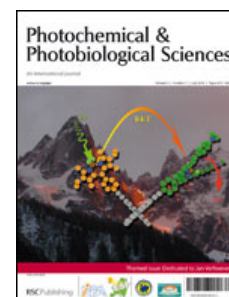This article is published as part of a themed issue of
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Photoinduced ligand isomerisation in a pyrazine-containing ruthenium polypyridyl complex†

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Photochemically-induced ligand rearrangements for the N2 and N4 coordination isomers of the complex $[Ru(bpy)_2(Hpztr)]^{2+}$ and its deprotonated analogue $[Ru(bpy)_2(pztr)]^+$, where bpy is 2,2′-bipyridyl and Hpztr is pyrazine-1,2,4-triazole ligand, are reported. ^1H NMR spectroscopic and HPLC studies indicate that in acetone and acetonitrile the complexes are photostable when the triazole ring is deprotonated. Irradiation of the protonated N2 isomer in acetone results in formation of the N4 isomer, with the N4 isomer being photostable. In acetonitrile both isomers show photolability of the triazole-based ligand and full dissociation to form $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ is observed. The activation parameters for the population of the ^3MC state from the lowest ^3MLCT manifold, as obtained from temperature-dependent emission lifetime studies, are reported and their relevance to the observed photochemical behaviour is considered. The results obtained are discussed in relation the analogous pyridine-triazole complexes.

Introduction

Following the early work of Adamson[1] and others,[2] the investigation of photoinduced processes has developed substantially over the last 50 years. This development was further intensified with the application of ruthenium polypyridyl complexes as dyes for solar cells,[3] oxygen sensors,[4] and as bioprobes[5] and molecular machines and devices, such as molecular wires, motors and switches.[6] Recently these studies have received further interest due to the potential application of polypyridyl compounds in the development of sustainable and environmentally friendly energy such as photocatalytic hydrogen generation[7] and CO_2 reduction.[8]

Over the last number of years we have reported a series of studies of photoinduced ligand rearrangements of ruthenium polypyridyl complexes containing pyridine-1,2,4-triazole (Hpytr) ligands. Recently such ligands have seen widespread application in iridium(III) based OLED systems also.[9] The complex $[Ru(bpy)_2(pytr)]^+$ (Fig. 1), which contains a deprotonated pyridine-1,2,4-triazolato ligand is photostable upon irradiation in basic acetone and acetonitrile. This photostability is related to the strong σ-donor capacity of the deprotonated triazole ring that provides for a considerable destabilization of the ^3MC state that has been identified as being involved in the photochemical activity of ruthenium polypyridyl complexes.[10] Because of the destabilisation this excited state is not populated significantly at

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Fig. 1 N2 isomers of $[Ru(bpy)_2(pztr)]^{2+}$ **1**, (left) and $[Ru(bpy)_2(pytr)]^{2+}$ **2**, (right); bpy = 2,2′-bipyridine.

room temperature. However, for complexes containing protonated or methylated triazole ligands the ^3MC level is stabilised and photolability observed.[11,12,13] As a result photoinduced ligand dissociation processes are observed where the triazole ligand is not anionic. For $[Ru(bpy)_2(Hpytr)]^{2+}$ there are two coordination isomers possible where the Hpytr ligand is bound via either the N2 or the N4 nitrogen atom of the triazole ring (Fig. 2). Irradiation in CH_2Cl_2 of either the N2 or N4 isomer leads to a photostationary state with a N4 : N2 ratio of 4 : 1.
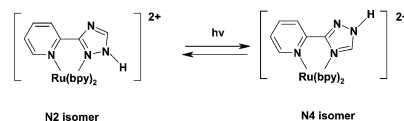
Fig. 2 Reversible N2–N4 isomerisation observed for compound **2H**.

For the analogous pyrazine triazole (Hpztr) based complexes (e.g., Fig. 1) photochemically induced ligand isomerisations have not been reported. There have however been extensive photophysical studies[14,15] that have shown that contrary to that which is observed for the Hpytr based complexes, where the emitting state is bpy based, the lowest energy triplet state in complexes containing the protonated ligand is based on the pyrazine ring.

In this contribution we report the photochemically induced rearrangements observed for the complex [Ru(bpy)$_2$(Hpztr)]$^{2+}$ (**1H**). The photochemical processes observed are discussed in terms of the structure and the electronic properties of the complex and are compared with those observed for the analogous complex **2H** based on the Hpytr ligand.

Experimental

Synthesis and materials

All solvents employed in spectroscopic measurements were of spectroscopic grade (Sigma-Aldrich). All other solvents were of HPLC grade or better. *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O,[16] and the N2 and N4 isomers of [Ru(bpy)$_2$(pztr)](PF$_6$)$_2$ **1**[14a] were prepared as reported before. [Ru(bpy)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$ was available from earlier studies.[13b]

N2-/N4-isomer [Ru(bpy)$_2$(pztr)]PF$_6$

cis-[Ru(bpy)$_2$Cl$_2$]·2H$_2$O (185 mg, 0.36 mmol) and Hpztr-H (80 mg, 0.54 mmol) were added to a mixture of EtOH (30 mL) and H$_2$O (30 mL). After heating at reflux for 8 h, EtOH was removed *in vacuo* and the reaction mixture was left to stand overnight. The crude product was flash chromatographed on a silica column with 7 : 3 (v/v) CH$_3$CN–H$_2$O saturated with KNO$_3$. A drop of NH$_3$ solution and NH$_4$PF$_6$ (30 mg, 0.18 mmol) was added in turn to each of the two fractions collected. Each solution was washed with dichloromethane (3 × 20 mL) and the solvent was evaporated. The N2-isomer (second fraction of silica column) was purified further by column chromatography on an alumina column (neutral) with CH$_3$CN as eluant. The solvent was evaporated *in vacuo* and the solid was recrystallised by slow evaporation from 2 : 1 MeOH–H$_2$O. The N4-isomer (first fraction from the silica column) was chromatographed on an alumina column (neutral) with first CH$_3$CN, then 1 : 20 MeOH–CH$_3$CN, 1 : 10 MeOH–CH$_3$CN and 1 : 5 MeOH–CH$_3$CN. The solvent was evaporated *in vacuo* and the solid recrystallised by slow evaporation of 2 : 1 MeOH–H$_2$O. Yield: 51 mg of the N2-isomer (0.09 mmol, 25%), 90 mg of N4-isomer (0.16 mmol, 45%). The ^{1}H NMR spectra were in accordance with literature values.[15a,c]

^{1}H-NMR spectra were recorded on a Bruker Advance 400 MHz NMR spectrometer. Data are relative to residual solvent absorptions. UV/vis absorption spectra were recorded on a JASCO 570 UV/vis/NIR spectrophotometer using a 1 cm pathlength quartz cells. Temperature dependent luminescence lifetime studies were carried out using a Spectra Physics Q-switched Nd-YAG laser system as described elsewhere.[14e] Analytical High Performance Liquid Chromatography (HPLC) experiments were carried out using an analytical HPLC system consisting of a Varian Prostar HPLC pump fitted with a 20 µL injection loop, a Varian Prostar PDA detector connected to a dedicated PC, and a HiChrom Partisil P10SCX-3095 cation exchange column. Mobile phase CH$_3$CN : H$_2$O : CH$_3$OH with volume ratio 75 : 20 : 5 containing 0.12 M KNO$_3$. Flow rate: 2.0 cm^3 min^{-1}; detection wavelength: 430 nm. The photochemistry of complexes **1**, **2**, **1H** and **2H** was monitored by HPLC and ^{1}H NMR spectroscopy. HPLC samples were irradiated in acetonitrile or acetone with an array of 60 Kingbright L-7113PBC-Gblue 470± 20 nm LEDs. Photolysis studies monitored by ^{1}H NMR spectroscopy were carried out by irradiating the compounds in NMR tubes and placing them before a 20 W tungsten filament light source slide projector (Kodak Carousel S-AV 2020). Sample heating was prevented using a water filter. The protonation state of the triazole ring of the complexes was controlled by addition of 100 µl triethylamine or trifluoroacetic acid to the 2 mL NMR sample.

Results and discussion

Both isomers show strong ^{1}MLCT bands in the visible part of the spectrum as expected.[15c] The absorption maxima of both protonated compounds are very similar with a λ_{max} of 440 nm for the N2 isomer and a value of 439 nm for the N4 species. Upon deprotonation the absorption maxima of the N2 and N4 isomers shift to 456 and 457 nm respectively. Because of the similarity of these values and also in the shape of the absorption spectra these features can not be used to discriminate between the two isomers.

Irradiation in acetonitrile

The photochemical properties of **1** and **1H** were investigated using ^{1}H NMR spectroscopy and HPLC. Irradiation of the compounds was carried out in both acetonitrile and acetone.

The HPLC chromatogram obtained for a mixture of the N2 and N4 isomers is shown in Fig. 3. The N4 isomer is observed to have a retention time of 5.4 min, while the N2 is observed at 6.7 min. The same elution order is observed for the pyridinetriazole analogues (*e.g.*, **2**).[11] In contrast to **2**, the UV/Vis spectra of the two isomers of **1/1H** are almost identical and cannot be used for identification as a result. The two species are identified by their ^{1}H NMR spectra however. Of most importance for the identification of the nature of the isomer obtained are the ^{1}H NMR absorptions than can be attributed to the pyrazine and the triazole rings. The pyrazine absorptions appear as a singlet (H3) in the range 9.1–9.5 ppm, while H5 appears at *ca.* 7.8 ppm and H6 at *ca.* 8.2 ppm; the exact location depending on whether the compound is protonated or not. The most indicative feature identifying the isomeric form is the position of the H5 proton of the triazole ring. For the protonated N2 isomer (*N2***1H**) this proton is observed at 8.91 ppm and for the deprotonated N2 isomer at 8.0 ppm. For the N4 isomer the corresponding values are at *ca.* 8.4 and 7.4 ppm respectively. These values were obtained in acetone and vary substantially depending on the amount of acid added and the water content of the solvent. The rather large difference between the values observed for the
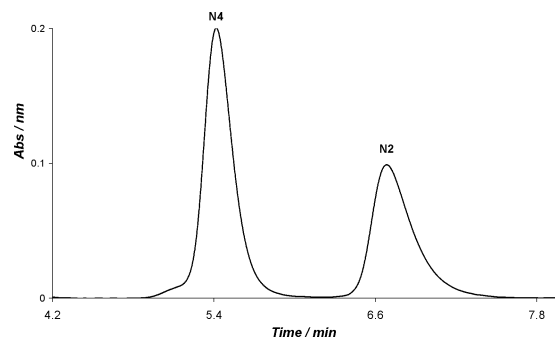
Fig. 3 HPLC trace of N2 and N4 isomers of **1**. Mobile phase CH$_3$CN : H$_2$O : CH$_3$OH with volume ratio 75 : 20 : 5, 0.12 M KNO$_3$, flow rate: 2.0 cm^3 min^{-1}; detection wavelength: 430 nm, 20 °C.

H5 protons for the two isomers is related to the through space interaction between these protons and neighbouring bpy ligands especially in the case of the N4 isomer.[15c,16] This through space interaction results in the considerable shift to lower ppm values for the proton in the N4 isomer compared with the N2 species.

HPLC and ^{1}H NMR spectroscopic studies indicate that both isomers of the deprotonated compound **1** are photostable in the presence of the base TEA in acetonitrile and in acetone. This is in agreement with the reported behaviour of compound **2**.[11] However, acidification of the solution prior to irradiation allows for photoinduced changes to be observed. The photoinduced changes observed for *N4***1H** in acetonitrile monitored by HPLC are shown in Fig. 4.
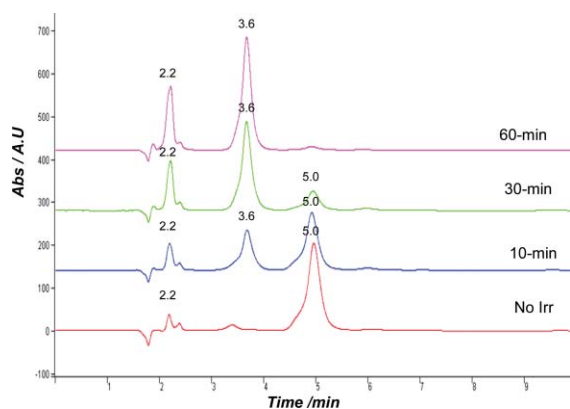
Fig. 4 HPLC trace following the irradiation of the N4 isomer in CH_3CN with CF_3CO_2H (mobile phase $CH_3CN : H_2O : CH_3OH$ with volume ratio 75 : 20 : 5, 0.12 M KNO_3). Flow rate: 2.0 cm^3 min^{-1}; detection wavelength: 430 nm, 20 °C.

The decrease in the signal for the N4 isomer (retention time of 5.0 min) with irradiation is accompanied by the appearance of a new peak at 3.6 min. This signal which shows an absorption maximum at 425 nm is identified as the $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ by comparison with an authentic sample. The appearance of a second product with a retention time of 2.2 min ($\lambda_{max} = 472$ nm) is observed also. The nature of these species could not be determined unambiguously but may be related to the intermediate observed in the ^{1}H NMR spectrum in Fig. 5. The irradiation of *N2***1H**
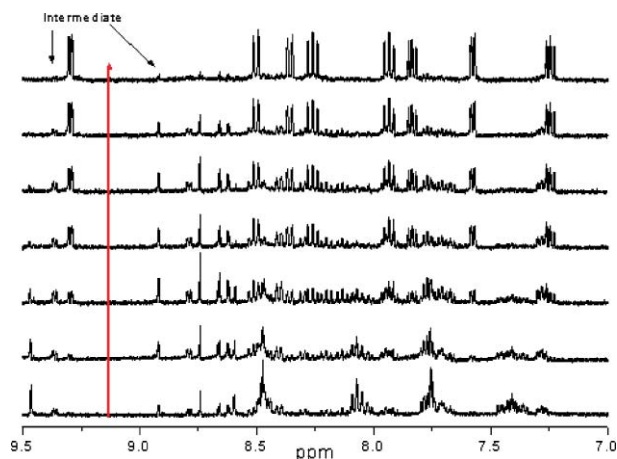
Fig. 5 Irradiation of N2 isomer of $[Ru(bpy)_2(Hpztr)]^{2+}$ in acetonitrile with CF_3CO_2H.

in acetonitrile was monitored by ^{1}H NMR spectroscopy also (Fig. 5). ^{1}H NMR spectra show that upon irradiation of both the N2 and the N4 isomers of **1H** in acidic acetonitrile results in formation of the same final product, $[Ru(bpy)_2(CH_3CN)_2]^{2+}$, which was confirmed by comparison with the spectrum of an authentic sample.

As observed in the HPLC traces an intermediate is observed with signals at 8.0, 8.9 pm and 9.3 pm which disappear upon further photolysis. The observed isomerisation process could suggest that in this intermediate the pyrazine ring remains attached to the metal centre, since this allows for reorientation of the triazole ring in the sterically most favoured position. However, our earlier studies have shown that an alternative intermediate species is formed upon photolysis of the related complex $[Ru(bpy)_2(L-L')]^{2+}$ where L-L' is 4-methyl-3-(pyridine-2-yl)-1,2,4-triazole. In this intermediate the triazole ring is bound to the N1 atom as shown in Fig. 6.[13b] Such a species can be formed starting from both **1H** isomers and hence the formation of the isomer where the triazole ring is coordinated to the metal centre *via* the N1 atom of the triazole ligand can not be excluded.
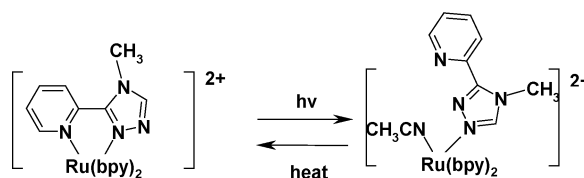
Fig. 6 Photo- and thermally-induced coordination changes for $[Ru(bpy)_2(L-L')]^{2+}$ where L-L' is 4-methyl-3-(pyridine-2-yl)-1,2,4-triazole.

Irradiation in acetone

The photostability of the protonated complex **1H** in acetone was investigated. Surprisingly, irradiation of the N4 isomer of **1H** does not result in any observed changes over at least a 2 h period. The N2 isomer, by contrast, shows photoreactivity as illustrated in Fig. 7. Initially the N2 isomer is observed at a retention time of 7.4 min. After irradiation the N4 isomer is present as the main product with a retention time of 5.6 min. As observed in the ^{1}H NMR spectra the formation of other minor products is observed also (Fig. 8).
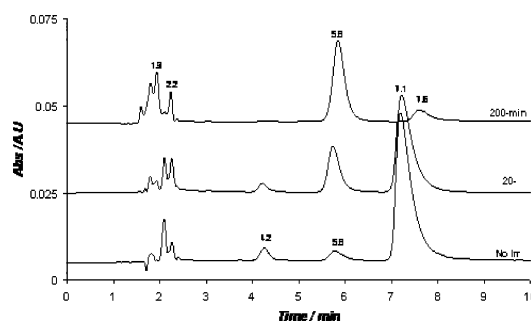
Fig. 7 HPLC assessment of the photoisomerisation of N2 isomer of **1H** in acetone in the presence of CF_3COOH.

Most indicative for the isomerisation from the N2 to the N4 isomer are the changes observed for the pzH3 peak which changes from 9.63 ppm for the N2 isomer to 9.54 pm. Additionally the peak
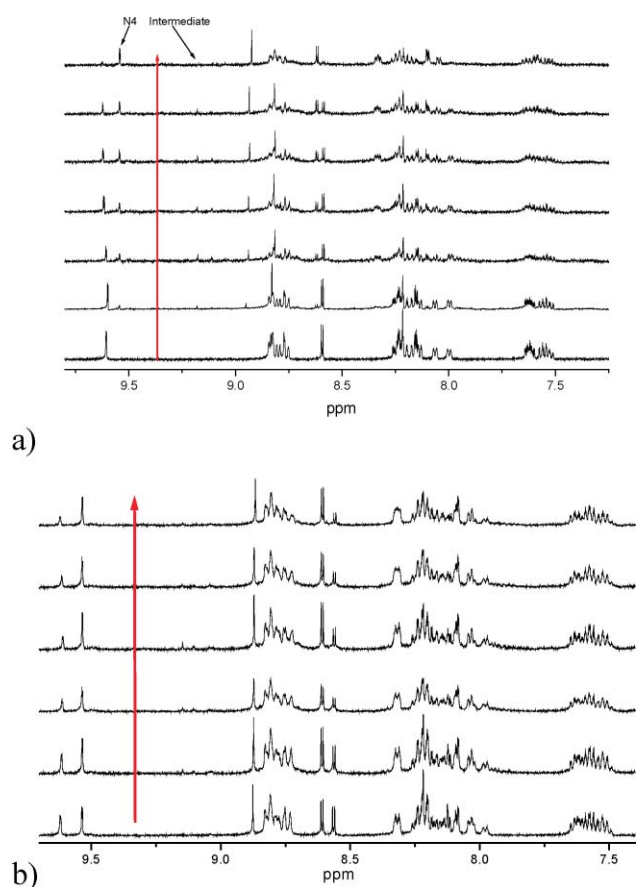
Fig. 8 (a) Irradiation of the N2 isomer of [Ru(bpy)$_2$(Hpztr)]$^{2+}$ (**1H**) in acetone with CF$_3$CO$_2$H. (b) Irradiation of a 1 : 1 mixture of the N2 and N4 isomer of [Ru(bpy)$_2$(Hpztr)]$^{2+}$ (**1H**) in acetone with CF$_3$CO$_2$H. Spectra run from bottom to top in each case.

of the pzH5 shifts from 8.58 pm to 8.61 pm. During irradiation two peaks appear at 9.1 pm and 9.17 pm and disappear in the final spectrum, indicating (as in the HPLC traces, *i.e.* at 4.2 and 2.0 min) the formation of a small amount of an intermediate. The concentrations of these species are however to low to allow for definitive assignment.

Activated crossing from the ^{3}MLCT to ^{3}MC states

Ligand exchange *via* cleavage of metal–ligand bonds is a paradigm photochemical reaction and is central to results discussed here. Meyer and co-workers,[17] in their studies of ruthenium(II) polypyridyl complexes, identified the triplet metal centred (^{3}MC) state as being responsible for the photochemical ligand dissociation observed for these compounds. The state corresponds to population of the antibonding (e_g) orbitals which is accessed at room temperature from the lowest ^{3}MLCT state manifold. This process is thermally activated and the difference in energy between the ^{3}MLCT and ^{3}MC states can be estimated indirectly from the temperature dependence of the emission lifetime. The activation parameters obtained in an ethanol–methanol (4 : 1) solvent system over the temperature range 150–300 K are shown in Table 1 and are compared with related data for Hpytr based compounds *N2***2** and *N4***2**. For example values of the ^{3}MLCT–^{3}MC energy gap for **1H** complexes are similar to those obtained for their **2H** analogues.

Table 1 Activation parameters and kinetic data for ruthenium(II) pyrazine triazole complexes and related pyridine triazole analogues

	E_a/cm^{-1} ^{a}	A/s^{-1}	$k_{77\,K}$/s^{-1}
*N4***1**	1300	5.1×10^9	2.2×10^5
*N2***1**	1200	3.6×10^9	2.4×10^5
*N4***1H**	2950	1.5×10^{13}	1.5×10^5
*N2***1H**	2200	9.0×10^{11}	1.4×10^5
*N4***2**^{b}	600	3.1×10^7	6.4×10^5
*N2***2**^{b}	550	4.7×10^7	4.1×10^5
*N4***2H**^{b}	2850	9.2×10^{13}	2.8×10^5
*N2***2H**^{b}	1700	6.0×10^{10}	2.8×10^5

^{a} Data obtained in ethanol–methanol (4 : 1) at temperatures 150–300 K. Rate constant errors ± 5%, activation parameters ± 10%. ^{b} Values obtained from reference 11.

The temperature dependent lifetime data in the temperature range 150–300 K were analysed by assuming that the excited state decay consists of a temperature independent intrinsic decay from the ^{3}MLCT state and a single thermally activated non-radiative decay process according to eqn (1):

$$\frac{1}{\tau_{obs}} = k_{77\,K} + A \exp\left(\frac{-E_a}{RT}\right) \qquad (1)$$

where $k_{77\,K} = k_{nr} + k_r$ (the sum of the temperature-independent radiative and non-radiative decays from the ^{3}MLCT direct to the ground state), A is the preexponential factor and E_a is the activation energy for crossing from the ^{3}MLCT to the ^{3}MC excited state. $k_{77\,K}$ is obtained at 77 K, assuming that k_{nr} and k_r are temperature independent above 77 K and that population of the ^{3}MC states is effectively prevented at 77 K

Activation parameters obtained for ruthenium polypyridyl complexes usually fall into one of two categories:

(a) small activation energies (<800 cm^{-1}) and low prefactors (<10^9 s^{-1});

(b) large activation energies (>2000 cm^{-1}) and large prefactors (>10^{11} s^{-1}).

Complexes exhibiting the former behaviour are typically unreactive towards photosubstitution. This is indeed observed for the deprotonated species. The low prefactor suggests the process involves the population of an MLCT state of largely singlet character that is weakly coupled to the ^{3}MLCT state.[18] Complexes exhibiting the second type of behaviour are typically photochemically active and the activation process has been ascribed as being due to population of a ^{3}MC state. If relaxation of the ^{3}MC state is rapid relative to crossover from the ^{3}MC state back to the ^{3}MLCT state, the measured E_a represents the activation energy for ^{3}MLCT–^{3}MC internal conversion. For such a process the prefactor is expected to be large (10^{13}–10^{14}). The N4 isomers for both **1H** and **2H** fall in this catagory.

The N2 isomer of [Ru(bpy)$_2$(Hpztr)]$^{2+}$ (*i.e.* *N2***1H**) intermediate behaviour was observed, with an activation barrier of 2200 cm^{-1} and a prefactor of 9.0×10^{11}. This may indicate that the ^{3}MLCT and ^{3}MC states are in equilibrium. In this case the measured activation energy corresponds approximately to the energy gap between the two states.[19] For compound *N2***2H** this intermediate behaviour was also observed.[11]

Population of the ^{3}MC state is a key step in the photochemistry of the protonated pyrazyltriazole complexes. pK_a data indicate

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that triazole is a stronger σ-donor when coordinating *via* the N2 nitrogen than *via* the N4 nitrogen.[11,14a] Hence for the N2 isomers of **1H** and **2H** the ^{3}MC state would be expected to lie higher in energy than the for the corresponding N4 isomers. Consequently the larger activation energy for population of the ^{3}MC state from the ^{3}MLCT state is expected to be higher for the N2 isomers compared with the N4 isomers. However, this is not found to be the case, suggesting that population of the ^{3}MC excited state is not the rate determining step in the photochemistry of the protonated pyrazoletriazole complexes. Instead, the rate-determining step may be governed by the formation of the monodentate species during the photoisomerisation and the subsequent ground state thermal self-annealing process. This may be related to the difference observed between the N4 and N2 isomers in the deactivation mechanism for the ^{3}MC state. While the prefactors for the N2 isomers suggest the existence of an equilibrium with the ^{3}MCLT state, fast deactivation of the ^{3}MC state is taking place *via* other pathways.

Conclusions

The aim of this study is to compare the photochemical properties of the [Ru(bpy)$_2$(pztr)]$^+$ **1**, and [Ru(bpy)$_2$(pytr)]$^+$ **2** and their protonated analogues **1H** and **2H**. Earlier studies have shown that for **1**, **2** and **2H** the LUMO and lowest emissive ^{3}MLCT state is based on the bpy ligands,[11] while for **1H** the LUMO and lowest emissive ^{3}MLCT state is pyrazine based.[14d,e] The purpose of this study is therefore to investigate whether the difference in the location of the LUMO/^{3}MLCT state affects the photolability of the complexes. The deprotonated complexes **1** and **2** are both photostable in acetonitrile and acetone. This is not unexpected since the activation parameters (Table 1) for these compounds indicate the population of the ^{3}MC excited state is not significant. The photochemical behaviour of **1H** and **2H** in CH$_3$CN is again the same, with ligand loss occurring with the formation of [Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$ as the final product. Differences are however observed upon photolysis in acetone. As reported earlier photoinduced interconversion of the N2 and N4 isomers of **2H** is observed in CH$_2$Cl$_2$, with a steady-state equilibrium of N4 : N2 of 4 : 1. Upon irradiation of **1H** however, it was found that the N4 isomer is photostable while the N2 species isomerises to the N4 species *via* an intermediate. The results obtained therefore indicate that for these compounds the location of the LUMO in **1H** and **2H** does not affect the photolytic behaviour fundamentally. The photostability of the N4 isomer of **1H** is however an important point but is likely to be associated with the thermal stability of the primary photoproduct, *i.e.* the species that contains a monodentate coordinated ligand.

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