 4 H_g); 4.0-3.0 (*m*, 8 H, $H_{a,a',b,b'}$); 2.5 (*m*, 4 H_f); 1.3 (*m*, 6 H, H_d or $H_{d'}$, H_e); 1.40 (*s*, 2 Me); 1.2 (*m*, 2 H, H_d or $H_{d'}$). 2D-ROESY NMR. ES-MS: 2053.7 ([**26**(PF_6)]$^+$, calc. 2053.1), 954.4 ([**26**]$^{2+}$; calc. 954.05).

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