Octahedral Complexes with Predetermined Helical Chirality: Xylene-Bridged Bis([4,5]-pineno-2,2′-bipyridine) Ligands (Chiragen[*o*-, *m*-, *p*-xyl]) with Ruthenium(II)

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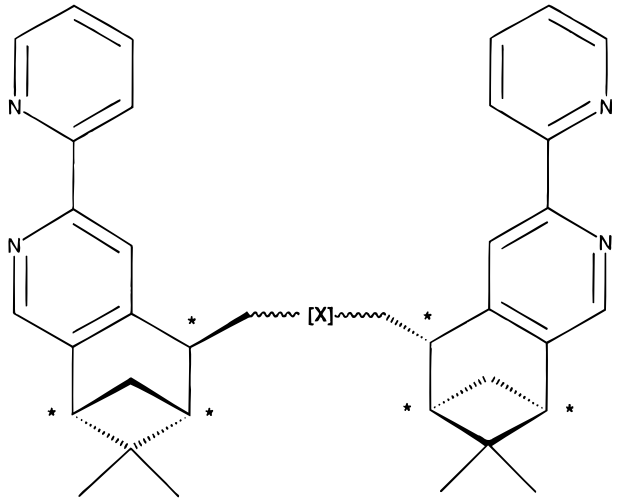
Tetradentate ligands are obtained by joining two optically active [4,5]-pineno-2,2′-bipyridine molecules in a stereoselective reaction, where two new stereogenic centers are created. These ligands are new members of the chiragen family that form *OC*-6 complexes with predetermined helical chirality. Ru(II) complexes with 4,4′-dimethyl-2,2′-bipyridine occupying the remaining coordination sites have been synthesized with all three new ligands. Characterization of the ruthenium complexes by NMR spectroscopy confirm C_2-symmetric structures in solution. CD spectra show that the complexes are composed of only one helical diastereomer with the expected absolute configurations. In addition, a strong chiral amplification is observed, if precursors of low enantiomeric purity are used. This is due to the inability of ligands that are heterochiral in the two bpy moieties to coordinate to one center. X-ray structural data were obtained for the complex Δ-[RuCG[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$. Crystal data (Mo Kα, 298 K): trigonal, space group *R*3, $a = 52.986(4)$ Å, $c = 10.545(1)$ Å, $V = 25639(4)$ Å^3, $Z = 18$, R1 = 0.087, and wR2 = 0.0986 for 2609 observed reflections.

Introduction

Predetermination of the helical chirality around a metal center can occur if the ligands themselves are chiral. Several cases have been reported for octahedral coordination geometry (*OC*-6), where a hexa- or pentadentate ligand forms complexes with predetermined helical chirality. In the case of hexadentate ligands, e.g. (*R*)-*N*,*N*,*N*′,*N*′-Tetrakis(2-aminoethyl)-1,2-propanediamine or analogs thereof,[1,2] the complex is coordinatively saturated, whereas in the case of a pentadentate ligand, e.g. (*R*,*R*)-alamp or (*R*,*R*)-promp,[3,4] one coordination site can be occupied by an additional monodentate ligand. We were interested in achieving chiral predetermination with *tetradentate* ligands in *OC*-6 complexes, so that the remaining two sites *cis* to each other can be occupied by either two monodentate ligands or one bidentate ligand. Such complexes can be used, for example, as enantiomerically pure chiral building blocks[5,6] for the synthesis of polynuclear metal complexes containing several metal centers with helical chirality. Unlike synthesis with ligands that are not preorganized, the formation of a large number of diastereomers does not occur. This is an essential requirement for the possibility to characterize such species often used in supramolecular assemblies investigated as photochemical systems.[7] Another reason for the synthesis of coordination species with tetradentate ligands, predisposed for one absolute configuration in *OC*-6, is their application in enantioselective catalysis. Often two adjacent coordination sites are required for the substrate to be coordinated to the central metal. Control of the chirality at the metallic center can therefore be essential for the determination of the chirality of the product in a catalytic reaction.



[X] = $(CH_2)_n$ with n = 2 (CG[4]), 3 (CG[5]) and 4 (CG[6])
[X] = *o*-xylene (CG[o-xyl]), *m*-xylene (CG[m-xyl]) and *p*-xylene (CG[p-xyl])

Figure 1. The tetradentate chiragen ligand family. All molecules have C_2 symmetry. They contain six stereogenic carbon atoms, which are marked with asterisks.

The so-called chiragen ligands (Figure 1) have been designed for the purpose of chiral predisposition around a metal center.[8] The synthetic pathway followed allows for a large choice of the bridging groups [X]. (−)-[4,5]-Pineno-2,2′-bipyridines linked with aliphatic chains were among the first tetradentate ligands reported that are able to control the helical chirality in octahedral metal complexes.[9] Depending on the absolute

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configuration of the starting pinene enantiomer, only the Λ or Δ complex is formed for steric reasons. Δ-[Ru(CG[6])(4,4′-DMbpy)]$(CF_3SO_3)_2$, Δ-[Ru(CG[5])(4,4′-DMbpy)]$(PF_6)_2$, and Δ-[Ru(CG[4])(4,4′-DMbpy)]$(PF_6)_2$ (4,4′-DMbpy = 4,4′-dimethyl-2,2′-bipyridine) were synthesized and characterized.[9] The rather low overall yields (CG[6], 20%; CG[5], 24%; CG[4], 12%) were explained by the formation of polynuclear material in the complexation step.

In replacing the totally flexible aliphatic chains by more rigid bridges, we hoped to increase these yields. A totally rigid system should be avoided, however, in order to allow the tetradentate ligand to arrange itself around one metal center. Additionally, we wished to demonstrate the chiral amplification due to the stereoselective complexation of ligands derived from starting material of low optical purity.

Experimental Section

(a) Measurements and Materials. The NMR studies (^{1}H and ^{13}C NMR, 2D-COSY, ^{1}H^{13}C HETCOR, and decoupling experiments) were performed on a Varian Gemini 300 instrument using solvent as the internal standard. Electronic spectra were measured using a Perkin-Elmer Lambda 5 UV/VIS spectrophotometer. Mass spectral data were collected with a VG Instruments 7070E mass spectrometer with an FAB inlet system (complexes) and a Hewlett-Packard HP5988A mass spectrometer (ligands). Microanalyses were carried out by Ciba AG, Forschungszentrum Marly, Switzerland. CD spectra were measured on a Jobin-Yvon Mark V autodichrograph. Rotation angles have been obtained with a Perkin-Elmer MC 241 polarimeter. Electrochemical measurements were carried out at room temperature by using a PAR 273A electrochemical analysis system with the 270 research electrochemistry software. Cyclic voltammograms were obtained in acetonitrile solution by using a micro cell equipped with a stationary platinum-disk electrode, a platinum-disk counter electrode, and a SCE reference electrode with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. $[Ru(bpy)_3](PF_6)_2$ was used as standard, taking its oxidation potential equal to +1260 mV *vs* SCE.[10] The electrochemical window examined was between +1.6 and −2.0 V. The scanning speed was 200 mV s^{-1}. Half-wave potentials were calculated as an average of the cathodic and the anodic peaks. All values are *vs* SCE. The emission spectra were measured on a Perkin-Elmer LS 50B spectrometer.

Unless otherwise specified, commercial chemicals were used as supplied. $RuCl_3 \cdot 3H_2O$ was obtained from Johnson & Matthey, (1*R*)-(−)-myrtenal and 4,4′- dimethyl-2,2′-bipyridine were purchased from Aldrich, and α,α-dibromoxylenes were obtained from Merck. All other materials were obtained from Fluka. THF was distilled under N_2 from sodium. Thin-layer chromatography was conducted on Kieselgel 60 H F_{254} plates (Merck). All bipyridine compounds can be detected as red spots on TLC with Fe(II) solutions.

(b) Ligand Synthesis. Ligands Derived from (1*R*)-(−)-Myrtenal. (−)-[4,5]-Pineno-2,2′-bipyridine was synthesized according to the literature.[8] Instead of 1-(2-acetylpyridyl)pyridinium iodide, the more conveniently prepared bromide salt was used.[11] To 50.0 g (0.41 mol) of 2-acetylpyridine in 150 mL of refluxing CCl_4 was added 66.0 g (0.41 mol) of bromine dropwise. The yellow precipitate was collected by filtration, dissolved in water, neutralized with Na_2CO_3, and extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and the volume reduced to approximately 150 mL. Pyridine (39.0 g, 0.49 mol) was added dropwise to the refluxing solution. The yellow precipitate was filtered off and dried *in vacuo* for 2 days; yield 50%. The Kröhnke reaction was unaffected by this change of the counterion. The syntheses of the xylene-bridged (−)-[4,5]-pineno-2,2′-bipyridines were carried out according to the literature[8] with the following modifications. The quenched reaction mixture is evaporated to dryness, dissolved in 50 mL of dichloromethane and washed twice with 25 mL of water. After addition of approximately 4 g of silica gel, the dichloromethane is slowly evaporated under reduced pressure. The dry powder is transferred on top of a silica gel column and eluted with hexane/ethyl acetate/triethylamine (3:2:0.1). Yields: (−)-*o*-xylene-bridged bis[4,5]-pinenobipyridine), 85%; (−)-*m*-xylene-bridged bis[4,5]-pinenobipyridine), 94%; (−)-*p*-xylene-bridged bis[4,5]-pinenobipyridine), 75%.

(−)-*o*-Xylene-Bridged Bis([4,5]-pineno-2,2′-bipyridine) ((−)-CG-[*o*-xyl]). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.60 (2H, ddd, J = 4.8, 1.8, 1.7 Hz), 8.40 (2H, s), 8.34 (2H, dt, J = 7.9, 0.9 Hz), 8.21 (2H, s), 7.77 (2H, dt, J = 7.9, 1.9 Hz), 7.3−7.2 (4H, m), 7.28 (2H, d, J = 2.8 Hz), 3.36 (2H, dd, J = 13.8, 3.0 Hz), 3.28 (2H, dm, J = 11.3 Hz), 2.88 (2H, dd, J = 13.2, 10.9 Hz), 2.82 (2H, dd, J = 5.4, 5.4 Hz), 2.53 (2H, dt, J = 9.8, 4.0 Hz), 1.93 (2H, dt, J = 6.3, 1.8 Hz), 1.34 (2H, d, J = 9.5 Hz), 1.29 (6H, s), 0.55 (6H, s). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 156.5, 154.8, 149.0, 148.5, 145.6, 142.7, 138.7, 136.7, 130.1, 126.5, 123.3, 120.8, 119.7, 45.0, 43.5, 42.7, 40.9, 35.9, 28.9, 26.2, 20.9. MS (*m*/*e*; EI): 602 (8%, $M^+ - 1$), 353 (10, $M - C_{17}H_{17}N_2$,), 249 (41, $M - C_{25}H_{25}N_2$), 207 (100, $M - C_{28}H_{19}N_2$,), 104 (31, $M - C_{34}H_{34}N_4$), 78 (24, py^+). $[\alpha]_D = -65°$, 25 °C, 23.9 mg in 20 mL CH_2Cl_2. Anal. Calcd for $C_{42}H_{42}N_4 \cdot 0.2H_2O$: C, 82.7; H, 7.1; N, 9.2. Found: C, 82.8; H, 7.3; N, 9.1.

(−)-*m*-Xylene-Bridged Bis([4,5]-pineno-2,2′-bipyridine) ((−)-CG-[*m*-xyl]). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.66 (2H, ddd, J = 4.5, 1.8, 1.7 Hz), 8.42 (2H, s), 8.36 (2H, dt, J = 8.1, 1.0 Hz), 8.23 (2H, s), 7.78 (2H, dt, J = 7.6, 1.7 Hz), 7.28 (2H, ddd, J = 7.5, 4.7, 1.2 Hz), 7.26 (1H, s), 7.1−7.0 (3H, m), 3.41 (2H, dd, J = 13.5, 3.6 Hz), 3.26 (2H, dm, J = 10.9 Hz), 2.80 (2H, dd, J = 5.4, 5.4 Hz), 2.65 (2H, dd, J = 13.5, 11.4 Hz), 2.50 (2H, dt, J = 9.7, 5.7 Hz), 1.93 (2H, dt, J = 5.9, 2.4 Hz), 1.34 (2H, d, J = 9.9 Hz), 1.26 (6H, s), 0.54 (6H, s). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 156.6, 154.8, 149.1, 148.8, 145.7, 142.8, 140.1, 136.9, 129.8, 128.6, 127.2, 123.4, 120.9, 119.6, 45.1, 43.1, 42.6, 41.0, 39.5, 28.1, 26.3, 21.0. MS (*m*/*e*; EI): 603 (7%, M^+), 354 (16, $M - C_{17}H_{17}N_2$), 249 (90, $M - C_{25}H_{25}N_2$), 207 (100, $M - C_{28}H_{19}N_2$), 104 (27, $M - C_{34}N_{34}N_4$), 78 (23, py^+). $[\alpha]_D = -95°$, 28 °C, 21.9 mg in 20 mL of CH_2Cl_2. Anal. Calcd for $C_{42}H_{42}N_4 \cdot 0.1H_2O$: C, 83.2; H, 7.1; N, 9.2. Found: C, 83.1; H, 7.4; N, 9.2.

(−)-*p*-Xylene-Bridged Bis([4,5]-pineno-2,2′-bipyridine) ((−)-CG-[*p*-xyl]). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.68 (2H, ddd, J = 4.8, 1.8, 1.8 Hz), 8.41 (2H, s), 8.31 (2H, dt, J = 8.0, 1.1 Hz), 8.24 (2H, s), 7.81 (2H, dt, J = 8.0, 1.7 Hz), 7.28 (2H, m), 7.17 (4H, s), 3.43 (2H, dd, J = 13.5, 3.6 Hz), 3.32 (2H, dm, J = 11.1 Hz), 2.87 (2H, dd, J = 5.5, 5.5 Hz), 2.79 (2H, dd, J = 13.5, 11.3 Hz), 2.58 (2H, dt, J = 10.1, 5.5 Hz), 2.04 (2H, dt, J = 5.9, 2.4 Hz), 1.41 (2H, d, J = 9.9 Hz), 1.35 (6H, s), 0.59 (6H, s). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 156.7, 154.8, 149.1, 148.8, 145.7, 142.8, 137.8, 136.9, 129.3, 123.4, 121.0, 119.7, 45.2, 43.0, 42.7, 41.1, 39.3, 28.1, 26.3, 21.0. MS (*m*/*e*; EI): 603 (6%, M^+), 602 (12, $M - 1$), 353 (9, $M - C_{17}H_{17}N_2$), 249 (66, $M - C_{25}H_{25}N_2$), 207 (100, $M - C_{28}H_{19}N_2$), 104 (31, $M - C_{34}H_{34}N_4$), 78 (11, py^+). $[\alpha]_D = -101°$, 27 °C, 26.6 mg in 20 mL of CH_2Cl_2. Anal. Calcd for $C_{42}H_{42}N_4 \cdot 0.4H_2O$: C, 81.7; H, 7.1; N, 9.1. Found: C, 81.9; H, 7.3; N, 8.7.

Ligands Derived from (+)-α-Pinene. (+)-[4,5]-Pineno-2,2′-bipyridine and (+)-CG[*m*-xyl] were synthesized as in the (−)-[4,5]-pineno-2,2′-bipyridine case, with (1*S*)-(+)-myrtenal as starting material, which was obtained by oxidation of (+)-α-pinene with SeO_2.[12]

(+)-[4,5]-Pineno-2,2′-bipyridine. Yield: 54%. $[\alpha]_D = +76°$, 25 °C, 49.4 mg in 25 mL of CH_2Cl_2. Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.6; H, 7.3; N, 11.2. Found: C, 81.4; H, 7.6; N, 11.1.

(+)-*m*-Xylene-Bridged Bis([4,5]-pinenobipyridine) (+)-CG[*m*-xyl]. Yield: 83%. $[\alpha]_D = +84°$, 29 °C, 29.7 mg in 20 mL of CH_2Cl_2. Anal. Calcd for $C_{42}H_{42}N_4 \cdot 0.2H_2O$: C, 82.7; H, 7.1; N, 9.2. Found: C, 82.9; H, 7.3; N, 8.9.

(c) Complex Synthesis. In a typical preparation, 121 mg (0.25 mmol) of $Ru(dmso)_4Cl_2$[13] was refluxed in 5 mL of acetonitrile for 2 h. After the mixture was cooled to room temperature, $Ru(NCCH_3)_4Cl_2$ was precipitated with about 80 mL of diethyl ether and filtered through

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a glass frit. The residue was dissolved in 250 mL of ethanol. A 150 mg (0.25 mmol) amount of xylene-bridged chiragen was also dissolved in 250 mL of ethanol. The two solutions are added simultanously to 300 mL of refluxing ethanol over 12 h. After a further 2 h under refluxing conditions, the brown solution was evaporated to dryness. The residue was redissolved in 5 mL of 2-methoxyethanol, 46 mg (0.25 mmol) of 4,4′-dimethyl-2,2′-bipyridine was added, and the mixture was refluxed for 5 min in a modified microwave oven.[14] The solution is diluted with 80 mL of water and then heated to 80 °C. The complex was precipitated with 1 g of NH_4PF_6 and then filtered through Celite. The residue was dissolved in a minimum of dry acetone and then purified by column chromatography on neutral Al_2O_3 (activity II) eluted with dry acetone. The first orange fractions were collected and further purified by preparative thick-layer chromatography eluted with ethanol/water/NH_4OOCCH_3 (1:1:0.3) as eluent. Yields: Δ-[RuCG[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$, 14%; Δ-[RuCG[*m*-xyl](4,4′-DMbpy)]$(PF_6)_2$, 17%; Λ-[RuCG[*m*-xyl](4,4′-DMbpy)]$(PF_6)_2$, 13%; Δ-[RuCG[*p*-xyl](4,4′-DMbpy)]$(PF_6)_2$, 4%.

Δ-[RuCG[*o*-xyl](4,4′-DMbpy)](PF$_6$) (Δ-1). ^{1}H-NMR (acetone-d_6, 300 MHz): δ 8.82 (2H, m), 8.53 (2H, d, J = 7.8 Hz), 8.47 (2H, s), 8.45 (2H, d, J = 6.1 Hz), 8.15 (2H, dt, J = 7.8, 1.5 Hz), 7.93 (2H, dm, J = 5.6 Hz), 7.52 (2H, ddd, J = 7.6, 5.6, 1.3 Hz), 7.40 (2H, dm, J = 5.8 Hz), 7.30 (2H, s), 7.3−7.2 (4H, m), 3.90 (2H, m), 3.01 (2H, dd, J = 15.0, 7.3 Hz), 2.63 (6H, s), 2.60 (2H, dd, J = 5.5, 5.5 Hz), 2.46 (2H, dd, J = 15.1, 6.3 Hz), 2.26 (2H, dt, J = 10.4, 5.0 Hz), 2.13 (2H, m), 1.30 (6H, s), 1.05 (2H, d, J = 10.2 Hz), 0.71 (6H, s). ^{13}C NMR (acetone-d_6, 75.44 MHz): δ 159.4, 157.9, 157.5, 154.5, 153.5, 152.6, 150.6, 148.2, 145.6, 138.6, 138.1, 131.0, 128.5, 127.3, 125.9, 124.4, 121.7, 45.1, 43.3, 41.2, 40.5, 26.9, 25.7, 21.0, 20.8. MS (*m*/*e*; FAB): 1034 (60%, $M^+ - PF_6$), 887 (36, $M^+ - 2PF_6$), 417 (36), 289 (100). UV−vis (λ in nm (ε); (acetonitrile, 1.171×10^{-5} M): 450 (sh, 10 900), 436 (11 800), 287 (61 700). CD (acetonitrile λ in nm (Δε)): *c* 1.171×10^{-5} M (250−350 nm) 306 (-130), 283 (76); c 7.115×10^{-5} M (350−700 nm) 519 (2), 461 (3), 429 (4), 371 (4). Cyclic voltammetry (0.1 M (TBA)PF_6, acetonitrile, mV *vs* SCE): +1140 (85), −1470 (85), −1680 (100), third reduction peak irreversible. Emission (acetonitrile, 1.489×10^{-5} M): excitation 454 nm, emission 608 nm.

Δ-[RuCG[*m*-xyl](4,4′-DMbpy)](PF$_6$)$_2$ (Δ-2). ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.82 (2H, m), 8.74 (2H, s), 8.69 (2H, d, J = 8.1 Hz), 8.43 (2H, d, J = 5.8 Hz), 8.15 (2H, dt, J = 7.9, 1.5 Hz), 7.94 (2H, dm, J = 5.6 Hz), 7.53 (2H, ddd, J = 7.6, 5.6, 1.3 Hz), 7.39 (2H, dm, J = 5.8 Hz), 7.31 (2H, s), 7.1−7.0 (3H, m), 5.95 (1H, s), 3.87 (2H, dd, J = 15.8, 1.3 Hz), 3.61 (2H, dm, J = 6.6 Hz), 3.12 (2H, dd, J = 16.0, 6.6 Hz), 2.62 (6H, s), 2.54 (2H, dd, J = 5.5, 5.5 Hz), 2.19−2.13 (4H, m), 1.26 (6H, s), 1.07 (2H, dm, J = 9.8 Hz), 0.61 (6H, s). ^{13}C NMR (acetone-d_6, 75.44 MHz): δ 159.1, 157.4, 157.1, 153.3, 152.4, 150.7, 151.9, 147.6, 147.1, 138.4, 137.9, 130.2, 129.3, 128.5, 127.6, 125.9, 124.5, 121.8, 45.3, 45.1, 43.1, 40.3, 39.8, 28.1, 25.6, 21.0, 20.7. MS (*m*/*e*; FAB): 1033 (48%, $M^+ - PF_6$), 888 (35, $M^+ - 2PF_6$), 722 (21), 603 (100), 531 (27). UV−vis (λ in nm (ε); (acetonitrile, 2.101×10^{-5} M): 451 (13 400), 436 (sh, 7200), 292 (65 600), 268 (22 400). CD (acetonitrile λ in nm (Δε), 1.372×10^{-5} M): 480 (−5), 332 (7), 303 (−120), 284 (81). $[\alpha]_{365} = -3090°$, 27 °C, 0.453 mg in 20 mL of acetonitrile. Cyclic voltammetry (0.1 M (TBA)PF_6, acetonitrile, mV *vs* SCE): +1140 (80), −1485 (75), −1680 (100), third reduction peak irreversible. Emission (acetonitrile, 1.563×10^{-5} M): excitation 454 nm, emission 613 nm.

Λ-[RuCG[*m*-xyl](4,4′-DMbpy)](PF$_6$)$_2$ (Λ-2). UV−vis (λ in nm (ε); acetonitrile, 4.197×10^{-5} M): 451 (12 100), 436 (sh, 11 700), 293 (62 500). CD (acetonitrile λ in nm (Δε), 4.197×10^{-5} M): 479 (4), 333 (−7), 305 (129), 284 (−79). $[\alpha]_{365} = -2730°$, 25 °C, 0.247 mg in 25 mL of acetonitrile.

Δ-[RuCG[*p*-xyl](4,4′-DMbpy)](PF$_6$)$_2$ (Δ-3). ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.76 (2H, m), 8.48 (2H, d, J = 7.9 Hz), 8.31 (2H, s), 8.20 (2H, d, J = 5.8 Hz), 8.09 (2H, dt, J = 1.5, 8.0 Hz), 7.96 (2H, dm, J = 6.3 Hz), 7.49 (2H, ddd, J = 7.6, 5.6, 1.3 Hz), 7.36 (2H, dm, J = 5.8 Hz), 7.21 (2H, s), 6.85 (4H, s), 3.85 (2H, dm, J = 10.7 Hz), 3.58 (2H, dd, J = 14.6, 9.9 Hz), 2.90 (2H, dd, J = 14.6, 1.4 Hz), 2.64 (2H, dd, J = 5.5, 5.5 Hz), 2.60 (6H, s), 2.58 (2H, dt, J = 10.4, 5.2 Hz), 2.42 (2H, dt, J = 5.8, 3.5 Hz), 1.80 (2H, d, J = 10.0 Hz), 1.40 (6H, s), 0.62 (6H, s). ^{13}C NMR (acetone-d_6, 75.44 MHz): δ 152.7, 152.1, 147.0, 138.3, 129.1, 128.4, 127.5, 125.8, 124.7, 123.8, 45.6, 45.4, 40.6, 39.1, 27.7, 25.8, 20.9, 20.8. MS (*m*/*e*; FAB): 1034 (10%, $M^+ - PF_6$), 889 (23, $M^+ - 2PF_6$), 444 (20), 307 (100). UV−vis (λ in nm (ε); acetonitrile, 3.013×10^{-5} M): 456 (13 300), 436 (sh, 11 600), 289 (62 000). CD (acetonitrile λ in nm (Δε), 3.013×10^{-5} M): 474 (−5), 429(4), 330 (7), 304 (-111), 285 (83). Emission (acetonitrile, 1.486×10^{-5} M): excitation 454 nm, emission 613 nm.

Table 1. Crystallographic Data for Δ-[RuCG[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$

chem formula	$[C_{54}H_{54}N_6Ru](PF_6)_2 \cdot {}^1/_{12}H_2O$
fw	1179.2
cryst syst	trigonal (on hexagonal axes)
$a = b$, Å	52.986(4)
c, Å	10.545(1)
V, Å^3	25639(4)
Z	18
space group	$R3$ (No. 146)
T, °C	−60
ρ_{calcd}, g cm^{-3}	1.377
λ(Mo Kα), Å	0.710 73
μ(Mo Kα), cm^{-1}	3.90
R1 (obsd data/all data)[a]	0.0867/0.316
wR2 (obsd data/all data)[b]	0.0986/0.138
goodness of fit, S	0.78
residual density(max/min), e Å^{-3}	+0.46/−0.70

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ [b] $wR2 = (\sum[w(F_o^2 - F_c^2)^2]^2]/\sum[wF_o^4])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0001P)^2]$; $P = {}^1/_3(F_o^2) + {}^2/_3(F_c^2)$.

(d) X-ray Structure Determination. Suitable crystals of Δ-[RuCG-[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$ were grown from ethanol/water as orange-red blocks. Intensity data were collected at −60 °C on a Stoe AED2 four-circle diffractometer using Mo Kα graphite-monochromated radiation (λ = 0.710 73 Å) with $\omega/2\theta$ scans in the 2θ range 5−50°. The lattice parameters were optimized from the $\pm\omega$ values of 12 reflections (plus equivalents) in the θ range 10−11.5°. Two standard reflections measured every 1 h showed no intensity variation. Some of the crystallographic data are summarized in Table 1. The structure was solved by direct methods using the program SHELXS-86.[15] There are two independent molecules (A and B) in the asymmetric unit. The refinement and all further calculations were carried out using SHELXL-93.[16] No absorption correction was applied. In view of the very low observed reflection ($I > 2\sigma(I)$) to parameter ratio (2609/818), only the Ru, N, P, and F atoms were refined anisotropically while the C atoms were refined isotropically, using weighted full-matrix least squares on F^2. All of the H atoms were included in calculated positions and allowed to ride on the corresponding C atom ($U_{iso} = (1.2 \text{ or } 1.5)U(C)_{eq}$). In a final difference electron density map a disordered partially occupied water molecule was located on a 3-fold axis.

Selected bond distances and angles for molecule A are given in Table 2. The absolute configuration of the molecule was confirmed by the chirality of the pinene moieties and the absolute structure parameter 0.04(6) (=0 within 3 esd for the correct absolute structure[17]). Full tables of atomic parameters and bond lengths and angles may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; on quoting the full journal citation. The molecular structure of molecule A and the crystallographic numbering scheme used are illustrated in Figure 2.

Results and Discussion

Synthesis. The ligand synthesis, where the key step is a Kröhnke-type reaction, follows the same line as given[8] for the chiragens with aliphatic chains. The xylene-bridged ligands (−)-CG[*o*-xyl], (−)-CG[*m*-xyl], and (−)-CG[*p*-xyl] were obtained in good overall yields (85%, 94%, and 75%, respectively) and are therefore easily available in gram quantities. The synthesis of the ruthenium complexes, carried out in a way

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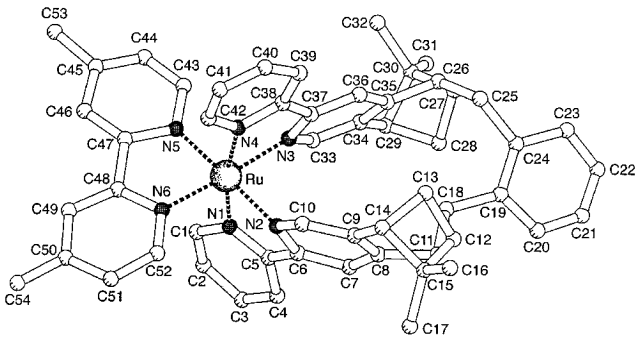

Figure 2. X-ray structure of the Δ-[RuCG[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$ complex. Hydrogen atoms and counterions have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Molecule A of Δ-[RuCG[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$

Ru(1)−N(1)	1.99(2)	C(11)−C(12)	1.50(3)	C(33)−C(34)	1.38(3)
Ru(1)−N(5)	2.01(2)	C(11)−C(18)	1.65(3)	C(34)−C(35)	1.44(3)
Ru(1)−N(2)	2.02(2)	C(12)−C(13)	1.52(3)	C(35)−C(36)	1.41(3)
Ru(1)−N(6)	2.03(2)	C(12)−C(15)	1.55(3)	C(36)−C(37)	1.40(3)
Ru(1)−N(4)	2.05(2)	C(13)−C(14)	1.54(3)	C(37)−C(38)	1.45(3)
Ru(1)−N(3)	2.05(2)	C(14)−C(15)	1.59(3)	C(38)−C(39)	1.37(3)
N(1)−C(5)	1.32(3)	C(15)−C(17)	1.56(3)	C(39)−C(40)	1.39(3)
N(1)−C(1)	1.40(3)	C(15)−C(16)	1.56(3)	C(40)−C(41)	1.33(3)
N(2)−C(6)	1.33(3)	C(18)−C(19)	1.52(3)	C(41)−C(42)	1.35(3)
N(2)−C(10)	1.40(2)	C(19)−C(20)	1.38(3)	N(5)−C(47)	1.39(3)
N(3)−C(37)	1.33(3)	C(19)−C(24)	1.41(3)	N(5)−C(43)	1.39(3)
N(3)−C(33)	1.38(3)	C(20)−C(21)	1.32(3)	N(6)−C(52)	1.31(3)
N(4)−C(42)	1.34(2)	C(21)−C(22)	1.31(3)	N(6)−C(48)	1.35(3)
N(4)−C(38)	1.36(3)	C(22)−C(23)	1.35(3)	C(43)−C(44)	1.34(3)
C(1)−C(2)	1.30(3)	C(23)−C(24)	1.44(3)	C(44)−C(45)	1.32(3)
C(2)−C(3)	1.38(3)	C(24)−C(25)	1.57(3)	C(45)−C(46)	1.42(3)
C(3)−C(4)	1.36(3)	C(25)−C(26)	1.54(3)	C(45)−C(53)	1.51(3)
C(4)−C(5)	1.44(3)	C(26)−C(35)	1.49(3)	C(46)−C(47)	1.38(3)
C(5)−C(6)	1.45(3)	C(26)−C(27)	1.54(3)	C(47)−C(48)	1.56(3)
C(6)−C(7)	1.43(3)	C(27)−C(28)	1.55(3)	C(48)−C(49)	1.41(3)
C(7)−C(8)	1.42(3)	C(27)−C(30)	1.63(3)	C(49)−C(50)	1.39(3)
C(8)−C(9)	1.40(3)	C(28)−C(29)	1.52(3)	C(50)−C(51)	1.42(3)
C(8)−C(11)	1.58(3)	C(29)−C(34)	1.52(3)	C(50)−C(54)	1.44(3)
C(9)−C(10)	1.43(3)	C(29)−C(30)	1.60(3)	C(51)−C(52)	1.41(3)
C(9)−C(14)	1.48(3)	C(30)−C(31)	1.46(3)		

N(1)−Ru(1)−N(5)	98.5(8)	N(2)−Ru(1)−N(4)	92.3(7)
N(1)−Ru(1)−N(2)	77.5(7)	N(6)−Ru(1)−N(4)	100.0(7)
N(5)−Ru(1)−N(2)	175.9(7)	N(1)−Ru(1)−N(3)	93.5(7)
N(1)−Ru(1)−N(6)	88.3(8)	N(5)−Ru(1)−N(3)	96.7(7)
N(5)−Ru(1)−N(6)	80.8(8)	N(2)−Ru(1)−N(3)	82.8(7)
N(2)−Ru(1)−N(6)	99.8(8)	N(6)−Ru(1)−N(3)	177.2(8)
N(1)−Ru(1)−N(4)	167.9(8)	N(4)−Ru(1)−N(3)	78.6(7)
N(5)−Ru(1)−N(4)	91.6(7)		

analogous to that previously described,[9] gave the complexes Δ-[RuCG[X](4,4′-DMbpy)]$(PF_6)_2$. The yields are dependent on the bridging group (X) with an optimum of 17% for the *m*-xylene case. *o*-Xylene and *p*-xylene bridges gave lower yields of 14% and 4%, respectively. These low values indicate that the problem of formation of polynuclear material is not eliminated by the use of the more rigid bridges. Experiments in glassware specially designed for high-dilution reactions[18] did not improve the yields.

The complex $[RuCG[m\text{-xyl}](4,4'\text{-DMbpy})]^{2+}$ was prepared in both absolute configurations, Λ and Δ. The Δ form was obtained by starting from (1*R*)-(−)-myrtenal, a product available commercially in high enantiomeric purity (ee = 98%). (1*S*)-(+)-Myrtenal is not commercially available and was prepared by oxidation of (+)-α-pinene (Fluka purum, ee = 76%) with SeO_2.[12] The difference in optical purity of the CG[*m*-xyl] ligands from these two sources is clearly reflected in the values for the rotation angle ($[\alpha]_D^{28} = -95°$ and $[\alpha]_D^{29} = +84°$, respectively). In the reaction step where the two pinenobipyridine moieties are connected to form the chiragen ligand, three isomers, namely *R/R*, *R/S*, and *S/S*, are formed (*R* and *S* signify the chiralities of the bridgehead carbon centers). Statistical considerations show that from a source material with an enantiomeric excess given by ee, a tetradentate ligand with ee′ is obtained, where $ee' = 2ee/(ee^2 + 1)$. The optically inactive *R/S* form is produced with a yield of $y_{R/S} = 0.5(ee^2 + 1)$. The latter cannot complex to one metal center because of steric constraints. The total yield for the C_2-symmetric complexes is therefore given by $y_{R/R} + y_{S/S} = 0.5(1 - ee^2)$. Under the assumption that the ee values do not change during any step of the ligand synthesis, the enantiomeric purities and yields given in Table 3 are expected.

Table 3. Expected Enantiomeric Purities and Relative Yields for Chiragen Complexes Obtained from Various Source Materials

source material	ee, %	complex	ee′, %	relative yield $y_\Delta + y_\Lambda$, %
(1*R*)-(−)-myrtenal	98	Δ-[Ru(CG[*m*-xyl])-(4,4′-DMbpy)]$^{2+}$	99.98	98
(1*S*)-(+)-myrtenal	76	Λ-[Ru(CG[*m*-xyl])-(4,4′-DMbpy)]$^{2+}$	96.3	79

Table 4. Dihedral Angles (deg) between the Two Pyridine Rings in Bipyridine-Type Ligands (Esd's in Parentheses)

$Ru(bpy)_3(PF_6)_2$[19]	2.2(1)
$Ru(bpym)_3(PF_6)_2$[19]	5(1)
$Ru(bpz)_3(PF_6)_2$[19]	4(1)
Δ-[RuCG[6](4,4′-DMbpy)]$(CF_3SO_3)_2$[9a]	8(1)/9(1)
Δ-[RuCG[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$[a]	24(1)/12(1), molecule A 22(1)/13(1), molecule B

[a] Values for the two bipyridine subunits of the chiragen ligand only.

The complex Λ-[RuCG[*m*-xyl](4,4′-DMbpy)]$(PF_6)_2$ was isolated with an overall yield of 13%. This result is in accordance with the expected lowering of the yield by 20% compared to the Δ enantiomer. The isolated complexes Δ-**2** and Λ-**2** are of similar enantiomeric purity, which is shown by the almost identical values for Δε in CD spectra and the rotation angle. The chiral amplification from 76% to 96% predicted for the ligand derived from (+)-α-pinene is therefore experimentally confirmed.

X-ray Structure Analysis. Characterization by X-ray diffraction proves the expected structure for Δ-[RuCG[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$. There are two independent molecules (A and B) per asymmetric unit (molecule A is shown in Figure 2, which also illustrates the numbering scheme used). Of the 10 124 reflections measured, only one-fifth could be considered observed ($I > 2\sigma(I)$); hence, the analysis is rather poor (see Experimental Section for details) with large standard deviations in the bond lengths and angles (Table 2). However, within experimental error, they are similar to comparable bond lengths and angles observed in previously reported Ru(II) tris(bipyridine) type structures.[9,19,20] The two independent molecules do not appear to differ in a significant manner, and the accuracy of the data does not merit a detailed analysis. In both molecules, A and B, the *o*-xylene bridge distorts the two bpy moieties of (−)-CG[*o*-xyl] from their idealized positions. This gives rise to dihedral angles between the two pyridine groups of 24 and 12° in molecule A and 22 and 13° in molecule B. In Table 4 these values are compared with those found for four analogous complexes. It can be seen that the same angle for the normal chelates bpy, bpym, and bpz lies between 2 and 5°, while this value is significantly greater in the CG[6] ligand complex.[9]

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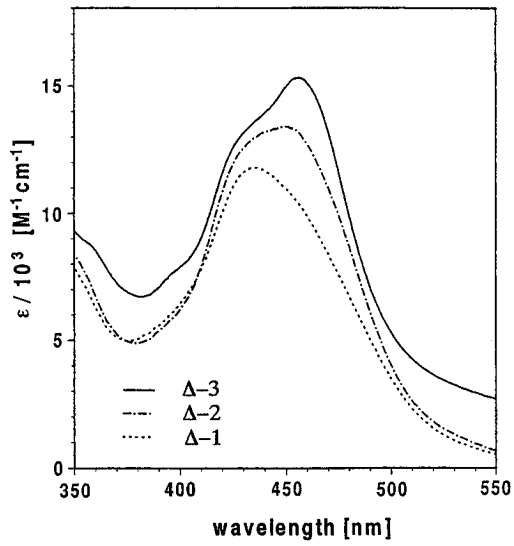

Figure 3. MLCT region of the absorption spectra of the Δ-[RuCG-[X](4,4′-DMbpy)]$(PF_6)_2$ complexes with xylene-bridged chiragen ligands. For better visualization, 2000 M^{-1} cm^{-1} was added to the spectrum of Δ-**3**.

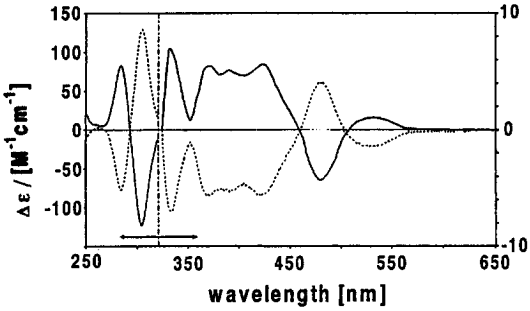

Figure 4. CD -spectra of Λ-**2** (dashed line) and Δ-**2** (solid line) in acetonitrile. Above 320 nm the scale on the right is valid.

UV−vis Spectra. The absorption spectra of the complexes are basically similar to those for other Ru(tris-diimine)$^{2+}$ compounds. A closer look at the shape of the MLCT absorption band reveals what appears to be an influence of the strain imposed on the complexes by the different lengths of the xylene bridges (see Figure 3). Δ-**3** has a spectrum almost identical with that for $Ru(bpy)_3^{2+}$, namely a maximum at 452 nm with a shoulder at 430 nm. With the complex Δ-**1** the relative importance of the shoulder and the maximum are inverted, resulting in a blue or hypsochromic shift of the absorption maximum by approximately 20 nm. The spectrum of Δ-**2** lies between these two extremes, resulting in a broad band without pronounced absorption maximum. This observation could be an effect caused by the increased dihedral angle between the pyridine subunits discussed above.

CD Spectra. All ligands synthesized show no activity in their CD spectra between 700 and 250 nm in dichloromethane as well as in 4 M hydrochloric acid. However, the complexes show behavior similar (shape and $\Delta\epsilon$) to that for the complexes with aliphatic linked chiragens.[9] As expected, an exact mirror image for Δ-**2** and Λ-**2** (see Figure 4) was found. In addition, the spectra for the two complexes match those of the enantiomers of $Ru(bpy)_3^{2+}$,[21] giving further proof for their absolute configuration.

Cyclic Voltammetry. The pinenobipyridine ligands shift all redox potentials to more negative values as compared to [Ru(bpy)$_3$]$(PF_6)_2$. The value of this shift (−0.12 V) is in good agreement with reported data for the complex [Ru(4,4′-DMbpy)$_3$]$(PF_6)_2$.[22] No influence of the different CG[xyl] ligands on the half-wave potentials was observed. It is therefore assumed that the inductive influence of the pinene substituents in these complexes is equivalent to that of the methyl groups in the homoleptic complex with three 4,4′-dimethyl-2,2′-bipyridine ligands.

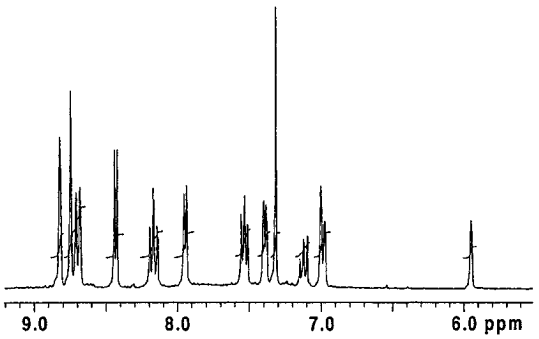

Figure 5. Aromatic region of the ^{1}H NMR of the Δ-[RuCG[*m*-xyl]-(4,4′-DMbpy)]$(PF_6)_2$ complex measured in acetone-d_6.

^{1}H NMR. The ^{1}H NMR spectra are relatively simple for all complexes, owing to the C_2 symmetry of the species. As an example, the aromatic part of the spectrum of Δ-**2** is given in Figure 5. A noteworthy feature is the singlet signal for the proton between the two substituents of the *m*-xylene bridge. It appears at a relatively high field (5.95 ppm) due to its position in the complex between two pyridine rings. The region of the nonaromatic protons also shows clearly the C_2-symmetric behavior. The complexes with *p*- and *o*-xylene bridges behave analogously.

Emission Spectra. All complexes emit at room temperature at approximately 610 nm with a somewhat lower intensity than $Ru(bpy)_3^{2+}$.

Conclusions

The successful synthesis of the ligands chiragen[*o*-xyl], chiragen[*m*-xyl], and chiragen[*p*-xyl] demonstrates that the synthetic method used is both simple and general. These tetradentate ligands are predisposed for coordination to octahedral metal centers with determined absolute configuration due to steric interactions. The geometry of the ligand can be finely tuned through variations in the bridge. The synthesis of both enantiomers of chiragen[*m*-xyl] shows that it is possible to obtain octahedral complexes of both absolute configurations from chiral pool molecules. Even in cases where the molecules from the chiral pool are not available in high enantiomeric purity, a relatively high purity is obtained with the metal complexes through the phenomenon of statistical chiral amplification. As will be shown in subsequent papers, the two remaining coordination sites in *cis* positions can be occupied by many other ligands, including easily replaceable halides. Such species represent very useful enantiomerically pure chiral building blocks, yielding polynuclear species with well-defined stereochemistry.

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Supporting Information Available: Tables of crystallographic data for Δ-[RuCG[*o*-xyl](4,4′-DMbpy)]$(PF_6)_2$ containing positional and displacement parameters and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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