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Photochemical ligand ejection from non-sterically promoted Ru(II)bis(diimine) 4,4'-bi-1,2,3-triazolyl complexes†

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Complexes of the form $[\text{Ru}(\text{diimine})_2(\text{btz})]^{2+}$ (btz = 1,1'-dibenzyl-4,4'-bi-1,2,3-triazolyl) are observed to undergo photochemical ejection of the btz ligand in the absence of any promotion through steric congestion to generate *cis*-bis(solvent) complexes $[\text{Ru}(\text{diimine})_2(\text{solvent})_2]^{2+}$.

Oligopyridine complexes of ruthenium(II) represent one of the most extensively investigated chemical systems due to their photophysical and electrochemical properties¹ that present opportunities for application in various areas from artificial photosynthesis to luminescent biological probes. More recently, this class of complexes has received growing attention for their application as photodynamic anti-cancer agents whereby DNA binding sites at the metal are generated by photoreactive ligand ejection.^{2–4}

The optical absorption spectra of these complexes are typically dominated by moderately strong absorption bands associated with metal-to-ligand-charge-transfer (MLCT) transitions which involve promotion of a Ru d-orbital localised electron to π^* orbitals centred on the oligopyridine ligand. Due to the spin-orbit coupling effect of the heavy metal ion these initially formed ¹MLCT states undergo rapid and efficient intersystem crossing to yield ³MLCT states. In themselves these ³MLCT states are inert toward ligand dissociation reactions. Instead, this involves higher lying metal-centred (MC) states associated with excitation of an electron into the Ru–N σ^* antibonding orbitals. If in close enough proximity, however, ³MC states can become efficiently thermally populated from photoexcited ³MLCT states resulting in isomerisation or ligand loss reactions. Photochemical reactivity can therefore be tuned by stabilisation of ³MC states with respect to ³MLCT states or by destabilisation of ³MLCT states with respect to ³MC states.

In studies of tris(diimine) Ru(II) complexes, photochemical ligand ejection has been facilitated by steric congestion

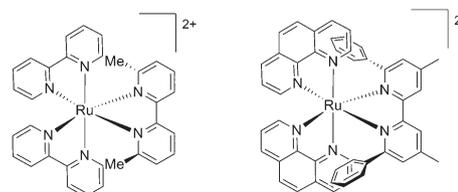


Fig. 1 Examples of ruthenium diimine complexes that exhibit photochemical ligand loss reactivity.

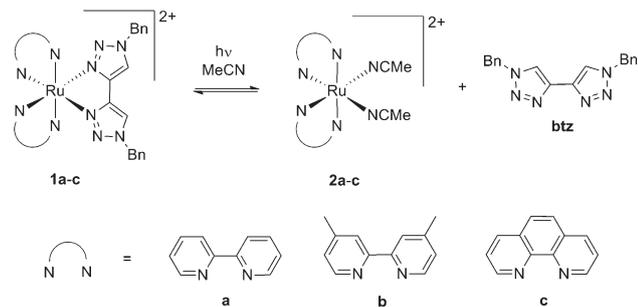
through the inclusion of substituents in the positions adjacent to the coordinating N-atoms of the ligand that is lost (Fig. 1).^{5–9} This steric congestion results in a stabilisation of the ³MC states such that they become thermally accessible and undergo efficient population from photo-excited ³MLCT states. Photoreactivity can also be achieved through inclusion of terdentate terpyridyl type ligands.¹⁰ This will stabilise ³MC states through their constrained coordination geometry involving a deviation from an ideal octahedral environment about the Ru centre.

We have previously reported the synthesis and photophysical characterisation of the series of complexes $[\text{Ru}(\text{bpy})_{3-n}(\text{btz})_n]^{2+}$ (bpy = 2,2'-bipyridyl) which undergo destabilisation of MLCT states with sequential replacement of bpy by btz.¹¹ We reasoned that this destabilisation might confer increasing photoreactivity with the number of btz ligands. Indeed, computational studies suggest that the lowest singlet and triplet excited states of the homoleptic btz complex $[\text{Ru}(\text{btz})_3]^{2+}$ in fact have MC character. We have recently reported on the photochemistry exhibited by the heteroleptic complex $[\text{Ru}(\text{bpy})(\text{btz})_2]^{2+}$ which undergoes loss of btz when illuminated using a domestic fluorescent lamp over a period of about a day in acetonitrile to yield *trans*- $[\text{Ru}(\text{bpy})(\text{btz})(\text{NCMe})_2]^{2+}$.¹² Significantly, this occurs in the absence of any steric congestion as is required in related system alluded to above. More significantly, this proceeds *via* an intermediate species, *trans*- $[\text{Ru}(\text{bpy})(\kappa^2\text{-btz})(\kappa^1\text{-btz})(\text{NCMe})]^{2+}$, containing a monodentate btz ligand. This intermediate forms quantitatively from the starting

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Scheme 1 Photochemical reactivity of complexes **1a** to **1c**.

material and shows remarkable stability allowing its unambiguous identification and even crystallographic characterisation.¹³

Here we report the photochemical reactivity of the series of complexes $[\text{Ru}(\text{diimine})_2(\text{btz})_2]^{2+}$ (diimine = bpy (**1a**); 4,4'-dimethyl-2,2'-bipyridyl (**1b**); 1,10-phenanthroline (**1c**)). Complexes **1a-c** are observed to undergo loss of the btz ligand to yield the complexes $\text{cis-}[\text{Ru}(\text{diimine})_2(\text{NCMe})_2]^{2+}$ (**2a-c**, Scheme 1), again in the absence of any steric promotion. Whilst no comparable intermediate is observed, ultimate ligand loss occurs on a much faster timescale than for $[\text{Ru}(\text{bpy})(\text{btz})_2]^{2+}$ and presents possible avenues for the development of new photodynamic DNA-binding anticancer reagents with electronically, rather than sterically, controlled photoreactivity.

Complexes **1b** and **1c** were prepared as their PF_6^- salts similarly to the previously reported complex **1a**.¹¹ Whilst **1b** was prepared in moderate yield synthesis of **1c** proved problematic, requiring column chromatography for purification and was isolated in only 5% yield. This low yield for this complex we attribute to difficulty in avoiding photochemical decomposition during purification procedures. As a consequence the entirety of the sample obtained was utilised for subsequent analysis by UV-visible absorption spectroscopy, ¹H NMR characterisation and subsequent monitoring of photochemical conversion.

Freshly prepared solutions of **1a-c** in d_3 -acetonitrile exhibit expected ¹H NMR spectra showing inequivalent donor rings of the diimine ligands and single singlet resonances for the triazole ring protons at approximately δ 8.3. Additionally, resonances are observed in each case at δ 5.39 to 5.51 for the methylene protons of the btz ligand. In the case of **1c** this appears as a pair of roofed geminal doublets due to the C_2 symmetry of the complex which renders these protons diastereotopic.

UV-visible absorption spectra of freshly prepared solutions of complexes **1a** to **1c** are presented in Fig. 2. **1a** and **1b** exhibit intense bands for diimine-based intraligand $\pi \rightarrow \pi^*$ transitions at about 285 nm whereas a similar band for **1c** appears at 263 nm. All complexes show diimine-based ¹MLCT bands between 380 and 480 nm. The profile of these bands for **1a** and **1b** have very similar appearance with maxima at about 444 nm and are blue-shifted with respect to those of

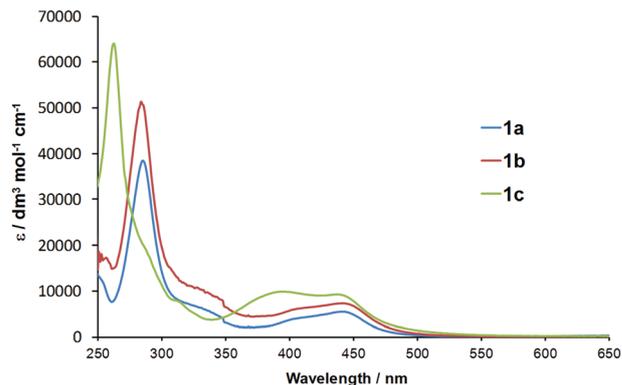


Fig. 2 UV-visible absorption spectra of complexes **1a** to **1c** in acetonitrile.

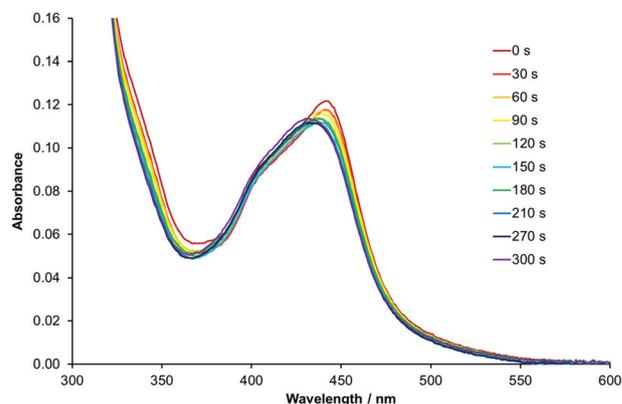


Fig. 3 UV-visible absorption spectra recorded during the photolysis of complexes **1a** in acetonitrile.

$[\text{Ru}(\text{bpy})_3]^{2+}$ (452 nm). That of **1c** is broader with maxima at 397 and 438 nm. All complexes also show a shoulder on the intraligand $\pi \rightarrow \pi^*$ band between 300 to 330 nm attributed to btz-centred ¹MLCT transitions.¹¹

Photochemical conversion of these complexes to complexes **2a** to **2c** occurs cleanly and can be conveniently achieved by suspending cuvettes or NMR sample tubes between the tubes of a domestic 23 W 1450 lumen fluorescent lamp. Using this simple set up, cuvettes containing solutions of **1a-c** were periodically removed from the lamp and their UV-visible absorption spectra recorded before returning for further illumination. Overlaid spectra recorded during the photolysis of **1a** are depicted in Fig. 3. As the reaction the ¹MLCT band is observed to undergo a slight blue-shift. Additionally, the btz-centred ¹MLCT shoulder between 300 and 350 nm is observed to bleach consistent with the loss of the btz ligand from the complex. After 5 to 10 minutes little further change is observed in the spectra.

¹H NMR spectroscopic monitoring of the photolysis reactions of **1a-c** was carried out in a similar manner (representative spectra are shown in Fig. 4 and ESI†). The resonances for the triazole ring and methylene protons of **1a-c** are observed



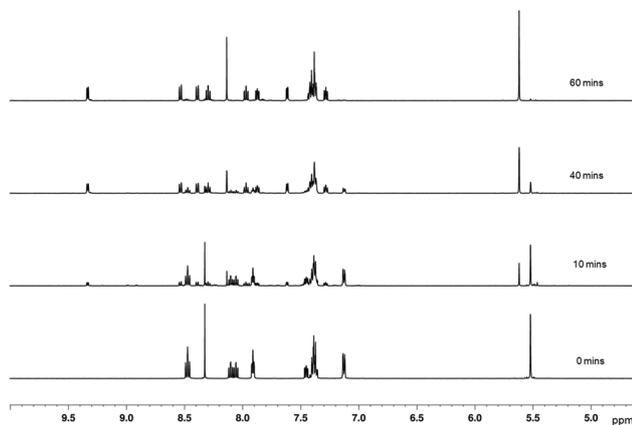


Fig. 4 ^1H NMR spectra of **1a** in d_3 -acetonitrile during photolysis to yield **2a**.

to diminish whilst new signals for the methylene and triazole ring protons of free btz are observed to grow at δ 5.6 and 8.1 respectively. Similarly, resonances for diimine protons of **1a–c** are observed to decay and are replaced by clearly identifiable resonances characteristic of **2a–c** with retention of C_2 stereochemistry. On conversion the protons *ortho* to the nitrogen atoms of the diimine ligand ring *cis* to the coordination sites vacated by the ejected btz are significantly deshielded with the resonance appearing at δ 9.11 to 9.76. The shift is observed due to these protons no longer residing above and hence no longer feeling the effect of the triazole π -system ring current. Under identical photolysis conditions no changes are observed in ^1H NMR spectra for samples of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$. Since the btz ligand is not sterically encumbered, indeed less so than bpy due the absence of H-atom substituents adjacent to the coordinated N-atoms,¹² the observed photochemical conversion is likely to be electronically promoted rather than induced by steric demands.

Unlike the case of the bis-btz complex $[\text{Ru}(\text{bpy})(\text{btz})_2]^{2+}$ no signals indicative of intermediate complexes were observed during the course of these experiments. The reaction of **1a** is observed to go to completion within an hour with that of **1b** occurring on a similar timescale. Loss of btz from **1c**, however, appears to take longer and goes to completion in over 3 hours. Despite the absence of an observed intermediate, as was seen during photolysis of the $[\text{Ru}(\text{bpy})(\text{btz})_2]^{2+}$, ultimate btz ligand ejection occurs at a significantly faster rate (approximately 2 days for the bis-btz complex). These timescales are however at odds with those observed in UV-visible absorption measurements and may possibly be an effect of the higher concentration of the samples used for NMR analysis.

In summary we have demonstrated that heteroleptic bitriazolyl complexes, $[\text{Ru}(\text{diimine})_2(\text{btz})]^{2+}$, undergo photochemical conversion with loss of btz. Mattiuzzi *et al.* have reported photodissociative decomposition of the $[\text{Ru}(\text{tap})_2(\text{btz})]^{2+}$ from UV-visible absorption data.¹⁴ Recently reported results from the group of Zysman-Colman show that an aryltriazole-based biscyclometalated iridium(III) complex with a btz ancillary

ligand also undergoes photoreactive ligand loss reactions as a route to decomposition.¹⁵ Whilst triazole-based ligands have resulted in complexes with attractive photophysical properties such as high luminescent quantum yield^{16–21} they also seem to promote photodissociative decomposition. Previously reported photodissociative systems involving tris(bidentate) ruthenium complexes proceed through ^3MC state stabilisation by the inclusion of substituents which impart steric congestion around the metal. Here, photoreactivity appears to be electronic in origin and derived by the destabilisation of the $^3\text{MLCT}$ state caused by the presence of btz. This therefore paves the way for the development of new systems where photoreactive tuning is electronically rather than sterically controlled. The *cis* stereochemistry of the solvent coordination sites generated upon btz ejection are set up to coordinate DNA in a cisplatin like manner. Complexes of this type may therefore form the basis of new photodynamic DNA-binding anticancer agents. Initial investigations of the anticancer properties of these complexes are currently under way.

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