Chiral $[Ru(pp)_2(CO)_2]^{2+}$ Species (pp = Bidentate Polypyridyl Ligand) and Their Use in the Stereoselective Synthesis of Ligand-Bridged Dinuclear Complexes

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Polymetallic supramolecular assemblies have considerable potential for application to *photochemical molecular devices* (PMDs),[1,2] and the spatial interrelationship of the component metal centers is likely to influence intramolecular energy and electron transfer processes. In photobiological systems, there is no ambiguity in the geometry of the natural assembly, as the building blocks of the enzymic matrix are chiral amino acids or phosphate sugars. By analogy, in the construction of covalent artificial polymetallic assemblies, spatial control will depend on the availability of building blocks with predetermined stereochemistry: however, this problem has rarely been addressed.

We previously reported a general synthetic methodology for tris(heteroleptic) complexes of ruthenium(II), $[Ru(pp)(pp')(pp'')]^{2+}$ (pp etc. are bidentate polypyridyl ligands), via the dicarbonyl species $[Ru(pp)(pp')(CO)_2]^{2+}$.[3,4] The scheme may be extended to dinuclear and higher polynuclear species.[5]

Significantly, we have also shown that, in cases where pp and pp′ are unsymmetrical, and therefore geometric isomers of $[Ru(pp)(pp')CO_2]^{2+}$ may exist, the stereochemical relationship of the two bidentate ligands is retained on conversion to $[Ru(pp)(pp')(pp'')]^{2+}$.[6] We have now extended those studies to demonstrate the maintenance of chirality in such reactions and the utilization of the dicarbonyl species as "building blocks" in the formation of dinuclear species in which the chirality of the two metal centers is predetermined.

The dicarbonyl precursor complexes $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(Me_2bpy)_2(CO)_2]^{2+}$, and $[Ru(phen)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridine; Me₂bpy = 4,4′-dimethyl-2,2′-bipyridine; phen = 1,10-phenanthroline) were synthesized and characterized as outlined previously[3,4] and resolved by the following general method: $[Ru(pp)_2(CO)_2](PF_6)_2$ was converted to $[Ru(pp)_2(CO)_2]Br_2$ by metathesis in 2-butanone solution using $[(n\text{-}C_4H_9)_4N]Br$, collected, and dissolved in distilled water. The solution was stirred in the dark for 30 min with 2 equiv of Ag[(+)-SbOtart]. The AgBr precipitate was separated from the mixture by filtration and the water removed to yield $[Ru(pp)_2(CO)_2][(+)\text{-SbOtart}]_2$, which was fractionally recrystallized from methanol.

The enantiomeric purity of the recrystallized dicarbonyl complexes was determined by ^1H NMR techniques using the chiral lanthanide-induced shift reagent tris{3-[(trifluoromethyl)hydroxymethylene]-(+)-camphorato}europium(III), $Eu(tfc)_3$.[7] The complexes were converted to chloride salts using anion-exchange chromatography, and the ^1H NMR spectra were measured in CD_2Cl_2 solution {for $[Ru(Me_2bpy)_2(CO)_2]Cl_2$} or CD_3CN {for $[Ru(bpy)_2(CO)_2]Cl_2$ and $[Ru(phen)_2(CO)_2]Cl_2$} in the presence of increasing amounts of the shift reagent. The effect of the shift reagent in discriminating between the enantiomers of $[Ru(Me_2bpy)_2(CO)_2]^{2+}$ (CH_2Cl_2 solution) is shown in Figure 1. Greater induced shifts and selectivities were observed in dichloromethane, whereas differentiation between the enantiomers in acetonitrile required increased amounts of the chiral shift reagent, probably because of greater competition for the reagent by that solvent.

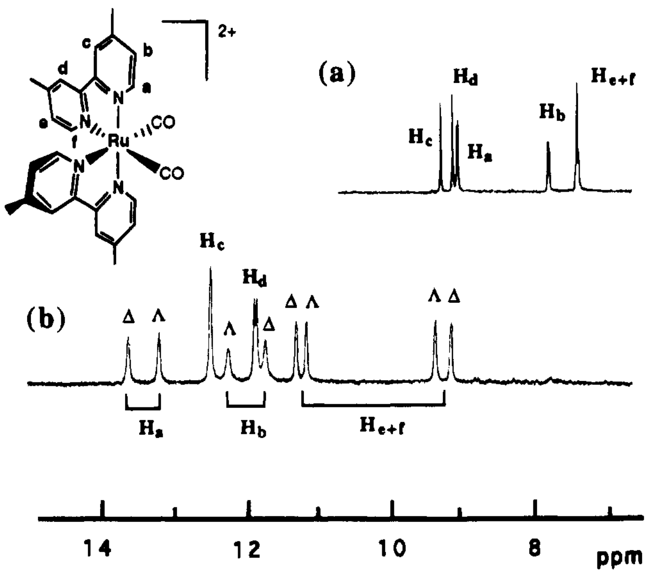

Figure 1. 300 MHz ^1H NMR spectra of $[Ru(Me_2bpy)_2(CO)_2]Cl_2$ in CD_2Cl_2 solution: (a) with no $Eu(tfc)_3$; (b) with added $Eu(tfc)_3$. [The numbering system for the Me₂bpy ligand in the complex is indicated in the structure (the two bidentate ligands are related by C_2 symmetry).]

The less soluble fractions in the resolutions of the dicarbonyl complexes $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(Me_2bpy)_2(CO)_2]^{2+}$, and $[Ru(phen)_2(CO)_2]^{2+}$ exhibited molecular rotations, $[M]_{365}$, of −4820°, +4430° and +12 080°, respectively, measured as the chloride salts. Following conversion to the hexafluorophosphate salt by metathesis, decarbonylation of $(-)\text{-}[Ru(bpy)_2CO_2](PF_6)_2$ (with 3 equiv of TMNO in 2-methoxyethanol solution containing 10 equiv of bpy, under stirring at room temperature for 3 days) yielded $\Delta\text{-}(-)\text{-}[Ru(bpy)_3](PF_6)_2$,[8] establishing the Δ configuration of the dicarbonyl precursor. The $\Delta\text{-}[Ru(bpy)_3](PF_6)_2$ product was converted to the iodide salt, which showed a molecular rotation $[M]_D$ of −6740°, compared to the literature value of −6750°,[9] indicating complete retention of configuration during the decarbonylation process. The decarbonylation reactions were carried out in the absence of light as a precautionary measure, although no photoracemization of the $[Ru(pp)_2(CO)_2]^{2+}$ species was observed under normal laboratory lighting conditions.

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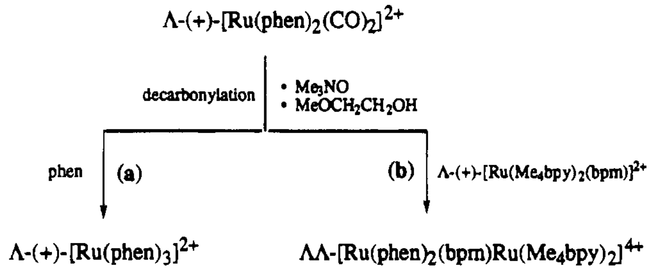
Scheme 1



Λ-(+)-[Ru(phen)$_3$]$^{2+}$ [8] was formed by decarbonylation of (+)-[Ru(phen)$_2$(CO)$_2$]$^{2+}$ in the presence of excess phen, but otherwise under conditions identical to those described above for the reaction of (−)-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$ with bpy (Scheme 1(a)). The product showed $[M]_{546}$ = +13 100°, indicating an optical purity of approximately 100%,[10] which was confirmed using the chiral lanthanide-induced shift reagent. The decarbonylation of (+)-[Ru(Me$_2$bpy)$_2$(CO)$_2$]$^{2+}$ under the same conditions in the presence of excess Me$_2$bpy realized (+)-[Ru(Me$_2$bpy)$_3$]$^{2+}$, for which $[M]_{546}$ = +6280° compared with $[M]_{546}$ = 6750° for the chromatographically-resolved product (see below), suggesting an optical purity of approximately 93% (96% as determined by the chiral lanthanide-induced shift experiment). These results indicate that the stereochemical integrities of Δ-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$ and Λ-[Ru(phen)$_2$(CO)$_2$]$^{2+}$ are maintained during the course of the decarbonylation reaction whereas (+)-[Ru(Me$_2$bpy)$_2$(CO)$_2$]$^{2+}$ undergoes minor racemization.

During the course of this work, a cation-exchange chromatographic technique was developed[11] for resolution of tris(bidentate)ruthenium(II) complexes based on the differential association of the enantiomeric forms with a chiral organic counteranion.[5,12−14] The complexes [Ru(Me$_2$bpy)$_3$]$^{2+}$ and [Ru(phen)$_3$]$^{2+}$ were resolved on a column of SP-Sephadex C-25 cation exchanger using 0.2 mol dm^{-3} NaCl/0.125 mol dm^{-3} sodium (−)-*O*-*O*′-dibenzoyl-L-tartrate solution as the eluent. In both cases, the enantiomers were clearly separated, and following isolation from the bands by precipitation as the PF$_6^-$ salts, the molecular rotations $[M]_{546}$ (acetonitrile solution) for [Ru(Me$_2$bpy)$_3$](PF$_6$)$_2$ were −6950° (eluted first) and +6750° and those for [Ru(phen$_3$](PF$_6$)$_2$ were −12 540° (eluted first) and +12 740°. The latter complex was also converted to the chloride salt, and $[\alpha]_D$ values (aqueous solution) of −1310 and +1400° were obtained (literature values of −1330 and +1340°).[10]

The chromatographic resolution technique was also extended to mononuclear ruthenium(II) complexes containing bridging ligands [Ru(pp)(pp′)(BL)]$^{2+}$: [Ru(Me$_4$bpy)$_2$(bpm)](PF$_6$)$_2$ (bpm = 2,2′-bipyrimidine and Me$_4$bpy = 4,4′,5,5′-tetramethyl-2,2′-bipyridine) was synthesized and resolved in this manner, giving $[M]_{546}$ values of −4440 and +4750° for the enantiomers as PF$_6^-$ salts in acetonitrile solution.

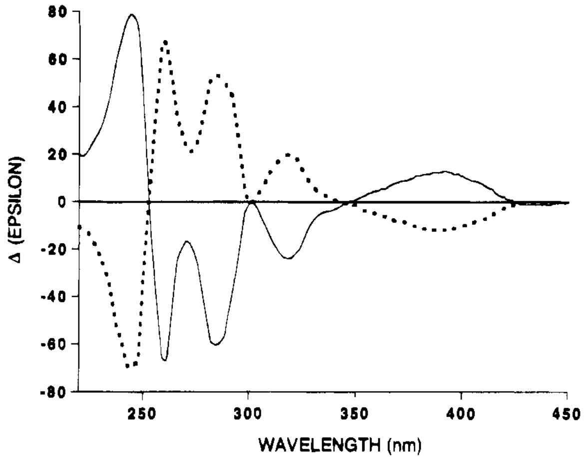


Figure 2. CD spectra of [(phen)$_2$Ru(bpm)Ru(Me$_4$bpy)$_2$](PF$_6$)$_4$ (acetonitrile solution): ΔΔ enantiomer (—); ΛΛ enantiomer (•••).

The synthesis of dinuclear species may be achieved by reaction under decarbonylation conditions of a dicarbonyl precursor {[Ru(pp)(pp′)(CO)$_2$]$^{2+}$} with the tris(bidentate) complex [Ru(pp)(pp′)(BL)]$^{2+}$ containing a bridging ligand.[5] In the present case (+)-[Ru(Me$_4$bpy)$_2$(bpm)](PF$_6$)$_2$ was added to a solution of 2-methoxyethanol containing 4 equiv of Λ-(+)-[Ru(phen)$_2$(CO)$_2$](PF$_6$)$_2$ and 4 equiv of TMNO, and the mixture was stirred at 30−35 °C in the dark for 14 days to yield ΛΛ-[(phen)$_2$Ru(bpm)Ru(Me$_4$bpy)$_2$](PF$_6$)$_2$ (Scheme 1(b)), confirmed by ^{1}H NMR measurements.[5] The NMR spectrum also indicated the presence only a very minor amount (<2%) of the ΛΔ diastereoisomer, confirming retention of chirality during the decarbonylation reaction. Accordingly, the absolute configuration of (+)-[Ru(Me$_4$bpy)$_2$(bpm)]$^{2+}$ can be confirmed as Λ, consistent with the configuration/rotatory dispersion relationship reported for [Ru(bpy)$_3$]$^{2+}$, [Ru(phen)$_3$]$^{2+}$, and their bis(heteroleptic) analogues.[8,15−17] The ΔΔ isomer was obtained by reacting Δ-(−)-[Ru(Me$_4$bpy)$_2$(bpm)](PF$_6$)$_2$ with 3 equiv of *rac*-[Ru(phen)$_2$(CO)$_2$](PF$_6$)$_2$ and 3 equiv of TMNO in 2-methoxyethanol at reflux for 3 h. The two diastereoisomers formed (ΔΔ and ΔΛ) were separated by ion-exchange chromatography (SP Sephadex C-25 cation exchanger) with 0.25 mol dm^{-3} sodium toluene-4-sulfonate as eluent.[5]

The circular dichroism of the ΔΔ and ΛΛ forms of [(phen)$_2$Ru(bpm)Ru(Me$_4$bpy)$_2$]$^{4+}$ are shown in Figure 2, demonstrating the enantiomeric nature of the two species.

The results reported exemplify the application of our synthetic methodology to the synthesis of an extended range of dinuclear species from the precursors [Ru(pp)(pp′)(CO)$_2$]$^{2+}$ and [Ru(pp)(pp′)(BL)]$^{2+}$, where pp and pp′ may or may not be identical. Furthermore, these building blocks enable the predetermination of the stereochemistry of the metal centers in dinuclear species, and in this sense the study is complementary to an earlier report.[18] However, the present scheme has greater versatility in terms of the variation of ligand environment and is more readily extended to the synthesis of higher nucleate assemblies.[3,4,19] The methodology will be exploited to enable us to probe the effect of stereochemical aspects on electron and energy transfer processes in such assemblies.

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