Unexpected Synthesis of an 8-Shaped Macrocycle Instead of an Interlocking-Ring System

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Introduction

Since the early days of template synthesis using transition metal complexes to build macrocycles, the field has undergone spectacular development. From Schiff base ligands, originally used by Busch and co-workers,[1−3] the family of organic fragments which have been utilized and incorporated into cyclic structures has gradually expanded.

Several years ago, a three-dimensional template strategy affording interlocking ring structures[4] (catenanes) and knots[5] in high yields was proposed. The preparation of a [2]catenane is based on a very simple concept. In a first step, one forms a molecular "tangle" by intertwining two threads around a transition metal center. Subsequently, the four ends of the tangle are interconnected in the appropriate fashion so as to produce the interlocking ring topology. (See Figure 1).

This construction principle, using a 2,9-diaryl-1,10-phenanthroline in combination with copper(I) as assembling and templating center has proven particularly successful.[6] The catenane so obtained contains a tetrahedral coordination site and is particularly well suited to transition metals in low oxidation states[7] (copper(I), nickel(I), cobalt(I), etc.). To prepare interlocking ring ligands able to complex metals in high oxidation states, 6-coordinate systems are preferable. This prompted us to use 2,2′:6′,2″-terpyridine (terpy) motifs. Due to the harsh conditions required for the cyclization step, however, the intertwined precursor had to be a ruthenium(II) complex which could not subsequently be demetalated.[8] Very recently, a molecular knot incorporating $Fe(terpy)_2^{2+}$ fragments has been reported.[9]

By combining the high efficiency of the methodology based on the ring-closing metathesis[10] (RCM) of olefins and the high stability of bis(terpyridine)iron(II) complexes, we planned to construct catenanes by following the strategy depicted in Figure 2 (route a).

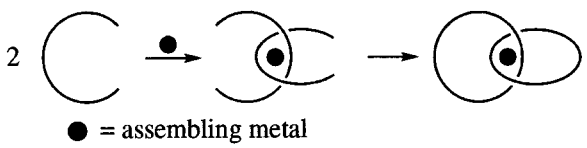

Figure 1. Template synthesis of a [2]catenane.

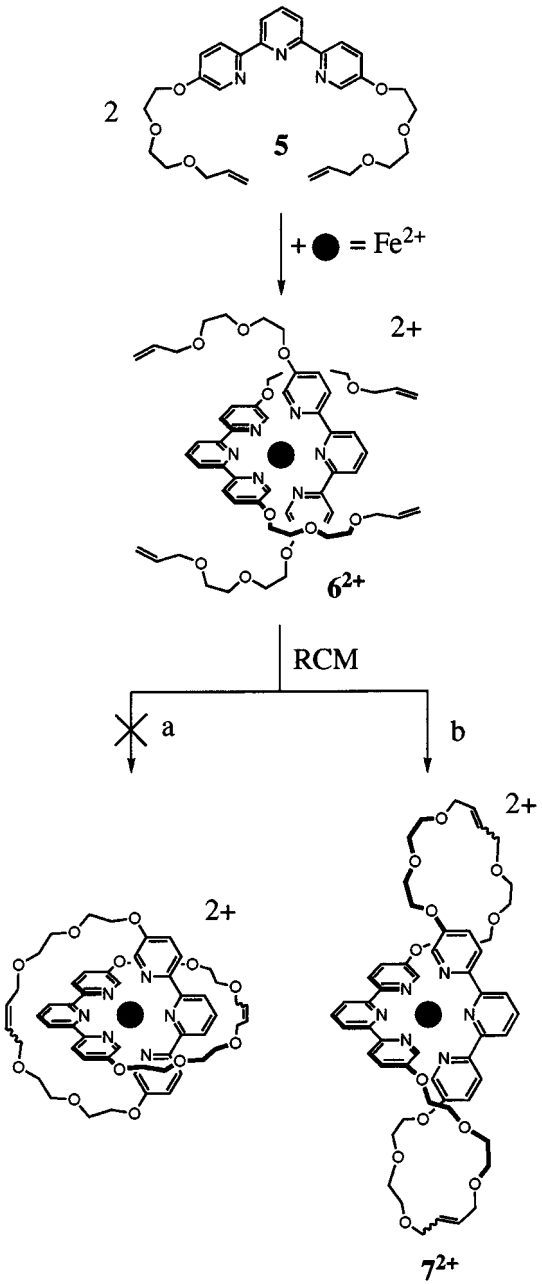

Figure 2. Formation of complex $\mathbf{6}^{2+}$ and the cyclization step. As indicated in the diagram, the double bonds are either cis or trans.

Experimental Section

Solvents were of reagent grade and were used as received unless otherwise stated. Reagents, except where otherwise noted, were purchased from various commercial sources and used as received. FAB mass spectral measurements were performed on a ZAB-HF apparatus, using NBA as the matrix. Proton NMR spectra were recorded on Bruker WP 200 SY (200 MHz) and AM (400 MHz) spectrometers.

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Compound **1** was prepared according to the literature.[11]

Preparation of 5,5″-Diethoxy-2,2′:6′,2″-terpyridine (2).[12] In 39 mL of DMSO, the following reagents were dissolved in succession: finely crushed KOH (7.8 g, 118 mmol), absolute ethanol (4.5 mL, 78 mmol), and **1** (600 mg, 1.9 mmol). This mixture was stirred at 50 °C for 24 h. After cooling, excess ethanol was evaporated under reduced pressure. The resulting mixture was diluted with 300 mL of water, upon which a brown solid precipitated. This solid was filtered off, dried in air, and dissolved in $CHCl_3$, and the solution was filtered over alumina (short column on sintered glass). Evaporation of the solvent afforded 422 mg of **2** (1.3 mmol, 71% yield) as a brown-beige solid (mp 175 °C). ^{1}H NMR ($CDCl_3$; δ): 8.54 (d, 2H, H_3, $H_{3''}$, ^3J = 8.9 Hz), 8.38 (d, 2H, H_6, $H_{6''}$, ^4J = 2.9 Hz), 8.3 (d, 2H, $H_{3'}$, $H_{5'}$, ^3J = 7.9 Hz), 7.89 (dd, 1H, $H_{4'}$, ^3J = 7.6 Hz, $^3J'$=8.1 Hz), 7.34 (dd, 2H, H_4, $H_{4''}$, ^3J = 8.7 Hz, ^4J = 2.8 Hz), 4.18 (q, 4H, $-CH_2$-, ^3J = 7 Hz), 1.49 (t, 6H, $-CH_3$, ^3J = 7 Hz).

Preparation of 5,5″-Dihydroxy-2,2′:6′,2″-terpyridine (3).[13] Technical grade pyridine (16 mL) was poured into a 100 mL three-necked round-bottomed flask fitted with a thermometer and a magnetic stirrer. Under rapid stirring, concentrated hydrochloric acid (17.6 mL) was added. The flask was equipped for distillation, and water was distilled from the mixture until its internal temperature rose to 210 °C. After the mixture was cooled to ∼140 °C, **2** (390 mg, 1.2 mmol) was added all at once as a solid and the reaction flask was fitted with a reflux condenser connected to a source of argon. The mixture was stirred and heated to reflux for 3 h (190° < T < 200 °C), after which it was cooled to ∼110 °C and carefully diluted with 60 mL of warm water. This mixture was neutralized with NaOH solution (end point: pH = 7.32), upon which **3** precipitated as a green solid, which was dried in air and utilized without further purification (293 mg, 1.1 mmol, 91% yield). ^{1}H NMR (DMSO-d_6; δ): 8.44 (d, 2H, H_3, $H_{3''}$, ^3J = 8.6 Hz), 8.23 (d, 2H, H_6, $H_{6''}$, ^4J = 2.5 Hz), 8.19 (d, 2H, $H_{3'}$, $H_{5'}$, ^3J = 7.4 Hz), 7.93 (dd, 1H, $H_{4'}$, ^3J = 7.1 Hz, $^3J'$ = 8.4 Hz), 7.36 (dd, 2H, H_4, $H_{4''}$, ^3J = 8.6 Hz, ^4J = 2.9 Hz).

Preparation of 4. Finely crushed Cs_2CO_3 (2 g, 6.1 mmol) was added to a solution of **3** (293 mg, 1,1 mmol) in DMF (120 mL). The mixture was heated to 75 °C under vigorous stirring. After 1 h at 75 °C, a solution of 2-(2-chloroethoxy)ethanol (0.35 mL, 3.3 mmol) in DMF (20 mL) was added dropwise over 15 min. This mixture was stirred at 75 °C for 6 h. Then another solution of 2-(2-chloroethoxy)ethanol (0.35 mL, 3.3 mmol) in DMF (20 mL) was added dropwise, and the reaction mixture was maintained at 75 °C under argon for 6 h. DMF was evaporated (0.1 mmHg, 50 °C), and the residue was dissolved in a 1:1 $H_2O/CHCl_3$ mixture. The organic phase was decanted, and the aqueous phase was extracted three times with 100 mL of $CHCl_3$. The organic phases were combined, dried over $MgSO_4$, and filtered. Evaporation of the solvent afforded 363 mg of **4** (0.8 mmol, 75% yield) as a beige solid (mp 105 °C). ^{1}H NMR ($CDCl_3$; δ): 8.55 (d, 2H, H_3, $H_{3''}$, ^3J = 8.6 Hz), 8.41 (d, 2H, H_6, $H_{6''}$, ^4J = 2.5 Hz), 8.30 (d, 2H, $H_{3'}$, $H_{5'}$, ^3J = 7.9 Hz), 7.89 (dd, 1H, $H_{4'}$, ^3J = 7.4 Hz, $^3J'$ = 8.1 Hz), 7.39 (dd, 2H, H_4, $H_{4''}$, ^3J = 8.8 Hz, ^4J = 2.9 Hz), 4.4−3.7 (m, 16H, H_α, H_β, H_γ, H_δ).

Preparation of Ligand 5. To a degassed solution of **4** (100 mg, 0.23 mmol) in DME (50 mL) was added NaH (2.5 mmol) under argon. The mixture was stirred at room temperature for 10 min, and then allyl bromide (0.5 mL, 6 mmol) was added via a syringe. The mixture was heated to reflux for 12 h. After cooling, excess NaH was destroyed by adding 5 mL of ethanol. Solvents were then evaporated, and the residue was dissolved in a 1:1 H_2O/CH_2Cl_2 mixture. The organic phase was decanted, and the aqueous phase was extracted three times with 100 mL of CH_2Cl_2. The organic phases were combined, dried over $MgSO_4$, and filtered. Evaporation of the solvent afforded 112 mg of **5** (0.21 mmol) in a quantitative yield as a beige solid (mp < 50 °C). ^{1}H NMR ($CDCl_3$; δ): 8.54 (d, 2H, H_3, $H_{3''}$, ^3J = 8.8 Hz), 8.4 (d, 2H, H_6, $H_{6''}$, ^4J = 2.5 Hz), 8.3 (d, 2H, $H_{3'}$, $H_{5'}$, ^3J = 7.6 Hz), 7.89 (t, 1H, $H_{4'}$, ^3J = 7.9 Hz), 7.38 (dd, 2H, H_4, $H_{4''}$, ^3J = 8.7 Hz, ^4J = 2.8 Hz), 5.94 (qd of t, 2H, H_b, $^3J_{trans}$ (bc′) = 17.2 Hz, $^3J_{cis}$(bc) = 10.4 Hz, ^3J(ba) = 5.6 Hz), 5.29 (m, 2H, $H_{c'}$), 5.20 (m, 2H, H_c), 4.05 (m, 4H, H_a), 4.4−3.6 (m, 16H, H_α, H_β, H_γ, H_δ).

Preparation of 6^{2+}. A solution of $FeSO_4$ (100 mg, 0.36 mmol) in water (100 mL) was added to a solution of **5** (112 mg, 0.21 mmol) in hot acetone. The solution, which immediatly turned deep purple, was heated to 55 °C for 30 min, and the acetone was evaporated. The iron complex was then precipitated by the addition of a saturated solution of KPF_6 (100 mL). The suspension was left for 2 h in a refrigerator, and the solid was filtered off, washed with water, and redissolved in CH_2Cl_2. This organic phase was washed three times with water, dried over $MgSO_4$, and filtered. Evaporation of the solvent afforded 142 mg of $\mathbf{6}^{2+}$ (0.1 mmol, 95% yield) as a fuschia red solid. ^{1}H NMR (acetone-d_6; δ): 8.98 (d, 4H, $H_{3'}$, $H_{5'}$, ^3J = 7.9 Hz), 8.8−8.6 (m, 6H, H_3, $H_{3''}$, $H_{4'}$), 7.65 (dd, 4H, H_4, $H_{4''}$, ^3J = 9.1 Hz, ^4J = 2.7 Hz), 6.88 (d, 4H, H_6, $H_{6''}$, ^4J = 2.5 Hz), 5.94 (qd of t, 4H, H_b, $^3J_{trans}$(bc′) = 17.3 Hz, $^3J_{cis}$(bc) = 10.3 Hz, ^3J(ba) = 5.7 Hz), 5.17 (m, 4H, $H_{c'}$), 5.05 (m, 4H, H_c), 3.87 (m, 8H, H_a), 4.1−3.3 (m, 32H, H_α, H_β, H_γ, H_δ).

Preparation of 7^{2+}. Complex $\mathbf{6}^{2+}$ (280 mg, 201 μmol) and the catalyst (Grubbs's ruthenium(II) carbene, 33 mg, 20% mol) were dissolved at room temperature in freshly distilled and degassed dichloromethane (25 mL), so as to obtain a ∼0.01 M solution. After 40 h, the solvent was evaporated. The crude product was then purified by column chromatography (Al_2O_3; eluent CH_2Cl_2/0−5% MeOH) and the impure fractions were purified by preparative TLC (SiO_2; eluent 100 mL of CH_3CN/20 mL of H_2O/1 mL of saturated KNO_3) to give 129 mg of $\mathbf{7}^{2+}$ (97 μmol, 48% yield), as a fuschia red solid. ^{1}H NMR (acetone-d_6, 400 MHz; δ): 8.99 (d, 4H, $H_{3'}$, $H_{5'}$, ^3J = 8 Hz), 8.74 (t, 2H, $H_{4'}$, ^3J = 8 Hz), 8.66 (d, 4H, H_3, $H_{3''}$, ^3J = 9.1 Hz), 7.72 (dd, 4H, H_4, $H_{4''}$, ^3J = 8.9 Hz, ^4J = 2.5 Hz), 6.89 (d, 4H, H_6, $H_{6''}$, ^4J = 2.4 Hz), 5.17−5.05 (m, 4H, H_b (*Z* or *E*)), 4.01 (m, 8H, H_a), 4.3−3.3 (m, 32H). Anal. Calcd for $C_{54}H_{62}F_{12}FeN_6O_{12}P_2$: C, 48.66; H, 4.69; N, 6.31. Found: C, 48.55; H, 4.81; N, 6.10.

Crystals suitable for X-ray diffraction were obtained by slow diffusion of benzene into a concentrated solution of complex $\mathbf{7}^{2+}$ in methylene chloride.

X-ray Crystallography for 7^{2+}. Suitable red single crystals of $\mathbf{7}^{2+}(PF_6^-)_2 \cdot CH_2Cl_2 \cdot C_6H_6$ were obtained as described above: $C_{61}H_{74}N_6O_{12}P_2F_{12}Cl_2Fe$, MW = 1499.98, triclinic; a = 12.4620(6), b = 16.7810(9), c = 17.3060(5) Å; α = 79.368(3), β = 84.937(3), γ = 72.513(2)°; V = 3390.7(4) Å^3, space group $P\bar{1}$, Z = 2, d_{calc} = 1.47 g cm^{-3}, μ = 0.445 mm^{-1}. Data were collected at −100 °C on a Nonius KappaCCD diffractometer using standard data collection procedures (2.5 < θ < 32.5°) and Mo Kα graphite-monochromated radiation (λ = 0.710 73 Å) for a crystal of dimensions 0.20 × 0.10 × 0.05 mm^3. A total of 26 324 reflections were collected, 8148 having $I > 3\sigma(I)$. The structure was solved using direct methods and refined against $|F|$. Atoms O9, O4, and C24 are disordered over two positions. These positions were refined with multiplicities of 0.5/0.5. Hydrogen atoms, with the exception of those related to the disorder, were introduced in structure factor calculations as fixed contributors at their computed positions; d(C−H) = 0.95 Å, B(H) = 1.3B_{eqv}(C). Final results: R = 0.062, R_w = 0.089, GOF = 1.551, largest peak in final difference map = 0.77 e Å^3. For all computations, the OpenMoleN[14] package was used.

Preparation of 8^{2+}. Complex $\mathbf{7}^{2+}$ (95 mg, 71 μmol) was dissolved in a 1:1 mixture of CH_2Cl_2/EtOH (40 mL). The catalyst (Pd/C, 5% mol in Pd) was then added. At room temperature and under vigorous stirring, the solution was maintained under a hydrogen atmosphere for 15 h. The reaction could be monitored by ^{1}H NMR spectroscopy, since the signal of the olefin progressively disappeared. The solvents were evaporated, and the crude mixture was purified by column chromatography (Al_2O_3; eluent CH_2Cl_2/0−5% MeOH) to give 85 mg of $\mathbf{8}^{2+}$ (64 μmol, 90% yield) as a fuschia red solid. ^{1}H NMR (acetone-d_6; δ): 8.99 (d, 4H, $H_{3'}$, $H_{5'}$, ^3J = 7.9 Hz), 8.73 (dd, 2H, $H_{4'}$, ^3J = 8.61 Hz, $^3J'$=7.38 Hz), 8.68 (d, 4H, H_3, $H_{3''}$, ^3J = 8.9 Hz), 7.71 (dd, 4H, H_4,

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$H_{4''}$, $^3J = 9$ Hz, $^4J = 2.7$ Hz), 6.9 (d, 4H, H_6, $H_{6''}$, $^4J = 2.5$ Hz), 4.3−3 (m, 48H, H_a, H_α, H_β, H_γ, H_δ).

Preparation of 9.[15] A solution of $\mathbf{8}^{2+}$ (19.1 mg, 14.3 μmol) dissolved in a 1:1 mixture of H_2O/CH_3CN (10 mL) was made alkaline by the addition of aqueous potassium hydroxide (440 mg, 66.7 mmol in 2 mL of water). H_2O_2 solution (30%) was then added slowly until the purple color disappeared. The suspension was filtered to remove iron oxides, and the filtrate was extracted with $CHCl_3$. This organic phase was washed with water, dried over $MgSO_4$, and filtered. Evaporation of the solvent afforded 10 mg of **9** (10 μmol, 70% yield) as a beige solid (mp 158 °C). ^{1}H NMR (acetone-d_6; δ): 8.49 (d, 4H, H_3, $H_{3''}$, ^3J = 8.8 Hz), 8.36 (d, 4H, H_6, $H_{6''}$, $^4J = 2.8$ Hz), 8.27 (d, 4H, $H_{3'}$, $H_{5'}$, ^3J = 7.8 Hz), 7,85 (t, 2H, $H_{4'}$, $^3J = 7.8$ Hz), 7.31 (dd, 4H, H_4, $H_{4''}$, ^3J = 8.8 Hz, $^4J = 2.9$ Hz), 4.2−3.4 (m, 48H, H_a, H_α, H_β, H_γ, H_δ). FAB$^+$-MS: *m*/*z* found 991.4 (MH^+), calcd 991.5.

Results and Discussion

The synthesis of the acyclic ligand **5**, consisting of a 5,5″-disubstituted terpyridine bearing terminal olefins, was carried out in several steps from 5,5″-dinitroterpyridine **1**.[11]

By reaction of **1** with ethanol and crushed KOH in DMSO[12] at 50 °C, the diethoxyterpyridine **2** was obtained in 71% yield. **2** was then converted to the dihydroxyterpyridine **3** in molten pyridinium chloride at 210 °C in 91% yield.[13] The reaction of **3** with 2-(2-chloroethoxy)ethanol and Cs_2CO_3 in DMF at 75 °C afforded ligand **4** (75%), which was quantitatively converted into its diolefinic derivative **5** by generating the dialcoholate with NaH and reacting the latter with a large excess of allyl bromide in refluxing DME. (See Figure 3).

5 was readily converted into its iron(II) complex by reaction with aqueous ferrous sulfate. Addition of an excess of saturated aqueous KPF_6 solution allowed complex $\mathbf{6}^{2+}$ to be obtained in quantitative yield as its hexafluorophosphate salt. ^{1}H NMR spectroscopy yielded clear evidence that $\mathbf{6}^{2+}$ is composed of two terpyridine ligands **5** entwined around the iron(II) center in a highly symmetrical geometry. Protons H_6 and $H_{6''}$ are upfield shifted by about 1.5 ppm, since in the complex they are located in the shielding cone of the central pyridine of the opposite ligand.

Cyclization of the precursor complex $\mathbf{6}^{2+}$ by ring-closing metathesis of its terminal olefins was performed in dichloromethane at room temperature in the presence of Grubbs' catalyst (ruthenium(II) dichloride phenylmethylene bis(tricyclohexylphosphine) [$RuCl_2$(PhCH,(PCy_3)$_2$)]). The double-ring-closure reaction, easily monitored by ^{1}H NMR, was complete after 40 h and afforded complex $\mathbf{7}^{2+}$ as a dark red solid in 48% yield after a chromatographic purification over Al_2O_3. The ^{1}H NMR spectrum of $\mathbf{7}^{2+}$ did not allow the determination of the *E*/*Z* ratio because of poorly resolved signals. These olefins were easily reduced (H_2, 5% Pd/C), affording the corresponding complex $\mathbf{8}^{2+}$ (not presented here) in 90% yield. This complex was subsequently demetalated to give compound **9** (not presented here) in 70% yield.[14]

To our surprise, the cyclization product turned out *not to be interlocked* but simply macrocyclic.

^{1}H NMR spectroscopy showed first that the cyclization product $\mathbf{7}^{2+}$ was not the expected catenate (route a of Figure 2) but merely a large 58-membered macrocycle twisted around the central iron(II) core (route b). Indeed, the signals corresponding to the various $-OCH_2CH_2O-$ units of the polyoxyethylenic chains (H_α, H_β, H_γ, and H_δ, between 4.1 and 3.3 ppm for $\mathbf{6}^{2+}$ and between 4.3 and 3.3 ppm for $\mathbf{7}^{2+}$), as well as those of the allylic protons (H_a, 3.87 ppm for $\mathbf{6}^{2+}$ and 4.01 ppm for $\mathbf{7}^{2+}$), appear for both the precursor $\mathbf{6}^{2+}$ and the final cyclic complex

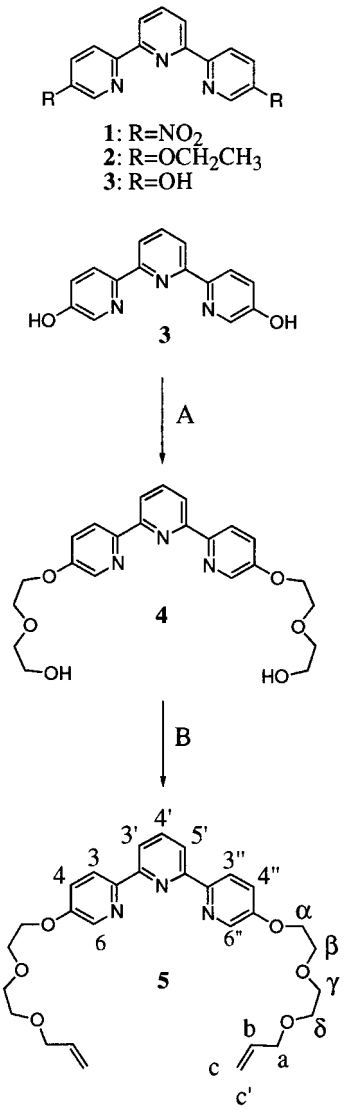

Figure 3. Terpyridine precursors leading to ligand **5**. A: (1) Cs_2CO_3, DMF, 75 °C, 1 h; (2) 2-(2-chloroethoxy)ethanol, DMF, 75 °C, 12 h. B: (1) NaH, DME, room temperature, 10 min; (2) allyl bromide, DME, 85 °C, 12 h.

$\mathbf{7}^{2+}$ at almost identical positions. Such identical chemical shifts would of course not be expected in the spectrum of an interlocked structure in which the proton resonances of the polyoxyethylenic chains located very near the various pyridine nuclei should differ significantly (deshielding ring current or shielding cone).

The X-ray structure of the reaction product $\mathbf{7}^{2+}$, depicted in Figure 4, shows that, after cyclization, the two chains remain far remote from the central bis(terpyridine) core.

This surprising result, reminiscent of that recently reported by Busch and co-workers,[16] indicates that if the precursor is not "intertwined" sufficiently, the cyclization reaction takes place laterally instead of "beyond" the metal. The new macrocyclic complex adopts the shape of a figure 8 with a twisted core. Considering the relative spatial locations and orientations of the four oxygens O1, O6, O7, and O12 (see Table 1), two oxygen atoms belonging to one terpyridine are further apart than two such atoms belonging to two different terpyridine moieties (Table 1).

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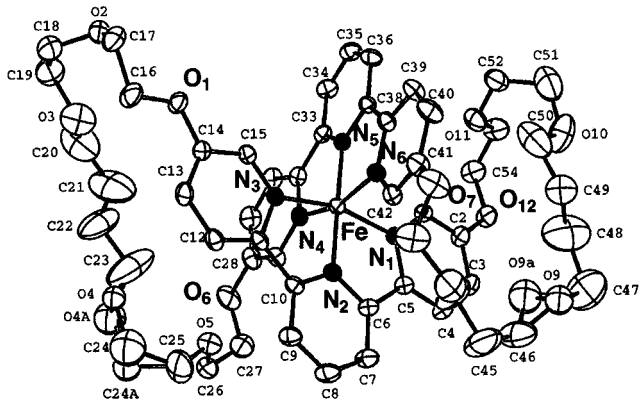

Figure 4. ORTEP diagram for the X-ray structure of $\mathbf{7}^{2+}$, with hydrogen atoms omitted for clarity. The unit cell contains both enantiomers, and the complex represented corresponds to a P helix.

Table 1. Distances (Å) between Oxygens in Complex $\mathbf{7}^{2+}$

distances between oxygens of the same terpyridine		distances between oxygens of two different terpyridines			
$d(O_1,O_{12})$	10.3	$d(O_1,O_6)$	7.6	$d(O_6,O_{12})$	7.8
$d(O_6,O_7)$	10.5	$d(O_1,O_7)$	7.4	$d(O_7,O_{12})$	8.3

The reaction between terminal olefins in the cyclization step of $\mathbf{6}^{2+}$ has certainly taken place by the less hindered pathway, since formation of one ring of the corresponding catenane is likely to be slower as a result of steric hindrance between the bulky catalyst and the other perpendicular terpyridine.

In conclusion, the synthesis of transition-metal-containing catenanes is not as simple as it might appear today, especially if the strategy is not based on the well established copper(I)−bis(2,9-diaryl-1,10-phenanthroline) synthon. On the other hand, the compound obtained contains a large macrocyclic ligand (58-membered ring) whose synthesis would certainly not be straightforward without the assistance of an $Fe(terpy)_2^{2+}$ core used as a template. Interestingly, the two lateral portions of the twisted ring, with their six oxygen atoms each, are reminiscent of crown ethers and could be used to complex various cations and thus allow control of the electronic properties of the central iron(II) complex.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, and listings of crystal data, X-ray experimental details, atomic coordinates, thermal parameters, and bond distances and angles for $\mathbf{7}(PF_6)_2 \cdot CH_2Cl_2 \cdot C_6H_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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