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Article

Zinc(II)-Templated Synthesis of a [2]-Catenane Consisting of a 2,2′,6′,2′′-Terpyridine-Incorporating Cycle and a 1,10-Phenanthroline-Containing Ring

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A nonsymmetrical [2]-catenane has been synthesized, with a 5-coordinated metal center (Zn^{2+}) as template. One of the two rings contains a terdentate ligand (2,2′,6′,2′′-terpyridine) and the other one incorporates a bidentate chelate (1,10-phenanthroline). The first ring was prepared separately and, subsequently, Zn^{2+} was used as the gathering and threading element to pass the stringlike component through the ring. This open-chain species bears two terminal olefins, which were reacted with Grubbs first-generation catalyst (ring-closing metathesis) to afford the desired catenane. Hydrogenation of the double bond and removal of the zinc(II) template afforded the final free [2]-catenane in 40% yield from the terdentate ligand-containing cycle and the diolefinic compound. Complexation studies on this new pentacoordinating catenane were carried out with Fe(II) or Cu(II). The most interesting observation is that the 5-coordinated complexes obtained are strongly stabilized. Their electrochemical reduction occurs at negative potentials.

Introduction

Catenanes have experienced a spectacular revival in the course of the last 20 years thanks to the introduction of template approaches.[1−7] These strategies make interlocking molecules much more accessible from a preparative viewpoint than before they were proposed.[8] Besides their fascinating topological and structural features, these compounds display highly interesting properties, in particular as prototypes of molecular machines.[9−12] An electronic switch has even been described recently that relies on a [2]-catenane with two stable conformations.[13]

Transition metal centers have been the first templating species used in catenane synthesis. Copper(I) turned out to be particularly efficient as a gathering and templating metal for the construction of catenanes. The prototypical set of reactions is represented in Figure 1. The free ligand ("catenand") of Figure 1 is a tetradentate ligand, especially well adapted to the coordination of tetrahedral metal centers. Subsequently, various approaches have been proposed that rely on octahedral metal centers. Ru(II) has been used in conjunction with two 2,2′,6′,2′′-terpyridine (terpy) derivatives but the procedure is not really preparative.[14] An impressive example has recently been published that leads to very high yields of 6-coordinated metal-complexed catenanes.[15] It is based on divalent first-raw transition metals, able to gather and orient two tridentate chelates perpendicular to one

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(1) Sauvage, J.-P.; Dietrich-Buchecker, C., Eds.; *Molecular Catenanes, Rotaxanes and Knots: A Journey Through the World of Molecular Topology*; 1999.

(2) Chambron, J.-C.; Dietrich-Buchecker C.; Sauvage, J.-P. *Compehensive Supramolecular Chemistry*; Pergamon Press: Oxford, U.K., 1996; Vol. 9, p 43.

(3) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725.

(4) Vögtle, F.; Safarowsky, O.; Heim, C.; Affeld, A.; Braun, O.; Mohry, A. *Pure Appl. Chem.* **1999**, *71*, 247.

(5) Hunter, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 5303.

(6) Johnston, A. G.; Leigh, D. A.; Nezhat, L.; Smart, J.-P.; Deegan, M. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1209.

(7) (a) Birhada, K.; Fujita, M. *Adv. Supramol. Chem.* **2000**, *6*, 1. (b) Fujita, M.; Ogura, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1471.

(8) Schill, G. *Catenanes, Rotaxanes and Knots*; Academic Press: New York, 1971.

(9) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611.

(10) Balzani, V.; Gomez-Lopez, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405.

(11) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348.

(12) *Acc. Chem. Res.* **2001**, *34*; Special issue.

(13) Collier, C. P.; Matterstei, G.; Wong, E. W.; Luo, Y.; Berverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289* (582), 1172.

(14) Sauvage, J.-P.; Ward, M. D. *Inorg. Chem.* **1991**, *30*, 3869.

(15) Leigh, D. A.; Lusby, P. J.; Teat, S. J.; Wilson, A. J.; Wong, J. K. Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1538.

10.1021/ic020381c CCC: $25.00

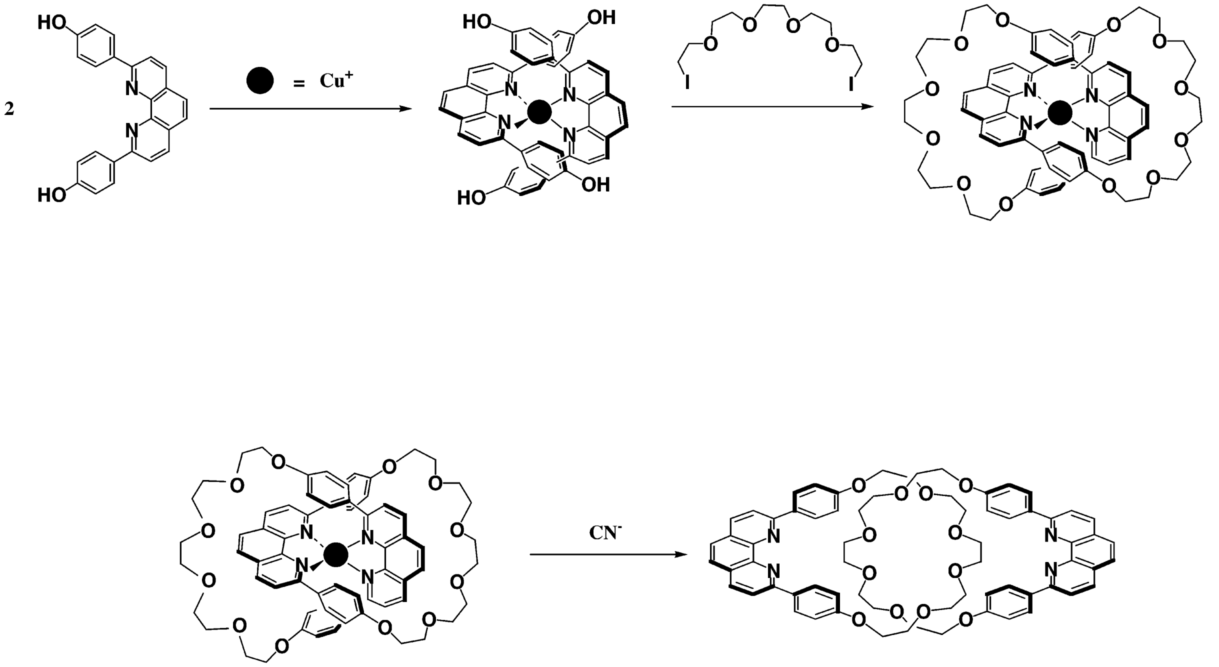


Figure 1. Preparation of the copper(I) catenane and subsequent demetalation to the catenand.

another. To our knowledge, 5-coordinated metals have never been used as template for synthesising [2]-catenanes. The present report is dealing with the use of Zn^{2+} as an assembling species for making an interlocking ring system consisting of two different cycles, the rings containing a bidentate and a terdentate ligand, respectively.

Experimental Section

^1H NMR spectra were acquired on either a Bruker WP200 SY (200 MHz) or a Bruker AC 300 (300 MHz) spectrometer, with the deuterated solvent as the lock and residual solvent as the internal reference. Fast atom bombardment mass spectroscopy (FAB MS) data were recorded in the positive ion mode with a xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a ZAB-HF mass spectrometer. A VG BIOQ triple-quadrupole spectrometer was used for the electrospray mass spectrometry measurements (ES-MS), also in the positive ion mode. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectra were taken on a Brücker Spectrometer Protein Tof with α-cyano-4-hydroxycinnamic acid as matrix. Electrochemical experiments were performed on an EG&G PAR model 273A potentiostat with a standard three-electrode configuration. Potentials are referenced to an Ag wire pseudo-reference electrode with 0.1 mol.L^{-1} tetrabutylammonium tetrafluoroborate as supporting electrolyte. The potentials were verified by use of ferrocene as internal standard and then referred to a saturated calomel electrode (SCE). Absorption spectra were recorded with an Uvikon XS spectrophotometer.

Synthesis. Oxygen- or water-sensitive reactions were conducted under a positive pressure of argon in oven-dried glassware, by Schlenk techniques. Common reagents and materials were purchased from commercial sources. The following materials were prepared according to literature procedures: **1**,[18] **2**,[19] and 2-(2′-iodoethoxy)ethyl-2″-tétrahydropyranyl ether.[28] The solvents were distilled over the appropriate drying agents.

5,5″-Di(ϵ-tetrahydropyranyl-(2-(2′-ethoxy)ethyl))terpyridine (3). A degassed solution of 5,5″-dimethylterpyridine (2.61 g, 10 mmol) in anhydrous tetrahydrofuran (THF, 50 mL) was cooled to −78 °C. While this temperature was maintained, a freshly prepared solution of LDA (23 mmol in THF) was added via the cannula transfer technique. The solution turned blue and was stirred at −78°C for a further 3 h. The temperature was then allowed to rise to 0 °C and brought down to −78 °C again. A solution of 2-(2′-bromoethoxy)ethyl-2″-tetrahydropyranyl ether (7 g, 27.6 mmol) in freshly distilled THF was then added into the blue solution. The solution was then stirred for 36 h at room temperature and was hydrolyzed with 10 mL of water. The solution turned brown. After evaporation of the THF, the residue was taken up in a CH_2Cl_2/H_2O mixture and the organic layer was dried over $MgSO_4$. After the solvent was evaporated, the resulting brown oil was chromatographed (Al_2O_3; eluent hexane/ether 60/40 to hexane/ether/methanol 59.5/40/0.5) to give pure **3** as a white powder in 24% yield (1.135 g, 1.87 mmol). ^1H NMR (200 MHz,CD_2Cl_2): δ (ppm) 8.54 (s, 2H), 8.52 (d, 2H, $J = 8.1$ Hz), 8.37 (d, 2H, $J = 8$ Hz), 7.92 (t, 1H, $J = 8.1$ Hz), 7.67 (dd, 2H, $^3J = 8.0, 2.0$ Hz), 4.66 (m, 2H), 3.86 (m, 4H), 3.60 (m, 12H), 2.80 (t, 4H, $J = 6.1$ Hz), 1.52−2.03 (m, 16H). ^{13}C NMR (200 MHz, CD_2Cl_2): 155.7, 154.2, 149.6, 138.0, 137.9, 137.0, 120.7, 120.5, 99.2, 70.5, 66.9, 62.3, 31.2, 30.9, 29.5, 25.8, 19.9. Anal. Calcd for $C_{35}H_{47}N_3O_6$: C, 69.40; H, 7.82; N, 6.94. Found: C, 69.50; H, 8.31; N 6.94. MALDI-TOF MS: *m*/*z* = 605.70 $[M^+ + 1]$.

5,5″-Di(ϵ-hydroxy -(2-(2′-ethoxy)ethyl))terpyridine (4). Terpyridine **3** (1.322 g, 2.2 mmol), dissolved in 100 mL of ethanol, was brought to reflux under argon before 2 drops of 37% HCl was added. The solution was refluxed for 3 h and ethanol was then removed. The residue was taken up in CH_2Cl_2/H_2O. The aqueous layer was washed with 20 mL of a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2 (2 × 50 mL). The organic layers were combined and dried over $MgSO_4$, and the solvent was removed. The crude mixture was chromatographed (Al_2O_3, eluent CH_2Cl_2/0−2% MeOH) to give **4** as a white powder in 90% yield (0.904 g). ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.56 (s, 2H), 8.52 (d, 2H, $J = 7.8$ Hz), 8.39 (d, 2H, $J = 8.0$ Hz), 7.93 (t, 1H, $J = 7.8$ Hz), 7.68 (dd, 2H, $J = 8.0, 2.0$ Hz), 3.75 (t, 4H, $J = 5.9$ Hz), 3.53 (m, 8H), 2.81 (t, 4H, $J = 6.0$ Hz), 1.97 (m, 4H). ^{13}C NMR (200

MHz, $CDCl_3$): 155.5, 154.4, 149.5, 138.2, 137.7, 137.3, 121.3, 120.9, 72.3, 70.3, 62.2, 31.2, 29.7. MALDI-TOF MS: $m/z = 438.12$ [$M^+ + 1$].

5,5″-Di(ϵ-mesilyl-(2-(2′-ethoxy)ethyl))terpyridine (5). A solution of the terpyridine **4** (0.90 g, 2.07 mmol) in 45 mL of anhydrous CH_2Cl_2 in the presence of freshly distilled triethylamine (3.2 mL, 22.7 mmol) was cooled to −5 °C under argon. A solution of mesyl chloride (0.8 mL, 10.4 mmol) in 10 mL of anhydrous CH_2Cl_2 was added dropwise to the previous solution. The temperature was maintained below 0 °C as the reaction is very exothermic. After 3 h of stirring at −5 °C, the mixture was brought to room temperature. The color of the solution turned from colorless to yellow. The reaction mixture was washed with H_2O and dried over $MgSO_4$. After the evaporation of the solvent, the crude product was filtered over Al_2O_3 (eluent CH_2Cl_2/hexane 80:20) to give **5** as a white powder in 87% yield. ^1H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.55 (s, 2H), 8.52 (d, 2H, $J = 7.5$ Hz), 8.41 (d, 2H, $J = 8.0$ Hz), 7.93 (t, 1H, $J = 7.5$ Hz), 7.69 (dd, 2H, $J = 8.0$, 2.0 Hz), 4.38 (m, 4H), 3.71 (m, 4H), 3.53 (t, 4H, $J = 6.0$ Hz), 3.07 (s, 6H), 2.79 (t, 4H, $J = 6.0$ Hz), 1.97 (m, 4H). MALDI-TOF MS: $m/z = 593.61$ [$M^+ + 1$].

5,5″-Di(ϵ-bromo-(2-(2′-ethoxy)ethyl))terpyridine (6). The terpyridine **5** (0.62 g, 1.04 mmol) was dissolved in acetone (70 mL) and the solution was refluxed in the presence of lithium bromide (0.9 g, 10 mmol) under argon. The reaction was monitored by TLC and was finished after 3 h. After the solvent was removed, the crude mixture was taken up in CH_2Cl_2/H_2O. The organic layers were combined and dried over $MgSO_4$, and the solvent was evaporated. The crude product was filtered over Al_2O_3 (eluent CH_2Cl_2/hexane 60:40) to give **6** as a white powder in 86% yield. ^{1} H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.56 (s, 2H), 8.52 (d, 2H, $J = 7.1$ Hz), 8.39 (d, 2H, $J = 8.0$ Hz), 7.94 (t, 1H, $J = 7.1$ Hz), 7.71 (dd, 2H, $J = 8.0$, 1.9 Hz), 3.77 (t, 4H, $J = 6.0$ Hz), 3.50 (m, 8H), 2.82 (t, 4H, $J = 6.0$ Hz), 1.97 (m, 4H). ^{13}C NMR (200 MHz, $CDCl_3$): 155.7, 154.6, 149.6, 138.1, 137.5, 137.2, 121.1, 120.8, 71.0, 69.9, 31.2, 10.8, 29.5. Anal. Calcd for $C_{25}H_{29}Br_2N_3O_2$: C, 53.30; H, 5.19; N, 7.46. Found: C, 53.41; H, 5.15; N, 7.34.

Macrocycle (7). A mixture of the terpyridine **6** (0.5 g, 0.87 mmol) and commercial 4,4′-isopropylidenediphenol (0.199 g, 0.87 mmol) in 80 mL of degassed dimethylformamide (DMF) was introduced in a high-dilution funnel fitted on a 1-L round-bottom flask containing Cs_2CO_3 (0.89 g, 2.73 mmol) in suspension in 180 mL of degassed DMF. The vessel was heated at 60 °C and the mixture in the funnel was added dropwise during 20 h. After 18 more hours of stirring, the solvent was removed and the residue was taken up into CH_2Cl_2/H_2O. The organic layers were combined and dried over $MgSO_4$, and after the solvent was removed, the resulting brown oil was chromatographed (Al_2O_3, eluent CH_2Cl_2/hexane 70:30) to give pure **7** as a white solid in 54% yield. ^1H NMR (200 MHz, CD_2Cl_2): δ (ppm) 8.52 (s, 2H), 8.48 (d, 2H, $J = 8$ Hz), 8.44 (d, 2H, $J = 7.8$ Hz), 7.92 (t, 1H, $J = 8.0$ Hz), 7.66 (dd, 2H, $J = 7.8$, 1.9 Hz), 7.08 (d, 4H, $J = 8.8$ Hz), 6.87 (d, 4H, $J = 8.8$ Hz), 4.09 (m, 4H), 3.73 (m, 4H), 3.47 (t, 4H, $J = 6.0$ Hz), 2.84 (t, 4H, $J = 6.5$ Hz), 1.97 (m, 4H), 1.61 (s, 6H). ^{13}C NMR (200 MHz, CD_2Cl_2): 156.9, 155.7, 154.1, 149.7, 143.6, 138.0, 137.9, 137.8, 127.9, 120.6, 120.4, 114.3, 69.5, 69.2, 67.9, 41.8, 30.9, 30.5, 29.0. Anal. Calcd for $C_{40}H_{43}N_3O_4$: C, 76.28; H, 6.88; N, 6.67. Found: C, 76.14; H, 7.05; N, 6.56. MALDI-TOF MS: $m/z = 630.19$ [$M^+ + 1$].

Zn(7)(H_2O)(OTf)$_2$ (8). A solution of $Zn(OTf)_2$ (31 mg, 0.085 mmol) in EtOH (5 mL) was added to a solution of macrocycle **7** (53.5 mg, 0,085 mmol) dissolved in CH_2Cl_2 (5 mL) at room temperature. The mixture was then stirred for 2 h. The solvents were evaporated in a vacuum to give **8** as a white powder in quantitative yield. ^1H RMN (200 MHz, CD_2Cl_2): δ (ppm) 8.68 (dd, 2H, $J = 1.9$ Hz), 8.29−8.13 (m, 5H), 7.96 (dd, 2H, $J = 7.1$, 1.9 Hz), 7.10 (d, 4H, $J = 8.8$ Hz), 6.83 (d, 4H, $J = 8.8$ Hz), 4.09 (m, 4H), 3.72 (m, 4H), 3.48 (t, 4H, $J = 5.8$ Hz), 2.92 (t, 4H, $J = 7.3$ Hz), 1.94 (m, 4H), 1.61 (s, 6H). ^{13}C RMN (200 MHz, CD_2Cl_2): 164.1, 157.0, 150.5, 148.3, 145.3, 143.7, 143.5, 142.8, 141.0, 127.9, 121.9, 121.6, 114.5, 69.5, 69.1, 68.1, 41.7, 30.7, 30.5, 29.4.

Threaded Complex (9). To a solution of **8** (31 mg, 0.031 mmol) in distilled CH_2Cl_2 (5 mL) was added **1** (19.5 mg, 0.031 mmol) dissolved in CH_2Cl_2 (5 mL) at room temperature. The solution, initially colorless, turned clear yellow. The solution was stirred for 20 min and then the solvent was removed under high vacuum: a clear yellow solid of crude **9** was obtained in quantitative yield (49 mg). Compound **9** was used without further purification. ^1H RMN (200 MHz, CD_2Cl_2): δ (ppm) 8.55 (m, 5H), 8.35 (d, 2H, $J = 8.2$ Hz), 8.00 (d, 2H, $J = 8.2$ Hz), 7.91 (dd, 2H, $J = 8.2$, 1.9 Hz), 7.77 (s, 2H), 7.35 (d, 4H, $J = 8.5$ Hz), 7.23 (dd, 2H, $J = 1.9$ Hz), 6.92 (d, 4H, $J = 8.6$ Hz), 6.64 (d, 4H, $J = 8.5$ Hz), 6.39 (d, 4H, $J = 8.6$ Hz), 6.00−5.81 (m, 2H), 5.30−5.11 (m, 4H), 4.00 (m, 4H), 3.86−3.58 (m, 20H), 3.44 (m, 4H), 3.11 (t, 4H, $J = 5.7$ Hz), 2.48 (t, 4H, $J = 6.9$ Hz), 1.73 (s, 6H), 1.60 (m, 4H).

[2]-Catenane (11). Precatenane **9** (136 mg, 0.084 mmol) and the catalyst **10** [Grubbs ruthenium(II) carbene; 14.9 mg, 20% mol] were dissolved at room temperature in freshly distilled and degassed CH_2Cl_2 (8.4 mL, to obtain a 0.01 M solution). After 10 min, the solution turned brown-black. The mixture was stirred at room temperature for 3 days (the reaction mixture was regularly purged by a small vacuum, to remove the ethylene gas formed during the reaction, and a further 10% mol of the catalyst (2 mg) was added the second day). The solvent was then evaporated and the crude mixture was used in the next step without purification.

Reduction of the Cyclic Olefins (12). The previous crude **11** (130 mg, mmol) was dissolved in a 1:1 mixture of CH_2Cl_2/EtOH (3 mL). The catalyst (Pd/C, 10 mol % in Pd) was then added. The solution was vigorously stirred at room temperature under a hydrogen atmosphere for 15 h. At this step, an attempt at purification was tried but the progressive demetalation of the complex was observed during the elution.

Free Catenane (13). The previous crude **12** was dissolved in CH_2Cl_2 (4 mL). NaOH (0.5 M in water) was added to the former solution. The demetalation reaction was monitored by TLC and was complete after 2 h of stirring. The mixture was then extracted with CH_2Cl_2 and the resulting organic layer was washed with water and dried over Na_2SO_4. The solvent was removed and the crude was then purified on a preparative plate (Al_2O_3, CH_2Cl_2/MeOH 0−0.5%) to give the demetalated catenane **13** as a colorless solid (42 mg). The yield over these last three steps is 40%. ^1H RMN (200 MHz,CD_2Cl_2): δ (ppm) 8.61 (d, 2H, $J = 8.1$ Hz), 8.45 (d, 2H, $J = 1.9$ Hz), 8.33 (d, 2H, $J = 7.8$ Hz), 8.28 (d, 2H, $J = 8.8$ Hz), 8.20 (d, 2H, $J = 8.0$ Hz), 7.95 (d, 2H, $J = 8.0$ Hz), 7.82 (t, 1H, $J = 7.8$ Hz), 7.71 (s, 2H), 7.61 (dd, 2H, $J = 8.1$, 1.9 Hz), 7.02 (d, 4H, $J = 8.8$ Hz), 6.85 (d, 4H, $J = 8.8$ Hz), 6.76 (d, 4H, $J = 8.8$ Hz), 4.05 (t, 4H, $J = 5.2$ Hz), 3.88 (t, 4H, $J = 6.0$ Hz), 3.68 (t, 4H, $J = 5.2$ Hz), 3.53 (t, 4H, $J = 6.0$ Hz), 3.37−3.31 (m, 12H), 3.18 (m, 4H), 2.71 (t, 4H, $J = 6.2$ Hz), 1.88 (m, 4H), 1.54 (s, 6H), 1.44 (m, 4H). FAB-MS: $m/z = 1224.7$ [$M^+ + 1$]. UV/vis (CH_2Cl_2): λ_{max}, nm (ϵ, liters per mole per centimeter) = 286 (107 000).

Zn(II) Catenane (12). $Zn(OTf)_2$ (1.2 mg, 0.003 mmol) dissolved in EtOH (1 mL) was added to a solution of **13** (3.6 mg, 0.003 mmol) in CH_2Cl_2. The solution turned pale yellow. The solvents were then removed to afford the complex as a pale yellow solid (4.7 mg) quantitatively. ^1H RMN (300 MHz,CD_2Cl_2): δ (ppm) 8.77 (t, 1H,

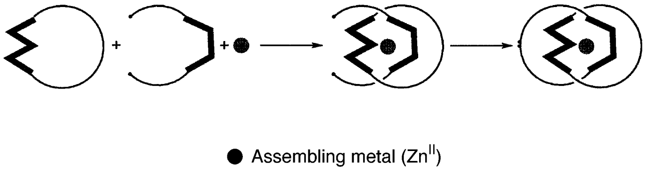


Figure 2. Strategy used to prepare the [2]-catenane **12**.

$J = 7.8$ Hz), 8.48 (d, 2H, $J = 7.8$ Hz), 8.38 (d, 2H, $J = 8.1$ Hz), 8.03 (d, 2H, $J = 8.4$ Hz), 7.97 (dd, 2H, $J = 8.1$, 1.5 Hz), 7.77 (s, 2H), 7.40 (m, 6H), 7.24 (d, 2H, $J = 1.5$ Hz), 6.91 (d, 4H, $J = 8.6$ Hz), 6.68 (d, 4H, $J = 8.5$ Hz), 6.39 (d, 4H, $J = 8.6$ Hz), 3.87 (m, 4H), 3.83 (m, 4H), 3.73 (m, 12H), 3.60 (m, 4H), 3.48 (m, 4H), 3.17 (t, 4H, $J = 5.7$ Hz), 2.52 (t, 4H, $J = 6.9$ Hz), 1.80 (s, 6H), 1.77 (m, 4H), 1.67 (m, 4H). ES-MS: $m/z = 1436.6$ [M − OTf]$^+$, 644.4 [M − 2OTf]$^{2+}$/2.

Cu(II) Catenane (14). Compound **13** (6 mg, 0.005 mmol) in CH_2Cl_2 (2 mL) was introduced into a 5 mL flask, and 0.85 mL of a 6 mM pale blue solution of $Cu^{II}(BF_4)_2$ in CH_3CN was added. The solution turned into pale green. The solvents were then removed to afford the crude complex as a pale green solid (7.3 mg). UV/Vis (CH_2Cl_2): λ_{max}, nm (ϵ, liters per mole per centimeter) = 593 nm (165). ES-MS: $m/z = 1374.6$ [M − BF_4]$^+$; 643.5 [M − 2BF_4]$^{2+}$/2.

Fe(II) Catenane (15). Compound **13** (4.7 mg, 0.004 mmol) in CH_2Cl_2 (2 mL) was introduced into a 5 mL flask and 1.4 mg of $Fe^{II}\cdot 6H_2O\cdot(BF_4)_2$ in EtOH was then added. The color turned bright yellow. The solvents were then removed to afford the crude complex as an orange solid (5.8 mg). UV/Vis (CH_2Cl_2): λ_{max}, nm (ϵ, liters per mole per centimeter) = 339 (18 176), 276 (27 704). ES-MS: $m/z = 1366.7$ [M − BF_4]$^+$; 640.0 [M − 2BF_4]$^{2+}$/2.

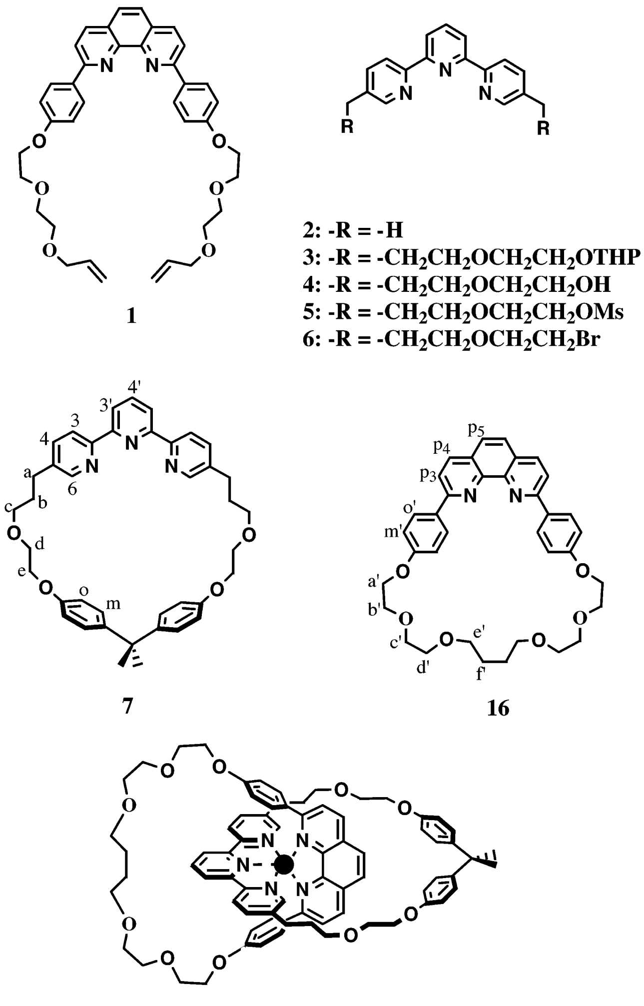
X-ray Structural Study. Single crystals suitable for X-ray analysis were obtained for complex **8** by slow diffusion of diethyl ether vapors into a solution of **8** in CH_2Cl_2. Crystal data and details of data collection are provided in Table 2

Results and Discussion

Design and Principle. To make a 5-coordinated catenate, Zn^{2+} seemed to be an appropriate template. This cation forms stable pentacoordinated complexes with nitrogen-containing ligands, contrary to the most frequently used template Cu(I). A terpy and a phen (phen = 1,10-phenanthroline) form a convenient set of ligands that has recently been used for setting in motion a "muscle"-like molecular assembly.[16] The construction principle is depicted in Figure 2.

To avoid formation of 6-coordinated complexes containing two terdentate ligands,[17] it is compulsory to include the terpy fragment in the ring, in an endotopic fashion. In principle, the use of the bidentate chelates not belonging to a ring could lead to 4-coordinated complexes. This would be the case with copper(I) but the situation will be very different with Zn^{2+}. Formation of a 5-coordinated complex implies that the system be threaded. The preference of Zn^{2+} for 5-coordinated complexes will thus be the driving force for the threading reaction.

Chart 1. Phen- and Terpy- Containing Precursors to the Cyclic Compounds and the Catenane



1

2: -R = -H
3: -R = $-CH_2CH_2OCH_2CH_2OTHP$
4: -R = $-CH_2CH_2OCH_2CH_2OH$
5: -R = $-CH_2CH_2OCH_2CH_2OMs$
6: -R = $-CH_2CH_2OCH_2CH_2Br$

7

16

12

Synthesis of the Organic Precursors. The phen- and terpy-containing precursors to the cyclic compounds and the catenane are represented in Chart 1.

The phen-incorporating fragment, compound **1**, was obtained according to a modified literature procedure.[18] The terpy-containing ring was prepared in five steps from 5,5″-dimethyl-2,2′,6′,2″-terpyridine **2**.[19] Compound **2** was reacted with lithium diisopropylamide (LDA) in THF, at low temperature, and to the resulting anion was added a solution of $ICH_2CH_2OCH_2CH_2OTHP$. The bis-THP compound **3** was isolated in 24% yield. The THP protective groups was cleaved by acidic treatment (HCl in refluxing ethanol; 90% yield), and the resulting diol **4** was converted to the bismesylate **5** (MsCl, NEt_3; 87% yield) and subsequently to the dibromo compound **6** (LiBr, acetone; 86% yield). Compound **6** was reacted with bis-phenol A[20] [2,2′-(*p*-hydroxyphenyl)propane] in the presence of Cs_2CO_3 (DMF at 60 °C; high dilution). The macrocyclic compound **7** was obtained in 54% yield from **6** as a white solid.

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(16) Jiménez-Molero, M. C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Eur. J.* **2002**, *8*, 1456.

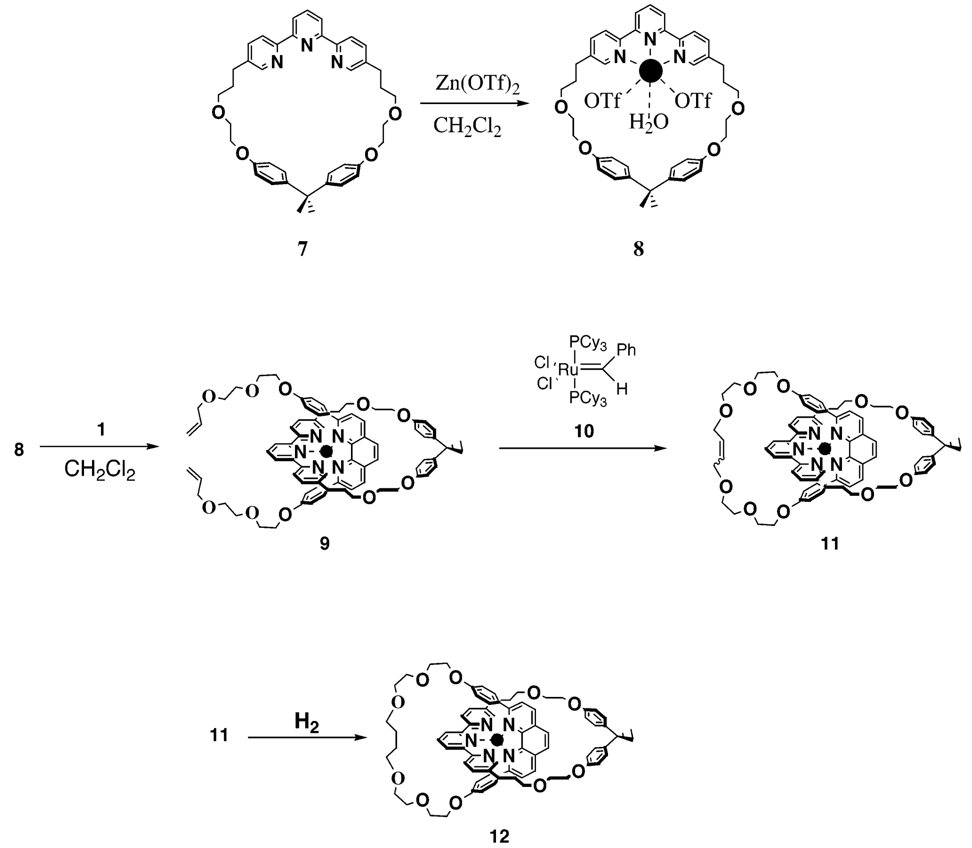
(17) (a) Albano, G.; Balzani, V.; Constable, E. C.; Maestri, M.; Smith, D. R. *Inorg. Chim. Acta* **1998**, *277*, 225. (b) Loiseau, F.; Di Pietro, C.; Serroni, S.; Campagna, S.; Licciardello, A.; Manfredi, A.. Pozzi, G.; Quici, S. *Inorg. Chem.* **2001**, *40*, 6901.

(18) (a) Weck, M.; Mohr, B.; Sauvage, J.-P.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 5463. (b) Mohr, B.; Weck, M.; Sauvage, J.-P.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1308.

(19) Cardenas, D. J.; Sauvage, J.-P. *Synlett* **1996**, *9*, 916.

(20) Katz, H. E. *Tetrahedron Lett.* **1984**, *25*, 4905.

Scheme 1. Synthesis of the [2]-catenane **12** Following the Strategy Depicted in Figure 2



Preparation of the Zinc(II) Catenane. The first step consists of threading the open-chain compound **1** through the 34-membered ring **7**, with Zn^{2+} acting as gathering and threading metal center. This reaction and the subsequent cyclization step are represented in Scheme 1.

A stoichiometric amount of zinc(II) triflate in ethanol is added to a solution of **7** in CH$_2$Cl$_2$. After the solvents are pumped off, the macrocyclic Zn^{2+} complex $\mathbf{8}^{2+}$ is obtained (white solid; quantitative). The formation of $\mathbf{8}^{2+}$ was clearly evidenced by ^{1}H NMR spectroscopy (see Experimental Section). In particular, some of the protons belonging to the terpy fragment undergo a significant downfield shift, in agreement with formation of a complex with a divalent metal.

A single crystal of $\mathbf{8}^{2+}\cdot 2\mathrm{OTf}^-$ was obtained and the X-ray structure of the complex was solved. The structure is shown in Figure 3 and the crystallographic data are given in Table 1. Zn^{2+} is 6-coordinate, with a distorted octahedral geometry. Three equatorial positions are occupied by the nitrogen atoms of the terpy nucleus, with the fourth equatorial position being occupied by a water molecule. The axial ligands are the triflate anions. As usually observed for terpy complexes,[21] the terpy ligand is slightly pinched so as to minimize the distortions around the metal (N−Zn−N′ angles ~ 76°). The Zn···0 and Zn···N distances have normal values (Zn···0, d = 2.18 Å; Zn···N, d = 2.12 Å).

Compound **1** was added to **8** in CH$_2$Cl$_2$ to afford quantitatively the catenane precursor **9** as a pale yellow complex. The quantitative formation of **9** and its threaded nature were demonstrated by ^{1}H NMR. The two aromatic nuclei borne by the phen group are located above and below the terpy plane, i.e., in the shielding region induced by this motif. The upfield shift experienced by the H$_{o'}$ and H$_{m'}$ protons upon complexation is indeed very significant ($\Delta\delta$ = −1.45 ppm for H$_{o'}$ and −0.71 ppm for H$_{m'}$). Analogously, the 6 and 6″ protons of the terpy fragment are strongly upfield-shifted ($\Delta\delta$ ~ −1.29 ppm) due to the ring current effect of the phen nucleus. These effects are reminiscent of similar upfield shifts observed in tetrahedral copper(I) complexes or 6-coordinated ruthenium(II) complexes con-

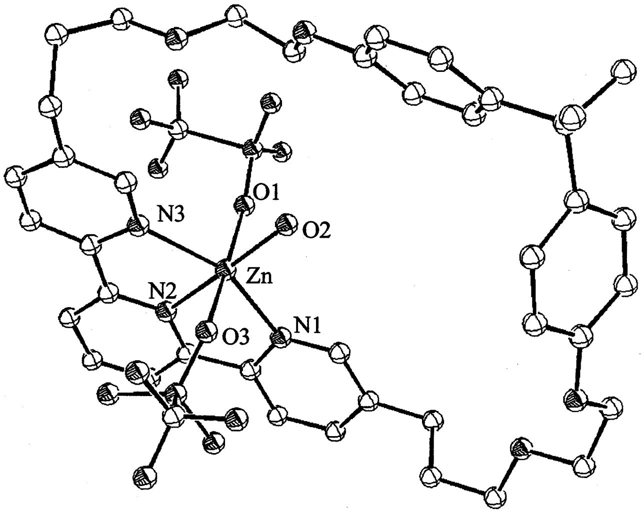


Figure 3. ORTEP diagram for the X-ray structure of $\mathbf{8}^{2+}$. Hydrogen atoms are omitted for clarity.

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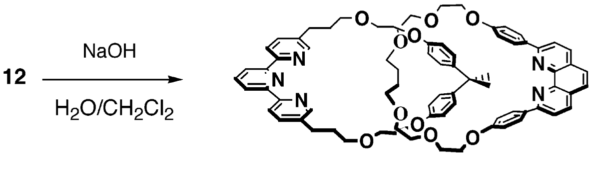
[21] Constable, E. C. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 69.

Table 1. Crystallographic Data for **8**$^{2+}$

formula	$C_{46}H_{57}F_6N_3O_{13}S_{13}Zn$
nolecular weight	1103.47
crystal system	triclinic
space group	*P*1
a (Å)	9.0624(1)
b (Å)	13.8674(3)
c (Å)	21.3164(4)
α (deg)	97.352(5)
β (deg)	96.995(5)
γ (deg)	98.293(5)
V (Å^3)	2602.09(8)
Z	2
color	colorless
D_{calc} (g cm^{-3})	1.41
μ (mm^{-1})	0.636
temp (K)	173
wavelength (Å)	0.710 73
R[a]	0.054
R_w[b]	0.063

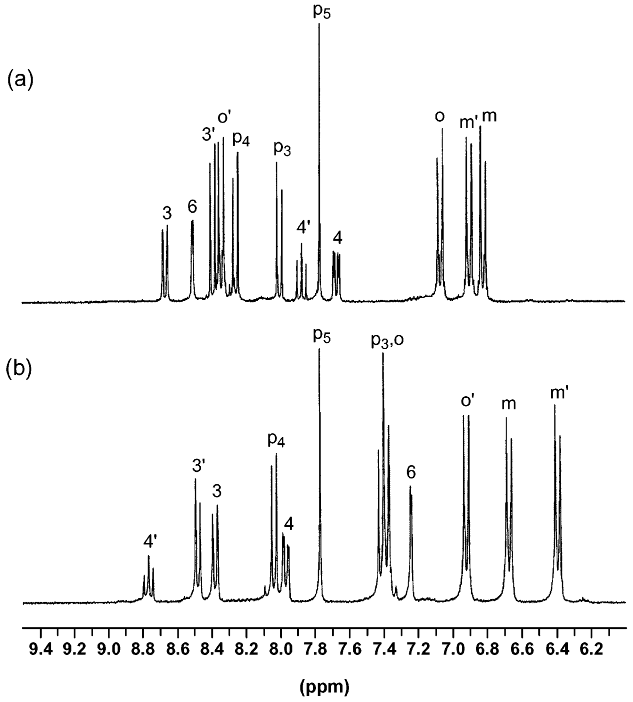
[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$.

Scheme 2. Demetalation of the [2]-catenane **12** to Yield the [2]-catenand **13**

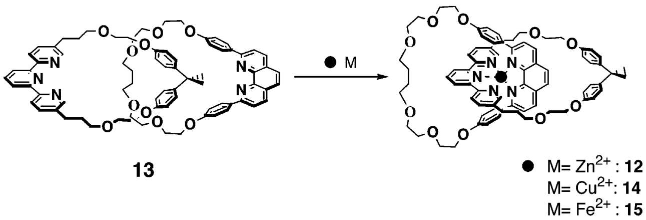


13

Figure 4. ^{1}H NMR spectra (300 MHz, aromatic region) in CD_2Cl_2 of (a) **13** and (b) **12**.



Scheme 3. Remetalation of **13** with Zn^{II} and Metallation of **13** with Cu^{II} and Fe^{II}



taining two aromatic ligands disposed perpendicularly to one another and arranged in an "entwined" fashion.[14,22]

The threaded species **9** was subsequently subjected to ring-closing metathesis with Grubbs first-generation catalyst **10**, at room temperature, in CH_2Cl_2. The stability of the zinc complex **11** being only limited, the chromatographic separation has been carried out on the partly demetalated crude reaction product, before incorporating back Zn^{2+}. The mixture of stereoisomers (*E* or *Z* double bonds) was then hydrogenated (H_2, room temperature, Pd/C) to afford catenane **12** from the threaded complex **9**.

The free catenand **13** was prepared from **12**, by removing the zinc cation with a base: **12** was dissolved in CH_2Cl_2 and stirred with an aqueous NaOH solution (biphasic reaction; Scheme 2). After chromatographic separation, **13** was obtained in quantitative yield from **9** as a white solid.

The FAB-MS spectrum of catenane **13** displays the characteristic pattern for catenated species, with the absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles.[23] Thus, the spectrum shows the molecular peak ([**13** + H]$^+$) and the next highest peaks are those of each constitutive macrocycle: $m/z = 1224.5$ for [**13** + H]$^+$, $m/z = 630.4$ for [**13** − **7**]$^+$, and $m/z = 595.4$ for [**13** − **16**]$^+$.

The electronic absorption spectrum of **13** in dichloromethane exhibits an intense maximum at $\lambda = 286$ nm ($\epsilon = 107\,000$). On the basis of literature data, this peak may be assigned to a spin-allowed $\pi-\pi^*$ transition centered on the terpy ligand.[24]

Coordination Chemistry of the Free Ligand 13. The free ligand **13** was then remetalated with Zn^{II} or metalated with Cu^{II} or Fe^{II} (Scheme 3). The Zn^{II}-catenane **12** was made by mixing stoichiometric amounts of $Zn(OTf)_2$ and ligand in CH_2Cl_2. The complex was obtained quantitatively.

The aromatic region of the spectra of the free ligand **13** and its Zn^{2+} complex **12** are given in Figure 4.

As observed previously for the precatenane **9**, the entwined topography of the molecular system is evidenced by the typical proton chemical shifts. The two coordinating subunits (terpy and dpp) of **13** are remote from one another and their corresponding protons show normal chemical shift values. On the other hand, the system undergoes a complete rearrangement during the complexation process, which brings the two coordinating fragments to close proximity. As a consequence, some particular protons such as $H_{o'}$ and $H_{m'}$ of the dpp unit (see Chart 1 for numbering) become located above and below the terpyridine nuclei. In the same manner,

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(22) Dietrich-Buchecker, C.; Marnot, P. A.; Sauvage, J.-P.; Kintzinger, J.-P.; Maltèse, P. *Nouv. J. Chim.* **1984**, *8*, 573.

(23) (a) Vetter, W.; Logemann, E.; Schill, G. *Org. Mass. Spectrom.* **1977**, *12*, 351. (b) Livoreil, A.; Sauvage, J.-P.; Armaroli, N.; Balzani, V.; Flamigni, L.; Ventura, B. *J. Am. Chem. Soc.* **1997**, *119*, 12114.

(24) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, 84, 85−277. (b) De Armond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.

the protons H_6 and $H_{6''}$ of the terpy unit become located in the shielding cone of the 1,10-phenanthroline nuclei. Due to intense ring current effects, the corresponding resonance signals move to higher field as compared to their position in the free ligand spectrum ($\Delta\delta = -1.37$ ppm for $H_{o'}$, $\Delta\delta = -0.46$ ppm for $H_{m'}$, and $\Delta\delta = -1.21$ ppm for H_6 and $H_{6''}$).

The Fe^{2+} and Cu^{2+} catenanes were made by mixing stoichiometric amounts of metal salts (BF_4^-) and ligand dissolved in EtOH and CH_2Cl_2, respectively. The resulting complexes are paramagnetic. They were characterized by UV and mass spectroscopy. Due to difficult purification, the crude products were used for the subsequent studies, including in particular electrochemical measurements. The UV spectrum of the Cu^{2+} catenane **14** is as expected for a 5-coordinated species complexed by a dpp and a terpy unit:[25] it shows a d−d absorption band centered at $\lambda = 593$ nm ($\epsilon = 166$).

The UV spectrum of Fe^{2+} catenane **15** shows two intense bands centered at 339 and 276 nm ($\epsilon = 18\,716$ and 2704). These bands correspond to ligand-centered transitions (LCT): ($\pi \rightarrow \pi^*$). The ES-MS spectra of **14** and **15** indicate the formation of the metalated species. Thus, for **14**, the spectrum shows the molecular peak ($[\mathbf{14}]^+$) at $m/z = 1367.2$ (obtained by loss of the counterion BF_4^-).

Electrochemical Study. The new 5-coordinated complexes **12**, **14**, and **15** were compared to their analogous 4-coordinated complexes with cat-30.[26] The electrochemical study was performed by cyclic voltammetry on a Pt electrode. The electrochemical data are collected in Table 2.

The redox processes observed in the course of the present study might involve either metal-centered reactions (d orbitals) or electron transfer to the organic ligand (π^* orbitals of the tpy subunits).[27]

Table 2. Electrochemical Properties of the Catenanes **12**, **14**, and **15** and Their Tetracoordinated Analogues[a]

	Zn		Cu		Fe	
charge	+2/+1	+1/0	+2/+1	+1/0	+2/+1	+1/0
medium	CH_2Cl_2	CH_2Cl_2	CH_3CN	CH_3CN	CH_2Cl_2	CH_2Cl_2
cat-30[26]	−0.96	−1.26	+0.57	−1.65	−0.72	−1.26
13	−1.19	−1.44	−0.13	/	−0.92	−1.32

[a] $E_{1/2}$ values were determined by cyclic voltametry. All potentials refer to SCE; the systems are reversible.

In each case, the lowest oxidation state is strongly stabilized in the 4-coordinated catenane as compared to the presently described series. It must be noted that the redox states indicated in Table 2 are only formal. For instance, reduction of the Zn^{2+} complexes (**12** or Zn•cat-30^{2+}) occurs on the ligands to afford a one- or two-electron reduction product. As far as the copper complexes are concerned, the first reduction process from the divalent state clearly occurs on the metal. In this case, the Cu(II)/Cu(I) potential is shifted to cathodic values by a difference of 0.7 V when going from the 4-coordinated species to $\mathbf{14}^{2+/1+}$.

In conclusion, the presently reported [2]-catenane, consisting of a terdentate ligand inscribed in a cycle and a bidentate chelate incorporated in a ring, displays coordination properties that are markedly different from those of the classical 4-coordinate catenane reported long ago. In particular, stable complexes with divalent transition metals could be prepared [Cu(II) or Fe(II)]. Their reduction potentials are negative, that of the copper complex being substantially shifted cathodically ($\Delta E \approx -0.7$ V) compared to the tetrahedral system.

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(25) Hasenknopf, B.; Lehn, J.-M.; Baum, G.; Fenske, D. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 1397.

(26) Dietrich-Buchecker, C.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 7791.

(27) Berger, R. M.; McMillin, D. R. *Inorg. Chem.* **1988**, *27*, 4245.

(28) Fyles, T. M.; McGavin, C. A.; Whitfield, D. M. *J. Org. Chem.* **1984**, *49*, 753.