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Preparation and structural elucidation of novel *cis* ruthenium(II) bis(bipyridine) sulfoxide complexes †

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Four novel *cis*-ruthenium bis(bipyridine) sulfoxide complexes with the general formula *cis*-[Ru(A)$_2$(B)(Cl)]X (**2**, A = 2,2′-bipyridine (bpy), B = dimethyl sulfoxide (DMSO); **3**, A = 4,4′-dimethyl-2,2′-bipyridine (dmbpy), B = DMSO; **4**, A = bpy, B = tetramethylene sulfoxide (TMSO); and **5**, A = dmbpy, B = TMSO; X = Cl^-, I^-, PF_6^- or ClO_4^-) were synthesized from *cis*-[Ru(bpy)$_2$Cl$_2$] **1** or *trans*-[Ru(dmbpy)$_2$Cl$_2$] **6** in the substrate sulfoxide solutions at 60–120 °C, *i.e.* by a thermal process. This *cis* selectivity is in contrast to previously reported results. However, photoirradiation of **1** in the presence of DMSO selectively produced *trans*-ruthenium bis(bipyridine) sulfoxide; when **6** was photoirradiated in the presence of DMSO *cis*-[Ru(dmbpy)$_2$(DMSO)Cl]Cl was the sole product. These complexes were fully characterized by elemental analysis, IR, UV/vis, ^{1}H, ^{13}C and 2-D NMR spectroscopy. The sulfoxide ligands co-ordinate through a Ru–S bond in all cases. The NMR studies of **2** imply that no rotation around the Ru–S bond occurs, in accord with quantum mechanics calculations. Crystallographic structural determinations of **2**·PF_6^- (from acetone–diethyl ether) and **2**·I^- (from water) showed that both complexes share similar octahedral geometries, but different conformations were found for the sulfoxide ligands with Cl–Ru–S–O dihedral angles of 121.6 and 56.3°, respectively, thus demonstrating that a different energetically favored conformation may exist in low or high dielectric environment. The stability of complexes **2**–**5** allowed separation into their Δ and Λ enantiomers, and the circular dichroism spectra were obtained. Thermal substitution reactions were also carried out using **2**·Cl^- which was converted into *cis*-[Ru(bpy)$_2$Cl$_2$] **1** or *cis*-[Ru(bpy)$_2$I$_2$] **7**. Several examples in which the resolved complex Δ-**2**·PF_6^- reacts with bipyridine nucleophiles with nearly complete retention of chirality are also given.

Introduction

Ruthenium tris(bipyridine) complexes remain highly important in modern inorganic chemistry, and are increasingly finding roles in multicomponent systems which perform light- or redox-induced functions.[1–5] However, one aspect of their synthesis that has been largely overlooked is the control of the Δ or Λ helical stereochemistry of the metal center. The methods used to facilitate the preparation of such asymmetric complexes normally rely on chromatographic separation[6,7] or optical resolution.[8,9] These methods inevitably necessitate the preparation and subsequent resolution of a racemic mixture, which eventually gives the desired enantiopure complex in 50% yield at the best. Only one asymmetric synthesis of ruthenium bipyridine complexes, that of von Zelewsky and co-workers,[10,11] has been reported, although this technique is somewhat limited in that the ligand architecture of the final product must contain the "chiragen" ligand. This means that although impressive diastereomeric excesses can be obtained, the number of products that can be prepared is somewhat limited. Another approach that has been put forward by Hua and von Zelewsky[12,13] and Keene and co-workers[6,14] involves the preparation of chiral ruthenium bis(bipyridine) reagents ([Ru(bpy)$_2$(py)$_2$]$^{2+}$ and [Ru(bpy)$_2$(CO)$_2$]$^{2+}$, respectively), which react with a third bipyridine to give the desired complex with retention of stereochemistry at the metal center. Although there is an initial resolution step in this synthetic sequence at the stage where the ruthenium bis(bipyridine) precursors have been prepared, the more precious tris(bipyridine) complex is subsequently prepared in the most efficient way in a high optical yield. These reagents are readily synthesized, and have the advantage of allowing access to a wide range of asymmetric complexes with maximum control and minimum wastage. We have sought to add to this small number of highly valuable reagents, and have discovered that ruthenium bis(bipyridine) sulfoxides, that can readily be made and resolved, are alternative chiral reagents to the other two proven methods for the synthesis of asymmetric ruthenium tris(bipyridine) complexes.[15] Many papers are devoted to sulfoxide–transition metal bond formation, and some of these results are summarized in review articles,[16,17] yet surprisingly *cis*-[Ru(bpy)$_2$(DMSO)Cl]X has not previously been reported, even though the first reports on transition metal complexes employing sulfoxide derivatives are found as early as the late 1950s.[18,19] It is noteworthy that S-bonded ruthenium sulfoxide complexes generally assume a *trans* configuration to O-bonded ligands or halide ions.[20,21] The thermal and photochemical synthesis, structural and spectral characteristics of several complexes, with the general formula *cis*-[Ru(A)$_2$(B)(Cl)]X (**2**, A = 2,2′-bipyridine (bpy), B = dimethyl sulfoxide (DMSO); **3**, A = 4,4′-dimethyl-2,2′-bipyridine (dmbpy), B = DMSO; **4**, A = bpy, B = tetramethylene sulfoxide (TMSO); **5**, A = dmbpy, B = TMSO; with X = Cl^-, I^-, PF_6^- or ClO_4^-) are described below. These complexes have been found to be thermally stable, allowing them to be separated into their Δ and Λ forms, although they are found to undergo degradation upon prolonged exposure to light. The solid state structures of **2**·PF_6^- and **2**·I^- show a preferred conformation where an

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/3701/

Also available: NMR, CD and IR spectra, HPLC data. For direct electronic access see http://www.rsc.org/suppdata/1999/3701/, otherwise available from BLDSC (No. SUP 57656, 25 pp) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

intramolecular [S–O · · · H–C] hydrogen bond is formed, and similar structures can be proposed for **3**, **4** and **5**. This conformation appears to remain in solution, as shown by NMR spectroscopy, which precludes the expected free rotation about the ruthenium–sulfur bond over a temperature range of −100 to +100 °C. Finally, several reactions of optically pure *cis*-[Ru(bpy)$_2$(DMSO)Cl]X are described which exhibit a retention of chirality at the metal center, demonstrating the use of this complex as a chiral reagent in the synthesis of ruthenium tris(bipyridine) complexes.

Results

Thermal *vs*. photoreactions in the preparation of *cis*- and *trans*-ruthenium bis(bipyridine) sulfoxide complexes

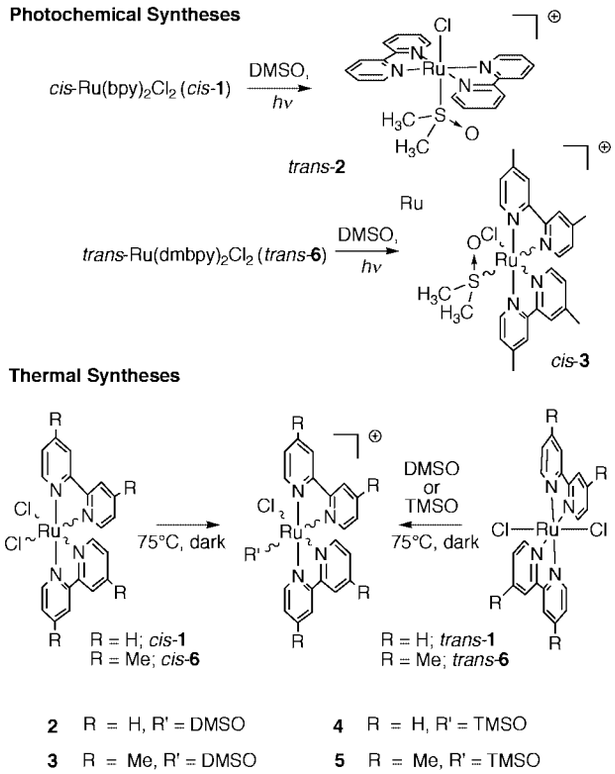
It has been reported that the reaction of *trans*-[Ru(bpy)$_2$-(H$_2$O)$_2$][CF$_3$SO$_3$]$_2$ with dimethyl sulfoxide leads to the quantitative formation of *trans*-[Ru(bpy)$_2$(DMSO)$_2$][CF$_3$SO$_3$]$_2$ in the absence of light.[21] However, under dark conditions thermal processes were found to promote the opposite configurational preference, *i.e.* the *cis* conformation, and in order to obtain a *trans*-ruthenium bis(bipyridine) sulfoxide complex photoirradiation was required. The ^{1}H NMR spectra recorded 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, was followed. The *cis* configuration was clearly defined by eight different proton resonances at $t = 0$ h, which 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**·Cl$^-$), with less than 5% of the *cis* product observed.[22] This was in spectral agreement with *S*-bonded *trans*-[Ru(bpy)$_2$(DMSO)Cl]PF$_6$ reported by Coe *et al*.[21] However, when the same reaction was carried out thermally in the absence of light *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 stable enough to allow resolution of the product into the Δ and Λ isomers, and this work is described below in more detail.

We considered that steric effects might also play a role in determining the preferred configuration of these sulfoxide complexes, and thus a sample of *trans*-[Ru(dmbpy)$_2$Cl$_2$] **1** was prepared, which was subsequently photoirradiated in the presence of DMSO-d_6. In contrast to the *trans* selectivity observed for the photochemical process involving [Ru(bpy)$_2$Cl$_2$], only *cis*-[Ru(dmbpy)$_2$(DMSO)Cl]Cl **4** was formed. When the same reaction was carried out thermally in the absence of light again only the *cis* product was observed.

Syntheses of *cis*-[Ru(A)$_2$(B)(Cl)]X 2–5

The thermal conversion of *cis*-[Ru(bpy)$_2$Cl$_2$] **1** or *trans*-[Ru(dmbpy)$_2$Cl$_2$] **6** into the corresponding DMSO and TMSO complexes could be carried out conveniently, and the product purified by recrystallization. Under the reaction conditions described above, *only cis*-ruthenium sulfoxide complexes were detected (Scheme 1).

The chloride salts are bright red crystalline solids, which are soluble in aprotic polar solvents such as acetonitrile, THF or CH$_2$Cl$_2$, and are found to be stable under dark conditions. The solution state stability of the complexes varies, depending strongly on the temperature, ionic strength of the solution[23] and counter ion used. The enantiomerically enriched PF$_6^-$ salts, which are prepared by anion exchange during the chiral HPLC separation process, are insoluble in water, and crystallize as a racemate from several different acetone–ether mixed solvent systems. Conversely, the Cl$^-$ salts are highly soluble in water, but gradually decompose to give the solvated starting materials *cis*-[Ru(bpy)$_2$(Cl)(H$_2$O)]Cl or *cis*-[Ru(dmbpy)$_2$(Cl)(H$_2$O)]Cl. The *cis*-[Ru(bpy)$_2$(DMSO)Cl]I salt (**2**·I$^-$) could be prepared by



Scheme 1 Photochemical and thermal preparations of *cis*- and *trans*-ruthenium bipyridine sulfoxides.

stirring *cis*-[Ru(bpy)$_2$(DMSO)Cl]Cl (**2**·Cl$^-$) in a warm 0.1 M NaI aqueous solution, affording long yellow needles upon cooling, interestingly with no sign of hydrolysis. Thus crystals from both non-polar (**2**·PF$_6^-$) and polar solvents (**2**·I$^-$) were prepared, and the structures of these two complexes, prepared from very different solvent systems, are discussed below. The dmbpy complexes **3**·Cl$^-$ and **5**·Cl$^-$ were found to decompose rapidly during the purification process. In order to prevent this the final step of the synthetic procedure was modified, and the derivatives were isolated and characterized as the perchlorate salts **3**·ClO$_4^-$ and **5**·ClO$_4^-$ following rapid extraction from the aqueous layer with dichloromethane in the presence of an excess of NaClO$_4$. All of the above mentioned compounds exhibit high stability in the solid state if they are stored under an inert atmosphere and are not exposed to light. However, the ruthenium sulfoxide derivatives are sensitive to photoinduced decomposition, both in the solution and solid states. Several problems were encountered during our attempts to elucidate this phenomenon, especially in the solution phase, and these factors were not readily anticipated. For example, if a sample of purified, optically active complex was left standing in the HPLC eluent for a short time, the enantiomeric excess (ee) was found to decrease as a result of photodegradation.[24]

Crystal structures of complexes 2·PF$_6^-$ and 2·I$^-$

X-Ray crystallographic studies were carried out in order to examine the structural characteristics of complexes **2**·PF$_6^-$ and **2**·I$^-$, and thus gain an insight into possible intramolecular interactions. The crystals were grown in the less polar, acetone–ether mixed solvent for **2**·PF$_6^-$, and in water for **2**·I$^-$. The structures are shown in Fig. 1, using a common atomic numbering scheme. It should be noted that both compounds are racemic in nature and crystallize in centrosymmetric space groups, although the torsion angles quoted below are taken from the Δ isomer. The assignment of labels A–D to the four pyridine rings is based on the following: the pyridine ring *trans* to the sulfoxide ligand is B, which is covalently linked to ring A, and the ring *trans* to the chloride ligand is C, and this is covalently linked to

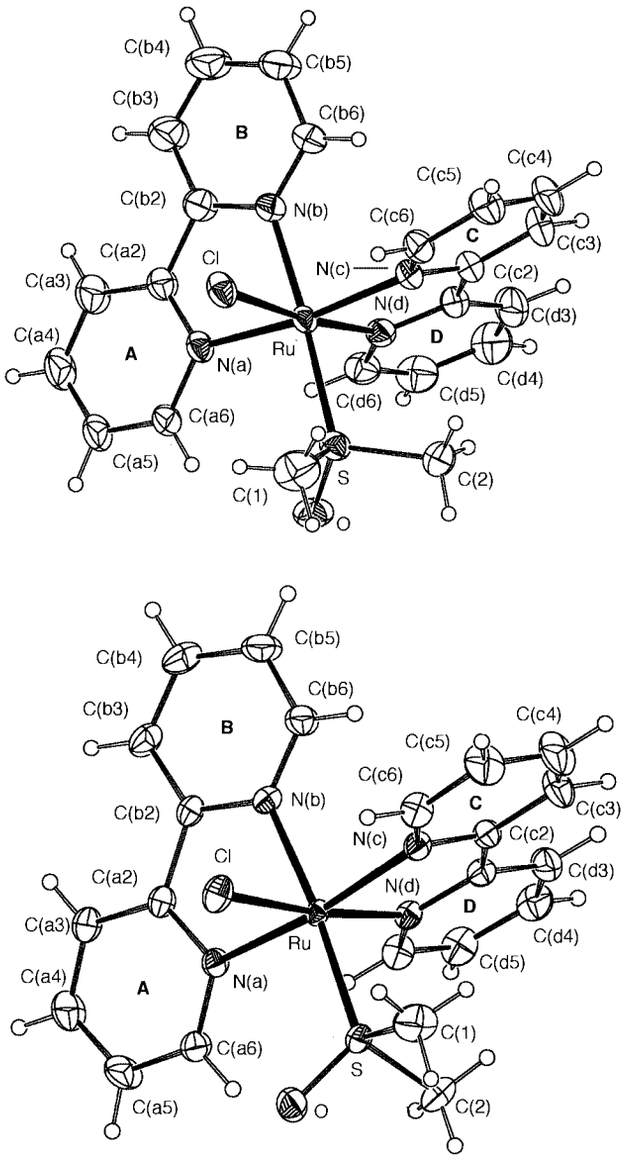


Fig. 1 An ORTEP[25] drawing of complex **2**·PF_6^- (top) and of **2**·I^- (bottom). Ellipsoids are shown at 50% probability. The counter ions and solvent molecules have been omitted for clarity.

ring D. If the sulfoxide ligand is rotated arbitrarily such that the N(a)–Ru–S–O torsion angle is 0°, the methyl group adjacent in space to the chloride ligand is labeled Me1, and the methyl group that lies above the C/D rings is labeled Me2. Both **2**·PF_6^- and **2**·I^- show very similar geometries for the metal atom, which is located in an octahedral environment bonded to two bidentate bipyridine ligands, a chloride ion and a DMSO ligand through the sulfur atom. Interestingly, in both structures, the nitrogen atom N(c) from ring C, *trans* to the chloride, participates in a Ru–N bond which is *ca.* 0.04 Å shorter than the three other Ru–N bonds.

However, there is some variation in the bond angles, particularly involving S(1), *e.g.* N(c)–Ru–S which are 90.05 and 95.18° in complexes **2**·PF_6^- and **2**·I^- respectively, and S–Ru–Cl, which is 94.16 and 88.04°. These differences are a result of the different conformations that are observed for the two DMSO ligands in environments of different polarity. While in both structures the oxygen atom of the DMSO forms a hydrogen bond to H(a6) from ring A, the conformations of the structures are subtly different. In **2**·PF_6^- the H(a6)···O distance is 2.26 Å and the oxygen atom is on the opposite side of the bipyridine A, B ring plane to the chloride ligand. The Cl–Ru–S–O torsion angle is 121.6°, and the Cl–Ru–S–C torsion angles are −4.6 and −117.4°, such that Me1 is *cis* to the chloride along the Ru–S bond. However in **2**·I^- the H(a6)···O distance is 2.39 Å and the oxygen atom is on the same side of bipyridine A, B ring plane as the chloride atom. In this arrangement the Cl–Ru–S–O torsion angle is 56.3° and the Cl–Ru–S–C(2) and the Cl–Ru–S–C(1) torsion angles are −68.2 and 179.1°, such that Me2 is now *trans* to the chloride. Thus in the two structures the Cl–Ru–S–O dihedral angle, and thus the conformation of the DMSO ligand, differs by *ca.* 60° despite the C–H···O–S hydrogen bond being maintained.

In complex **2**·I^- both Me1 and Me2 are close to the bipyridine C and D rings, as indicated by the closest interatomic distances which are H(2A)···N(1c) 2.86, H(2A)···C(c2) 3.06, H(2A)···C(c6) 3.35, H(1B)···N(1d) 2.73, H(1B)···C(d2) 3.24 and H(1B)···C(d6) 2.87 Å. In **2**·PF_6^- only one methyl group is in the proximity of the pyridine D ring with interatomic distances H(2A)···N(d1) 2.73, H(2A)···C(d6) 3.16, H(2A)···C(d2) 3.02 Å, but it also is close to the C ring with H(2B)···N(c1) 2.99, H(2B)···C(c2) 2.91 and H(2B)···C(c6) 3.68 Å.

Quantum mechanics (QM) calculations

Following on from the solid-state analysis of complexes **2**·PF_6^- and **2**·I^-, quantum mechanics calculations using density functional theory (DFT) were carried out to ascertain if the two structures obtained bore close resemblance to a calculated global minimum. The starting model for the Δ isomer examined was taken from the crystal structure of racemic **2**·PF_6^- and the structure was then geometry optimized to convergence using the generalized gradient approximation. The minimized structure gave a Cl–Ru–S–O torsion angle of 99.4°. The O···H–C distance was 1.865 Å, which suggests a strong intramolecular hydrogen bonding interaction. This could imply that the DFT method has over-exaggerated the importance of the hydrogen bond interaction. However, there have been many studies of hydrogen bonding by DFT, and while there is little evidence that the technique in general gives distorted results, there are examples of shorter than experimental distances being observed.[26,27] The torsion angle O–S–Ru–N is reduced from 25.2° in the crystal to 10.2° in the geometry-optimized structure, thus reducing the O···H–C distance and increasing the strength of the hydrogen bonding interaction.

The distances between the methyl groups and bipyridine ligands are similar to those of van der Waals contacts, the shortest distances to the C ring being 2.804, 2.824 and 3.007 Å for H(2A) and 2.689, 2.954 and 2.866 Å for H(2B). It is interesting that when the geometrical arrangement taken from the crystal structure of **2**·I^- was used as the starting model, the geometry optimization led to a structure identical to that obtained from **2**·PF_6^-. Since these QM calculations were carried out in the gas phase, it is not surprising that the two different geometry optimizations lead to the same final structure. Clearly the minimum energy structure can be varied by packing effects in the crystal, but the intramolecular hydrogen bond is of sufficient importance to be maintained in both crystal structures.

IR Spectroscopy

The IR spectral evidence agrees with the mode of DMSO coordination established by the crystal structure determinations. Thus, the spectrum of $[Ru(bpy)_2(DMSO)Cl]Cl$ **2** recorded in KBr pellet and Nujol shows an intense absorption band at 1120 cm^{-1}, which is assigned to the S–O stretching vibration of DMSO covalently bonded to the metal through the S atom.[28] No strong absorption was observed in the region 900–1000 cm^{-1}, where the stretching vibration of *O*-bonded DMSO is expected.

UV/vis Spectroscopy

The conversion of $[Ru(bpy)_2Cl_2]$ **1** into both DMSO and TMSO complexes (**2**·Cl^- and **4**·Cl^-) was monitored by UV/vis

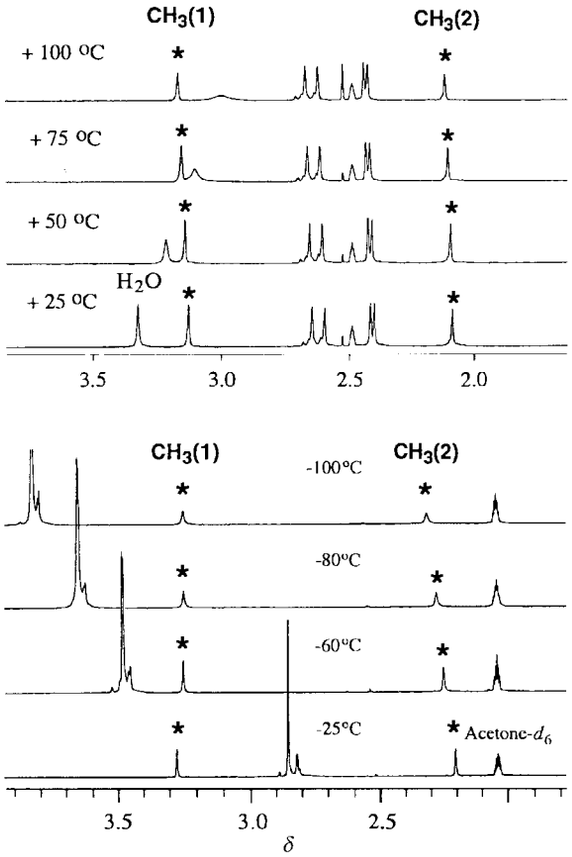


Fig. 2 Variable temperature ^{1}H NMR measurements for complexes **2**·PF_6^- (−100 to −25 °C in acetone-d_6) and **4**·PF_6^- (25 to 100 °C in DMSO-d_6).

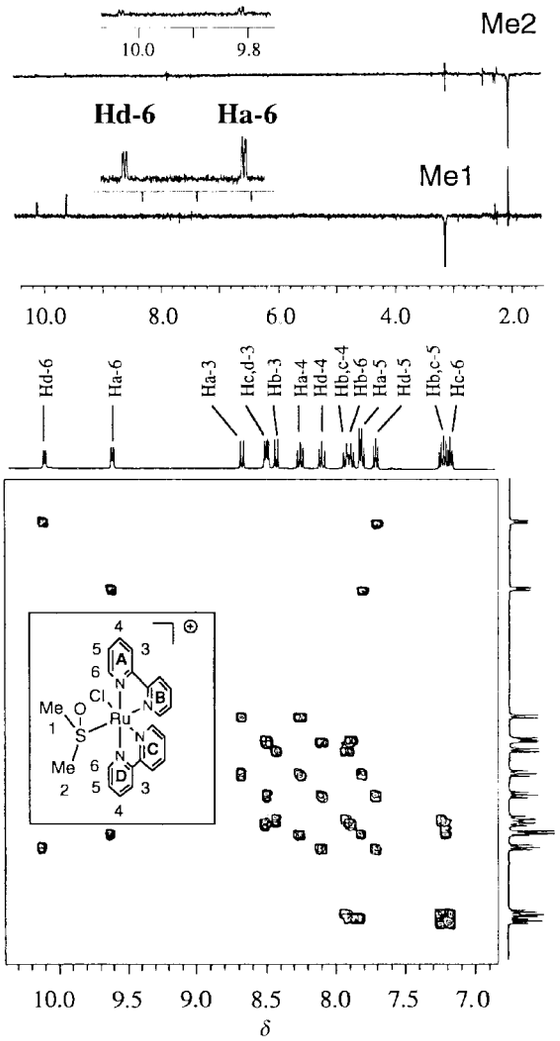


Fig. 3 DIFNOE Experiments and the aromatic region of the H–H COSY spectrum of complex **2**·Cl^- recorded at 400 MHz in CD_3CN showing the crosspeaks of the proton resonances. The chemical shift data and full assignment of **2**·Cl^- are listed in the Experimental section. The labeling system for **2** is also shown; the other complexes described also follow the same labeling protocol.

spectroscopy in DMSO or TMSO, allowing observation of changes in the electronic spectra of the reaction mixture. For the formation of **4**·Cl^- three isosbestic points were seen at 355, 408 and 497 nm, and changes in peaks at 386 and 567 (gradually decreasing, from **1**) and at 432 nm (gradually emerging, attributable to **4**·Cl^-) were observed, but no by-products. Unfortunately, further investigations concerning the reaction kinetics were severely limited by the sensitivity of the reaction to the solvent, *etc*. The use of a more polar solvent was considered likely to lead to undesired *O*-bonded intermediates, and the integrity of the product was also thought to be at risk. Indeed, using protic solvents such as MeOH, or the dipolar aprotic solvent DMF, led to a large number of by-products, and this was attributed to the product decomposition under the reaction conditions. Owing to the solvent limitations that were imposed upon the reaction, it was difficult to envisage a set of conditions under which the dependence of the rate of reaction upon the sulfoxide concentration could be investigated, and we chose not to pursue this matter further.

NMR Spectroscopy

The evolution of ^{1}H NMR (DMSO-d_6) spectral changes were monitored when complex **1** was heated at 85 °C for 2 h. The development of sharp signals was observed, indicating that *cis*-[Ru(bpy)$_2$(DMSO-d_6)Cl]Cl (**2**·Cl^-) had formed in high yield with no detectable by-products, and no *trans*-[Ru(bpy)$_2$-(DMSO-d_6)Cl]Cl could be detected at the ^{1}H NMR sensitivity level. As a result of its structural similarity to the other derivatives in this study, complex **2**·PF_6^- was chosen as a representative for an extensive NMR investigation. The resonances of all protons attached to pyridine and methyl groups in the ruthenium sulfoxide complexes exhibit non-equivalence, confirming an asymmetric C_1 structure, which must exclude *trans* isomers. Sixteen anisochronous signals are seen in the low-field region from δ 7.1 to 10.6; these are characteristic of protons attached to inequivalent bipyridine units. Two equal integration single resonances in the aliphatic region resulting from the magnetically non-equivalent methyl groups of the dimethyl sulfoxide (δ 3.13 and 2.06) reflect the non-symmetrical substitution at the Ru atom.

We shall now focus our attention on the two sulfoxide methyl groups, which are central to the complete assignment of the ^{1}H NMR. It might appear at first sight that in the sulfoxide complexes free rotation will occur around the Ru–S bond. However, ^{1}H NMR shows a large difference in the resonance frequencies of the two methyl groups, indicating that the chemical environments experienced by these two groups are non-identical, a situation that cannot occur in a completely freely rotating system, where positional averaging should lead to chemical equivalence. We decided to carry out a series of variable temperature ^{1}H NMR (VT NMR) measurements (see Fig. 2), in an attempt to coalesce the two methyl group signals, initially by cooling a sample of **2**·PF_6^- from −25 to −100 °C in acetone-d_6. A significant movement of the peak for the residual water in the sample was seen, but the two methyl groups remained essentially in the same positions, with a slight broadening attributable to a slowing of the rotation of the S–C bonds. A sample of **4**·PF_6^- was then warmed from 25 to 100 °C in DMSO-d_6, and although the system had been altered slightly, the result that

was observed was surprising. No significant shift was observed for the two signals, *i.e.* the increase in temperature had not affected the Ru–S bond, implying that some factor stabilizes the structure of the complex. We next decided to consider the through space interactions of the two methyl groups with other protons in the complex using the difference nuclear Overhauser enhancement (DIFNOE) method (see Fig. 3). The saturation of the methyl group at δ 2.06 failed to cause any effect in the remainder of the spectrum, indicating that no other protons are in spacial proximity. However, when the proton at δ 3.13 was irradiated two signals were observed in the aromatic region of the spectrum. An inspection of the H–H COSY (see Fig. 3) indicated that these two signals correspond to Ha6 and Hd6, although it was not immediately clear which was which, and it should be noted that this is a crucial point in the assignment process, as it leads ultimately to an assignment of all of the other aromatic protons through the H–H COSY experiment. By rotating the OMe2 moiety around the Ru–S bond in the computer generated three-dimensional model of the complex it was possible to calculate the average atomic separations, these being 3.40 (C-Ha6) and 4.56 Å (C-Hd6). From these average distances it is clear that the strongest NOE is likely to arise from the interaction of one of the methyl groups with Ha6, which is located at δ 9.8. The upfield shift of the methyl group at δ 2 (C2) as compared to that at δ 3 (C1) is probably caused by its inclusion in the shielding cone that lies above the C/D rings, and from this evidence it is reasonable to postulate a structure where there is the possibility of an intramolecular interaction between the oxygen and Ha6, and where a restricted rocking motion always leaves C2 above the C/D rings, with C1 located on the same side of the complex as the Cl ligand, in good agreement with the solid state and quantum mechanics calculation structures.

Optical resolution

The structure and optical behavior of a variety of optically active ruthenium tris(bipyridine) complexes have been well established. However, only a limited amount of information could be found for chiral *cis*-Ru(bpy)$_2$XY complexes, and thus circular dichroism (CD) spectra of the enantiomerically pure complexes are rarely obtained. It is also important to note that resolution processes that use cocrystallization techniques with chiral anions run the risk of having the optical properties of the complex modified by the chiral centers in the anion, and thus may not always be a true representation of the complex itself. Thus, the CD spectra of complexes **2**–**5** were measured by us. The need to prepare a reasonable amount of enantiomerically pure material for full characterization and investigation prompted the development of a new separation method. Attempts to resolve racemic **2**·Cl$^-$ by diastereoselective crystallization (using ammonium (+)-*O*,*O*′-dibenzoyl-D-tartrate),[6] and crystallizations seeded with a small crystal of pure enantiomer (obtained from analytical scale chiral HPLC), were both unsuccessful. Resolution was ultimately achieved by chiral stationary phase HPLC. This technique has several advantages in that (i) the optical purity of the resolved complex can reproducibly be verified with only a small experimental error, (ii) the desired product is obtained directly, and (iii) there is no risk of contamination from unbound chiral resolving agents, which may affect the values of extrema in the CD spectra. Using the HPLC conditions described above, all reported compounds, except **5**·ClO_4^-, were readily resolved into Δ and Λ enantiomers as the PF_6^- salts. Every care was taken to handle all fractions in the absence of light. For *cis*-[Ru(bpy)$_2$(DMSO)Cl]PF_6 (**2**·PF_6^-), the specific rotation ($[a]_D^{20}$) of the first fraction was $-300.2 \pm 7°$ (97.2% ee, *c* 3.06×10^{-4}, CH_3CN), and that of the second fraction was $+315.5 \pm 10°$ (80.3% ee, *c* 3.4×10^{-4}, CH_3CN) (NB ees were determined separately by chiral HPLC analysis). The observed discrepancies are probably the result of a gradual photoinduced decomposition of the solution state samples during the measurement period, and this underlines the need to handle these complexes in light free conditions.

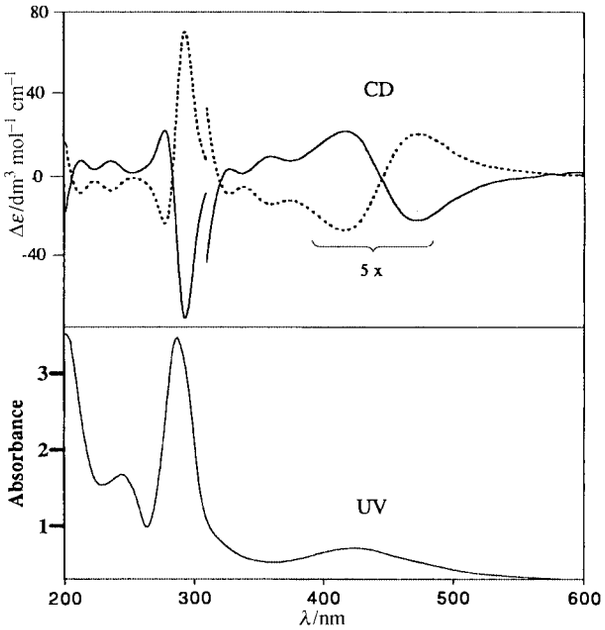


Fig. 4 The CD (top) and UV/vis spectra (bottom) of the first and second HPLC fractions of complex **2**·PF_6^- in CH_3CN at 25 °C.

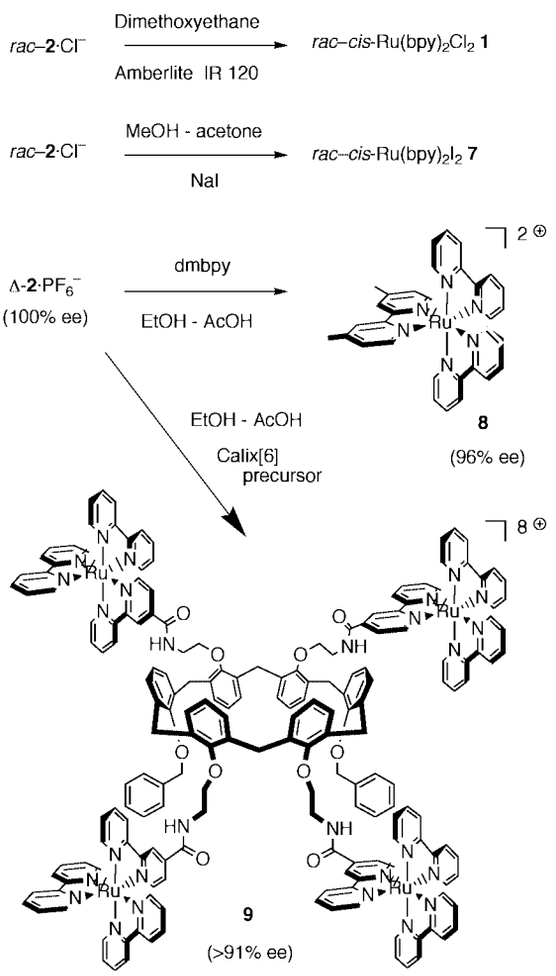
Fig. 4 shows the CD spectra of the resolved enantiomers Λ- and Δ-enantiomers of complex **2**·PF_6^- (7.5×10^{-5} M, acetonitrile) and their UV/vis spectra. These spectra have been assigned by comparison with previously reported ruthenium tris(bipyridine) and bis(bipyridine) complexes.[4,29,30] The strong absorptions at *ca.* 210 and 285 nm were assigned as ligand centered (LC) bands, which arise as a result of exciton coupling between the two long axis polarized transitions of the 2,2′-bipyridine ligands. From these bands we were able to assign the (−) and (+) isomers, obtained as the first and second fractions from HPLC, as having Δ and Λ configurations, respectively. The MLCT band centered around 425 nm changes from a negative (446 nm) to a positive (320 nm) Cotton effect for the Δ isomer. The observed CD spectra are mirror images. Although the UV/vis spectrum of $[Ru(bpy)_3]^{2+}$ exhibits a metal-centered (MC) d–d transition (weak shoulders at 323 and 345 nm, and peaks at 238 and 250 nm), **2**·PF_6^- simply shows a broad absorption band at *ca.* 240 nm and no absorption bands around 330 nm. However, the CD spectra of Δ and Λ-**2**·PF_6^- exhibit small hyperfine structures at both 240 and 330 nm, and these are assigned as the MC d–d transition. Satisfyingly Δ-**2**·PF_6^- was shown not to undergo racemization upon heating in DMSO at 105 °C for 3 h, thus demonstrating the thermal stability of this complex.

Reactions of *cis*-[Ru(bpy)$_2$(DMSO)Cl]X **2**·X$^-$ and *cis*-[Ru(dmbpy)$_2$(DMSO)Cl]X **4**·X$^-$: chiral reagents for ruthenium tris(bipyridine) syntheses

Several problems are apparent with the use of enantiomerically enriched *cis*-[Ru(bpy)$_2$Cl$_2$] **1** as a starting material in the synthesis of chiral octahedral ruthenium complexes, even though it is frequently used in exactly this role to give racemic products. It is well known that the solubility of **1** is poor, and the necessary polar acidic reaction conditions that are required to drive the reaction may result in racemization, or even product degradation. Although attempts have been made to resolve **1** into its Λ and Δ forms, the results of this work are not encouraging,[31] and the preparation of enantiomerically pure materials from **1** is unlikely to succeed in the near future. Only one asymmetric synthesis of ruthenium bipyridine complexes has been

reported,[10,11] affording a product that contains the "chiragen" ligand, severely limiting the synthetic scope of this method. Another approach involves the preparation of chiral ruthenium bis(bipyridine) reagents ($[Ru(bpy)_2(py)_2]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$, respectively), which reacts with a third bipyridine to give the desired complex with retention of stereochemistry at the metal center.[6,12–14] Compounds $[Ru(L–L)_2(CO)_2]^{2+}$ and $[Ru(L–L)_2(L'–L')(py)_2]^{2+}$ [14,32] have also been used for this purpose. Attention is also drawn to the use of chiral Δ- and Λ-$[Ru(L–L)_2(py)_2]^{2+}$ building blocks for the preparation of dinuclear complexes,[12] and as precursors for the synthesis of enantiomerically pure *cis*-$[Ru(bpy)_2(py)(H_2O)][ClO_4]_2$.[33]

Solubility and reactivity problems encountered when complex **1** is used as a starting material appear to have been overcome when the sulfoxide complex is used instead. The complexes that we have described are readily soluble in polar and non-polar solvents, and the enantiomers can readily be resolved. Satisfyingly, we found complexes **2**·X^- and **4**·X^- to be suitable building blocks for the synthesis of other octahedral ruthenium complexes under very mild conditions. Initially we investigated two simple reactions that involved the displacement of the sulfoxide and chloride ligands with other monodentate ligands. Heating racemic or resolved **2**·Cl^- in methanol gave racemic **1** in quantitative yield. However, when the same process was carried out in 1,2-dimethoxyethane in the presence of a catalytic amount of Amberlite® IR-120 the reaction again went to completion, but the product was found to have an active CD spectrum. The formation of racemic *cis*-$[Ru(bpy)_2I_2]$ **7** starting from racemic **2**·I^- occurred in good yield in the presence of NaI (Scheme 2). The discovery that some optical activity was transferred to the product of the reaction using a resolved sulfoxide complex led us to attempt



Scheme 2 Reactions of racemic and optically resolved complex **2**·Cl^-.

several reactions where a bipyridine derived nucleophile was used. As we have stated, the sulfoxide complexes are soluble in most organic solvents, rendering them suitable as precursors to ruthenium tris(bipyridine) complexes. Thus, we treated Δ **2**·PF_6^- with dmbpy in an 8:1 mixture of ethanol and acetic acid for 2 h at 75 °C. This gave $[Ru(bpy)_2(dmbpy)][PF_6]Cl$ in 97% yield, with 96.8% ee.[34] A more ambitious attempt was made to react the 39,42-dibenzyloxy-37,38,40,41-tetrakis(2,2′-bipyridine-4-carboxamidoethoxy)calix[6]arene nucleophile with Δ **2**·PF_6^-. This reaction also gave the desired tetrasubstituted product in excellent yield, with >90% ee, a remarkable result bearing in mind that four centers have been modified in the course of this reaction.[15]

Conclusion

The synthetic routes described above offer convenient access to a new family of octahedral ruthenium complexes. Through a combination of solid state analysis, quantum mechanics calculations and NMR spectroscopy, we have given good evidence for the formation of an intracomplex hydrogen bond, which stabilizes the configuration of the *cis*-ruthenium bis(bipyridine) sulfoxide complexes, thus allowing the resolution of the enantiomers into valuable, optically pure antipodes. The thermal stability towards racemization of *cis*-Δ-$[Ru(bpy)_2(DMSO)]Cl$ has been demonstrated, even upon prolonged heating in DMSO. Furthermore, the preferred solid state conformations of the complexes can readily be controlled through the choice of solvents with the appropriate polarity. Importantly, these ruthenium bis(bipyridine) sulfoxide complexes can be used as precursors in the preparation of other octahedral ruthenium complexes under mild conditions. As well as providing access to racemic complexes, it has been shown that the enantiomerically pure complex *cis*-Δ- or *cis*-Λ-$[Ru(bpy)_2(DMSO)]Cl$ can be converted into ruthenium tris(bipyridine) complexes in excellent yield with almost complete retention of the stereochemistry at the metal center. It is likely that the interesting conformation and reactivity features that we have elucidated should lead to the use of this family of sulfoxide complexes in the design and preparation of novel, optically active ruthenium complexes of the future.

Experimental

Physical measurements

The IR spectra were obtained from KBr disks using a JEOL JIR 6500 instrument, circular dichroism spectra on a JASCO J-720WI spectropolarimeter at 25 °C in acetonitrile or in the HPLC eluent ($NaPF_6$ (aq)–CH_3CN). The concentrations of the solutions were determined by UV/vis measurements. Optical resolution was performed on the preparative scale using a JAI LC-908 recycling liquid chromatograph equipped with a preparative chiral column, Daicel Chiralcel OD-R (20 × 250 mm). A CH_3CN–0.1 M $NaPF_6$ (aq.) eluent with a flow rate of 3 ml min^{-1} was used. The chromatograph was monitored at 292 nm with a UV detector. Monitoring the products of the synthetic reactions and the optical purity of the separated fractions was performed using an analytical HPLC system (JASCO GULLIVER series) equipped with an analytical chiral column, Daicel Chiralcel OD-R (4.6 × 250 mm), a PU-980 HPLC pump, a DG-980-50 3-line Degasser, a UV-970 UV/vis detector, and an 860-CO column oven. The eluent (CH_3CN–0.1 M $NaPF_6$ (aq.)) flow rate was 0.4 ml min^{-1}, and the chromatogram was monitored at 425 nm and recorded with a JASCO 807-IT integrator. Optical rotations were measured with a Perkin-Elmer model 341 polarimeter in the HPLC eluent. Analytical thin-layer chromatography was performed with plastic backed silica sheets (Merck Kieselgel 60 F_{254}). All new compounds were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis.

NMR spectroscopy

The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 400 spectrometer, operating at 399.65 and 100.40 MHz, respectively. Unless indicated, spectra were recorded in acetonitrile-d_3 or acetone-d_6 solutions. Chemical shifts are reported relative to either the solvent reference or internal standard tetramethylsilane (TMS, δ 0.00) for ^{1}H NMR and solvent for ^{13}C NMR. Pulsed field gradient experiments were used for H–H and C–H correlations (VCOSYNH and VCHSHF pulse sequences, respectively).

Crystallographic measurements

Data collection for X-ray analysis was carried out on compounds **2**·PF_6^- and **2**·I^- using a Rigaku AFC7R diffractometer with filtered Mo-Kα radiation and a rotating anode generator. Details of the data collection and refinement are given in Table 1. The structures were solved using direct methods. Final refinement on F^2 was carried out with the SHELXL program.[35] In both structures all non-hydrogen atoms in the cations were refined with anisotropic thermal parameters. Hydrogen atoms were added in geometric positions. Methyl groups were refined as rigid groups with allowed rotation. The thermal parameters of the hydrogen atoms were constrained to 1.2 times that of the atom to which they were bonded. In **2**·PF_6^- the PF_6^- anion was disordered with two sets of octahedral fluorine atoms refined with occupation factors x and $1 - x$; x refined to 0.74(1). The phosphorus atoms were refined anisotropically and the fluorine atoms isotropically. A disordered diethyl ether solvent molecule was located. This was given 50% occupancy, but there were two positions for each of the two terminal methyl groups and these four atoms were all given 25% occupancy. In addition a water molecule was located which was given 50% occupancy. These solvent molecules were given isotropic thermal parameters and no hydrogen atoms were included. In **2**·I^- the I^- anion was refined anisotropically. Two solvent water molecules were located and the oxygen atoms refined anisotropically, but their hydrogen atoms could not be located and were not included.

CCDC reference number 186/1647.

See http://www.rsc.org/suppdata/dt/1999/3701/ for crystallographic files in .cif format.

Materials

The reagents in these studies were reagent grade or better, used without further purification. Solvents were purified according to published methods. Dimethyl sulfoxide and tetramethylene sulfoxide were dried overnight over molecular sieves 4A, distilled and stored under argon.

Syntheses

The compounds *cis*-[$Ru(bpy)_2Cl_2$] and *trans*-[$Ru(dmbpy)_2Cl_2$] are either commercially available, or prepared according to the literature procedure.[36]

General procedure for the preparation of *cis*-[$Ru(bpy)_2$(DMSO)Cl]Cl (2·Cl^-) and *cis*-[$Ru(dmbpy)_2$(DMSO)Cl]Cl (3·Cl^-). A 0.5 g sample of complex **1** or **6** was added to 30 mL of dried, deaerated DMSO, and the stirred reaction mixture heated to 85 °C under nitrogen for 5 h. The solvent was then removed *in vacuo* (water bath temperature = 85 °C). The red oil was subsequently decanted with diethyl ether (50 mL), then hot acetone (150 mL) was added to the partially solidified material. Upon cooling, the resulting red precipitate was collected by filtration and dried. An elemental analysis sample was further purified by recrystallization from acetone–ether. Crystals of **2**·PF_6^- were grown by slow evaporation of an acetone–diethyl ether solution in the presence of ammonium hexafluorophosphate. Crystals of **2**·I^- were grown in 0.1 M NaI aqueous solution.

Table 1 Summary of the crystal data and structure refinement for complexes **2**·PF_6^- and **2**·I^-

	2·PF_6^-	**2**·I^-
Empirical formula	$C_{24}H_{28}ClF_6N_4O_2PRuS$	$C_{22}H_{26}ClIN_4O_3RuS$
Formula weight	718.05	689.95
T/K	298	298
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	13.594(3)	8.171(2)
b/Å	17.951(4)	10.372(3)
c/Å	14.171(3)	16.133(3)
α/°		79.83(2)
β/°	114.44(1)	76.82(2)
γ/°		72.49(2)
μ/mm^{-1}	0.76	2.07
Reflections collected	15404	12650
Unique reflections/ R(int)	7247/0.012	5871/0.028
Data/restraints/ parameters	7247/0/353	5854/0/301
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0434, 0.1269	0.0387, 0.1021
[all data]	0.0532, 0.1356	0.0453, 0.1301
Largest difference peak and hole/e Å^{-3}	1.196, −0.826	1.405, −1.746

2·Cl^-. Yield 0.50 g (89%). A sample for analysis was prepared by recrystallization using a vapor diffusion technique (ether solvent diffusing into an acetone solution of **2**·Cl^-). Water is observed in this compound, probably arising at the crystallization stage from the undried acetone solvent. Calc. for $C_{22}H_{22}Cl_2N_4ORuS·H_2O$: C, 45.51; H, 4.17; N, 9.65. Found: C, 44.98; H, 3.96; N, 9.41%. ^{1}H NMR (CD_3CN): δ 10.12 (d, J = 5.6, 1 H, Hd-6), 9.63 (dd, J = 5.6, 1.3, 1 H, Ha-6), 8.68 (d, J = 8.4, 1 H, Ha-3), 8.53 (m, 2 H, Hc,d-3), 8.44 (d, J = 8.4, 1 H, Hb-3), 8.27 (t, J = 7.6, 1 H, Ha-4), 8.12 (t, J = 7.6, 1 H, Hd-4), 7.93 (m, 2 H, Hb,c-4), 7.86 (d, J = 5.2, 1 H, Hb-6), 7.84 (t, J = 8.0, 1 H, Ha-5), 7.73 (t, J = 8.0, 1 H, Hd-5), 7.24 (m, 2 H, Hb,c-5), 7.20 (d, J = 4.8 Hz, 1 H, Hc-6), 3.13 (s, 3 H, CH_3(1)) and 2.06 (s, 3 H, CH_3(2)). ^{13}C NMR (CD_3CN): δ 158.9 (s, C-2), 158.8 (s, C-2), 158.5 (s, C-2), 157.1 (s, C-2), 156.5 (d, C-6), 154.3 (d, C-6), 154.1 (d, C-6), 150.3 (d, C-6), 139.4 (d, C-4), 139.3 (d, C-4), 138.5 (d, C-4), 138.3 (d, C-4), 128.7 (d, C-5), 127.9 (d, C-5), 127.6 (d, C-5), 127.5 (d, C-5), 125.7 (d, C-3), 125.3 (d, C-3), 124.6 (d, C-3), 124.1 (d, C-3), 44.6 (q, CH_3) and 42.5 (q, CH_3).

3·Cl^-. Yield 0.53 g (89%). A sample for analysis was prepared by recrystallization using a vapor diffusion technique (ether diffusing into an acetonitrile solution of **3**·Cl^-). Calc. for $C_{26}H_{30}Cl_2N_4ORuS·2H_2O$: C, 47.70; H, 5.23; N, 8.56. Found: C, 47.00; H, 4.87; N, 8.47%. ^{1}H NMR (CD_3CN): δ 9.92 (d, J = 6, 1 H, H-6), 9.39 (d, J = 6, 1 H, H-6), 8.46 (s, 1 H, H-3), 8.32 (s, 1 H, H-3), 8.30 (s, 1 H, H-3), 8.26 (s, 1 H, H-3), 7.63 (m, 2 H, H-5), 7.55 (d, J = 6, 1 H, H-6), 7.08 (m, 2 H, H-5), 7.03 (d, J = 6 Hz, 1 H, H-6), 3.13 (s, 3 H, CH_3), 2.68, 2.60, 2.43 and 2.40 (4 × s, 12 H, dmbpy CH_3) and 2.08 (s, 3 H, CH_3). ^{13}C NMR (CD_3CN): δ 158.5 (s, C-2), 158.3 (s, C-2), 158.1 (s, C-2), 158.0 (s, C-2), 156.8 (d, C-6), 155.8 (d, C-6), 153.4 (d, C-6), 153.1 (d, C-6), 152.0 (s, C-4), 151.7 (s, C-4), 150.8 (s, C-4), 149.4 (s, C-4), 129.5 (d, C-5), 128.7 (d, C-5), 128.3 (d, C-5), 128.2 (d, C-5), 126.1 (d, C-3), 125.8 (d, C-3), 125.2 (d, C-3), 124.7 (d, C-3), 44.8 (q, CH_3), 42.6 (q, CH_3), 21.5 (q, CH_3), 21.1 (q, 2 × CH_3) and 21.1 (q, CH_3).

***cis*-[$Ru(bpy)_2$(TMSO)Cl]Cl (4·Cl^-).** A 0.53 g sample of *cis*-[$Ru(bpy)_2Cl_2$] **1** was added to 20 mL of dried, deaerated TMSO, and the mixture heated under nitrogen, with stirring at 85 °C for 5 h. The reaction solution was allowed to cool to room temperature, and the solvent evaporated to dryness *in vacuo* (water-bath temperature = 85 °C). The resulting red oil was redissolved in a small amount of acetone, and diethyl ether slowly added.

After stirring at room temperature for 1 h the precipitate formed was vacuum filtered. This solid was then dissolved in the minimum of hot acetone and an excess of ether slowly added. The resulting red precipitate was collected by filtration and dried. Yield 0.37 g (82%). A sample for analysis was prepared by recrystallization using a vapor diffusion technique (ether solvent diffusing into an acetone solution of **4**·Cl^-) Calc. for $C_{24}H_{24}Cl_2N_4ORuS·H_2O$: C, 47.52; H, 4.32; N, 9.27. Found: C, 47.65; H, 4.38; N, 8.92%. ^{1}H NMR (CD_3CN): δ 9.83 (dd, J = 5.6, 1.2, 1 H, H-6), 9.46 (dd, J = 5.6, 1.2, 1 H, H-6), 8.50 (d, J = 8.4, 1 H, H-3), 8.38 (d, J = 8.4, 1 H, H-3), 8.34 (d, J = 8.2, 1 H, H-3), 8.31 (d, J = 8.2, 1 H, H-3), 8.12 (t, J = 7.6, 1 H, H-4), 7.99 (t, J = 7.6, 1 H, H-4), 7.81 (t, J = 7.6, 1 H, H-4), 7.76 (t, J = 7.6, 1 H, H-5), 7.70 (m, 2 H, H-4, H-5), 7.61 (t, J = 8.0, 1 H, H-5), 7.13 (m, 2 H, H-6), 7.08 (t, J = 8.0 Hz, 1 H, H-5), 3.75 (m, 1 H, CH_2), 3.20 (m, 1 H, CH_2), 2.20 (m, 1 H, CH_2), 1.80 (m, 1 H, CH_2) and 1.60 (m, 1 H, CH_2). ^{13}C NMR (CD_3CN): δ 159.0 (s, C-2), 158.9 (s, C-2), 158.7 (s, C-2), 157.4 (s, C-2), 156.6 (d, C-6), 154.2 (d, C-6), 150.5 (2 × d, C-6), 139.4 (d, C-4), 139.4 (d, C-4), 138.6 (d, C-4), 138.2 (d, C-4), 128.8 (d, C-5), 127.9 (d, C-5), 127.7 (d, C-5), 127.5 (d, C-5), 125.5 (d, C-3), 125.0 (d, C-3), 124.7 (d, C-3), 124.2 (d, C-3), 57.5 (t, CH_2), 54.5 (t, CH_2), 25.5 (t, CH_2) and 25.4 (t, CH_2).

***cis*-[Ru(dmbpy)$_2$(TMSO)Cl]ClO_4 (5·ClO_4^-).** A 0.53 g of complex **6** was added to 20 mL of dried, deaerated TMSO, and the stirred mixture heated to 85 °C under nitrogen for 5 h. The solvent was then removed *in vacuo*. The resulting red oil was dissolved in a small amount of water–acetone (3 : 1) and 100 mL of 0.1 M $NaClO_4$ were added. Dichloromethane (100 mL) was added and the organic layer subsequently separated and extracted several times with distilled water. The organic solvent was then removed under reduced pressure until *ca*. 3 mL remained. The complex **5**·ClO_4^- was then precipitated by addition of an excess of diethyl ether (yield 85%). **CAUTION**: perchlorate salts are potentially explosive, and should be handled with due care. Calc. for $C_{28}H_{34}Cl_2N_4ORuS·Cl_2O_4$: C, 45.19; H, 4.33; N, 7.53. Found: C, 45.32; H, 4.27; N, 7.38%. ^{1}H NMR (CD_3CN): δ 9.77 (d, J = 6, 1 H, H-6), 9.35 (d, J = 6, 1 H, H-6), 8.35 (s, 1 H, H-3), 8.30 (s, 1 H, H-3), 8.24 (s, 1 H, H-3), 8.18 (s, 1 H, H-3), 7.60 (m, 4 H, H-5), 7.12 (d, J = 6, 1 H, H-6), 7.03 (d, J = 6 Hz, 1 H, H-6), 3.90 (m, 1 H, CH_2), 3.40 (m, 1 H, CH_2), 2.65, 2.60, 2.43 and 2.41 (4 × s, 12 H, dmbpy CH_3), 2.27 (m, 2 H, CH_2), 2.10 (m, 1 H, CH_2), 1.90 (m, 1 H, CH_2) and 1.76 (m, 1 H, CH_2). ^{13}C NMR (CD_3CN): δ 158.4 (2 × s, C-2), 158.3 (s, C-2), 158.1 (s, C-2), 156.9 (d, C-6), 155.9 (d, C-6), 153.4 (d, C-6), 153.1 (d, C-6), 151.9 (s, C-4), 150.7 (s, C-4), 150.6 (s, C-4), 149.6 (s, C-4), 128.5 (2 × d, C-5), 128.2 (2 × d, C-5), 126.4 (2 × d, C-3), 125.2 (d, C-3), 124.8 (d, C-3), 57.0 (t, CH_2), 54.5 (t, CH_2), 25.5 (t, CH_3), 25.4 (t, CH_2), 21.5 (q, CH_3), 21.4 (q, CH_3), 21.2 (q, CH_3) and 21.1 (q, CH_3).

***cis*-[Ru(bpy)$_2$Cl$_2$] 1.** Complex **2**·Cl^- (0.58 g, 1 mmol) was suspended in dry 1,2-dimethoxyethane (50 mL), and a catalytic amount of Amberlite® IR-120 (Cl^- form) resin was added. The mixture was heated to 90 °C for 20 min under nitrogen, then allowed to cool to room temperature. The solution was poured into rapidly stirring diethyl ether (100 mL). After standing for 2 h the precipitate was isolated by vacuum filtration and washed with diethyl ether. Following vacuum drying, **1** was isolated as a violet-black powder in quantitative yield. ^{1}H NMR (DMSO-d_6): δ 9.99 (2 H, d, J = 6, H-6), 8.65 (2 H, d, J = 6, H-3), 8.50 (2 H, d, J = 6, H-3), 8.07 (2 H, t, J = 6, H-4), 7.76 (2 H, t, J = 8.5, H-5), 7.67 (2 H, t, J = 8.5, H-4), 7.50 (2 H, d, J = 5.5, H-6) and 7.11 (2 H, t, J = 6 Hz, H-5).

***cis*-[Ru(bpy)$_2$I$_2$] 7.** Complex **2**·I^- (0.67 g, 1 mmol) was dissolved in methanol–acetone (1 : 10 v/v, 50 mL) and anhydrous NaI (0.45 g, 3 mmol) and a catalytic amount of Amberlite® IR-120 resin were added. The mixture was heated to reflux for 3 h under nitrogen, allowed to cool to room temperature, and the solvent removed *in vacuo*. The crude material was then dissolved in a small volume of acetone, and the resultant precipitate isolated by vacuum filtration. Following vacuum drying, **7** was isolated as a violet-black powder. Yield 0.53 g, 79%. Calc. for $C_{20}H_{16}I_2N_4Ru$: C, 36.00; H, 2.42; N, 8.40. Found: C, 36.12; H, 2.40; N, 8.33%. ^{1}H NMR (DMSO-d_6): δ 10.43 (2 H, d, J = 6, H-6), 8.66 (2 H, d, J = 6, H-3), 8.50 (2 H, d, J = 6, H-3), 8.07 (2 H, t, J = 6, H-4), 7.74 (4 H, m, H-5, H-4), 7.55 (2 H, d, J = 5.5, H-6) and 7.18 (2 H, t, J = 6 Hz, H-5). ^{13}C NMR (DMSO-d_6): δ 159.5, 157.9, 157.7, 151.2, 134.9, 134.1, 126.0, 125.5, 123.1 and 122.8.

General procedure for the photoreactions of *cis*-[Ru(bpy)$_2$Cl$_2$] and *trans*-[Ru(dmbpy)$_2$Cl$_2$] in DMSO-d_6

The photochemical reaction was carried out in a 0.5 mm tube equipped with removable gas inlet. The tube was charged with argon and then with 1 mL of DMSO-d_6, and 0.1 mmol of *cis*- or *trans*-**1** added. The reaction mixture was cooled to 15 °C and irradiated for 300 min with a low-pressure mercury lamp, filtered through the Pyrex walls of the NMR tube. The progress of the photochemical reaction was followed by ^{1}H NMR and thin layer chromatography. After photoirradiation the sample was analyzed by HPLC. The observed product composition was determined from the crude mixture and characterized by comparison with authentic samples.

Quantum mechanics calculations

The structure of *cis*-[Ru(bpy)$_2$(DMSO)Cl]$^+$ **2** was investigated using the Amsterdam Density Functional Program (ADF)[37] running on an Origin 2000 Supercomputer at the University of Reading. The generalized gradient approximation method was used, while the basis set employed in the calculation was a triple-zeta set with two polarization functions.

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References

1 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.
2 A. Magnuson, H. Berglund, P. Korall, L. Hammarström, B. Åkermark, S. Styring and L. Sun, *J. Am. Chem. Soc.*, 1997, **119**, 10720.
3 T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**, 163.
4 K. Kalyanasundaram, *Coord. Chem. Rev.*, 1982, **46**, 159.
5 P. R. Ashton, R. Ballardini, V. Balzani, E. C. Constable, A. Credi, O. Locian, S. J. Langford, J. A. Preece, L. Prodi, E. R. Schofield, N. Spencer, J. F. Stoddart and S. Wenger, *Chem. Eur. J.*, 1998, **4**, 2413.
6 T. J. Rutherford, P. A. Pellegrini, J. Aldrich-Wright, P. C. Junk and F. R. Keene, *Eur. J. Inorg. Chem.*, 1998, 1677.
7 N. C. Fletcher, P. C. Junk, D. A. Reitsma and F. R. Keene, *J. Chem. Soc., Dalton Trans.*, 1998, 133.
8 T. Tada, *J. Sci. Hiroshima Univ., Ser. A: Phys. Chem.*, 1982, **46**, 73.
9 J. A. Arce Sagues, R. D. Gillard, D. H. Smalley and P. A. Williams, *Inorg. Chim. Acta*, 1980, **43**, 211.
10 H. Mürner, P. Belser and A. von Zelewsky, *J. Am. Chem. Soc.*, 1996, **118**, 7989.
11 N. C. Fletcher, F. R. Keene, H. Viebrock and A. von Zelewsky, *Inorg. Chem.*, 1997, **36**, 1113.
12 X. Hua and A. von Zelewsky, *Inorg. Chem.*, 1991, **30**, 3796.
13 X. Hua and A. von Zelewsky, *Inorg. Chem.*, 1995, **34**, 5791.
14 T. J. Rutherford, M. G. Quagliotto and F. R. Keene, *Inorg. Chem.*, 1995, **34**, 3857.
15 D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda and M. G. B. Drew, *Tetrahedron: Asymmetry*, 1998, **9**, 4089.

16 M. Calligaris and O. Carugo, *Coord. Chem. Rev.*, 1996, **153**, 83.
17 J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 115.
18 F. A. Cotton and R. Francis, *J. Inorg. Nucl. Chem.*, 1961, **17**, 62.
19 I. Lindquist and P. Einarrson, *Acta Chem. Scand.*, 1959, **13**, 420.
20 M. Calligaris, P. Faleschini, F. Todone, E. Alessio and S. Geremia, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1653.
21 B. J. Coe, T. J. Meyer and P. S. White, *Inorg. Chem.*, 1993, **32**, 4012.
22 D. Hesek, Y. Inoue and S. R. L. Everitt, *Chem. Lett.*, 1999, 109.
23 M. Khan, G. Ramachandraiah and R. Shukla, *Polyhedron*, 1992, **11**, 3075.
24 D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda and M. G. B. Drew, unpublished work.
25 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
26 H. Guo, S. Sirois, D. Nguyen and D. R. Salahub, *Density functional theory and its applications to hydrogen bonded systems. Theoretical treatment of hydrogen bonding*, ed. H. Hadzi, Wiley, New York, 1997.
27 S. Sirois, E. Proynov, D. Nguyen and D. R. Salahub, *J. Chem. Phys.*, 1997, **107**, 6770.
28 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 204.
29 P. S. Braterman, B. C. Noble and R. D. Peacock, *J. Phys. Chem.*, 1986, **90**, 4913.
30 B. Bosnich, *Inorg. Chem.*, 1968, **7**, 2379.
31 A. Yamagishi, K. Naing, Y. Goto, M. Taniguchi and M. Takahashi, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2085.
32 B. T. Patterson and F. R. Keene, *Inorg. Chem.*, 1998, **37**, 645.
33 X. Hua and A. G. Lappin, *Inorg. Chem.*, 1995, **34**, 992.
34 D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda and M. G. B. Drew, *Chem. Commun.*, 1999, 403.
35 G. M. Sheldrick, SHELXL, University of Göttingen, 1997.
36 P. A. Lay, A. M. Sargeson and H. Taube, *Inorg. Synth.*, 1986, **24**, 291.
37 G. te Velde and E. J. Baerends, *J. Comput. Phys.*, 1992, **99**, 84.

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