Conformational Switching in the Thermal and Photochemical Synthesis of *cis*- and *trans*-Ruthenium Bis(bipyridine) Sulfoxide Complexes

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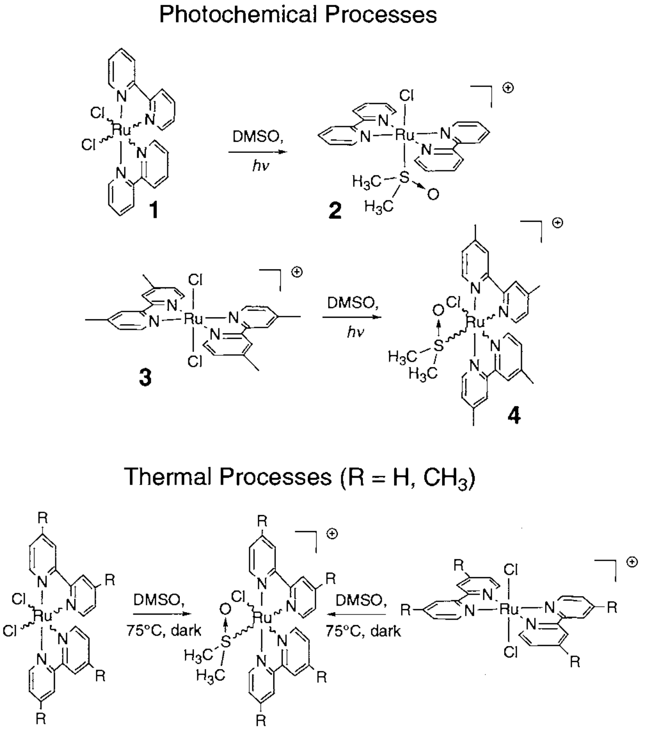
The preparation of ruthenium bis(bipyridine) sulfoxides has been carried out under thermal or photochemical conditions, leading to good yields of products with *trans* or *cis* configurations, and the configuration of the starting material has also been observed to influence the preferred structure of the final product.

Many literature examples describe the use of light to modify the configuration of a molecule,[1-3] and we have sought to use photochemical processes in several areas of our work.[4,5] As part of our ongoing search for photosensitizers we have recently focused attention on ruthenium bis- and tris(bipyridine) complexes, as these are known to exhibit photochemical responses.[6] Our research led to the discovery of a new group of ruthenium bis(bipyridine) sulfoxide complexes, which we have used as conveniently resolvable precursors for the synthesis of optically active ruthenium tris(bipyridine) complexes.[7] Chiral sulfoxides have been used to carry out the asymmetric synthesis of these types of ruthenium bis(bipyridine) sulfoxide complexes.[7] During the course of these investigations, an interesting phenomenon concerning configurational selectivity came to light. Coe *et al.*[8] reported that the reaction of *trans*-[Ru(bpy)$_2$(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$ with dimethyl sulfoxide (DMSO) led to the quantitative formation of *trans*-[Ru(bpy)$_2$(DMSO)$_2$](CF$_3$SO$_3$)$_2$ in the absence of light. However, we discovered that under dark conditions, the opposite configurational preference *i.e.* the *cis* conformation was observed. In order to obtain a *trans*-ruthenium bis(bipyridine) sulfoxide complex, photoirradiation was required. Figure 1 shows the evolution of the ^{1}H NMR spectra taken during the reaction of *cis*-Ru(bpy)$_2$Cl$_2$ **1** in DMSO-d$_6$ under photoirradiation from a low pressure mercury lamp, filtered through the Pyrex walls of an NMR tube. The *cis*-configuration, clearly defined by the eight different proton resonances at $t = 0$ h, showed a gradual broadening, until completion of the reaction at $t = 5$ h. At this time the major product was *trans*-[Ru(bpy)$_2$(DMSO)Cl]Cl, **2**, with less than 5% of the *cis* product observable. This was in spectral agreement with *S*-bonded *trans*-[Ru(bpy)$_2$(DMSO)Cl]PF$_6$ reported by Coe *et al.*[8] However, when the same reaction was carried out thermally, under dark conditions, *cis*-[Ru(bpy)$_2$(DMSO)Cl]Cl was formed in near quantitative yield, with no observable by-products. Indeed, the *cis* configuration was found to be sufficiently stable to allow resolution of the product into the Δ- and Λ-isomers, as demonstrated by the strongly active molar circular dichroism (CD) spectra of the two isomers.[9]



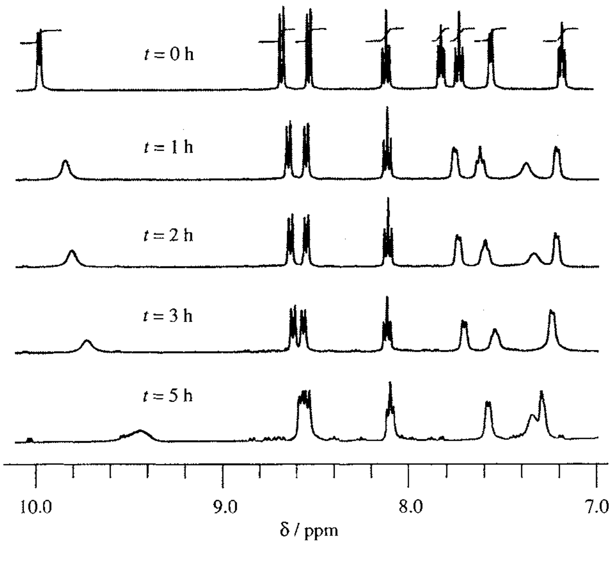


Figure 1. The evolution of the ^{1}H NMR spectra for the formation of *trans*-[Ru(bpy)$_2$(DMSO)Cl]Cl (**2**).

We considered that a steric effect might also play a role in determining the preferred configuration of these sulfoxide complexes, and thus we prepared a sample of *trans*-Ru(dmbpy)$_2$Cl$_2$ **3** (dmbpy = 4,4'-dimethyl-2,2'-bipyridine), which was reacted with DMSO-d$_6$ under photoirradiation conditions. The evolution of the ^{1}H NMR over 5 h is shown in

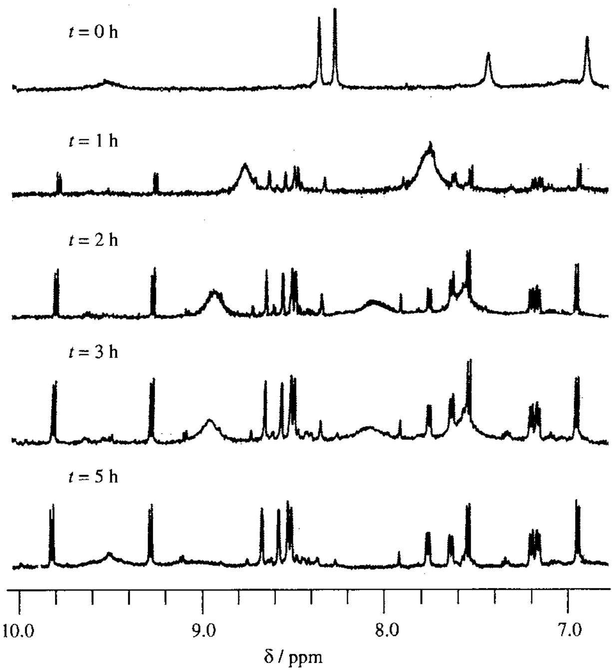


Figure 2. The evolution of the ^1H NMR spectra for the formation of *cis*-[Ru(dmbpy)$_2$(DMSO)Cl]Cl (**4**).

Figure 2. In contrast to the bipyridine liganded photochemical process, only *cis*-[Ru(dmbpy)$_2$(DMSO)Cl]Cl **4** was observed, even though the methyl groups might have been expected to impose a greater steric strain on the *cis* product than the *trans* product. When this reaction was carried out thermally, only *cis*-[Ru(dmbpy)$_2$(DMSO)Cl]Cl **4** was observed.

We have been able to use photoirradiation to selectively prepare a *trans*-ruthenium bis(bipyridine) sulfoxide. However, in contrast to previously reported details,[8] ruthenium bis(bipyridine) dimethyl sulfoxide complexes appear to adopt the *cis* configuration preferentially. This structural selectivity is observed when the sulfoxide ligation is carried out thermally, starting from both *cis* and *trans* precursors. *Cis* selectivity is also observed when *trans*-Ru(dmbpy)$_2$Cl$_2$ is used as the starting material. However, the mechanism that lies behind the *cis*/*trans* configuration control that is afforded through the use of photoirradiation and thermal processes is still not fully understood, and we are currently investigating this phenomenon. This work will be the subject of future reports from our laboratory.

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9 The CD spectrum of Δ-*cis*-[Ru(bpy)$_2$(DMSO)Cl]Cl shows an MLCT band centered around 450 nm, and a large LC band at 300 nm ($\Delta\varepsilon = -65$ dm^3·mol^{-1}·cm^{-1}). An X-ray structure for *cis*-Δ-[Ru(bpy)$_2$(DMSO)Cl]PF$_6$ has been lodged with the Cambridge crystal structure database, deposition number 101690.