Photochemistry

Unambiguous Characterization of a Photoreactive Ligand-Loss Intermediate**

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The photophysics and photochemistry of the complex [Ru-(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridyl) and its many N^N trischelate analogues have been the subject of enormous interest over the past four decades.[1] The interest stems primarily from their attractive photophysical and electrochemical properties, with potential applications in light harvesting, solar energy conversion, and artificial photosynthesis. One drawback however of [Ru(N^N)$_3$]$^{2+}$ type complexes can be photochemical ligand loss or isomerization reactions.[2] Whilst ordinarily an inconvenient side-reaction, such ligand loss pathways have been exploited, for example, in the development of photodynamic anticancer agents.[3] In these examples, ligand loss is often sterically promoted through inclusion of substituents adjacent to the N-donor atoms of the ligand that is ejected.[4]

The dominant features in the visible region of their optical absorption spectra are the characteristic metal-to-ligand charge-transfer (MLCT) bands. Absorption at wavelengths in these bands involves excitation of a metal d-orbital-centered electron to vacant π* orbitals on the N^N chelate ligands. Rapid intersystem crossing (ISC) then converts these initially formed ^{1}MLCT states into ^{3}MLCT states. It is these latter triplet states that are primarily responsible for phosphorescent emission exhibited by these complexes. In themselves, these ^{3}MLCT states are inert toward ligand loss and isomerization reactions. Instead, it is higher-lying metal-centered (MC) states, characteristic of population of the metal–ligand antibonding dσ* orbitals, that are associated for ligand dechelation and ligand dissociation pathways and quenching of luminescent emission. Population of ^{3}MC states can be effected by absorption of high-energy light in the UV or two-photon absorption.[5] If close enough in energy, however, ^{3}MC states can undergo efficient thermal population from ^{3}MLCT states.

Population of ^{3}MC states in [Ru(N^N)$_3$]$^{2+}$ type complexes was long thought to result in dechelation of one of the N^N ligands to form a coordinatively unsaturated species of the form [Ru(κ^2-N^N)$_2$(κ^1-N^N)]$^{2+}$, which is subsequently trapped by a solvent molecule. Isomerism or dissociation of the monodentate N^N ligand may then occur. More recently, computational calculations by Alary et al. suggest that the initially formed species as a result of ^{3}MC state population in [Ru(bpy)$_3$]$^{2+}$ and related complexes is the four-coordinate [Ru(κ^2-bpy)(κ^1-bpy)$_2$]$^{2+}$ in which two ligands dechelate through elongation of two mutually *trans* Ru−N bonds.[6]

Tachiyashiki and co-workers[7] reported HPLC and electrospray mass spectrometry detection of the species [Ru-(bpy)$_2$(3,3′-dmbpy)(NCMe)]$^{2+}$ (3,3′-dmbpy = 3,3′-dimethyl-2,2′-bipyridyl). Signals for the methyl groups were also observed by ^{1}H NMR spectroscopy that are suggestive of the formation of this intermediate in which the 3,3′-dmbpy ligand is coordinated in a monodentate fashion. Here, dechelation is presumably facilitated by the steric repulsion between the methyl groups of the dmpby ligand. The relatively long lifetime of the intermediate species then presumably results from inhibition of rechelation for the same reason. To the best of our knowledge, there have been no other reports of the directly observed intermediates for photochemical ligand loss from [Ru(bpy)$_3$]$^{2+}$ analogue complexes.

Herein we present the first unambiguous observation and characterization by NMR spectroscopy of a metastable ligand-loss intermediate with a monodentate N^N ligand for a non-sterically promoted [Ru(N^N)$_3$]$^{2+}$ type complex. Furthermore, this intermediate is observed to form quantitatively, reverting to the starting material with a long lifetime. Additionally we report a novel concomitant rearrangement in which the two remaining bidentate ligands adopt a square-coplanar geometry.

We have previously reported[8] the synthesis and photophysical investigation of the series of complexes [Ru(bpy)$_{3−n}$-(btz)$_n$]$^{2+}$ (*n* = 0 to 3, btz = 1,1′-dibenzyl-4,4′-bi-1,2,3-triazolyl). Sequential replacement of bpy by btz results in destabilization of the bpy π*-based LUMO in these complexes and a resultant blue-shift in the ^{1}MLCT bands. We reasoned that this destabilization might promote photochemical reactivity through enhanced ^{3}MC state population. Indeed, we report herein the unprecedented observation and characterization of the quantitatively formed ligand-loss intermediate *trans*-[Ru-(κ^2-bpy)(κ^2-btz)(κ^1-btz)(NCMe)]$^{2+}$ (**2**) from [Ru(bpy)-(btz)$_2$]$^{2+}$ (**1**) and its subsequent conversion to *trans*-[Ru(bpy)-(btz)(NCMe)$_2$]$^{2+}$ (**3**; Scheme 1).

Upon examination of NMR spectroscopy samples of **1** as the hexafluorophosphate salt in [D$_3$]acetonitrile that had been left in the laboratory in ambient daylight, numerous new signals were observed. On closer repeat examination of fresh
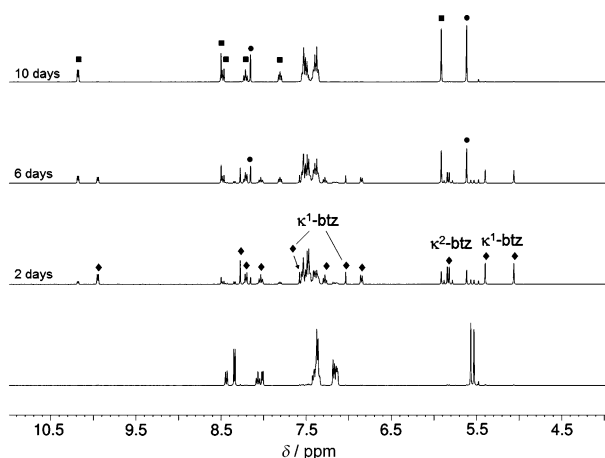
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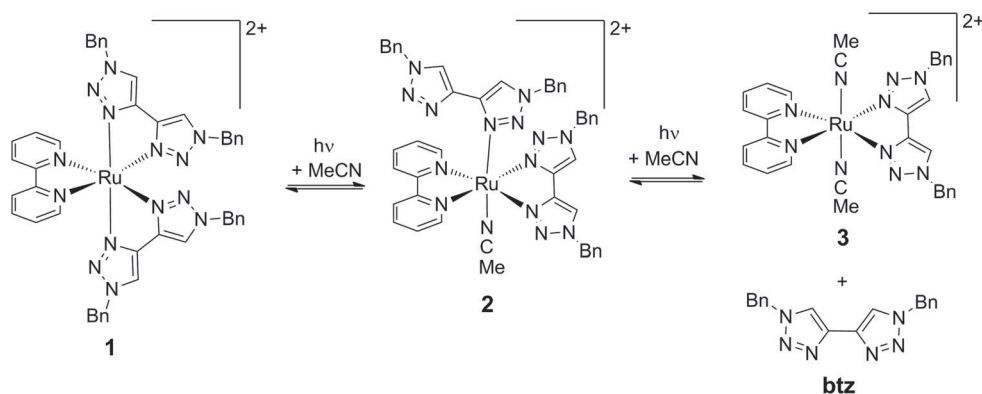
Scheme 1. Photochemical conversion of complex **1** into **3** with ejection of btz via monodentate btz-containing intermediate **2**.

ligand mandate a coplanar arrangement of these two ligands with presumably two acetonitrile ligands occupying the remaining *trans* coordination sites. Samples of **3** in CH_3CN were examined by electrospray mass spectrometry. Ions with m/z 328.1, 307.6, and 287.1 were observed corresponding to the dications **3**, [Ru(bpy)(btz)(NCMe)]$^{2+}$, and [Ru(bpy)(btz)]$^{2+}$, respectively, confirming the formation of a species containing two solvent ligands. Each signal exhibited the expected isotope pattern for a mononuclear ruthenium complex.

After prolonged illumination of concentrated solutions of **1** in acetonitrile, free btz was observed to precipitate. The liquor from these samples was decanted, the solvent removed and redissolved in CH_3CN. Crystals of X-ray diffraction quality were then obtained by slow vapor diffusion of diisopropylether. The molecular structure of the cation **3** is depicted in Figure 2 (see the Experimental Section and

Figure 1. Representative ^1H NMR spectra following the photochemical conversion of **1** into **3** via intermediate **2** in [D$_3$]acetonitrile at room temperature in ambient daylight (♦ **2**, ■ **3**, ● free btz).

samples of **1**, similarly left in daylight, clean conversion of **1** into a new complex **3** along with one equivalent of free btz is observed to occur. The process was observed to proceed through the intermediate species **2**. Representative spectra for this conversion are presented in Figure 1. Samples in which **1** had converted into **2** and which were subsequently left in the dark were observed to revert to the starting material. Samples that had been left to undergo full conversion into **3**, a process that therefore appears to require a second photon, were observed to be unchanged after similar storage in the dark. This indicates that re-coordination of ejected btz does not occur or is at least very slow.
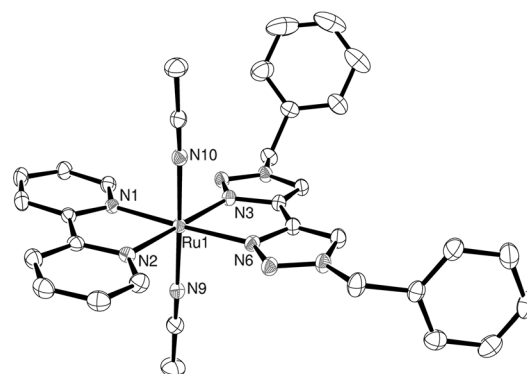
Along with the signals for free btz, the ^1H NMR spectrum of a fully converted sample containing **3** exhibits four resonances for the bpy ligand, which indicates that it retains the magnetic equivalence of the two pyridyl rings. The remaining coordinated btz ligand gives rise to a singlet resonance for the two triazole ring protons at δ 8.50 and a further singlet for the benzyl substituent methylene protons at δ 5.91.

The observed magnetic equivalence of the two triazole rings combined with the symmetrical environment for the bpy

Figure 2. ORTEP of the structure of the cation [Ru(bpy)(btz)(MeCN)$_2$]$^{2+}$ (hydrogen atoms and counterions removed for clarity, ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ru–N1 2.051(1), Ru–N2 2.053(1), Ru–N3 2.078(1), Ru–N6 2.097(1), Ru–N9 2.018(2), Ru–N10 2.021(2); N1-Ru-N2 79.04(6), N3-Ru-N6 76.67(5), N1-Ru-N6 177.38(6), N2-Ru-N3 179.51(6), N9-Ru-N1 178.45(6)).

Supporting Information). The complex adopts a distorted octahedral geometry with two *trans* acetonitrile ligands and coplanar bpy and btz ligands, in agreement with NMR data.

For complexes of the type [Ru(bpy)$_2$(N^N)]$^{2+}$, the resultant products from photochemical N^N ligand ejection have the form *cis*-[Ru(bpy)$_2$(solvent)$_2$]$^{2+}$ rather than the *trans* geometry as observed here. Density functional calculations were performed to determine optimized geometries for the *cis* and *trans* isomers of complexes **3** and [Ru(bpy)$_2$(NCMe)$_2$]$^{2+}$ (Supporting Information). *Cis*-[Ru(bpy)$_2$-

$(NCMe)_2]^{2+}$ is calculated to be some 40 kJ mol^{-1} more stable than its *trans* isomer, whereas *trans*-**3** is 7.76 kJ mol^{-1} more stable than its corresponding *cis* isomer. In the case of $[Ru(bpy)_2(NCMe)_2]^{2+}$, the 6/6′-position CH groups result in a severe steric clash between the two bpy ligands, giving rise to a significant deviation from planarity of the two ligands observed crystallographically[9] and is reproduced in our calculations. The absence of H-substituents adjacent to the coordinated N-atoms of the btz ligand in **3** means that similar steric congestion does not occur, allowing for the observed coplanarity and formation of the *trans* isomer.

The definitive stereochemical characterization of the product **3** enabled straightforward elucidation of the structural nature of the intermediate **2**. ^{1}H NMR spectra of samples in which **1** had converted into **2** again show four resonances for the bpy ligand and a singlet resonance for the two triazole ring protons of the κ^2-btz ligand. Rather than appearing as a singlet, the methylene protons of this κ^2-btz ligand give rise to a pair of roofed geminal doublets centered at δ 5.84. The data confirm the coplanarity of the bpy and κ^2-btz ligands as exhibited by **3**, but show that the two remaining mutually *trans* ligands are different from each other. Further signals for a second btz ligand in which the two triazole rings are magnetically inequivalent are also observed; two singlet resonances are observed δ 7.03 and 7.58 for the triazole ring protons along with two further singlet resonances for the methylene protons at δ 5.06 and 5.40. Owing to the stereochemical arrangement of the two bidentate ligands, this third ligand must therefore be coordinated in a monodentate fashion with the sixth coordination site *trans* to it occupied by a solvent molecule. We therefore assign the structure of **2** as *trans*-$[Ru(bpy)(\kappa^2$-btz$)(\kappa^1$-btz$)(NCMe)]^{2+}$. This is further supported by electrospray mass spectrometry data on partially converted samples of **1** in CH$_3$CN, which show signals along with that for **1** for an ion with m/z 445.1, in agreement with the proposed structure of **2**.

It was found that the photochemical conversion process could be dramatically accelerated if conducted by placing the NMR sample between the tubes of a domestic 23 W 1450 lumen fluorescent bulb. Cooling through the use of an electric fan allowed maintenance of the sample temperature at 40 °C. In this simple experimental set-up and with periodic NMR spectroscopic interrogation, near-complete conversion of **1** into **2** occurs in 30 min, with subsequent formation of **3** occurring over a period of 2 days. Samples in which **1** had converted into **2** were transferred and left in the bore of the spectrometer in the dark at 40 °C and were monitored every 20 min. Complex **2** is observed to revert to **1** in a first-order process with an approximate half-life of 13.75 h. Whilst monitoring these backward reactions, concentrations of **3** were observed to remain constant.

This extremely long life-time of the intermediate **2** with respect to reversion to **1** is partially explained by the

stereochemistry of the intermediate. The rearrangement of the bidentate ligands to give a coplanar arrangement will inhibit the re-coordination of the pendant triazole of the κ^1-btz ligand. Furthermore, the ^{1}H NMR resonances for the phenyl protons of the btz ligand in complexes such as **1** are generally ill-resolved and overlapping. ^{1}H NMR spectra for **2**, however, show clearly resolved and well-separated signals for the *ortho*- and *meta*-positions for one of the κ^1-btz phenyl rings. This could be indicative of some intramolecular π-stacking interaction that may further stabilize **2** to conversion back into **1** and indeed ultimately to subsequent ligand loss to yield **3**. No further evidence from nOe data could be obtained to corroborate this however.

We propose a tentative mechanism for the formation of **2** upon photoexcitation of **1** (Scheme 2). Visible excitation of **1** yields a ^{1}MLCT state, which rapidly undergoes ISC to yield
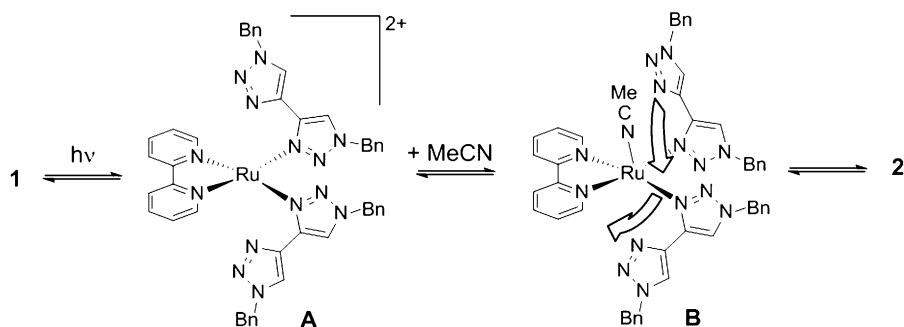
Scheme 2. Proposed mechanism for the formation of intermediate **2** after photoexcitation of **1**.

the corresponding ^{3}MLCT state. Owing to the destabilization of this ^{3}MLCT state relative to the ^{3}MC state when compared to those states of $[Ru(bpy)_3]^{2+}$, efficient thermal interconversion to the ^{3}MC state occurs. This results in the formation of the bis(dechelation) photoproduct $[Ru(bpy)(\kappa^1$-btz$)_2]^{2+}$ (**A**),[6,8] which is trapped by a solvent molecule to form the species $[Ru(bpy)(\kappa^1$-btz$)_2(NCMe)]^{2+}$ (**B**). The incoming solvent ligand deflects the adjacent pendant triazole ring of btz ligand which then re-coordinates to establish the coplanar bpy/btz arrangement. In the process, the second btz ligand is induced to migrate to the coordination site *trans* to the new solvent ligand, thereby forming **2**.

In summary, we have reported the unprecedented quantitative formation and unambiguous characterization of a long-lived photochemical ligand-loss intermediate containing a monodentate N^N ligand. Further, the process involves a novel concomitant rearrangement of the other two chelate ligands such that they become coplanar. These results therefore point the way to numerous possible applications of this new class of complex. These include the possibility of utilizing complexes of this type for the photogeneration of supramolecular synthons, as components in light-activated molecular machines and switches, and as potential new photodynamic anticancer drugs.

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