Isolation of Enantiomers of a Range of Tris(bidentate)ruthenium(II) Species Using Chromatographic Resolution and Stereoretentive Synthetic Methods

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A range of chiral building blocks of the type Δ- or Λ-$[Ru(pp)_2(CO)_2]^{2+}$ {pp = bidentate ligands bpy (2,2′-bipyridine), phen (1,10-phenanthroline) and Me_2bpy (4,4′-dimethyl-2,2′-bipyridine)} have been synthesized, and their enantiomeric purity and absolute configurations determined by CD and NMR studies. Decarbonylation using trimethylamine oxide in the presence of the respective pp ligand at room temperature produced the corresponding tris(bidentate) species $[Ru(pp)_3]^{2+}$ with retention of configuration at the ruthenium(II) centre. A general chromatographic technique for resolution of tris-homoleptic complexes of the type $[Ru(pp)_3]^{2+}$ was investigated, with the absolute configurations of the resolved complexes confirmed by CD studies, and the X-ray structural analyses of Δ-(–)-$[Ru(Me_2bpy)_3]$[(–)-*O*,*O*′-dibenzoyl-L-tartrate] and Λ-(+)-$[Ru(phen)_3]$[(+)-*O*,*O*′-di-4-toluoyl-D-tartrate]. Resolution is also reported for the analogous species containing three potential bridging ligands, $[Ru(bpm)_3]^{2+}$ and $[Ru(HAT)_3]^{2+}$ (bpm = 2,2′-bipyrimidine; HAT = 1,4,5,8,9,12-hexaazatriphenylene). The versatility of the chromatographic procedure was demonstrated by the resolution of a series of bis-heteroleptic complexes $[Ru(pp)_2(pp')]^{2+}$ {pp′ = dpq (dipyrido[3,2-*d*:2,3′-*f*]quinoxaline), dpqc (dipyrido[3,2-*a*:2,3-*d*]-6,7,8,9-tetrahydrophenazine), and dppz {dipyrido[3,2-*a*:2,3′-*d*]phenazine)}.

Introduction

Ruthenium(II) complexes of polypyridyl ligands have received considerable attention as potential chromophoric components in photochemical molecular devices,[1] largely as a consequence of their synthetic versatility, and favourable photophysical and redox properties.[2][3][4]

For polynuclear assemblies based on such octahedral metal centres, stereoisomerism may occur by virtue of chirality or geometrical isomerism in the individual components, particularly when bidentate ligands are involved.[5][6][7] Since the initial chiral resolution of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine),[8][9][10] increasing attention has been drawn to the stereochemistry of this species and its analogues as a result of the differential interactions of the enantiomeric forms {e.g. of Δ- and Λ-$[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline)} with certain biological molecules such as DNA or oligonucleotides.[11][12][13][14] Additionally, the chiral resolution of $[Ru(pp)_2(BL)]^{2+}$,[15] $[Ru(pp)(pp')(BL)]^{2+}$,[16] {pp = bidentate polypyridyl ligand and BL = bridging ligand}, $[Ru(pp)_2(X)_2]^{n+}$ {X = py, CO, Cl^-, and CN^-},[15][17][18][19][20] and $[Ru(pp)(pp')(py)_2]^{n+}$[16] species have also been investigated in terms of their potential use as chiral building blocks for oligonuclear assemblies with predetermined stereochemistry.[6][7]

In the utilization of these species as chiral building blocks in stereoselective syntheses, or in the investigation of chiral interactions, it is required that they be available in optically pure form and have known absolute configurations. Generally, the chiral resolutions of bis(bidentate)- and tris(bidentate)ruthenium(II) complexes of polypyridyl ligands have been achieved by diastereoisomeric salt formation,[8][10][15][19][20][21][22][23][24] or chromatographic techniques.[15][16][25][26][27][28][29][30][31] The absolute configuration of a number of these enantiomeric forms have been assigned by exciton analysis of their circular dichroism (CD) spectra,[19][32][31][32][33][34][35][36] although more recently X-ray analyses have unambiguously confirmed the absolute configurations of Λ-$[Ru(bpy)_2(py)_2]^{2+}$[37] and Λ-$[Ru(phen)_3]^{2+}$.[38]

We recently communicated details of the chiral resolution of a series of dicarbonyl complexes of the type $[Ru(pp)_2(CO)_2]^{2+}$ {where pp = bpy, phen, and Me_2bpy (= 4,4′-dimethyl-2,2′-bipyridine)} and demonstrated their potential as chiral building blocks in the stereoselective synthesis of oligonuclear assemblies with predetermined stereochemistry.[15] We now report in detail the chiral resolution procedures and assignment of their absolute configurations, an NMR method of determining their optical purity, and the stereochemical consequences of their decarbonylation reactions. Also discussed is the development of a general chromatographic resolution technique for a variety of tris(bidentate)ruthenium(II) species and the factors which in-

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fluence this resolution procedure. X-ray structural analyses of Δ-(−)-[Ru(Me_2bpy)$_3$]{(−)-*O,O′*-dibenzoyl-L-tartrate} and Λ-(+)-[Ru(phen)$_3$]{(+)-*O,O′*-di-4-toluoyl-D-tartrate} were used in combination with CD studies to confirm the absolute configurations of the tris(bidentate) species.

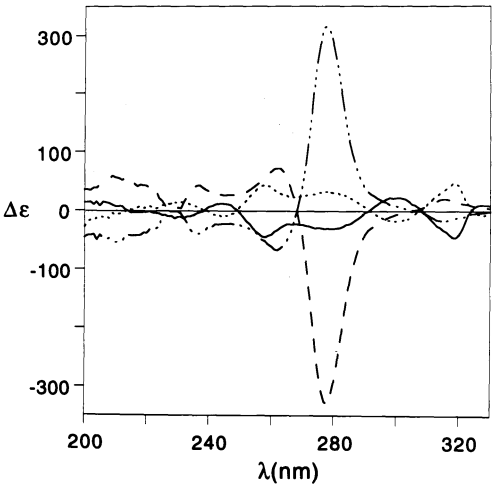
Results and Discussion

Dicarbonyl Species

Stereochemistry

Chiral resolutions of the cations [Ru(bpy)$_2$(CO)$_2$]$^{2+}$, [Ru(phen)$_2$(CO)$_2$]$^{2+}$, and [Ru(Me_2bpy)$_2$(CO)$_2$]$^{2+}$ were achieved by conventional diastereoisomeric salt formation as the antimonyl-(+)- or -(−)-tartrate salts. The CD spectra of the Λ-(+)- and Δ-(−)-[Ru(phen)$_2$(CO)$_2$](PF$_6$)$_2$ and Λ-(+)- and Δ-(−)-[Ru(bpy)$_2$(CO)$_2$](PF$_6$)$_2$ are shown in Figure 1; assignments of the absolute configurations of the three cations are discussed below.

Figure 1. CD spectra of the enantiomeric forms of [Ru(bpy)$_2$(CO)$_2$]$^{2+}$; Δ (——) and Λ (·····), and [Ru(phen)$_2$(CO)$_2$]$^{2+}$; Δ (------) and Λ (-·-·-·-)

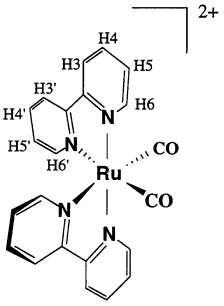


Cation-exchange chromatography utilizing a chiral eluent {e.g. sodium (−)-*O,O′*-dibenzoyl-L-tartrate}[15] was attempted as a resolution procedure but was found to be experimentally difficult due to the colourless character of these dicarbonyl complexes.

Chiral Lanthanide-Shift Reagent Studies

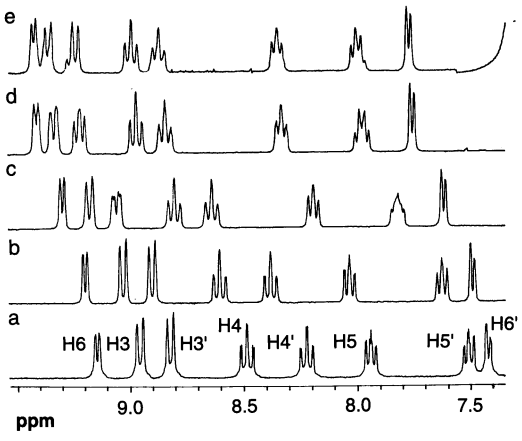
^{1}H-NMR techniques have provided an accurate and definitive method for the determination of enantiomeric purity of a variety of ruthenium(II) complexes of polypyridyl ligands. Such studies involve the addition to the complex of a chiral lanthanide-induced shift reagent[15][20][39][40][41][42] or tartrate derivative,[28] which causes a discrimination in the chemical shifts between the two enantiomeric forms. In the present work, the lanthanide-shift reagent studies of [Ru(pp)$_2$(CO)$_2$]Cl$_2$ (pp = bpy, phen, and Me_2bpy) were performed in [D_3]acetonitrile or [D_2]dichloromethane solutions: a non-polar solvent such as [D_2]dichloromethane is preferable in such studies,[40] but for solubility reasons [D_3]acetonitrile was required for the former two complexes. For all three dicarbonyl complexes, chemical shift discriminations between the enantiomeric forms were observed upon the addition of tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III), Eu(tfc)$_3$, with the largest and most pronounced effects occurring for [Ru(Me_2bpy)$_2$(CO)$_2$]Cl$_2$ measured in [D_2]dichloromethane solution.

The effect of the sequential addition of Eu(tfc)$_3$ on the ^{1}H-NMR spectrum of [Ru(bpy)$_2$(CO)$_2$]Cl$_2$ is shown in Figure 2, where all the protons exhibited an induced downfield chemical shift of a magnitude influenced by their environment. The distinction between the enantiomers can be seen most clearly by comparison of the H3′ and H5′ proton resonances in Figures 2d and 2e (the racemate and a sample enriched in the Λ-(+) form, respectively, under similar conditions).



The complexes [Ru(phen)$_2$(CO)$_2$]Cl$_2$ and [Ru(Me_2bpy)$_2$(CO)$_2$]Cl$_2$ also showed an induced downfield chemical shift and chiral descrimination. Intersection of initial and final slopes in plots of the induced perturbation in chemical shift as a function of added [Eu(tfc)$_3$] for [Ru(phen)$_2$(CO)$_2$]Cl$_2$ and [Ru(bpy)$_2$(CO)$_2$]Cl$_2$ indicated a ca. 1:1 adduct with the shift reagent. For the complex [Ru(Me_2bpy)$_2$(CO)$_2$]Cl$_2$, the ratio of shift reagent to complex exceeded unity.

Figure 2. The effect of [Eu(tfc)$_3$] on the ^{1}H-NMR (300 MHz; CD_3CN) spectrum of [Ru(bpy)$_2$(CO)$_2$]Cl$_2$; {a = no Eu(tfc)$_3$; b = 0.25 equiv.; c = 0.6 equiv.; d = 1 equiv.; e ≈ 1 equiv.; sample enriched in Λ isomer}; ^{1}H labelling scheme shown in text}



Stereochemical Consequences of the Decarbonylation Reaction

The stereochemical consequences of the decarbonylation reaction with trimethylamine *N*-oxide (TMNO) were investigated by treating the enantiomerically pure Λ-(+)-$[Ru(phen)_2(CO)_2]^{2+}$, Δ-(−)-$[Ru(bpy)_2(CO)_2]^{2+}$ and Λ-(+)-$[Ru(Me_2bpy)_2(CO)_2]^{2+}$ species (see below for absolute configuration assignments) with the ligands phen, bpy, and Me_2bpy under a variety of conditions, as given in Table 1. The $[Ru(pp)_3]^{2+}$ products from the reactions were isolated and the corresponding $[\alpha]_D$ values compared with those of the independently fully resolved products, allowing an assessment of the enantiomeric excess (*ee*) of the products formed under the various decarbonylation conditions. ^{1}H-NMR techniques utilizing the chiral shift reagent $[Eu(tfc)_3]$ were also used to confirm these *ee* determinations.

Previous studies[15][43] of the decarbonylation reactions of enantiomerically-enriched $[Ru(bpy)_2(CO)_2]^{2+}$ indicated that the three parameters which most significantly influenced the degree of stereoretention were temperature, solvent and ligand concentration. In order to maintain chiral integrity during the decarbonylation process, reaction conditions involved use of the solvent 2-methoxyethanol, ligand concentrations of ca. 10-fold or higher excess and low reaction temperatures. Photoracemization was not observed, but light was excluded in this study as a precaution.[15][43]

Table 1. Stereochemical consequences of the decarbonylation reactions of Δ- or Λ-$[Ru(pp)_2(CO)_2]^{2+}$ {where pp = phen, bpy, or Me_2bpy}

$[Ru(pp)_2(CO)_2]^{2+}$ precursor	Reaction conditions[a]	$[Ru(pp)_3]^{2+}$ product $[\alpha]_D$	Column resolution $[\alpha]_D$	Literature[b] $[\alpha]_D$	Enantiomeric excess (*ee*)
Λ-(+)-[pp = phen]	25°C	+1395	+1400	+1340	> 0.99
	45°C	+1330			0.95
	60°C	+1134			0.82
	120°C	+980			0.74
	200°C[c]	+938			0.70
Δ-(−)-[pp = bpy]	25°C	−816	−823	−819	> 0.99
	120°C	−254			0.50
	120°C[d]	−300			0.53
Λ-(+)-[pp = Me_2bpy]	25°C	+1000[e]	+1045[e]		0.96
	120°C	+920[e]			0.88

[a] All reactions were performed in subdued light using 2-methoxyethanol as solvent, with 10-fold excess of pp and 3-fold excess of TMNO unless otherwise specified. − [b] Optical rotations measured in water as Cl^- or I^- salt for phen and bpy, respectively. − [c] Reaction conditions of ethylene glycol as solvent and heating under microwave conditions. − [d] Reaction conditions of 30-fold excess of bpy, 20-fold excess of TMNO and 2-methoxyethanol as solvent. − [e] Optical rotations measured as PF_6^- salts in CH_3CN as solvent at λ = 546 nm.

All reactions were observed to proceed with complete or near-complete retention of configuration at room temperature, whereas racemization occurred to varying degrees for all complexes at elevated temperatures. The most likely stage at which racemization might occur is subsequent to the removal of one carbonyl group, when competition for the "free" (or solvated) coordination site may occur between the uncoordinated nitrogen of an incoming monodentate pp ligand and a rearrangement involving one of the coordinated bidentate pp ligands. The extent of *racemization* during the decarbonylation reaction agrees with work previously completed by the authors, which demonstrated that retention of *geometric* integrity of an analogous dicarbonyl complex incorporating two non-symmetrical polypyridyl ligands occurred at 25°C, but isomerization took place at elevated temperatures.[44]

Absolute Configuration Determinations

Assignment of the absolute configurations of (+)- and (−)-$[Ru(phen)_2(CO)_2]^{2+}$ and (+)- and (−)-$[Ru(bpy)_2(CO)_2]^{2+}$ was achieved by their reaction with a third bidentate ligand to yield a tris(bidentate) product of known chirality. To ensure the decarbonylation reactions occurred with complete retention of configuration, the reactions were performed at room temperature and in subdued light (see above). The decarbonylation of (−)-$[Ru(bpy)_2(CO)_2]^{2+}$ with TMNO in 2-methoxyethanol in the presence of a 10-fold excess of bpy yielded the product Δ-(−)-$[Ru(bpy)_3]^{2+}$[36] with $[\alpha]_D = -816$ (compared with the literature value of −819[9]). This observation established a Δ configuration for (−)-$[Ru(bpy)_2(CO)_2]^{2+}$ and confirmed complete retention of configuration under those decarbonylation reaction conditions.

The absolute configuration of Λ-(+)-$[Ru(phen)_3]^{2+}$ has been assigned by CD[36] and X-ray crystallographic studies[38] and confirmed in the present work. It was formed by decarbonylation of (+)-$[Ru(phen)_2(CO)_2]^{2+}$ in the presence of phen, but otherwise under identical conditions to those described above for the formation of Δ-(−)-$[Ru(bpy)_3]^{2+}$, thus indicating the Λ configuration for (+)-$[Ru(phen)_2(CO)_2]^{2+}$ (see above). The product showed $[\alpha]_D = +1395$ compared with the literature value of +1340.[10]

The decarbonylation of (+)-$[Ru(Me_2bpy)_2(CO)_2]^{2+}$ under the same conditions described above but in the presence of Me_2bpy yielded the Λ-(+)-$[Ru(Me_2bpy)_3]^{2+}$ product (configuration determined by X-ray structural determination, Figure 4). The synthesized Λ-(+)-$[Ru(Me_2bpy)_3]^{2+}$ showed $[\alpha]_{546} = +1000$ compared to the independently resolved (+)-$[Ru(Me_2bpy)_3]^{2+}$ complex (see below) where $[\alpha]_{546} = +1045$, which may suggest that minor racemization (< 4%) occurs under the above reaction conditions.

The electronic spectrum of $[Ru(phen)_2(CO)_2]^{2+}$ exhibited a strong absorption band at ca. 275 nm which is assigned to an intraligand π→π* transition, while the weak bands at

340 and 350 nm are most likely to be dπ→π* transitions.[45][46] The intense circular dichroism band at ca. 280 nm (phen long-axis polarization transition) for (+)-$[Ru(phen)_2(CO)_2]^{2+}$ is strongly positive and the circular dichroism band at higher energy (ca. 260 nm) negative (Figure 1), confirming the (+) isomer as having the Λ absolute configuration.[33]

The electronic spectrum of $[Ru(bpy)_2(CO)_2]^{2+}$ was dominated by π→π* transitions in the region of ca. 200−300 nm.[45][46] The long-axis polarized transitions of bpy occur at ca. 300 nm:[33] the CD band at 315 nm for the (+)-enantiomer is strongly positive and the high energy band at 300 nm is negative (Figure 1), confirming the assignment as Λ-(+)-$[Ru(bpy)_2(CO)_2]^{2+}$. For the complexes $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(phen)_2(CO)_2]^{2+}$, the lower energy long-axis polarized transitions were red-shifted relative to those reported for the $[Ru(pp)_2(py)_2]^{2+}$ analogues,[19][33] presumably due to the electron-withdrawing carbonyl ligands. Accordingly, the two methods used to determine the absolute configurations of the chirally resolved dicarbonyl complexes (i.e. stereoselective syntheses and CD studies) were in agreement.

Tris(bidentate) Complexes

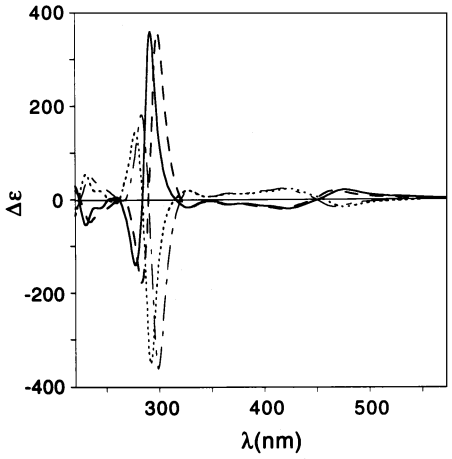
Stereochemistry

During the course of this study, a chromatographic technique was developed for the resolution of tris(bidentate)ruthenium(II) complexes. The technique is based on a cation-exchange mechanism (SP Sephadex C-25 support) with the mode of resolution significantly influenced by the differential association of the chiral anions of the eluent with the enantiomeric forms of the complex.[30][31] As Sephadex has a dextran base and is itself chiral, it believed to significantly influence the resolution procedure, as demonstrated by the chiral resolution of $[\{Ru(Me_2bpy)_2\}_2(\mu\text{-bpm})]^{4+}$[30] and $[Ru(bpq)_3]^{2+}$ {bpq = 2,3-bis(2-pyridyl)quinoxaline} with the achiral eluent sodium toluene-4-sulfonate.[47]

The resolutions of a number of ruthenium(II) complexes involving α,α′-diimine ligands have recently been reported using CM and SP Sephadex C-25 and (+ or −)-SbOtart salts as eluents.[25][27][28] Generally, these resolution procedures have required the collection of a series of fractions to obtain the resolved complex. The procedure reported below resulted in the clear separation into two bands (i.e. the two enantiomeric forms) of every mononuclear complex examined.

The study was based primarily on the resolution of the four tris-homoleptic tris(bidentate) complexes $[Ru(pp)_3]^{2+}$ (pp = bpy, phen, Me_2bpy, and Me_4bpy), although a number bis-heteroleptic complexes $[Ru(pp)_2(pp')]^{2+}$ were examined to demonstrate the generality of the resolution procedure. The CD spectra of Δ- and Λ-$[Ru(bpy)_3]^{2+}$ and Δ- and Λ-$[Ru(phen)_3]^{2+}$ resolved by the technique were in excellent agreement with the spectra reported previously.[35] The CD spectra of Δ-(−)- and Λ-(+)-$[Ru(Me_2bpy)_3]^{2+}$ and Δ- and Λ-$[Ru(Me_4bpy)_3]^{2+}$ are shown in Figure 3 (the determination of the absolute configuration of Δ-(−)-$[Ru(Me_2bpy)_3]^{2+}$ is discussed below). The Cotton effects of the three complexes $[Ru(pp)_3]^{2+}$ (pp = bpy, Me_2bpy, and Me_4bpy) were near identical, as expected because of their electronic and structural similarity.

Figure 3. CD spectra of the enantiomeric forms of $[Ru(Me_2bpy)_3]^{2+}$; Δ (·····) and Λ (——), and $[Ru(Me_4bpy)_3]^{2+}$; Δ (-···-···-) and Λ (------)



Chromatographic Resolutions of Tris-homoleptic Tris(bidentate) Species

In the chromatographic resolutions, large variations in efficiencies were observed between the different eluents for the same complex and between different complexes for the same eluent {where a decreased distance for column resolution ("effective column length", ECL) indicates a more efficient resolution}, as shown in Table 2. ^{1}H-NMR studies have suggested that there is a differential association between the above complexes and the anions in the eluent solutions which involves π-stacking and hydrophobic interactions.[30][31] This is further supported by the X-ray structure of Λ-$[Ru(bpy)_2(py)_2]$\{(+)-*O,O′*-dibenzoyl-L-tartrate\}[37] Δ-$[Ru(Me_2bpy)_3]$\{(−)-*O,O′*-dibenzoyl-L-tartrate\} and Λ-(+)-$[Ru(phen)_3]$\{(+)-*O,O′*-di-4-toluoyl-D-tartrate\}; the latter two are reported herein. The associations leading to the chromatographic resolution are believed to involve three-way interaction between the complex, the chiral eluent and the Sephadex support.[31]

Chromatographic resolution using aqueous sodium (−)-*O,O′*-dibenzoyl-L-tartrate as the eluent is significantly more efficient in complexes containing methyl-substituted ligands {$[Ru(bpy)_3]^{2+}$ (ECL = 55 cm) > $[Ru(Me_2bpy)_3]^{2+}$ (ECL = 30 cm) > $[Ru(Me_4bpy)_3]^{2+}$ (ECL = 20 cm) or $[Ru(Me_4bpy)_2(bpm)]^{2+}$ (ECL = 25 cm) > $[Ru(Me_4bpy)_3]^{2+}$ (ECL = 20 cm)}. For these complexes in which there is an increase in resolution efficiency, it is also noted that there is an enhanced rate-of-travel down the column.

While sodium (−)-*O,O′*-di-4-toluoyl-L-tartrate is more efficient than sodium (+)-*O,O′*-di-4-toluoyl-D-tartrate solution as an eluent in the resolution of $[Ru(bpy)_3]^{2+}$ (ECL = 30 cm and 55 cm, respectively), the opposite is true for $[Ru(Me_2bpy)_3]^{2+}$ (ECL = 80 cm and 30 cm, respectively)

Table 2. Chromatographic resolution efficiency for a range of polypyridyl complexes of ruthenium(II)

Complex	Effective column length (ECL)[a] sodium (−)-*O,O′*-dibenzoyl-L-tartrate[b]	sodium (+)-*O,O′*-dibenzoyl-D-tartrate[b]	sodium (−)-*O,O′*-di-*p*-toluoyl-L-tartrate[b]	sodium (+)-*O,O′*-di-*p*-toluoyl-D-tartrate[b]
$[Ru(bpy)_3]^{2+}$	55		30	120
$[Ru(bpy)_2(Me_2bpy)]^{2+}$				65
$[Ru(Me_2bpy)_2(bpy)]^{2+}$				70
$[Ru(Me_2bpy)_3]^{2+}$	30	> 120	80	22
$[Ru(phen)_3]^{2+}$	70	24	80	25
$[Ru(Me_4bpy)_3]^{2+}$	20		40	> 120
$[Ru(Me_4bpy)_2(bpm)]^{2+}$ [15]	25			
$[Ru(bpm)_3]^{2+}$	60			
$[Ru(Me_4bpy)(phen)(bpm)]^{2+}$ [16]	45			
$[Ru(HAT)_3]^{2+}$	50			
$[Ru(bpy)_2(HAT)]^{2+}$ [48]			> 400	ca. 300
$[Ru(phen)_2(HAT)]^{2+}$ [48]	200			

[a] ECL given in cm; error ± 2.5 cm. − [b] Eluent concentrations at 0.075 M.

and $[Ru(Me_4bpy)_3]^{2+}$ (ECL = 40 cm and 20 cm, respectively). The apparent anomaly may arise from increased steric interactions between the toluoyl substituent in the anion and the methyl substituents on the ligands, which diminish the association between the eluent anion and the substrate cation and thus reduce the degree of chiral discrimination.

Chromatographic resolution using sodium (+)-*O,O′*-di-4-toluoyl-D-tartrate solution as the eluent is also more efficient for resolution of complexes with increased numbers of methyl-substituted ligands, although not with the same predicability as in the case above {e.g. $[Ru(bpy)_3]^{2+}$ (ECL = 120 cm) > $[Ru(bpy)_2(Me_2bpy)]^{2+}$ (ECL = 65 cm) ≈ $[Ru(bpy)(Me_2bpy)_2]^{2+}$ (ECL = 70 cm) compared with $[Ru(Me_4bpy)_3]^{2+}$ (ECL > 120 cm)}. The apparent anomaly in the resolution efficiency of $[Ru(Me_4bpy)_3]^{2+}$ may also have its origins in competing steric interactions, as described above.

The degree of aromaticity of the polypyridyl ligand also has a significant influence in the resolution efficiency. For example, the resolution of $[Ru(phen)_3]^{2+}$ was significantly more efficient than $[Ru(bpy)_3]^{2+}$ using both the (+)-tartrate salts as eluents.

The order of elution of the two enantiomeric forms was also observed to be significantly influenced by the chirality of the eluent. For example, elution of the complex $[Ru(bpy)_3]^{2+}$ with sodium (−)-*O,O′*-di-4-toluoyl-L-tartrate solution or sodium (−)-*O,O′*-dibenzoyl-L-tartrate solutions resulted in resolution with the first eluted band (Band 1) as the Δ-(−) enantiomer and the second eluted band (Band 2) as Λ-(+) enantiomer. This elution order is reversed when eluting with aqueous sodium (+)-*O,O′*-di-4-toluoyl-D-tartrate and sodium (+)-*O,O′*-dibenzoyl-D-tartrate (Table 3). This observation suggests the Δ enantiomer of the complex has a higher degree of association with the (−) forms of the two anions, reducing its effective charge (relative to the Λ enantiomer), and thus leading to the resolution.

However, this "band switching" was not observed in the complexes containing ligands with one or more methyl-substituents (e.g. $[Ru(bpy)_2(Me_2bpy)]^{2+}$ and $[Ru(Me_2bpy)_3]^{2+}$); in those cases the (−)-enantiomer was eluted first independent of the eluent or its chirality. This is presumably a result of the increased hydrophobic interactions between the Sephadex support and the methyl-substituted ligands, leading to the chirality of the Sephadex dominating the elution order of the enantiomeric forms. For the elution order of the enantiomers of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ to be dependent on the chirality of the eluent, the interaction between the complex and the eluent must be significantly greater than the interaction of the enantiomeric forms with the Sephadex support. The involvement of the support in the chromatographic resolution of dinuclear complexes has also been reported previously.[30] These simultaneous interactions of the target cation with the support itself and the chiral anion of the eluent may be cooperative or in opposition, with the consequence that the two enantiomeric forms of the eluent have unequal efficiencies in achieving the resolution of a particular substrate.

The study demonstrates the effectiveness of the technique for the chiral resolution of tris(bidentate) polypyridyl complexes of ruthenium, and provides an appreciation of the factors involved for efficient chiral resolution in terms of the nature of the interactions between the complex, Sephadex support and the chiral eluent.

X-ray Structural Studies

The X-ray crystal structures of (−)-$[Ru(Me_2bpy)_3]${(−)-*O,O′*-dibenzoyl-L-tartrate}·6 H_2O (**1**; Figure 4) and (+)-$[Ru(phen)_3]${(+)-*O,O′*-di-4-toluoyl-D-tartrate}·8 H_2O (**2**; Figure 5) are reported. The incorporation of an anion of known chirality allowed ready and unambiguous assignment of the absolute configuration of the respective cations as Δ and Λ. Such assignments are significant: while there have been a number of structural determinations of tris(bidentate)ruthenium(II) complexes containing polypyridyl ligands, a vast majority have involved racemic samples. There are in fact very few structural confirmations of chirality within complexes of this genre, and in view of recent interest in the control of the stereochemistry of polymetallic assemblies incorporating such centres as components,[6][7][49] such confirmations are timely. In this case, the determination of the chirality of the (+)-$[Ru(phen)_3]^{2+}$ cation as Λ

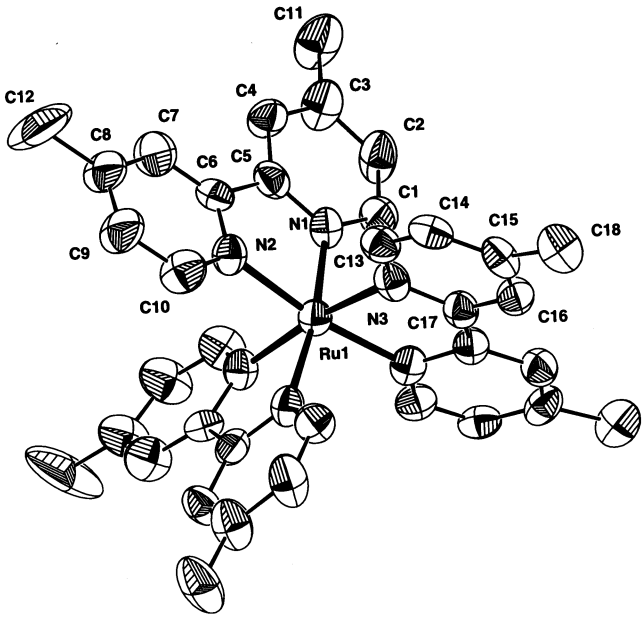
Table 3. Chromatographic elution order for the enantiomeric forms of $[Ru(pp)_2(pp')]^{2+}$ and $[Ru(pp)_3]^{2+}$ with various resolving agents as eluents

Complex	Elution band (Band 1 eluted first)	Elution order of the enatiomeric forms: sodium (−)-*O,O′*-dibenzoyl-L-tartrate[a]	sodium (+)-*O,O′*-dibenzoyl-D-tartrate[a]	sodium (−)-*O,O*-di-*p*-toluoyl-L-tartrate[a]	sodium (+)-*O,O*-di-*p*-toluoyl-D-tartrate[a]
$[Ru(bpy)_3]^{2+}$	Band 1	Δ-(−)		Δ-(−)	Λ-(+)
	Band 2	Λ-(+)		Λ-(+)	Δ-(−)
$[Ru(bpy)_2(Me_2bpy)]^{2+}$	Band 1				Δ-(−)
	Band 2				Λ-(+)
$[Ru(Me_2bpy)_2(bpy)]^{2+}$	Band 1				Δ-(−)
	Band 2				Λ-(+)
$[Ru(Me_2bpy)_3]^{2+}$	Band 1	Δ-(−)	Δ-(−)	Δ-(−)	Δ-(−)
	Band 2	Λ-(+)	Λ-(+)	Λ-(+)	Λ-(+)
$[Ru(phen)_3]^{2+}$	Band 1	Δ-(−)	Λ-(+)	Δ-(−)	Λ-(+)
	Band 2	Λ-(+)	Δ-(−)	Λ-(+)	Δ-(−)
$[Ru(Me_4bpy)_3]^{2+}$	Band 1	Δ-(−)		Δ-(−)	Δ-(−)
	Band 2	Λ-(+)		Λ-(+)	Λ-(+)

[a] Eluent concentration 0.075 M.

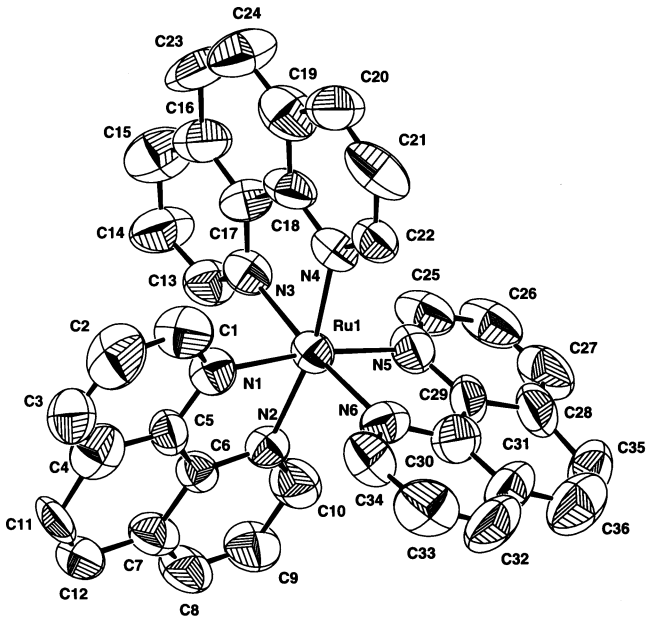
confirms earlier CD analyses based on exciton theory,[32][33][34][35][36] and the recent structural determination by Maloney and MacDonnell,[38] which utilised the technique of fractal analysis in the assignment. Bond lengths and angles are typical for such complexes.[38][50][51][52][53]

Figure 4. X-ray structure of one of the unique Δ-(−)-$[Ru(Me_2bpy)_3]^{2+}$ cations in compound (−)-$[Ru(Me_2bpy)_3]$\{(−)-*O,O′*-dibenzoyl-L-tartrate\} (**1**) which resides on a two-fold rotation axis; hydrogen atoms have been omitted for clarity



The packing diagram for the structure of **2** is shown in Figure 6, and attention is draw to a particular feature. The $[Ru(phen)_3]^{2+}$ cations form layers which alternate with layers containing water molecules. The (+)-*O,O′*-di-4-toluoyl-D-tartrate anions are positioned such that the tartrate backbone (containing the two carboxylate functionalities) reside in the water layer (hydrophilic), while the toluoyl rings penetrate into a virtually hydrophobic region in the complex cations where they essentially π-stack with the phenanthroline rings. The distance between the toluoyl and phenanthroline rings varies in the range 3.4−3.9 Å, which is consistent with π-stacking, for which a spacing of ca. 3.5 Å is considered normal.[54] While this present observation is made in the solid state, the interaction supports our proposal for the mode of association of anions with such complexes in solution (based on ^{1}H-NMR evidence),[30][31] which we assert is a major contributing factor to the mechanism of separation of complexes (and their stereoisomers) in cation-exchange chromatographic techniques involving the organic counter-anions in the eluents.

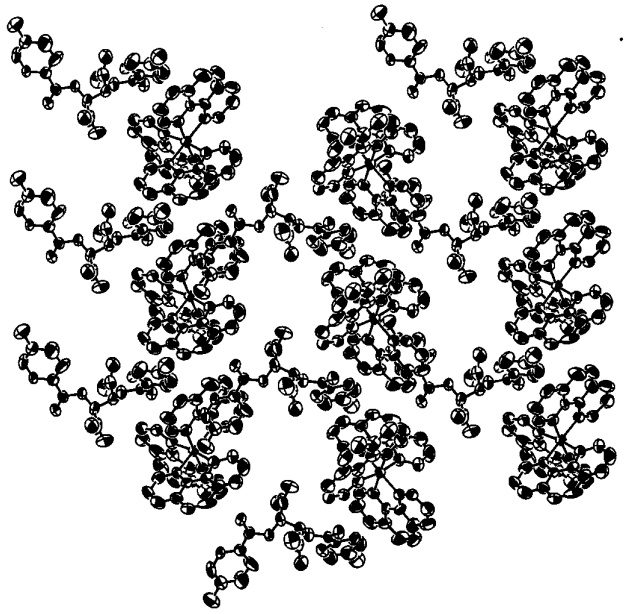
Figure 5. X-ray structure of the Λ-(+)-$[Ru(phen)_3]^{2+}$ cation in complex Λ-(+)-$[Ru(phen)_3]$\{(+)-*O,O′*-di-4-toluoyl-D-tartrate\}·8 H_2O (**2**); hydrogen atoms have been omitted for clarity



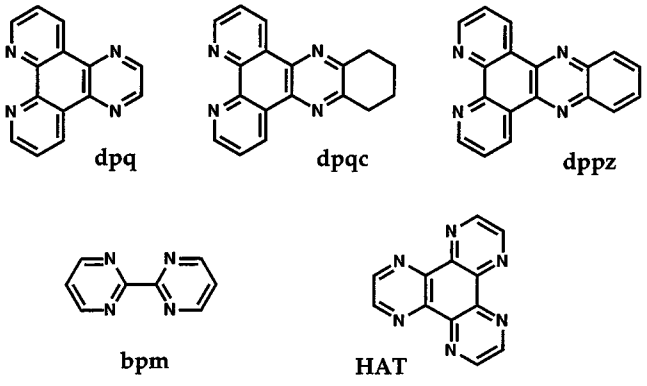
Chiral Resolutions of Heteroleptic Tris(bidentate) Species

To demonstrate the versatility of the chromatographic techniques and stereoretentive synthetic procedures, a range of bis-heteroleptic complexes $[Ru(pp)_2(pp')]^{2+}$ were also re-

Figure 6. Packing diagram for Λ-(+)-[Ru(phen)$_3$]{(+)-*O,O′*-di-4-toluoyl-D-tartrate}·8 H_2O (**2**) showing penetration of the toluoyl residues of the anion into the hydrophobic cationic layer; the carboxylate groups reside in the hydrophilic layer; water molecules have been omitted for clarity



solved. Each of the complexes [Ru(bpy)$_2$(pp′)]$^{2+}$ and [Ru(Me$_2$bpy)$_2$(pp′)]$^{2+}$ {pp′ = phen (1,10-phenanthroline), dpq (dipyrido[3,2-*d*:2,3′-*f*]quinoxaline), dpqc (dipyrido[3,2-*a*:2,3-*d*]-6,7,8,9-tetrahydrophenazine), and dppz {dipyrido[3,2-*a*:2,3′-*d*]phenazine)}, and [Ru(phen)$_2$(pp′′)]$^{2+}$ (pp′′ = dpq, dpqc, and dppz) were resolved by the cation-exchange chromatographic procedure on SP Sephadex C-25 support using sodium (−)-*O,O′*-dibenzoyl-L-tartrate solution as eluent. Aqueous K (+)-SbOtart solution was also used as eluent for the resolution of [Ru(phen)$_2$(dpqc)]$^{2+}$ and [Ru(phen)$_2$(dppz)]$^{2+}$. Additionally, [Ru(bpy)$_2$(dpqc)]$^{2+}$ and [Ru(bpy)$_2$(dppz)]$^{2+}$ were also obtained in specific enantiomeric forms by the reaction of the respective ligands with resolved [Ru(bpy)$_2$(py)$_2$]$^{2+}$.[19]



This general method for chiral resolution is significant as there have been a number of studies of the nature of the interaction of such complexes with polynucleotides, aimed at the assessment of their potential as photoprobes in sequencing and in cleavage reactions of DNA.[12][13][14]

Analogous bis-heteroleptic complexes [Ru(Me$_2$bpy)$_2$(bpy)]$^{2+}$, [Ru(Me$_2$bpy)(bpy)$_2$]$^{2+}$, [Ru(Me$_2$bpy)$_2$(phen)]$^{2+}$, and [Ru(bpy)(phen)$_2$]$^{2+}$ were also resolved chromatographically {aqueous sodium (+)-*O,O′*-dibenzoyl-D-tartrate solution eluent}. It is also noted that we have previously reported the chromatographic resolution of a tris-heteroleptic species, [Ru(phen)(Me$_4$bpy)(bpm)]$^{2+}$, using aqueous sodium (−)-*O,O′*-dibenzoyl-L-tartrate solution as eluent.[16]

The incorporation of potential bridging ligands such as 2,2′-bipyrimidine (bpm) or 1,4,5,8,9,12-hexaazatriphenylene (HAT) in such chiral tris(bidentate) metal centres provides the potential basis of stereochemical control in the construction of polymetallic ligand-bridged assemblies.[6][7] In such a context, we also chromatographically resolved the tris-homoleptic complexes [Ru(bpm)$_3$]$^{2+}$ and [Ru(HAT)$_3$]$^{2+}$ by these techniques using 0.1 M sodium (−)-*O,O′*-dibenzoyl-L-tartrate solution as eluent.

Summary

The chiral building blocks Δ- and Λ-[Ru(pp)$_2$(CO)$_2$]$^{2+}$ (where pp = bpy, phen, and Me$_2$bpy) were obtained by diastereoisomeric salt formation, and their enantiomeric purity established by ^{1}H-NMR spectroscopy using the chiral lanthanide-shift reagent [Eu(tfc)$_3$]. These species were demonstrated to undergo decarbonylation to form tris(bidentate) complexes with retention of stereochemical integrity under certain reaction conditions. Their absolute configurations were established by comparison of the configuration of the products with the the X-ray crystal structure determinations of the diastereoisomeric salts Δ-(−)-[Ru(Me$_2$bpy)$_3$]{(−)-*O,O′*-dibenzoyl-L-tartrate} and Λ-(+)-[Ru(phen)$_3$]{(+)-*O,O′*-di-4-toluoyl-D-tartrate}, and comparison of CD spectra with compounds whose configuration has previously assigned by exciton analysis.

The development of a cation-exchange chromatographic resolution procedure provided an efficient means of obtaining a wide range of enantiomerically-pure tris(bidentate)ruthenium(II) complexes containing polypyridyl ligands, which have application as chiral building blocks for oligomeric assemblies, or as chiral probes for biological molecules (e.g. polynucleotides, DNA).

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Experimental Section

Materials, Instrumentation, and Techniques: The following chemicals were used without further purification: 2,2′-bipyridine (bpy, 99+%; Aldrich), 1,10-phenanthroline (phen, 99+% anhydrous; Aldrich), 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy, 99%; Aldrich),

tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium-(III) {Eu(tfc)$_3$, 97%; Fluka}, ruthenium(III) chloride hydrate ($RuCl_3$, 99.9%; Strem), potassium hexafluorophoshate (KPF_6, 98%; Aldrich), 2,3-bis(2-pyridyl)pyrazine (dpp, 98%; Aldrich), 2,2′-bipyrimidine (bpm, 98+%; Lancaster), sodium hydroxide (BDH), sodium chloride (BDH), sodium toluene-4-sulfonate (95%; Aldrich), potassium antimonyl (+)-tartrate hydrate {K(+)-SbOtart, 99+%, $[\alpha]_D$ = +141; Aldrich}, (−)-*O,O′*-di-4-toluoyl-L-tartaric acid (98+%, $[\alpha]_D$ = −139; Fluka), (+)-*O,O′*-di-4-toluoyl-D-tartaric acid (97%, $[\alpha]_D$ = +139; Aldrich), (+)-*O,O′*-dibenzoyl-D-tartaric acid (99%, $[\alpha]_D$ = +117; Fluka), (−)-*O,O′*-dibenzoyl-L-tartaric acid (99+%, $[\alpha]_D$ = −117; Fluka), tetra-*n*-butylammonium bromide (TBABr, 99%; Aldrich), tetra-*n*-butylammonium iodide (TBAI, 98+%; BDH) and tetraethylammonium chloride (TEACl, > 98%; Fluka).

The ligands dpq,[55] dpqc,[56] and dppz[57] were prepared as reported previously.

$[Ru(pp)_2Cl_2]$,[58] $[Ru(CO)_2Cl_2]_n$, $[Ru(pp)(CO)_2Cl_2]$, and $[Ru(pp)_2(CO)_2](PF_6)_2$ pp = Me_2bpy, phen, and bpy),[59] $[Ru(OH_2)_6]$(toluene-4-sulfonate)$_2$,[60] and $[Ru(DMSO)_4Cl_2]$ (DMSO = dimethyl sulfoxide)[61] were prepared as reported previously. $[Ru(bpy)_3](PF_6)_2$, $[Ru(Me_2bpy)_3](PF_6)_2$, $[Ru(bpy)_2(Me_2bpy)](PF_6)_2$ $[Ru(Me_2bpy)_2(bpy)](PF_6)_2$, $[Ru(Me_4bpy)_3](PF_6)_2$ and $[Ru(phen)_3](PF_6)_2$ were synthesized in a manner similar to the literature methods,[62] except that they were isolated as the PF_6^- salts by addition of KPF_6. Their ^{1}H-NMR and electronic spectra were in agreement with those reported previously.[4][63][64] Δ- and Λ-$[Ru(bpy)_2(py)_2]^{2+}$ were obtained by diastereoisomeric salt fomation with the chiral anion *O,O′*-dibenzoyltartrate, as described previously.[18][19]

Trifluoromethanesulfonic acid (3 M) was distilled under vacuum prior to use. Trimethylamine *N*-oxide hydrate (TMNO, Aldrich) was sublimed under vacuum at 120°C and stored under argon. 4,4′,5,5′-Tetramethyl-2,2′-bipyridine (Me_4bpy) was kindly supplied by Michael Quagliotto and was prepared according to a literature method.[16][65] Silver antimonyl (−)-tartrate {Ag (−)-SbOtart} and silver antimonyl (+)-tartrate {Ag (+)-SbOtart} were prepared according to a literature method.[66]

Electronic spectra, elemental analyses, and optical rotations were recorded as described previously.[48] CD (circular dichroism) spectra were measured using either a Jobin Yvon Dichrograph 6 or a JASCO-500C spectropolarimeter. Mass spectra were recorded with a Fisons/VG Biotech Quattra (Altrinchem, U.K.) instrument which is a tandem mass spectrometer with quadrupoles for MS1 and MS2, each with a mass range of 4000 amu for single-charged ions, a hexapole collision cell and photomultiplier detectors. The samples were dissolved in acetonitrile (50−100 pmol/μl).

Chromatographic procedures were carried out using SP Sephadex C-25 cation exchanger as the support and aqueous sodium chloride, sodium toluene-4-sulfonate, sodium (−)-*O,O′*-dibenzoyl-L-tartrate, sodium (+)-*O,O′*-dibenzoyl-D-tartrate, sodium (−)-*O,O′*-di-4-toluoyl-L-tartrate or sodium (+)-*O,O′*-di-4-toluoyl-D-tartrate solutions as eluents. The tartrate salts were prepared by the neutralization of the respective acids with sodium hydroxide. The support was contained in a column approximately 100 cm long × 2 cm diameter and the flow rate was controlled at ca. 1.5 ml/min. When necessary, the column was sealed enabling the complex to be recycled several times down its length with the aid of a peristaltic pump: in these cases, an "effective column length" (ECL) for the separation represents the length of support travelled by the sample for visual band separation. All chromatography was carried out in subdued light.

X-Ray Crystal Structure Determinations: Crystals of (−)-$[Ru(Me_2bpy)_3]$[(−)-*O,O′*-dibenzoyl-L-tartrate} (**1**) and (+)-$[Ru(phen)_3]$[(+)-*O,O′*-di-4-toluoyl-D-tartrate} (**2**) were grown by slow concentration of aqueous solutions of the respective salts. Unique room-temperature diffractometer data sets ($T \approx 295$ K; monochromatic Mo-K_α radiation, $\lambda = 0.7107_3$ Å; 2θ/θ scan mode; 2−50°) were measured on an Enraf-Nonius CAD4 diffractometer, yielding N_o independent reflections, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the large-block least-squares refinements.

For both compounds, anisotropic thermal parameters were refined for all non-hydrogen atoms, except the oxygen atoms of the hydration water molecules (due to high thermal motion and disorder, see below). Hydrogen atoms were placed in calculated positions and were not refined. Two oxygen atoms in compound **1** were disordered and were successfully modelled with half occupancies {O(5w), O(6w), O(7w) and O(8w)}. Likewise in compound **2** two water molecules were also disordered and were modelled with half occupancies {O(1w), O(4w), O(5w) and O(7w)}. Conventional residuals R, R_w on F are quoted, statistical weights derivatives of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed, and computation was by the XTAL 3.4 program system, implemented by S. R. Hall.[67] A summary of crystal data and data collection is compiled in Table 4 and structures are shown in Figures 4 and 5; material deposited comprises all atomic coordinates and thermal parameters, complete bond lengths and angles and full non-hydrogen atom geometries.

Synthetic and Stereochemical Studies

Homoleptic Dicarbonyl Ruthenium(II) Complexes: The $[Ru(phen)_2(CO)_2](PF_6)_2$ species was converted to the bromide salt by metathesis with TBABr in acetone. For ^{1}H-NMR, UV/Vis, and ORD measurements, the bromide salt was converted to the chloride by anion-exchange chromatography. $[Ru(Me_2bpy)_2(CO)_2](PF_6)_2$ and $[Ru(bpy)_2(CO)_2](PF_6)_2$ were converted to the respective bromide salts by metathesis with TBABr in 2-butanone. The chloride salts were obtained as described above.

^{1}H NMR ([D$_3$]acetonitrile): *$[Ru(phen)_2(CO)_2]Cl_2$:* δ = 7.63 [m, 4 H], 8.25 [d, 2 H, J = 9 Hz], 8.29 [dd, 2 H, J = 5.5, 8 Hz], 8.36 [d, 2 H, J = 9 Hz], 8.71 [dd, 2 H, J = 5.5, 1.5 Hz], 9.10 [d, 2 H, J = 8 Hz], 9.60 [d, 2 H, J = 5 Hz]. *$[Ru(bpy)_2(CO)_2]Cl_2$*: δ = 7.42 [d, 2 H, J = 5 Hz], 7.51 [ddd, 2 H, J = 8, 6, 1 Hz], 7.94 [ddd, 2 H, J = 8, 6, 1 Hz], 8.22 [td, 2 H, J = 8, 1 Hz], 8.48 [td, 2 H, J = 8, 1 Hz], 8.82 [d, 2 H, J = 8 Hz], 8.96 [d, 2 H, J = 8 Hz], 9.14 [d, 2 H, J = 5 Hz]. − ^{1}H NMR ([D$_2$]dichloromethane): *$[Ru(Me_2bpy)_2(CO)_2]Cl_2$:* δ = 2.57 [s, 6 H], 2.61 [s, 6 H], 7.37 [m, 4 H], 7.78 [d, 2 H, J = 5.5 Hz], 9.04 [d, 2 H, J = 5.5 Hz], 9.11 [s, 2 H], 9.28 [s, 2 H]. UV/Vis [λ (ε), H_2O]: *$[Ru(phen)_2(CO)_2]Cl_2$:* 226 nm (57900), 274 (52100), 305 (15000). *$[Ru(bpy)_2(CO)_2]Cl_2$:* 210 nm (35600), 250 (26200), 306 (24800). *$[Ru(Me_2bpy)_2(CO)_2]Cl_2$:* 214 nm (43800), 252 (26900), 302 (23300), 312 (22900).

Λ-$[Ru(phen)_2(CO)_2]${(+)-SbOtart}$_2$·3 H_2O: $[Ru(phen)_2(CO)_2]Br_2$ (1.369 g, 2.019 mmol) was stirred in the minimum of distilled water for dissolution, and Ag(+)-SbOtart (1.589 g, 4.038 mmol) added. The mixture was stirred over glass balls for ca. 30 min in subdued light, then filtered through Celite to remove AgBr, and the filtrate concentrated to dryness. Yield 2.00 g, 90%. − $C_{33}H_{26}N_4O_{17}RuSb_2$: calcd. C 36.2, H 2.39, N 5.1%; found: C 36.2, H 2.25, N 5.0%.

(+)-$[Ru(phen)_2(CO)_2]${(+)-SbOtart}$_2$ was dissolved in a minimum volume of hot water and methanol added dropwise until the appearance of a faint cloudiness. The mixture was stored at 4°C

Table 4. Crystal data and summary of data collection for complexes **1** and **2**

Compound	(−)-[Ru(Me_2bpy)$_3$]{(−)-*O,O′*-dibenzoyl-L-tartrate}·6 H_2O (**1**)	(+)-[Ru(phen)$_3$]{(+)-*O,O′*-di-4-toluoyl-D-tartrate}·8 H_2O (**2**)
Molecular formula	$C_{54}H_{60}N_6O_{14}Ru$	$C_{56}H_{56}N_6O_{16}Ru$
Molecular weight	1118.2	1170.2
Crystal system	Monoclinic	Monoclinic
Space group	*C*2 (no. 5)	$P2_1$ (no. 4)
F(000)	2328	1212
Cell constants		
a [Å]	16.520(5)	10.597(2)
b [Å]	26.279(2)	24.921(2)
c [Å]	15.073(3)	11.634(2)
α [deg]	90	90
β [deg]	115.47(2)	99.78(1)
γ [deg]	90	90
V [Å^3]	5908(4)	3028.2(8)
Molecules/unit cell (*Z*)	4	2
D_c [g cm^{-3}]	1.257	1.265
μ [cm^{-1}]	3.3	3.3
A* min., max.	1.107, 1.138	1.125, 1.144
Crystal dimensions [mm]	0.62 × 0.40 × 0.36	0.42 × 0.42 × 0.38
σ cutoff	3σ	2σ
No. reflcections collected *(N)*	5326	5456
No. observed reflections (N_o)	4128	3512
No. parameters varied	655	680
R	0.058	0.064
R_w	0.067	0.071

overnight, the product collected and the precipitation procedure repeated a further two times. The precipitate was collected and either converted to the Cl^- salt by anion exchange or precipitated by the addition of KPF_6 to yield [Ru(phen)$_2$(CO)$_2$]Cl$_2$ or [Ru(phen)$_2$(CO)$_2$](PF_6)$_2$, respectively. Λ-(+)-[Ru(phen)$_2$(CO)$_2$]Cl$_2$: $[\alpha]_{365}$ (water) = +2320, $[M]_{365}$ (water) = +13640. Λ-(+)-[Ru(phen)$_2$(CO)$_2$](PF_6)$_2$: CD [λ (Δε), CH_3CN] = 211 nm (−55), 236 (−40), 262(−67), 278 (+315), 316 (−17).

The enantiomeric form was obtained in an analogous manner, using Ag(−)-SbOtart.

Δ-(−)-[Ru(phen)$_2$(CO)$_2$]Cl$_2$: $[\alpha]_{365}$ (water) = −2330 and $[M]_{365}$ (water) = −13710. Δ-(−)-[Ru(phen)$_2$(CO)$_2$](PF_6)$_2$: CD [λ (Δε), CH_3CN] = 211 nm (+54), 236(+41), 262 (+70), 278 (−322), 316 (+19).

Λ-[Ru(bpy)$_2$(CO)$_2$]{(+)-SbOtart}$_2$·2 H_2O: [Ru(bpy)$_2$(CO)$_2$]-{(+)-SbOtart}$_2$·2 H_2O was prepared in an identical manner to that described above, using [Ru(bpy)$_2$(CO)$_2$]Br$_2$ in place of [Ru(phen)$_2$-(CO)$_2$]Br$_2$. − $C_{29}H_{24}N_4O_{16}RuSb_2$: calcd. C 33.8, H 2.35, N 5.3; found C 33.8, H 2.31, N 5.3. − The diastereoisomer was recrystallized four times from methanol, the collected product being washed with cold methanol, ether, and air-dried. The product was then converted to the chloride and hexafluorophosphate salts as described above. Δ-(−)-[Ru(bpy)$_2$(CO)$_2$]Cl$_2$: $[\alpha]_{365}$ (water) = −1020 and $[M]_{365}$ (water) = −5570. Δ-(−)-[Ru(bpy)$_2$(CO)$_2$](PF_6)$_2$: CD [λ (Δε), CH_3CN] = 231 nm (−13), 244 (+11), 258 (−46), 278 (−31), 301 (+22), 319 (−47), 327 (+9).

The enantiomeric form was obtained in an analogous manner, using Ag(−)-SbOtart. Λ-(+)-[Ru(bpy)$_2$(CO)$_2$]Cl$_2$: $[\alpha]_{365}$ (water) = +1025 and $[M]_{365}$ (water) = +5545. Λ-(+)-[Ru(bpy)$_2$(CO)$_2$](PF_6)$_2$: CD [λ (Δε), CH_3CN] = 231 nm (+13), 244 (−10), 258 (+43), 278 (+31), 301 (−18), 319 (+45), 327 (−8).

(+)-[Ru(Me$_2$bpy)$_2$(CO)$_2$]{(+)-SbOtart}$_2$·H_2O: [Ru-(Me_2bpy)$_2$(CO)$_2$]{(+)-SbOtart}$_2$·H_2O was prepared in an identical manner to that described above using [Ru(Me_2bpy)$_2$(CO)$_2$]Br$_2$ in place of [Ru(phen)$_2$(CO)$_2$]Br$_2$. − $C_{33}H_{30}N_4O_{15}RuSb_2$: calcd. C 37.1, H 2.83, N 5.3; found C 37.4, H 2.72, N 5.3. − The disasteroisomer was recrystallized twice from methanol. The product was stirred with boiling methanol (ca. 20 ml) and collected by filtration while hot. The precipitate was washed with methanol, ether, and air-dried. The product was then converted to the chloride and hexafluorophosphate salts as described above. (+)-[Ru(Me_2bpy)$_2$-(CO)$_2$]Cl$_2$: $[\alpha]_{365}$ (water) = +840 and $[M]_{365}$ (water) = +5006.

Decarbonylation Reactions of Δ- or Λ-[Ru(pp)$_2$(CO)$_2$]$^{2+}$

Λ-(+)-[Ru(phen)$_3$]Cl$_2$: (+)-[Ru(phen)$_2$(CO)$_2$](PF_6)$_2$ (20 mg, 0.0247 mmol) was dissolved in 2-methoxyethanol (10 ml) and the solution purged with N_2 for 20 min prior to the addition of phen (44 mg, 0.247 mmol). TMNO (12 mg, 0.116 mmol) was then added and the reaction mixture stirred at room temperature in subdued light for 72 h. The reaction mixture was diluted with water and the product purified by cation exchange chromatography (SP Sephadex C25, eluent 0.2 M NaCl). The orange band was collected and precipitated as the PF_6^- salt by the addition of a saturated solution of KPF_6, which was collected by filtration and washed with water, ether, and air dried. Yield: 8 mg, 40%. NMR spectra were in agreement with those published previously for [Ru(phen)$_3$]$^{2+}$.[63][68] Λ-(+)-[Ru(phen)$_3$](PF_6)$_2$: $[\alpha]_{546}$ (CH_3CN) = +2000. The complex was converted to the chloride salt by metathesis from acetone solution using TEACl. $[\alpha]_D$ (water) = +1385; ref.[10][35] +1340.

The above reaction was repeated at a series of temperatures and reaction times, with all other conditions remaining identical, and $[\alpha]_D$ values measured as the chloride salts in water: 45°C for 24 h; yield 48%, $[\alpha]_D$ = +1330; 60°C for 6 h; yield 62%, $[\alpha]_D$ = +1134; 120°C for 3 h; yield 75%, $[\alpha]_D$ = +980. Microwave (low power) using ethylene glycol/10% water for 40 s; yield 78%, $[\alpha]_D$ = +938.

Δ-(-)-[Ru(bpy)$_3$]I$_2$: Bpy (30 mg, 0.197 mmol) was dissolved in 2-methoxyethanol (5 ml) and the solution purged with N_2 for 20 min. (−)-[Ru(bpy)$_2$(CO)$_2$](PF_6)$_2$ (15 mg, 0.0197 mmol) and TMNO (10 mg, 0.133 mmol) were added and the mixture stirred at room temperature for 72 h in subdued light, and after addition of water purification was achieved as described for Λ-(+)-[Ru(phen)$_3$]Cl$_2$.

Yield: 9 mg, 58%. The NMR spectrum was in agreement with the literature.[63][68] The complex was converted to the iodide salt by metathesis with TBAI in 2-butanone solution. $[\alpha]_D$ and $[M]_D$ (water) = −816 and −6740 respectively; ref.[9][35] $[\alpha]_D$ and $[M]_D$ = −819and −6750, respectively.

The above reaction was repeated at 120°C for 3 h with all other conditions identical; yield 81%, $[\alpha]_D$ = −254.

The above reaction was repeated at 120°C for 3 h with a 30-fold excess of bpy and 20-fold excess of TMNO with all other conditions identical; yield 85%, $[\alpha]_D$ = −300.

Λ-(+)-[Ru(Me$_2$bpy)$_3$]Cl$_2$: (+)-[Ru(Me$_2$bpy)$_3$]Cl$_2$ was formed by the decarbonylation of (+)-[Ru(Me$_2$bpy)$_2$(CO)$_2$](PF$_6$)$_2$ in the presence of an excess of Me$_2$bpy, but otherwise under identical conditions to those described for Λ-(+)-[Ru(phen)$_3$]Cl$_2$; yield 40%. The NMR spectrum was in agreement with that described previously.[63] Λ-(+)-[Ru(Me$_2$bpy)$_3$](PF$_6$)$_2$ $[\alpha]_{546}$ (CH$_3$CN) = +972 and $[M]_{546}$ = +9164. Chromatographically resolved Λ-(+)-[Ru(Me$_2$bpy)$_3$](PF$_6$)$_2$ (see below): $[\alpha]_{546}$ = +1045 and $[M]_{546}$ = +9845. (See above for X-ray structural determination of absolute configuration.)

The above reaction was repeated at 120°C for 3 h with all other conditions identical; yield 84%, $[\alpha]_D$ = +920.

Chromatographic Resolutions: The chromatographic resolutions of the mononuclear complexes were all achieved by cation-exchange chromatography (SP Sephadex C-25) using 0.075 M solutions of the eluent specified in the text. The impact of the enantiomeric identity of the eluent anion on the efficiency of the chromatographic resolution procedure {quoted as ECL for the chiral resolution (cm)}, and on the order of elution of the chiral forms of the cation (sign of optical rotation quoted at 589 nm, or the sign of Δε from the CD spectra at the MLCT absorption maximum at ca. 450 nm), was investigated by separately examining the resolution of complex {30 mg} with the eluents sodium (+)- and (−)-*O,O′*-dibenzoyltartrate and sodium (+)- and (−)-*O,O′*-di-4-toluoyltartrate.

Δ.Λ-[Ru(phen)$_3$]$^{2+}$: Chromatographic resolution was achieved using aqueous sodium (−)-*O-O′*-dibenzoyl-L-tartrate solution as the eluent (ECL ≈ 60 cm). The two bands were collected and the products isolated as the PF_6^- salts by addition of a saturated aqueous solution of KPF_6. The two products were converted to the chloride salts by anion exchange. By comparisons with the literature,[35][38] Band 1 (eluted first) was assigned as Δ-(−)-[Ru(phen)$_3$]$^{2+}$ and Band 2 (eluted second) as Λ-(+)-[Ru(phen)$_3$]$^{2+}$ with $[\alpha]_D$ (water) = −1310 and +1400 respectively (literature values of −1330 and +1340).[10] − CD [λ (Δε), CH$_3$CN]: Δ-(−): 227 nm (−19), 234 (33), 259 (437), 268 (−602), 296 (−72), 385 (+7), 419 (15), 464 (−22); Λ-(+): 227 (10), 234 (−33), 259 (−430), 268 (582), 296 (87), 385 (−7), 419 (−15), 464 (23).

Elution with sodium (−)-*O,O′*-dibenzoyl-L-tartrate, sodium (+)-*O,O′*-dibenzoyl-D-tartrate, sodium (−)-*O,O′*-di-4-toluoyl-L-tartrate and sodium (+)-*O,O′*-di-4-toluoyl-D-tartrate solutions demonstrated resolution at ECL ≈ 70 cm (Band 1 having a negative and Band 2 a positive rotation), ECL ≈ 30 cm (Band 1 positive), ECL ≈ 80 cm (Band 1 negative) and ECL ≈ 25 cm (Band 1 positive) respectively.

Δ.Λ-[Ru(bpy)$_3$]$^{2+}$: Chromatographic resolution was achieved for [Ru(bpy)$_3$]$^{2+}$ using aqueous sodium (−)-*O,O′*-dibenzoyl-L-tartrate solution at ECL ≈ 55 cm {$[\alpha]_{546}$ (water; I^- salt) − Band 1 = −824 and Band 2 = +817} (literature values of −819[9][35]), sodium (−)-*O,O′*-di-4-toluoyl-L-tartrate at ECL ≈ 30 cm (Band 1 negative rotation) and sodium (+)-*O,O′*-di-4-toluoyl-D-tartrate at ECL ≈ 120 (Band 1 positive rotation). − CD [λ (Δε), CH$_3$CN]: Δ-(−): 240 nm (24), 257 (−12), 278 (149), 292 (−331), 323 (21), 358 (12), 418 (23), 469 (−18); Λ-(+): 240 (−23), 257 (12), 278 (−147), 292 (347), 323 (−20), 358 (−12), 418 (−22), 469 (18).

Λ-(+)/Δ-(−)-[Ru(Me$_2$bpy)$_3$]$^{2+}$: Chromatographic resolution was achieved for [Ru(Me$_2$bpy)$_3$]$^{2+}$ using aqueous sodium (−)-*O,O′*-dibenzoyl-L-tartrate solution at ECL ≈ 30 cm, $[\alpha]_{546}$ and $[M]_{546}$ (CH$_3$CN; PF_6^-): Band 1 = −1060 and −10027 respectively and Band 2 = +1045 and +9845, respectively; sodium (−)-*O,O′*-di-4-toluoyl-L-tartrate at ECL ≈ 80 cm (Band 1 negative rotation); and sodium (+)-*O,O′*-di-4-toluoyl-D-tartrate at ECL ≈ 22 cm (Band 1 negative). − CD [λ (Δε), CH$_3$CN]: Δ-(−): 231 (54), 260 (−7), 277 (142), 292 (−351), 328 (18), 367 (11), 424 (21), 477 (−17); Λ-(+): 231 (−55), 260 (4), 277 (−141), 292 (357), 328 (−18), 367 (−11), 424 (−21), 477 (19).

Λ-(+)/Δ-(−)-[Ru(Me$_4$bpy)$_3$]$^{2+}$: Chromatographic resolution was achieved for [Ru(Me$_4$bpy)$_3$]$^{2+}$ using aqueous sodium (−)-*O,O′*-dibenzoyl-L-tartrate solution at ECL ≈ 20 cm, $[\alpha]_{546}$ and $[M]_{546}$ (CH$_3$CN; PF_6^-): Band 1 = −831 and −8530 respectively and Band 2 = 839 and +8631 respectively, and for sodium (−)-*O,O′*-di-4-toluoyl-L-tartrate eluent at ECL ≈ 40 cm (Band 1 negative rotation), sodium(+)-*O,O′*-di-4-toluoyl-D-tartrate eluent at ECL > 120 cm (Band 1 negative). − CD [λ (Δε), CH$_3$CN]: Δ-(−): 234 nm (49), 283 (180), 299 (−361), 329 (19), 366 (12), 418 (22), 468 (−17); Λ-(+): 234 (−48), 283 (−178), 299 (357), 329 (−19), 366 (−12), 418 (−22), 468 (17).

(+)/(−)-[Ru(Me$_2$bpy)$_2$(bpy)]$^{2+}$ and [Ru(Me$_2$bpy)(bpy)$_2$]$^{2+}$: Chromatographic resolution was observed for [Ru(Me$_2$bpy)$_2$(bpy)]$^{2+}$ and [Ru(Me$_2$bpy)(bpy)$_2$]$^{2+}$ using aqueous sodium (+)-*O,O′*-di-4-toluoyl-D-tartrate solution as eluent, where ECL ≈ 65 and 70 cm, respectively (Band 1 negative rotation).

[Ru(pp)$_2$(pp′)](PF$_6$)$_2$ {pp = bpy or Me$_2$bpy; pp′ = phen, dpq, dpqc, or dppz} and [Ru(phen)$_2$(pp′′)](PF$_6$)$_2$ {pp′′ = dpq, dpqc, or dppz} were synthesized by a literature procedure.[69] The respective [Ru(pp)$_2$Cl$_2$] precursor in 50% aqueous ethanol was refluxed in the presence of a slight excess of the third bidentate ligand for 2 h. Ethanol was evaporated from the solution, which was filtered before the dropwise addition of a saturated solution of KPF_6 to give an orange precipitate which was collected by filtration, washed with ice/water, and dried at 100°C. The complexes were purified by chromatography on alumina (acetonitrile eluent). the major band collected and concentrated to dryness. Yields were typically in the range 60−80%. Mass spectra *m/z* observed for all species were within 0.5 amu of the values calculated for [Ru(pp)$_2$(pp′)](PF$_6$)$^+$. ^{1}H-NMR spectra were consistent with the complex formulations. Visible spectra [λ_{max} (MLCT) (ε), CH$_3$CN]: [Ru(bpy)$_2$(phen)]$^{2+}$ 452 (14900); [Ru(bpy)$_2$(dpq)]$^{2+}$ 449 (14500); [Ru(bpy)$_2$(dpqc)]$^{2+}$ 451 (16200); [Ru(bpy)$_2$(dppz)]$^{2+}$ 448 (16400); [Ru(Me$_2$bpy)$_2$(phen)]$^{2+}$ 456 (14100); [Ru(Me$_2$bpy)$_2$(dpq)]$^{2+}$ 439 (13900); [Ru(Me$_2$bpy)$_2$(dpqc)]$^{2+}$ 452 (15200); [Ru(Me$_2$bpy)$_2$(dppz)]$^{2+}$ 443 (16100); [Ru(phen)$_2$(dpq)]$^{2+}$ 446 (17300); [Ru(phen)$_2$(dpqc)]$^{2+}$ 448 (14300); [Ru(phen)$_2$(dppz)]$^{2+}$ 439 (16100).

Chiral Resolution of [Ru(pp)$_2$(pp′)]$^{2+}$ Cations: All cations were chromatographically resolved on SP Sephadex C-25 support using as eluent aqueous 0.1 M sodium (−)-*O,O′*-dibenzoyl-L-tartrate solution containing 5% acetone to maintain complex solubility. In all cases, two distinct enantiomer bands were observable within ECL ≈ 1.5−2 m, and the separated bands were collected after 3 m of passage down the column. The enantiomer with a negative Δε in the CD spectrum at the absorption maximum (ca. 450 nm) was invariably eluted first; by comparison with the CD characteristics of similar complexes (see above), these were assigned the Δ

absolute configuration. CD [λ (Δε), CH_3CN]: $[Ru(bpy)_2(phen)]^{2+}$ Δ 380 nm (58), 457 (−56) and Λ 380 (−59), 457 (55); $[Ru(bpy)_2(dpq)]^{2+}$ Δ 400 (79), 461 (−67) and Λ 400 (−81), 461 (66); $[Ru(bpy)_2(dpqc)]^{2+}$ Δ 412 (62), 468 (−54) and Λ 412 (−64), 468 (54); $[Ru(bpy)_2(dppz)]^{2+}$ Δ 395 (64), 461 (−58) and Λ 395 (−70), 461 (58); $[Ru(Me_2bpy)_2(phen)]^{2+}$ Δ 400 (53), 465 (−54) and Λ 400 (−59), 457 (56.5); $[Ru(Me_2bpy)_2(dpq)]^{2+}$ Δ 415 (53.6), 476 (−38.8) and Λ 415 (−54), 476 (40); $[Ru(Me_2bpy)_2(dpqc)]^{2+}$ Δ 386 (51), 464 (−46) and Λ 386 (−60), 464 (46); $[Ru(Me_2bpy)_2(dppz)]^{2+}$ Δ 390 (63), 467 (−51) and Λ 390 (−70), 467 (51);$[Ru(phen)_2(dpq)]^{2+}$ Δ 396 (30), 456 (−52) and Λ 396 (−33), 456 (51); $[Ru(phen)_2(dpqc)]^{2+}$ Δ 407 (40), 467 (−54) and Λ 407 (−43), 467 (58); $[Ru(phen)_2(dppz)]^{2+}$ Δ 405 (41), 458 (−49) and Λ 405 (−55), 458 (61) {incomplete separation}.

The complexes $[Ru(phen)_2(dpqc)]^{2+}$ and $[Ru(phen)_2(dppz)]^{2+}$ could also be separated using aqueous 0.1 M potassium antimonyl (+)-tartrate solution (containing 10% acetone) as eluent (ECL ≈ 3 m).

The enantiomers of the complexes $[Ru(bpy)_2(dpqc)]^{2+}$ and $[Ru(bpy)_2(dppz)]^{2+}$ were also obtained by the stereoretentive reactions of Δ- or Λ-$[Ru(bpy)_2(py)_2]^{2+}$ with dpqc or dppz, in an analogous manner to that described previously.[18][19]

Synthesis of $[Ru(bpm)_3](PF_6)_2$: $[Ru(H_2O)_6]$(toluene-4-sulfonate)$_2$[60] (100 mg, 0.079 mmol) and bpm (62 mg, 0.394 mmol) were added to ethylene glycol (30 ml) and heated in a microwave oven (medium high) for 45 s. The reaction mixture was diluted with distilled water and purified by cation-exchange chromatography (SP Sephadex C-25, 0.2 M NaCl). The product was precipitated from the orange band by addition of KPF_6, collected and washed with water and diethylether. Yield = 140 mg, 62%. − $C_{24}H_{18}F_{12}N_{12}P_2Ru$: calcd. C 33.3, H 2.09, N 19.4; found: C 33.2, H 2.08, N 19.4. − UV/Vis data was in agreement with the literature.[70] − ^{1}H NMR ([D_3]acetonitrile): δ = 9.12 (dd, 6 H, *J* = 5, 2 Hz], 8.15 (dd, 6 H, *J* = 5, 2 Hz], 7.59 (t, 6 H, *J* = 5.5 Hz].

Resolution of $[Ru(bpm)_3]^{2+}$: Resolution was achieved by cation-exchange chromatography using 0.1 M sodium (−)-*O,O′*-dibenzoyl-L-tartrate as the eluent (ECL ≈ 150 cm). The two bands were collected and the enantiomers precipitated by the addition of a saturated solution of KPF_6, reprecipitated twice from acetone/water solution by the addition of KPF_6, collected, washed with cold water and diethyl ether. Comparisons with similar compounds,[15][19][35] enabled the assignment of Δ-(−)-$[Ru(bpm)_3]^{2+}$ (Band 1) $[\alpha]_{546}$ = −909 and $[\alpha]_D$ = −454, CD [λ (Δε), CH_3CN]: 235 nm (+51), 254 (+45), 268 (−210), 320 (−19), 411 (+22), 468 (−14) and Λ-(+)-$[Ru(bpm)_3]^{2+}$ (Band 2) $[\alpha]_{546}$ = +890 and $[\alpha]_D$ = +451, CD [λ (Δε), CH_3CN]: 235 nm (−48), 254 (−40), 268 (+200), 320 (+19), 411 (−21), 468 (+14).

Synthesis of $[Ru(HAT)_3](PF_6)_2$: $[Ru(HAT)_3]^{2+}$ was synthesiszd in a similar manner to that described by Kirsch-De Mesmaeker et al.[71] $[Ru(DMSO)_4Cl_2]$ (65 mg, 0.2 mmol) was dissolved in distilled water (60 ml) and degassed with N_2 for 20 min. HAT (233 mg, 0.99 mmol) was added and the mixture refluxed for 48 h. The reaction mixture was allowed to cool, then filtered to remove unreacted HAT. The orange product was purified by cation-exchange chromatography (SP Sephadex C-25, 0.2 M NaCl) and collected as described above. Yield 140 mg, 64%. − UV/Vis [λ (ε), CH_3CN]: 212 (63800), 274 (64300), 414 (sh), 436 (14180).[71][72] − ^{1}H NMR ([D_3]acetonitrile): δ = 9.40 (s, 6 H), 9.14 (d, 6 H, *J* = 2.5 Hz), 8.43 (d, 6 H, *J* = 2.5 Hz).

Resolution of $[Ru(HAT)_3]^{2+}$: Resolution was achieved by cation-exchange chromatography using 0.1 M sodium (−)-*O,O′*-dibenzoyl-L-tartrate solution as the eluent (ECL ≈ 80 cm). The two bands were collected and precipitated by the addition of a saturated solution of KPF_6, reprecipitated twice from acetone/water solution by the addition of KPF_6, collected, washed with cold water, and diethyl ether. Comparisons with similar compounds,[15][19][35] Λ-(+)-$[Ru(HAT)_3]^{2+}$ (Band 1) $[\alpha]_{546}$ = +974 and $[\alpha]_{589}$ = +623, CD [λ (Δε), CH_3CN]: 232 (+8), 250 (−15), 262 (+4), 282 (−6), 314 (+48), 406 (−13), 462 (+12) and Δ-(−)-$[Ru(HAT)_3]^{2+}$ (Band 2) $[\alpha]_{546}$ = −940 and $[\alpha]_{589}$ = −618, CD (λ nm (Δε), CH_3CN): 232 (−8), 250 (+15), 262 (−2), 282 (+7), 314 (−45), 406 (+14), 462 (−11).

Chiral Lanthanide Shift Reagent Studies: All complexes were converted to the Cl^- salts for the chiral-lanthanide shift reagent (CLSR) studies, which were performed on *rac*- and Δ- or Λ-$[Ru(bpy)_2(CO)_2]Cl_2$, $[Ru(phen)_2(CO)_2]Cl_2$, $[Ru(Me_2bpy)_2(CO)_2]Cl_2$ and $[Ru(Me_4bpy)_2(CO)_2]Cl_2$ in [D_3]acetonitrile for the former two and [D_2]dichloromethane for the latter two complexes. Mol ratios of [Complex]/[CLSR] varied from 0 to 2, depending on solvent and complex. Shift reagent studies were also performed on $[Ru(Me_2bpy)_3]Cl_2$ in [D_2]dichloromethane and $[Ru(Me_4bpy)_3]Cl_2$ in [D_2]dichloromethane and [D_3]acetonitrile. Complexes were dissolved in the solvent at concentrations between $3\cdot10^{-2}$ M and $3\cdot10^{-3}$ M.

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