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Photochemistry of Mixed-Metal Bimetallic Complexes Containing Pentacyanoferrate(II) or Pentaammineruthenium(II) Metal Centers. Evidence for Some Intramolecular Energy-Transfer Reactions[1]

Kathy J. Moore, Liangshiu Lee, Joseph E. Figard, Janette A. Gelroth, Angela J. Stinson, H. David Wohlers, and John D. Petersen*

Contribution from the Department of Chemistry, Clemson University, Clemson, South Carolina 29631. *Received August 11, 1982*

Abstract: The series of complexes $B_5MLM'B'_5$, where $B_5M = (NH_3)_5Ru^{II}$ or $(CN)_5Fe^{II}$, L = 4-cyanopyridine (4-CNpy), pyrazine (pz), or 4,4'-bipyridine (4,4'-bpy), and $M'B'_5 = Rh^{III}(NH_3)_5$ or $Co^{III}(CN)_5$, display highly absorbing metal-to-ligand charge-transfer (MLCT) bands in the visible spectral region that can be assigned as predominantly $M(d_\pi) \rightarrow L(p_\pi{}^*)$ in character. MLCT irradiation of these complexes generally leads to cleavage of either the M–L or L–M' bonds. Cleavage of the L–M' bond, a reaction characteristic of an excited state localized on M' (not the metal center initially involved in photon absorption), is a result of intramolecular, energy-transfer processes. This phenomenon is observed only for the 4-CNpy- and 4,4'-bpy-bridged Ru(II)/Rh(III) bimetallic complexes. The pz-bridged Ru(II)/Rh(III) bimetallic complex shows little photoreactivity at either metal center. All of the Fe(II) bimetallic complexes show Fe(II)–L bond breaking as the sole photochemical process with no evidence of any intramolecular energy transfer. The quantum yields for reactions driven by intramolecular energy transfer are small ($10^{-4} < \Phi \leq 10^{-2}$), but photochemical reactions normally requiring ultraviolet incident irradiation can be driven by visible light by using these highly absorbing, antenna fragments as internal sensitizers.

The photochemical reactivity of transition-metal complexes is dependent, in many instances, on the nature of the lowest or reactive excited state.[2] The ligand-field (LF) excited states of d^6, low-spin complexes of Fe(II), Co(III), Ru(II), and Rh(III) generally undergo ligand labilization, owing to the increase in σ^* electron density.[2-15] On the other hand, the metal-to-ligand charge-transfer (MLCT) excited states of d^6 complexes, which may be conceptualized as an oxidized metal/reduced ligand species, are usually unreactive toward photosubstitution reactions and either interconvert to lower energy, excited states or deactivate directly back to the ground state.[16-18]

The series of complexes $Fe(CN)_5L^{3-}$, $Ru(NH_3)_5L^{2+}$, and $W(CO)_5L$ all have intense MLCT bands in the visible region of the spectrum.[16-18] The energy of the MLCT maximum is very sensitive to substituent changes on L (i.e., the energy of the π^* orbitals of free L), with more electron-withdrawing substituents causing red shifts in the MLCT maximum as well as greater ground-state delocalization of d_π electron density into L (π-back-bonding).[19] The extreme sensitivity of the MLCT wavelength maximum in $Fe(CN)_5L^{3-}$, $Ru(NH_3)_5L^{2+}$, and $W(CO)_5L$ complexes to substituents on L (L is a substituted pyridine or pyrazine) has led to a large variability in the quantum yield for photosubstitution of L.[16-18] For $Fe(CN)_5L^{3-}$ [16] and $Ru(NH_3)_5L^{2+}$,[17] photosubstitution of L can drastically be reduced when the MLCT maximum is shifted to frequencies below 2.1 μm^{-1}. The interpretation[16,17] of these data is that the shift to lower frequencies causes the MLCT state to cross under the ^{3}LF excited state and cut off photochemical reactions characteristic of ^{3}LF (i.e., M–L cleavage). A similar type of tuning of excited states is apparent in the metal carbonyl photochemistry. The photochemistry and emission spectroscopy of $W(CO)_5L$ (L = substituted pyridine) show that changes in the nature of the lowest excited state affect the quantum yield of photosubstitution and the emission lifetime.[18]

The $Fe(CN)_5L^{3-}$ and $Ru(NH_3)_5L^{2+}$ complexes, being highly absorbing in the visible region of the spectrum, have the basic prerequisite necessary for generation of chemical potential energy from the absorption of sunlight. To convert the radiant energy into usable chemical potential energy, the absorbing molecule must either undergo direct reactions[11,20,21] or transfer its energy[22-24] or an electron[25-35] to a second, reacting molecule. These latter

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processes are plagued by the inefficiency inherent to bimolecular quenching processes in dilute aqueous solution, and in the case of excited-state electron transfer, with very efficient back electron transfer by ground-state products.[26–28] Our goal is to eliminate the inherent inefficiencies of the above-mentioned bimolecular processes by bringing the absorbing and reacting metal complex together in the same molecular species. The methodology is to absorb the visible photon at a highly absorbing, but unreactive, $Fe(CN)_5L$ or $Ru(NH_3)_5L$ metal center (antenna fragment), transfer the energy through L to a remote metal center, and drive photochemical reactions at the remote metal center (reactive fragment). The fact that the reactive center does not have to be the highly absorbing center adds flexibility to the usable photochemistry that can be accomplished with the polymetallic systems.

We have prepared a series of bimetallic complexes, $B_5MLM'B'_5$, where $B_5M = (NH_3)_5Ru^{II}$ or $(CN)_5Fe^{II}$, L = pyrazine (pz), 4-cyanopyridine (4-CNpy), or 4,4′-bipyridine (4,4′-bpy), and $M'B'_5 = Rh^{III}(NH_3)_5$ or $Co^{III}(CN)_5$, as model systems to probe the possibility of intramolecular energy-transfer reactions in mixed-metal bimetallic complexes. Previous thermal substitution and stability studies,[36] Mössbauer studies[37] on the Fe(II) complexes, and electrochemical studies[38] on the Fe(II) and Ru(II) complexes have shown that the main effect of the remote center on the properties of $(CN)_5FeL$ and $(NH_3)_5RuL$ is that of a Lewis acid substituent on L. Herein we report the results of the photochemistry[1] of these bimetallic systems and discuss the possible general utility of intramolecular energy-transfer reactions.

Experimental Section

Materials. Analytical reagent compounds were used for all preparations described in this work. Water used for synthesis and photochemical studies was either redistilled from alkaline permanganate in an all-glass apparatus or passed through a Bantam demineralizer after distillation.

Syntheses. The complexes $[Rh(NH_3)_5L](ClO_4)_3$, $K_2[Co(CN)_5L]$, $[(CN)_5FeLRh(NH_3)_5]$, and $Na_3K_2[(CN)_5FeLCo(CN)_5]$ were prepared as previously reported.[36] The Ru(II)/Rh(III) bimetallic complexes, $[(NH_3)_5RuLRh(NH_3)_5](ClO_4)_5$, were prepared by the procedure of Creutz and Taube[39] for the L = pz complex. The purity of all complexes was determined by comparison of the electronic spectrum with previously reported values[36,39] or by elemental analysis for complexes previously unreported. Electronic spectra (Table I) and photochemical experiments utilized a Cary 14 or a Bausch-Lomb Spectronic 2000 spectrophotometer. Elemental analysis were performed by Galbraith Laboratories, Knoxville, TN, or Atlantic Microlabs, Atlanta, GA.

Photolysis Apparatus. Quantum yields were determined by using a continuous beam photolysis apparatus consisting of an Oriel Universal Arc-Source Lamp with a 200-W high-pressure mercury lamp, 1-in. diameter Oriel mercury-line interference filters (1.57, 1.73, 1.83, 2.29, and 3.19 μm^{-1}), an ESCO A-1, 4-in. focal length, fused quartz, collimating lens, and a hollow brass thermostated cell compartment (controlled by a Forma Temp. Jr. constant-temperature circulating bath) all mounted on an Ealing 22-6894 optical bench. Usable light intensities from this experimental configuration were measured by ferrioxalate[40] ($\nu_{irr} \geq 2.29$ μm^{-1}) or Reineckate[41] actinometry ($\nu_{irr} \leq 2.29$ μm^{-1}) and ranged from 10^{17} to 10^{19} quanta/min depending on the selection of the interference filter and the age of the lamp.

Photolysis Procedures. The solutions used for the photolysis studies were generated and transferred into 10-cm quartz cells under argon gas, using previously described techniques and apparatus.[42] Samples were irradiated for time intervals ranging from 30 s to 30 min. Five to seven of these time periods were used to monitor the first 20–25% of each photolysis reaction. Spectroscopic changes in the photolysis sample were determined after each time interval at the wavelength of irradiation and the wavelength maximum of the MLCT band. All spectroscopic measurements were corrected for thermal reactions which were negligible in general.

Table I. Electronic Spectrum and Molar Extinction Coefficients of the Bimetallic Complexes $B_5MLM'B'_5$

complex	ν_{max}^a (MLCT), μm^{-1}	ϵ_{max}(MLCT), M^{-1} cm^{-1}
$(CN)_5Fe4,4'\text{-}bpyCo(CN)_5{}^{5-}$	2.20	5.7×10^3
$(CN)_5Fe4,4'\text{-}bpyRh(NH_3)_5$	2.08 1.94^b	5.4×10^3
$(NH_3)_5Ru4\text{-}CNpyRh(NH_3)_5{}^{5+}$	2.05	1.3×10^4
$(CN)_5FepzCo(CN)_5{}^{5-}$	1.90	4.2×10^3
$(NH_3)_5RupzRh(NH_3)_5{}^{5+}$	1.89^c	$1.8 \times 10^{4\ c}$
$(NH_3)_5Ru4,4'\text{-}bpyRh(NH_3)_5{}^{5+}$	1.87	1.6×10^4
$(CN)_5FepzRh(NH_3)_5$	1.75	9.3×10^3

[a] ν_{max} for the Fe(II) → L or Ru(II) → L MLCT transition. [b] Solid-state (KBr pellet) electronic spectrum: Yeh, A.; Haim, A.; Tanner, M.; Ludi, A. *Inorg. Chim. Acta* 1979, *33*, 51. [c] Reference 39.

The Ru(II)/Rh(III) and Fe(II)/Rh(III) bimetallic complexes are very stable thermally to substitution reactions which prevents complications in the photochemical studies. The formation constant for the Fe(II)/Co(III) bimetallic complexes are on the order 10^3–10^4 M^{-1} so the presence of $Fe(CN)_5H_2O^{3-}$, $Co(CN)_5L^{2-}$ in addition to $(CN)_5FeLCo(CN)_5{}^{5-}$ in dilute aqueous solution needed to be considered. Corrections due to initial monometallic complexes present in solution and corrections due to thermal back reaction of the monometallic fragments formed during irradiation were applied to the quantum yield calculations. These latter corrections also were applied to the Fe(II)/Rh(III) bimetallic system.

Quantum Yield Calculations. Two types of calculations were used to determine quantum yields for bimetallic complexes. For complexes in which depletion of the MLCT band is the only spectral change (i.e., Fe(II)/Rh(III), Fe(II)/Co(III), Ru(II)-pz-Rh(III)), the formula used to calculate the quantum yield at various time periods, Φ_t, is

$$\Phi_t = (\Delta A V / l \Delta\epsilon) / (I_0{}^i t F)$$

where ΔA = the change in optical density at the MLCT maximum of the starting material from $t = 0$ to $t = t$ (corrected for dark reaction), $\Delta\epsilon$ = corresponding extinction coefficient difference between the starting material at the MLCT maximum and the product (usually O) in M^{-1} cm^{-1}, V = volume of the photolysis cell in L, l = pathlength of the photolysis cell in cm, $I_0{}^i$ = incident light intensity as determined by chemical actinometry[40,41] in einstein/min, t = irradiation time in min, and F = average fraction of light absorbed at the irradiation wavelength over the time period t. The Φ_t value for each photolysis reaction was plotted vs. percent reaction with initial quantum yields obtained by extrapolation to 0% reaction. Multiple runs were recorded on each complex and the average value reported.

The second type of quantum yield calculation was necessary for Ru(II)/Rh(III) bimetallic complexes containing 4-CNpy and 4,4′-bpy bridging ligands. Photolysis of the complexes result in an appreciable amount of $Ru(NH_3)_5L^{2+}$ being formed. This complex, like the starting complex, has an intense MLCT band, will competitively compete with the bimetallic complex for photons, and is capable of undergoing secondary photochemical reactions.[17] The calculations of the quantum yields for these systems utilized an IBM 3033 computer and a Runge–Kutta, fourth-order numerical integration program, and the results and mechanism for this calculation will be described in the Results section.

Results

Electronic Spectra. The electronic spectra and molar extinction coefficients for the complexes used in this study are listed in Table I. All of the complexes have intense bands in the visible region of the spectrum with molar extinction coefficients ranging from 3×10^3 to 2×10^4 M^{-1} cm^{-1}. This intense transition is assigned as a metal-to-ligand charge-transfer (MLCT) transition localized mainly between Fe(II) → L or Ru(II) → L as previously proposed by Creutz and Taube.[39]

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Table II. Quantum Yields for Photosubstitution in $B_5MLM'B'_5$ Bimetallic Compounds

complex	ν_{max}(MLCT),[a] μm^{-1}	ν_{irr},[b] μm^{-1}	Φ_B,[c] mol/einstein M-L	Φ_C,[d] mol/einstein L-M
$(CN)_5Fe4,4'$-bpy$Co(CN)_5{}^{5-}$	2.20[e]	1.83	0.60	$<10^{-2}$
$(CN)_5Fe4,4'$-bpy$Rh(NH_3)_5$	2.08[e]	2.29	0.060	$<10^{-4}$
		1.83	0.013	$<10^{-4}$
$(NH_3)_5Ru4$-CNpy$Rh(NH_3)_5{}^{5+}$	2.05[f]	3.19	$<10^{-4}$	2.2×10^{-2}
		2.29	$<10^{-4}$	3.3×10^{-3}
		1.83	$<10^{-5}$	3.0×10^{-4}
$(CN)_5$Fepz$Co(CN)_5{}^{5-}$	1.90[e]	1.83	0.60	$<10^{-2}$
$(NH_3)_5$Rupz$Rh(NH_3)_5{}^{5+}$	1.89[f]	2.29	7.3×10^{-5}	
		1.83	2.8×10^{-6}	
$(NH_3)_5Ru4,4'$-bpy$Rh(NH_3)_5{}^{5+}$	1.87[g]	2.29	4.2×10^{-3}	9.8×10^{-3}
$(CN)_5$FePz$Rh(NH_3)_5$	1.75[h]	2.29	0.11	$<10^{-3}$
		1.83	0.23	$<10^{-3}$
		1.73	0.16	$<10^{-3}$
		1.57	0.07	$<10^{-4}$

[a] ν_{max} for the Fe(II) → L or Ru(II) → L MLCT transition. [b] ν_{irr} is the frequency of light used to irradiate the sample. [c] Quantum yield for cleavage of the Fe(II)-L or Ru(II)-L bond in mol/einstein (Φ_B in text). [c] Quantum yield for cleavage of the L-Rh(III) or L-Co(III) bond in mol/einstein (Φ_C in text). [e] $LiClO_4$, 0.5 M, pH 8.4. [f] $HClO_4$, pH 6.0 or 2.0. [g] $HClO_4$, pH 2.0. [h] $LiClO_4$, 1.0 M, pH 7.0.

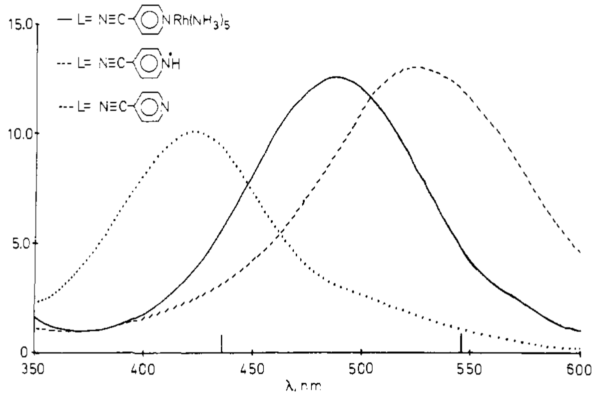

Figure 1. Electron absorption spectrum of $Ru(NH_3)_54$-$CNpy^{2+}$ (···), $Ru(NH_3)_54$-$CNpyH^{3+}$ (- -), and $(NH_3)_5Ru4$-$CNpyRh(NH_3)_5{}^{5+}$ (–) in aqueous solution. The vertical lines on the abscissa correspond to ν_{irr} of 2.29 and 1.83 μm^{-1} (436 and 546 nm, respectively).

Every bimetallic complex ($B_5MLM'B'_5$) in this study has a MLCT maximum at lower frequency than the corresponding monometallic system (B_5ML). Spectroscopically, the remote metal center, $M'B'_5 = Rh(NH_3)_5{}^{3+}$ or $Co(CN)_5{}^{2-}$, is functioning as a Lewis acid, electron-withdrawing substituent that stabilizes the π^* orbitals on L and thus lowers the MLCT, transition energy. Figure 1 illustrates this point by showing the electronic absorption spectrum of $Ru(NH_3)_54$-$CNpy^{2+}$ and the complexes generated when H^+ or $Rh(NH_3)_5{}^{3+}$ are bound to the remote end of the pyridine ring. The red shift observed for the $Rh(NH_3)_5{}^{3+}$ adduct is not as large as that observed for H^+. The position of the MLCT transition with respect to the length of the bridging ligand and remote metal center has been discussed previously.[36]

Quantum Yield Calculation. A general scheme for the photosubstitution of bimetallic complexes by metal-bridge bond cleavage is outlined in eq 1 and 2. Initial excitation of the bimetallic

$$\underset{A}{B_5MLM'B'_5} \xrightarrow[H_2O]{h\nu\ \Phi_B} B_5MOH_2 + \underset{B}{LM'B'_5} \qquad (1a)$$

$$A \xrightarrow[H_2O]{h\nu\ \Phi_C} \underset{C}{B_5ML} + \underset{D}{H_2OM'B'_5} \qquad (1b)$$

$$C \xrightarrow[H_2O]{h\nu,\ \Phi_E} \underset{E}{B_5MOH_2 + L} \qquad (2)$$

complex, A, could lead to bond cleavage at the M-L (Φ_B) or L-M′ (Φ_C) side of the bridge. Since the highly absorbing chromophore in this system is the MLCT transition associated with M and L, only the bimetallic and monometallic species, A and C, respectively, will absorb any appreciable amount of light. Thus, reactions following the channel in eq 1a will lead to nonabsorbing photolysis products, while reactions following the channel in eq 1b will form the highly absorbing B_5ML complex (C) and be susceptible to secondary photochemical reaction (eq 2). By use of the above mechanism, the following rate equations can be generated for the species A–E:

$$\frac{d[A]}{dt} = -(\Phi_B + \Phi_C)\left(\frac{I_0}{V}\right)\left(\frac{\epsilon_A[A]}{\epsilon_A[A] + \epsilon_C[C]}\right)(1-10^{-(\epsilon_A[A]l+\epsilon_C[C]l)}) \qquad (3)$$

$$\frac{d[B]}{dt} = \Phi_B\left(\frac{I_0}{V}\right)\left(\frac{\epsilon_A[A]}{\epsilon_A[A] + \epsilon_C[C]}\right)(1-10^{-(\epsilon_A[A]l+\epsilon_C[C]l)}) \qquad (4)$$

$$\frac{d[C]}{dt} = (\Phi_C\epsilon_A[A] - \Phi_E\epsilon_C[C])\left(\frac{I_0}{V}\right)\left(\frac{1}{\epsilon_A[A] + \epsilon_C[C]}\right) \times (1-10^{-(\epsilon_A[A]l+\epsilon_C[C]l)}) \qquad (5)$$

$$\frac{d[D]}{dt} = \Phi_C\left(\frac{I_0}{V}\right)\left(\frac{\epsilon_A[A]}{\epsilon_A[A] + \epsilon_C[C]}\right)(1-10^{-(\epsilon_A[A]l+\epsilon_C[C]l)}) \qquad (6)$$

$$\frac{d[E]}{dt} = \Phi_E\left(\frac{I_0}{V}\right)\left(\frac{\epsilon_c[C]}{\epsilon_A[A] + \epsilon_C[C]}\right)(1-10^{-(\epsilon_A[A]l+\epsilon_C[C]l)}) \qquad (7)$$

where Φ_B, Φ_C, and Φ_E are quantum yields for the formation of B, C, and E, respectively (mol/einstein), I_0 is the incident intensity at the irradiation frequency (einstein/min), V is the cell volume (L), ϵ_A and ϵ_C are the molar extinction coefficients (M^{-1} cm^{-1}) at the irradiation frequency for A and C, respectively, and l is the pathlength of the cell (cm). For each experiment modeled by eq 3–7, I_0, V, ϵ_A, ϵ_c, and l are parameters that come directly from the experiment. A value for Φ_E is independently determined by direct irradiation of B_5ML. The values of Φ_B and Φ_C are approximated, then varied to obtain the best fit with respect to changes in the electronic spectrum as a function of irradiation time. (It should be noted that it is easier for computer modeling procedures not to combine the B_5MOH_2 formed in eq 1a with that formed in eq 2.).

Photochemical Data. The quantum yields for the photochemical decomposition of the bimetallic complexes are listed in Table II. There are four different classes of behavior observed for the complexes in Table II. All of the pentacyanoferrate(II) complexes, $(CN)_5FeLM'B'_5$ where L = pz or 4,4′-bpy and $M'B'_5$ = $Rh(NH_3)_5{}^{3+}$ or $Co(CN)_5{}^{2-}$, show relatively high quantum efficiencies (0.01–0.6 mol/einstein) for Fe(II)–L bond breaking (eq 1a). This process is monitored by the decrease, without wavelength shift, of the MLCT absorption due to $(CN)_5FeLM'B'_5$. There is no evidence, within the experiment limits, for any energy-transfer process (eq 1b) occurring with the Fe(II) systems.

The pentaammineruthenium(II) complexes in Table II, $(NH_3)_5RuLRh(NH_3)_5{}^{5+}$, show different photochemistry for all three entries, L = pz, 4-CNpy, and 4,4′-bpy. For L = pz, a very slow photodegredation of the bimetallic complex is observed as the MLCT band slowly decays during irradiation. Since there is only decay and no shift of the MLCT band that could be explained by loss of NH_3 or cleavage of the pz-Rh(III) bond to form $Ru(NH_3)_5pz^{2+}$, the spectral change is attributed to Ru(II)-pz bond breaking with a quantum yield of 7.3×10^{-5} and 2.8×10^{-6} mol/einstein at ν_{irr} of 2.29 and 1.83 μm^{-1}, respectively. The loss of NH_3 from the Ru(II) side of the molecule, which is an observed process for the monometallic Ru(II) complexes,[3,17] was not a significant pathway but could not be accurately determined under the experimental conditions (i.e., [complex] $\cong 10^{-5}$ M).

The 4-CNpy complex, $(NH_3)_5Ru4\text{-}CNpyRh(NH_3)_5^{5+}$, shows a markedly different photochemical pattern than the L = pz analogue. Irradiation of $(NH_3)_5Ru4\text{-}CNpyRh(NH_3)_5^{5+}$ in pH 6.0 aqueous solution at ν_{irr} of either 2.29 or 1.83 μm^{-1} (436 and 546 nm, respectively), leads to a depletion of the MLCT band centered at 2.05 μm^{-1} (488 nm) and a growth in and subsequent depletion of a band at 2.35 μm^{-1} (425 nm). Initially, this corresponds to the formation of $Ru(NH_3)_54\text{-}CNpy^{2+}$ (Figure 1) by the photochemical process outlined in eq 1b, followed by the subsequent, secondary photolysis of $Ru(NH_3)_54\text{-}CNpy^{2+}$ to give $Ru(NH_3)_5H_2O^{2+}$ and free 4-CNpy (eq 2). The quantum yield for this latter process[1] is 1.7×10^{-3} or 2.3×10^{-2} mol/einstein at ν_{irr} of 1.83 or 2.29 μm^{-1}, respectively. The isosbestic point at ~450 nm, expected from Figure 1 for the primary photochemical process, is maintained in the initial portions of the photolysis experiments.

Secondary photochemical processes can be minimized for $(NH_3)_5Ru4\text{-}CNpyRh(NH_3)_5^{5+}$ by irradiating the bimetallic complex in pH 2.0 solution where the primary photolysis product is $Ru(NH_3)_54\text{-}CNpyH^{3+}$. The protonated, monometallic complex has a MLCT maximum at 1.88 μm^{-1} (532 nm) and smaller substitution quantum yields of 3.2×10^{-5} and 1.5×10^{-3} mol/einstein at ν_{irr} of 1.83 and 2.29 μm^{-1}, respectively.[1] The lower quantum yield for photosubstitution of the protonated 4-CNpy monometallic complex, with respect to the unprotonated version, is consistent with the reactive/unreactive classification of $Ru(NH_3)_5L^{2+}$ complexes.[17]

The third Ru(II) bimetallic complex, $(NH_3)_5Ru4,4'\text{-}bpyRh(NH_3)_5^{5+}$, shows photochemical behavior different from either the L = pz or L = 4-CNpy complexes. Irradiation of the 4,4′-bpy bimetallic complex at pH 2.0 aqueous solution at 2.29 μm^{-1} (436 nm) leads to a decrease in absorbance at wavelengths longer than 460 nm and a slight increase in absorbance at wavelengths less than 460 nm. As was the case for L = 4-CNpy, the MLCT maximum shifted during irradiation and no isosbestic points were maintained very long into the photolysis experiment. Unlike the L = 4-CNpy case, the photochemistry cannot be explained solely by eq 1b and 2. The quantum yield for loss of 4,4′-bpy from $Ru(NH_3)_54,4'\text{-}bpy^{2+}$ at ν_{irr} = 2.29 μm^{-1} is 4.0×10^{-4} mol/einstein.[43] In order to account for the increase in absorption at $\lambda < 460$ nm and the appropriate decrease at ~520 nm, computer modeling using eq 1b and 2 would indicate that a relatively large increase in absorbance should be observed in the 580–600-nm region. This is not observed in the experimental data. However, if eq 1a is in competition with eq 1b, a good fit can be obtained for the experimental data. The values that best fit eq 3–7 are $\Phi_B = 4.2 \times 10^{-3}$ mol/einstein, $\Phi_C = 9.8 \times 10^{-3}$ mol/einstein, and $\Phi_E = 4.0 \times 10^{-4}$ mol/einstein (determined independently).

Discussion

Electronic Spectra. The electronic spectra of the bimetallic complexes in this study (Table I) show spectral characteristics expected of attaching electron-withdrawing substituents to L. When $Rh(NH_3)_5^{3+}$ or $Co(CN)_5^{2-}$ are attached to remote sites on L, the position of the MLCT band, associated mainly with the d_π (Fe or Ru) → p_π^* (L) transition, is shifted to lower frequency. This MLCT frequency shift is attenuated by distance (i.e., larger for L = pz than for L = 4,4′-bpy) and greater when the Lewis acid is cationic (i.e., $Rh(NH_3)_5^{3+}$) than when it is anionic (i.e., $Co(CN)_5^{2-}$). The shifts are not as large as those observed for CH_3^+ or H^+ (Figure 1) but still reflect a substantial stabilization of the π^* orbitals on L and the corresponding lower MLCT energy. There is no indication from the electronic spectrum that these remote metal centers are functioning other than as Lewis acid, electron-withdrawing substitutents on L.

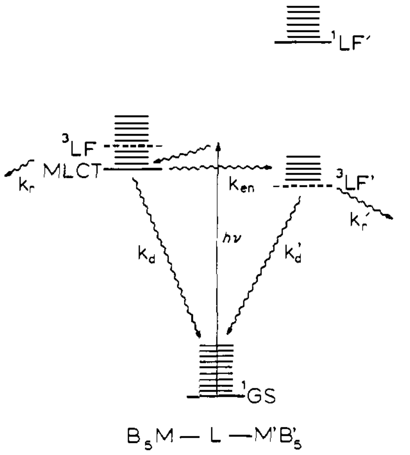

Figure 2. Excited-state diagram for the bimetallic complexes $B_5M\text{–}L\text{–}M'B'_5$. Excited states on the left side of the diagram are localized mainly on B_5ML while those on the right side with $LM'B'_5$.

Photochemistry of the Monometallic Fragments. The photochemistry of the monometallic complexes associated with the antenna fragment, $Fe(CN)_5L^{3-}$ [16] and $Ru(NH_3)_5L^{2+}$,[17] was discussed in the introduction. The result is that shifting of the MLCT band maximum below ~2.1 μm^{-1} turns off photosubstitution by placing a MLCT excited state, which is unreactive toward photosubstitution reactions, below a reactive ligand-field state.[16,17] The unreactive complexes ($\nu_{max} < 2.1$ μm^{-1}) show small, wavelength-dependent quantum yields for loss of L.

The remote metal center in the bimetallic complexes, $Rh(NH_3)_5L^{3+}$ and $Co(CN)_5L^{2-}$, demonstrate photochemistry characteristic of a lowest energy, ligand-field excited state.[7,15] That is, the quantum yields for photosubstitution of L are relatively high, approximately independent of irradiation wavelength, and maintain the same type of general behavior regardless of the substituent on L.[15]

Photochemistry of Bimetallic Complexes. The photochemistry of the bimetallic complexes can be discussed by using Figure 2. In Figure 2, a qualitative energy level diagram is given for the general system $B_5MLM'B'_5$. The left side of the diagram represents metal-to-ligand charge transfer (MLCT) and ligand-field (LF) excited states localized mainly on the highly absorbing, antenna fragment, $Fe(CN)_5L^{2-}$ or $Ru(NH_3)_5L^{2+}$, whiile the right side of the diagram deals with LF states localized mainly on the remote metal fragment, $Rh(NH_3)_5L^{3+}$ or $Co(CN)_5L^{2-}$. Excited states shown by dashed lines are nonspectroscopically observed (e.g., spin forbidden). The exact ordering of the states on the left side with respect to each other and the ^{1}LF′ and ^{3}LF′ from the remote fragment are dependent on the nature of B_5M, L, and $M'B'_5$. The approximate energy of the ^{3}LF and the spectroscopically observed MLCT state come from photochemical studies on the monometallic antenna fragments.[16,17] (Preliminary emission studies[44] also confirm the excited state diagram in Figure 2.) The relative energies of the ^{1}LF′ and ^{3}LF′ states associated with the remote metal fragment, $LM'B'_5$, are approximated from absorption[7,15] and emission[7] studies on the monometallic complexes.

The photochemistry of the Ru(II)/Rh(III) bimetallic complexes are the most interesting in that the three complexes show three different types of reactivity. By analogy with the monometallic complexes of $Ru(NH_3)_5L^{2+}$,[17] the bimetallic species have MLCT maxima that are <2.1 μm^{-1} and should be unreactive toward photosubstitution at the Ru(II) metal center. For $(NH_3)_5RuLRh(NH_3)_5^{5+}$, L = 4-CNpy and pz, with ν_{max} (MLCT)

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[43] Moore, K. J., unpublished data.

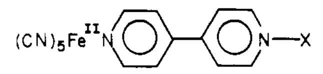
[44] Watts, R. J.; Petersen, J. D., work in progress.

= 2.05 and 1.89 μm^{-1}, respectively, this is the case. Irradiation of the L = 4-CNpy complex at 3.19, 2.29, or 1.83 μm^{-1} shows no measurable Ru(II)-L bond breaking[45] but gives rise to 4-CNpy-Rh(III) bond breaking with a quantum yield of 2.2×10^{-2}, 3.3×10^{-3}, and 3.0×10^{-4} mol/einstein, respectively. The breaking of the Rh(III)-L bond is a reaction characteristic of the $^3LF'$ state in the monometallic remote complex and we believe it comes about by intramolecular energy transfer (k_{en} in Figure 2) from excited states localized mainly on Ru(II) to those localized mainly on Rh(III). This process is in competition with non-radiative deactivation from the $^3LF/MLCT$ excited states (k_d) and is dependent on ν_{irr}. This dependence on irradiation frequency could arise from nonunitary efficiencies in the interconversion of the excited states initially populated on Ru(II), or by competitive intramolecular energy transfer/vibrational relaxation of the MLCT manifold initially populated. The quantum efficiencies of Rh(III)-L bond cleavage are much less for the bimetallic complex than for direct irradiation of $Rh(NH_3)_5(4\text{-CNpy})^{3+}$ ($\Phi = 6 \times 10^{-2}$ mol/einstein[1] when $\nu_{irr} = 3.19$ μm^{-1}), but the monometallic photochemistry must be driven by initial population of $^1LF'$, conversion to $^3LF'$, and reaction (k_r'). Initial population of $^1LF'$ requires ν_{irr} to be 3.19 μm^{-1} (313 nm) while in the bimetallic system the same reaction, albeit less efficient, can be driven with lower frequency (1.83 μm^{-1}, 546 nm) light.

The pz-bridged complex, $(NH_3)_5RupzRh(NH_3)_5^{5+}$, is much less reactive photochemically than the 4-CNpy-bridged complex. The only photochemical pathway observed is breaking of the Ru(II)-pz bond with very low quantum yields of 7.3×10^{-5} and 2.8×10^{-6} mol/einstein at $\nu_{irr} = 2.29$ and 1.83 μm^{-1}, respectively. These quantum yields are ~2 orders of magnitude less than the quantum yields observed for the energy transfer with L = 4-CNpy. The lack of energy transfer for L = pz is due to the lower energy MLCT state for L = pz vs. L = 4-CNpy. This makes the energy-transfer step (k_{en}) endothermic for L = pz, and k_{en} is no longer competitive with k_d (see Figures 1 and 2 in ref 1).

The third Ru(II)/Rh(III) complex, $(NH_3)_5Ru4,4'\text{-bpyRh}(NH_3)_5^{5+}$, has a MLCT maximum at lower frequency (1.87 μm^{-1}) than either the 4-CNpy (2.05 μm^{-1}) or pz (1.89 μm^{-1}) bimetallic complexes. Initial expectations were that the 4,4'-bpy-bridged complex would mimic the pz-bridged species, be unreactive to Ru(II)-L bond breaking ($\nu_{max} < 2.1$ μm^{-1}), and be thermodynamically unfavorable for energy-transfer processes ($E(MLCT) < E(^3LF')$). However, this is not the case, as Table II indicates competitive cleavage of Ru(II)-4,4'-bpy and Rh(III)-4,4'-bpy bonds. The quantum yields for these processes are 4.2×10^{-3} and 9.8×10^{-3} mol/einstein, respectively. These quantum yields are comparable to Ru(II) monometallic complexes which are reactive toward photosubstitution, and energy-transfer reactions that are as efficient as the 4-CNpy-bridged complex. There is no simple explanation for this photochemical reactivity. The bandwidths at half-height is approximately the same for L = 4,4'-bpy as for L = 4-CNpy and L = pz. This rules out any Stokes shift differences that would invert the MLCT and ^3LF excited states. The only experimental data that shows any marked differences in the three complexes are cyclic voltammetry studies.[38] The Ru(III)/Ru(II) reduction potentials (vs. NHE) of $(NH_3)_5RuLRh(NH_3)_5^{5+}$ are 0.68 V (L = 4,CNpy), 0.68 V (L = pz), and 0.39 V (L = 4,4'-bpy). The greater ease of oxidation of the 4,4'-bpy bimetallic complex may indicate that the Ru(II)/4,4'-bpy orbital overlap, and ground-state π-back-bonding are much different than the other two systems and that ν_{max} (MLCT) and $\Delta_{1/2}$ are misleading in approximating the relative energies of MLCT and ^3LF. However, it should be noted as well the monometallic complex, $Ru(NH_3)_5\text{-}4,4'\text{-bpy}^{2+}$, has a reduction potential of 0.33 V[38], a ν_{max} (MLCT) of 2.06 μm^{-1},[17] and a photochemical reactivity at Ru(II) that is a factor of 10 lower than the Ru(II)/Rh(III) bimetallic complex.

Table III. Electronic Spectra, Photochemistry, and Electrochemistry of $Fe(CN)_54,4'\text{-bpy-X}$ Complexes



X	ν_{max}- (MLCT),[a] μm^{-1}	Φ,[b] mol/einstein	$E^{\circ\prime}$,[c] V
lone pair	2.32	0.34[d]	0.507
$Co^{III}(CN)_5$	2.20	0.60	0.53
$Rh^{III}(NH_3)_5$	2.08	0.013-0.060[e]	0.52
CH_3^+	1.92	0.016[d]	0.538

[a] Maximum of the Fe(II) → 4,4'-bpy-X MLCT transition. [b] Quantum yield for Fe^{II}-4,4'-bpy-X bond breaking. [c] Fe(III)/Fe(II) reduction potential vs. NHE measured by cyclic voltammetry, ref 38. [d] Reference 16. [e] Quantum yield is dependent on irradiation frequency; see Table II.

An alternate mechanism for the remote center reactivity observed in the 4-CNpy and 4,4'-bpy bimetallic complexes could be proposed. This mechanism would involve an electron-transfer process from the MLCT excited state to produce $(NH_3)_5Ru^{III}LRh^{II}(NH_3)_5^{5+}$. Although the Ru(III) metal center would be inert to thermal substitution processes, the Rh(II) metal center should be axially labile. Cleavage of the Rh(II)-L and Rh(II)-*trans*-NH_3 bonds, followed by reverse outer-sphere electron transfer would result in $Ru(NH_3)_5L^{2+}$ and *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ products. Under the conditions used in these experiments ([complex] ≅ 10^{-5} M), we would not be able to distinguish between $Rh(NH_3)_5H_2O^{3+}$ and *trans*-$Rh(NH_3)_4(H_2O)_2^{3+}$ in the photolyte solution by pH or electronic spectral changes. However, this latter mechanism does not explain why the pz-bridged complex, which has a ν_{max} (MLCT) similar to the 4-CNpy-bridged complex and an identical ground-state Ru(III)/Ru(II) reduction potential, does not undergo the same reaction. It would also seem fortuitous that the competition between excited-state electron transfer and bond breaking at Ru(II) for the 4,4'-bpy bimetallic complex would be in such close competition. Thus, we favor an intramolecular, energy-transfer mechanism to explain reactivity at the remote center in the Ru(II)/Rh(III) bimetallic systems.[46]

The pentacyanoferrate(II) bimetallic complexes, $(CN)_5FeLM'B'_5$, show a straightforward photochemical behavior which is relatively efficient Fe(II)-L bond breaking. There is no evidence for any energy-transfer reactions for the Fe(II) bimetallic complexes. These data are not in accord with our previous interpretation[16] of the monometallic Fe(II) complexes, $Fe(CN)_5L^{n-}$. For the monometallic systems, as the maximum of the MLCT band shifts below ~2.1 μm^{-1} the quantum yield for photosubstitution of L decreases drastically. In the bimetallic systems, this is not the case. Even the complex $(CN)_5FepzRh(NH_3)_5$, with $\nu_{max}(MLCT) = 1.75$ μm^{-1}, has a large quantum yield (0.07-0.23 mol/einstein) for Fe(II)-pz bond breaking.

If we ignore, for the moment, the pz-bridged Fe(II)/Co(III) and Fe(II)/Rh(III) systems and concentrate on the two 4,4'-bridged complexes, the photochemical results are compatible with the monometallic Fe(II) systems. Table III summarizes the electronic spectra, photochemistry, and electrochemistry[38] for the series of complexes $Fe(CN)_54,4'\text{-bpy-X}$, where X is a Lewis acid bound to the remote pyridyl nitrogen. As the MLCT maximum is shifted to lower frequency, there is a slight tendency for a larger reduction potential. This trend has been interpreted as a tendency to increase π-back-bonding in going down from top to bottom in Table III. However, in this case, the effect is small due to the large distance between the Fe(II) center and X and the ability of the bridging ligand to undergo rotation around the 4,4' C-C bond.[38] The quantum yields for $Fe^{II}4,4'\text{-bpy-X}$ bond cleavage are high (>0.3 mol/einstein) when ν_{max} (MLCT) >2.1 μm^{-1} and much smaller (<0.06 mol/einstein) when ν_{max}(MLCT < 2.1 μm^{-1}. This behavior and the irradiation frequency dependence for X =

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(45) Ru(II)-L bond breaking occurs in $Ru(NH_3)_54\text{-CNpy}^{2+}$ as a secondary photolysis process.

(46) Even in the event that an electron-transfer process is supported, the fact still remains that the antenna fragment is driving a photochemical reaction at a much lower irradiation frequency than would be necessary by direct irradiation of the monometallic remote center.

$Rh^{III}(NH_3)_5$ is all consistent with $E(^3LF) < E(MLCT)$ for X = lone pair and $Co^{III}(CN)_5$ and $E(MLCT) < E(^3LF)$ for X = $Rh^{III}(NH_3)_5$ and CH_3^+. In the case of $(CN)_5Fe4,4'\text{-bpyCo}(CN)_5^{5-}$, the reduction of the quantum yield by lowering the MLCT state has still not made the k_{en} process competitive with k_r and k_d (Figure 2) and the Fe(II)–L bond breaking process is the only pathway observed.

The most surprising data in the study comes from the photochemistry of the pz-bridged Fe(II) bimetallic complexes, $(CN)_5FepzCo(CN)_5^{5-}$ and $(CN)_5FepzRh(NH_3)_5$. These complexes have ν_{max} (MLCT) values of 1.90 and 1.72 μm^{-1}, respectively. On the basis of the discussion above and the results of the monometallic photochemistry,[16] these bimetallic complexes should not show much photochemical reactivity toward Fe(II)–pz bond breaking. On the contrary, the Fe(II)/Co(III) system has a quantum yield of 0.60 mol/einstein and the Fe(II)/Rh(III) system has a quantum yield of 0.07–0.23 mol/einstein for Fe(II)–pz bond breaking.

One possible explanation for this behavior is that the attachment of the remote metal center is perturbing the σ/π system in such a way that the ligand field excited state has to be shifted to lower frequency along with the MLCT excited state. This explanation suffers from the fact that the electrochemistry[38] and Mössbauer spectroscopy[37] on these complexes, along with other monometallic and bimetallic pentacyanoferrate(II) complexes, show that the addition of the remote metal center modifies the properties of the complex just as any other electron-withdrawing substituent. There is no evidence for any drastic shift in ^3LF when a remote metal center is bound to $Fe(CN)_5pz^{3-}$.

The second, and more reasonable explanation for the large quantum yields in the pz-bridged Fe(II) systems, is a modification of the MLCT reactivity at Fe(II). If we first look at $(CN)_5FepzRh(NH_3)_5$, the quantum yield is dependent on irradiation frequency with a minimum of 0.07 mol/einstein at ν_{irr} = 1.57 μm^{-1} and a maximum of 0.23 mol/einstein at ν_{irr} = 1.83 μm^{-1}. This dependence has been observed for other monometallic pentacyanoferrate(II)[16] and pentaammineruthenium(II)[17] systems, where $E(MLCT)$ is assumed to be lower than $E(^3LF)$, internal conversion from MLCT to ^3LF is competitive with MLCT vibrational relaxation, and the reverse process ($^3LF \rightarrow MLCT$) does not occur with unitary efficiency.[20,47] The lower limit quantum yield, 0.07 mol/einstein, is higher than those of the MLCT lowest excited-state monometallic complexes,[16] but still much less reactive than the complexes where the ^3LF state is assumed to be lower in energy than the MLCT state populated by photon absorption.

The most difficult photochemical data to rationalize is that of $(CN)_5FepzCo(CN)_5^{5-}$. With $\nu_{max}(MLCT)$ = 1.90 μm^{-1}, the quantum yield of 0.60 for Fe(II)–pz bond breaking is much larger than expected or larger than can be attributed to a slight increase in MLCT excited-state reactivity. However, there is a lot of electrostatic repulsion between $Fe(CN)_5^{3-}$ and $Co(CN)_5^{2-}$ through the very small pz bridge. This is reflected in the formation rate constant when the bimetallic complex is prepared by the reaction of $Fe(CN)_5H_2O^{3-}$ and $Co(CN)_5pz^{2-}$ (k_2 = 0.5 M^{-1} s^{-1}).[36] The formation rate constant is much slower than any of the others observed for the Fe(II) bimetallic complexes in this study.[36] This electrostatic repulsion may contribute heavily in the k_r process for this complex and dominate all other deactivation pathways.

Conclusion

Highly absorbing or antenna metal fragments can be chemically coupled to a second metal center and used to drive reactions at the remote center via intramolecular energy-transfer processes. For these reactions to occur, the following two conditions must be met: (1) The excited-state ordering and character of the antenna fragment must be constrained to prevent reactions at the antenna fragment from competing with energy transfer to excited states localized mainly on the remote metal, and (2) The energy-transfer process must be kinetically and thermodynamically feasible within the lifetime of the donor excited state. Both conditions are met for the complex $(NH_3)_5Ru4\text{-CNpyRh}(NH_3)_5^{5+}$ and irradiation of the Ru(II) → 4-CNpy MLCT band leads to reactions characteristic of the ^3LF state on Rh(III). For the complex $(NH_3)_5Ru4,4'\text{-bpyRh}(NH_3)_5^{5+}$, condition 2 is met but condition 1 is only partially met, resulting in competitive reactions characteristics of excited states of both Ru(II) and Rh(III). The $(NH_3)_5RupzRh(NH_3)_5^{5+}$ complex meets condition 1 but does not meet condition 2 and very little reactivity is observed at either metal center. Using the less expensive but analogous pentacyanoferrate(II) in place of pentaammineruthenium(II), we could generate the series of compounds, $(CN)_5FeLRh(NH_3)_5$ (L = pz, 4,4'-bpy) and $(CN)_5FeLCo(CN)_5^{5-}$ (L = pz, 4,4'-bpy). The Fe(II)/Co(III) bimetallic complexes are not very stable thermally,[36] and all Fe(II) bimetallic complexes fail to meet condition 1.

The results on these model systems indicate that photochemical reactions can be run by absorbing light in one portion of the molecule and using that photonic energy to drive reactions in another portion of the molecule. The two greatest problems appear to be maintaining the metal-bridging ligand bonds and communicating effectively between the antenna fragment and remote fragment through the bridging ligand. We hope to overcome these problems by using short, unsaturated, chelate bridging ligands such as 2,2'-bipyrimidine with both Ru(II)[48] and Fe(II)[49] metal centers.

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