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Templating and Clipping Coordination Reactions Leading to Heteronuclear Trimetallic Complexes Containing Interlocking Rings

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We report the preparation of heterotrimetallic complexes with a Cu-complexed [2]-catenate structure, containing two other metals within the rings. Starting from a multidentate ligand **1** containing two terpy units (terpy 2,2′:6′,2″-terpyridine) and one dpp fragment (dpp 2,9-diphenyl-1,10-phenanthroline), a 29-membered macrocycle **2** was prepared in 59% yield by clipping of both terpy moieties of **1** with Ru(DMSO)$_4$Cl$_2$ under high-dilution conditions. Threading of an additional equivalent of ligand **1** through macrocycle **2** was achieved by reaction with Cu(I), which acts as a template, forming a Cu(dpp)$_2^+$-type complex bearing two free terpy ligands. Reaction of this complex with different salts of Cu(II), Co(II), Fe(II), and Zn(II) gave the corresponding heteronuclear trimetallic catenates, as mixtures of diastereomers, again by clipping of both terpy units with the metal. The kinetic stability of the Ru complex prevents ligand scrambling. A somewhat different strategy, i.e., simultaneous formation of two rings from Cu(**1**)$_2^+$ by reaction with Ru(DMSO)$_4$Cl$_2$, afforded a catenate containing two Ru(terpy)$_2^+$ complexes within the rings. The high stability of these Ru species allows the selective demetalation of Cu(I) to give a catenane containing a free tetrahedral coordination site.

Introduction

Transition metals have been used extensively in the preparation of multicomponent systems. Their ability to gather and dispose ligands in a given predictable geometry, along with the possibility of ligand design, allows the preparation of very different structures.[1−4] In most cases, only one transition metal species is used, which leads to homonuclear complexes. Recently, the development of multidentate ligands containing subunits having different coordinating properties has enabled the preparation of heterodinuclear complexes with helical[5] and catenate[6] structures. On the other hand, catenates and catenanes containing transition metals within the rings are not very common. A family of such of those catenanes have been described by Fujita[7] and Stang,[8] and some other examples have been published.[6,9−12]

In this work we report the preparation of complexes presenting a [2]-catenate structure containing *three* different transition metals, one of which is employed as a template, the other two ones being included into the rings. We have taken advantage of both the different coordinating properties of several metals and the different kinetic stabilities of their complexes. Thus, with a suitable choice of metals, the same coordinating fragment can be used in the stepwise construction of heteronuclear trimetallic species showing a nontrivial topology.

Experimental Section

Materials and General Procedures. Cu(MeCN)$_4$PF$_6$[13] and Ru(DMSO)$_4$Cl$_2$[14] were prepared according to the literature procedures. All other chemicals were of the best commercially available grade and were used without further purification. Dry MeCN and CH$_2$Cl$_2$ were obtained by distillation over CaH$_2$ under Ar. 1,2-Dichloroethane (SDS,

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(1) *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Sauvage, J.-P.; Hosseini, W., volume Eds.; Pergamon Press: Oxford, U.K., 1996; Vol. 9.

(2) Maverick, A. W.; Ivie, M. L.; Waggenspack, J. H.; Fronczek, F. R. *Inorg. Chem.* **1990**, *29*, 2403. Maverick, A. W.; Buckingham, S. C.; Yao, Q.; Bradbury, J. R.; Stanley, G. G. *J. Am. Chem. Soc.* **1986**, *108*, 7430.

(3) Saalfrank, R. W.; Trummer, S.; Krautscheid, H.; Schünemann, V.; Trautwein, A. X.; Hien, S.; Stadler, C.; Daub, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2206. Saalfrank, R. W.; Burak, R.; Breit, A.; Stalke, D.; Herbst-Irmer, R.; Daub, J.; Porsch, M.; Bill, E.; Müther, M.; Trautwein, A. X. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1621. Saalfrank, R. W.; Hörner, B.; Stalke, D.; Salbeck, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1179. Saalfrank, R. W.; Stark, A.; Bremer, M.; Hummel, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 311.

(4) Some recent works: Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1838. Benelli, C.; Parsons, S.; Solan, G. A.; Winpenny, R. E. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1825.

(5) Constable, E. C.; Edwards, A. J.; Raithby, P. R.; Walker, J. V. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1465. Piguet, C.; Hopfgartner, G.; Bocquet, B.; Schaad, O.; Williams, A. F. *J. Am. Chem. Soc.* **1994**, *116*, 9092.

(6) Piguet, C.; Bernardinelli, G.; Williams, A. F.; Bocquet, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 582.

(7) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *J. Chem. Soc., Chem. Commun.* **1996**, 1535. Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720. Fujita, M.; Ibukuro, F.; Seki, H.; Kamo, O.; Imanari, M.; Ogura, K. *J. Am. Chem. Soc.* **1996**, *118*, 899. Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. Fujita, M.; Nagao, S.; Iida, M.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574. Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645.

(8) Stang, P. J.; Olenyuk, B.; Fan, J.; Arif, A. M. *Organometallics* **1996**, *15*, 904. Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273. Stang, P. J.; Whiteford, J. A. *Organometallics* **1994**, *13*, 3776. Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. Stang, P. J.; Chen, K.; Arif, A. M. *J. Am,. Chem. Soc.* **1995**, *117*, 8793. Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667.

(9) Grohmann, A. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 2107. Beer, P. D.; Rothin, A. S. *Polyhedron* **1989**, *8*, 1251.

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

(11) Mingos, D. M. P.; Yan, J.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 17.

(12) Cárdenas, D. J.; Gaviña, P.; Sauvage, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 2657.

(13) Kubas, G. J. *Inorg. Synth.* **1990**, *28*, 68.

(14) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204. According to this reference, the *trans* isomer was prepared, since the crude complex was not recrystallized.

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synthesis grade), EtOH (Normapur, analytical reagent), and MeOH (Carlo Erba, analytical grade) were used as received. Reactions were performed under Ar, but chromatographic separations were done in air. UV−visible spectra were recorded on a Kontron Instruments Uvikon 860 spectrophotometer. ^{1}H NMR spectra were recorded on either Brucker WP 200SY (200 MHz) or WP 400SY (400 MHz) spectrometers (using the deuterated solvent as the lock and residual solvent as the internal reference). Fast atom bombardment mass spectra (FABMS) were recorded in the positive ion mode with either a krypton primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a Kratos MS80RF mass spectrometer coupled to a DS90 system or a xenon primary atom beam with the same matrix and a ZAB-HF mass spectrometer. Electrochemical measurements were performed with a three-electrode system consisting of a platinum working electrode, a platinum-wire counter electrode and a standard reference calomel electrode (SCE), vs which all potentials are reported. All measurements were carried out under argon, in degassed spectroscopic grade solvents, using 0.1 M *n*-Bu_4NBF_4 solutions as supporting electrolyte. A potentiostat (EG&G Princeton Applied Research Model 273A) connected to a computer was used (software, Programme Research Electrochemistry Software), as well as a potentiostat Bruker E130M, connected to a printing table.

Macrocyclic Complex Ru(1)(PF$_6$)$_2$ (2). A degassed solution of ligand **1** (500 mg, 0.53 mmol) in 1,2-dichloroethane−EtOH (0.75 L + 1 L) was heated at 70 °C and treated dropwise with a solution of Ru(DMSO)$_4$Cl$_2$ (257 mg, 0.53 mmol) in EtOH (1 L). After the addition had finished (∼12 h), the resulting red solution was further heated at 70 °C for 6 h. After cooling to 23 °C, solvent was evaporated and the residue was chromatographed (SiO_2 column; eluent: from MeCN−H_2O (95:5) to MeCN−H_2O−$KNO_{3(sat)}$ (90:10:0.2)). The violet byproducts that are eluted first were not characterized. The red complex **2** was isolated as its PF_6^- salt by the following procedure: the eluted nitrate was evaporated to dryness and the residue was redissolved in the minimum amount of MeCN (and some drops of H_2O if necessary). Then, it was treated with an excess of a saturated KPF_6 solution in MeCN. The complex was precipitated as a red solid by addition of H_2O. It was filtered, washed with H_2O and dried under vacuum (416 mg, 59%). ^{1}H NMR (acetone-d_6, 200 MHz): δ 9.09 (d, J = 8.1 Hz, 2H), 8.86 (d, J = 8.1 Hz, 2H), 8.69 (d, J = 8.4 Hz, 2H), 8.64 (d, J = 8.4 Hz, 2H), 8.58 (d, J = 8.4 Hz, 2H), 8.23 (t, J = 8.1 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H), 8.09 (d, J = 8.4 Hz, 4H), 8.03 (s, 2H), 7.87 (br d, J = 8.4 Hz, 2H), 7.80 (dd, J = 8.3, 1.7 Hz, 2H), 7.54 (br s, 2H), 7.41 (d, J = 1.5 Hz, 2H), 6.62 (d, J = 8.8 Hz, 4H), 3.98 (m, 2H), 3.72 (m, 2H), 2.59 (t, J = 6.7 Hz, 4H), 2.1−1.8 (m, 4H), 1.99 (br s, 6H). UV−visible (MeCN) λ (nm) (ϵ, mol^{-1} L cm^{-1}): 474 (12 800), 313 (76 100), 276 (68 900), 254 (43 900), 236 (44 900). Electrochemical data (McCN): *E*[Ru(III)/Ru(II)] = +1.23 V (ΔE = 95 mV), *E*[Ru(II)/Ru(I)] = −1.34 V (ΔE = 100 mV). FAB-MS *m/z*: 1330.0 (M$^+$, calcd 1330.1), 1185.3 ([M − PF$_6$]$^+$, calcd 1185.2), 1039.3 ([M − 2PF$_6$]$^+$, calcd 1040.1). Anal. Calcd for $C_{62}H_{50}F_{12}N_8O_2P_2Ru$: C, 55.98; H, 3.79; N, 8.42. Found: C, 56.04; H, 3.99; N, 8.29.

Macrocyclic Dimer Ru$_2$(1)$_2$(PF$_6$)$_4$ (3). This complex was obtained from the reaction described above, as a second red fraction from the column chromatography, when the eluent polarity was increased (90:10:0.5). The compound (red solid) was also isolated as the PF_6^- salt (21 mg, 2%). ^{1}H NMR (acetone-d_6, 200 MHz): δ 8.79 (m, 8H), 8.70−8.30 (m, 28 H), 8.03 (s, 2H), 8.02 (s, 2H), 7.90−7.70 (m, 8H), 7.37 (m, 4H), 7.25 (m, 4H), 6.90 (d, J = 8.7 Hz, 4H), 6.88 (d, J = 8.7 Hz, 4H), 3.73 (m, 4H), 3.45 (m, 4H), 2.47 (br t, J = 7.5 Hz, 8H), 1.91 (br s, 12H), 1.78 (m, 8H). UV−visible (MeCN) λ (nm) (ϵ, mol^{-1} L cm^{-1}): 474 (19 100), 315 (130 400), 278 (129 500), 245 (92 200). Electrochemical data (MeCN): *E*[Ru(III)/Ru(II)] = +1.23 V (ΔE = 65 mV), *E*[Ru(II)/Ru(I)] = −1.32 V (ΔE = 85 mV). FAB-MS *m/z*: 2516.4 ([M − PF$_6$]$^+$, calcd 2515.3), 2369.7 ([M − 2PF$_6$]$^+$, calcd 2370.3), 2224.5 (M − 3PF$_6$]$^+$, calcd 2225.4).

Synthesis of Precatenate 4. This common intermediate in the syntheses of the complexes **5**−**8** was prepared by the following two-step one-pot procedure. A solution of Cu(MeCN)$_4$PF$_6$ (10.1 mg, 0.027 mmol) in degassed MeCN (5 mL) was transferred via a cannula to a stirred solution of macrocyclic complex **2** (36 mg, 0.027 mmol) in MeCN (10 mL) under argon. The resulting red solution was stirred at 23 °C for 0.5 h. Then, a degassed solution of ligand **1** (25.4 mg, 0.027 mmol) in CH_2Cl_2 (30 mL) was added, resulting in the immediate formation of a brown-red solution which was stirred under argon at 23 °C for 1 h. Once the complex is formed, it is stable in air. Evaporation of the solvent gave a brown solid which was used without further treatment (see text below).

[RuCu$_2$(1)$_2$](PF$_6$)$_5$ (5). A solution of **4** (26 mg, 0.010 mmol) in degassed MeCN (15 mL) was treated with a solution of Cu(OAc)$_2$·H_2O (2.1 mg, 0.010 mmol) in MeOH. The resulting mixture was stirred at 23 °C for 2 h. After evaporation of the solvent, the residue was column chromatographed (SiO_2; MeCN−H_2O (9:1) containing 0.2−1% aqueous saturated KNO_3), and the brown complex was isolated as a PF_6^- salt (27 mg, 96%). UV−visible (MeCN) λ (nm) (ϵ, mol^{-1} L cm^{-1}): 474 (13 100), 316 (115 000), 276 (103 000), 250 (122 000), 209 (142 000). Electrochemical data (MeCN): *E*[Ru(III)/Ru(II)] = +1.25 V (ΔE = 55 mV), *E*[Ru(II)/Ru(I)] = −1.32 V (ΔE = 65 mV), *E*[tetracoord Cu(II)/Cu(I)] = +0.61 V (ΔE = 60 mV), *E*[hexacoord Cu(II)/Cu(I)] = −0.04 V (irreversible). FAB-MS *m/z*: 2686.7 ([M − PF$_6$]$^+$, calcd 2686.3), 2541.5 ([M − 2PF$_6$]$^+$, calcd 2541.3), 2396.1 ([M − 3PF$_6$]$^+$, calcd 2396.3), 1198.3, 1002.6 (Cu(**1**)$^+$, calcd 1002.7). Anal. Calcd for $C_{124}H_{100}F_{30}N_{16}O_4P_5Cu_2Ru$: C, 52.60; H, 3.56; N, 7.92. Found: C, 52.70; H, 3.60; N, 7.88.

[RuCuCo(1)$_2$](PF$_6$)$_5$ (6). A solution of **4** (39 mg, 0.016 mmol) in degassed MeCN (15 mL) was treated with a solution of CoCl$_2$·6H_2O (3.7 mg, 0.016 mmol) in MeCn (3 mL). The resulting mixture was stirred at 23 °C for 8 h. Solid KPF_6 was added, the solvent was evaporated, and the brown residue was rinsed with MeOH and dried under vacuum. Column chromatography (Al_2O_3; CH_2Cl_2 containing 0.7% of MeOH) furnished the brown complex, which was recrystallized from MeCN−Et_2O (18 mg, 40%). UV−visible (MeCN) λ (nm) (ϵ, mol^{-1} L cm^{-1}): 473 (12 400), 316 (101 000), 276 (86 000), 251 (96 000). Electrochemical data (MeCN): *E*[Ru(III)/Ru(II)] = +1.30 V (ΔE = 55 mV), *E*[Ru(II)/Ru(I)] = −1.27 V (ΔE = 60 mV), *E*[Cu(II)/Cu(I)] = +0.66 V (ΔE = 55 mV), *E*[Co(III)/Co(II)] = +0.20 V (ΔE = 95 mV), *E*[Co(II)/Co(I)] = 0.76 V (ΔE = 60 mV). FAB-MS *m/z*: 2682.1 ([M − PF$_6$]$^+$, calcd 2681.7), 2536.7 ([M = 2PF$_6$]$^+$, calcd 2536.7), 2391.8 ([M − 3PF$_6$]$^+$, calcd 2391.7).

[RuCuFe(1)$_2$](PF$_6$)$_5$ (7). In a similar procedure, a solution of **4** (79 mg, 0.032 mmol) in MeCN−acetone (2:1, 8 mL) was treated with a solution of Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H_2O (12.5 mg, 0.032 mmol) in H_2O−MeOH (1:1, 2 mL), and the mixture was stirred at 23 °C for 15 h. Column chromatography of the reside resulting from evaporation of the solvent (SiO_2; MeCN−H_2O (9:1) containing 0.2−1% aqueous saturated KNO_3) followed by anion exchange gave complex **7** as a brown-violet solid (30 mg, 30%). ^{1}H NMR (acetone-d_6, 400 MHz): δ 9.31 (t, J = 7.6 Hz, 4H), 9.18 (d, J = 8.0 Hz, 2H), 9.17 (d, J = 8.3 Hz, 2H), 9.12 (d, J = 7.5 Hz, 2H), 9.11 (d, J = 7.8 Hz, 2H), 9.14−8.98 (m, 12H), 8.89 (m, 4H), 8.70 (d, J = 8.8 Hz, 4H), 8.67 (d, J = 9.1 Hz, 4H), 8.59 (t, J = 8.0 Hz, 2H), 8.58 (t, J = 8.3 Hz, 2H), 8.08 (m, 4H), 8.03 (dd, J = 8.3, 1.9 Hz, 2H), 7.95−7.72 (m, 30H), 7.61 (br s, 2H), 7.60 (d, J = 1.6 Hz, 2H), 7.56 (br s, 4H), 7.30 (m, 12H), 7.23 (m, 8H), 6.21 (s, 2H), 6.19 (s, 2H), 6.02 (s, 2H), 5.97 (s, 2H), 5.94 (m, 16H), 3.47 (m, 16H), 2.27 (m, 16H), 2.04 (s, 12H), 1.99 (s, 12H), 1.28 (m, 16H). UV-vis (MeCN) λ (nm) (ϵ, mol^{-1} L cm^{-1}): 548 (12 100), 475 (19 500), 325 (134 300), 316 (137 400), 277 (124 700), 252 (125 200). Electrochemical data (MeCN): *E*[Ru(III)/Ru(II)] = +1.26 V (ΔE = 65 mV), *E*[Ru(II)/Ru(I)] = −1.29 V (ΔE = 700 mV), *E*[Cu(II)/Cu(I)] = +0.63 V (ΔE = 70 mV), *E*[Fe(III)/Fe(II)] = +1.10 V (ΔE = 65 mV), *E*[Fe(II)/Fe(I)] = 1.37 V (ΔE = 65 mV). FAB-MS *m/z*: 2678.7 ([M − PF$_6$]$^+$, calcd 2678.6), 2533.7 ([M − 2PF$_6$]$^+$, calcd 2533.6), 2388.8 ([M − 3PF$_6$]$^+$, calcd 2388.6).

[RuCuZn(1)$_2$](PF$_6$)$_5$ (8). A solution of **4** (79 mg, 0.032 mmol) in degassed MeCN (10 mL) was treated with a solution of Zn(OAc)$_2$·2H_2O (7.0 mg, 0.032 mmol) in MeOH (8 mL), and the resulting mixture was stirred at 23 °C for 15 h. Solvent was evaporated and the residue was chromatographed (SiO_2 column; MeCN−H_2O (9:1) containing 0.2−1% aqueous saturated KNO_3) to yield a brown solid isolated as a PF_6^- salt (22 mg, 25%). ^{1}H NMR (acetone-d_6, 200 MHz): δ 9.11 (m, 8H), 9.09 (d, J = 8.0 Hz, 4H), 9.01 (m, 12H), 8.88 (t, J = 8.0 Hz, 2H), 8.87 (d, J = 8.0 Hz, 2H), 8.75 (d, J = 8.3 Hz, 2H), 8.74 (d, J = 8.0 Hz, 2H), 8.69 (d, J = 8.3 Hz, 2H), 8.68 (d, J = 8.0 Hz, 2H), 8.60 (d, J = 8.3 Hz, 2H), 8.56 (d, J = 8.0 Hz, 2H), 8.38 (dd, J = 8.3, 1.8 Hz, 2H), 8.24 (m, 6H), 8.18 (br d, J = 8.3 Hz, 2H), 8.11 (d, J = 8.3 Hz, 4H), 8.01 (m, 4H), 7.91 (m, 10H), 7.83 (d, J = 8.3 Hz, 2H), 7.81−7.69 (m, 14H), 7.56 (br s, 2H), 7.53 (br s, 2H), 7.31 (m, 12H), 7.25 (d,

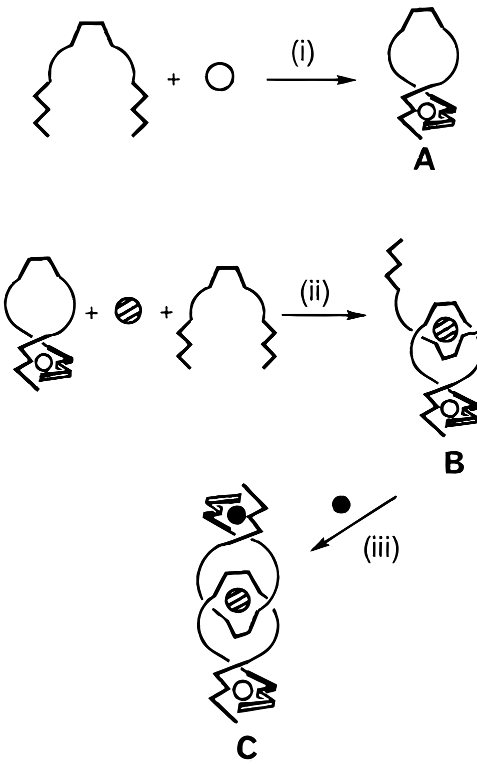

Figure 1. Synthesis of disymmetrical [2]-catenates incorporating two different transition metals in their constitutive rings (black and white dots) and constructed around a third transition metal center used as template. The starting coordinating string contains one central bidentate ligand (symbolized by a U) and two lateral terdentate fragments (symbolized by a stylized W).

J = 8.8 Hz, 4H), 6.36 (s, 2H), 6.32 (s, 2H), 6.23 (s, 2H), 6.16 (s, 2H), 5.95 (m, 16H), 3.60−3.30 (m, 16H), 2.45−2.20 (s, 16H), 2.16 (s, 12H), 2.05 (s, 12H), 1.50−1.30 (m, 16H). UV−visible (MeCN) λ (nm) (ϵ, mol^{-1} L cm^{-1}): 618 (1123), 473 (14 600), 327 (115 400), 316 (130 500), 276 (122 900), 250 (135 100). Electrochemical data (MeCN): E[Ru(III)/Ru(II)] = +1.32 V (ΔE = 70 mV), E[Ru(II)/Ru(I)] = −1.25 V (ΔE = 70 mV), E[Cu(II)/Cu(I)] = +0.68 V (ΔE = 70 mV). FAB-MS m/z: 2688.3 ([M − PF$_6$]$^+$, calcd 2688.1), 2541.7 ([M − 2PF$_6$]$^+$, calcd 2543.1), 2396.4 [(M − 3PF$_6$]$^+$, calcd 2398.1), 1002.2 (Cu(**1**)$^+$, calcd 1002.7).

[Ru$_2$Cu(1)$_2$](PF$_6$)$_5$ (10). Method A. A solution of **1** (110 mg, 0.117 mmol) in degassed CH_2Cl_2 (125 mL) was treated with a solution of Cu(MeCN)$_4$PF$_6$ (22 mg, 0.059 mmol) in MeCN (50 mL) under Ar. The resulting brownish red mixture was stirred at 23 °C for 0.5 h. After evaporation of the solvent, the residue was dissolved in degassed 1,2-dichloroethane−EtOH (200 + 100 mL), the mixture was heated at 70 °C and treated dropwise with a degassed solution of Ru(DMSO)$_4$Cl$_2$ (59 mg, 0.112 mmol) in EtOH (250 mL) for 12 h. After the addition had been completed, the mixture was heated for three more hours. The residue resulting from evaporation of the solvent was chromatographed (SiO$_2$ column; MeCN−H$_2$O (9:1) containing up to 0.8% aqueous saturated KNO$_3$). The brown complex was isolated as the PF$_6^-$ salt (17 mg, 10%).

Method B. A mixture of the complex **5** (85 mg, 0.0301 mmol) and Ru(DMSO)$_4$Cl$_2$ (14.6 mg, 0.0301 mmol) in MeCN−EtOH (7 + 40 mL, respectively) was heated under refulx for 5 h. Then, an additional 1 equiv of Ru(DMSO)$_4$Cl$_2$ (14.6 mg) was added and the solution was heated overnight. After evaporation of the solvent, the residue was chromatographed as above and the complex isolated as the PF$_6^-$ salt (11 mg, 12%). ^{1}H NMR (acetone-d_6, 400 MHz): δ 9.11 (d, J = 8.0 Hz, 2H), 9.09 (d, J = 8.0 Hz, 2H), 9.07 (d, J = 8.6 Hz, 2H), 9.00 (m, 6H), 8.69 (d, J = 8.3 Hz, 2H), 8.68 (d, J = 8.3 Hz, 2H), 8.59 (t, J = 8.0 Hz, 2H), 8.57 (t, J = 8.2 Hz, 2H), 8.14 (dd, J = 8.3, 1.6 Hz, 2H), 7.99 (dd, J = 8.3, 1.6 Hz, 2H), 7.91 (m, 8H), 7.84 (d, J = 8.6 2H), 7.82 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.56 (br s, 2H), 7.55 (br s, 2H), 7.31 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.6 Hz, 4H), 6.20 (s, 2H), 6.16 (s, 2H), 5.95 (d, J = 8.6 Hz, 4H), 5.94 (d, J = 8.6 Hz, 4H), 3.45 (m, 8H), 2.27 (m, 8H), 2.00 (s, 12H), 1.35 (m, 8H). UV−visible (MeCN) λ (nm) (ϵ, mol^{-1} L cm^{-1}): 473 (21 800), 315 (146 000), 276 (115 000), 251 (117 000). Electrochemical data (MeCN): E[Ru(III)/Ru(II)] = +1.26 V (ΔE = 70 mV), E[Ru(II)/Ru(I)] = −1.29 V (ΔE = 65 mV), E[Cu(II)/Cu(I)] = +0.64 V (ΔE = 70 mV). FAB-MS m/z: 2723.6 ([M − PF$_6$]$^+$, calcd 2723.8), 2579.0 ([M − 2PF$_6$]$^+$, calcd 2578.8), 2433.5 ([M = 3PF$_6$]$^+$, calcd 2433.8). Anal. Calcd for $C_{124}H_{100}F_{30}N_{16}O_4P_5CuRu_2$: C, 51.91; H, 3.51; N, 7.81. Found: C, 51.61; H, 3.63; N, 7.77.

Catenane [Ru$_2$(1)$_2$](PF$_6$)$_5$ (11). A solution of **10** (16 mg, 5.6 μmol) in MeCN (6 mL) was treated with a solution of KCN (18 mg, 0.28 mmol) in H$_2$O (2 mL). After stirring at 70 °C for 20 h, the resulting red solution was extracted with CH_2Cl_2 and washed with H$_2$O. The

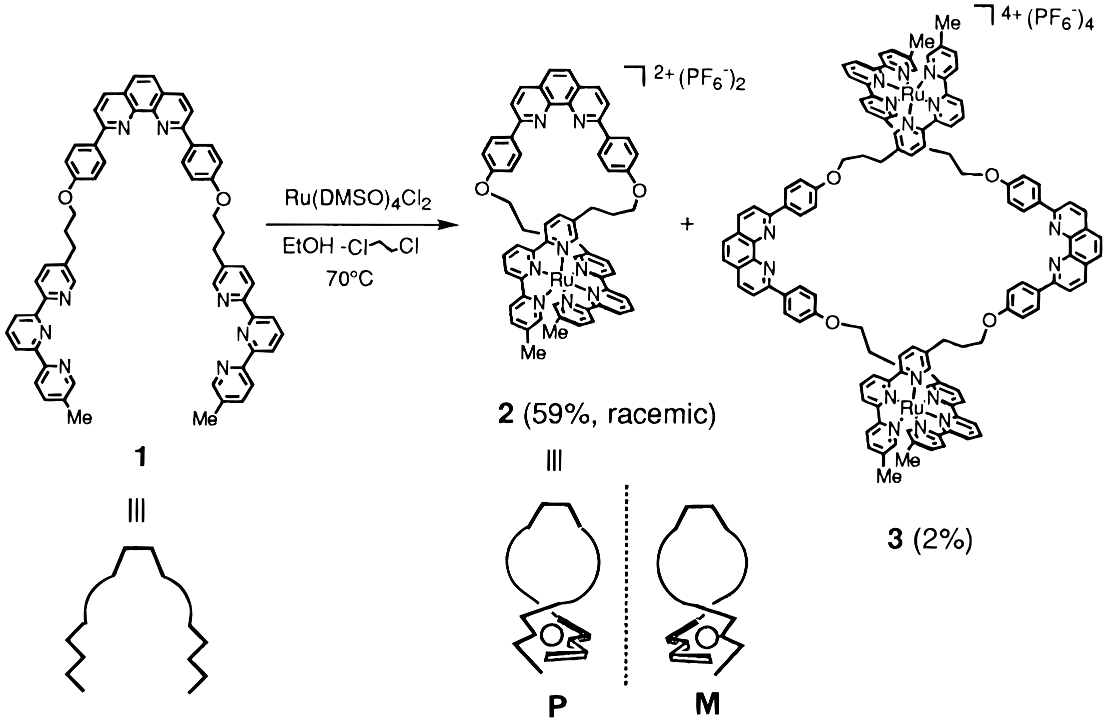

Figure 2. Preparation of the Ru(terpy)$_2^{2+}$-based macrocyclic compounds.

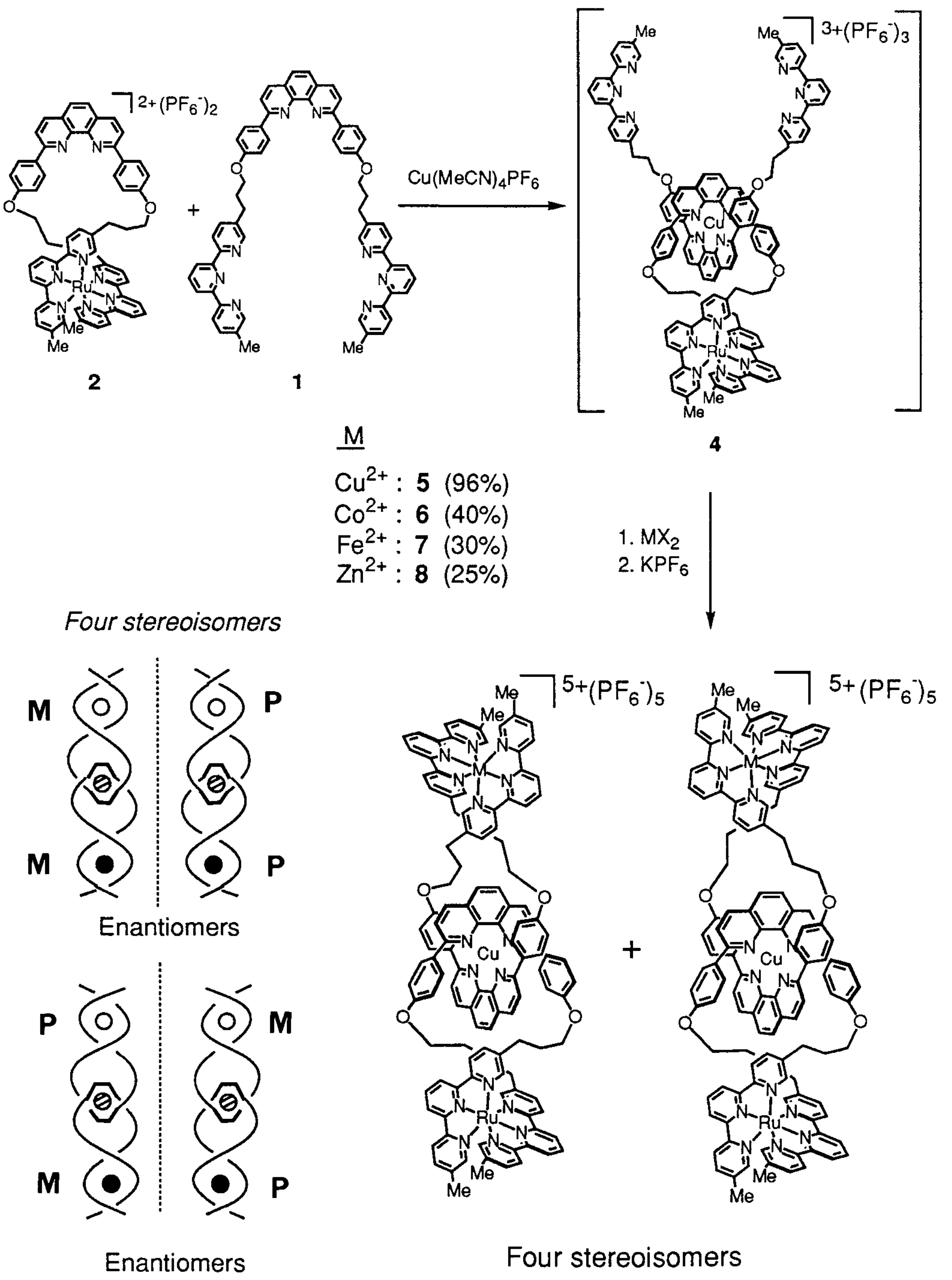

Figure 3. Two-step synthesis of trimetallic catenates: Cu(I)-directed threading of **1** through **2** followed by cyclization using an additional metal center.

residue resulting from the evaporation of the organic phase was chromatographed (SiO_2 column; MeCN−H_2O (9:1) containing up to 0.5% of saturated aqueous KNO_3), and the complex was isolated as the PF_6^- salt (11 mg, 74%). ^1H NMR (acetone-d_6, 400 MHz): δ 8.87 (d, J = 8.1 Hz, 2H), 8.84 (d, J = 8.1 Hz, 2H), 8.82 (d, J = 8.1 Hz, 2H), 8.71 (d, J = 8.1 Hz, 2H), 8.62 (d, J = 8.6 Hz, 2H), 8.60 (d, J = 8.1 Hz, 2H), 8.56 (d, J = 8.4 Hz, 2H), 8.38 (t, J = 8.1 Hz, 2H), 8.36 (d, J = 8.3 Hz, 2H), 8.30 (t, J = 8.1 Hz, 2H), 8.21 (d, J = 8.3 Hz, 4H), 8.05 (d, J = 8.3 Hz, 2H), 7.99 (br s, 2H), 7.97 (d, J = 8.6 Hz, 4H), 7.95 (br s, 2H), 7.85 (br d, J = 8.8 Hz, 6H), 7.81 (br d, J = 8.6 Hz, 2H), 7.80 (s, 4H), 7.73 (d, J = 8.3 Hz, 2H), 7.58 (br d, $J \sim 8$ Hz, 2H), 7.43 (br s, 2H), 7.37 (br s, 2H), 7.13 (br d, $J \sim 8$ Hz, 2H), 6.29 (d, J = 8.6 Hz, 4H), 6.22 (d, J = 8.8 Hz, 4H), 3.6−3.4 (m, 8H), 2.23 (m, 8H), 2.02 (s, 6H), 1.99 (s, 6H), 1.48 (m, 8H). FAB-MS *m/z*: 2516.9 ($[M - PF_6 + H]^+$, calcd 2516.3), 2370.4 ($[M - 2PF_6]^+$, calcd 2370.3), 2225.3 ($[M - 3PF_6]^+$, calcd 2225.3). UV−visible (MeCN) λ (nm) (ϵ, mol^{-1} L cm^{-1}): 474 (22 750), 315 (160 000), 276 (141 100), 251 (116 400). Electrochemical data (MeCN): E[Ru(III)/Ru(II)] = +1.25 V (ΔE = 70 mV), E[Ru(II)/Ru(I)] = −1.30 V (ΔE = 70 mV).

Results and Discussion

The strategy followed to prepare the polynuclear trimetallic complexes is shown in Figure 1: (i) a multidentate ligand containing two terpy units (terpy) 2,2′:6′,2″-terpyridine and one dpp fragment (dpp 2,9-diphenyl-1,10-phenanthroline) is reacted with a *metal preferring the terpy ligands* to afford a macrocyclic bis(terpy)octahedral complex (**A**). This complex must be kinetically stable to avoid further ligand scrambling. (ii) A second metal, *which binds selectively to the dpp moieties*, is used as a template to *direct the threading* of a second molecule of ligand through the macrocycle. Thus, a heterobimetallic precatenate with two free terpy units is formed (**C**). (iii) Addition of a suitable third metal will lead to a [2]-catenate (**C**) containing two octahedral metal complexes included in the backbones of the rings.

Compound **1**[15] (Figure 2) was chosen as the multidentate ligand. It contains the necessary terpy and dpp units joined by

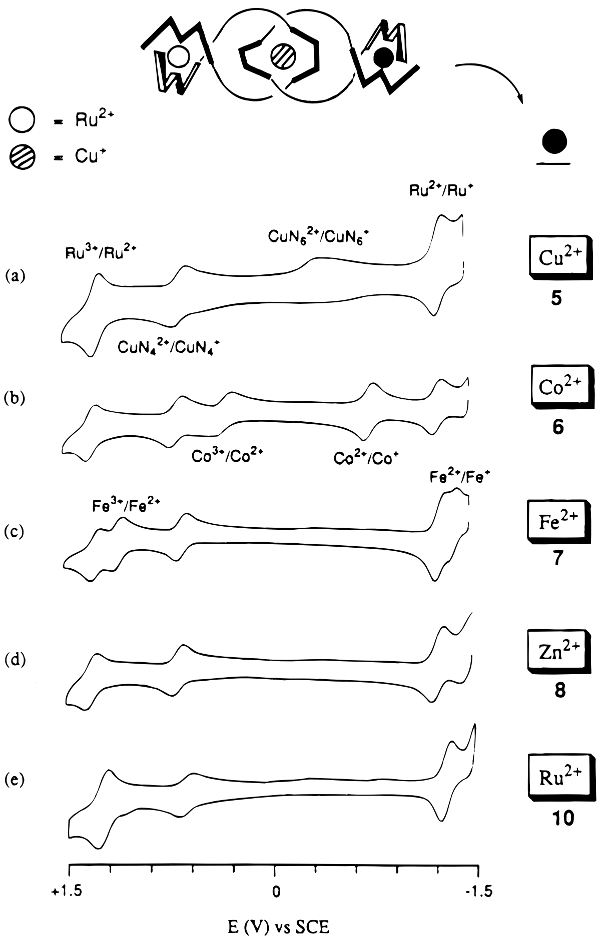

Figure 4. Cyclic voltammetry studies of the four catenates containing three different metals (**5**−**8**) and clearly showing the distinct electrochemical response of each subunit. The fifth compound (**10**) contains two Ru atoms and one central Cu, the relative heights of the three waves Ru(III)/Ru(II), Cu(II)/Cu(I), and Ru(II)/Ru(I) being in accordance with this stoichiometry. Of course, it should be kept in mind that the formal Ru(II)/Ru(I) couple corresponds to a ligand-localized process, with no change of the metal oxidation state (+2).

linkers long enough to permit the formation of the interlocked structure. Ru(II) was thought to be a suitable metal to prepare a macrocyclic complex from **1**, due to its ability to give octahedral Ru(terpy)$_2^{2+}$ complexes and because of the high kinetic stability of these units toward ligand dissociation and scrambling. Ru(DMSO)$_4$Cl$_2$[14] was employed as the Ru source (instead of the more usual RuCl$_3$) since it requires less drastic conditions to react with 2 equiv of terpy. A solution of **1** in 1,2-dichloroethane−EtOH (3×10^{-4} M) was treated dropwise with a solution of Ru(DMSO)$_4$Cl$_2$ in EtOH (5.3×10^{-4} M) at 70 °C to give the desired macrocyclic complex **2** (PF$_6^-$ salt, 29-membered ring) as a red solid in 59% yield after column chromatography (Figure 2). Attempts to improve the yield by using higher dilution conditions were unsuccessful.[16] The reaction of Ru with the dpp ligand probably limits the yield of the desired complex.[17] The complex **2** is chiral, and it is obtained as a racemic mixture of enantiomers. We did not try to resolve them. A second minor red species was also isolated. It was shown to be the 58-membered ring dimer **3** (2% yield). Both complexes (**2** and **3**) show an absorption at 474 nm in their UV−visible spectrum typical of the Ru(terpy)$_2^{2+}$ complexes. Their cyclic voltammograms exhibit reversible waves for both Ru oxidation and (ligand centered) reduction at the usual values (+1.23, −1.34 V; and +1.23, −1.32 V vs SCE, for **2** and **3**, respectively, in MeCN). Satisfactory FAB mass spectra were also obtained. The ^{1}H NMR spectra show an appreciable difference in the chemical shifts of the phenyl H atoms in ortho to the O atom (0.26 ppm) for complexes **2** and **3**. An upfield shift is observed in the case of the locked complex **2**. In the case of the more flexible **3**, these hydrogens show the usual chemical shift for this kind of phenyl ring (6.88 ppm).

The next step is based on the Cu-templated synthesis of cantenanes and rotaxanes developed some years ago.[18] dpp fragments have been shown to be excellent ligands for Cu(I) coordination. Reaction of **2** with Cu(MeCN)$_4$PF$_6$ in MeCN at 23 °C led to the dpp complex Cu(**2**)(MeCN)$_2$PF$_6$, which was treated *in situ* with a CH$_2$Cl$_2$ solution of **1** to give the threaded species **4** (Figure 3, top). Coordination takes place *selectively* on the dpp fragment of **1**, due to the higher stability of this kind of tetrahedral Cu(I) complex as compared to the pentacoordinate ones, as has been observed for related systems.[19,20] This complex could not be isolated as a pure compound by column chromatography (Al$_2$O$_3$) or crystallization since it is partially dissociated in solution as shown by ^{1}H NMR (acetone-d_6 or CD$_2$Cl$_2$). Nevertheless it is present in ∼80% in the equilibrium. The ^{1}H NMR spectrum shows the usual upfield-shifted signals found for the phenyl rings in this kind of entwined Cu(dpp)$_2^+$-type complex (5.97 and 6.13 ppm for the H ortho to the O atom; 7.34 and 7.52 ppm for the meta H).[18,19] Since only a small amount of free **2** (∼20%) was observed, the formation of Cu(**1**)$_2^+$ as the main species was discarded. This behavior is probably due to the relative instability of the threaded species. It has been also observed in a different but related Cu(I) complex containing a Ru(bipy)$_3^{2+}$ unit,[21] and it may be a consequence of the electrostatic repulsion between the close Ru(II) and Cu(I) complexes.[22] The crude mixture was thus employed for the following coordination reactions.

The preparation of the catenates was achieved by reacting different metal salts with the crude precatenate **4** in suitable mixtures of solvents (see the Experimental Section). Thus, the reaction of **4** with Zn(OAc)$_2$·2H$_2$O, Cu(OAc)$_2$·H$_2$O, Fe(NH$_4$)$_2$-

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(15) Compound **1** was prepared by double alkylation of 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline with 5″-methyl-5-(3-trifluoromethanosulfonyl-1-propyl)-2,2′:6′,2″-terpyridine. The synthesis will be reported elsewhere.

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

(17) Some minor violet byproducts are obtained from the chromatography. Although they were not characterized, they probably are dpp cyclometalated species. In fact, cyclometalated complexes of related dpp ligands have been obtained: Collin, J.-P.; Kayhanian, R.; Sauvage, J.-P., unpublished results. For similar cyclometalation reactions see, for example: Reveco, P.; Cherry, W. R.; Medley, J.; Garber, A.; Gale, R. J.; Selbin, J. *Inorg. Chem.* **1996**, *25*, 1842. Reveco, P.; Schmehl, R. H.; Cherry, W. R.; Fronczec, F. R.; Selbin, J. *Inorg. Chem* **1985**, *24*, 4078. Beley, M.; Chodorowsky, S.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L.; Barigelletti, F. *Inorg. Chem.* **1994**, *33*, 2543. Constable, E. C.; Cargill Thompson, A. M. W.; Greulich, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1444. Constable, E. C.; Cargill Thompson, A. M. W. *New. J. Chem.* **1996**, *20*, 65, and references cited therein.

(18) Dietrich-Buchecker, C.; Sauvage, J.-P. *Tetrahedron* **1990**, *46*, 503. Chambron, J.-C.; Chardon-Noblat, S.; Dietrich-Buchecker, C. O.; Heitz, V.; Sauvage, J.-P. *Macrocycle Synthesis. A Practical Approach*; Parker, D., Ed.; Oxford University Press: Oxford, U.K., 1996, p 207. Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Tetrahedron Lett.* **1983**, *24*, 5091. Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J.-P. *Tetrahedron Lett.* **1983**, *24*, 5098.

(19) Cárdenas, D. J.; Gaviña, P.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1996**, 1915.

(20) (a) Livoreil, A.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 9299. (b) Collin, J.-P.; Gaviña, P.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1996**, 2005. (c) Cárdenas, D. J.; Livoreil, A.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 11980.

(21) Chambron, J.-C.; Sauvage, J.-P. *New J. Chem.* **1990**, *14*, 883.

(22) Difficulties have been encountered in the metalation of a “trefoil knot” with divalent but not monovalent metals, which suggest a similar effect between the two coordinating sites: Dietrich-Buchecker, C. O., personal communication. Synthesis of the knot: Dietrich-Buchecker, C. O.; Sauvage, J.-P.; De Cian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2231.

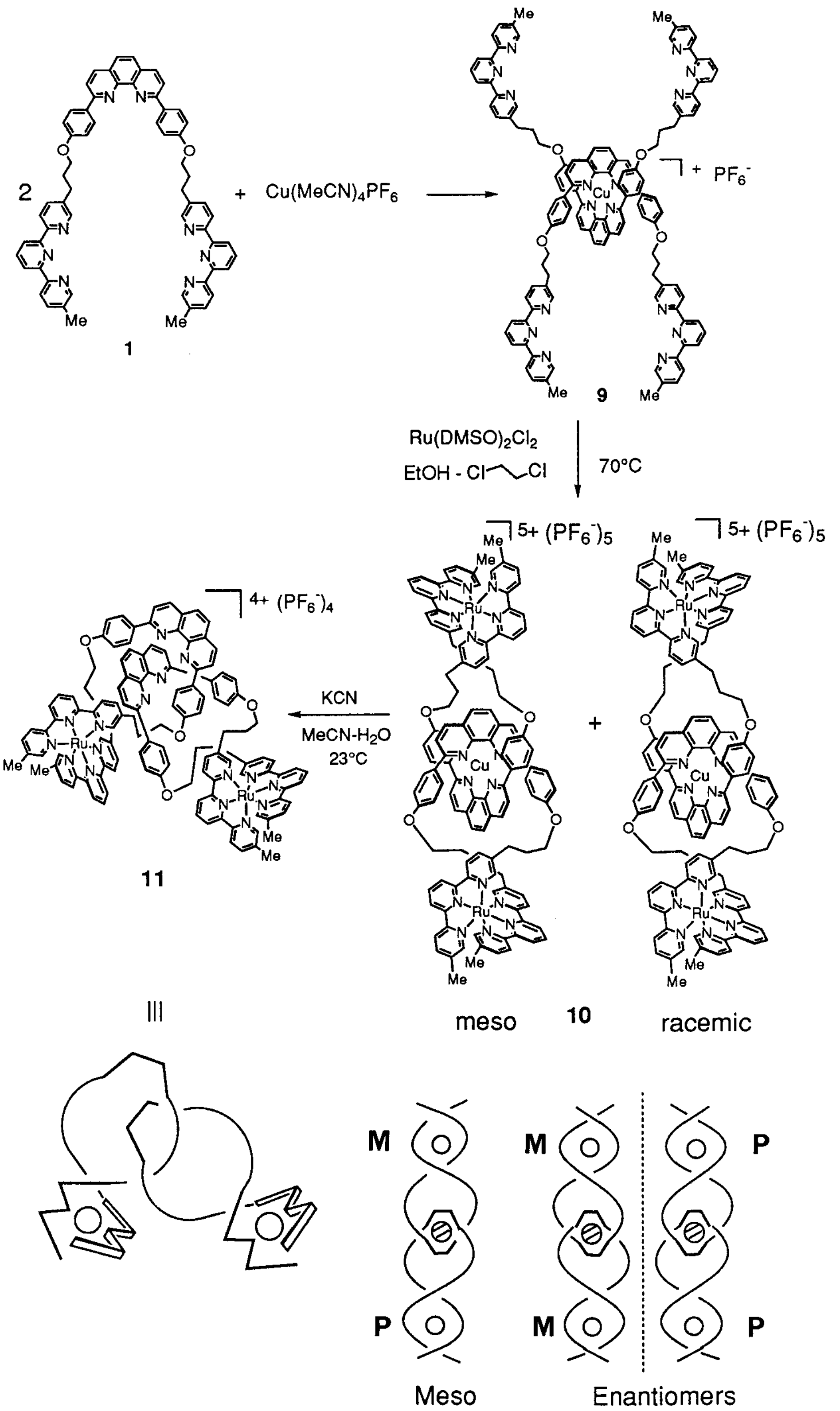

Figure 5. Entwining reaction, involving 2 equiv of the coordinating fragment **1** and 1 equiv of Cu(I), followed by the double-clipping step with formation of the Ru(terpy)$_2^{2+}$ units, to afford **10**. The catenate **10** can be selectively demetalated to give catenane **11**.

$(SO_4)_2{\cdot}6H_2O$, and $CoCl_2{\cdot}6H_2O$ gave the corresponding catenates **5**−**8**, which were isolated as PF_6^- salts after column chromatography (Figure 3). The Cu(II) complex **5** was also obtained in 49% yield when we tried to purify precatenate **4** by column chromatography on SiO_2, the Cu(II) being formed *in situ* by oxidation of Cu(I). The yield was nearly quantitative based on the Cu(II) that may be formed from **4**, provided that the equilibrium of formation of **4** is displaced to completion by this process. Satisfactory FAB mass spectra were obtained for all these complexes. They show monocharged peaks corresponding to the loss of one, two, and three PF_6^- anions from the molecular ion (reduction takes place under the experimental conditions). In principle, all the complexes **5**−**8** should be obtained as mixtures of four isomers, two racemic mixtures of diastereomers, since they contain two different chiral centers in their structure (the octahedral complexes). In all cases, the chromatographic separations rely on the differences of charge among the several complexes that may be formed, and no separation between both diastereomers is expected to take place. This could be confirmed in the case of the diamagnetic complexes **7** and **8** by

^{1}H NMR. The spectra of complexes **7** and **8** show the usual high-field shift of the signals corresponding to the phenyl hydrogens of each dpp ligand (~1.2 ppm as compared to the free ligand), due to the electronic influence of the phenanthroline fragment of the partner in the entwined Cu(I) complex.[18,19,21] Interestingly, the hydrogen atoms of the phenanthroline central rings also appear at high field (between 6.0 and 6.4 ppm), which indicates that the Ru(terpy)$_2^{2+}$ complexes they face have an important influence on their chemical shifts. For these hydrogens, four well-separated signals are observed, two for each diastereomer. Analysis of the integrals show that a weak diastereoselection takes place in both complexes (54:46 for **7**, and 55:45 for **8**). The relative configurations for the major and minor species were not determined.

The cyclic voltammograms for complexes **5**−**8** are presented in Figure 4. They all show reversible waves for the Ru(III)/Ru(II) couples at ~+1.3 V vs SCE. The ligand centered reduction to Ru(I) is reversible, too (~1.3 V). The potential of the tetrahedral Cu(II)/Cu(I) redox couple lies between +0.6 and +0.7 V, as has been previously observed for this kind of complex.[20] The Co(II)- and Fe(II)-containing (**6** and **7**, respectively) show additional reversible or quasi-reversible waves for the M(III)/M(II) and M(II)/M(I) couples. On the other hand, an irreversible behavior is observed for the hexacoordinate Cu(terpy)$_2^{2+}$ moiety of complex **5**. This is due to the low stability of the bis(terpy) complexes of Cu(I), which decompose on the time scale of the cyclic voltammetry, as has been observed before for related species.[20c] As expected, the Zn(II) fragment of complex **8** does not suffer electrochemical changes.

The UV-vis spectra for the trimetallic catenates **5**−**8** display very similar features. Absorptions of the Ru(terpy)$_2^{2+}$ moieties, which have greater ϵ values, dominate and hide the absorption corresponding to the other fragments in the visible region. Only in the case of the Fe(II) complex **7** is a different well-defined absorption at 548 nm observed.

We also tried to obtain the Ru(II)-containing complex analogous to **5**−**8** by clipping the free terpy units of precatenate **4** with a Ru(II) precursor. The negative results obtained led us to try different conditions. After much experimental work, the desired catenate, containing two Ru(terpy)$_2^{2+}$ units, could be prepared using a *simultaneous two-ring-construction strategy* as shown in Figure 5.

Gathering of two molecules of **1** with Cu(MeCN)$_4$PF$_6$ in CH$_2$Cl$_2$−MeCN gave the bis(dpp) Cu(I) derivative of **1** (**9**, Figure 5), which was reacted with Ru(DMSO)$_4$Cl$_2$ under high-dilution conditions to give catenate **10** in 10% yield after column chromatography on SiO$_2$. This compound could also be prepared by reaction of **5** with Ru(DMSO)$_4$Cl$_2$. In this case, we hoped that Cu(II) would act as a template, bringing together both terpy units and preventing dethreading, but unfortunately, the yield could not be significantly increased (12%). The cyclic voltammogram of complex **10** shows the above mentioned waves for the Ru and Cu fragments, the signals corresponding to the Ru complexes having double the intensity of the one for the Cu, as expected for the 2:1 stoichiometry (Figure 4e). The ^{1}H NMR spectrum shows features similar to those for complexes **7** and **8**. In the case of **10**, the two singlets corresponding to the phenanthroline central rings of both diastereomers (a racemic mixture and a meso form) have the same intensity. This indicates that the two isomers are formed at the same rate, but not necessarily that they both have the same stability, since the Ru−terpy coordination is irreversible. It is because of the inertness of the Ru(terpy)$_2^{2+}$ complexes toward ligand scrambling that **10** could be selectively demetalated.[12,19] Demetalation was also useful to determine that only catenates, and not helical complexes, had been formed in the case of **10**. Reaction of **10** with KCN in MeCN−H$_2$O at 23 °C afforded the free catenand **11** (74%), in which, as expected, the Ru complexes remain unaltered. This complex is a topologically more complicated isomer of macrocycle **3** (although both compounds are not topological isomers). Its FAB mass spectrum shows the same signals as **3** for the molecular ions resulting from the loss of PF$_6^-$ anions (δ 2515.5, 2370.3, 2225.2), but in this case, signals corresponding to only one of the rings also appear (1185.4 for **2**-PF$_6^-$, and 1039.9 for **2**-2PF$_6^-$), confirming the catenate structure. The ^{1}H NMR spectrum of **11** is different from that corresponding to **3**. The phenyl hydrogen signals appear at high field (δ 6.29 and 7.97 for one of the isomers, and δ 6.22 and 7.85 for the other one) even in the absence of Cu(I), which implies that the phenyl rings are probably affected by the Ru complexes in the interlocked structure. So, the double clipping reaction is selective for the formation of catenates. Complex **11** contains a free tetrahedral coordinating site that could be remetalated with suitable metals to give complexes with promising electron transfer and photochemical properties.

Conclusion

The preparation of heteronuclear trimetallic complexes with catenated structures and whose ring backbones incorporate metal−ligand bonds has been described. We have taken advantage of the different coordinating properties of several metals. Starting from a three-ligand molecular string containing two different types of coordinating units (terpy, dpp), a Ru(terpy)$_2^{2+}$-containing macrocycle (**2**) has been prepared in a very good yield, in spite of the possibility of oligomerization and competition of the dpp moiety. The high kinetic stability of the Ru(terpy)$_2^{2+}$ complexes permits us to employ this macrocycle, which contains a free dpp ligand, in further coordination reactions without encountering the problem of ligand scrambling. Besides, the high affinity of Cu(I) for the dpp ligands allows the regioselective threading of the multidentate string through the metal-containing ring. Thus, a heterodinuclear complex still containing two dangling free terpy units can be prepared. It has been shown that reaction of this intermediate with different metals allows the preparation of heterotrimetallic complexes containing interlocked rings as mixtures of diastereomers. A two-ring simultaneous construction approach has been employed to prepare a Cu(I) [2]-catenate containing two Ru(II) atoms, one within each ring. Due to the above mentioned stability of the Ru(terpy)$_2^{2+}$ complexes, selective removal of Cu(I) can be achieved to give a catenane having two metal atoms as elements of its skeleton. In summary, this work illustrates fundamental aspects of synthetic coordination chemistry and presents a way of preparing multicomponent transition metal complexes employing coordination reactions only.

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