Molecular Architecture of Polynuclear Ruthenium Bipyridyl Complexes with Controlled Metal Helicity

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The synthesis of di- and trinuclear ruthenium(II) complexes is reported, where each metal center has a tris(bidentate) octahedral coordination sphere with predetermined stereochemistry. New members of the "Chiragen" ligand series, consisting of two linked chiral 4,5-pineno-2,2′-bipyridine groups, have been prepared, with small spacer units between the coordination centers ($-(CH_2)_n$ {$n = 0, 3$} and $-CH_2(bpy)CH_2-$). X-ray structural data were obtained for the ligand Chiragen[3]. (Crystal data: orthorhombic, space group $P2_12_12_1$, $a = 12.229(1)$ Å, $b = 12.790(1)$ Å, $c = 20.215(1)$ Å, $V = 3161.8(4)$ Å^3, $Z = 4$.) Combination of the ligands with $Ru(bpy)_2Cl_2$ (where bpy is 2,2′-bipyridine) led to a mixture of diastereomers, while the use of enantiomerically pure Δ- or Λ-$[Ru(bpy)_2(py)_2]$(dibenzoyltartrate) or Δ-Ru(CG[*m*-xyl])Cl_2 led to almost complete stereoselectivity in the products. Circular dichroism spectra show that the complexes are composed of one helical diastereomer, with the expected absolute configuration predetermined by the chiral building block used. Additionally, ^{1}H-NMR spectroscopy indicates C_2 point group symmetry for the structures in solution, confirming the absence of ΔΛ diastereomers.

Introduction

Ruthenium complexes of polypyridyl ligands, in particular 2,2′-bipyridyl (bpy), have been extensively studied during the last few decades, due to their unique combination of chemical stability, redox properties, reactivity, and luminescence emission from the metastable excited triplet state.[1,2] As a consequence, they have been applied to such areas as photocatalysis,[3] molecular recognition (host guest) chemistry,[4−6] DNA intercalation,[7,8] and artificial photosynthesis/charge separation.[9−12]

By nature of tris(bidentate) octahedral six-coordinate (*OC*-6) species, such as $[Ru(bpy)_3]^{2+}$, there is an inherent helical chirality at the metal center (Δ or Λ), which until recently was significantly overlooked. Much attention has been devoted to the synthesis of polynuclear transition metal complexes, stimulated by attempts to design and construct multicomponent (supramolecular) species.[13] With the inclusion of more six-coordinate octahedral (*OC*-6) centers, the number of possible diastereomers that are theoretically possible increases exponentially. This is especially true for the larger species recently reported,[14−18] where it would be expected that the diastereomers would have different photophysical and electrochemical behaviors. In addition, the wide range of diastereomers typically prepared greatly hampers the characterization of the compounds by techniques such as NMR, while preventing the simple growth of crystals suitable for X-ray structural determination.

Over recent years we attempted to prepare suitable chiral building blocks to allow the synthesis of supramolecular species, where the chirality of the metal center is predetermined. To this end, we have published the separation of $[Ru(bpy)_2(py)_2]^{2+}$ into its two enantiomers by crystallization with dibenzoyltartrate, providing access to both the Δ and Λ forms, which do not undergo racemization upon replacement of the two pyridyl groups.[19,20] Similar units were recently used to prepare dinuclear[21] and linear polymetallic species.[22]

Additionally, we have found that, by using the specially designed chiral polypyridyl ligands from the "Chiragen" series, the helicity on the metal center can be predetermined from the

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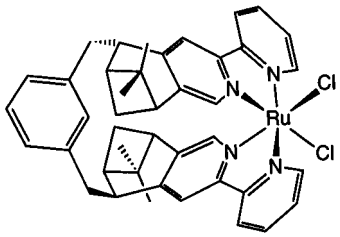

Figure 1. The chiral building block, prepared with Chiragen[*m*-xyl] (CG[*m*-xyl]).

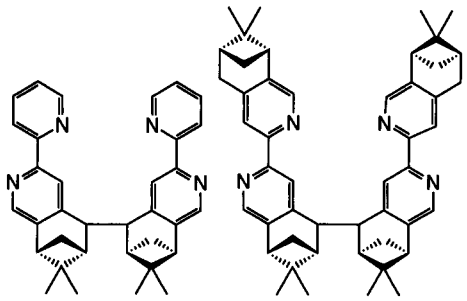

Figure 2. The tetradentate "Chiragen" ligand series. All molecules have C_2 symmetry, with six stereogenic carbon atoms.

chirality of readily available naturally-occurring terpenes.[23−25] These tetradentate ligands, when combined with ruthenium trichloride, give only one diastereomer (Figure 1), with the further advantage that they are unable to undergo photoracemization due to steric constraints.[24] Subsequent replacement of the two chloride ligands facilitates the preparation of octahedral complexes with predetermined chirality.

In this paper we illustrate how these building blocks can be applied to chiral bridging ligands of the "Chiragen" series, to produce diastereomerically and enantiomerically pure di- and trinuclear ruthenium complexes of polypyridyl ligands.

Experimental Section

(a) Measurements and Materials. NMR spectra were obtained on a Varian Gemini-300 spectrometer operating at 300 MHz for ^{1}H and 75.46 MHz for ^{13}C and on a Bruker Avance DRX500 operating at 500 MHz for ^{1}H, using the solvent as internal reference relative to TMS. UV/vis spectral data were recorded on a Perkin-Elmer Lambda 2 spectrometer, and CD spectra, on a Jobin Yvon spectrophotometer [λ_{max}, nm ($\Delta\epsilon$)]. Optical rotation values were obtained with a Perkin-Elmer MC 241 polarimeter using a 10 cm cell, with a sample concentration of approximately 1×10^{-2} M in chloroform. FAB MS data were obtained with a VG Instruments 7070E mass spectrometer (*m*/*z*), and electrospray MS data, with a Bruker BioApex 30e FT ion cyclotron mass spectrometer, with the samples dissolved in MeOH (0.1 mg/mL) (*m*/*z*). Melting points were recorded using a Büchi 520 melting point apparatus and are uncorrected. The elemental analyses were performed in The Research Center, Marly, Ciba AG. Emission spectra were recorded on a Perkin-Elmer LS 50B spectrometer. Emission quantum yields (Φ_{em}) were calculated by using $[Ru(bpy)_3](PF_6)_2$ as a standard in CH_3CN (0.062).[26−28] Electrochemical measurements were carried out at room temperature using a PAR 273A electrochemical analysis system with 270 research electrochemistry software. Cyclic voltammograms were obtained in CH_3CN, using a microcell equipped with a stationary platinum disk electrode with tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as base electrolyte. $[Ru(bpy)_3](PF_6)_2$ was used as the standard, taking the oxidation potential as +1.26 V, vs SCE.[29−31] Half-wave potentials were calculated as an average of the cathodic and anodic peaks.

Unless otherwise stated, commercial grade reagents were used without further purification. Tetrahydrofuran (THF) was predried by distillation from sodium. (1*R*)-(−)-Myrtenal was obtained from Fluka, >97%, $[\alpha]^{20}_D$ −14.6°.

5,5′-Bis(bromomethyl)-2,2′-bipyridine,[32] 4,5-pineno-2,2′-bipyridine,[25,33] the 4,5-pineno-2,2′-bipyridine dimer (Chiragen-[0]), the 4,5:4′,5′-dipineno-2,2′-bipyridine dimer (SuperChiragen-[0]),[34] $Ru(bpy)_2Cl_2$,[35] Δ-/Λ-$[Ru(bpy)_2(py)_2]$(dibenzoyltartrate),[19] and Δ-RuCG[*m*-xyl]Cl_2[24] were prepared according to the literature methods.

(b) Ligand Syntheses. (i) The 4,5-Pineno-2,2′-bipyridine Dimer (CG[3]). To a solution of 4,5-pineno-2,2′-bipyridine (602 mg, 2.41 mmol) in dry THF (10 mL) was added lithium diisopropylamine (LDA) solution (1.5 M; 1.5 mL, 2.25 mmol) in dry THF (10 mL) over 30 min at −40 °C. The reaction mixture was kept below −40 °C for 3 h; then 1,3-dibromopropane (220 mg, 1.09 mmol) dissolved in dry THF (10 mL) was added. During the addition, the color changed from blue to red. The mixture was stirred overnight, and the reaction was quenched with water (2 mL). The solution was concentrated *in vacuo*. After addition of a saturated aqueous solution of sodium hydrogen carbonate (30 mL), the mixture was extracted with dichloromethane (3 × 30 mL). The organic phase was dried over magnesium sulfate and filtered. Following removal of the solvent, the residue was purified by column chromatography on silica gel with hexane/ether/triethylamine (14:6:1) as eluent. Yield: 511 mg (79%). Recrystallization from methanol/dichloromethane gave colorless crystals. Mp: 120.5−121.5 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.64 (dd, 1H, J = 4.8, 0.9 Hz, H-6′), 8.35 (d, 1H, J = 8.0 Hz, H-3′), 8.29 (s, 1H, H-6), 8.20 (s, 1H, H-3), 7.77 (ddd, 1H, J = 7.7, 7.7, 1.7 Hz, H-4′), 7.25 (m, 1H, H-5′), 3.01 (d, 1H, J = 9.9Hz, H-7), 2.87 (dd, 1H, J = 5.4, 5.4 Hz, H-10), 2.60 (ddd, 1H, J = 9.9, 5.8, 5.8 Hz, H-9b), 2.30 (ddd, J = 5.8, 5.8, 2.2 Hz, 1H, H-8), 2.03 (m, 1H, H-15), 1.60 (m, 2H, H-14), 1.44 (s, 3H, H-13), 1.30 (d, 1H, J = 9.7 Hz, H-9a), 0.61 (s, 3H, H-12). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 156.7, 154.9, 149.7, 148.9, 145.4, 142.6, 136.8, 123.2, 120.8, 119.6, 45.1, 43.2, 41.2, 40.9, 33.5, 28.3, 26.4, 26.2, 21.0. MS (FAB (NBA), *m*/*z*): 563 (16, MNa^+), 541 (100, MH^+). Anal. Calcd for $C_{37}H_{40}N_4$·MeOH: C, 79.7; H, 7.7; N, 9.8. Found: C, 80.1; H, 7.7; N, 9.8. Optical rotation: $[\alpha]^{22}_D$ = −70°.

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(ii) The 4,5-Pineno-2,2′-bipyridine Dimer (CG[bpy]). A procedure analogous to that for CG[3] was followed, using 4,5-pineno-2,2′-bipyridine (500 mg, 2.00 mmol) in dry THF (10 mL), 1.5 M LDA solution (1.4 mL, 2.10 mmol), and 5,5′-bis-(bromomethyl)-2,2′-bipyridine (341 mg, 0.99 mmol) dissolved in dry THF (10 mL). Yield: 212 mg (32%). Recrystallization from methanol/dichloromethane gave colorless crystals. Mp: 217.5−218.5 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.62 (dd, 1H, J = 4.8, 0.8 Hz, H-6′), 8.48 (d, 1H, J = 1.92 Hz, H-6″), 8.42 (s, 1H, H-6), 8.34 (d, 1H, J = 8.0 Hz, H-3′), 8.31 (d, 1H, J = 8.4 Hz, H-3″), 8.21 (s, 1H, H-3), 7.75 (ddd, 1H, J = 7.6, 7.6, 1.8, Hz, H-4′), 7.64 (dd, 1H, J = 8.2, 2.2 Hz, H-4″), 7.23 (m, 1H, H-5′), 3.46 (dd, 1H, J = 3.6, 13.8 Hz, H-14a), 3.26 (dd, 1H, J = 11.3 Hz, H-7), 2.84 (dd, 1H, J = 5.5, 5.5 Hz, H-10), 2.75 (dd, 1H, J = 11.2, 14.0 Hz, H-14b), 2.54 (ddd, 1H, J = 9.9, 5.5, 5.5 Hz, H-9b), 1.95 (dd, J = 5.8, 5.8 Hz, 1H, H-8), 1.36 (d, 1H, J = 10.0 Hz, H-9a), 1.28 (s, 3H, H-13), 0.53 (s, 3H, H-12). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 156.4, 154.8, 154.3 149.8, 149.0 148.0, 145.7, 142.7, 137.6, 136.9, 135.3 123.4 (CH-5′), 120.9, 120.6, 119.3, 45.0, 42.8, 42.4, 41.0, 36.4, 28.0, 26.2, 20.9. MS (FAB (NBA), *m*/*z*): 703 (9, MNa^+), 681 (48, MH^+), 432 (20, M − pineno − bpy$^+$). Anal. Calcd for $C_{46}H_{46}N_6\cdot 2.5H_2O$: C, 76.1; H, 6.8; N, 11.6. Found: C, 76.1; H, 6.8; N, 11.6. Optical rotation: $[\alpha]^{22}_D = +133°$.

(c) Complex Syntheses Using Ru(bpy)$_2$Cl$_2$. (i) Diastereomeric Mixture of [{(bpy)$_2$Ru}$_2$-μ-CG[3]](PF$_6$)$_4$. In a typical experiment, CG[3] (53.4 mg, 0.10 mmol) and $Ru(bpy)_2Cl_2$ (106 mg, 0.20 mmol) were heated in ethylene glycol (10 mL; 10% water) at 100 °C for 20 h, after which the volume was reduced to 1 mL by vacuum distillation, and the product was precipitated with the addition 10% aqueous ammonium hexafluorophosphate solution. The red solid was filtered, dried at 50 °C, and purified by repeated passage down a Sephadex LH20 column (50% methanol/acetonitrile eluent), collecting the first fraction. Yield: 165 mg (85%). MS (FAB (NBA), *m*/*z*): 1804 ([M − PF_6]$^+$), 1656 ([MH − 2PF_6]$^+$), 1513 ([MH_2 − 3PF_6]$^+$). Anal. Calcd for $C_{77}H_{72}N_{12}F_{24}P_4Ru_2\cdot H_2O$: C, 47.1; H, 3.8; N, 8.5. Found: C, 47.1; H, 3.8; N, 8.5.

(ii) Diastereomeric Mixture of [{(bpy)$_2$Ru}$_2$-μ-CG[0]](PF$_6$)$_4$. Yield: 74%. MS (FAB (NBA), *m*/*z*): 1761 ([M − PF_6]$^+$), 1615 ([MH − 2PF_6]$^+$). Anal. Calcd for $C_{74}H_{66}N_{12}F_{24}P_4Ru_2\cdot 2H_2O$: C, 45.8; H, 3.6; N, 8.7. Found: C, 45.8; H, 3.8; N, 8.4.

(iii) Diastereomeric Mixture of [{(bpy)$_2$Ru}$_2$-μ-SCG[0]](PF$_6$)$_4$. Yield: 82%. MS (FAB (NBA), *m*/*z*): 1947 ([M − PF_6]$^+$), 1806 ([MH − 2PF_6]$^+$). Anal. Calcd for $C_{88}H_{85}N_{12}F_{24}P_4Ru_2\cdot 1.5H_2O$: C, 49.8; H, 4.2; N, 7.9. Found: C, 49.9; H, 4.3; N, 7.7.

(iv) Diastereomeric Mixture of [{(bpy)$_2$Ru}$_3$-μ-CG[bpy]](PF$_6$)$_6$. Yield: 57%. MS (FAB (NBA), *m*/*z*): 2648 ([M − PF_6]$^+$), 2500 ([MH − 2PF_6]$^+$). Anal. Calcd for $C_{106}H_{92}N_{18}F_{36}P_6Ru_3\cdot 1.5H_2O$: C, 44.9; H, 3.6; N, 8.7. Found: C, 44.8; H, 3.7; N, 8.5.

(d) Complex Syntheses Using Δ-/Λ-[Ru(bpy)$_2$(py)$_2$](dibenzoyltartrate). (i) [{(bpy)$_2$-Δ-Ru}$_2$-μ-CG[3]](PF$_6$)$_4$. In a typical experiment, CG[3] (21.6 mg, 40.0 μmol) and Δ-[Ru(bpy)$_2$(py)$_2$](dibenzoyltartrate) (101.8 mg, 89.0 μmol) were heated in ethylene glycol (10 mL; 10% water) at 100 °C for 20 h, after which the volume was reduced to 1 mL by vacuum distillation, and the product was precipitated with the addition 10% aqueous ammonium hexafluorophosphate solution. The red solid was filtered off, dried at 50 °C, and purified by preparative thick-layer plate silica chromatography using *N*,*N*-dimethylformamide (DMF)/water (4:1) containing 10% ammonium chloride as eluent (SCG[0]: DMF/water (10:1)). The product was extracted from the lowest fraction with acetone containing 10% ammonium hexafluorophosphate. Yield: 37 mg (41%). MS (electrospray, *m*/*z*): 1803 ([M − PF_6]$^+$), 829 ([M − 2PF_6]$^{2+}$), 504 ([M − 3PF_6]$^{3+}$).

(ii) [{(bpy)$_2$-Λ-Ru}$_2$-μ-CG[3]](PF$_6$)$_4$. Yield: 85%. MS (electrospray, *m*/*z*): 1803 ([M − PF_6]$^+$), 829 ([M − 2PF_6]$^{2+}$), 504 ([M − 3PF_6]$^{3+}$).

(iii) [{(bpy)$_2$-Δ-Ru}$_2$-μ-CG[0]](PF$_6$)$_4$. Yield: 46%. MS (electrospray, *m*/*z*): 1761 ([M − PF_6]$^+$), 1125 ([2M − 3PF_6]$^{3+}$), 808 ([M − 2PF_6]$^{2+}$), 490 ([M − 3PF_6]$^{3+}$).

(iv) [{(bpy)$_2$-Λ-Ru}$_2$-μ-CG[0]](PF$_6$)$_4$. Yield: 88%. MS (electrospray, *m*/*z*): 1761 ([M − PF_6]$^+$), 1125 ([2M − 3PF_6]$^{3+}$), 808 ([M − 2PF_6]$^{2+}$), 490 ([M − 3PF_6]$^{3+}$).

(v) [{(bpy)$_2$-Δ-Ru}$_2$-μ-SCG[0]](PF$_6$)$_4$. Yield: 22%. MS (electrospray, *m*/*z*): 1948 ([M − PF_6]$^+$), 902 ([M − 2PF_6]$^{2+}$), 553 ([M − 3PF_6]$^{3+}$).

(vi) [{(bpy)$_2$-Λ-Ru}$_2$-μ-SCG[0]](PF$_6$)$_4$. Yield: 55%. MS (electrospray, *m*/*z*): 1948 ([M − PF_6]$^+$), 1251 ([2M − 3PF_6]$^{3+}$), 902 ([M − 2PF_6]$^{2+}$), 553 ([M − 3PF_6]$^{3+}$), 378 ([M − 4PF_6]$^{4+}$).

(vii) [{(bpy)$_2$-Δ-Ru}$_3$-μ-CG[bpy]](PF$_6$)$_6$. Yield: 37%. MS (electrospray, *m*/*z*): 1251 ([M − 2PF_6]$^{2+}$), 785 ([M − 3PF_6]$^{3+}$), 553 ([M − 4PF_6]$^{4+}$), 413 ([M − 5PF_6]$^{5+}$), 384 ([M − 5PF_6 − HPF_6]$^{5+}$).

(viii) {(bpy)$_2$-Λ-Ru}$_3$-μ-CG[bpy]](PF$_6$)$_6$. Yield: 39%. MS (electrospray, *m*/*z*): 1251 ([M − 2PF_6]$^{2+}$), 785 ([M − 3PF_6]$^{3+}$), 553 ([M − 4PF_6]$^{4+}$), 413 ([M − 5PF_6]$^{5+}$), 384 ([M − 5PF_6-HPF_6]$^{5+}$).

(e) Complex Syntheses Using Δ-RuCG[*m*-xyl]Cl$_2$. (i) [{CG[*m*-xyl]-Δ-Ru}$_2$-μ-CG[3]](PF$_6$)$_4$. In a typical experiment, CG[3] (17.5 mg, 32.4 μmol) and Δ-[Ru(CG[*m*-xyl])Cl_2] (50.8 mg, 65.6 μmol) were heated in ethylene glycol (10 mL; 10% water) at 100 °C for 20 h, after which the volume was reduced to 1 mL by vacuum distillation, and the product was precipitated with the addition 10% aqueous ammonium hexafluorophosphate solution. The red solid was filtered off, dried at 50 °C, and purified by preparative thick-layer plate silica chromatography with acetonitrile/butan-1-ol/water (4:1:1) containing 10% potassium nitrate as eluent. The product was extracted from the lowest fraction with acetone containing 10% ammonium hexafluorophosphate. Yield: 62 mg (76%). MS (FAB (NBA), *m*/*z*): 2385 ([M − PF_6]$^+$), 2239 ([MH − 2PF_6]$^+$), 2089 ([MH_2 − 3PF_6]$^+$). Anal. Calcd for $C_{121}H_{124}N_{12}F_{24}P_4Ru_2\cdot 4MeOH$: C, 56.5; H, 5.3; N, 6.3. Found: C, 56.7; H, 5.4; N, 5.9.

(ii) [{CG[*m*-xyl]-Δ-Ru}$_2$-μ-CG[0]](PF$_6$)$_4$. Yield: 50%. MS (FAB (NBA), *m*/*z*): 2341 ([M − PF_6]$^+$), 2196 ([MH − 2PF_6]$^+$), 2053 ([MH_2 − 3PF_6]$^+$). Anal. Calcd for $C_{118}H_{118}N_{12}F_{24}P_4Ru_2\cdot 5H_2O$: C, 55.0; H, 5.0; N, 6.5. Found: C, 54.5; H, 5.3; N, 5.5.

(iii) [{CG[*m*-xyl]-Δ-Ru}$_2$-μ-SCG[0]](PF$_6$)$_4$. Yield: 39%. MS (electrospray, *m*/*z*): 1193 ([M − 2PF_6]$^{2+}$), 764 ([M − 3PF_6]$^{3+}$), 524 ([M − 4PF_6]$^{4+}$). Anal. Calcd for $C_{132}H_{138}N_{12}F_{34}P_4Ru_2\cdot 7H_2O$: C, 56.6; H, 5.5; N, 6.0. Found: C, 56.4; H, 5.4; N, 5.9.

(iv) [{CG[*m*-xyl]-Δ-Ru}$_3$-μ-CG[bpy]](PF$_6$)$_6$. Yield: 29%. MS (electrospray, *m*/*z*): 1687 ([M − 2PF_6]$^{2+}$), 1076 ([M − 3PF_6]$^{3+}$), 771 ([M − 4PF_6]$^{4+}$), 588 ([M − 5PF_6]$^{5+}$), 465 ([M − 6PF_6]$^{6+}$). Anal. Calcd for $C_{172}H_{170}N_{18}F_{36}P_6Ru_3\cdot 7H_2O$: C, 54.5; H, 4.9; N, 6.7. Found: C, 54.6; H, 5.1; N, 6.5.

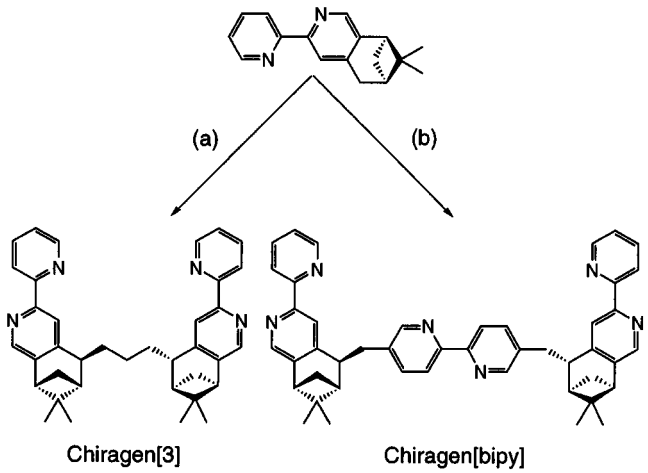
All of the complexes were fully characterized by ^{1}H-NMR, details of which are supplied in the Supporting Information. Additionally, see Table 1 and Figures 4 and 5.

(f) X-ray Structural Determination of CG[3]. The data set was collected on a Stoe AED2 four-circle diffractometer, using the $\omega/2\theta$ scan mode and Mo Kα graphite-monochromated radiation (λ 0.7107 3 Å) at room temperature. The crystals are

Table 1. Numbers and Positions of the Pineno Methyl Signals in the ^{1}H-NMR Spectra

complex	no. of methyl peaks obsd	ppm (rel integration ± 10%)												
[{(bpy)$_2$Ru}$_2$-μ-CG[3]]$^{4+}$	6	1.38 (2)	1.32 (2)	0.70 (1)	0.69 (1)	0.29 (1)	0.28 (1)							
[{(bpy)$_2$-Δ-Ru}$_2$-μ-CG[3]]$^{4+}$	2	1.38 (2)			0.69 (1)									
[{(bpy)$_2$-Λ-Ru}$_2$-μ-CG[3]]$^{4+}$	2		1.31 (2)			0.29 (1)								
[{CG[*m*-xyl]-Δ-Ru}$_2$-μ-CG[3]]$^{4+}$	5	1.42 (1)	1.28 (1)	1.27 (1)	0.77 (1)	0.59 (2)								
[{(bpy)$_2$Ru}$_2$-μ-CG[0]]$^{4+}$	8	1.29 (1)	1.23 (1)	1.19 (1)	1.12 (1)	0.82 (1)	0.79 (1)	0.41 (1)	0.38 (1)					
[{(bpy)$_2$-Δ-Ru}$_2$-μ-CG[0]]$^{4+}$	2	1.29 (1)					0.79 (1)							
[{(bpy)$_2$-Λ-Ru}$_2$-μ-CG[0]]$^{4+}$	2			1.19 (1)				0.41 (1)						
[{CG[*m*-xyl]-Δ-Ru}$_2$-μ-CG[0]]$^{4+}$	4	1.28 (2)	0.91 (1)	0.60 (1)	0.58 (2)									
[{(bpy)$_2$Ru}$_2$-μ-SCG[0]]$^{4+}$	15	1.35 (1)	1.34 (1)	1.29 (2)	1.28 (1)	1.22 (1)	1.18 (1)	1.12 (1)	0.83 (1)	0.80 (1)	0.73 (1)	0.71 (1)	0.41 (1)	0.39 (1)	0.35 (1)	0.33 (1)
[{(bpy)$_2$-Δ-Ru}$_2$-μ-SCG[0]]$^{4+}$	4	1.36 (1)					1.19 (1)			0.81 (1)	0.74 (1)					
[{(bpy)$_2$-Λ-Ru}$_2$-μ-SCG[0]]$^{4+}$	4			1.29 (1)	1.28 (1)								0.42 (1)		0.34 (1)	
[{CG[*m*-xyl]-Δ-Ru}$_2$-μ-SCG[0]]$^{4+}$	8	1.39 (1)	1.28 (1)	1.28 (1)	1.26 (1)	0.93 (1)	0.81 (1)	0.59 (1)	0.58 (1)							
[{(bpy)$_2$Ru}$_3$-μ-CG[bpy]]$^{6+}$	8	1.22 (1)	1.16 (1)	1.15 (1)	1.09 (1)	0.79 (1)	0.61 (1)	0.49 (1)	0.21 (1)	0.09 (1)						
[{(bpy)$_2$-Δ-Ru}$_3$-μ-CG[bpy]]$^{6+}$	2			1.16 (1)				0.50 (1)								
[{(bpy)$_2$-Λ-Ru}$_3$-μ-CG[bpy]]$^{6+}$	2		1.17 (1)						0.21 (1)							
[{CG[*m*-xyl]-Δ-Ru}$_3$-μ-CG[bpy]]$^{6+}$	8	1.26 (1)	1.26 (1)	1.16 (1)	1.01 (1)	0.62 (1)	0.58 (1)	0.55 (1)	0.39 (1)							

Scheme 1. Preparation of Additional "Chiragen" Ligands[a]



[a] Route a: (i) LDA, THF, <−40 °C; (ii) 1,3-dibromopropane. Route b: (i) LDA, THF, <−40 °C; (ii) 5,5′-bis(bromomethyl)-2,2′-bipyridine.

orthorhombic, of space group $P2_12_12_1$. Cell dimensions: a = 12.229(1) Å, b = 12.790(0) Å, c = 20.215(1) Å, and V = 3161.8(4) Å^3. D_{calc} = 1.170 g cm^{-3}; Z = 4; R = 0.0554. Additionally, a disordered molecule of water was located in the unit cell.

Results and Discussion

Synthesis. We previously published the preparation of the "Chiragen" ligand system consisting of two linked 4,5-pineno-2,2′-bipyridines.[23−25,33] To ensure unambiguous characterization of the bridged coordination complexes of this type of system by techniques such as NMR, it was necessary to design new analogues where the link between the two bipyridyl coordination sites is as small as possible. As a consequence, it would be possible to identify the diastereomers present following coordination to an octahedral transition metal center. To this end we recently described the synthesis of "Chiragen[0]" (CG[0]) and "SuperChiragen[0]" (SCG[0]), with a direct linkage between two pinene moieties. Due to the close proximity of the bulky pinene groups, a severely hindered rotation around the linkage was demonstrated, as indicated by a significant effect observed by both polarimetry and circular dichroism (CD) spectroscopy.[34]

To extend the series, "Chiragen[3]" (CG[3]), with a propylene spacer, was prepared in high yield (Scheme 1) by following the previously described procedure. Disappointingly, similar procedures to prepare the analogous ligands Chiragen[1] and Chiragen[2] (with a methylene and an ethylene spacer, respectively) were unsuccessful. Crystals of CG[3] suitable for X-ray structure determination were produced by slow evaporation from methanol/dichloromethane, giving the structure illustrated in Figure 3. The structure indicates that the coupling reaction occurs with the introduction of a pair of chiral centers on C7 and C7a, as previously described.[23−25,33]

To increase the possible number of coordination sites to three, 5,5′-bis(bromomethyl)-2,2′-bipyridine was used to form a bridge between the two pinenobipyridine groups (Scheme 1), giving "Chiragen[bpy]" (CG[bpy]). This new ligand provides three bidentate coordination sites, suitable for the preparation of trinuclear species.

Ligands CG[0], SCG[0], and CG[3] were subsequently coordinated to ruthenium(II), using an excess of the transition metal precursors, by heating in ethylene glycol containing 10% water. Ru(bpy)$_2$Cl$_2$ gave a mixture of all the possible dinuclear diastereomers in over 70% yield. In the case of the trinuclear ligand (CG[bpy]), 57% of the desired product was obtained as

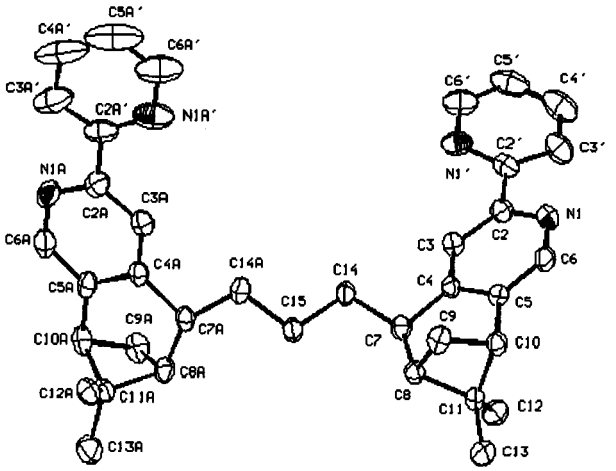


Figure 3. Thermal motion ellipsoid plot of Chiragen[3], with ellipsoids drawn at 30% probability.

a mixture of diastereomers, with a small but significant amount of a dinuclear species being observed during the purification. The complexes were purified by repeated passage of the hexafluorophosphate salt down a Sephadex LH20 column, eluting with 50% acetonitrile/methanol, giving the larger desired species first.

Using the resolved chiral building blocks Δ- and Λ-[Ru(bpy)$_2$-(py)$_2$](dibenzoyltartrate), only one of the possible diastereomers was obtained following purification by preparative plate silica chromatography eluting with a DMF/water (4:1) mixture containing 10% ammonium chloride. The complexes derived from SCG[0] indicated a greater hydrophobicity, due to the increased number of pinene groups as compared to CG[0], and were eluted with a mixture containing a higher proportion of DMF (10:1). In all cases, the slowest moving fraction was collected, while species of lower nuclearity were observed to travel much faster on the plate. The products were characterized by CD and ^{1}H-NMR spectroscopy, as described below. Additionally, electrospray mass spectroscopy gave a number of assignable peaks in accordance with the proposed species; this observation is the subject of further study. The yields proved to be disappointingly lower than that obtained with the use of Ru(bpy)$_2$Cl$_2$ due to retention of the product on the silica during purification.

The precursor, Δ-RuCG[*m*-xyl]Cl$_2$, with a predetermined helicity due to the nature of the supplementary tetradentate Chiragen[*m*-xylyl] ligand, gave only one of the possible diastereomers. Again, these were purified by preparative plate silica chromatography, eluting with acetonitrile/butan-1-ol/water (4:1:1) containing 10% potassium nitrate. It was noted that an appreciable amount of the product was retained on the silica. Compounding this, lower yields were obtained than expected for the species with the smaller bridges, CG[0], SCG[0], and CG[bpy], which we assume to be due to unfavorable steric interactions of the bulky pinene groups, preventing the formation of dinuclear (trinuclear) species. Due to the natural chirality of the ligands and the control of helicity at the ruthenium metal centers, only one diastereomer was prepared, indicated by ^{1}H-NMR and CD spectroscopy (see below). This is even the case with the complex [{CG[*m*-xyl]-Δ-Ru}$_3$-μ-CG[bpy]](PF$_6$)$_6$ containing 27 stereogenic sites, including three chiral metal centers.

^{1}H-NMR Spectroscopy. The dinuclear species prepared from Ru(bpy)$_2$Cl$_2$ contains all three diastereomers, ΔΔ, ΛΛ, and ΔΛ, in the expected statistical ratios (from integration). While each of these possesses either C_2 or C_s symmetry, a very complex spectrum occurs as a consequence of the diastereomeric mixture, where definite identification of individual peaks is extremely difficult. In each case, the pineno methyl peaks gave a good indication of the number of isomers present (Table 1). Using the chirally resolved precursor, either Δ- or Λ-[Ru(bpy)$_2$-

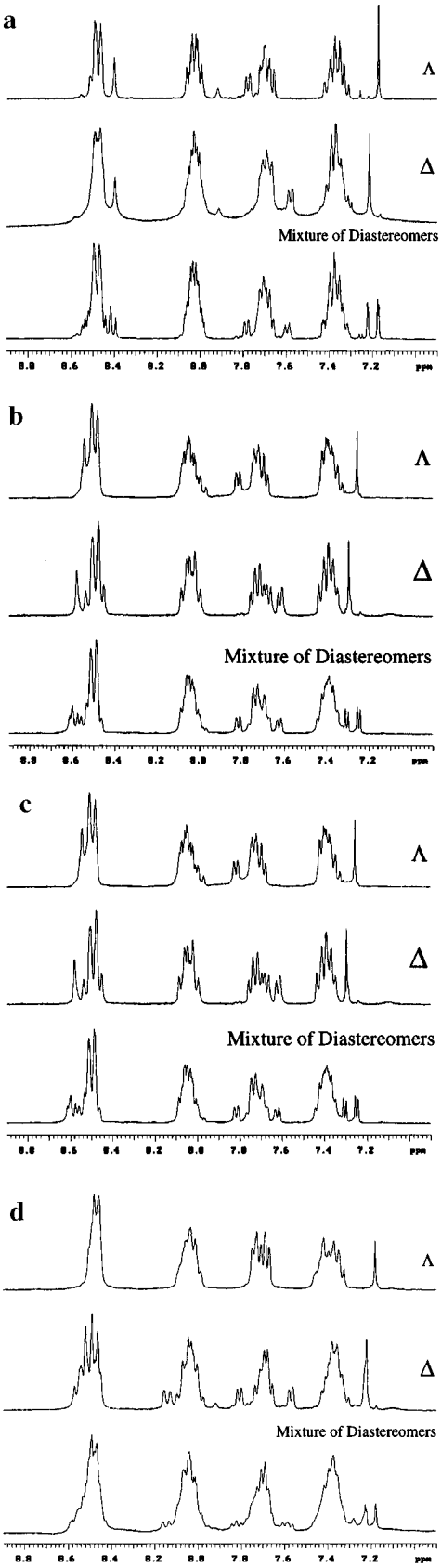


Figure 4. The aromatic region of the ^{1}H-NMR for the di- and trinuclear Λ, Δ and mixed ruthenium species of the ligands (a) [{(bpy)$_2$Ru}$_2$-μ-CG[3]](PF$_6$)$_6$, (b) [{(bpy)$_2$Ru}$_2$-μ-CG[0]](PF$_6$)$_6$, (c) [{(bpy)$_2$Ru}$_2$-μ-SCG[0]](PF$_6$)$_6$, and (d) [{(bpy)$_2$Ru}$_3$-μ-CG[bpy]](PF$_6$)$_6$.

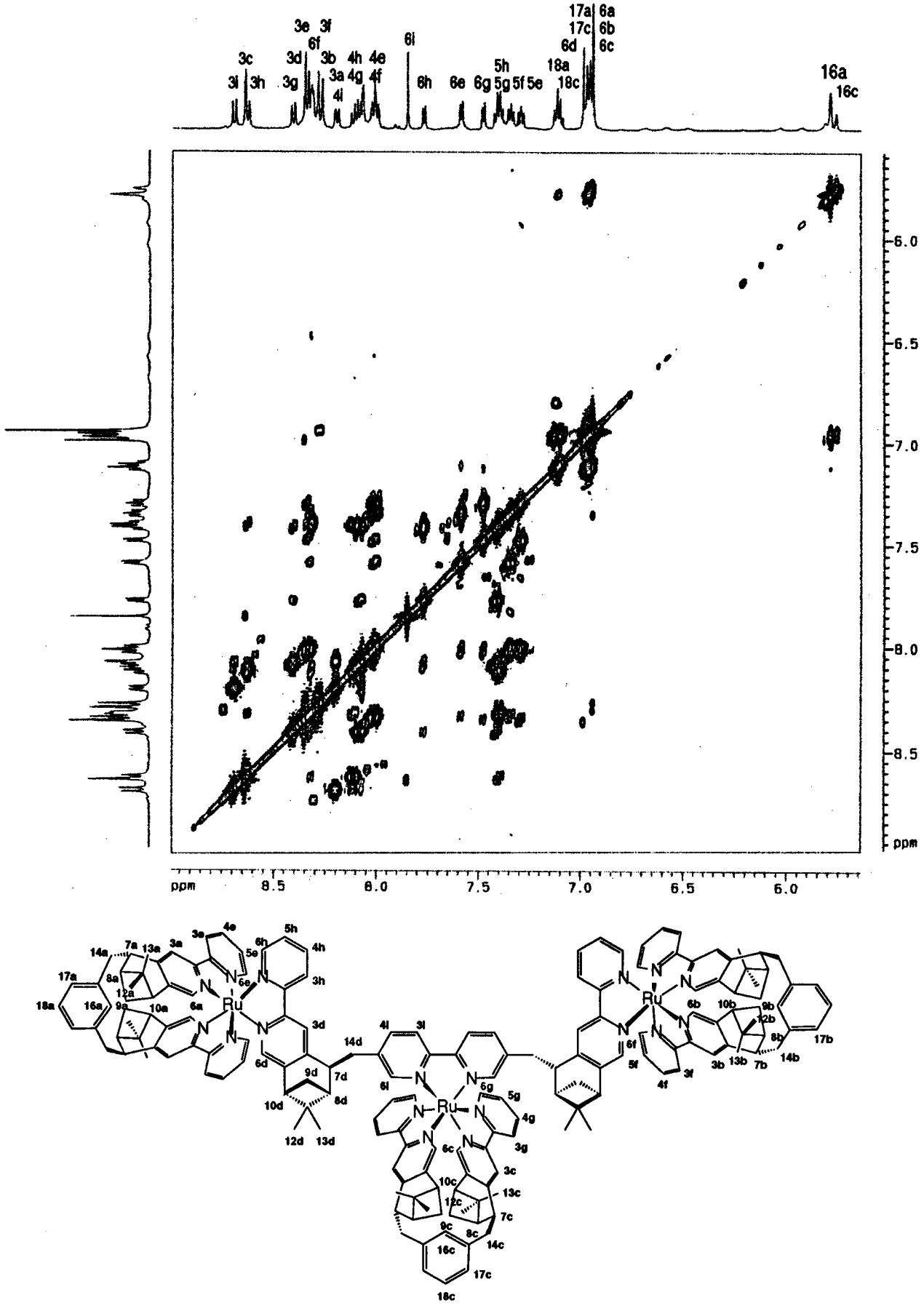


Figure 5. An H,H-COSY spectrum of $[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_3\text{-}\mu\text{-}CG[bpy]](PF_6)_6$, with assignments shown below, run in CD_3CN (500 MHz).

$(py)_2$](dibenzoyltartrate), the ^{1}H-NMR spectrum indicates that only one of the three diastereomers was present in the product (see CD spectra), with an estimated ee of over 95%, as determined from the integration of the methyl peaks. The

Table 2. Electrochemical and Photophysical Properties in CH_3CN at 298 K

	$E_{1/2}$, V vs SCE		E_{red}, V vs SCE	LC		MLCT		emission	
complex	oxidn	redn	redn	$\lambda_{max} \pm 2$, nm	$10^{-3}\epsilon$	$\lambda_{max} \pm 2$, nm	$10^{-3}\epsilon$	$\lambda_{em} \pm 2$, nm	$\Phi_{em} \pm 5\%$
$[Ru(bpy)_3]^{2+}$	1.26	−1.37	−1.59	286	102.3	452	16.1	610	0.062
$[\{(bpy)_2Ru\}_2\text{-}\mu\text{-}CG[3]]^{4+}$	1.21	−1.38	−1.63	288	175.1	452	37.8	613	0.049
$[\{(bpy)_2\text{-}\Delta\text{-}Ru\}_2\text{-}\mu\text{-}CG[3]]^{4+}$				288	169.6	452	36.1	615	0.052
$[\{(bpy)_2\text{-}\Lambda\text{-}Ru\}_2\text{-}\mu\text{-}CG[3]]^{4+}$				288	174.0	452	36.6	615	0.048
$[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_2\text{-}\mu\text{-}CG[3]]^{4+}$	1.13	−1.48	−1.69	295	155.4	450	30.0	610	0.018
$[\{(bpy)_2Ru\}_2\text{-}\mu\text{-}CG[0]^{4+}$	1.23	−1.37	−1.60	288	154.5	452	31.1	611	0.053
$[\{(bpy)_2\text{-}\Delta\text{-}Ru\}_2\text{-}\mu\text{-}CG[0]]^{4+}$				288	153.5	452	34.7	614	0.055
$[\{(bpy)_2\text{-}\Lambda\text{-}Ru\}_2\text{-}\mu\text{-}CG[0]]^{4+}$				288	157.6	452	36.7	612	0.055
$[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_2\text{-}\mu\text{-}CG[0]]^{4+}$	1.14	−1.48	−1.69	296	144.3	452	29.2	610	0.013
$[\{(bpy)_2Ru\}_2\text{-}\mu\text{-}SCG[0]]^{4+}$	1.16	−1.40	−1.64	288	158.9	452	29.9	618	0.043
$[\{(bpy)_2\text{-}\Delta\text{-}Ru\}_2\text{-}\mu\text{-}SCG[0]]^{4+}$				288	143.9	452	31.1	618	0.044
$[\{(bpy)_2\text{-}\Lambda\text{-}Ru\}_2\text{-}\mu\text{-}SCG[0]]^{4+}$				288	133.6	452	26.1	623	0.044
$[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_2\text{-}\mu\text{-}SCG[0]]^{4+}$	1.10	−1.49	−1.75	298	143.1	438	29.2	611	0.019
$[\{(bpy)_2Ru\}_3\text{-}\mu\text{-}CG[bpy]]^{6+}$	1.22	−1.38	−1.63	288	244.9	452	56.3	614	0.061
$[\{(bpy)_2\text{-}\Delta\text{-}Ru\}_3\text{-}\mu\text{-}CG[bpy]]^{6+}$				288	230.0	452	54.1	614	0.064
$[\{(bpy)_2\text{-}\Lambda\text{-}Ru\}_3\text{-}\mu\text{-}CG[bpy]]^{6+}$				288	237.5	452	52.2	612	0.060
$[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_3\text{-}\mu\text{-}CG[bpy]]^{6+}$	1.15	−1.48	−1.67	298	213.3	451	38.3	604	0.016

spectrum in each case simplifies considerably when compared to those of the diastereomeric mixtures (Figure 4).

Using the potential trinuclear ligand CG[bpy], the number of possible diastereomers increases to 6; *viz.*, ΔΔΔ, ΔΔΛ, ΔΛΔ, ΔΛΛ, ΛΔΛ, and ΛΛΛ. This leads to a very complex spectrum (Figure 4d). However, because the two extreme coordination centers are unable to sense each other's presence, the number of isomers observed is reduced to 3 (while in reality all six are present). By using the Δ- or Λ- $[Ru(bpy)_2(py)_2]$-(dibenzoyltartrate) precursor, only one of the respective stereoisomers is produced (see CD spectra), as with the dinuclear complexes.

Using the predetermined building block Δ-RuCG[*m*-xyl]Cl_2, only one of the possible diastereomers is observed by ^{1}H-NMR. While this series of complexes demonstrate extremely intricate ^{1}H-NMR spectra, especially for the trinuclear $[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_3\text{-}\mu\text{-}CG[bpy]]^{6+}$, they can be assigned using H,H-COSY techniques (Figure 5) and comparison with previously characterized species such as $[\Delta\text{-}Ru(CG[m\text{-xyl}])(bpy)]^{2+}$.[24]

Cyclic Voltammetry. The complexes all gave similar CV spectra, with a quasi-reversible Ru(II/III) couple in the range 1.13−1.22 V. The first reduction wave demonstrated reversibility, at approximately −1.4 V. The subsequent wave was irreversible, and consequently the peak potential for reduction ($E_{p,c}$) is given in Table 2. The pinenobipyridyl ligands shift all redox potentials to a more negative (cathodic) potential, when compared to the case of $[Ru(bpy)_3](PF_6)_2$, as illustrated in Table 2, where larger shifts are given for complexes with a greater number of pinene groups per coordination center. No difference between the pairs of diastereomers was observed electrochemically, despite there being considerable structural differences between them.

UV/Vis Absorption and Emission Spectra. The complexes of the type $[\{(bpy)_2\text{-}Ru\}_n\text{-}\mu\text{-}L](PF_6)$ ($n = 2$, L = CG[0], SCG-[0], CG[3]; $n = 3$, L = CG[bpy]) each demonstrated spectra similar to that of $[Ru(bpy)_3]^{2+}$, where the absorption is proportional to the number of chromophoric centers (Table 2). Additionally, they exhibit strong luminescence at approximately the same wavelength (610 nm) and quantum yield (0.06) (within experimental error) as those of $[Ru(bpy)_3]^{2+}$ per chromophoric center. Again, in each case, it was observed that the individual orientations at the metal centers of the ΛΛ and ΔΔ complexes did not demonstrate any significant difference in behavior.

The complexes prepared from RuCG[*m*-xyl]Cl_2 did not conform to the above observations however (Figure 6). The

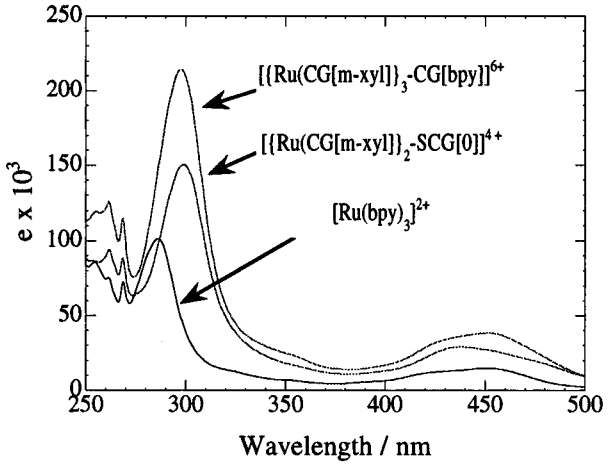


Figure 6. UV/vis absorption spectra of $[Ru(bpy)_3](PF_6)_2$, $[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_2\text{-}\mu\text{-}SCG[0]](PF_6)_6$, and ΔΔΔ-$[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_3\text{-}\mu\text{-}CG[bpy]](PF_6)_6$.

ligand-centered (LC) absorption is bathochromically shifted by 10 nm to 298 nm. A strong shoulder is evident in the metal-to-ligand charge transfer band (MLCT) at approximately 430 nm. With the complex $[\{CG[m\text{-xyl}]\text{-}\Delta\text{-}Ru\}_2\text{-}\mu\text{-}SCG[0]]^{4+}$ the shoulder and the maxima are inverted resulting in a hypsochromic shift of 18 nm (Table 2). Additionally, the emission is much weaker than those of the above complexes, though still at 610 nm. It is assumed that these effects are a result of additional steric constraints caused by the larger number of bulky pinene groups, forcing a deviation from the ideal octahedral coordination ligand arrangement.

Circular Dichroism Spectra. All the ligands, except CG-[3], exhibit a significant Cotton effect, observed by circular dichroism (CD) spectroscopy in the LC $\pi-\pi^*$ transitions at approximately 300 nm.[34] It has been assumed that this is due to steric constraints in the rotation along the linkage, leading to a dominant solution conformation. With the mixture of diastereomers prepared using the racemic precursor $Ru(bpy)_2Cl_2$, a weak Cotton effect is evident in the solution, despite the NMR indicating a statistical mixture of the diastereomers, with small $\Delta\epsilon$ values being observed only on the LC transitions. While for the CG[3] complex the effect is small, and could be caused by a slight excess of the ΛΛ diastereomer, the effect is much more evident for the other complexes, with a pattern that does not resemble those of the single diastereomers discussed below. Thus, this observed signal is a consequence of the ligand

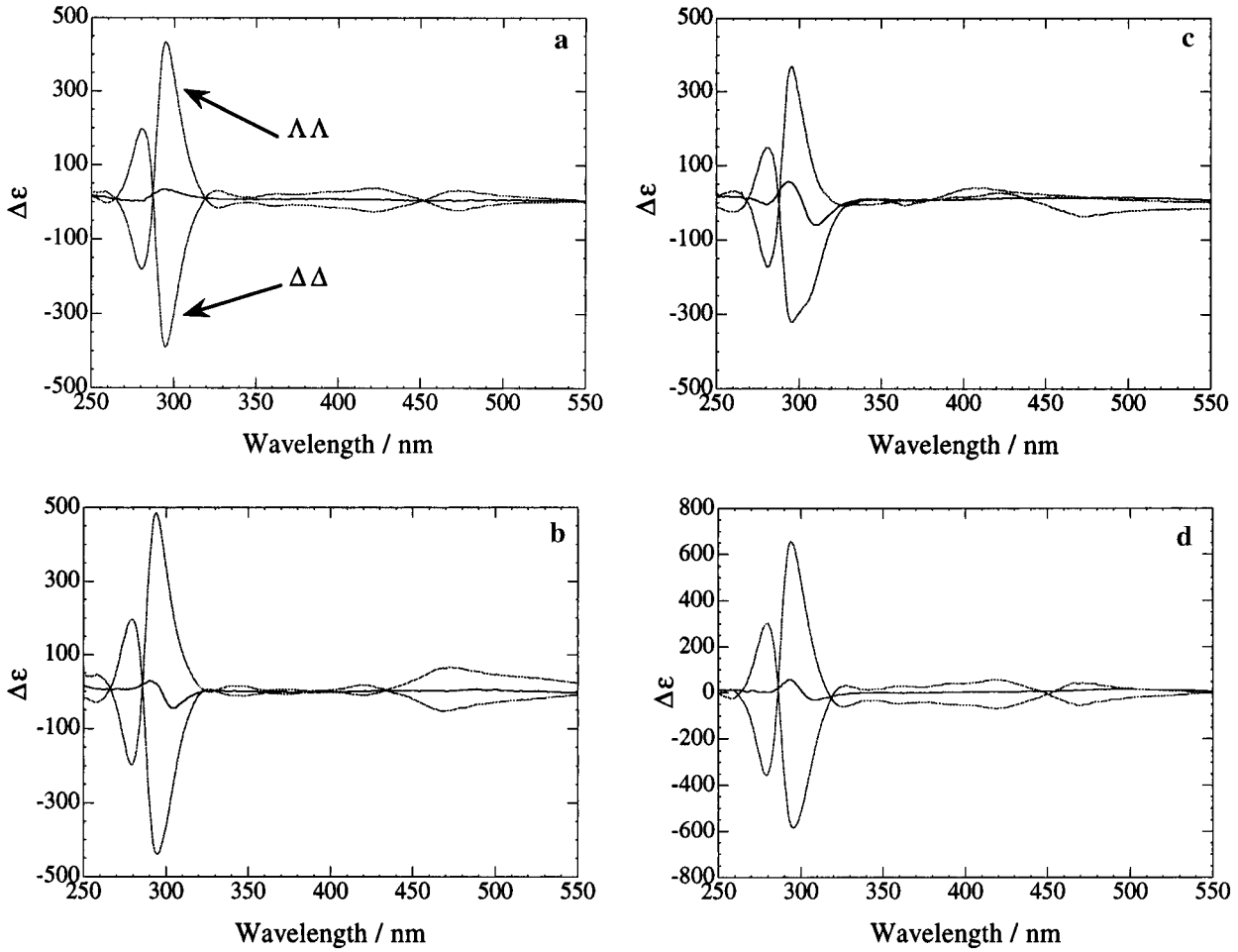


Figure 7. CD spectra of ΛΛ, ΔΔ, and mixed ruthenium species of the ligands (a) CG[3], (b) CG[0], (c) SCG[0], and (d) the trinuclear ΛΛΛ, ΔΔΔ, and mixed ruthenium species CG[bpy].

Table 3. CD Maxima Observed in Acetonitrile at 298 K

complex	$\lambda \pm 3$, nm ($\Delta\epsilon$)					
$[\{(bpy)_2Ru\}_2$-μ-CG[3]$]^{4+}$	281 (2)	294 (35)				
$[\{(bpy)_2$-Δ-$Ru\}_2$-μ-CG[3]$]^{4+}$	281 (197)	295 (−389)	326 (31)		419 (39)	470 (−22)
$[\{(bpy)_2$-Λ-$Ru\}_2$-μ-CG[3]$]^{4+}$	281 (−181)	295 (435)	327 (−15)		420 (−24)	472 (30)
$[\{CG[m$-xyl]-Δ-$Ru\}_2$-μ-CG[3]$]^{4+}$	286 (266)	304 (−380)	335 (21)	352 (5)	425 (26)	475 (−3)
$[\{(bpy)_2Ru\}_2$-μ-CG[0]$]^{4+}$	277 (5)	290 (30)	305 (−45)			
$[\{(bpy)_2$-Δ-$Ru\}_2$-μ-CG[0]$]^{4+}$	279 (198)	295 (−439)	326 (5)		420 (17)	468 (−53)
$[\{(bpy)_2$-Λ-$Ru\}_2$-μ-CG[0]$]^{4+}$	279 (−197)	294 (485)	328 (−1)		420 (11)	473 (66)
$[\{CG[m$-xyl]-Δ-$Ru\}_2$-μ-CG[0]$]^{4+}$	287 (212)	305 (−291)	335 (5)	351 (−6)	422 (10)	475 (−12)
$[\{(bpy)_2Ru\}_2$-μ-SCG[0]$]^{4+}$	280 (−5)	294 (56)	310 (−60)			
$[\{(bpy)_2$-Δ-$Ru\}_2$-μ-SCG[0]$]^{4+}$	281 (149)	296 (−320)	327 (−8)		422 (26)	476 (−37)
$[\{(bpy)_2$-Λ-$Ru\}_2$-μ-SCG[0]$]^{4+}$	281 (−174)	296 (369)	310 (sh)		363 (−7)	407 (40)
$[\{CG[m$-xyl]-Δ-$Ru\}_2$-μ-SCG[0]$]^{4+}$	288 (271)	307 (−415)	337 (12)	354 (−1)	429 (22)	485 (−15)
$[\{(bpy)_2Ru\}_3$-μ-CG[bpy]$]^{6+}$	280 (1)	294 (58)	309 (−31)			
$[\{(bpy)_2$-Δ-$Ru\}_3$-μ-CG[bpy]$]^{6+}$	279 (301)	295 (−585)	327 (+31)		417 (58)	469 (−56)
$[\{(bpy)_2$-Λ-$Ru\}_3$-μ-CG[bpy]$]^{6+}$	279 (−356)	294 (657)	326 (−60)		419 (−69)	471 (43)
$[\{CG[m$-xyl]-Δ-$Ru\}_3$-μ-CG[bpy]$]^{6+}$	286 (384)	307 (−520)	335 (30)	352 (−17)	417 (33)	471 (−1)

conformation by nature of restricted rotation along the linkage. This confirms the NMR data indicating that a statistical distribution of the diastereomers is present.

With the complexes prepared from the chiral building block, Δ- or Λ-$[Ru(bpy)_2(py)_2]^{2+}$, strong signals were obtained in the CD spectra, where in the majority of cases the ΔΔ and ΛΛ diastereomers were almost exact mirror images of each other (Table 3 and Figure 7). Only the complexes of SCG[0] deviated significantly. It is assumed that the greater number of chiral centers on the ligand play a more important role with the additional bulky pinene moieties, which force two different average solution conformations for the ΔΔ and ΛΛ isomers, thus giving distinctively different patterns (Figure 7).

Complexes prepared from RuCG[*m*-xyl]Cl_2 all demonstrated strong signals in the CD spectra, as has been observed with previously described mononuclear species,[24] with the $\Delta\epsilon$ in proportion to the number of metal centers present in the complex (Figure 8).

Comparison of Building Blocks and Conclusions

The successful synthesis of two new members of the "Chiragen" ligand series, CG[3] and CG[bpy], illustrates the

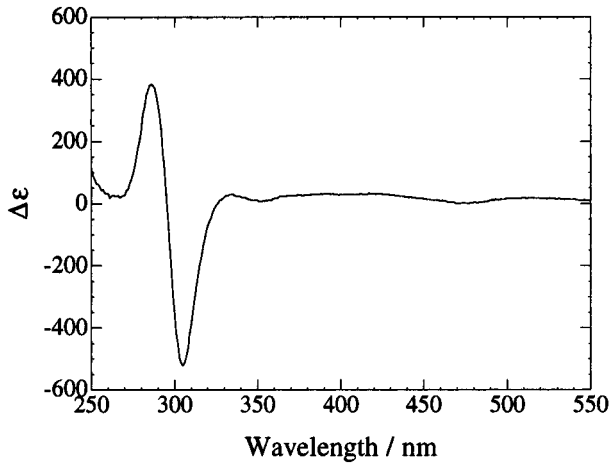


Figure 8. CD spectrum of ΔΔΔ-[{CG[*m*-xyl]-Δ-Ru}$_3$-μ-CG[bpy]]-$(PF_6)_6$.

great versatility of this stereospecific route to chiral bridging ligands. These can then be readily coordinated to ruthenium using $Ru(bpy)_2Cl_2$; however, this leads to a large number of diastereomers, which are clearly evident by ^{1}H-NMR spectroscopy. Using one of the enantiomerically pure precursors Δ- and Λ-$[Ru(bpy)_2(py)_2]^{2+}$, only one of the possible diastereomers is obtained, with high stereoisomeric purity in a known configuration. While in these examples all the isolated diastereomers exhibit the same electrochemical and photophysical behavior within the limits of experimentation, systems can be envisaged where the helicity of the metal center will play a greater role in the overall structure and relative distances between individual components in a supramolecular assembly. Additionally, the prepared individual diastereomers were not observed to photoracemize, despite being left in the daylight for a number of weeks. However, it must be stated that similar systems have been observed to undergo photoracemization.[36,37]

Using the building block RuCG[*m*-xyl]Cl_2, optically pure polynuclear complexes of a well-defined stereochemistry have been obtained. Due to the chiral nature of the tetradentate CG-[*m*-xyl] ligand, these complexes will not undergo the possible photoracemization alluded to above. Unfortunately, as a consequence of these same steric constraints, the photoemission is reduced, when compared to the analogous species previously described.

In conclusion, the results indicate that by the use of preprepared chiral starting materials, it is possible to design and build polynuclear transition metal complexes containing octahedral coordination sites with controlled stereochemistry, high optical purity, and a predetermined configuration. These methods are general and invaluable as the size of supramolecular assemblies expand.

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Supporting Information Available: Textual presentation of the ^{1}H-NMR data for all complexes described (6 pages). Ordering information is given on any current masthead page

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