Enantiomerically Pure Chiral $Ru^{II}(L\wedge L)_2$ Building Blocks for Coordination Compounds

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The synthesis of dinuclear complexes, where each metal center has a tris-bidentate coordination sphere, with defined stereochemistry is reported. Using Δ- and Λ-$[Ru(L\wedge L)_2(py)_2]^{2+}$ (L∧L = 2,2′-bipyridine and 1,10-phenanthroline) as enantiomerically pure chiral building blocks, the three possible isomers (ΔΔ, ΛΛ, and ΔΛ) of $[Ru(phen)_2-bpym-Ru(phen)_2]^{4+}$ and two diastereoisomers (ΔΔ and ΔΛ) of the dinuclear complex $[Ru(bpy)_2-4,6\text{-dppm}-Ru(bpy)_2]^{4+}$ were characterized by means of CD and NMR spectroscopy (bpym = 2,2′-bipyrimidine, 4,6-dppm = 4,6-di-2-pyridylpyrimidine). A study of substitution of the two pyridine ligands with (*R*,*R*)-1,2-diaminocyclohexane (*R*,*R*-dach) was carried out with the same enantiomerically pure chiral building blocks. It was found that substitution occurs under retention of configuration.

Introduction

Ruthenium tris(diimine) complexes, including mono- and polynuclear species have been among the most extensively studied and most widely used molecules in fundamental research in the fields of photochemistry, photophysics, photocatalysis, electrochemistry, photoelectrochemistry, chemi- and electrochemiluminescence, and electron and energy transfer during the past two decades.[1] Strong interest has also been developed in the areas of application of these luminescent complexes to sensor technologies,[2] as well as their use as probes[3] for DNA. Other applications comprise the development of instruments capable of measuring the time dependence of circular polarization in the light emitted by chiral molecules[4] and a method to study intra- and inter-protein electron transfer through covalently attached $[Ru(bpy)_3]^{2+}$.[5] The most common starting material for the complexes used in these applications is *cis*-$Ru(L\wedge L)_2Cl_2$ (L∧L = bpy and phen), which is chiral. Attempts to resolve these compounds into the enantiomers have not been successful so far.[6] Polynuclear and multifunctional species that are built from chiral units yield up to 2^N (where N is the number of chiral units involved) isomers, depending on the overall symmetry of the species, if racemic starting material is used. If artificial, self-assembling structures are envisaged with a large number of centers, the number of isomers may therefore soon become very large. This leads to a system that can be described as having *"fuzzy stereochemistry"*. The functions of such systems are necessarily not very well defined, and the possibilities to characterize them are severely limited.[7] Some efforts have been devoted to solving this isomer problem.[8] In a communication[9] we introduced the enantiomerically pure chiral building block Λ-$[Ru(phen)_2(py)_2]^{2+}$ in the preparation of dinuclear complexes with well-defined stereochemistry. It was found[9] that the two pyridine ligands in Δ- or Λ-$[Ru(phen)_2(py)_2]^{2+}$ can be substituted under certain conditions with retention of the configuration.

Given the high thermal stereochemical stability of these chiral building blocks, it is interesting to explore how general the method is in practice. Here we describe the synthesis of all three possible isomers (ΔΔ, ΛΛ, and ΔΛ) of the ruthenium dinuclear complexes $[Ru(phen)_2-bpym-Ru(phen)_2]^{4+}$ and the new, enantiomerically pure chiral building blocks Δ- and Λ-$[Ru(bpy)_2(py)_2]^{2+}$. The latter have been used to synthesize two diastereoisomers of a dinuclear complex, ΔΔ- and ΔΛ-$[Ru(bpy)_2-4,6\text{-dppm}-Ru(bpy)_2]^{4+}$, which are characterized by means of CD and NMR. (See Chart 1 for pertinent structures.)

Experimental Section

Materials and Instrumentation. All solvents (p.a.) were used without further purification. The bridging ligand 4,6-dppm was obtained in this laboratory, and the other ligands were obtained from commercial sources. *cis*-$[Ru(bpy)_2Cl_2]$,[10] *cis*-$[Ru(bpy)_2(py)_2]Cl_2$,[11] *cis*-$[Ru(phen)_2Cl_2]$,[10] and *cis*-$[Ru(phen)_2(py)_2]Cl_2$[11] were prepared according to literature methods. *cis*-$[Ru(phen)_2(py)_2]Cl_2$[11] was resolved by recrystallization of diastereomeric salts. All reactions involving chiral ruthenium complexes were carried out in the dark. UV/vis data were collected using a Perkin-Elmer Lambda 5 spectrophotometer [λ_{max}, nm (ϵ)]. CD spectra were measured on a Jobin Yvon auto dichrograph Mark V [λ_{max}, nm ($\Delta\epsilon$)]. Optical rotation values were obtained with a Perkin-Elmer MC 241 polarimeter using a 10 cm cell. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker AM-360 spectrometer (360.13 and 90.56 MHz, respectively) and a Varian Gemini-300 spectrometer (300.075 and 75.462 MHz, respectively). Chemical shifts

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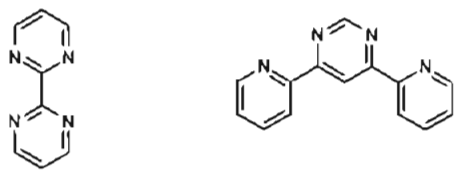
Chart 1



bpym 4,6-dppm

Λ,Λ-[Ru(phen)$_2$-bpym-Ru(phen)$_2$]$^{4+}$ Δ,Λ-[Ru(phen)$_2$-bpym-Ru(phen)$_2$]$^{4+}$

are given in ppm relative to internal TMS; coupling constants J are given in Hz. NOE's: observed signal (% enhancement {irradiation frequency, ppm}). MS data were obtained with a VG Instruments 7070E mass spectrometer equipped with a FAB inlet system (*m/z*). The elemental analyses were performed in the Research-Center Marly, CIBA AG.

Resolution of [Ru(bpy)$_2$(py)$_2$]$^{2+}$. A 45-mL aqueous solution of 0.5 M disodium (+)-*O,O'*-dibenzoyl-D-tartrate was added to a solution of *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (4.5 g) in 90 mL of water. The mixture was stirred for 10 min. In a dark room, the solvent was allowed to evaporate naturally. After 8−10 days, red crystals of Δ-[Ru(bpy)$_2$(py)$_2$][(+)-*O,O'*-dibenzoyl-D-tartrate]·12H$_2$O were formed and collected by filtration. This diastereoisomer was washed with cold water and air-dried; yield 2.2 g. Anal. Calcd for $C_{48}H_{60}N_6O_{20}Ru$: C, 50.38; H, 5.47; N, 7.35. Found: C, 50.30; H, 5.47; N, 7.25.

Syntheses. [Ru(bpy)$_2$(*R,R*-dach)](PF$_6$)$_2$. *rac,cis*-[Ru(bpy)$_2$(py)$_2$]-Cl$_2$ (100 mg) and (*R,R*)-1,2-diaminocyclohexane (*R,R*-dach) (50 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 4 h, cooled to room temperature, and diluted with 6 mL of H$_2$O. The resultant mixture was then filtered. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the filtrate until no more precipitate formed. The solid material was then collected by filtration, redissolved in acetonitrile, and reprecipitated by addition to diethyl ether. The compound was purified by recrystallization from acetonitrile/water; yield 85%. Anal. Calcd for $C_{20}H_{32}$-$F_{12}N_6P_2Ru$: C, 38.20; H, 3.70; N, 10.28. Found: C, 37.97; H, 3.63; N, 10.06.

Λ-[Ru(bpy)$_2$(*R,R*-dach)](PF$_6$)$_2$. Λ-[Ru(bpy)$_2$(py)$_2$][(−)-*O,O'*-dibenzoyl-L-tartrate]·12H$_2$O (150 mg) and *R,R*-dach (50 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 4 h, cooled to room temperature, and diluted with 6 mL of H$_2$O. The resultant mixture was then filtered. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the filtrate until no more precipitate formed. The solid material was then collected by filtration, redissolved in acetonitrile, and reprecipitated by addition to diethyl ether. The compound was purified by recrystallization from acetonitrile/water; yield 80%, *RR*/Λ > 98%. Anal. Calcd for $C_{20}H_{32}$-$F_{12}N_6P_2Ru$: C, 38.20; H, 3.70; N, 10.28. Found: C, 38.02; H, 3.69; N, 10.20. ^{1}H-NMR (300 MHz, acetonitrile-d_3, aromatic region): 9.10 (d, J = 5.4, 2H); 8.49 (d, J = 8.1, 2H); 8.32 (d, J = 8.1, 2H); 8.17 (ddd, J = 8.1, 7.6, 1.3, 2H); 7.82−7.76 (m, 4H); 7.61 (d, J = 5.7, 2H); 7.14 (ddd, J = 7.6, 5.4, 1.4, 2H).

Δ-[Ru(bpy)$_2$(*R,R*-dach)](PF$_6$)$_2$. The complex was prepared in the same way as the Λ form described above using the chiral building block Δ-[Ru(bpy)$_2$(py)$_2$][(+)-*O,O'*-dibenzoyl-D-tartrate]·12H$_2$O, *RR*/Δ > 98%. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 8.99 (d, J = 5.6, 2H); 8.47 (d, J = 8.2, 2H); 8.31 (d, J = 8.1, 2H); 8.17 (ddd, J = 8.2, 7.6, 1.4, 2H); 7.83−7.76 (m, 4H); 7.62 (d, J = 5.7, 2H); 7.16 (ddd, J = 7.6, 5.7, 1.4, 2H).

Δ-[Ru(bpy)$_2$(phen)](PF$_6$)$_2$. Δ-[Ru(bpy)$_2$(py)$_2$][(+)-*O,O'*-dibenzoyl-D-tartrate)·12H$_2$O (150 mg) and 1,10-phenanthroline (60 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 6 h, cooled to room temperature, and diluted with 6 mL of H$_2$O. The resultant mixture was then filtered. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the filtrate until no more precipitate formed. The solid material was then collected by filtration, redissolved in acetonitrile, and reprecipitated by addition to diethyl ether. The compound was purified by recrystallization from acetonitrile/water; yield 80%. Anal. Calcd for $C_{32}H_{24}$-$F_{12}N_6P_2Ru$: C, 43.50; H, 2.74; N, 9.51. Found: C, 43.31; H, 2.81; N, 9.35. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 8.60 (dd, J = 8.3, 1.3, 2H); 8.51 (dd, J = 8.0, 1.1, 2H); 8.47 (dd, J = 8.3, 1.3, 2H); 8.23 (s, 2H); 8.11−8.05 (m, 4H); 7.96 (ddd, J = 8.1, 7.6, 1.4, 2H); 7.83 (dd, J = 5.7, 1.4, 2H); 7.51 (ddd, J = 5.6, 1.4, 0.7, 2H); 7.43 (ddd, J = 7.7, 5.6, 1.4, 2H); 7.20 (ddd, J = 7.6, 5.7, 1.4, 2H). CD: 468 (-15.2); 416 (15.8); 291 (-209); 265 (81.9). $[\alpha]_D$ = −905° (3.81 mg/10 mL of acetonitrile).

[(Ru(bpy)$_2$)$_2$(4,6-dppm)](PF$_6$)$_4$·2H$_2$O. *rac,cis*-[Ru(bpy)$_2$Cl$_2$] (150 mg) and 4,6-dppm (34 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 6 h in the dark. The solution was cooled to room temperature and diluted with 6 mL of H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the solution until no more precipitate formed, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography (silica gel) using ethanol−H$_2$O (containing 10% NaCl) as an eluant. The deep red band was collected, and the complex was precipitated and dried; yield 70%. Anal. Calcd for $C_{54}H_{46}F_{24}N_{12}O_2P_4$-$Ru_2$: C, 38.68; H, 2.76; N, 10.02. Found: C, 38.60; H, 2.76; N, 9.94. UV/vis: 568 (sh) (14 000); 532 (18 300); 430 (24 000); 282 (106 000); 246 (41 000).

Δ,Δ-[(Ru(bpy)$_2$)$_2$(4,6-dppm)](PF$_6$)$_4$·2H$_2$O. Δ-*cis*-[Ru(bpy)$_2$(py)$_2$]-[(+)-*O,O'*-dibenzoyl-D-tartrate)]·12H$_2$O (200 mg) and 4,6-dppm (25 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 6 h in the dark, cooled to room temperature, and diluted with 6 mL of H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the solution until no more precipitate formed, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography (silica gel) using ethanol−H$_2$O (containing 10% NaCl) as an eluant. The deep red band was collected, and the complex was precipitated and dried; yield 60%, ΔΔ > 96%. Anal. Calcd for $C_{54}H_{46}F_{24}N_{12}O_2P_4Ru_2$: C, 38.68; H, 2.76; N, 10.02. Found: C, 38.95; H, 2.70; N, 9.87. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 9.34 (s, 1H); 9.02 (d, J = 8.1, 2H); 8.45−8.38 (m, 6H); 8.24−8.18 (m, 4H); 8.15 (ddd, J = 8.1, 7.6, 1.4, 2H); 8.07−8.00 (m, 4H); 7.89 (ddd, J = 8.2, 7.6, 1.5, 2H); 7.79 (d, J = 5.6 2H); 7.74 (dd, J = 5.6, 1.4, 2H); 7.58 (d, J = 0.9, 1H); 7.57−7.51 (m, 6H); 7.37 (ddd, J = 7.6, 5.6, 1.3, 2H); 7.22−7.12 (m, 8H). NOE's (360 MHz, acetonitrile): 9.02 (27% {9.34}); 8.21 (−4.0% {9.34}); 9.34 (12% {9.02}); 8.21 (13.7% {9.02}). UV/vis: 568 (sh) (16 130); 532 (18 900); 430 (237 000); 282 (109 000); 246 (41 400). CD: 587 (−8.52); 405 (23.1); 293 (−220); 275 (62.8).

***meso*-(Δ,Λ)-[(Ru(bpy)$_2$)$_2$(4,6-dppm)](PF$_6$)$_4$·2H$_2$O.** Δ-[Ru(bpy)$_2$-(py)$_2$][(+)-*O,O'*-dibenzoyl-D-tartrate)·12H$_2$O (100 mg) and 4,6-dppm (60 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 ° C for 4 h in the dark, cooled to room temperature, and diluted with 6 mL of H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the solution until no more precipitate formed, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography (silica gel) using ethanol−H$_2$O (containing 10% NaCl) as an eluant. The orange band was collected, and the monomeric complex Δ-[Ru(bpy)$_2$(4,6-dppm)](PF$_6$)$_2$ was precipitated and dried (yield 85%). Then, Δ-[Ru(bpy)$_2$(4,6-dppm)]-(PF$_6$)$_2$ (75 mg) and Λ-[Ru(bpy)$_2$(py)$_2$][(−)-*O,O'*-dibenzoyl-L-tartrate]·12H$_2$O (85 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for another 4 h in the dark, cooled to room temperature, and diluted with 6 mL of H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added dropwise to the solution until no more precipitate formed, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography (silica gel) using ethanol −

H_2O (containing 10% NaCl) as an eluant. The deep red band was collected, and the meso form of the dinuclear complex was precipitated and dried; yield 70%, $\Delta\Lambda$ > 96%. Anal. Calcd for $C_{54}H_{46}F_{24}N_{12}O_2P_4Ru_2$: C, 38.68; H, 2.76; N, 10.02. Found: C, 38.56; H, 2.79; N, 9.97. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 9.29 (d, J = 0.8, 1H); 9.00 (d, J = 7.9, 2H); 8.47 (d, J = 8.0, 2H); 8.46 (d, J = 8.1, 2H); 8.37 (d, J = 8.0, 2H); 8.29 (d, J = 8.1, 2H); 8.23−8.17 (m, 4H); 8.11 (ddd, J = 8.1, 7.6, 1.4, 2H); 8.06−7.98 (m, 4H); 7.91 (ddd, J = 8.1, 7.6, 1.4, 2H); 7.74 (dd, J = 5.6, 0.8, 2H); 7.63 (d, J = 0.8, 1H); 7.53−7.44 (m, 8H); 7.41 (dd, J = 5.6, 0.8, 2H); 7.31 (ddd, J = 7.6, 5.6, 1.3, 2H); 7.18 (ddd, J = 7.6, 5.6, 1.3, 2H); 7.05 (ddd, J = 7.6, 5.6, 1.3, 2H). NOE's (360 MHz, acetonitrile): 9.01 (33% {9.29}); 8.21 (-4.0% {9.29}); 8.21 (3% {7.63}); 7.47 (2.4% {7.63}). UV/vis: 568 (sh) (14 000); 532 (18 200); 430 (24 300); 282 (103 000); 246 (38 700).

[Ru(phen)$_2$(*R,R*-dach)](PF$_6$)$_2$·2H$_2$O. *rac,cis*-[Ru(phen)$_2$(py)$_2$]Cl$_2$ (100 mg) and *R,R*-dach (50 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 4 h, cooled to room temperature, and diluted with 6 mL of H_2O. The resultant mixture was then filtered. A saturated aqueous solution of NH_4PF_6 was added dropwise to the filtrate until no more precipitate formed. The solid material was then collected by filtration, redissolved in acetonitrile, and reprecipitated by addition to diethyl ether. The compound was purified by recrystallization from acetonitrile−water; yield 80%. Anal. Calcd for $C_{30}H_{34}F_{12}N_6OP_2Ru$: C, 40.68; H, 3.88; N, 9.49. Found: C, 40.98; H, 3.54; N, 9.42.

Λ-[Ru(phen)$_2$(*R,R*-dach)](PF$_6$)$_2$. Λ-[Ru(phen)$_2$(py)$_2$]Cl$_2$ (100 mg) and *R,R*-dach (50 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 4 h, cooled to room temperature, and diluted with 6 mL of H_2O. The resultant mixture was then filtered. A saturated aqueous solution of NH_4PF_6 was added dropwise to the filtrate until no more precipitate formed. The solid material was then collected by filtration, redissolved in acetonitrile, and reprecipitated by addition to diethyl ether. The compound was purified by recrystallization from acetonitrile−water; yield 80%, *RR*/Λ > 97%. Anal. Calcd for $C_{30}H_{32}F_{12}N_6P_2Ru$: C, 41.53; H, 3.72; N, 9.69. Found: C, 41.17; H, 3.52; N, 9.42. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 9.59 (dd, J = 5.3, 1.2, 2H); 8.76 (dd, J = 8.2, 1.2, 2H); 8.30 (dd, J = 8.2, 1.2, 2H); 8.25 (d, J = 8.9, 2H); 8.17 (dd, J = 8.2, 5.3, 2H); 8.12 (d, J = 8.9, 2H); 7.86 (dd, J = 5.3, 1.2, 2H); 7.35 (dd, J = 8.2, 5.3, 2H). UV/vis: 480 (12 100); 264 (76 100).

Δ-[Ru(phen)$_2$(*R,R*-dach)](PF$_6$)$_2$. The complex was prepared in the same way as the Λ form by using Δ-[Ru(phen)$_2$(py)$_2$]Cl$_2$; *RR*/Δ > 97%. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 9.50 (dd, J = 5.3, 1.2, 2H); 8.76 (dd, J = 8.2, 1.2, 2H); 8.30 (dd, J = 8.2, 1.2, 2H); 8.24 (d, J = 8.9, 2H); 8.17 (dd, J = 8.2, 5.3, 2H); 8.12 (d, J = 8.9, 2H); 7.88 (dd, J = 5.3, 1.2, 2H); 7.37 (dd, J = 8.2, 5.3, 2H).

Λ-[Ru(phen)$_2$bpy](ClO$_4$)$_2$·2H$_2$O. Λ-[Ru(phen)$_2$(py)$_2$]Cl$_2$ (100 mg) and 2,2′-bipyridine (60 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 6 h, cooled to room temperature, and diluted with 6 mL of H_2O. The resultant mixture was then filtered. Aqueous $NaClO_4$ was added dropwise to the filtrate until no more precipitate formed. The compound was purified by recrystallization from acetonitrile−water; yield 80%. Anal. Calcd for $C_{34}Cl_2H_{28}N_6O_{10}Ru$: C, 47.90; H, 3.31; N, 9.86. Found: C, 48.33; H, 3.11; N, 9.86. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 8.64 (dd, J = 8.2, 1.3, 2H); 8.54 (dd, J = 8.2, 1.3, 2H); 8.51 (d, J = 7.9, 2H); 8.25 (d, J = 8.9, 2H); 8.19 (dd, J = 5.3, 1.2, 2H); 8.02 (ddd, J = 7.9, 7.6, 1.4, 2H); 7.87 (dd, J = 5.3, 1.2, 2H); 7.78 (dd, J = 8.2, 5.3, 2H); 7.66 (ddd, J = 5.7, 1.4, 0.8, 2H); 7.55 (dd, J = 8.2, 5.3, 2H); 7.28 (ddd, J = 7.6, 5.7, 1.4, 2H). UV/vis: 445 (17 100); 262 (91 300). CD: 261 (−183.9); 269 (173.2); 288 (126.4); 419 (−13.7); 467 (15.0). $[\alpha]_D$ = +1080° (4 mg/10 mL of H_2O).

[(Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$·2H$_2$O. *rac,cis*-[Ru(phen)$_2$Cl$_2$] (90 mg) and bpym (11 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 6 h in the dark, cooled to room temperature, and diluted with 6 mL of H_2O. A saturated aqueous solution of NH_4PF_6 was added dropwise to the solution until no more precipitate formed, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography (silica gel) using ethanol−H_2O (containing 10% NaCl) as an eluant. The green band was collected, and the complex was precipitated and dried; yield 50%. Anal. Calcd for $C_{56}H_{42}F_{24}N_{12}O_2P_4Ru_2$: C, 39.62; H, 2.50; N, 9.90. Found: C, 39.77; H, 2.68; N, 9.77. UV/vis: 591 (9000), 406 (33 100), 260 (135 000).

Λ,Λ-[Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$·2H$_2$O. Λ-[Ru(phen)$_2$(py)$_2$]Cl$_2$ (100 mg) and bpym (11 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 6 h in the dark, cooled to room temperature, and diluted with 6 mL of H_2O. A saturated aqueous solution of NH_4PF_6 was added dropwise to the solution until no more precipitate formed, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography (silica gel) using ethanol−H_2O (containing 10% NaCl) as an eluant. The green band was collected, and the complex was precipitated and dried; yield 50%, ΛΛ > 95%. Anal. Calcd for $C_{56}H_{42}F_{24}N_{12}O_2P_4Ru_2$: C, 39.62; H, 2.50; N, 9.90. Found: C, 39.72; H, 2.70; N, 9.74. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 8.83 (dd, J = 8.3, 1.2, 4H); 8.60 (dd, J = 8.3, 1.2, 4H); 8.35 (d, J = 8.9, 4H); 8.28 (dd, J = 5.3, 1.2, 4H); 8.27 (d, J = 8.9, 4H); 7.97 (d, J = 5.7, 4H); 7.83 (dd, J = 5.3, 1.2, 4H); 7.80 (dd, J = 8.3, 5.3, 4H); 7.58 (dd, J = 8.3, 5.3, 4H); 7.21 (t, J = 5.7, 2H). NOE's (360 MHz, acetonitrile): 8.28 (3.5% {7.98}); 7.83 (2.1% {7.98}); 7.20 (12% {7.98}). ^{13}C-NMR (75.44 MHz, acetonitrile-d_3): 167.83, 160.46, 154.96, 154.19, 148.50, 148.32, 139.05, 138.79, 132.35, 132.16, 129.19, 129.13, 127.48, 127.09, 126.92. UV/vis: 591 (8800), 406 (33 200), 260 (135 000). CD: 589 (3.66); 548 (3.66); 432 (14.1); 397 (−12.9); 295 (93.8); 281 (90.4); 259 (−55.2); 248 (−77.3).

Δ,Δ-[(Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$·2H$_2$O. The complex was prepared in the same way as for the Λ form described above using the chiral building block Δ-[Ru(phen)$_2$(py)$_2$]Cl$_2$; ΔΔ > 95%. Anal. Calcd for $C_{56}H_{42}F_{24}N_{12}O_2P_4Ru_2$: C, 39.62; H, 2.50; N, 9.90. Found: C, 39.92; H, 2.65; N, 9.73. CD: 590 (−4.84); 548 (−4.49); 434 (−13.55); 397 (12.08); 295 (−108.3); 283 (−98.3); 258 (64.0); 250 (78.02).

***meso*-(Δ,Λ)[(Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$·2H$_2$O.** Λ-[Ru(phen)$_2$(py)$_2$]-Cl$_2$ (100 mg) and bpym (70 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for 4 h in the dark, cooled to room temperature, and diluted with 6 mL of H_2O. A saturated aqueous solution of NH_4PF_6 was added dropwise to the solution until no more precipitate formed, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography (silica gel) using ethanol−H_2O (containing 10% NaCl) as an eluant. The orange band was collected, and the monomeric Λ-[Ru(phen)$_2$(bpym)](PF$_6$)$_2$ was precipitated and dried (yield 85%). Then, Λ-[Ru(phen)$_2$(bpym)(PF$_6$)$_2$ (100 mg) and Δ-[Ru(phen)$_2$(py)$_2$]Cl$_2$ (76 mg) were added to 4 mL of ethylene glycol (10% water) in a 25-mL flask. The solution was heated to 120 °C for another 4 h in the dark, cooled to room temperature, and diluted with 6 mL of H_2O. A saturated aqueous solution of NH_4PF_6 was added dropwise to the solution until no more precipitate formed, and the mixture was filtered. The precipitated complex was dried, dissolved in a small amount of acetonitrile, and purified by chromatography (silica gel) using ethanol−H_2O (containing 10% NaCl) as an eluant. The green band was collected, and the meso form of the dinuclear complex was precipitated and dried; yield 60%, ΔΛ > 96%. Anal. Calcd for $C_{56}H_{42}F_{24}N_{12}O_2P_4Ru_2$: C, 39.62; H, 2.50; N, 9.90. Found: C, 39.36; H, 2.60; N, 9.68. ^{1}H-NMR (300 MHz, acetonitrile-d_3): 8.74 (dd, J = 8.3, 1.2, 4H); 8.67 (dd, J = 5.2, 1.2, 4H); 8.59 (dd, J = 8.3, 1.2, 4H); 8.25 (d, J = 8.9, 4H); 8.22 (d, J = 8.9, 4H); 8.06 (dd, J = 8.3, 5.2, 4H); 7.91 (m, 8H); 7.62 (dd, J = 8.3, 5.2, 4H); 7.19 (t, J = 5.7, 2H). ^{13}C-NMR (75.44 MHz, acetonitrile-d_3): 168.04, 160.16, 155.22, 154.17, 148.34, 148.30, 138.85, 138.77, 132.18, 132.12, 129.17, 129.05, 127.43, 127.12, 127.06. UV/vis: 591 (8900), 406 (33 500), 259 (136 000).

Results and Discussion

Chiral Building Blocks. The determination of optical purity of the chiral building blocks is of basic importance. The retention or partial loss of optical purity in the course of a reaction can often give valuable information, provided the optical purities of the starting material and the product are known. Accurate knowledge of the optical purity is especially important in the area of polynuclear metal complex synthesis. Due to the multiplication effect, a relatively small amount of

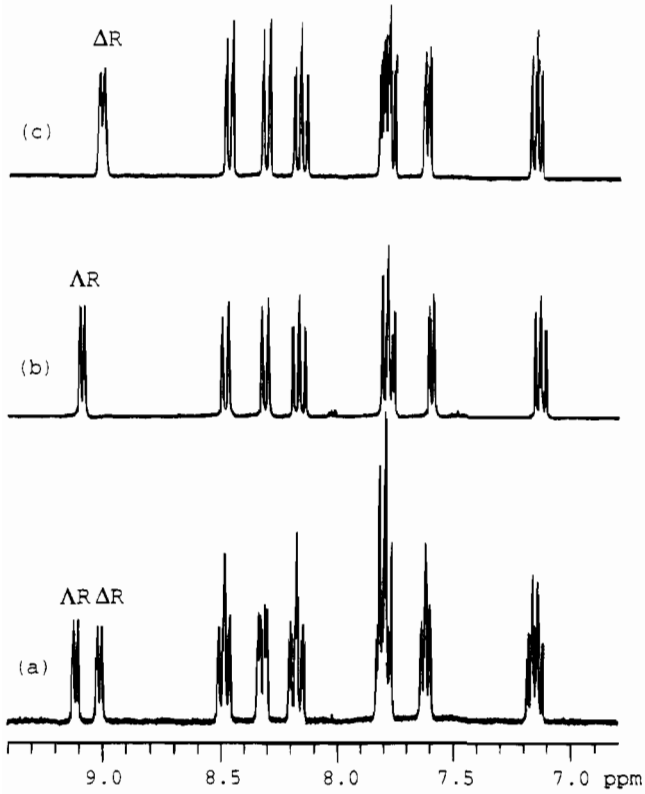


Figure 1. ^{1}H-NMR spectra (300 MHz) of (a) *rac*-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$, (b) Λ-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$, and (c) Δ-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$ in acetonitrile-d_3.

the other enantiomer already yields isomerically mixed products, even if the reactions proceed with retention of configuration. E.g., in the case of a dinuclear species, an 80%/20% mixture of a chiral building block leads to 64% of one enantiomer, 4% of the other enantiomer, and 32% meso form.

Substitution of pyridine ligands by various anions in Δ- or Λ-[Ru(phen)$_2$(py)$_2$]$^{2+}$ was studied before by Dwyer et al.[11] These authors found retention if only one pyridine was substituted and complete loss of optical activity upon substitution of both pyridine ligands. Since we were interested in the use of these complexes as chiral building blocks, where the two pyridine ligands in general are replaced by bidentate ligands, we investigated this substitution reaction in some detail. At first, the replacement of the two pyridine ligands with an optically active bidentate ligand (*R,R*-dach) was studied.

A lower limit of the optical purity of the building blocks was determined by forming two diastereoisomers of Λ-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$ and Δ-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$ through a substitution reaction. The two diastereoisomers give different ^{1}H-NMR chemical shifts. Spectrum a in Figure 1 shows the proton NMR (aromatic region) of [Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$ prepared from racemic *cis*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$, clearly giving the signals of two diastereoisomers in a 1:1 molar ratio. Since each diastereoisomer possesses a C_2 axis, the corresponding bpy protons in the complex are equivalent, giving a total of only eight nonequivalent protons. Spectrum b in Figure 1 shows the NMR of Λ-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$ prepared from Λ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$, and spectrum c shows that of Δ-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$ prepared from Δ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$, clearly indicating the purity of the optically active chiral building blocks. Similar results were obtained for Δ- and Λ-[Ru(phen)$_2$(py)$_2$]$^{2+}$.[12] This method yields *a lower limit* for the value of the optical purity. It cannot, however, at this point be decided whether the reaction proceeds with retention or inversion of configuration.

(12) Hua, X. Ph.D. Dissertation, University of Fribourg, Switzerland, 1993.

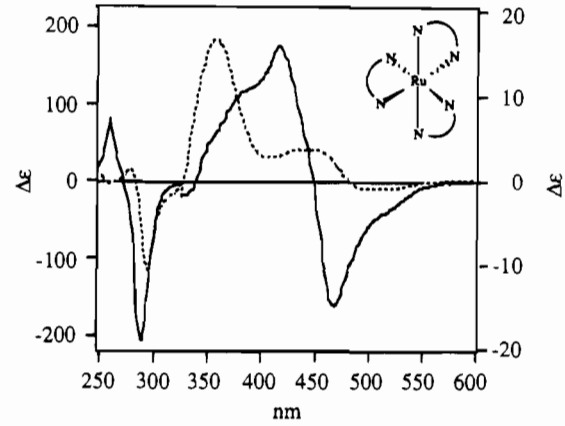


Figure 2. CD spectra: acetonitrile solution of (−)-*cis*-[Ru(bpy)$_2$(phen)]$^{2+}$ (solid line) prepared from (−)-Δ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (dotted line) which has the absolute configuration shown in the inset.

Assignment of the absolute configuration of the chiral building blocks and of the corresponding substituted products can be made by applying exciton theory;[13] i.e., in the regions of the long-axis-polarized transitions of the ligands bpy and phen, the circular dichroism will appear strongly positive at lower energies and strongly negative at higher energies if the molecule has the absolute configuration related to (−)-[Fe(phen)$_3$]$^{2+}$ (Λ form). In order to avoid complications, due to the presence of an inherently chiral ligand (*R,R*-dach), the substitution of pyridine by phen was also studied. From the CD spectrum (Figure 2), it can be seen that Δ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ and (−)-[Ru(bpy)$_2$(phen)]$^{2+}$, obtained from the former by the substitution reaction, show the same spectral pattern; i.e., under the long-axis-polarized band around 290 nm the circular dichroism is at low energies strongly negative and at higher energies positive. Therefore it is concluded that the substitution of the two pyridine ligands proceeds with retention of configuration.

The extension to the substitution of both pyridine ligands with the neutral monodentate ligands 4-methylpyridine and imidazole,[12] respectively, also shows retention of configuration.

Ruthenium Dinuclear Complexes. ^{1}H-NMR spectra of [Ru(phen)$_2$−bpym−Ru(phen)$_2$]$^{4+}$ prepared from racemic Ru(phen)$_2$Cl$_2$ and from chiral Λ-[Ru(phen)$_2$(py)$_2$]$^{2+}$ building blocks are shown in Figure 3a,b. It is clear from the spectra that, using a racemic building block, two diastereoisomers (ΔΔ/ΛΛ and ΔΛ) are obtained. The relative abundance of the meso form and of the enantiomeric pair in the dinuclear complex is ca. 60:40 (meso:enantiomer pair), not far from the 50:50 statistical value. Molecular modeling has indicated no significant energy preference for either diastereoisomer. The use of a chiral building block almost entirely avoids the formation of the different isomers. In a one-step reaction (below) homochiral ΔΔ or ΛΛ dinuclear complexes can be obtained. The preparation of the pure meso (Δ,Λ) form of [Ru(phen)$_2$−bpym−Ru(phen)$_2$]$^{4+}$ (see NMR spectrum in Figure 3c) requires a two-step reaction:

$$[\Lambda\text{-Ru(phen)}_2\text{(py)}_2]^{2+} + \text{bpym} \rightarrow [\Lambda\text{-Ru(phen)}_2\text{(bpym)}]^{2+}$$

$$[\Delta\text{-Ru(phen)}_2\text{(py)}_2]^{2+} + [\Lambda\text{-Ru(phen)}_2\text{(bpym)}]^{2+} \rightarrow [\Lambda\text{-Ru(phen)}_2\text{−bpym−}\Delta\text{-Ru(phen)}_2]^{4+}$$

The CD spectra (Figure 4) of the two enantiomers of the dinuclear complexes prepared from Δ and Λ chiral building

(13) Bosnich, B. *Inorg. Chem.* **1968**, *7*, 178. Bosnich, B. *Inorg. Chem.* **1968**, *7*, 2379.

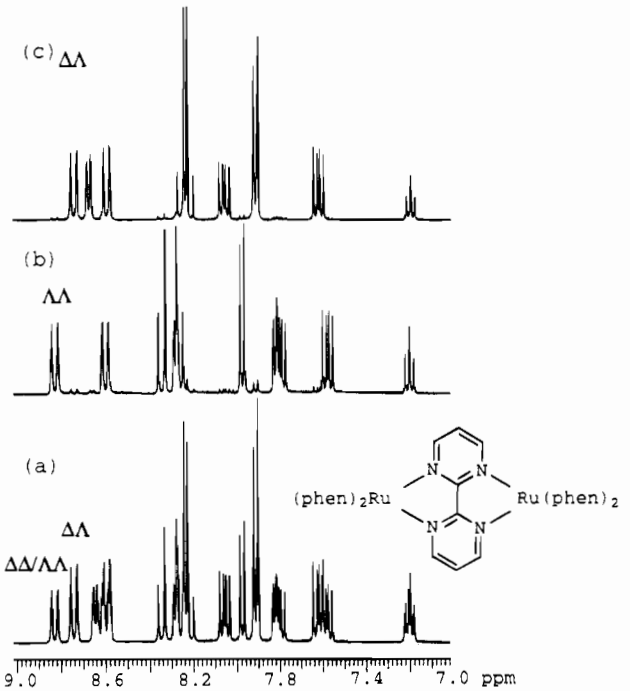


Figure 3. ^{1}H-NMR spectra of (a) [(Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$ prepared from *rac*-Ru(phen)$_2$Cl$_2$, (b) Λ,Λ-[(Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$, and (c) Δ,Λ−[(Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$ (300 MHz in acetonitrile-d_3).

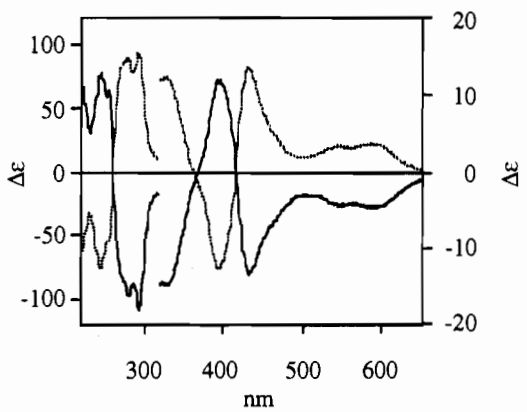


Figure 4. CD spectra: acetonitrile solutions of Δ,Δ-[(Ru(phen)$_2$)$_2$-bpym]$^{4+}$ (solid line) prepared from (−)-Δ-[Ru(phen)$_2$(py)$_2$]$^{2+}$ and of Λ,Λ-[(Ru(phen)^2)$_2$bpym]$^{4+}$ prepared from (+)-Λ-[Ru(phen)$_2$(py)$_2$]$^{2+}$ (dotted line).

blocks, respectively, clearly indicate Cotton effects of opposite signs, with absolute configurations corresponding to those of the building blocks, corroborating therewith the retention of configuration for substitution of the pyridine ligands. Also, it must be stressed that no equilibrium between ΔΔ or ΛΛ and ΔΛ forms has been observed in solution at room temperature, even for years. Furthermore, the results of ^{13}C-NMR studies[12] of the dinuclear complex are in complete agreement with those from ^{1}H-NMR.

Similar NMR results (Figure 5) were obtained for dinuclear complexes Δ,Δ- and Δ,Λ-[Ru(bpy)$_2$−4,6-dppm−Ru(bpy)$_2$]$^{4+}$ prepared from Λ- and Δ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$, respectively.

Detailed characterizations of dinuclear complexes of the type [Ru(L∧L)$_2$−BL−Ru(L∧L)$_2$]$^{4+}$ by NMR are given below:

[Ru(phen)$_2$−bpym−Ru(phen)$_2$]$^{4+}$. The D_2 symmetry of Λ,Λ-[Ru(phen)$_2$−bpym−Ru(phen)$_2$]$^{4+}$ requires the equivalence of the four phenanthroline ligands. Since each ligand is no longer symmetric, an AMX, AB, A′M′X′ spectrum results. In addition, the bridging ligand bpym should give an AX$_2$ pattern in the spectrum. A total of 10 magnetically nonequivalent

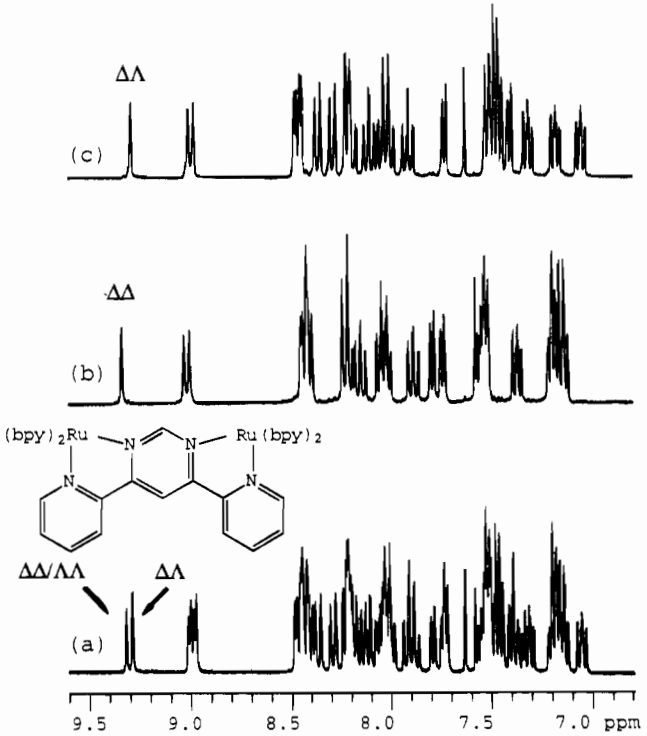


Figure 5. ^{1}H-NMR spectra of (a) [(Ru(bpy)$_2$)$_2$-4,6-dppm](PF$_6$)$_4$ prepared from *rac*-Ru(bpy)$_2$Cl$_2$, (b) Δ,Δ-[(Ru(bpy)$_2$)$_2$-4,6-dppm](PF$_6$)$_4$, and (c) Δ,Λ-[(Ru(bpy)$_2$)$_2$-4,6-dppm](PF$_6$)$_4$ (300 MHz in acetonitrile-d_3).

protons is therefore expected. Indeed, from the ^{1}H-COSY spectrum, combined with the coupling constant values $J_{23} = J_{89} = 5.2$ Hz, $J_{24} = J_{79} = 1.2$ Hz, $J_{34} = J_{78} = 8.3$ Hz, and $J_{56} = 9.0$ Hz, the AMX portion (protons 2−4) is distinguished from the A′M′X′ portion (protons 7−9). These two sets of protons are then identified by the relative degree of the diamagnetic anisotropy effects from the aromatic rings of the adjacent ligands. From Figure 6, it can be seen that proton H(2) lies above the bridging ligand bpym ring, while proton H(9) lies in the shielding cone of the adjacent phen rings. The diamagnetic anisotropic interactions between H(9) and phen are expected to be more pronounced than that between H(2) and the bpym ring on the basis of two arguments: (1) phen contains three aromatic rings, whereas bpym contains only two. (2) Two ruthenium centers, binding to bpym, cause a strong decrease of electron density in the bridging ligand. Therefore, proton H(2) is assigned to the downfield peak at 8.28 ppm. Protons H(a) and H(b) can easily be recognized by the coupling constant $J_{ab} = 5.7$ Hz on the basis of a typical AX$_2$ pattern. It is impossible to distinguish protons H(5) and H(6).

The very similar ^{1}H-NMR spectrum of *meso*-[Ru(phen)$_2$−bpym−Ru(phen)$_2$]$^{4+}$ (with symmetry C_s, but requiring the equivalence of the four phen ligands as well) also gives 10 different protons where eight are contributed from phen and two from bridging bpym. One set of three protons [defined as H(2), H(3), and H(4)] are associated with the rings *trans* to another phen ring of the same metal center; the other set of three protons [defined as H(7), H(8), and H(9)] are associated with the phen rings *trans* to the bridging bpym (see Figure 7). By use of the same arguments as described above for interpreting the ΛΛ form, the spectrum of the meso form of the complex can also be fully interpreted. Furthermore, the relatively large change in the chemical shifts of proton H(2) of the meso form of the complex compared to that of the ΛΛ form of the complex is consistent with this first assignment, because only the rings with H(2), H(3), and H(4) (for both ΛΛ and ΔΛ) interact with

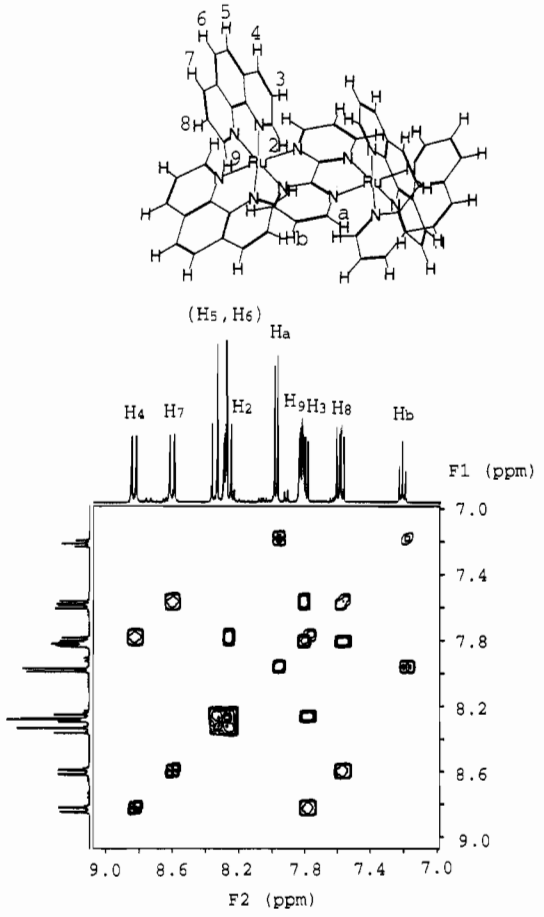


Figure 6. COSY ^{1}H-NMR spectrum of Λ,Λ-[(Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$ (300 MHz in acetonitrile-d_3).

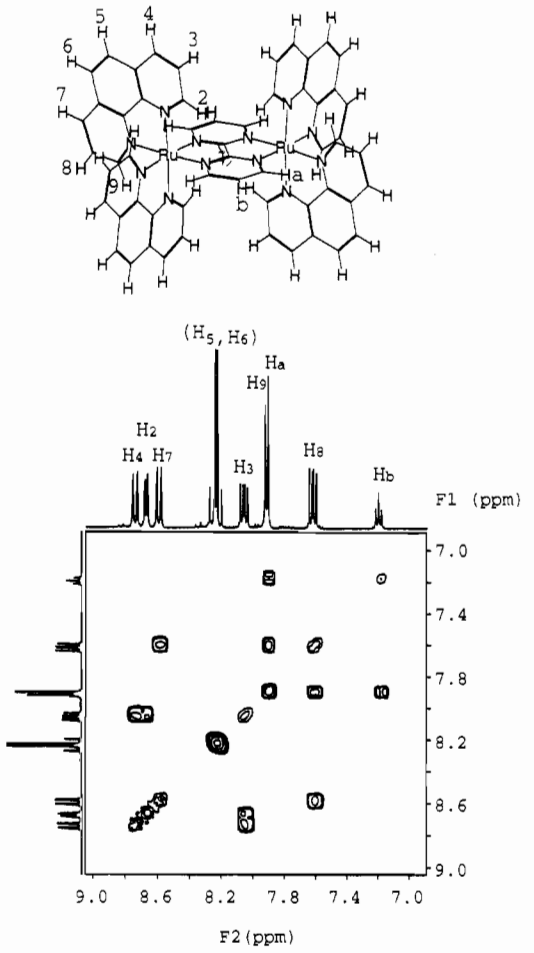


Figure 7. COSY ^{1}H-NMR spectrum of Δ,Λ-[(Ru(phen)$_2$)$_2$bpym](PF$_6$)$_4$ (300 MHz in acetonitrile-d_3).

each other in the dinuclear complex, while the rings with H(7), H(8), and H(9) are far away from each other.

The ^{13}C-NMR spectra of [Ru(phen)$_2$-bpym−Ru(phen)$_2$]$^{4+}$ are interpreted by comparing their chemical shifts with those of [Ru(phen)$_3$]$^{2+}$ and with those of the free ligands.[14] Signals assigned to specific carbon atoms are further confirmed by using 2D-HETCOR techniques.[12] The $\Lambda\Lambda$ or $\Delta\Delta$ and the meso forms of the complex each give 15 lines (12 lines from ligand phen and 3 lines from bpym). These results further support the results from molecular modeling; i.e., the D_2 symmetry of Λ,Λ-[-Ru(phen)$_2$−bpym−Ru(phen)$_2$]$^{4+}$ and C_s symmetry of Δ,Λ-[Ru(phen)$_2$−bpym−Ru(phen)$_2$]$^{4+}$ both require the equivalence of the four phen ligands. Each ligand is no longer symmetric, however. Chemical shift differences between the homochiral pair and the meso form of the complex with the analogous carbons are very small. They appear twinlike in the spectrum of the complex prepared from the racemic building blocks, and an assignment can only be obtained after isolation of the pure isomers.

[Ru(bpy)$_2$-4,6-dppm-Ru(bpy)$_2$]$^{4+}$. ^{1}H-NMR spectra of two diastereoisomers ($\Delta\Delta$ and $\Delta\Lambda$) of the dinuclear complex are illustrated in Figure 8. They are less easy to interpret than those of the phen analogs since they contain five sets of four coupled protons (with almost the same coupling constant for each pair), which are in very similar magnetic environments. For the $\Delta\Delta$ form of the complex (Figure 8), proton H(5) of the bridging ligand is assigned to the downfield signal with the highest ppm value 9.34 because of a strong deshielding interaction; H(2) can be found from the ^{1}H-COSY spectrum (Figure 8), which is upfield due to a strong shielding interaction. A large NOE effect of the doublet at 9.02 ppm during irradiation of the singlet H(5), combined with a coupling constant of $J_{3'4'} = 8.1$ Hz, unambiguously establishes this resonance to be due to H(3′) of the bridging ligand. The assignment of H(4′), H(5′), and H(6′) of this ligand follows from the ^{1}H-COSY spectrum. This leaves 16 signals identifiable with the bpy protons: one set of four protons [defined as H(3a), H(4a), H(5a), and H(6a)] associated with the rings *trans* to the bridging ligand 4,6-dppm and face to face with another pyridine ring from the other metal center, one set of four protons [defined as H(3a′), H(4a′), H(5a′), and H(6a′)] associated with the rings *trans* to a bpy, one set of four protons [defined as H(3b), H(4b), H(5b), and H(6b)] associated with the rings *trans* to a bpy and above the pyridine ring from another metal center, and one set of four protons [defined as H(3b′), H(4b′), H(5b′), and H(6b′)] associated with the rings *trans* to the bridging ligand 4,6-dppm. It is expected that both sets of H(4a), H(5a), H(6a) and H(4b), H(5b), H(6b) are in strong shielding regions, but H(4a) should be more upfield than H(4b) due to a much larger diamagnetic anisotropic interaction between the two rings (from two metal centers). Therefore, the triplet at 7.89 ppm is assigned to H(4a), while the triplet at 8.04 ppm is assigned to H(4b) with the help of the ^{1}H-COSY spectrum and the use of coupling constants. Then, H(3a), H(5a), H(6a) and H(3b), H(5b), and H(6b) can be easily "seen" from the ^{1}H-COSY spectrum, as indicated in the spectrum. The remaining set of four coupled protons H(3a′), H(4a′), H(5a′), H(6a′) and the other set of four coupled protons H(3b′), H(4b′), H(5b′), H(6b′) are identified by their relative degree of the diamagnetic anisotropy effects from the aromatic rings of the adjacent ligands; H(5b′) and H(6b′) lie above

(14) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G. *Org. Magn. Reson.* **1984**, *22*, 388.

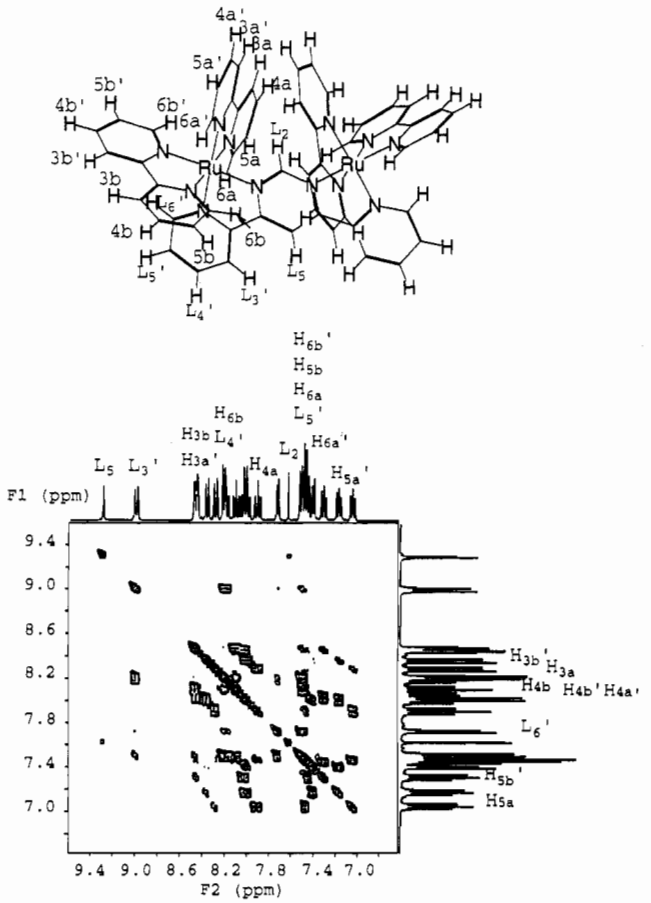


Figure 8. COSY ^{1}H-NMR spectrum of Δ,Δ-[(Ru(bpy)$_2$)$_2$-4,6-dppm](PF$_6$)$_4$ (300 MHz in acetonitrile-d_3).

pyridine rings of the adjacent ligands while H(5a′) and H(6a′) lie above aromatic rings of the bridging ligand, with less electron charge density due to the second metal bound to this ligand. Therefore, chemical shifts of protons H(5b′) and H(6b′) should be at higher fields than those of H(5a′) and H(6a′), as assigned in the spectrum.

Using the same technique, five sets of four coupled protons along with two coupled "singlet" protons from the bridging ligand 4,6-dppm (a total of 22 magnetically different protons) were observed and interpreted for the meso form of the dinuclear complex (Figure 9).

Concluding Remarks

CD and NMR experiments reveal that the *two* pyridine ligands in Δ- or Λ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ and Δ- or Λ-[Ru(phen)$_2$(py)$_2$]$^{2+}$, respectively, can be substituted with retention of the absolute configuration under certain circumstances. The successful synthesis of all possible isomers of dinuclear complexes proved that Δ- or Λ-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ and Δ- or Λ-[Ru(phen)$_2$(py)$_2$]$^{2+}$, respectively, can serve as enantiomerically pure chiral building blocks in the preparation of diverse oligomeric complexes containing Ru(L∧L)$_2$ moieties with defined stereochemistry. In principle, the results could be applied to the exploration of other chiral ruthenium building blocks having similar ligands for various purposes in the design of highly ordered systems.

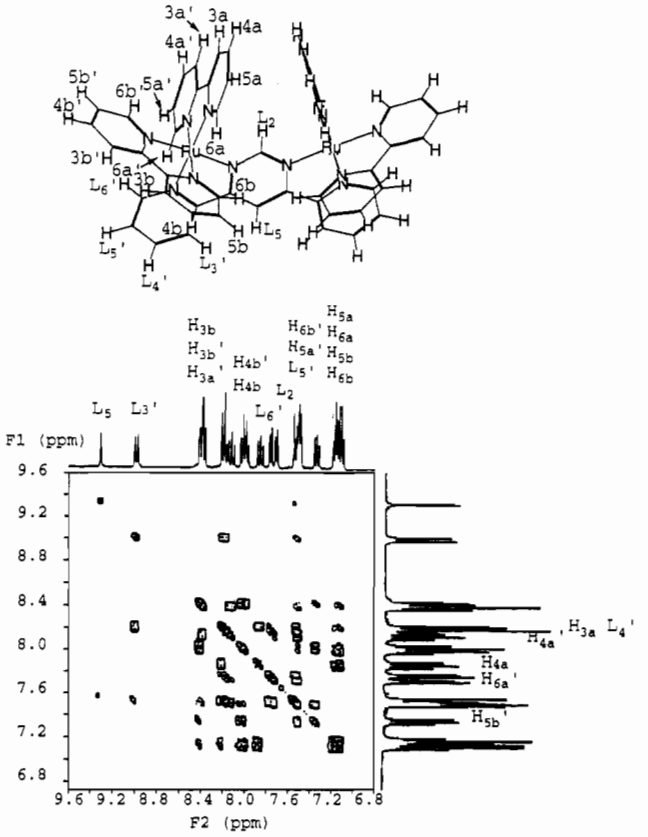


Figure 9. COSY ^{1}H-NMR spectrum of Δ,Λ-[(Ru(bpy)$_2$)$_2$-4,6-dppm](PF$_6$)$_4$ (300 MHz in acetonitrile-d_3).

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