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Excited-State Acid–Base Chemistry: Evidence for a Dissociative Excited State

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Excitation (410 nm) of the bimetallic $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ produces the MLCT state localized on the $(bpy)_2Ru(CN)_2$ ligand. Photoinduced cleavage of the bimetallic occurs in the presence of $[H^+]$, and the dependence yields a K_a equivalent to that for ground-state *cis*-$(bpy)_2Ru(CN)_2$ implying separation of the bimetallic prior to relaxation. The pH dependence and the emissivity of a bimetallic composed of components that individually quench at a diffusion controlled rate suggest that rupture of the RuCN–Rh bond is due to the reduction in electron density at the cyano ligand that occurs on population of the MLCT state. Unlike known photoinduced metal ligand dissociations, where the excitation energy is consumed in the dissociation, the dissociated "$(bpy)_2Ru(CN)_2$ ligand" remains excited.

Optical excitation of certain Ru(II) diimines produces immense changes in Bronsted acid–base properties.[1–3] In *cis*-$(bpy)_2Ru(CN)_2$, excitation transfers electron density to the diimine reducing the basicity of the cyano ligand by $\geq 10^5$ in the excited state.[4] Evidence presented here indicates that population of the MLCT state of the "$(bpy)_2Ru(CN)_2$ ligand"[5] in the bimetallic $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ leads to a dissociative excited state. Unlike known photoinduced ligand dissociations,[6] where the excitation energy is consumed in the ligand dissociation, the "$(bpy)_2Ru(CN)_2$ ligand"[5] remains excited. Dissociation occurs because of the reduction in electron density at the bridging cyano on population of the MLCT state.

In aqueous solution, $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ [7] exhibits an MLCT absorption at 418 nm ($\epsilon = 7.1 \times 10^3$ M^{-1} cm^{-1}),[7] while that in *cis*-$(bpy)_2Ru(CN)_2$ occurs at 429 nm ($\epsilon = 6.6 \times 10^3$ M^{-1} cm^{-1}).[4] The spectra are very similar with no bands attributable to the Rh(III) component evident at wavelengths $\geq$300 nm,[7] but both spectra are dependent on $[H^+]$. Increasing $[H_2SO_4]$ from 10^{-4} to 7 M shifts the bimetallic MLCT absorption from 418 to 362 nm, while that of *cis*-$(bpy)_2Ru(CN)_2$ first shifts from 429 to 390 nm as $[H_2SO_4]$ increases from 10^{-4} to 2 M and then from 390 to 355 nm as $[H_2SO_4]$ increases to 7 M. The spectral changes are independent of the acid used[4,8] and are reversible on addition of NaOH, and spectra recorded periodically over a period of hours show that the mono- and bimetallics are stable in these strong acid solutions.[3,4,8] The decline in absorbance at 418- nm as a function of $[H^+]$ yields $K_a = 4.13 \pm 0.59$ M^{-1} for $[(bpy)_2Ru(CN)(\mu\text{-}CNH)Rh(NH_3)_4Br]^{3+} \leftrightarrows [(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+} + H^+$. The initial change in the MLCT band of *cis*-$(bpy)_2Ru(CN)_2$ yields $K_{a2} = 1.54 \pm 0.23$ M^{-1} for *cis*-$(bpy)_2Ru(CN)(CNH^+) \leftrightarrows$ *cis*-$(bpy)_2Ru(CN)_2 + H^+$, while the subsequent change yields $K_{a1} = 4.42 \pm 0.10$ M^{-1} for *cis*-$(bpy)_2Ru(CNH^+)(CNH^+) \leftrightarrows$ *cis*-$(bpy)_2Ru(CN)(CNH^+) + H^+$.

In aqueous solution, the bimetallic exhibits an emission maximum at 610 nm, while that from *cis*-$(bpy)_2Ru(CN)_2$ occurs at 618 nm. At room temperature, the $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ emission decays exponentially with a lifetime of 175 ± 20 ns, while that from *cis*-$(bpy)_2Ru(CN)_2$ also decays exponentially with an equivalent lifetime of 190 ± 15 ns.

Photolysis (at 410 ± 5 nm) of an aqueous solution of the $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ leads to no detectable chemical change, indicating the quantum yield of decom-

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position is $\leq 2.7 \times 10^{-4}$. Increasing the hydrogen ion concentration, however, leads to a decline in the bimetallic's 418 nm absorbance and a corresponding increase of a shorter wavelength shoulder corresponding to the formation of the monoprotonated *cis*-$(bpy)_2Ru(CN)_2$. Neutralizing the photolyte with NaOH and resolving it on a Na^+-cation-exchange resin establishes *cis*-$(bpy)_2Ru(CN)_2$ and a Rh(III) tetraamine as the photoproducts with the amount of *cis*-$(bpy)_2Ru(CN)_2$ recovered within 11 ± 1% of that calculated from the photoinduced spectral changes. A plot of the observed quantum yield of bimetallic cleavage, Φ_{cl}^{obs}, versus $[H^+]$ achieves a maximum at $[H^+]$ = ca. 1 M and then declines at higher $[H^+]$. In the region where Φ_{cl}^{obs} declines with increasing $[H^+]$, $[(bpy)_2Ru(CNH)(\mu\text{-}CN)Rh(NH_3)_4Br]^{3+}$ is the dominant light absorbing species. Independent experiments in 5 M H_2SO_4, where ca. 60% of the bimetallic is present in the protonated form, yield $\leq 2.7 \times 10^{-4}$ for the quantum efficiency of dissociation of the protonated bimetallic, Φ_{cl}^{bim}. The inefficiency is attributed to a fast decay process promoted by protonation of the nonbridging cyanide. Protonation reduces its emission intensity by $\geq 10^2$ and reduces the emission lifetime from 175 ± 20 ns for the unprotonated bimetallic to 32 ± 7 ns for the protonated form.

The thermal rate of cleavage of $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ in 22 ± 1 °C neutral solutions and solutions containing 1 M H_2SO_4 and 3 M H_2SO_4 is $\leq 1.9 \times 10^{-12}$ M/s. In fact, no spectral change occurs in any acidified solution over a period of hours until the solutions are heated to 60 °C. At this temperature, the rate of decomposition measured spectrally at 418 nm is 1.3×10^{-12} M/s, establishing that the photoinduced changes are not biased by a thermal reaction.

The dependence of Φ_{cl}^{obs} on $[H^+]$ suggests two processes.[9] The decline in Φ_{cl}^{obs} at high $[H^+]$ is attributed to a larger fraction of the excitation absorbed by the protonated bimetallic, which exhibits little photoreactivity, $\Phi_{cl}^{obs} \leq 2.7 \times 10^{-4}$. In this case, Φ_{cl}^{obs} at a given $[H^+]$ is the quantum yield of cleavage for the unprotonated bimetallic, Φ_{cl}^{bi}, times the fraction of light absorbed by the unprotonated complex. Since the spectra of the protonated and unprotonated bimetallics are similar at the excitation wavelength, 410 nm, the fraction of light absorbed by the unprotonated bimetallic is taken as the fraction of the unprotonated complex at a given $[H^+]$, in which case, $\Phi_{cl}^{obs} = \Phi_{cl}^{bi}[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}/\{[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+} + [(bpy)_2Ru(CNH)(\mu\text{-}CN)Rh(NH_3)_4Br]^{3+}\}$. Assuming the concentrations of protonated and unprotonated species are governed by the ground-state acid−base equilibrium, then $\log(\Phi_{cl}^{bi}/\Phi_{cl}^{obs} - 1) = -pH + pK_a$, where K_a is the acid dissociation constant of the protonated bimetallic. Indeed, a plot of $\log(\Phi_{cl}^{bi}/\Phi_{cl}^{obs} - 1)$ versus pH (Figure 1) is linear and yields $K_a = 4.65 \pm 0.5$, which is in excellent agreement with the equilibrium constant obtained from the titration of the bimetallic with H_2SO_4, $K_a = 4.42 \pm 0.10$.

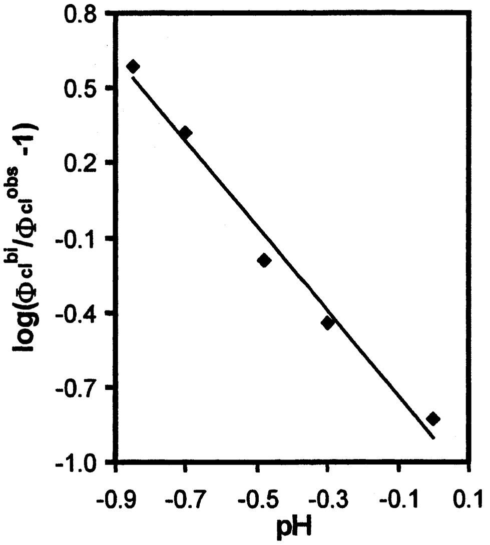

Figure 1. Plot of $\log(\Phi_{cl}^{bi}/\Phi_{cl}^{obs} - 1)$ as a function of pH.

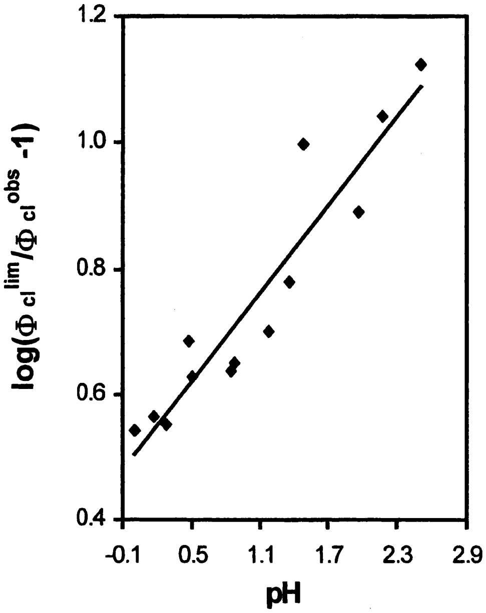

Figure 2. Plot of $\log(\Phi_{cl}^{lim}/\Phi_{cl}^{obs} - 1)$ as a function of pH.

The increase in Φ_{cl}^{obs} with increasing $[H^+]$ is attributed to the protonation of the product, ground-state *cis*-$(bpy)_2Ru(CN)_2$, which prevents the complex from recoupling with the Rh(III) fragment. Assuming protonation of *cis*-$(bpy)_2Ru(CN)_2$ is an equilibrium process, the ratio $\Phi_{cl}^{lim}/\Phi_{cl}^{obs}$ is given by $\log(\Phi_{cl}^{lim}/\Phi_{cl}^{obs} - 1) = pH + \log K_a$, where Φ_{cl}^{lim} is the limiting yield of dissociation of the unprotonated bimetallic. Extrapolation of a plot of $1/\Phi_{cl}^{obs}$ versus $1/[H^+]$ over the range $[H^+]$ = 0.066−0.14 M, where the fraction of light absorbed by the protonated bimetallic, $[(bpy)_2Ru(CNH)(\Phi\text{-}CN)Rh(NH_3)_4Br]^{3+}$, is ≤2% yields $3 \pm 2 \times 10^{-3}$ for Φ_{cl}^{lim}. Using the latter value, a plot of $\log(\Phi_{cl}^{lim}/\Phi_{cl}^{obs} - 1)$ versus pH (Figure 2) is linear and yields an intercept corresponding to $K_a = 2.2 \pm 1.0$ which agrees with the K_a obtained by titrating *cis*-$(bpy)_2Ru(CN)_2$ with H_2SO_4, $K_{a2} = 1.54 \pm 0.6$.

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(9) Attributing the observed dependence on ion pairing is discounted for the following reasons: First, the ground- and excited-state acid−base properties of $(bpy)_2Ru(CN)_2$ are independent of the acid used. Second, the quantum yield of cleavage of the bimetallic increases with increasing acid concentration, but at the point where protonation of the bimetallic increases its charge from 2+ to 3+, therefore increasing the probability of ion pairing, the quantum yield of cleavage declines. And last, it is extremely unlikely that the equilibrium constants for ion pairing would be numerically equal to those for protonation of both *cis*-$(bpy)_2Ru(CN)_2$ and $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$.

The uncertainty in the data is large because of the uncertainty in the extrapolation, but it is small in comparison to the 5 orders of magnitude difference in the basicities of the ground and excited states.[4] Consistent with the immense reduction in basicity on excitation of *cis*-$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$,[4] the H^+ dependence clearly corresponds to protonation of ground-state species thereby establishing that the molecule was separated prior to relaxation to the ground state and scavenging by the proton. Since the MLCT state is localized on the "$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ ligand"[5,7] and its population reduces the electron density at the cyano ligand, as evidenced by $\geq 10^5$ reduction in cyano basicity in the MLCT state,[4] we propose that excitation of $[(\mathrm{bpy})_2\mathrm{Ru(CN)}(\mu\text{-}\mathrm{CN})\mathrm{Rh(NH_3)_4Br}]^{2+}$ leads to a dissociative excited state. At this point, the data are consistent with a conventional photochemical reaction in which the excitation energy promotes the dissociation of the "$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ ligand".[5,6] However, the bimetallic, which is composed of components that as individual molecules quench at a diffusion controlled rate,[10] possesses the most intimate encounter accessible between a donor and quencher, i.e., chemically bonded to each other, and is electronically coupled through the cyano bridge,[7] is luminescent with an emission lifetime within experimental error of that of *cis*-$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$. Previous studies attribute the "anomalous emission" to *cis*-$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ impurities.[7] Cation-exchange chromatography of the bimetallic, however, gives no indication of $(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ impurities. To account for the emissivity of the bimetallic, we propose that, unlike known photoinduced ligand dissociations, where the excitation energy is consumed in the dissociation,[6] the excitation energy is *not* consumed in the RuCN−Rh bond rupture. Instead, the reduction in electron density at the cyano group that occurs on population of the MLCT state reduces the bonding between the excited "$^*(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ ligand"[5] and the Rh(III) complex.

$$[(\mathrm{bpy})_2\mathrm{Ru(CN)}(\mu\text{-}\mathrm{CN})\mathrm{Rh(NH_3)_4Br}]^{2+} \xrightarrow{h\nu} [{}^*(\mathrm{bpy})_2\mathrm{Ru(CN)}_2,\ \mathrm{Rh(NH_3)_4Br}^{2+}] \quad (1)$$

In eq 1, $[{}^*(\mathrm{bpy})_2\mathrm{Ru(CN)}_2,\ \mathrm{Rh(NH_3)_4Br}^{2+}]$ denotes the excited ruthenium complex and the dissociated rhodium fragment within a solvent cage. The equivalence of the emission lifetimes indicates the separated, excited "$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ ligand"[5] relaxes either radiatively or nonradiatively analogous to $(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$, as shown in eq 2.

$$[{}^*(\mathrm{bpy})_2\mathrm{Ru(CN)}_2,\ \mathrm{Rh(NH_3)_4Br}^{2+}] \rightarrow [(\mathrm{bpy})_2\mathrm{Ru(CN)}_2,\ \mathrm{Rh(NH_3)_4Br}^{2+}] + h\nu_{\mathrm{em}} + \mathrm{heat} \quad (2)$$

Relaxation occurs with a corresponding ca. 5-order-of-magnitude increase in the basicity of the dissociated "$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ ligand".[5] Provided the pair remains within the solvent cage, relaxation increases electron density at the coordination site of the "$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ ligand"[5] and the ligand recoordinates to the Rh(III) complex, as shown in eq 3.

$$[(\mathrm{bpy})_2\mathrm{Ru(CN)}_2,\ \mathrm{Rh(NH_3)_4Br}^{2+}] \rightarrow [(\mathrm{bpy})_2\mathrm{Ru(CN)}(\mu\text{-}\mathrm{CN})\mathrm{Rh(NH_3)_4Br}]^{2+} \quad (3)$$

In the presence of H^+, the proton reacts with ground-state $(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ prior to recoupling thereby preventing reformation of the bimetallic, eq 4.

$$[(\mathrm{bpy})_2\mathrm{Ru(CN)}_2,\ \mathrm{Rh(NH_3)_4Br}^{2+}] + \mathrm{H}^+ \rightarrow (\mathrm{bpy})_2\mathrm{Ru(CN)(CNH)}^+ + \mathrm{Rh(NH_3)_4Br(H_2O)}^{2+} \quad (4)$$

Consistent with reaction 4, the K_a derived from the pH dependence of $\Phi_{\mathrm{cl}}^{\mathrm{obs}}$, $K_\mathrm{a} = 2.2 \pm 1.0$, is equivalent to that obtained from the titration of ground-state $(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ with $\mathrm{H_2SO_4}$, $K_{\mathrm{a2}} = 1.54 \pm 0.6$. The limiting yield of $(\mathrm{bpy})_2\mathrm{Ru(CN)(CNH)}^+$, $3 \pm 2 \times 10^{-3}$, indicates that H^+ scavenges $\leq 1\%$ of the separated components after relaxation to the ground state with the majority recoupling to form the bimetallic.

Although water is a reasonably good ligand, the absence of decomposition of the bimetallic in neutral solution suggests water is unable to react with the dissociated Rh(III) fragment. This suggests the distortion involved in creating the dissociated excited state does not involve a large change in the $(\mathrm{bpy})_2\mathrm{Ru(CN)}_2{-}\mathrm{Rh(NH_3)_4Br}^{2+}$ distance. Rather, analogous to the dissociation of weak acids,[11] where the principal contributor to the ΔG of dissociation is *not* ΔH of bond breaking, but ΔS of solvent reorganization to accommodate the formation of charged species, a dissociative excited state may principally involve a reorganization of the surrounding water molecules to accommodate the redistributed charge, rather than large changes in the distances between, or relative orientations of, the dissociated fragments in the excited state. The energy needed for the reorganization is thought to arise from the Stokes shift, which with 410 nm excitation of $[(\mathrm{bpy})_2\mathrm{Ru(CN)}(\mu\text{-}\mathrm{CN})\mathrm{Rh(NH_3)_4Br}]^{2+}$ and its 635 nm emission corresponds to 24.5 kcal/mol since hydrogen bonding in HF is on the order of 4−9 kcal/mol.[12]

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Supporting Information Available: Electronic spectra of $(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ and $[(\mathrm{bpy})_2\mathrm{Ru(CN)}(\mu\text{-}\mathrm{CN})\mathrm{Rh(NH_3)_4Br}]^{2+}$ as functions of pH. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Quenching of *cis*-$(\mathrm{bpy})_2\mathrm{Ru(CN)}_2$ by Rh(III) bromo-tetraamine and -pentamines occurs with a rate constant of $\geq 1.6 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$; see: Lei, Y.; Buranda, T.; Endicott, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8820.

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