Switching pathways for reversible ligand photodissociation in Ru(II) polypyridyl complexes with steric effects

The absence of the steric (Thorpe-Ingold) effect of a methyl group in the ligand MeN4Py switches the reversible photodissociation of a pyridyl-CH$_2$- moiety in [Ru(CH$_3$CN)(MeN4Py)]$^{2+}$, to form one coordination isomer of the complex [Ru(CH$_3$CN)$_2$(MeN4Py)]$^{2+}$, to reversible photodissociation of pyridyl-moieties connected via a tertiary carbon in [Ru(CH$_3$CN)(N4Py)]$^{2+}$ resulting in reversible formation of two distinct thermally stable coordination isomers.

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4.1 Introduction
Compounds that undergo well defined and reversible structural changes following excitation with
UV and visible light provide insight into the fundamental photophysical processes that occur in
nature’s photoswitching systems and are of increasing interest due to the wide range of
applications that non-invasive control over molecular structure provides. Over the last half
century, organic photoswitches based on, primarily, light-induced pericyclic and E/Z isomerization
reactions have seen widespread application in areas as diverse as materials science and
photochemical control of catalysis, and biological activity.

More recently molecular photoswitching with transition metal complexes has emerged
especially in the control of structure and for selective small molecule release. With the exception of hybrid inorganic-organic photoswitches, transition metal based photochemistry is dominated
by a population of metal centered (dd) dissociative excited states, that is, promotion of electrons
to anti-bonding metal-ligand orbitals. Ruthenium(II) polypyridyl complexes are prominent in this
field due to their remarkable photophysical and photochemical properties including
photoluminescence, photoredox catalysis, photoisomerization, and photoinduced ligand
exchange reactions.

The photochemistry of ruthenium(II) complexes is dominated by the lowest triplet metal-to-
ligand charge transfer (3MLCT) and dissociative metal centered states, and is typified by
dissociative reactions in which excitation leads to partial or complete ligand dissociation followed
by coordination of a new ligand or by a different donor atom on the ligand already present (linkage
isomerism). Thermally reversible ligand photodissociation has been reported by several groups,
notably by Kojima and Sarkar and co-workers. The selectivity of thermal and photochemical
ligand dissociation in the complex [Ru(TPA)(bpy)] has been shown to be due to steric repulsion
within the equatorial plane and has been explored extensively recently with density functional
theory (DFT) methods.

Recently, we reported the first example of a ruthenium(II) complex based on the pentadentate
ligand MeN4Py [1,1-di(pyridin-2-yl)-N,N-bis(pyridin-2-yl-methyl)ethan-1-amine] in which nearly
complete reversible two-way photoswitching (and photochromism) is observed. The reversible
photochemical switching of [Ru(CH3CN)(MeN4Py)]2+ (1) was achieved by irradiation with visible
light to induce dissociation of a pyridine moiety, which was replaced by acetonitrile, to form the
thermally stable complex 1P as sole photoproduct.

Scheme 1. Reversible photochemistry of [Ru(CH3CN)(MeN4Py)]2+ (1) upon irradiation at 457 nm and
subsequently irradiation at 355 nm.
The highly reversible photochemistry of 1 is remarkable, especially in regard to the selective dissociation of the least sterically encumbered $\text{−CH}_2\text{-pyridyl}'s$. The introduction of the methyl group in the synthesis of MeN4Py involves lithiation and subsequent methylation of N4Py (1,1-di(pyridin-2-yl)-$N,N$-bis(pyridin-2-yl-methyl)methanamine) and hence the importance of the methyl group to the selectivity and especially reversibility of the photochromism of 1 prompted our study of its more easily prepared analogue $\text{[Ru(CH}_3\text{CN)(N4Py)]}^{2+}$ (2).

In this chapter, we show that the photochromism of 2 involves dissociation of pyridyl moieties as observed for 1, but is fundamentally different because of the absence of the methyl group. The photochemistry of 2 is shown through a combination of UV-vis absorption, FTIR, $^1\text{H}$ NMR, spectroscopy, ESI mass and X-ray crystallography, to be dominated by dissociation of the more encumbered $\text{−CH(pyridyl)}$ moieties (i.e. bound to the tertiary carbon), leading to the reversible formation of two coordination isomers that are not accessible through thermal chemistry.

Scheme 2. Photoswitching of coordination mode in $\text{[Ru(CH}_3\text{CN)(N4Py)]}^{2+}$ (2) by irradiation at 457 nm and subsequent irradiation at 355 nm; pathway I involves dissociation of pyridyl moieties attached to tertiary carbon (CH) to form $2a/2a'$, whereas pathway II involves the dissociation of pyridyl moieties attached via methylene units, followed by photoinduced rearrangement to form $2b/2b'$.

4.2 Results
4.2.1 Structure and spectroscopic characterization of $\text{[Ru(CH}_3\text{CN)(N4Py)]}[(\text{PF}_3)_2]$ (2).

The ESI mass spectrum of 2 in acetonitrile shows a base peak at $m/z$ 255.3 corresponding to the dication $\text{[Ru(CH}_3\text{CN)(N4Py)]}^{2+}$. The relative simplicity of the $^1\text{H}$ NMR spectrum of 2 in acetonitrile-$d_3$ reflects the plane of symmetry in the complex with two distinct sets of pyridyl signals and a singlet at 4.52 ppm assigned to the methylene signals (vide infra). The signal of the coordinated acetonitrile is at 2.74 ppm, confirming an exchange of the chlorido ligand of the precursor $\text{[Ru(Cl)(N4Py)]Cl}$ for acetonitrile (vide infra). The UV-vis absorption spectrum of 2 in acetonitrile shows two absorption bands at 350 nm and 425 nm which are assigned to metal to ligand charge transfer ($^1\text{MLCT}$) transitions, respectively, (Figure 1a) similar to its analog $\text{[Ru(CH}_3\text{CN)(MeN4Py)]}(\text{BF}_4)_2$ (1) (see in chapter 3). Raman ($\lambda_{\text{exc}}$ 785 nm) and IR spectra of 2 recorded in the solid state show a C≡N stretch mode at 2276 cm$^{-1}$ and pyridine modes in the region 1000-1600 cm$^{-1}$, which compare closely with those of $\text{[Fe(CH}_3\text{CN)(N4Py)]}(\text{ClO}_4)_2$.
4.2.2 Photochemistry of 2.

A complete loss in visible absorbance at 440 nm and a decrease in absorbance at 355 nm is observed, concomitant with the appearance of a new band at 376 nm, upon irradiation of 2 in CH$_3$CN at $\lambda_{\text{exc}}$ 457 nm (Figure 1a). Isosbestic points are maintained at 366 and 398 nm. The changes to the spectrum are consistent with dissociation of a pyridine moiety from the Ru(II) center, together with coordination of solvent as observed earlier for 1 (Chapter 3). However, in contrast to 1, the thermal reversion of the photoproduct to 2 does not occur even upon heating at 70 °C for an extended period of time. Subsequent irradiation at 355 nm lead to only a partial recovery of the initial spectrum of 2 (photostationary state, PSS ca. 20%, Figure 1b).

Repeated alternate irradiation between 457 nm and 355 nm (Figure 1c), was reversible indicating that the primary photoproducts exhibited photochromism also. The ESI mass spectrum of 2 in acetonitrile after irradiation at 457 nm shows a base peak at $m/z$ 275.8, which corresponds to the dication [Ru(CH$_3$CN)(CH$_3$CN)(N4Py)]$^{2+}$, and no significant signals other than that of 2. Notably, irradiation in acetonitrile-$d_3$ resulted in a base peak corresponding to [Ru(CH$_3$CN)(CD$_3$CN)(N4Py)]$^{2+}$ ($m/z$ 277.2) in which the original bound CH$_3$CN was retained. Subsequent irradiation at 355 nm resulted in the reappearance of the signal corresponding to [Ru(CH$_3$CN)(N4Py)]$^{2+}$ (2) at $m/z$ 255.3. The photochemical quantum yields were determined by actinometry with ferrioxalate as a reference (Appendix B). At 457 nm, the quantum yield for the conversion 2 to the mixture of products is 0.039, which is six-times greater than 1 ($\Phi = 0.0058$).

![Figure 1. UV-vis absorption spectra of 2 (0.1 mM) (red) in acetonitrile (a) with irradiation at 457 nm, (b) with subsequent irradiation at 355 nm and (c) absorbance at 457 nm after sequential irradiation at 457 and 355 nm.](image)

4.2.3 Temperature dependence of photoswitching.

As noted above, heating a solution of 2, after it has reached PSS$_{457\text{nm}}$, to 343 K did not result in further spectral changes. Furthermore, the rate (and hence quantum yields) at which the PSS$_{457\text{nm}}$ (a wavelength at which the photoproducts do not absorb) was reached the same at 343 and 293 K indicating that this photochemical process is not thermally activated (Figure 2a). In contrast,
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Irradiation at 355 nm, at 343 K, of a solution of 2 at PSS457 nm resulted in a 37% recovery of the initial spectrum of 2 compared with ca. 20% at room temperature (Figure 2b). Furthermore, the rate of recovery was greater at 343 K than at 293 K. These data indicate the photochemical reversion to the original state is thermally activated.

Figure 2. Change in absorbance of 2 in acetonitrile at 457 nm after irradiation at (a) 457 nm, (b) 355 nm at 293 K and 343 K.

4.2.4 1H NMR spectral analysis of photoproducts.
Although the changes observed for 2 upon irradiation at 457 nm are similar to those reported for 1, the 1H NMR spectrum of 2 in acetonitrile-d3 after irradiation at 457 nm shows that a mixture of two complexes (2a’ and 2b’) with lower symmetry than 2 is obtained (Figure 3). The ratio of the major product (2a’) to the minor product (2b’) was 2:1, determined by integration of the signals of the coordinated acetonitrile ligands at 2.77 ppm and 2.76 ppm, respectively. Subsequent irradiation of the PSS457 nm mixture of 2a’ and 2b’ at 355 nm, at room temperature for 18 h, resulted in the partial recovery of 2 with a ratio of 23:55:22 for 2:2a’:2b’ (Figure 3c).

Figure 3. 1H NMR spectrum of 2 in acetonitrile-d3 (a) before and (b) after irradiation at 457 nm for 7 h and (c) after subsequent irradiation at 355 nm 18 h.

The 4-fold increase in the number of resonances in the aromatic region and the appearance of doublets of the methylene protons (i.e. the CH2 protons are both diastereotopic and are all inequivalent) observed reflects the decrease in symmetry, consistent with dissociation of only one pyridine moiety in each case. The singlet of the tertiary alkyl proton (CH) of 2 is shielded in the
photochemical products moving from 6.49 ppm to 6.19 ppm and 5.68 ppm for 2a' and 2b', respectively (vide supra).

The spectral assignment was carried out using a combination of NOESY, COSY and HMBC NMR spectroscopy on the PSS457 nm mixture, however, complete assignment of only the major product was achieved; the assignment of the spectrum of the minor product was precluded by the overlap of signals and low concentration (see Appendix A). Although the signals of 2a' are temperature independent between 243 and 343 K, several of the signals of 2b' are temperature dependent over this range (Figure 4). The broad singlet at 6.50 ppm assigned to a hydrogen of a pyridyl moiety of 2b' narrowed with an increase in temperature from 298 K to 348 K. At 243 K, the signals of the alkyl protons and some of the pyridyl signals of 2b' broadened, consistent with hindered rotation of the unbound pyridyl ring.

Figure 4. VT 1H NMR spectrum of 2 in acetonitrile-d3 after irradiation at 457 nm at 243, 298, 308, 328 and 348 K.

Overall, the spectral data indicated that for both 2a' and 2b', one of pyridine moieties connected to tertiary alkyl carbon (CH) group was dissociated in contrast to the photochemistry observed for 1 in which one of the pyridyl moieties attached via a methylene unit is dissociated (Scheme 1). The structural assignment of 2a' and 2b' was facilitated by isolation of crystals from the PSS457 nm mixture, with the structure of 2a' confirmed unambiguously by X-ray crystallographic analysis (Figure 6 and Appendix A).

In situ irradiation at 420 nm of 2 and subsequently at 365 nm, with acquisition of 1H NMR spectrum at 5 min intervals (Figure 5), showed that the loss and recovery of 2, respectively, occurred without a change in the ratio of 2a' and 2b' (2:1, followed by the time dependence of the integral at δ = 9.13, 9.02 and 8.96 ppm, i.e. a pyridine H6 signal of 2b', 2a' and 2, respectively.
4.2.5 X-ray structural analysis.

A single crystal of photoproduct \(2a'\) suitable for structural analysis by X-ray diffraction was obtained, from a solution of \(2\) at \(PSS_{457\text{nm}}\). The Ru(II) ion in \(2a'\) is coordinated by four N atoms of the ligand N4Py (three pyridine N atoms and one amine N atom), one nitrogen atom from a CH3CN molecule and the sixth nitrogen from CD3CN. The non-coordinated pyridine is connected to the tertiary alkyl carbon (CH) and two pyridines connected in the ligand via the methylene units are arranged cis to each other (Figure 6).

The bond length between the central Ru(II) ion and the pyridine N atoms of N4Py are in the normal range and correspond to those in \([\text{Ru(II)}]([\text{N4Py}])\text{ClO}_4\text{-CH}_3\text{OH}\).\(^{24}\) The Ru–N1 amine bond (2.067 (3) Å) is longer than those reported for \([\text{Ru(II)}]([\text{N4Py}])\text{ClO}_4\text{-CH}_3\text{OH} \) and \([\text{Ru(OH}_2\text{)}(\text{N4Py})][\text{PF}_6]\)\(^{25}\) while the Ru–Nacn (N6 and N7) bond lengths are shorter than the Ru-Npyridine (N2, N4, and N5) and Ru-Namine bonds. The short bond between Ru and N (acetonitrile) is consistent with reported ruthenium(II) nitrile bond lengths. The bond angle of N1–Ru1–N2 (81.4(1) Å), in which N1 is connected to the tertiary (C1) atom of N4Py is similar to those reported elsewhere (e.g. \([\text{Ru(II)}]([\text{N4Py}])\text{ClO}_4\text{-CH}_3\text{OH}\)).\(^{24}\)

![Figure 6. Perspective view of \(2a'\)](image)

Although single crystals of 2b′ were obtained also, the quality of the diffraction data set is rather poor and only serves to establish the atom connectivity. It is apparent from the data that 2b′ is an isomer in which the two Py-CH$_2$ moieties are coordinated in a *trans* arrangement with respect to each other (Scheme 2, Appendix A).

4.2.6 Photoreactivity of 2a′
Although efforts to separate 2a′ and 2b′ chromatographically were unsuccessful, isolation of 2a′ (in a 92:8 ratio of 2a′/2b′) was achieved by fractional crystallization and allowed for the photochemistry of 2a′ to be explored in further detail. As observed for mixtures generated photochemically, the ratio of 2a′/2b′ was unaffected (determined by $^1$H NMR spectroscopy) by heating in acetonitrile-d$_3$ at 70 °C for 2 h. By contrast, irradiation of a dilute solution at 355 nm resulted in a rapid change in the UV-vis absorption spectrum to that corresponding to a 2:1 ratio of 2a′ and 2b′.

Notably, irradiation of 2a′ at a more concentrated solution at 355 nm showed the formation of a mixture of 2/2a′/2b′ in the ratio of 52:38:10, by $^1$H NMR spectroscopy, after 8 h, which confirms that the equilibrium between 2 and 2a′ is established more quickly than that between 2a′ and 2b′ (Figure 7). Hence, the conversion of 2a′ to 2b′ proceeds via 2 (vide infra).

**Figure 7.** $^1$H NMR spectrum of 2a′/2b′ (92:8) in acetonitrile-d$_3$ (a) before irradiation (b) after irradiation at 355 nm for 8 h.

4.3 Discussion
Complexes 2 and 1 are similar except for the replacement of a hydrogen with a methyl group in the ligand backbone (Scheme 1 and 2). In our early report$^{22}$ (chapter 3) of the photochemistry of 1, we demonstrated that irradiation at 457 nm resulted in the formation of 1P, in which one of the pyridyl moieties connected to a secondary carbon (CH$_2$) undergoes dissociation exclusively (Scheme 1).

In contrast to 1, complex 2 forms a mixture of two products upon irradiation (Scheme 2). UV-vis absorption, ESI mass spectrometry, $^1$H NMR spectroscopy experiments, and X-ray crystallography indicated that the photoproducts of 2 are isomers in which a tertiary pyridyl moiety is dissociated with a reduction in symmetry. The two photoproducts are thermally stable and are coordination isomers of each other each with an additional CH$_3$CN coordinated to the Ru(II) center (i.e. identical m/z).
The photoproducts interconvert photochemically via 2 or a common intermediate, manifested in the preservation of isosbestic points during irradiation at low concentration, and the variation in the ratio of 2a' and 2b' observed only when isolated 2a' was irradiated initially. The X-ray structures of the major product (2a') shows that the –CH2-pyridyls coordinate in a cis manner, whereas in the minor product (2b') these pyridyl moieties are arranged trans to each other. The assignment is confirmed by the structural assignments made by 2-D NMR spectroscopy (see Appendix A).

There are two reasonable pathways to access each of the photoproducts (pathways I and II in Scheme 3), with both pathways involving sequential dissociation of pyridyl units. The major product 2a can be generated (pathway I, Scheme 3) directly by dissociation of one of pyridyl units at the tertiary carbon with coordination of acetonitrile (specifically acetonitrile-d3 in the case of 2a'). The minor product 2b cannot be generated by a common intermediate as irradiation of 2a' leads first to conversion to 2 before the appearance of 2b. Dissociation of a methylene bound pyridyl unit is followed by coordination of solvent (pathway II, Scheme 3). The non-coordinated pyridyl unit subsequently rotates and re-coordinates to the Ru(II) center to form trans-2b. VT NMR experiments on the photoproducts confirm that 2a and 2b are not in thermal equilibrium.

1H NMR spectral data confirmed that 2a' and 2b' form directly from 2 upon visible irradiation with a ratio of 2:1. This ratio is maintained upon subsequent photochemical reversion to 2 upon irradiation at 355 or 365 nm. The 1H NMR spectrum of 2a' (containing ca. 8% of 2b') after irradiation at 355 nm shows that complex 2 is recovered without an increase in the concentration of 2b'. These data confirm that the two photoproducts do not interconvert with each other directly and that 2b' is generated from 2 directly. Formation of 2b' via la is unlikely given that irradiation of 2a' does not lead immediately to 2b'.

![Scheme 3. Proposed mechanism for the reaction of 2 in acetonitrile under irradiation at 457 nm.](image-url)
The importance of the methyl group of MeN4Py to the photochemistry of 1 observed is remarkable given that the electronic effects of such a group are expected to be minimal given the close similarity of the electronic and electrochemical properties of 1 and 2. In the forward reaction, the steric effect (Thorpe-Ingold) of the methyl group appears to preclude dissociation of the –C(CH₃)₂(pyridyl)₂ moieties (pathway I), with only the –CH₂-pyridyl moieties undergoing dissociation and substitution by solvent (Scheme 1, it should be noted also that in the case of complex 1, careful examination of the spectrum obtained upon irradiation with visible light shows very weak signals that indicate that very minor amounts of complexes analogous to 2a/2b are formed). In contrast, complex 2 is not subjected to such steric constraints and both types of pyridyl units can dissociate to form photoproducts. Hence, for 2 irradiation leads to both of photoproducts 2a and 2b and a photoproduct analogous to 1P is not observed.

4.4 Conclusions
The steric repulsion of the methyl group on ligand MeN4Py is the main reason for the photoreactivity of 1 which diverges from that of 2. The data presented here demonstrate that in the absence of a methyl group in the N4Py ligand photo-induced dissociation of pyridine units on both sides (pathway I and II, Scheme 3) can occur with the result that two thermally stable isomers are formed in which the pyridyl unit attached to –CH– moiety is no longer coordinated. The data indicate that these changes are reversible photochemically but not thermally. Finally, the photochemistry of 2 provides access to novel species of Ru(II) polymeric complexes that are not accessible by thermal reactions. These photoproducts are expected to show distinct chemical reactivity especially in catalytic oxidations of organic compounds and open up new opportunities in the fields of photochromism, photo switching and oxidation catalysis.

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4.6 References

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