Isolation of Geometric Isomers within Diastereoisomers of Dinuclear Ligand-Bridged Complexes of Ruthenium(II)

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The individual diastereoisomeric forms [*meso* (ΔΛ) and *rac* (ΔΔ and ΛΛ)] of the ligand-bridged dinuclear species $[\{Ru(phen)(Me_4bpy)\}_2(\mu\text{-bpm})]^{4+}$ [phen = 1,10-phenanthroline; Me_4bpy = 4,4′,5,5′-tetramethyl-2,2′-bipyridine; bpm = 2,2′-bipyrimidine] have been synthesized using chiral forms of the precursors $[Ru(phen)(Me_4bpy)(bpm)]^{2+}$ and $[Ru(phen)(Me_4bpy)(py)_2]^{2+}$. The *cis* and *trans* geometric isomers of both diastereoisomeric forms have been separated by cation exchange chromatography and characterized by NMR spectroscopy. We also report the first chiral resolutions of a heteroleptic tris(bidentate)ruthenium(II) complex, $[Ru(phen)(Me_4bpy)(bpm)]^{2+}$, and a heteroleptic bis(bidentate)bis(pyridine)ruthenium(II) complex, $[Ru(phen)(Me_4bpy)(py)_2]^{2+}$, in both cases using cation exchange chromatography.

Introduction

Ligand-bridged polymetallic molecular assemblies have potential application to photochemical devices,[1] and tris(bidentate)-ruthenium(II) centers involving polypyridyl ligands have frequently formed the basis of such assemblies by virtue of their favorable redox, spectral, and photophysical characteristics.[2] However, these moieties also introduce stereoisomerism, and there has been considerable interest by ourselves and others regarding stereochemical control in oligomeric assemblies.[3−18] Further, our initial studies have revealed that intramolecular electron and energy transfer processes depend on the spatial relationship of the components within such species.[16−20]

Dinuclear ligand-bridged complexes represent the simplest example of the genre, and stereochemical studies thus far have generally sought the stereoselective synthesis of individual diastereoisomeric or enantiomeric forms[3,4,6,7,9−14,16] or the separation of these individual stereoisomeric forms from a mixture.[5,6,16,18] However, in all such studies the individual metal centers have possessed two identical terminal (i.e. nonbridging) ligands; i.e., $[\{Ru(pp)_2\}_2(\mu\text{-BL})]^{n+}$ or alternatively $[\{Ru(pp)_2\}\{Ru(pp')_2\}(\mu\text{-BL})]^{n+}$ {pp and pp′ are symmetrical bidentate ligands such as 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) (Chart 1); BL is a bis-bidentate bridging ligand}. In the first case, only *meso* [ΔΛ (=ΛΔ)] and *racemic* (ΔΔ/ΛΛ) diastereoisomeric forms exist (with the latter being an enantiomeric pair; Figure 1), while in the second case there are analogous diastereoisomeric possibilities but with the ΔΛ and ΛΔ forms becoming enantiomeric.[5]

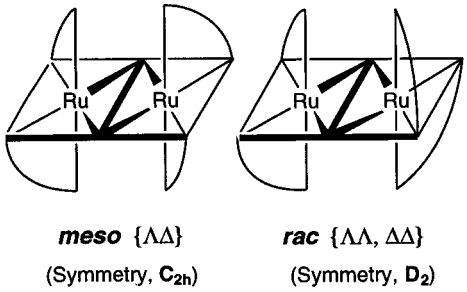
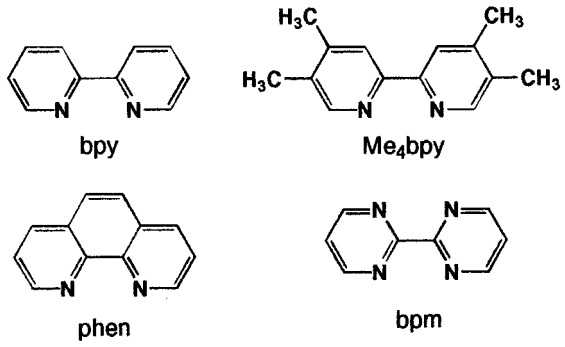


Figure 1. Schematic representation of the diastereoisomeric forms of the ligand-bridged dinuclear species $[\{Ru(pp)_2\}_2(\mu\text{-BL})]^{n+}$.

Chart 1



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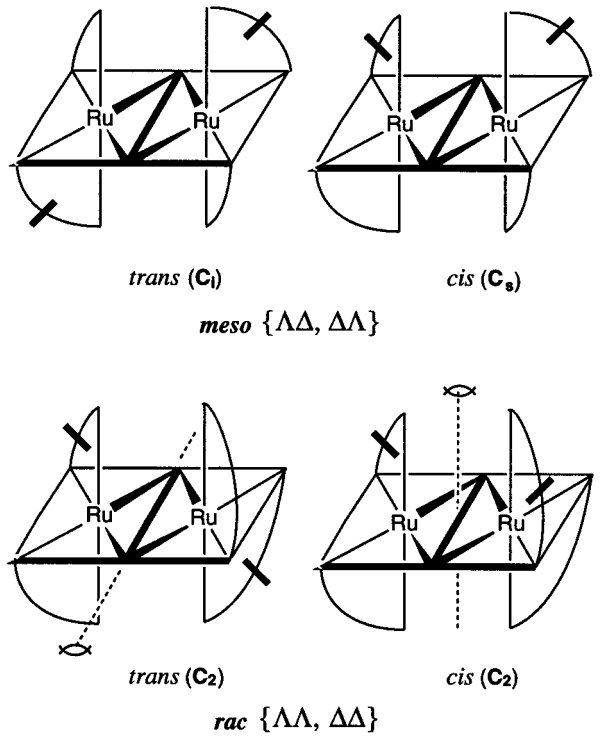

Figure 2. Schematic representation of the geometric isomers of the *meso*- and *rac*-$[\{Ru(pp)_2\}_2(\mu\text{-BL})]^{n+}$. For the *rac* forms, the C_2 axes are shown.

Clearly, the complexity in such dinuclear species may rapidly increase if the two terminal ligands on each center are not identical and/or the bridging ligand is not symmetrical. However, investigation of such systems has not been possible as the synthetic methodologies for such species have not been available. Recently reported synthetic schemes for tris(heteroleptic)ruthenium(II) centers via dicarbonyl precursors of the type $[Ru(pp)(pp')(CO)_2]^{2+}$ [21] allow extensive variation of the ligand environment, and together with the development of appropriate stereochemical techniques,[20] they provide the means to investigate these more complicated systems.

As a model for these studies, we chose the dinuclear complex $[\{Ru(phen)(Me_4bpy)\}_2(\mu\text{-bpm})]^{4+}$, in which the two terminal ligands (phen = 1,10-phenanthroline and Me_4bpy = 4,4′,5,5′-tetramethyl-2,2′-bipyridine) and the bridging ligand (bpm = 2,2′-bipyrimidine) are symmetrical. In such a case, there are again two possible diastereoisomeric forms (*meso* and *rac*), but each diastereoisomer may also possess two geometric forms (called *cis* and *trans*) in which the equivalent ligands on each metal center are disposed either on the same or on opposite sides of the plane of the bridge, respectively (Figure 2).

We report here the isolation and characterization (using NMR techniques) of all possible stereoisomeric forms of this complex by a combination of stereoselective syntheses and chromatographic separation methods.

Experimental Section

Materials. 1,10-Phenanthroline (phen; Aldrich), 2,2′-bipyrimidine (bpm; Lancaster), (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (*R*,*R*′-dach; Aldrich), potassium hexafluorophosphate (Aldrich), sodium toluene-4-sulfonate (Aldrich), ethylene glycol (Aldrich), 2-methoxyethanol (Fluka), and acetonitrile (Aldrich, 99.8%) were used as received. Trimethylamine *N*-oxide (TMNO) was obtained by vacuum sublimation at 120 °C of the dihydrate (Fluka). Aqueous solutions of sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate and sodium (−)-*O*,*O*′-di-4-toluoyl-L-tartrate were obtained by neutralization of the corresponding acids (Fluka) using sodium hydroxide. Pyridine (Ajax) and 3,4-lutidine (BDH) were dried (KOH) and distilled before use; all other solvents were of laboratory grade.

Measurements. ^1H and COSY experiments were performed on a Bruker Aspect 300 MHz NMR spectrometer (CD_3CN solutions). ORD (optical rotatory dispersion) curves were recorded using a Perkin-Elmer 141 polarimeter in a 1 dm cell. Specific rotation at λ: $[\alpha]_\lambda = 100\alpha/cl$, where α = absolute rotation (deg), c = concentration in g/100 cm^3, and l = cell path length (in dm). CD (circular dichroism) spectra were recorded in acetonitrile solution at concentrations of $\sim(1-3) \times 10^{-5}$ M at the University of Wollongong using a Jobin Yvon Dichrograph 6 instrument. CD spectra are presented as $\Delta\epsilon$ vs λ (nm). High-resolution mass spectra were obtained on a Brucker BioApex 47e ICR mass spectrometer with an electrospray source, using a ca. 2 μg/mL solution in methanol.

Elemental microanalyses were performed within the Department of Chemistry and Chemical Engineering at James Cook University of North Queensland.

Syntheses. The complexes $[Ru(phen)(CO)_2Cl_2]$, $[Ru(phen)(CF_3SO_3)_2(CO)_2]$ and $[Ru(phen)(Me_4bpy)(CO)_2](PF_6)_2$ were prepared using literature methods.[21]

4,4′,5,5′-Tetramethyl-2,2′-bipyridine (Me_4bpy) was synthesized by an adaption of a literature procedure.[22,23] Freshly distilled 3,4-lutidine (40 mL, 0.356 mol) was stirred with Pd/C (10%; 4 g) and the mixture refluxed for 13 days. The resulting solid was extracted (Soxhlet) with dichloromethane and decolorized with activated carbon (3 g) in refluxing dichloromethane. The solution was filtered through Celite, which was washed with several portions of hot toluene. The filtrate was evaporated to dryness, and the yellow residue was recrystallized from toluene to give a white crystalline product (22.5 g; 60%). ^1H NMR ($CDCl_3$): δ 2.28 (s), 2.33 (s), 8.11 (s), 8.36 (s).

$[Ru(phen)(Me_4bpy)(bpm)](PF_6)_2$. $[Ru(phen)(Me_4bpy)(CO)_2](PF_6)_2$ (30 mg; 0.0357 mmol) and 2,2′-bipyrimidine (22.6 mg; 0.143 mmol) were dissolved in 2-methoxyethanol (10 mL) and the solution deaerated with N_2 for 30 min. TMNO (27 mg; 0.36 mmol) was added, causing a rapid change from colorless to orange. The solution was refluxed for 3 h under subdued light and cooled, and the product was precipitated by the addition of a saturated aqueous solution of KPF_6 and collected. Further purification was achieved by cation exchange chromatography (SP Sephadex C-25; eluent 0.2 M NaCl). The major orange band was collected and the complex precipitated using KPF_6: it was reprecipitated twice by the addition of KPF_6 to an acetone/water solution of the complex, collected, washed with cold water (2 × 5 mL) and diethyl ether (2 × 10 mL), and dried in vacuo. Yield: 21 mg; 61%. Anal. Calcd for $RuC_{34}H_{30}F_{12}N_8P_2 \cdot C_3H_6O \cdot 2H_2O$: C, 43.4; H, 4.20; N, 10.7. Found: C, 43.5; H, 3.80; N, 10.5.

Chiral Resolution of $[Ru(phen)(Me_4bpy)(bpm)]^{2+}$. $[Ru(phen)(Me_4bpy)(bpm)](PF_6)_2$ was resolved into its Δ and Λ enantiomeric forms using cation exchange chromatography (SP Sephadex C-25; eluent 0.075 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate; effective column length (ECL) of 1.5 m). The two bands were collected, and the complexes were precipitated as their PF_6^- salts and purified as described above: band 1 (Δ), $\alpha_{589} = -3550°$; band 2 (Λ), $\alpha_{589} = +3680°$.

$[Ru(phen)(Me_4bpy)(py)_2](PF_6)_2$. $[Ru(phen)(Me_4bpy)(CO)_2](PF_6)_2$ (166 mg; 0.198 mmol) and pyridine (3 mL; excess) were dissolved in 2-methoxyethanol (30 mL), and the solution was deaerated with N_2 for 30 min. TMNO (55 mg; 0.73 mmol) was added causing a change from almost colorless to orange within 30 min. The solution was refluxed in subdued light under a nitrogen atmosphere for 3 h before cooling and precipitation with a saturated aqueous KPF_6 solution. The

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precipitate was purified using cation exchange chromatography (SP Sephadex C-25; eluent 0.2 M NaCl) and the product collected as described above. Yield: 130 mg; 70%. Anal. Calcd for $RuC_{36}H_{34}F_{12}N_6P_2$: C, 45.9; H, 3.61; N, 8.9. Found: C, 45.8; H, 3.59; N, 8.8.

Chiral Resolution of [Ru(phen)(Me$_4$bpy)(py)$_2$]$^{2+}$. [Ru(phen)(Me$_4$bpy)(py)$_2$](PF$_6$)$_2$ (130 mg) was converted to the chloride salt by anion exchange chromatography and applied to a column of SP Sephadex C-25 cation exchanger; the two enantiomers were separated using 0.075 M sodium (−)-*O*,*O*′-di-4-toluoyl-L-tartrate solution as eluent (ECL ∼ 2 m). Each band was collected, and the complexes were precipitated as their PF_6^- salts and purified (3×) as described above. Approximately 30 mg of each enantiomer was obtained: band 1 (Δ), $[\alpha]_{589} = -940°$; band 2 (Λ), $[\alpha]_{589} = +1000°$.

[Ru(phen)(Me$_4$bpy)(*R*,*R*′-dach)](PF$_6$)$_2$. The following reactions were carried out as a test for chiral purity of Δ- and Λ-[Ru(phen)(Me$_4$bpy)(py)$_2$]$^{2+}$, based on a method detailed previously.[4] In a typical experiment, [Ru(phen)(Me$_4$bpy)(py)$_2$](PF$_6$) (13.5 mg; 0.0143 mmol) and (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (*R*,*R*′-dach; 5 mg; 0.044 mmol) were dissolved in 50% aqueous ethylene glycol (2 mL), and the mixture was heated at 120 °C for 5 h under an inert atmosphere (N_2). The solution was cooled and the product precipitated using a saturated aqueous solution of KPF_6. The precipitate was collected and washed with copious amounts of diethyl ether and air-dried. Yield: 11.6 mg; 89%.

***meso*-[{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)](PF$_6$)$_4$.** Δ-[Ru(phen)(Me$_4$bpy)(bpm)](PF$_6$)$_2$ (15.6 mg; 0.0166 mmol) and Λ-[Ru(phen)(Me$_4$bpy)(py)$_2$](PF$_6$)$_2$ (19.4 mg; 0.0206 mmol) were dissolved in ethylene glycol (2 mL), and the solution was deaerated with N_2 and heated for 5 h at 100−110 °C. Upon cooling, water (3 mL) and saturated KPF_6 solution (2 mL) were added and the green precipitate was collected. Purification was achieved by cation exchange chromatography (SP Sephadex C-25; eluent 0.4 M NaCl). The green band was collected, and the complex was precipitated as the PF_6^- salt and purified as described above. Yield: 22.2 mg; 78%. As is the case in many dinuclear species of this type, microanalyses indicated the inclusion of acetone and water molecules in the crystals, rendering the data of dubious use in characterization. However, associated NMR and mass spectral data provided unambiguous assignment. Mass spectrum: observed *m*/*z* 1580.1702 (M^+: most abundant isotope peak within cluster); $[C_{60}H_{54}N_{12}Ru_2](PF_6)_3^+$ requires *m*/*z* 1580.1632.

Separation of Geometric Isomers of *meso*-[{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)]$^{4+}$. *meso*-[{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)](PF$_6$)$_4$ (40 mg) was converted to the chloride salt by anion exchange chromatography and the solution sorbed on to SP Sephadex C-25 cation exchanger. The complex was eluted using 0.25 M sodium toluene-4-sulfonate as eluent, and after continual recycling two bands were collected (ECL ∼ 12 m). Each band was collected, and the complexes were precipitated as the PF_6^- salts and purified (3×) as described above.

ΛΛ-[{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)](PF$_6$)$_4$. Λ-[Ru(phen)(Me$_4$bpy)(bpm)](PF$_6$)$_2$ (18 mg; 0.0191 mmol) and Λ-[Ru(phen)(Me$_4$bpy)(py)$_2$](PF$_6$)$_2$ (22.4 mg; 0.023 mmol) were dissolved in ethylene glycol (2 mL), and the solution was deaerated with N_2 and heated for 5 h at 100−110 °C. Upon cooling, water (3 mL) and saturated KPF_6 solution (2 mL) were added and the precipitate was collected. The green-brown solid was purified by cation exchange chromatography (SP Sephadex C-25; eluent 0.4 M NaCl). The resulting green band was collected, and the complex was precipitated as the PF_6^- salt and purified (3×) as described above. Yield: 27.2 mg; 83%.

Separation of Geometric Isomers of ΛΛ-[{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)]$^{4+}$. ΛΛ-[{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)](PF$_6$)$_4$ (60 mg) was converted to the chloride salt by anion exhange chromatography, sorbed onto SP Sephadex C-25 cation exchanger, and eluted using 0.25 M sodium toluene-4-sulfonate solution. On continual recycling of the samples, (ECL ∼ 20 m), two bands were collected, and the respective complexes precipitated as the PF_6^- salts and purified (3×) as described above.

Results and Discussion

Synthetic and Stereochemical Aspects. In developing a target dinuclear species of the type [{Ru(pp)(pp′)}$_2$(μ-BL)]$^{4+}$, we selected the system [{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)]$^{4+}$. The particular identity of the ligands was chosen for several reasons: the ^{1}H NMR spectrum of the Me$_4$bpy ligand comprises only singlets in the aromatic region, simplifying the spectral interpretation of its complexes; from earlier studies,[5,24] we have observed that the presence of phen and methyl-substituted "bpy"-type ligands facilitates chromatographic separation of the stereoisomers. Finally, bpm is a rigid symmetrical bridging ligand.

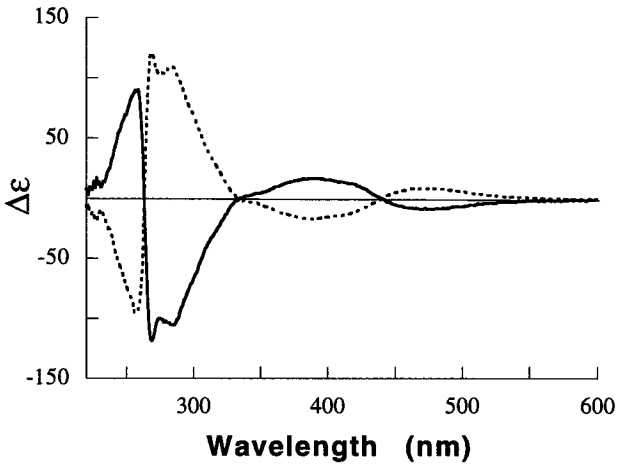

Figure 3. CD of [Ru(phen)(Me$_4$bpy)(bpm)]$^{2+}$ (CH_3CN solution): Δ (—); Λ (- - -).

Because of the potential isomeric complexity in the system, we directed our initial attention to the synthesis of the individual enantiomers of the two diastereoisomeric forms [i.e. ΔΔ and ΛΛ, ΔΛ (≡ΛΔ)], so that subsequent separation of the two geometric isomers (*cis* and *trans*) of each form was unencumbered by any uncertainty of the chiral identity. Such a stereoselective synthesis requires two chiral precursors: viz. the individual enantiomeric forms of the tris(heteroleptic) species [Ru(phen)(Me$_4$bpy)(bpm)]$^{2+}$, as well as the enantiomers of a [Ru(phen)(Me$_4$bpy)X$_2$]$^{2+}$ species (X = CO or py). In both instances, this posed an interesting challenge as there are no reported resolutions of either type of complex.

We have recently reported a general synthetic methodology for hetereoleptic tris(bidentate)ruthenium(II) complexes,[21,25] and the target complex [Ru(phen)(Me$_4$bpy)(bpm)]$^{2+}$ was conveniently obtained by this technique. We have also recently reported the routine resolution of mononuclear tris(bidentate)-ruthenium(II) species by cation exchange chromatographic methods,[20] and the complex was readily resolved using these techniques. The CD spectra of the two enantiomers are given in Figure 3. This is the first reported example of the chiral resolution of a hetereoleptic tris(bidentate)ruthenium(II) complex.

The second of the precursors was chosen as [Ru(phen)(Me$_4$bpy)(py)$_2$]$^{2+}$, rather than the dicarbonyl analogue. While both [Ru(pp)$_2$(py)$_2$]$^{2+}$ [3,4] and [Ru(pp)$_2$(CO)$_2$]$^{2+}$ [6] species have been shown to undergo the addition of a third bidentate ligand with retention of absolute configuration, the former complex reacts in higher yield, and our own studies have led to consistent resolution of bis(pyridine) complexes of this type into enantiomers by chromatographic methods. In the present instance, [Ru(phen)(Me$_4$bpy)(py)$_2$]$^{2+}$ was synthesized by decarbonylation

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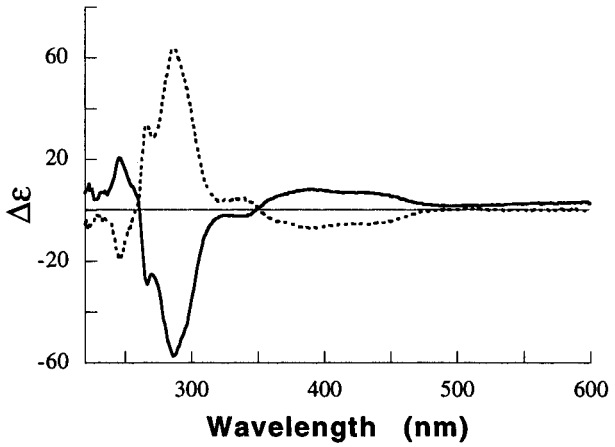


Figure 4. CD of $[Ru(phen)(Me_4bpy)(py)_2]^{2+}$ (CH_3CN solution): Δ (—); Λ (- - -).

of $[Ru(phen)(Me_4bpy)(CO)_2]^{2+}$ in the presence of pyridine, and it was chromatographically resolved. The CD spectra of the two enantiomers are shown in Figure 4. While complexes of the type $[Ru(pp)_2(py)_2]^{2+}$ (pp = a bidentate ligand) have been resolved into enantiomeric forms by diastereoisomeric formation involving chiral anions,[3,4] this is the first reported example of the resolution of a complex $[Ru(pp)(pp')(py)_2]^{2+}$ ($pp \neq pp'$), although we have previously reported the separation of geometrical isomers of such species in cases where pp and pp′ are unsymmetrical.[17]

The absolute configurations of (−)-$[Ru(phen)(Me_4bpy)(bpm)]^{2+}$ and (−)-$[Ru(phen)(Me_4bpy)(py)_2]^{2+}$ were assigned to the Δ form, using predictions made by the exciton theory[26−28] and comparisons of CD spectra with those of related species.[3,4]

The availability of the enantiomers of each of the precursors enables all diastereoisomers to be generated selectively, and route A in Scheme 1 is an example of a specific synthesis of one stereoisomer. In fact two specific diastereoisomers were obtained in this way: viz. ΛΛ and ΔΔ. In each case, cation exchange chromatography allowed the separation of two geometrical isomers, and these were characterized by a combination of 1D and 2D ^1H NMR studies, as described below.

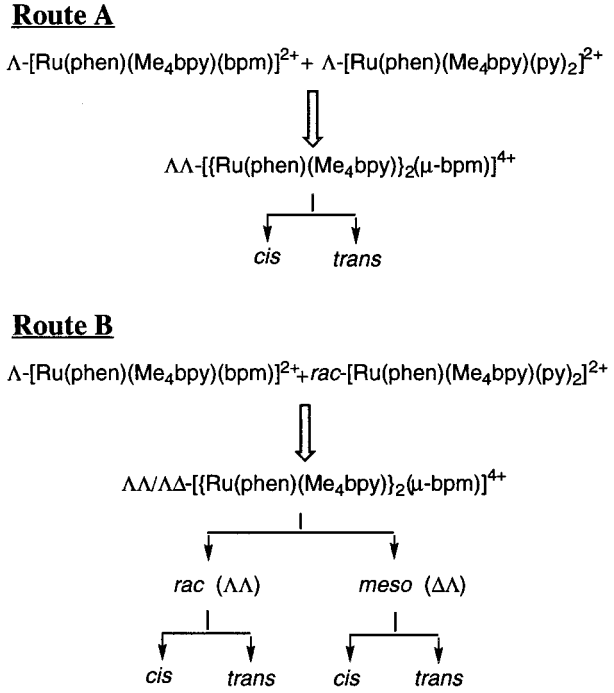
It is noted that in the chromatographic studies, the diastereoisomer separation occurred very much more easily than the separation of geometric isomers. Consequently, once that had been established, it was found more convenient to react either Δ- or Λ-$[Ru(phen)(Me_4bpy)(bpm)]^{2+}$ with *rac*-$[Ru(phen)(Me_4bpy)(py)_2]^{2+}$ producing a ΔΔ/ΔΛ (or ΛΔ/ΛΛ) mixture, which could then be readily separated into the individual diastereoisomers prior to the isolation of the geometric components (Scheme 1B).

The separation of the geometric isomers of the *meso* and *rac* diastereoisomeric forms of an analogous species $[\{Ru(Me_2bpy)(Me_4bpy)\}_2(\mu\text{-bpm})]^{4+}$ (Me_2bpy = 4,4′-dimethyl-2.2′-bipyridine) has also been achieved by similar techniques.[29]

NMR Studies. In the discussion of the NMR spectra, the conventional numbering schemes are used with the ligands phen, Me_4bpy, and bpm. In all four species, the two phen ligands are related by symmetry (as are the two Me_4bpy ligands), but in both cases the two halves of each ligand type are not equivalent (see below). While the assignments of resonances arising from these ligands can be made unambiguously, the actual ligand orientation is not specified. In principle, such additional assignments may be deduced by a detailed consideration of anisotropic effects,[5,6,16−18,30] but in the present case it was not necessary for the isomer characterization and was therefore not undertaken. For bpm, the nonprimed protons are positioned under the phen ligands in the *meso-cis* and *rac-trans* forms. In the *meso-trans* and *rac-cis* cases, the distinction between the rings is not important (as a consequence of symmetry), but the additional convention is adopted that the 4-positions are nearer the phen ligand.

For the bis(homoleptic) complex $[\{Ru(pp)_2\}_2(\mu\text{-BL})]^{4+}$, the point group symmetries of the *meso* and *rac* forms are C_{2h} and D_2, respectively (Figure 1). In the case of the bis(heteroleptic) species $[\{Ru(pp)(pp')\}_2(\mu\text{-BL})]^{4+}$ (Figure 2), for the *meso* diastereoisomer, the *trans* geometrical form adopts C_i point group symmetry, but that of the *cis* isomer is reduced to C_s. For the *rac* diastereoisomer, the symmetries of both the *cis* and *trans* geometrical isomers are C_2 but differ with respect to the orientation of the C_2 axis. However, the two halves of each nonbridging ligand are nonequivalent. In the case of the Me_4-bpy, this gives rise to four (4) singlet resonances in the aromatic region and four (4) $-CH_3$ aliphatic resonances. The phen ligands exhibit AMX and A′M′X′ coupling systems, with the expected coupling constants:[4] $J_{2,3} = J_{8,9} \sim 5$ Hz, $J_{2,4} \sim J_{7,9} = 1.5$ Hz, and $J_{3,4} = J_{7,8} \sim 8$ Hz. An AB-type coupling pattern, due to second-order effects ($J_{5,6} \sim 9$ Hz), was observable only in the *rac* (ΔΔ/ΛΛ) diastereoisomer.

Scheme 1. Synthetic Scheme for Isolation of Geometric Isomers of Diastereoisomeric Forms of $[\{Ru(phen)(Me_4Bpy)\}_2(\mu\text{-bpm})]^{4+}$ (A) through Stereoselective Synthesis of Individual Diastereoisomers of the Target Complex and (B) through a Combination of Partial Stereoselective Synthesis and Cation Exchange Chromatography[a]



[a] Synthetic procedures are indicated by double arrows, and chromatographic separations, by single arrows.

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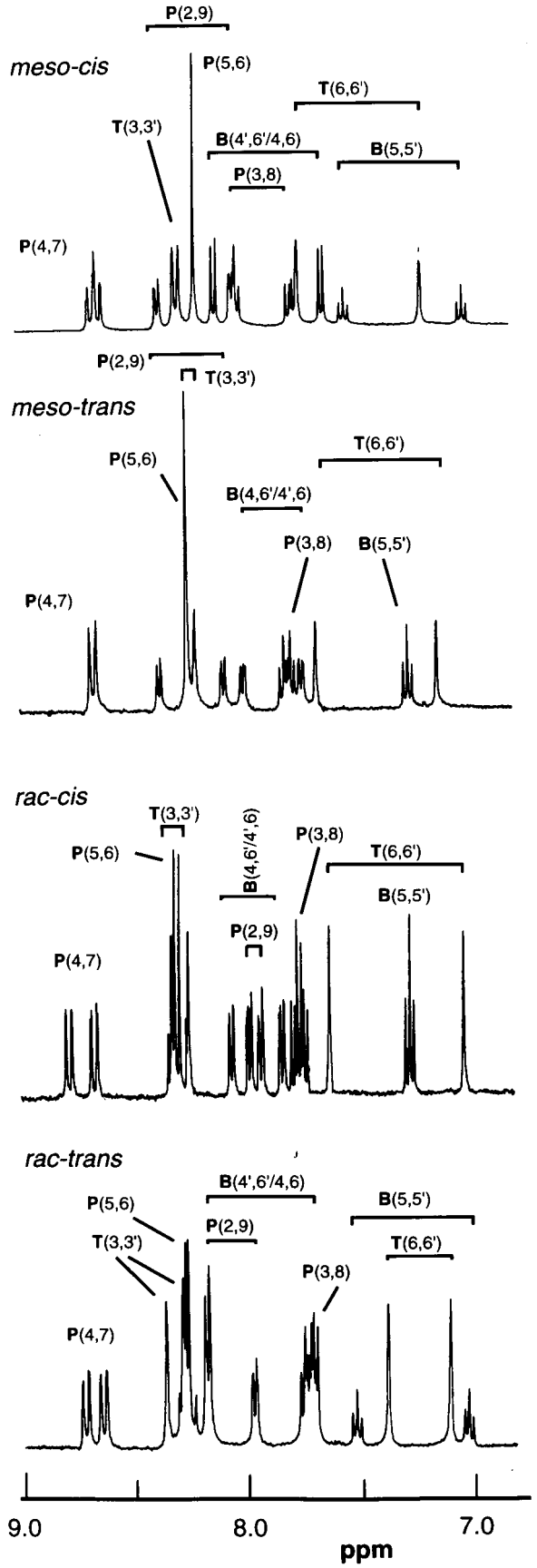

Figure 5. 300 MHz ^{1}H NMR spectra of [{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)]$^{4+}$: (a) $\Delta\Delta$-*cis*; (b) $\Delta\Lambda$-*trans*; (c) $\Lambda\Lambda$-*cis*; (d) $\Lambda\Lambda$-*trans*.

The ^{1}H NMR spectra of the four stereoisomers in the aromatic region are given in Figure 5. For each of the diastereoisomeric forms, the assignment of its geometric isomers as *cis* or *trans* was achieved using purely symmetry arguments, which could be applied as the precise form of the diastereoisomer was known from the synthetic route using enantiomerically pure precursors. The assignment is explained below for each specific isomer.

In *meso*-[{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)]$^{4+}$, the *trans* isomer (point group symmetry C_i) may be identified as the form that shows only one triplet (J = 5.7 Hz) since the center of symmetry renders the H5 and H5′ protons of the bpm bridge equivalent. The H4 and H6′ protons of the bpm bridge are also equivalent because of the inversion center, as are the H4′ and H6 protons. The resonances observed from these two sets of equivalent protons comprise two doublets of doublets arising from the $J_{4,5/4',5'}$ and the $J_{4,6/4',6'}$-type coupling (J = 5.7, 1.4 Hz; Figure 5b).

In the *meso-cis* form, the point group symmetry is lower (*viz.* C_s). The H5 and H5′ protons are no longer equivalent so that two triplets (J = 5.7 Hz) are observed. This nonequivalence of the two ends of the bpm ligand, along with the plane of symmetry which is orientated perpendicular to the plane of the bpm bridge incorporating the C5 and C5′ positions of the bpm and relates the H4/H6 and the H4′/H6′ protons, means that they each show only show a doublet (J = 4.3 Hz), arising from coupling to the H5 and H5′ protons, respectively. The comparison of the ^{1}H NMR spectra of the *meso-cis* and *meso-trans* forms are shown in Figure 5a,b, respectively.

For the *rac* diastereoisomer, both geometric isomers possess C_2 point group symmetry; however, in the *cis* isomers the C_2 axis is perpendicular to the plane of the bridging bpm ligand whereas in the *trans* isomer it is in the plane of the bpm ligand running through the long C5−C2−C2′−C5′ axis. In the former case, the axis renders the H5 and H5′ protons of the bridge equivalent, as well as the two pairs of protons H4/H6′ and H4′/H6. These equivalences are observed in the NMR spectrum as triplet (J = 5.7 Hz) and two doublets of doublets (J = 5.7, 1.4 Hz) resonances.

For the *trans* geometrical isomer, the C_2 axis renders the H4/H6 and the H4′/H6′ protons equivalent, giving rise to two doublets (J = 5.7 Hz). On the other hand, the H5 and H5′ protons are nonequivalent, resulting in a pair of triplets (J = 5.7 Hz). The comparison of the ^{1}H NMR spectra of the *rac-cis* and *rac-trans* forms are shown in Figure 5c,d, respectively.

Isomer Proportions. As the geometric isomers of each of the diastereoisomeric forms can be identified by ^{1}H NMR spectroscopy, the topic of stereospecificity in the synthesis may be revisited. The *cis*:*trans* ratios in the production of *meso*- and *rac*-[{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)]$^{4+}$ are 1:2 and 1:1, respectively, assessed from NMR studies by spectral integration. A study of models shows little difference in the interactions of the methyl groups of the Me$_4$bpy ligands in the two geometric forms of the *rac* diastereoisomer. However, in the *meso* form, there appears significant interaction of these groups specifically in the *cis* geometrical isomer, consistent with the observed proportions.

Conclusions

The *cis* and *trans* geometric isomers of both the *meso* and *rac* diastereoisomeric forms of the ligand-bridged dinuclear species [{Ru(phen)(Me$_4$bpy)}$_2$(μ-bpm)]$^{4+}$ have been separated by cation exchange chromatography and characterized by NMR spectroscopy. This is the first example of the isolation of geometric isomers of this type.

The individual diastereoisomers of the target complex were also synthesized stereoselectively. In developing the appropriate precursors, we have also achieved the first chiral resolutions of

a heteroleptic tris(bidentate)ruthenium(II) complex, $[Ru(phen)(Me_4bpy)(bpm)]^{2+}$, and a heteroleptic bis(bidentate)bis(pyridine)ruthenium(II) complex, $[Ru(phen)(Me_4bpy)(py)_2]^{2+}$, in both cases using cation exchange chromatography.

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