Efficient Asymmetric Synthesis of Δ- and Λ-Enantiomers of (Bipyridyl)ruthenium Complexes and Crystallographic Analysis of Δ-Bis(2,2′-bipyridine)(2,2′-bipyridine-4,4′-dicarboxylato)ruthenium: Diastereoselective Homo- and Heterochiral Ion Pairing Revisited

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Keywords: Ruthenium / Chiral resolution / Circular dichroism

Optically pure ruthenium complexes of the type Δ- or Λ-[Ru(bpy)$_2$(L–L)][PF$_6$]$_2$ [L–L = cmbpy = 4′-methyl-2,2′-bipyridine-4-carboxylic acid (**3a**, **b**); L–L = dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid (**4a**, **b**)] were prepared and fully characterized. The Ru^{II} carboxylate complexes Δ- and Λ-[Ru(bpy)$_2$(dcabpy)] (**5a**, **b**) (dcabpy = 2,2′-bipyridine-4,4′-dicarboxylate) were resolved efficiently by chiral column chromatography and isolated in good yields. The Δ-[Ru(bpy)$_2$(dcabpy)] (**5a**) enantiomer was crystallized and its X-ray molecular structure determined. The enantiomeric nature and the absolute configuration of the tris(bipyridyl)ruthenium complexes were confirmed by NMR and circular dichroism studies. In addition, ion-pairing interactions between Δ-Trisphat (Δ-**1**, D_3 symmetry) and each enantiomer of the (monocarboxylic acid)Ru^{II} complex (**3a** and **3b**, C_1 symmetry) and the dicarboxylic acid complex (**4a** and **4b**, C_2 symmetry) were examined by NMR spectroscopy.

Introduction

Octahedral hexacoordinated ruthenium(II) complexes bearing 2,2′-bipyridine ligands (bpy) have received considerable attention because of their potential use as chiral building blocks for supramolecular assemblies,[1] or as chiral probes for biological molecules (polynucleotides, DNA).[2] In addition, they exhibit photoluminescence and electroluminescence properties, making them promising light-emitting devices.[3] More recently, efforts have been devoted to the study of the stereochemistry of these complexes as a result of the different interactions that may arise when enantiomeric forms (Δ or Λ) interact with a variety of substrates.[4,5a,5b]

We, and others, have been working in the area of stereoselective synthesis of tris(bpy)metal complexes with D_3 symmetry.[5] The determination of their enantiomeric purity by ^{1}H NMR spectroscopy has become an easy and routine task in the presence of the Trisphat anion (**1**) [Trisphat = tris(tetrachlorobenzenediolato)phosphate(v)],[6] which acts as a chiral shift reagent.[7] Further investigations carried out by Lacour have also shown that homochiral association (Δ,Δ) or (Λ,Λ) is favored over heterochiral association (Δ,Λ) in a solvent of low polarity and proceeds with high selectivity.[8] More recently Le Bozec, Lacour, and co-workers also found that homochiral ion-pairing is also favored for the tris(DEAS-bpy)ruthenium complex {DEAS-bpy = 4,4′-bis(diethylaminostyryl)-[2,2′]-bipyridine}.[9] Very recently, Kol and co-workers reported that octahedral mono(eilatin)ruthenium complexes form discrete dimers held by π-stacking interactions in both the solid state and in solution. In contrast to the results outlined above, heterochiral association (Δ,Λ) was found to be strongly favored.[10]

In order to investigate this ion-pairing phenomenon, we decided to prepare the optically pure dicationic (bipyridyl)-Ru^{II} complexes Δ- and Λ-[Ru(bpy)$_2$(cmbpy)][PF$_6$]$_2$ (**3a**, **b**; cmbpy = 4′-methyl-2,2′-bipyridine-4-carboxylic acid) and Δ- and Λ-[Ru(bpy)$_2$(dcbpy)][PF$_6$]$_2$ (**4a**, **b**; dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid), with C_1 and C_2 symmetries, respectively. We anticipated that association of our model complexes with the Δ-Trisphat anion of D_3 symmetry should be the ideal probe to discriminate between homochiral and heterochiral ion-pairing association.

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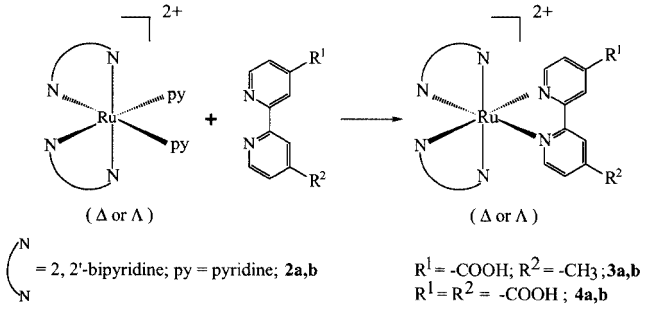
In this paper we report the synthesis and complete characterization of **3a**, **3b**, **4a**, and **4b**. We also report the X-ray crystal structure of the optically pure Ru^{II} dicarboxylate complex Δ-[Ru(bpy)$_2$(dcabpy)] (**5a**; dcabpy = 2,2′-bipyridine-4,4′-dicarboxylate). The solution behavior and NMR studies of these resolved complexes in the presence of Δ-Trisphat are presented and discussed.

Results and Discussion

Synthesis of the (Bipyridyl)ruthenium Complexes 3a, b and 4a, b

The optically pure ruthenium complexes **3a** and **3b** were prepared in a single step by treatment of the resolved ruthenium complexes Δ- and Λ-[Ru(bpy)$_2$py$_2$][dibenzoyltartrate-*O*,*O*′] (**2a**, **b**)[11] with the appropriate chelating ligands in ethylene glycol/H_2O for several hours (Scheme 1). These compounds were obtained as red microcrystalline solids in good yields and were fully characterized (the synthesis of racemic **3** has been reported previously[2f]). The absolute configurations of **3a** and **3b** (Δ and Λ, respectively) were assigned by circular dichroism (see Figure 2).



Scheme 1. Preparation of ruthenium complexes **3a**, **3b**, **4a**, and **4b**

The dicarboxylic acid complexes **4a** and **4b** were obtained by two different methods. The first involves direct treatment of **2a** and **2b** with the dcabpy ligand following the synthetic procedure described above. However, several weeks were required to obtain resolved crystals of either **2a** or **2b**. A more convenient method was thus used, involving the preparation of racemic [Ru(bpy)$_2$(dcbpy)][Cl]$_2$ by treatment of Ru(bpy)$_2$Cl$_2$ with dcabpy in a refluxing 1:1 water/methanol mixture.[2g] [Ru(bpy)$_2$(dcbpy)][Cl$_6$]$_2$ was easily resolved using HPLC chromatography,[12] affording initially the related carboxylate derivatives **5a** and **5b** in almost quantitative yields (see Exp. Sect.), which on subsequent protonation and workup gave optically pure **4a** and **4b** (vide infra).

The IR spectra of **5a** and **5b** recorded as KBr disks supported the formation of the Ru^{II} carboxylate species with ν(CO) = 1617 cm^{-1}, and the structure of **5a** was confirmed by X-ray structural analysis.

X-ray Structure of Δ-[Ru(bpy)$_2$(dcabpy)] (5a)

Suitable crystals of **5a** were obtained by slow concentration of a saturated acetonitrile solution. Complex **5a** crystallizes in the chiral C_2 space group. Crystallographic data for **5a** are given in Table 2 (Exp. Sect.) and selected bond lengths and angles are given in Table 1. The structure shows a hexacoordinated Ru^{II} center complexed by one dcabpy and two bpy ligands, and confirms that the functionalized bipyridine ligand has two deprotonated carboxylate groups at the 4 and 4′ positions.

Table 1. Selected interatomic distances [Å] and angles [°] for **5a** (* denotes dihedral angles)

Ru(1)−N(1)	2.072(7)
Ru(1)−N(1′)	2.046(7)
Ru(1)−N(2)	2.067(8)
Ru(1)−N(2′)	2.078(7)
Ru(1)−N(3)	2.060(7)
Ru(1)−N(3′)	2.045(8)
C(7)−O(1)	1.21(1)
C(7)−O(2)	1.25(1)
C(7′)−O(1′)	1.25(1)
C(7′)−O(2′)	1.23(1)
O(1)−C(7)−O(2)	124.7(10)
O(1′)−C(7′)−O(2′)	126.6(8)
(pyridyl ring)−[O(1)−C(7)−O(2)]*	17.2
(pyridyl ring)−[O(1′)−C(7′)−O(2′)]*	14.4

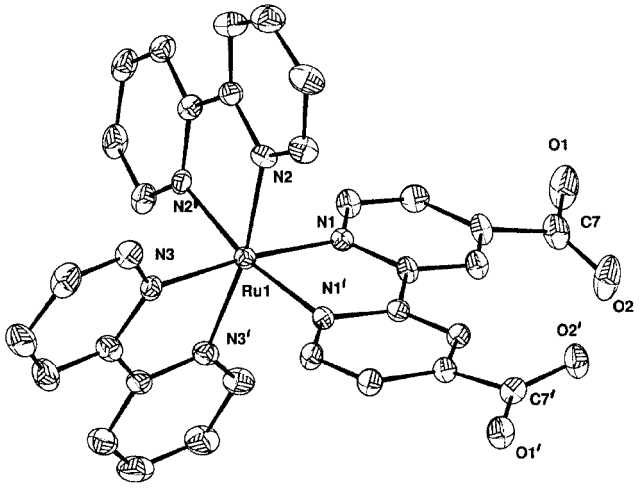


Figure 1. Molecular structure of **5a** with the atom numbering system; hydrogen atoms have been omitted for clarity

Figure 1 shows that the two carboxylate groups of the dcabpy ligand are coplanar with the substituted aromatic rings, suggesting an electronic delocalization throughout the conjugated π-systems. Although there has been a number of structural determinations of tris(bidentate ligand)ruthenium(II) complexes containing polypyridyl ligands,[13−15] the majority of these have involved racemic samples, and only a few structures confirming the absolute configuration of such complexes have been reported. Therefore our example is of interest, especially because several groups are currently interested in the polymetallic assembly involving optically pure ruthenium complexes as individual components.[1c] The absolute configurations of Δ and Λ for **5a** and **5b**, respectively, were also assigned by circular dichroism using the characteristic MLCT absorption band at λ_{max} = 295 nm (Figure 3). The $[\alpha]_D$ values of **5a** and **5b** were re-

corded in aqueous solution with $[\alpha]_D = -951$ ($c = 0.0063$, H_2O) for **5a** and $[\alpha]_D = +961$ ($c = 0.0083$, H_2O) for **5b**.

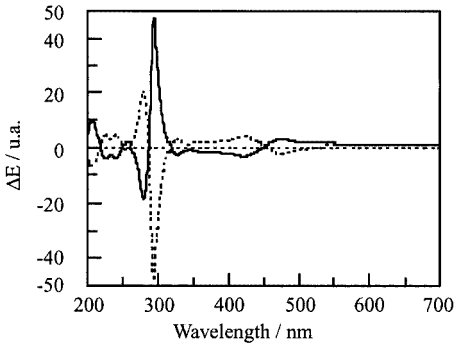


Figure 2. CD curves for **3a** (solid line) and **3b** (dotted line) in acetonitrile

We believe that the basic conditions used in the HPLC resolution (diethylamine/MeOH eluent) resulted in complete deprotonation of the acidic functions and led to the isolation of the deprotonated complexes **5a** and **5b**. The equilibrium between the carboxylate and carboxylic acid forms of the tris(bidentate ligand)ruthenium complexes can be monitored by ^{1}H NMR spectroscopy. Thus, addition of $HBF_4{\cdot}Et_2O$ to a racemic mixture of **5a** and **5b** in D_2O leads to significant changes in the ^{1}H NMR spectrum. For example, the signal corresponding to 3-H and 3′-H shifts downfield by 0.1 ppm. The spectrum of the starting material can be recovered by addition of excess triethylamine. Thus, starting from the pure enantiomers **5a** or **5b**, it is easy to obtain the related carboxylic acid complexes **4a** or **4b**.

Acidification of a solution of **5a** or **5b** in water (pH = 0.5, 1 M H_2SO_4), followed by addition of excess NH_4PF_6, leads to precipitation of **4a** or **4b**. These two enantiomers were characterized by elemental analyses, IR and ^{1}H NMR. It is noteworthy that the ν(CO) vibration in these complexes occurs at 1734 cm^{-1}, shifted by 117 cm^{-1} compared to the carboxylate starting materials. The circular dichroism curves for **4a** and **4b** (Figure 4) were recorded in CH_3CN solution, and show little change compared to those of the related starting carboxylates **5a** and **5b** (Figure 3). The $[\alpha]_D$ value for **4a** is −1058 ($c = 0.0152$, CH_3CN) and for **4b** is +1250 ($c = 0.0104$, CH_3CN).

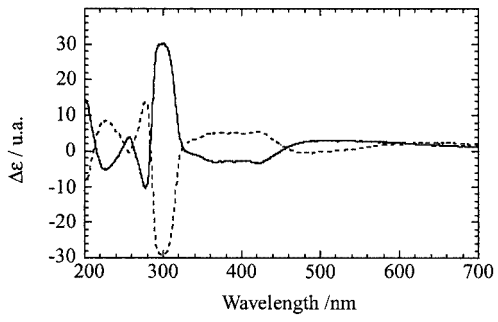


Figure 3. CD curves for **5a** (solid line) and **5b** (dotted line) in acetonitrile

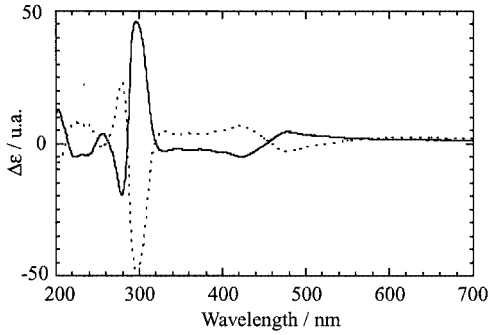


Figure 4. CD curves for **4a** (solid line) and **4b** (dotted line) in acetonitrile

Homo- and Heterochiral Ion-Pairing with Δ-Trisphat (Δ-1)

The determination of the enantiomeric purity of a variety of tris(bidentate ligand)Ru complexes by ^{1}H NMR techniques using the anion Δ-**1** as a chiral shift reagent has become a definitive and accurate method.[6] Thus, addition of Δ-**1** (D_3 symmetry) to D_3-symmetric ruthenium complexes causes a discrimination in the chemical shifts of the two enantiomeric forms. In fact several studies have suggested that the Δ−Δ homochiral ion-pairing interaction between the complex and Δ-**1** is stronger than that of the heterochiral triad based on geometrical criteria.[7,9]

We sought specific interactions between Δ-**1** and the ruthenium complexes of C_2 or C_1 symmetry in the hope that such complexes will act as appropriate probes to highlight this ion-pairing phenomenon; the results of these investigations are presented below.

i) C_2 Symmetry: Δ-Trisphat (Δ-1) and Δ- and Λ-[Ru(bpy)$_2$(dcbpy)][PF$_6$]$_2$ (4a, b)

Sequential addition of up to 5 equiv. of Δ-**1** to a racemic mixture of **4a** and **4b** in CD_2Cl_2/5%CD_3CN (v/v) was monitored by ^{1}H NMR spectroscopy at 293 K. Prior to addition of this chiral shift reagent, the ^{1}H NMR spectrum showed only one set of signals for the two magnetically equivalent enantiomers, in agreement with a C_2-symmetric topology. As shown in Figure 5, a splitting and a progressive chemical shift variation of specific signals are seen on successive addition of 0.5 equiv. aliquots of Δ-**1**. We attribute this result to the formation of a pair of diastereoisomers, **4a**−Δ-**1** and **4b**−Δ-**1**. The signals showing the largest changes in chemical shifts also broaden significantly. In order to discriminate between the two sets of signals ascribed to each diastereoisomeric pair, pure **4a** was added to the initial mixture. Full assignment of the ^{1}H NMR spectrum was achieved using standard 2D experiments (see Exp. Sect. and Supporting Information; see also footnote on the first page of this article).

The chemical shift variation upon addition of Δ-**1** is attributed to a fast exchange process between either Ru^{II} enantiomer (**4a**, **b**) and the ion-pair **4a**−Δ-**1** or **4b**−Δ-**1**, while the broad signals denote a slower dynamic phenomenon. These broad signals are assigned to the homochiral (Δ−Δ) ion-pair and these results therefore suggest that the interac-

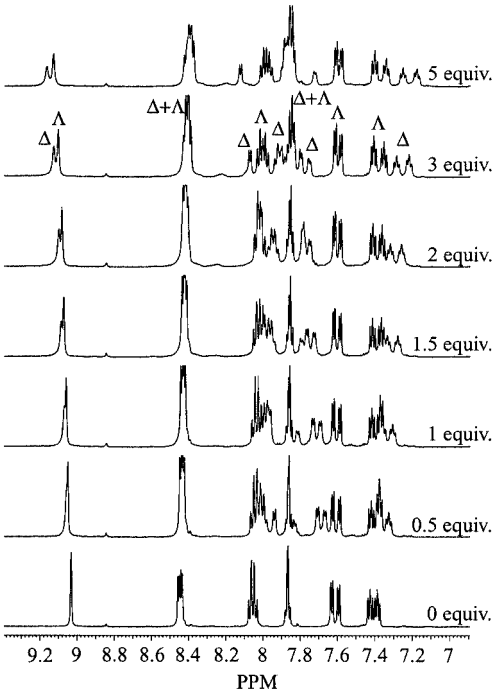
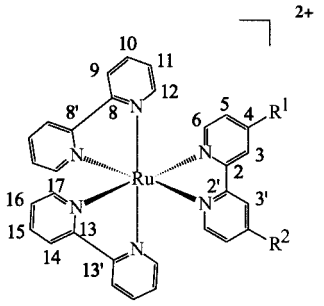


Figure 5. Section of the ^{1}H NMR spectra of racemic **4a**, **b** upon sequential addition of Δ-**1** from 0 to 5 equiv.; the symbols Δ and Λ, on the second trace from top, denote the diastereoisomers **4a**−Δ-**1** and **4b**−Δ-**1**, respectively

tions within the homochiral ion pair are stronger than those involved in the heterochiral ion pair. Moreover, the protons of the homochiral ion-pair exhibit the most pronounced shift of their resonance frequency upon addition of Δ-**1** (Figure 6 and Scheme 2). The resonance signals ascribed to the enantiomer **4a** are strongly spread out either upfield or downfield as a consequence of two concomitant effects; the intimate π-stacking with Δ-**1** and the coulombic attractions between the cationic metal center and the anionic phosphorus atom. The large shifts of the signals are clear evidence of the high vicinity of the octupoles within the homochiral association.



Scheme 2. Atom labelling for the NMR investigations

The heterochiral assembly is less favored, as suggested by the small variation in the chemical shifts of the signals of **4b**. We note that for this Λ−Δ ion-pair, only one C_2-related proton pair is shifted downfield, while the other proton signals remain unchanged or shift slightly upfield (Figure 6). From the ^{1}H NMR spectra, the retention of the twofold symmetry for both diastereoisomeric pairings is postulated. This suggests that in our model complex the pairing of one chiral object either with a homochiral species, or with a mirror-image partner, induces a decrease of symmetry for

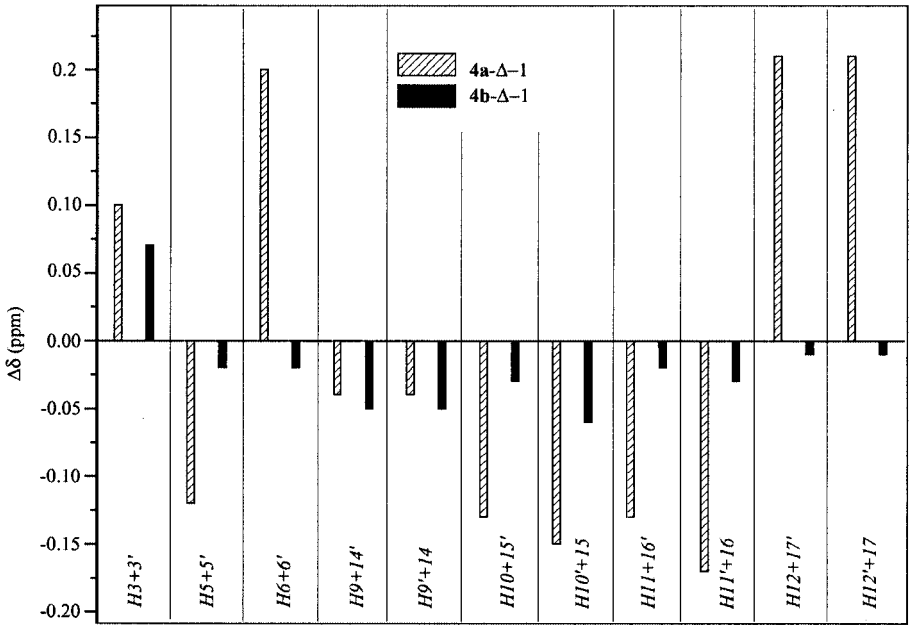


Figure 6. The differences, δ(**4a**−Δ-**1**) − δ(*rac*-**4a**, **b**) (white columns) and δ(**4b**−Δ-**1**) − δ(*rac*-**4a**, **b**) (black columns), point out the effect of Δ-Trisphat on the proton resonances; these values were measured in the presence of 3 equiv. of Δ-**1**

the whole supramolecular assembly i.e. C_2 symmetry in the latter case.

ii) C_1 Symmetry: Δ-Trisphat (Δ-1) and Δ- and Λ-[Ru(bpy)$_2$(cmbpy)][PF$_6$]$_2$ (3a, b)

We anticipated that both the homochiral (**3a**−Δ-**1**) and heterochiral (**3b**−Δ-**1**) ion-pairs should display the same NMR profile (i.e. the same number of signals). To avoid any complex NMR patterns, we studied the behavior of **3a** and **3b** separately in the presence of 4 equiv. of Δ-Trisphat in CD_2Cl_2/5%CD_3CN (v/v), and monitoring was performed by standard ^{1}H NMR techniques (see Exp. Sec. and Supporting Information). Our choice to run only one experiment in the presence of 4 equiv. of Δ-**1** is based on previous results that we obtained for **4a** and **4b**, where maximum separation of the signals of the enantiomers (Δδ) was achieved.

Surprisingly, the ^{1}H NMR spectrum of the homochiral ion-pair **3a**−Δ-**1** displays more signals than that of the heterochiral ion-pair **3b**−Δ-**1** (Figure 7). In the latter case the protons of the unsubstituted bipyridine ligands remain almost unchanged relative to the initial mixture (i.e. without chiral shift reagent) and this suggests that the ion-pairing interactions are weak.

In sharp contrast, the ^{1}H NMR spectrum of **3a**−Δ-**1** displays many signals, consistent with a C_1-symmetric ion-pair. Both the substituted and unsubstituted bipyridine ligands showed distinct signals (see Exp. Sect.) and we suggest this behavior is a result of a strong ion-pairing interaction in the homochiral self assembly **3a**−Δ-**1**. The NMR spectra of all samples remained unchanged over several weeks and we thus conclude that no enantiomeric conversion from **3a** to **3b** (i.e. the conversion from **3a**−Δ-**1** to **3b**−Δ-**1**) occurs. This observation suggests that these ruthenium complexes are configurationally rigid, in agreement with previous reports.[5d]

In summary, our NMR spectroscopic data suggest that the Δ−Δ homochiral ion-pairing interaction is stronger than that of the heterochiral triad. It appears that the initial geometry of the ionic partner is crucial in allowing an intimate association of the ions. The homosymmetry (D_3−D_3) criterion is not the sole defining parameter for the occurrence of ion-pairing; both D_3−C_2 and D_3−C_1 symmetries exhibit stable ion-pairs. These results represent the first investigation of ruthenium complexes with different symmetries.

Concluding Remarks

In this paper we have reported the synthesis of optically pure ruthenium complexes of the type Δ- or Λ-[Ru(bpy)$_2$(L−L)][PF$_6$]$_2$ [L−L = cmbpy = 4′-methyl-2,2′-bipyridine-4-carboxylic acid (**3a**, **b**); L−L = dcbpy = 2,2′-bipyridine-4,4′ dicarboxylic acid (**4a**, **b**)], including the X-ray crystal structure of the (dicarboxylato)ruthenium species Δ-[Ru(bpy)$_2$(dcabpy)] (**5a**). The enantiomeric nature and the absolute configuration of these tris(bidentate ligand)ruthenium complexes were confirmed by NMR and circular dichroism studies. NMR studies of **3a**, **3b**, **4a**, and **4b** in the presence of Δ-Trisphat (Δ-**1**) suggest that strong ion-pairing interactions are taking place, which favor a homochiral association (Δ−Δ), relative to the heterochiral ion pairing (Δ−Λ). We also note that the ^{1}H NMR spectrum of each ion-pair differs for each enantiomer, and depends on whether the cation possesses C_1 or C_2 symmetry. Further investigations are currently in progress with other ruthenium and osmium complexes.

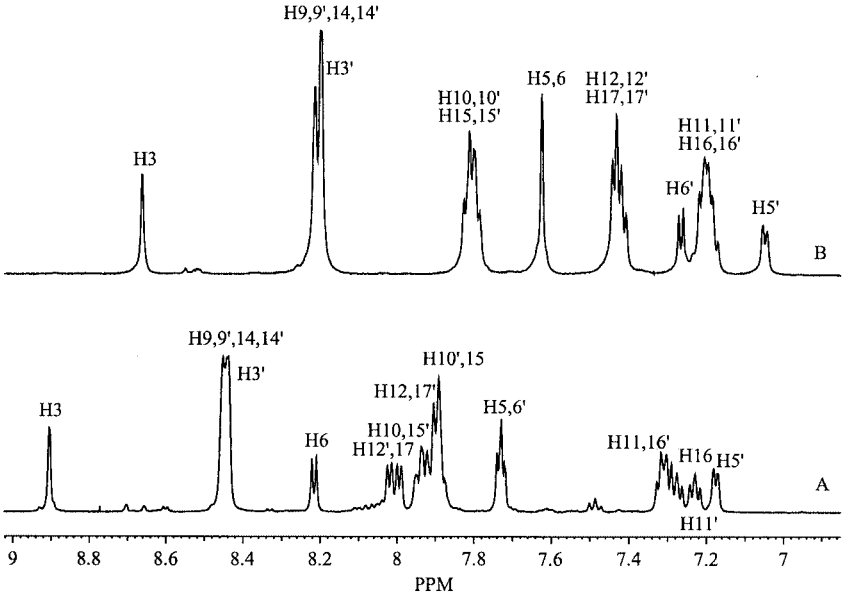


Figure 7. Section of the ^{1}H NMR spectra of **3a**−Δ-**1** (trace A) and **3b**−Δ-**1** (trace B), in the presence of 4 equiv. of Δ-**1**, showing the region of signals of aromatic protons

Experimental Section

General Procedures: All solvents used were reagent grade or better. Deuterated solvents were used as received. Commercially available reagents were used as received. The complexes Δ- and Λ-[Ru^{II}-$(bpy)_2(py)_2$][dibenzoyltartrate-*O*,*O*′],[11] [$Ru^{II}(bpy)_2(Cl)_2$],[16] and *rac*-[$Ru(bpy)_2(cmbpy)][PF_6]_2$ (**3a**,**b**),[2f] were prepared according to literature procedures. The ligand 2,2′-bipyridine-4,4′-dicarboxylate (dcbpy) was purchased from STREM Chemicals and used as received. ^1H NMR spectra were recorded with a Bruker AC-300 spectrometer and with a Bruker DRX-500 spectrometer, equipped with a Silicon Graphics workstation (vide infra). Chemical shifts are reported in ppm downfield from the tetramethylsilane signal and are referenced to the residual hydrogen signal of deuterated solvents (δ = 1.94 ppm, acetonitrile). IR spectra were recorded with a Bio-RAD IR-FT spectrophotometer as KBr disks in the 4000−250 cm^{-1} region. Specific rotations were measured at 20 °C, in a 1-dm cell using the sodium D-line of an Amber AA5 polarimeter. Circular dichroism spectra were measured using a Jasco model J-710 spectropolarimeter. HPLC was carried out using a CHIROSE-(R)C3 chiral column, (CHIRALSEP, La Frenaye, France) 50 mm diameter × 250 mm length, with methanol/diethylamine (100/0.1, v/v), as mobile phase; UV detection 275 nm. For a flow rate of 100 mL/min, retention times of 9.00 min for **5b** and 13.00 min for **5a** were observed. 60 mg of racemic mixture in 4 mL of acetonitrile was injected in each run.

Supporting Information: NMR spectra including complete assignments of the protons and carbon atoms of **3a**, **3b, 4a**, and **4b** (6 figures) are provided (see also footnote on the first page of this article).

Δ- or Λ-[$Ru(bpy)_2(cmbpy)][PF_6]_2$ (3a or 3b): Δ- or Λ-[$Ru^{II}(bpy)_2$-$(py)_2$][dibenzoyltartrate-*O*,*O*′] (390 mg, 419 μmol), cmbpy (220 mg, 1 mmol, 2.38 equiv.), sodium acetate (220 mg, 2.7 mmol, 5.65 equiv.), water (3 mL), and ethylene glycol (13 mL) were heated at 120 °C overnight, and the pH was then adjusted to 1 by addition of concentrated sulfuric acid. Water (30 mL) was added and the mixture was filtered to remove excess free ligand. The product was precipitated by addition of a saturated aqueous solution of NH_4PF_6, and filtration through a fine (porosity 5) glass frit gave a red powder. This was washed with water and dried under vacuum. Yield: 321 mg (85%). Spectroscopic data are similar to those reported for the racemic complexes.[2f]

***rac*-[$Ru(bpy)_2(dcbpy)][PF_6]_2$ (4a, b):** This product was prepared as described in the literature.[2h] Yield: 331 mg (85%). Selected IR data (KBr disk): $\tilde{\nu}$ = 1734 (C=O), 842 (P−F) cm^{-1}. ^1H NMR (300 MHz, CD_3CN): δ = 7.40 (qd, *J* = 5.7, *J*′ = 1.3 Hz, 4 H), 7.68 (dd, *J* = 6.5, *J*′ = 5.7 Hz, 4 H), 7.82 (dd, *J* = 5.7, *J*′ = 1.8 Hz, 2 H), 7.92 (d, *J* = 5.7 Hz, 2 H), 8.08 (qd, *J* = 7.5, *J*′ = 1.3 Hz, 4 H), 8.51 (dd, 4 H, *J* = 7.9, *J*′ = 2.6 Hz, 4 H), 9.11 (d, *J* = 0.9 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR (500 MHz, CD_3CN): C (quaternary): δ = 163.97 (C=O), 157.45, 156.53, 156.41, 138.57; =CH: δ = 152.59, 152.49, 151.54, 151.30, 138.09, 137.98, 127.59, 127.52, 127.45, 126.52, 124.17, 123.74, 123.60. $C_{32}H_{24}F_{12}N_6O_4P_2Ru{\cdot}3H_2O$ (1001.66): calcd. C 38.37, H 3.02, N 8.39; found C 38.68, H 3.03, N 8.10.

Δ- or Λ-[$Ru(bpy)_2$ (dcbpy)][$PF_6]_2$ (4a or 4b): These complexes were prepared in a similar fashion to **3a** and **3b** using Δ- or Λ-[Ru^{II}-$(bpy)_2(py)_2$][tartrate] (200 mg 215 μmol), dcbpy (110 mg, 426 μmol, 1.98 equiv.), sodium acetate (110 mg, 1.34 mmol, 6.23 equiv.), water (3 mL), and ethylene glycol (13 mL). The compounds were obtained as purple powders. Yield: 140 mg (67%). Spectroscopic data are similar to those reported for the racemic compound (vide supra).

NMR Studies and Experimental Conditions: NMR samples were prepared by dissolving the solid Ru^{II} complexes in 500 μL of CD_2Cl_2 + 5 vol-% of CD_3CN ($c \approx 10^{-2}$ M for each sample). The spectra were recorded with a Bruker DRX-500 spectrometer, equipped with a Silicon Graphics workstation. A 5-mm broad-band probe with a shielded z-gradient was used. The temperature was monitored with a BCU 05 temperature unit and fixed at 293 K. Data were processed with Silicon Graphics stations using GIFA (version 4.3).[17,18] Proton spectra were obtained in 16 scans of 16 K data points over a 5.12 kHz spectral width. A presaturation (60 dB) of the solvent residual signal was performed. The free induction decays were processed using standard Fourier transformation. COSY 2D NMR spectra in the absolute mode were recorded using the standard pulse sequence with a presaturation (60 dB) of the solvent signal during the relaxation delay. This 2.0-s relaxation delay was introduced between the 48 transients of each increment. 320 FIDs with 2 K data points in F_2 over a 5.12 kHz spectral width were collected. Zero-fillings were added to increase the resolution in F_1. Before 2D Fourier transformation, a sine-bell window function was applied to both dimensions. The transformed data were then symmetrized. For the $^1H-^1H$ dipolar contact analyses, 2D ROESY experiments were preferred because of the molecular weight of the concerned ions for which NOEs are weakly positive or zero. The chosen ROESY sequence[19] introduces trim pulses (180_X, 180_{-X}, ...) used as spinlock to avoid TOCSY effects. The 180° pulses were calibrated for a 20 dB power. These experiments were acquired in the TPPI mode. Solvent signal suppression was achieved by a low power transmitter pulse of presaturation (45 dB) during the relaxation delay. 2D ROESY data were recorded with 2 K points in t_2 over 5.12 kHz and 400 points in t_1. A 2.0-s relaxation delay and a mixing time of 600 ms were used for the 32 scans of each FID. Zero-fillings were added in F_1. Shifted sinebell window functions were applied in both dimensions before the Fourier transformation. Baselines were corrected using a polynomial function if necessary.

Table 2. Crystal data and structure refinement for **5a**

Empirical formula	$C_{32}H_{36}N_6O_{11}Ru$
Formula mass	781.74
Temperature [K]	295
Crystal system	monoclinic
Space group	*C*2
a [Å]	22.772(9)
b [Å]	13.336(4)
c [Å]	17.340(6)
β [°]	137.33(3)
V [$Å^3$]	3569(3)
Z	4
$\rho_{calcd.}$ [$g{\cdot}cm^{-3}$]	1.455
λ (Mo-K_α) [Å]	0.71069
μ [cm^{-1}]	4.92
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0532
$Rw = [\Sigma w(\|\|F_o\| - \|F_c\|\|)^2/\Sigma wF_o^2]^{1/2}$	0.0615

X-ray Structure Determination: Data for **5a** (Table 2) were collected with an Enraf−Nonius CAD4 diffractometer, Mo-K_α radiation (λ = 0.71069 Å) collection range 2θ = 2−50°, crystal dimensions 0.25 × 0.30 × 0.35 mm. An empirical absorption correction (DIFABS)[20] was applied (T_{min} = 0.89, T_{max} = 1). The structure was solved by direct methods and subsequent difference Fourier syn-

theses, and refined by full-matrix least squares on *F* by using the programs of the PC version of CRYSTALS. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier map and their coordinates were refined with an overall isotropic thermal parameter. CCDC-174554 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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