Ligand Selective Monosubstitution with Complete Enantiomeric Retention in Ruthenium Bis(bipyridine) Complexes

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Ruthenium bis(bipyridine) compounds of the type Ru(bpy)$_2$(X)(Y) possess extensive coordination and photo/electrochemical properties,[1] along with varied and complex chiral attributes such as: the interconversion between *cis*- and *trans*- isomers,[2] diastereomerically controlled synthesis,[3] and the generation and control of atropisomeric chirality.[4] However, despite such efforts by ourselves and other research groups, the ability to retain what may be seen as the most essential chiral feature of these systems, the Δ or Λ chirality around the ruthenium center on mono-ligand substitution without racemization, has remained elusive.

This inability to perform enantioretaining monosubstitution lies essentially in the fact that conventional thermal methods are not (typically) bond selective. Previously we described the synthesis and stereochemistry associated with the molecule *cis*-[Ru(bpy)$_2$(DMSO)(Cl)]PF$_6$,[3] and from our previous experience with these compounds, we were aware that we could selectively excite the ruthenium−sulfoxide bond over the adjacent ruthenium−chloride bond. Thus we felt it would be possible, in principle, to selectively substitute the sulfoxide group for a new ligand via a photochemical process.

The work detailed below reveals a new concept, that the sulfoxide moiety (DMSO) of enantiopure Δ- or Λ-*cis*-[Ru(bpy)$_2$(DMSO)(Cl)]PF$_6$ (**1**) can be specifically monosubstituted for a variety of ligands via irradiation of either the LC (288 nm) or MLCT (420 nm) bands, resulting in new products with complete Δ/Λ enantiomeric retention around the ruthenium center. The enantioretaining nature of these reactions can be seen by the retention of the 1st positive and 2nd negative Cotton effects (for the Λ isomer) in the LC region (250−330 nm) of the CD spectra for all ligands studied, which corresponds to the orientation of the two bipyridine groups around the Ru center (Figure 1).

Additionally, it is noted that the outcome of these reactions further resulted in inversions of the bisignate Cotton effects arising from the MLCT transitions (350−550 nm). This is not related to the Δ/Λ configuration around the metal center (as verified by the retention the bisignate CD coupling in the LC region), but indicates a subtle change in the stereochemistry of these transitions.

Initially, the anions F^-, Cl^-, I^-, and SCN^- were employed as new ligands to test if this photochemical approach to enantioretaining substitution was possible (Scheme 1). Remarkably all of these species were found to replace the sulfoxide ligand, showing quantitative conversion of **1** with complete retention of configuration. The reactions proceed by initially replacing the sulfoxide group; then at longer irradiation times, the chloride is also replaced as a result of the new ligands excess of approximately 10^5:1. However, when an I^- ligand was employed in a 1:1 ratio under the same conditions, only the enantiopure monosubstituted product was formed, showing that monosubstitution may be achieved, without bis-substitution contamination, by the amount of new ligand used. In contrast to this new photochemical method, the conventional thermal reaction as typified by the reaction with I^- results in the bisiodide substituted racemic product, *rac*-Ru(bpy)$_2$(I)$_2$. With the success of these simple ligands, we investigated the pyridyl ligand 4,4′-bipyridine (4,4′-bpy), which possesses two coordination sites. In particular, the ability to coordinate pyridyl groups with complete enantiomeric control is crucial, as pyridyl ligand coordination to numerous transition metals, including ruthenium, has shown great potential for the generation of useful molecular architectures[5,6] and bio-active species;[7] this reaction

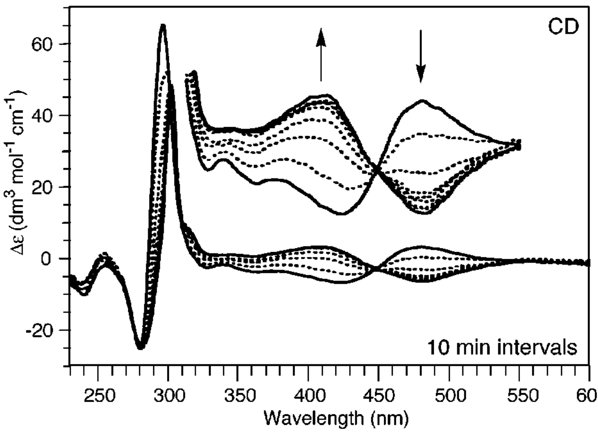
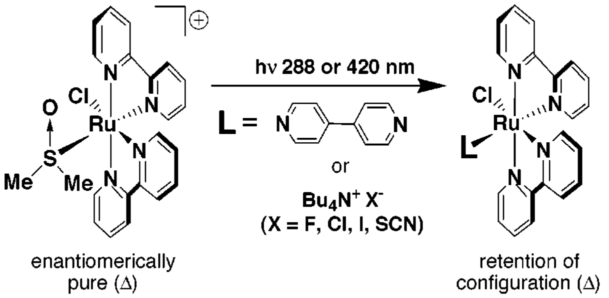


Figure 1. Variation in the CD spectra on substitution of the DMSO ligand of the Λ isomer of **1** for Cl^-.

Scheme 1. Bond Selective Photoinduced Substitution of the Sulfoxide Ligand in Δ-*cis*-Ru(bpy)$_2$(DMSO)(Cl)]PF$_6$ (**1**) by 4,4′-bpy, F−, Cl−, I−, and SCN− with Enantioretention (the Product Charge is Omitted for Clarity)



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was also found to proceed with complete retention of the enantiomeric configuration, in high chemical yield, to give Δ-*cis*-$[Ru(bpy)_2(4,4'\text{-bpy})(Cl)]^+$ (**2**).

The essential synthetic procedure is very simple. To 3 mL solutions of Λ-*cis*-$[Ru(bpy)_2(DMSO)(Cl)]^+$ (**1**) at 10^{-6} M in either 1,2-dichloroethane, MeCN, or THF/MeOH were added the new ligands (F^-, Cl^-, I^-, and SCN). In the weak intensity irradiation conditions employed for these reactions, MeCN was not found to be a competing coordinating ligand. These concentrations were used so that the reactions could be conveniently followed by either UV−vis or CD spectroscopy, or by chiral phase HPLC. The reaction mixtures were then irradiated using a Xe lamp (0.5 mW cm^{-2}) fitted with a monochromator to give wavelengths of either 288 or 420 nm (±5 nm); the enantioretaining nature of the reactions was found to be independent of the excitation wavelength. In all cases, after reaction times of 17−60 min, it was found that the reaction proceeded with 100% conversion of the starting material (as revealed by CD, UV−vis spectroscopy and HPLC analysis) to form the monosubstituted product (with small amounts of the bisproduct in the cases of ligand excesses of 10^5:1, as discussed previously). With the confirmation that this methodology worked at “analytical concentrations”, a conventional reaction concentration of 0.01 M of **1** was utilized for the more “practical” 4,4′-bpy ligand to evaluate if concentration affected the outcome of the reaction and, thus, the procedures applicability at these concentrations. The reaction was found to occur not only with complete enantioretention, but also with excellent efficiency, with the weak light source giving complete conversion from **1** to **2** in 10 h.

Notably, the 4,4′-bpy ligand only displaces the sulfoxide and never the chloride, even at long reaction times. This monosubstitution arises from a 4,4′-bpy excess of only 10:1 rather than the 10^5:1 previously employed. Further, and crucially, the 4,4′-bpy was only coordinated through one of the nitrogens, leaving the other free for further coordination to other species, as confirmed by X-ray analysis (Figure 2).[8] In this case, the crystal was grown from a racemic sample of **1** irradiated under the same conditions in the presence of 4,4′-bpy. This is a result of far-reaching consequence for the subsequent facile, rational design of chirally sophisticated molecules and materials.

The photoinduced bond-selective substitution of the Ru−S bond over the Ru−Cl bond in $[Ru(bpy)_2(DMSO)(Cl)]^+$ (**1**) was evaluated by determination of the quantum yield (Φ) for the replacement of the sulfoxide by SCN^-. Quantum yields were determined from CD and UV−vis spectral changes, carried out in deaerated 1,2-dichloromethane solution, and was found to be 0.6. Light intensity for irradiation experiments were determined by using ferrioxalate actinometry.[9] The quantum yield for replacement of the Ru−chloride in this molecule could not be determined due to its photoinertness, cf. the Ru−sulfoxide bond. This clearly shows that the photoreactivity of the Ru−chloride bond is significantly lower than that of the Ru−sulfoxide bond. Confirmation of quantitative enantioretention for these reactions is obtained by comparing the values of the molar CDs for enantiopure Λ-*cis*-$Ru(bpy)_2(Cl)_2$[10] with that of the Λ-*cis*-$Ru(bpy)_2(Cl)_2$ formed in the photoreaction of Λ-*cis*-$[Ru(bpy)_2(DMSO)(Cl)]^+$ with Bu_4NCl; these are found to be identical, confirming quantitative enantioretention. The efficiency of this reaction is such that the reaction carried out at 1 M using *cis*-$[Ru(bpy)_2(DMSO)(Cl)]PF_6$ (**1**) and an Xe light source, with a $\lambda > 420$ nm filter, went to completion in 4 h.

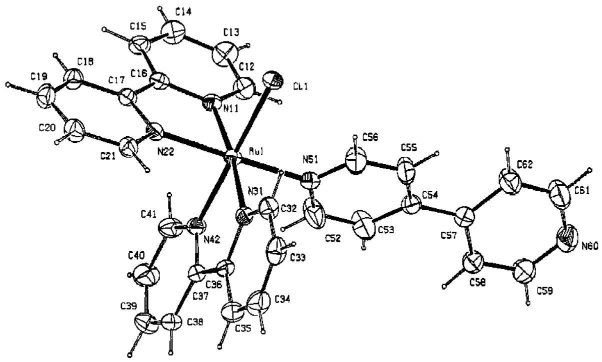

Figure 2. The ORTEP view of *cis-rac*-$[Ru(bpy)_2(4,4'\text{-bpy})(Cl)]PF_6$ at 50% probability level. The counteranion (PF_6) is omitted for clarity.

The wider significance of this result is enhanced by the monocoordination of 4,4′-bpy, as this leaves a reactive site for subsequent chirally controlled or racemic reactions. The mechanism for these reactions is likely to proceed via a two step process; first, photoinduced intramolecular isomerization from the thermodynamically stable S−bound DMSO species to the kinetically stable O−bound DMSO species,[11] second, rapid exchange of the O−bound DMSO for the new ligand.[12] The unambiguous determination of the reaction mechanism for the present case is currently being undertaken.

Supporting Information Available: ^1H and ^{13}C NMR spectra, CD and UV spectra, HPLC chromatogram charts and X-ray tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Data for **2** was collected on a Rigaku AFC7R four-circle diffractometer with filtered Mo Kα radiation and a rotating anode generator using the w scan technique, and the structure was solved using direct methods. Data for compound **2**: Monoclinic space group $P2_1/n$; $a = 13.0154(19)$, $b = 14.068(2)$, $c = 17.453(2)$ Å, _ = 99.703(12), $V = 3154.0(8)$ Å^3, $Z = 4$, $R = 0.0601$, $Rw = 0.1652$ for 4504 observed data. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center.

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