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Ligand substituent effects in transition metal photochemistry—The tuning of excited states

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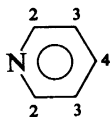
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I. Introduction

For decades the systematic application of substituent effects has been a mainstay of physical organic chemistry, and few chemistry students have escaped the influence of Hammett's elegant treatment of substituent effects on benzoic acid dissociation constants.¹ The application of substituent effects in transition metal chemistry has been much less extensive. However, in recent years, various researchers have used this powerful tool to probe the nature of metal complex electronic excited states in investigations of absorption and emission spectroscopy and of photochemistry. The purpose of this article is to review ligand substituent effects in transition metal photochemistry, particularly in mechanistic studies. Spectroscopic investigations relevant to the photochemical experiments will also be reviewed.

For the purpose of the work described here, the term substituent will be defined as a group replacing a hydrogen atom of a parent ligand and having the potential of changing the electronic character of that ligand. In addition, we

will limit our interest to those substituents which have little steric influence on the metal coordination site of the ligand. For example, substituents at the 3-(*meta*) and 4-(*para*) sites of pyridine are relatively remote from the coordination site and effects of this type of substitution can be considered largely in



terms of electronic effects. In contrast, a group located at the 2-(*ortho*) position may cause steric crowding at the coordination site or may even bind directly to the metal, leading to rather unsubtle perturbations of the ground and excited states. Nonetheless, even remote substituents may cause major modifications in the complex's spectroscopy, in the energetic order of relevant excited states, and in the reactivities and deactivation rates from these states. Thus, such molecular engineering of excited state properties provides a powerful tool for investigating photochemical mechanisms and for the design of chemical systems having practical applications as in the conversion of solar radiation to chemical potential energy.

To this reviewer's knowledge, the term "tuning" in the context of metal excited states was first introduced by Crosby, Watts, and Carstens² to describe the effects of ligands and of ligand substituents on the energies and the relative ordering of excited states. Substituent effects as discussed here would actually fall under their definition of "fine tuning." The first systematic application of the tuning concept to metal complex photochemistry³ and subsequent studies of similar genre have been largely concerned with d^6 metal complexes of the aromatic nitrogen heterocycles pyridine (py), 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen), and this review will concentrate on these systems. However, some substituent effect studies have also been carried out with tris(1,3-diketonate) complexes, the subject of a recent review.⁴ Lastly, it is clear that organometallic photochemistry has vast potential for substituent effect studies.

II. Spectroscopy

Since the central theme of this review is the use of substituent effects in the transition metal complex photochemistry, it is clearly very important to correlate spectroscopic substituent effects with those seen in photochemistry. The excited states of transition metal complexes are generally categorized according to their orbital parentages and the photoreactions are usually analyzable in terms of one or another of the following states:⁵ ligand field ($d \rightarrow d$), interligand ($\pi_L \rightarrow \pi_L^*$), metal to ligand charge transfer ($d \rightarrow \pi_L^*$), ligand to metal charge transfer (σ_L or $\pi_L \rightarrow d$), or charge transfer to solvent ($d \rightarrow ?$). These are illustrated in Figure 1. Characterizations based on spin multiplicities are also bandied about, but despite this common usage (including parts of the present

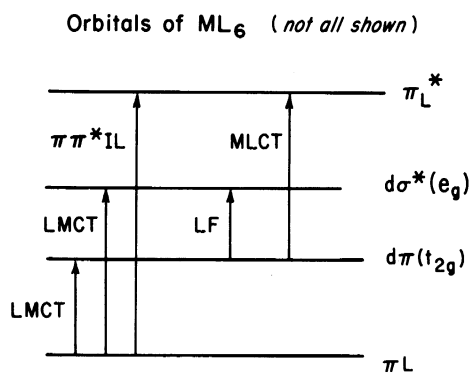


Figure 1. Schematic representation of the types of orbital electronic absorptions expected for a hexacoordinate complex ML_6 . (Not shown are the LMCT transitions $\sigma_L \rightarrow d_\pi$ or $\sigma \rightarrow d_\sigma$ or the IL transitions $n \rightarrow \pi^*$.) Relative energies of various transitions will depend on the nature of M and L.

review), it should be emphasized that spin orbit coupling may significantly modify the meaning of such designations, especially for the heavier metal systems.⁶

A. Ligand field states

According to crystal field theory, ligand (LF) states are derived from electronic excitation between one metal centered "d" orbital and another (Figure 1). However, it should be emphasized that in the generally more useful molecular orbital treatment these "d" orbitals may include considerable contributions from ligand orbitals. In this context the $t_{2g} \rightarrow e_g$ transition illustrated in Figure 1 represents a $\pi \rightarrow \sigma^*$ molecular orbital transition where the t_{2g} orbital is either π_{M-L}^* or π_{M-L}^b depending on the nature of the coordinated ligands. Thus, in considering the effects of ligand substituents on d orbital energies, one must take account of the effects on both σ and π bonding characteristics of the ligand.

The influence of a substituent x on the ligand properties of a *m*- or *p*-substituted pyridine (py-x) can be roughly separated into the *inductive*, *field*, and *resonance* effects.⁷ The inductive effect operates through bonds and corresponds to a displacement of electronic charge caused by the different electron withdrawing power of the two atoms forming a bond. It falls off rapidly with distance, although the nature of the atoms in the chain of transmission has a major influence on how rapidly the effect is attenuated. The field effect corresponds to charge/charge, charge/dipole, or dipole/dipole interactions through space. Lastly, the resonance effect is defined as operating *via* the π -orbitals of a π -unsaturated system thus is important for aromatic ligands but not for saturated ones. Therefore, although a parameter such as the Hammett sigma constant¹ (based on the acidity of substituted benzoic acids⁸) may give a qualitative idea

regarding the substituent effect on metal ligand interactions, quantitative comparisons suffer from the probability that the latter interactions have a different relative response to the inductive, field, and resonance properties⁹ of the substituents.

The LF absorption bands of various d^6 complexes of substituted pyridine L_5Mpy-x are relatively insensitive to x . For the hexacoordinate complex ML_6 , two spin allowed LF bands are expected, ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$, while in the approximately C_{4v} symmetry of ML_5py-x , these bands correspond to the representations 1A_2 , ${}^1E^a \leftarrow {}^1A_1$, 1B_2 , ${}^1E^b \leftarrow {}^1A_1$ respectively. However, band splitting in the latter case is often undetectable (Figure 2), and the observed

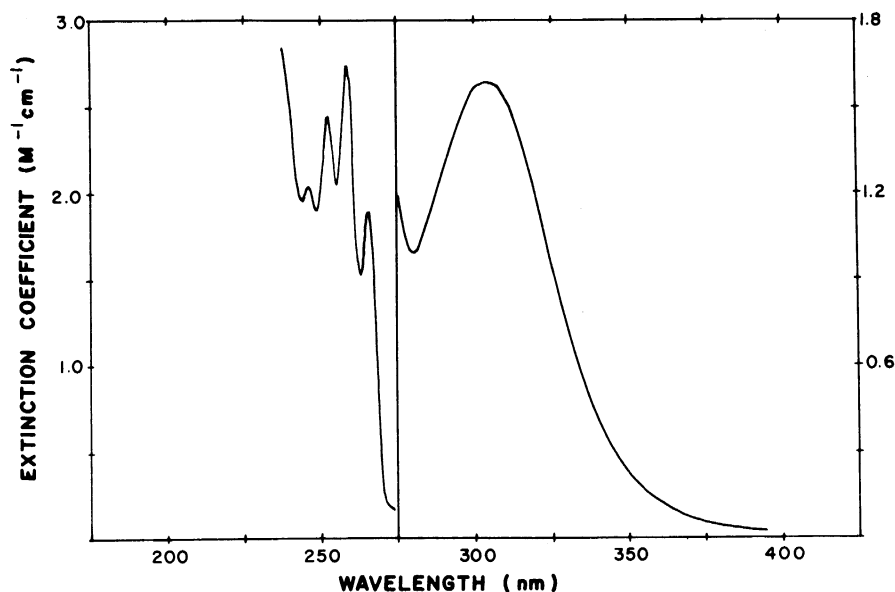


Figure 2. Spectrum of $Rh(NH_3)_5py^{3+}$ in aqueous solution (scale to left is $10^3 M^{-1} cm^{-1}$, scale to right is $10^2 M^{-1} cm^{-1}$).

λ_{max} values are functions of the average ligand field.¹⁰ Hence, comparison of the LF λ_{max} (e.g., ${}^1T_1 \leftarrow {}^1A_1$) of ML_6 to those (e.g., 1A_2 , ${}^1E^a \leftarrow {}^1A_1$) of various ML_5L' qualitatively positions L' in the spectrochemical series. The identical λ_{max} values (302 nm)¹¹ for the 1A_2 , ${}^1E^a \leftarrow {}^1A_1$ bands of the rhodium(III) complexes $Rh(NH_3)_5py-x^{3+}$ ($py-x = py, py-4-CH_3, \text{ or } py-3-Cl$) indicate that in this context the $py-x$ ligand field strengths are independent of the substituent. Also, comparison with the $Rh(NH_3)_6^{3+}$ spectrum (Figure 3, λ_{max} 305 nm for ${}^1T_1 \leftarrow {}^1A_1$) indicates that the various pyridines occupy a spectrochemical series position comparable to that of ammonia.

Absorption spectra of other d^6 L_5Mpy-x complexes give results similar to those seen with the Rh(III) complexes. For example, the homologous cobalt(III) complexes $Co(NH_3)_5py-x^{3+}$ show 1A_2 , ${}^1E^a \leftarrow {}^1A_1$ λ_{max} of 474 nm, 475 nm, and

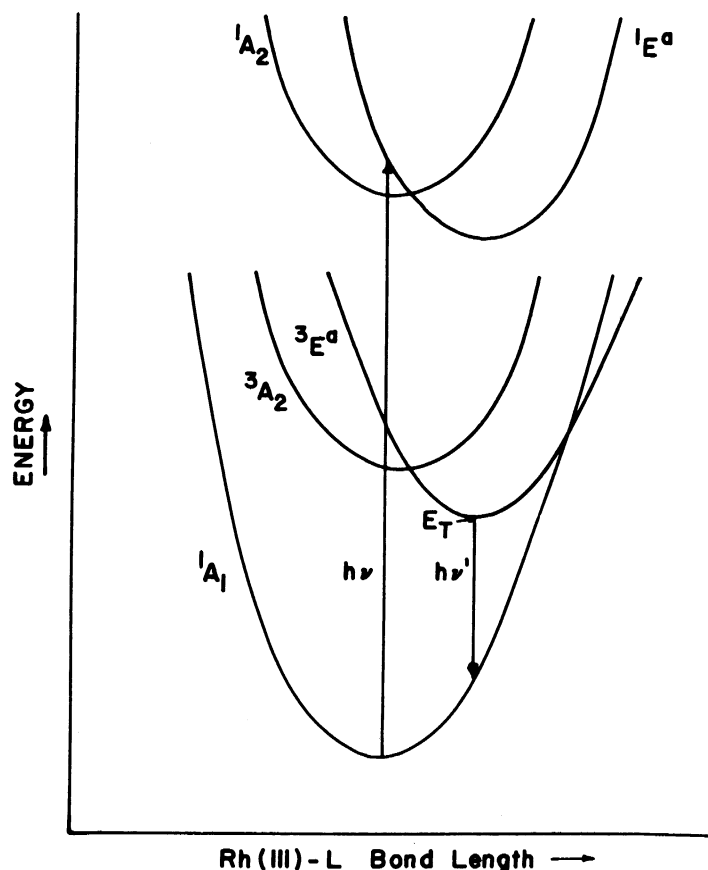


Figure 3. Proposed splitting of A_2 , E^a states as a function of the distortion along the Rh(III)-L band of $\text{Rh}(\text{NH}_3)_5\text{L}^{3+}$ illustrating how the absorption and emission experiments may lead to different conclusions regarding the relative ligand field strengths of NH_3 and L.

476 nm for py, py-4- CONH_2 , and py-3- CONH_2 respectively *vs* 475 nm for $\text{Co}(\text{NH}_3)_6^{3+}$.¹² For this series the higher energy ${}^1B_2, {}^1E^b \leftarrow {}^1A_1$ bands can also be identified in the absorption spectra and fall quite close to the ${}^1T_{2g} \leftarrow {}^1A_{1g}$ band of $\text{Co}(\text{NH}_3)_6^{3+}$. Similar patterns are seen for the rather different series $\text{W}(\text{CO})_5\text{py-x}$. Although the spectra of the tungsten(0) complexes are dominated by MLCT bands, LF absorptions (assigned as ${}^1E^a \leftarrow {}^1A_1$) were identified in the spectra of substituted pyridines as diverse as py-4-Me and py-4-CN.¹³ Again the LF λ_{max} values are little affected by x and are close to that for the piperidine (NC_5H_{11} , a saturated cyclic amine) complex.¹³

Since pyridine is a much weaker Bronsted base than ammonia, one might also expect it to be a weaker field ligand. The failure of this viewpoint with regard to the absorption spectra described here can be argued to be the result

of synergistic π bonding effects. The pyridine is a poorer σ -donor than NH_3 but is a better π -acceptor.^{14,15} Thus, it appears that the effect of an electron withdrawing substituent on pyridine is self compensating with regard to the spectrochemical series position; the lowered σ donor ability largely is cancelled by increased π -acceptor ability.

The luminescence spectra of the $\text{Rh}(\text{NH}_3)_5\text{py-x}^{3+}$ and $\text{W}(\text{CO})_5\text{py-x}$ species add complexity to the question of ligand field strengths. In low temperature (77°K) glasses the $\text{Rh}(\text{NH}_3)_5\text{py-x}^{3+}$ species emit from the lowest energy ligand field triplet state (${}^3\text{A}_2, {}^3\text{E}^a \rightarrow {}^1\text{A}_1$) and, in contrast to the absorption spectra, emission maxima are substituent dependent.¹¹ While $\text{Rh}(\text{NH}_3)_6^{3+}$ and $\text{Rh}(\text{NH}_3)_5\text{py}^{3+}$ have comparable emission energies (16.4 kK and 16.3 kK, respectively), emission from $\text{Rh}(\text{NH}_3)_5(\text{py-3-Cl})^{3+}$ occurs at a measurably lower energy (15.6 kK).¹¹ Similarly, LF emissions from $\text{W}(\text{CO})_5\text{py-x}$ show a definite sensitivity to the nature of x with ν_{max} energies ranging from 19.7 kK for $\text{W}(\text{CO})_5(\text{py-3,5}(\text{CH}_3)_2)$ to 18.1 kK for $\text{W}(\text{CO})_5(\text{py-3,5-Br}_2)$.¹³ Interpretation of the Rh(III) and W(0) data must focus on the nature of the thermally relaxed excited state from which emission originates.¹¹ The absorption and emission experiments are illustrated in Figure 3. The important point is that promotion of an electron from the $\pi^6 t_{2g}$ orbital to the $\sigma^* e_g$ orbital should lead to significant elongation of the metal ligand bonds.¹⁶ Given the view that $d_{\pi}\text{-p}_{\pi}$ overlap is a more sensitive function of M-L distance than is $d_{\sigma}\text{-p}_{\sigma}$ or $d_{\sigma}\text{-sp}_{\sigma}$ overlap,¹⁷ this elongation should decrease the contribution of π -bonding to the py-x ligand field strength relative to the ground state.¹¹ This argument is reinforced by viewing the thermally equilibrated excited (thexi) state as having depleted $\pi^6(t_{2g})$ orbitals relative to the ground state. Thus while the absorption spectra appear to reflect an approximate cancellation of the expected opposing influences of x on the py-x σ -donor and π -acceptor natures in the ground state, the emission spectra indicate that the relative ligand field strengths in the lowest energy thexi state are more strongly influenced by σ -donor effects. This feature has significance in considering the LF excited state reactivities (*vide infra*).

Tantalizing exceptions to the above examples are the emission spectra of the tetrachloro(1,10-phenanthroline) complexes $\text{MCl}_4(\text{phen-x})^-$, where M is Rh(III) or Ir(III).¹⁸ These all show low energy broad Gaussian bands attributed to LF emission. For both sets of complexes electron withdrawing substituents increase ν_{max} (the emission energy) and electron donating groups decrease ν_{max} with these tendencies much more pronounced for Ir(III). Thus ν_{max} for $\text{K}[\text{IrCl}_4(\text{phen})]$ is 15.1 kK while those for $\text{K}[\text{IrCl}_4(\text{phen-5,6}(\text{CH}_3)_2)]$ and $\text{K}[\text{IrCl}_4(\text{phen-4-Br})]$ are 14.7 kK and 16.2 kK respectively.

These results were interpreted as indicating that the π -bonding influences of the phenanthroline substituents outweighed the corresponding σ -donor changes especially for the Ir(III) complexes. The larger effect for Ir(III) would be expected given other indirect evidence for stronger interactions with π -unsaturated ligands than seen for Rh(III).¹⁸ Absorption spectra were not reported, so one cannot evaluate whether substituent effects on the absorption spectra are dominated by π effects as well or whether there is any attenuation of π -interactions between

the absorption and emission data. However, an important point to consider in comparing the $\text{IrCl}_4(\text{phen-x})^-$ spectra to those of $\text{Rh}(\text{NH}_3)_5\text{py-x}^{3+}$ and analogous species is that the Cl-Ir-Cl axis perpendicular to the phen plane is clearly the weakest field axis and it will be along this axis that the major distortion will occur for the lowest thexi state (*vide infra*). In that case, the arguments presented above for attenuation of the M-L π -bonding in going from the ground to the excited state are much less likely to carry much importance.

B. Metal-to-ligand charge transfer and intraligand π, π^* states

1. Pyridine complexes

Electronic transitions involving MLCT states (both absorption and emission) generally are quite substituent sensitive if the substituents are on the ligand directly involved. An early systematic study⁹ of substituent effects on MLCT absorption bands was concerned with the ruthenium(II) ions $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$. The spectrum of the parent $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ ion is shown in Figure 4. The broad

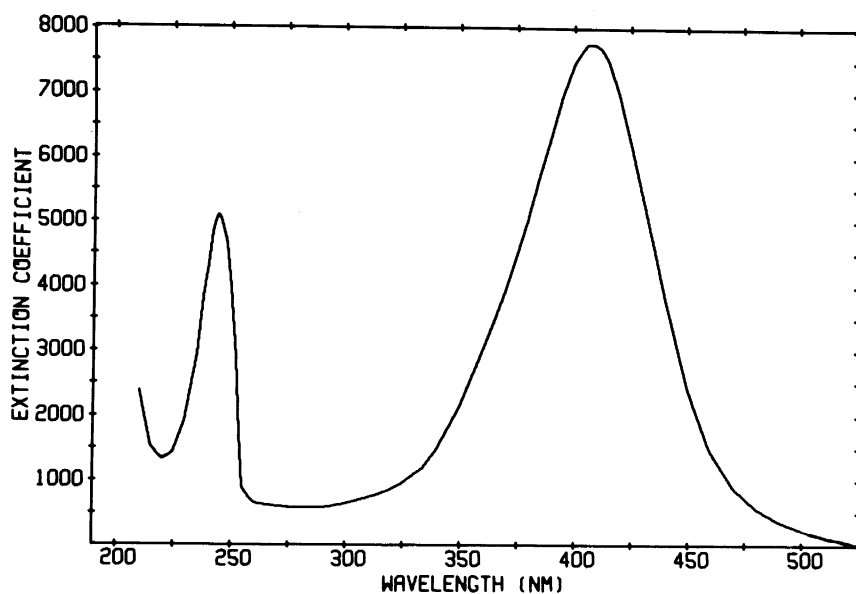
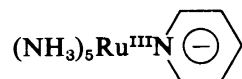


Figure 4. The spectrum of $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ in aqueous solution.

lower energy band centered at 407 nm was assigned⁹ as having MLCT character and the higher energy absorption as having π, π^* intraligand character. The observed single MLCT absorption band in this case may be more complex than is apparent since group theory analysis of the allowed transitions suggests that several of comparable energy are expected.⁹ Despite this conclusion, none of the $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$ complexes show any splitting of this MLCT band. A variety of other $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ complexes where L is a π unsaturated ligand

including such species as dinitrogen and various organonitriles also display MLCT absorptions in their electronic spectra.¹⁹

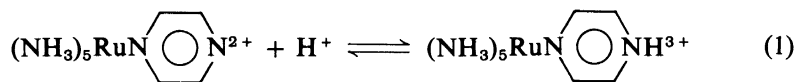
Substituent effects on the MLCT band energies respond in a manner consistent with the formal representation of the MLCT state as an oxidized metal center coordinated to a radical ion:



Electron donating substituents should destabilize this configuration while electron withdrawing groups, especially those which are π -unsaturated, should stabilize it. If there are no major substituent related changes in the Franck-Condon energies, the MLCT band maxima should respond similarly. This indeed is the case, and Table 1 summarizes the MLCT maxima for the aqueous solution spectra of various $\text{Ru}(\text{NH}_3)_5(\text{py}-x)^{2+}$ derivatives. Hammett σ constants and free ligand pK_a values are also listed for comparison.

Table 1 also summarizes the MLCT absorption maxima for the analogous pyridine complexes $\text{Fe}(\text{CN})_5\text{py}-x^{3-}$,^{20,21} $\text{W}(\text{CO})_5(\text{py}-x)$,¹³ and $(\eta^5-\text{C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{py}-x)^{22}$ ($\text{M} = \text{Re}$ or Mn). The energies of these transitions parallel qualitatively the behavior of the ruthenium(II) complexes, indicating the generality of the substituent effects. For example, comparison of the MLCT band energies for different substituents shows that the $\Delta\nu_{\text{max}}$ between $x = 4\text{-CH}_3$ and $x = 4\text{-CHO}$ is in the range 6–8 kK for each of the $\text{py}-x$ complexes listed in Table 1. Substituent effects have also been argued²³ as evidence for a MLCT assignment of bands in $\text{PtCl}_2(\text{CO})\text{py}-x$ and similar complexes; however, in these cases, the substituent effects are so small that it is unlikely that the transitions involve the same $\text{py}-x$ orbitals as those complexes listed in Table 1.

The spectral study of the $\text{Ru}(\text{NH}_3)_5(\text{py}-x)^{2+}$ complexes⁹ revealed several features particularly relevant to the characterization of the MLCT absorption bands. First, the complexes of the various diazines ($\text{N}_2\text{C}_2\text{H}_4$, pyrazine, pyrimidine, pyridazine) show a linear correlation between ν_{max} and the formal potentials for the one electron reductions of the free ligands. Second, protonation of the pyrazine complex (eq.(1)) causes a shift in the λ_{max} (MLCT) from



472 nm to 529 nm, indicating that the MLCT excited state is considerably more basic than the ground state.⁹ Third, the MLCT band position is very sensitive to the solvent medium. For example, in water the *isonicotinamide* complex $\text{Ru}(\text{NH}_3)_5(\text{py}-4\text{-CONH}_2)^{2+}$ has a λ_{max} (MLCT) at 479 nm but this is shifted to the blue (468 nm) in acetonitrile and to the red (511 nm) in dimethyl sulfoxide solution.²⁴ Similar solvent shifts of MLCT bands are noted with the tungsten and molybdenum carbonyl complexes, $\text{M}(\text{CO})_4\text{phen}$ and $\text{M}(\text{CO})_4(\text{bipy})$.²⁵ In

Table 1. MLCT λ_{\max} for some $L_5M(\text{py-x})$ complexes

py-x	σ^a	pK_a^b	MLCT, λ_{\max} (in nm)					
			$\text{Ru}(\text{NH}_3)_5(\text{py-x})^{2+}$ ^c	$\text{Fe}(\text{CN})_5(\text{py-x})^{3-}$ ^d	$\text{W}(\text{CO})_6(\text{py-x})^e$	$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{py-x})^f$	$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{py-x})^g$	
py-4-CH ₃	-0.17	6.1	398	356	351	380, 430 sh	390, 485 sh	
py	0.00	5.3	407	362	355	393, 445 sh	412, 495 sh	
py-4-Cl	0.23	3.8	422	383				
py-4-C ₆ H ₅	-0.01	5.6	446			417, 475 sh		
py-3,5-Cl ₂	0.7	0.7	447		407 ^o	435, 505 sh	470, 555	
pyrazine		0.6	472	452				
py-4-CONH ₂	0.27	3.6	479	435				
py-4-CO ₂ CH ₃	0.39	3.8	497					
py-4-COCH ₃	0.5	3.5	523 ^h	478 ⁱ	440	480, 555 sh	525, 640 sh	
py-4-CN	0.66	1.9	—	476	455	495, 585 sh	555, 670 sh	
py-4-CHO	—	—	545	505	470	320 ^j	455 ^j	
NH ₃	—	—	390 ^j	398 ^j	408, 440 sh ^j			

^a Hammett σ constant for -x taken from J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, NY, 1962, p. 87.

^b pK_a of py-x in aqueous solution, taken from K. Schofield, "Hetero-Aromatic Nitrogen Compounds," Plenum Press, New York, 1967.

^c In aqueous solution, data from Reference 9 except where noted.

^d In aqueous solution, data from Reference 20 except where noted.

^e In *isooctane*, data from Reference 13.

^f In *isooctane*, data from Reference 22.

^g Value for $\text{W}(\text{CO})_6(\text{py-3,5-Br}_2)$, λ_{\max} for overlapping CT and LF bands.

^h Reference 3.

ⁱ Reference 21.

^j Lowest energy LF absorptions.

contrast, LF absorption bands are relatively insensitive to solvent media,²⁶ and this difference can be used as a criterion for assigning spectral bands. The solvent sensitivity of MLCT band energies and the apparent insensitivity of the metal centered LF states also have important implications with regard to the photochemistry of these systems (*vide infra*).

Among the $ML_5(py-x)$ complexes, reliable data for MLCT emissions have been reported only for the $W(CO)_5(py-x)$ derivatives. The span of complexes which emit from a MLCT state is narrow; however, the emission ν_{max} of the $py-4-COCH_3$ (17.0 kK), $py-4-CN$ (16.6 kK) and $py-4-CHO$ (15.2 kK) complexes follow the same energy order as do the MLCT absorption maxima (Table 1).

2. Bipyridine and phenanthroline complexes

The absorption and emission spectra of d^6 metal complexes of bipyridine and phenanthroline have been the subject of considerable attention in recent years. Aspects of the emission spectra were reviewed²⁷ recently. Here we will be concerned only with the complexes of Ru(II) and Ir(III) both of which have been the subject of photochemical studies involving ligand substituents.

Emission studies have characterized the lowest energy states of $Ru(bipy)_3^{2+}$, of $Ru(phen)_3^{2+}$ and of the various tris $bipy-x$ and $phen-x$ derivatives as having MLCT character.²⁷⁻³¹ The absorption spectrum of $Ru(bipy)_3^{2+}$ displays bands at 453 nm ($\epsilon = 1.4 \times 10^4 M^{-1} cm^{-1}$) and 423 nm (sh) attributed to MLCT transitions and bands at 285 nm ($8 \times 10^4 M^{-1} cm^{-1}$) and 250 nm ($2.5 \times 10^4 M^{-1} cm^{-1}$) assigned as π, π^* intraligand transitions.²⁸ Since low extinction coefficient absorption ($< 10^3 M^{-1} cm^{-1}$) ~ 550 nm overlaps the higher energy component of the emission envelope (Figure 5), this may represent direct absorption into the emitting state(s). Earlier work described the emitting state as a triplet; however, Crosby and co-workers have since discarded this description as inadequate owing to the magnitude of the spin orbit coupling.^{30,32}

In general the energies of the absorption and emission bands of the $Ru(bipy-x)_3^{2+}$ and $Ru(phen-x)_3^{2+}$ species in fluid solutions are not particularly sensitive to the nature of the substituents.³³ For example the higher energy maximum of the $Ru(phen-x)_3^{2+}$ luminescence in 25° aqueous solution occurs at 605 nm for substituents as diverse as 3,4,7,8- $(CH_3)_4$, 5-Br and 5- NO_2 . The 4,7- $(CH_3)_2$ and 4,7- $(C_6H_5)_2$ derivatives have slightly lower energy emission (613 nm).^{33,34} Emission from $Ru(bipy-x)_2$ is more dependent on x with 4,4'- $(C_6H_5)_2$ shifting the higher energy component ~ 25 nm to the red (from 613 nm) with a comparable effect on absorption bands.³³ In low temperature glasses (77°K) both emission and absorption spectra are more structured than in fluid solution. As a consequence, the effect of substituents on band positions can be evaluated more definitely. For example, Figure 5 illustrates the spectra of $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$ and their phenyl substituted analogs. In each case both the MLCT absorption and emission maxima are shifted to the red by phenyl substitution but the effects are less dramatic than in the L_5Mpy-x examples described above. Significant substituent effects are seen on the lifetime and quantum yields for emission in low temperature glasses.²⁹

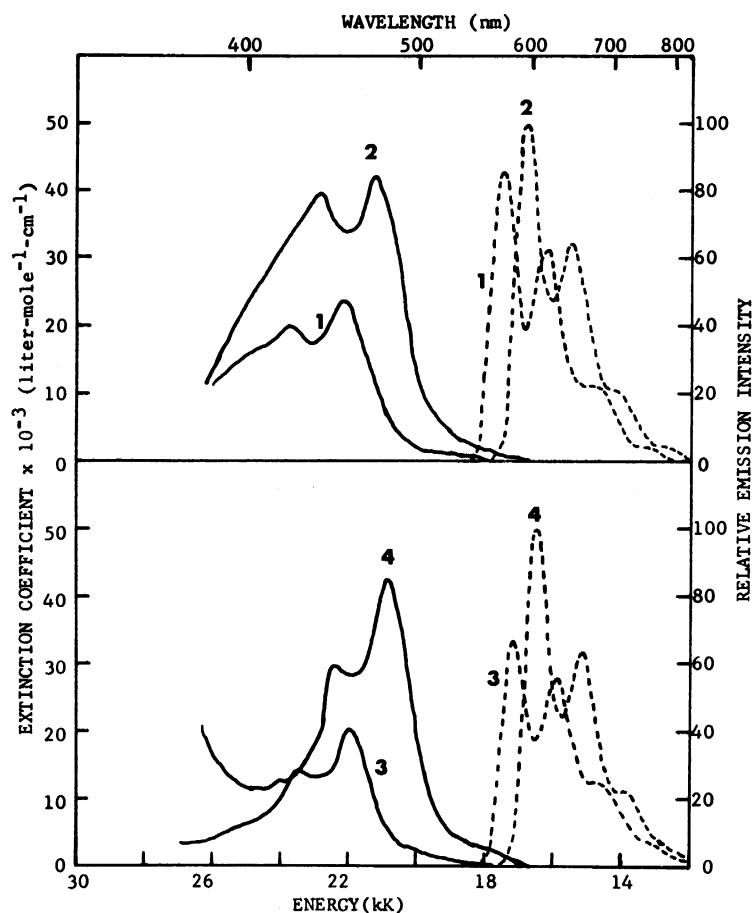


Figure 5. Absorption (solid lines) and emission spectra (dashed lines) of $\text{Ru}(\text{phen})_3^{2+}$ (1), $\text{Ru}(\text{phen-4,7-(C}_6\text{H}_5)_2)_2^{2+}$ (2), $\text{Ru}(\text{bipy})_3^{2+}$ (3), and $\text{Ru}(\text{bipy-4,4'-(C}_6\text{H}_5)_2)_2^{2+}$ (4), in EtOH/MeOH glasses (77°K).

In contrast to the symmetrically substituted tris complexes, e.g., $\text{Ru}(\text{phen-x})_3^{2+}$, more dramatic substituent effects have been reported by Wrighton and co-workers³⁵ for the spectra of $\text{Ru}(\text{phen})_2(\text{phen-4,7-(OH)}_2)^{2+}$ and its deprotonated analog $\text{Ru}(\text{phen})_2(\text{phen-4,7-(O}^-)_2)$. Emission from the 4,7-(OH)₂ species occurs at 635 nm and deprotonation shifts this to 720 nm. Marked changes in the absorption spectra are also seen. It appears, however, that the magnitude of these effects may very much be due to the unsymmetrical nature of the complex. Since the shift on deprotonation is in the opposite direction to that expected for a MLCT transition to the substituted ligand, it was concluded³⁵ that the deprotonated dihydroxyphenanthroline is acting as a π -donor to the Ru(II) thus lowering the energy of MLCT to the other phen ligands.

Emission spectra seen for various Ir(III) complexes containing phen-x or bipy-x derivatives as ligands may be LF, MLCT or π, π^* IL depending on the nature of the substituent x and on the balance of the ligand field. For example, the work of Crosby, Watts, and Carstens^{2a} has established that the luminescence of $\text{Ir}(\text{phen})_2\text{Cl}_2^+$, of $\text{Ir}(\text{phen}-5,6-(\text{CH}_3)_2)_2\text{Cl}_2^+$ and of $\text{Ir}(\text{phen})\text{Cl}_4^-$ in low temperature (77°K) aqueous methanol glass can be assigned as MLCT, IL and LF respectively. Thus, merely the replacement of several phenanthroline hydrogens by methyl groups is enough to change the character of the emitting state from MLCT to IL.³⁶ Since it has been proposed for these types of metal complexes that the luminescent state will be the lowest energy state or one which is in Boltzmann equilibrium with the lowest state,^{27,28} such changes in the character of the lowest state should have important implications with respect to the photochemistries of these systems (*vide infra*).

For Ir(III) complexes with two phen-x or bipy-x ligands coordinated, the low temperature emission is either MLCT or IL. The unsubstituted and phenyl substituted ligands favor MLCT emission while methyl substitution gives IL emission. Each of the complexes displays a reasonably intense absorption at ~ 400 nm which is shifted to the red somewhat by phenyl substitution while smaller blue shifts are seen for methyl substitution. Analogous shifts are also seen in the low temperature emission maxima.

The closeness of the MLCT and IL states in systems of these types leads to unusual kinetics for excited state deactivation when the two organic ligands are different, e.g., phenanthrolines with different sets of substituents. In some cases, e.g., $\text{IrCl}_2(\text{phen})(\text{phen}-4,7-(\text{CH}_3)_2)^+$ the interaction between two states, one IL in character, the other MLCT in character, is sufficiently weak that non-exponential decay curves are seen. For these, the low temperature emission spectra from the two states can be differentiated by time resolved spectroscopy.³⁷

An intriguing controversy has centred on the emission spectral assignments of $\text{Ir}(\text{phen})_2\text{Cl}_2^+$. This species has been reported to emit in ambient temperature, fluid solutions.^{38,39} However, while it is agreed that the low temperature emission is MLCT in character, Watts³⁹ has claimed that the fluid solution emission is from a lowest energy LF state while Ballardini and co-workers have argued first for a MLCT assignment,³⁸ then that the observation is an experimental anomaly resulting from trace impurities.⁴⁰ Watts disagrees with the latter conclusion and reports that even clean samples show both a green charge transfer emission and a red Gaussian emission as expected for a LF transition.⁴¹ If this last conclusion proves to be correct, it will have a major influence on mechanistic thinking with regard to metal complex excited states. For example, this introduces the possibility of significant energy barriers for the internal conversion from an excited state of one particular orbital parentage (d, π^* in this case) to a state having a different orbital parentage (e.g., d, d^*). Thus, emission spectra obtained at low temperatures may sometimes not reflect the nature of lowest excited state, in contrast to the premise stated earlier (*vide supra*).²⁸

III. Photochemistry

Effects of substituents on a photochemical process can result from a number of perturbations. Figure 6 presents a simplistic representation of some

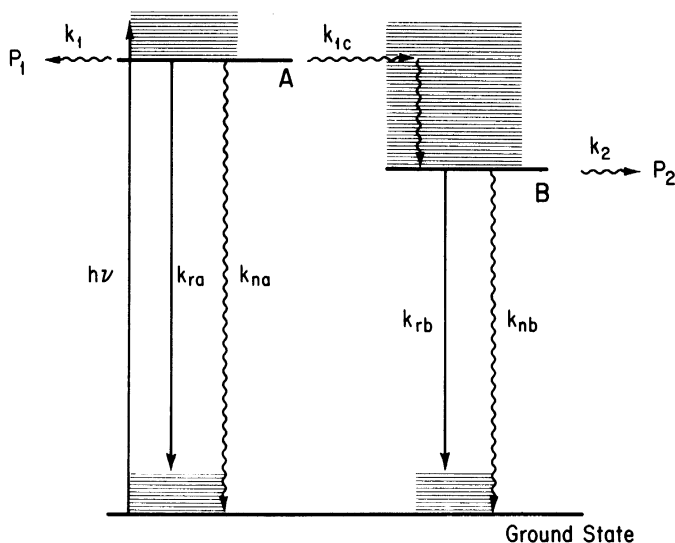


Figure 6. Illustration of possible processes subsequent to excitation into excited state A. The respective rate constants represent the formation of products P_1 (k_1) and P_2 (k_2), nonradiative (k_{na} and k_{nb}) or radiative (k_{ra} and k_{rb}) deactivation to ground state, and internal conversion (k_{ic}).

processes which might occur after excitation into an excited state designated as A. The quantum yield for P_1 formation would be

$$\Phi_1 = \frac{k_1}{k_1 + k_{na} + k_{ra} + k_{ic}} \quad (2)$$

while that for P_2 formation would be

$$\Phi_2 = \Phi_{ic} \frac{k_2}{k_2 + k_{nb} + k_{rb}} \quad (3)$$

where Φ_{ic} is the quantum yield for internal conversion to a different state B:

$$\Phi_{ic} = \frac{k_{ic}}{k_1 + k_{na} + k_{ra} + k_{ic}} \quad (4)$$

Substituents may have kinetic effects, that is, these may perturb any or all of the rate constants indicated in Figure 6. For example, a heavy atom substituent such as iodine may increase the rates of multiplicity forbidden processes owing to increased spin orbit coupling. In addition, if the energies of A and B have

different sensitivities to substituents, it may be possible to "tune" the relative energies in such a manner to reverse their ordering. It is this last substituent effect that may prove to have the most dramatic influence on the quantitative photochemistry.

A. Pyridine complexes

For each of the pyridine complexes for which ligand substituent effects have been explored, the π, π^* IL absorptions are high in energy relative to LF and MLCT absorptions, and photochemical studies have concentrated on these lower energy bands. While other reactions have been seen (*vide infra*) the bulk of the published work has been concerned with photosubstitution reactions.

1. $\text{Rh}(\text{NH}_3)_5(\text{py-x})^{3+}$

For the Rh(III) complexes both the lowest energy absorption bands (Figure 2) and the emitting states are ligand field in character.¹¹ In water, LF excitation (313 nm) gives only photoaquation of the unique ligand (eq. (5)).



Various sensitization studies⁶ point to the lowest energy LF triplet state as the direct precursor to the ligand aquation. Since the pyridines are weaker σ donors than is NH_3 , this state is the ${}^3\text{E}^*$, which qualitatively is derived from the $e(d_{xz}, d_{yz}) \rightarrow a_1(d_{z^2})$ promotion¹¹ (Figure 3). Given the σ^* character of the $a_1(d_{z^2})$ orbital, labilization along the unique axis is expected and this question is treated in several qualitative theories.⁴² The effect of pyridine substituents on photoaquation is summarized in Table 2 where it is notable that the quantum yield Φ_L follows the order $x = 4\text{-CH}_3^- < \text{H}^- < 3\text{-Cl}$, inverse to the orders of

Table 2. Excited state properties of $\text{Rh}(\text{NH}_3)_5\text{py-x}^{3+}$ ^a

<i>x</i>	$\text{pK}_a(\text{py-x})^b$	Φ_L^c (<i>mol einstein</i> ⁻¹)	E_T^d (kK)	τ_m^e (μs)
4-CH ₃ ⁻	6.0	0.091	21.4	18.6
H ⁻	5.3	0.14	21.0	17.1
3-Cl ⁻	2.8	0.34	20.0	13.6

^a Data from Reference 11.

^b pK_a of free ligand in aqueous solution.

^c Quantum yield for eq. (5) in 25°C aqueous solution, 313 nm irradiation.

^d Energy of the thermally equilibrated lowest triplet LF state as determined according to Reference 11.

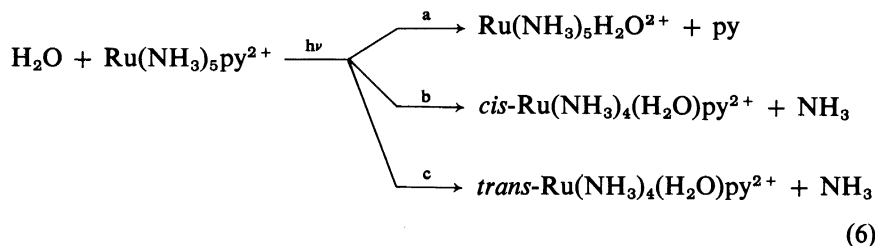
^e Measured lifetime of the ClO_4^- salt at 77°K in MeOH/H₂O (4/1, V/V) glass.

Bronsted basicities and of the triplet energies. Thus it can be argued that the effect of *x* on the excited state properties of $\text{Rh}(\text{NH}_3)_5\text{py-x}^{3+}$ can be correlated

with the σ -donor properties of py-x. The weaker a σ -donor py-x, the greater the distortion of the ${}^3E^g$ state along the unique axis, hence its lower energy and greater reactivity toward ligand substitution.

2. $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$

The spectra of the Ru(II) species are markedly different from their iso-electronic Rh(III) analogs. The prominent difference is the appearance of an intense, visible range, MLCT band in Ru(II) spectra (Figure 4, Table 1). Nonetheless, when aqueous $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ is irradiated into its MLCT band (405 nm), photoaquations are the principal reactions seen (eq. (6)).⁴³⁻⁴⁵



Rationalization of this photoreactivity is based on the excited state diagram shown in Figure 7a. In this scheme initial excitation involves the allowed MLCT transition but this is followed by rapid internal conversion to the lowest energy

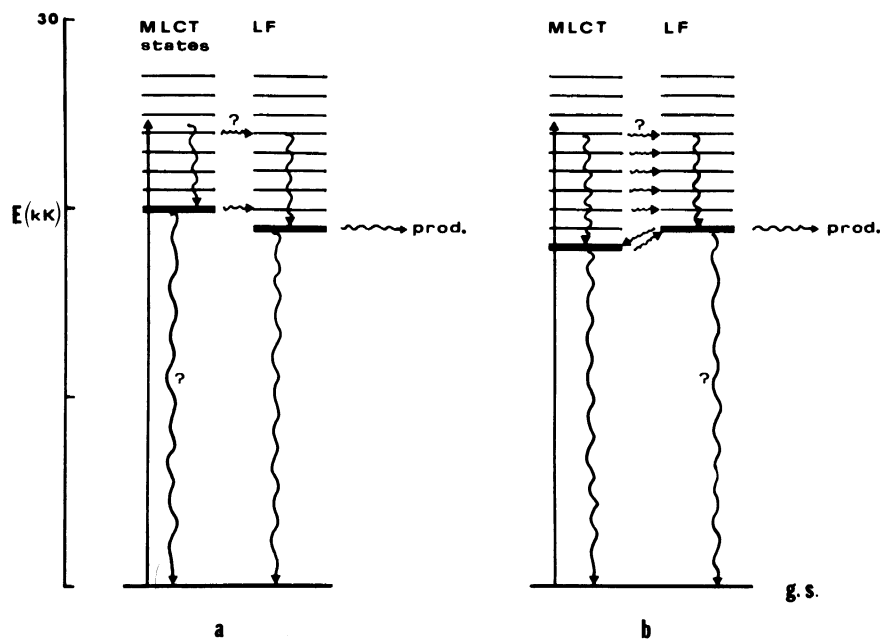


Figure 7. Excited state diagrams for $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$ complexes.

(a) photosubstitution reactive complexes.

(b) photosubstitution unreactive complexes.

excited state, the lowest LF state. From this state nonradiative deactivation to the ground state or ligand aquation occur (eq. (6)). The rationales behind this proposition are:

1) Given that Ru(III) amine complexes, e.g., $\text{Ru}(\text{NH}_3)_5\text{py}^{3+}$ are not substitution labile, the MLCT state would not be expected to be labile, especially toward NH_3 aquation.

2) Saturated amine complexes of Ru(II) display LF bands at wavelengths comparable to $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ λ_{max} , e.g., the lowest energy LF λ_{max} (${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$) of aqueous $\text{Ru}(\text{NH}_3)_6^{2+}$ occurs at 390 nm ($\epsilon = 39 \text{ M}^{-1} \text{ cm}^{-1}$). Direct excitation of this LF band leads principally to the aquation product $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ with $\Phi_{\text{NH}_3} = 0.3 \text{ mol einstein}^{-1}$.⁴⁶ Quantum yields for photoaquation of $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ are essentially independent of irradiation wavelength (λ_{irr}) over the range 436–254 nm, suggesting the interconversion of initially populated states to a common state.

The sensitivity of the MLCT absorption band and the relative insensitivity of the LF bands to ligand substituents (Section II) suggested the photochemical tuning experiments as a test of the model indicated in Figure 7a for the photochemistry of $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$. Systematic variation of x should give cases (i.e., if x is strongly electron withdrawing) for which the lowest excited state is a MLCT state. In such cases the excited state model would be that illustrated in

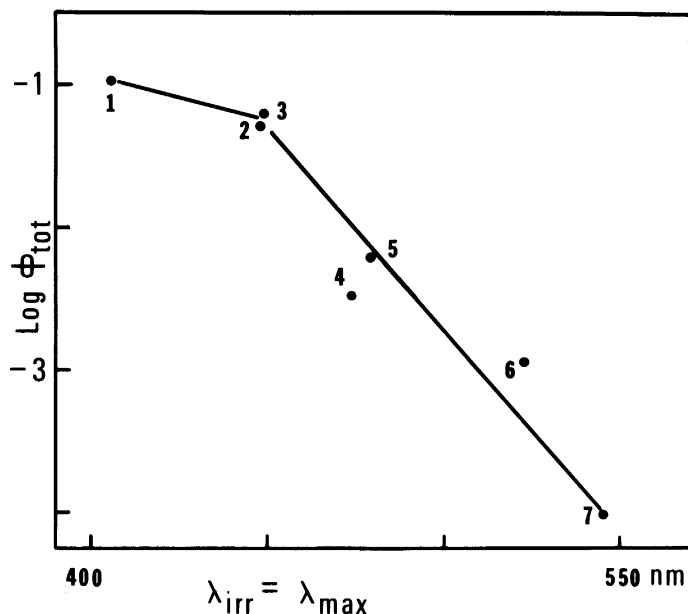


Figure 8. Φ_{TOT} for the photoaquation reactions of $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ as a function of λ_{max} (MLCT) ($\lambda_{\text{irr}} \cong \lambda_{\text{max}}$ (MLCT)). L = pyridine (1), 4-phenylpyridine (2), 3,5-dichloropyridine (3), pyrazine (4), isonicotinamide (5), 4-acetylpyridine (6), 4-formylpyridine (7).

Figure 7b and markedly different photochemical reactivity would be expected if relatively efficient interconversion from initially formed excited states to the lowest excited state occurs.

The success of the photochemical tuning experiment^{3,24} is illustrated in Figure 8 where $\log \Phi_{\text{TOT}} (= \Phi_{\text{L}} + \Phi_{\text{NH}_3})$ is plotted *vs* λ_{max} for λ_{irr} equal to the λ_{max} (MLCT) of the various aqueous $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$ complexes. Notably the complexes with shorter wavelength MLCT bands are relatively photoactive toward substitution with $\Phi_{\text{TOT}} \sim 0.1 \text{ mol einstein}^{-1}$. However, all complexes with λ_{max} (MLCT) longer than $\sim 460 \text{ nm}$ are significantly less active when irradiated at λ_{max} (MLCT) displaying Φ_{TOT} values as low as three orders of magnitude smaller. This pattern is consistent with the excited state models of Figure 7 and suggests that the crossover point between complexes with a LF state as the lowest energy state and those with a lowest energy MLCT state comes when λ_{max} (MLCT) is $\sim 460 \text{ nm}$.

An important consideration is the approximate energy of the lowest LF state which should be relatively independent of the pyridine substituent. Several different methods have been employed to estimate this value to be about 16–17 kK.⁴⁷

Complexes displaying relatively large Φ_{TOT} values can be termed “reactive” and according to the above model have a LF state as the lowest energy state while those displaying small Φ_{TOT} values can be termed “unreactive” and should have a lowest energy MLCT state. Notably, the terms “reactive” and “unreactive” apply here only to photosubstitution lability. Figure 9 offers another

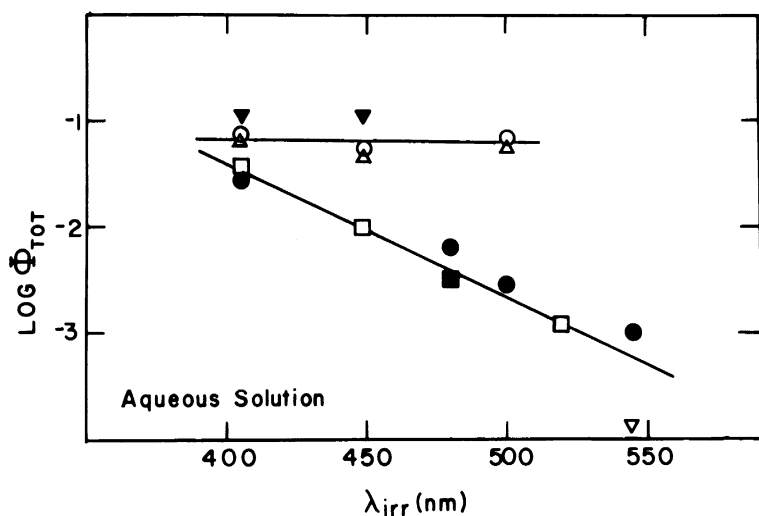


Figure 9. Wavelength dependence of $\log \Phi_{\text{TOT}}$ for the photolysis of $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ in aqueous solution. Symbols for various L's: ▼, pyridine; ○, 3,5-dichloropyridine; △, 4-phenylpyridine; ▽, methylpyrazinium; ●, *iso*-nicotinamide; ■, pyrazine; □, 4-acetylpyridine. Lines are drawn for illustrative purposes only.

way of differentiating these types. The "reactive" complexes such as those of pyridine (λ_{\max} 407 nm), 3,5-dichloropyridine (447 nm) and 4-phenyl pyridine (446 nm) show little Φ_{TOT} dependence on λ_{irr} , consistent with a mechanism where most excitation leads eventually to population of a substitution reactive, lowest energy LF state. In contrast, Φ_{TOT} values for the "unreactive" complexes (e.g., that of isonicotinamide (479 nm)) are very λ_{irr} dependent, a fact which suggests that after MLCT excitation there is some crossover into the manifold of LF* states in competition with internal conversion to the lowest energy MLCT* state.

The $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$ complexes display another remarkable example of excited state tuning, namely that by solvent effects. Although LF bands generally are insensitive to changes in the solvent,²⁶ MLCT absorption bands are markedly solvent dependent (*vide supra*). For example, λ_{\max} (MLCT) of the pyridine complex in DMSO appears ~ 40 nm to the red of its value in water.⁹ Thus, if a complex is borderline reactive in water (Figure 7a), dissolving it in DMSO may reverse the order of its lowest energy states to give a situation conforming to Figure 7b. Figure 10 demonstrates this effect. Although the patterns of behavior

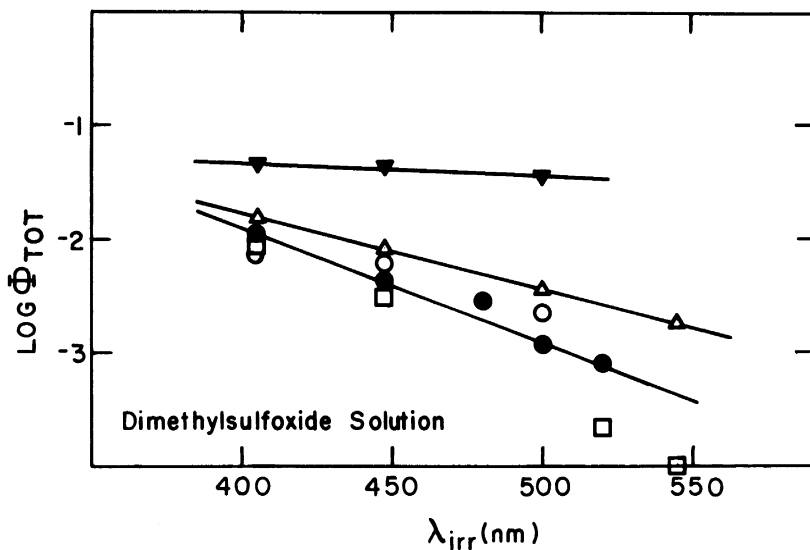


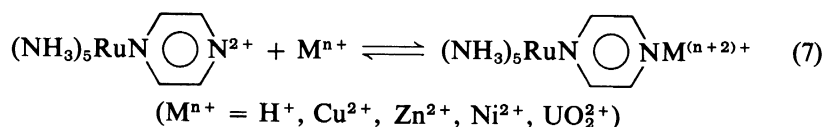
Figure 10. Wavelength dependence of $\log \Phi(\text{spec})$ for the photolysis of $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ in DMSO solution. Symbols as in Figure 9.

for the pyridine (λ_{\max} 407 nm in H_2O , 447 nm in DMSO) and isonicotinamide (479 nm in H_2O , 511 nm in DMSO) complexes remain consistent (reactive and unreactive respectively) in both solvents, the 4-phenylpyridine (446 nm in H_2O , 497 nm in DMSO) and 3,5-dichloropyridine (447 nm in H_2O , 491 nm in DMSO) complexes undergo behavioral changes. In water, both behave much like the reactive pyridine complex (relatively large, λ_{irr} independent quantum yields); in

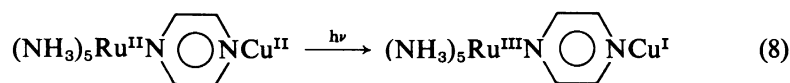
DMSO, their patterns are more similar to that of the unreactive isonicotinamide complex (relatively small, λ_{irr} dependent quantum yields). Behavioral changes explainable by this model have also been seen for the red shifting DMF solvent and for blue shifting acetonitrile solvent.²⁴ Thus, for those complexes where the lowest MLCT and LF states are reasonably close in energy, it appears possible to reverse the order of the lowest states and to change the general reactivity patterns by solvent variation alone.

Although the MLCT states of $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$ are unlikely to be active toward ligand substitution, these may be activated toward other processes, especially redox reactions. The formal representation of a MLCT state as $[(\text{NH}_3)_5(\text{Ru}^{\text{III}})(\text{L}^-)]^{2+}$ suggests reactivity such as electron transfer *from* another substrate to the oxidized metal center or *to* another substrate from the radical ion ligand. Other suggested processes would be structural rearrangement of L^- or electrophilic substitution on L^- .^{45,48} Attempts to detect bimolecular electron transfer reactions of excited $\text{Ru}(\text{NH}_3)_5\text{py-x}^{2+}$ have been unsuccessful presumably because the lifetime is too short to be quenched significantly by a second order process.⁴⁷ In contrast, bimolecular redox reactions for the long lived MLCT states of $\text{Ru}(\text{bipy})_3^{2+}$ and its derivatives are well characterized (*vide infra*).³³

The pyrazine complex, however, provides a different pathway for electron transfer. The organic ligand has a second coordination site which is a good base for hydrogen ion⁹ and for other metal cations⁴⁹ (eq. (7)).



Under continuous photolysis the pyrazine complex and its protonated analog are photosubstitution unreactive,²⁴ and flash photolysis of these and of the Zn^{2+} adduct (eq. (7)) give no evidence of the formation of transient species with lifetimes longer than $40 \mu\text{s}$. However, when M^{n+} is Cu^{2+} or UO_2^{2+} , transient bleaching is observed,⁵⁰ and the extent of bleaching is directly proportional to the percent of the Ru(II) complex present as the binuclear adduct. Thus, the bleaching pathway is interpreted as representing the electron transfer:



The system undergoes relaxation back to starting material, therefore is an example of *electron transfer photochromism*.⁵⁰

As will be apparent in the following sections, the photosubstitution behavior of the Ru(II) pentaammine complexes serves as a model for the reactivities seen for other pyridine complexes (Fe(II), Re(I), W(0)) where the lowest LF and

MLCT states lie close in energy. For each of these cases systematic application of ligand substituents demonstrates separation of the M-py-x complexes into two classes of photosubstitution behavior: i.e., those showing the photoreactivities expected for LF excited states or for a MLCT state. These patterns are explained by the model in which the predominant (but not exclusive) pathway for excited state deactivation involves internal conversion from states formed by initial excitation to the lowest excited state.

3. $W(CO)_5py-x$

The photochemistry of the tungsten pentacarbonyl pyridine complexes parallels qualitatively that of the Ru(II) pentaammine analogs. However, here the "LF" absorption bands are sufficiently strong to be prominent in the visible spectra and the low temperature (77°K) emission spectra and lifetimes can be routinely measured.¹³ Figure 11 illustrates the absorption spectra of the $W(CO)_5$

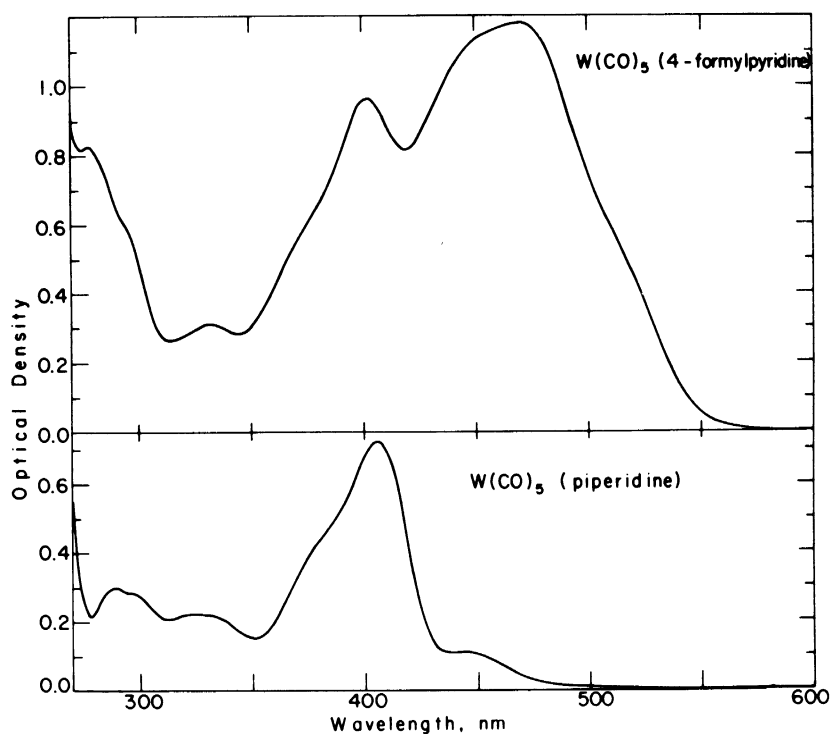
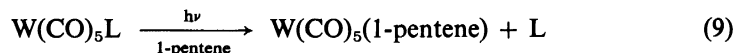


Figure 11. Comparison of the absorption spectra of $W(CO)_5$ (piperidine) and of $W(CO)_5$ (pyridine-4-CHO) at 298°K in *isooctane*. Reproduced with permission from the American Chemical Society.¹³

complexes of 4-formylpyridine and piperidine (pip) in *isooctane*. In the $W(CO)_5pip$ spectrum, the absorption maxima at 443 nm ($\epsilon = 560 M^{-1} cm^{-1}$) and 407 nm (3960) have been assigned to the LF transitions $^1A_1 \rightarrow ^3E$ and $^1A_1 \rightarrow ^1E$ respectively.⁵¹ The position of the $^1A_1 \rightarrow ^1E_1$ band is essentially the same

for the 4-formylpyridine complex; however, this species also displays an intense MLCT absorption with a λ_{\max} at 470 nm ($\epsilon = 6470$). As noted in Section II the MLCT band is markedly sensitive to substituents and in some cases the MLCT band occurs at an energy higher than the two LF bands (Table 1).

The photochemistry of these complexes in *isooctane/n-pentane* solvents is substitutional in nature (eq. (9)).



Replacement of the unique ligand predominates with only a small contribution from CO substitution ($\Phi_{\text{CO}} \leq 0.01$ mol einstein⁻¹ when L is py-x). For the piperidine complex Φ_{L} (0.5 mol einstein⁻¹) is essentially λ_{irr} independent over the range 366–436 nm while Φ_{CO} decreases from 0.03 to 0.006 mol einstein⁻¹ over the same range.^{51b} Although the experimental λ_{irr} range is narrow, these data imply that population of the state reactive toward piperidine labilization occurs with high efficiency and that CO labilization comes from higher energy states.

Quantum yields for eq. (9) and relevant spectroscopic data for the $\text{W(CO)}_5\text{py-x}$ complexes are summarized in Table 3. Both the spectral and photochemical data indicate that these complexes fall into two distinct classes:

Table 3. Photochemical quantum yields and spectral data for representative $\text{W(CO)}_5\text{L}$ complexes^a

L	λ_{\max} (CT) ^b nm	Φ^c		ν_{\max}^d kK	τ^e μs
		436 nm ^f	514 nm ^f		
Piperidine	407, ^g 443 sh ^h	0.58		18.3	0.81
py-4-CH ₃	351	0.55		19.6	1.1
py	355	0.62		19.1	0.86
py-3-Br	399 ⁱ	0.66		18.9	1.00
py-3-COC ₆ H ₅	400 ⁱ	0.73		18.5	1.25
py-4-COCH ₃	440	0.15	0.02	17.0	38.3
py-4-CN	455	0.12	0.02	16.6	33.0
py-4-CHO	470	0.05	0.002	15.2	15.0

^a Data from Reference 13.

^b λ_{\max} (in nm) of the MLCT absorption band at 298° in *isooctane*, except where noted.

^c Quantum yield in mol einstein⁻¹ for eq. (9) in 2:1 *isooctane/pentane*.

^d Frequency of emission maxima in 77° EPA glass.

^e Emission lifetimes in 77° EPA glass.

^f λ_{irr} .

^g "Singlet" LF absorption.

^h "Triplet" LF absorption.

ⁱ Overlapping LF and CT absorption.

1) those with lowest energy LF absorption bands, emission lifetimes close to 1 μsec and high Φ_{L} values (0.5–0.8 mol einstein⁻¹); and

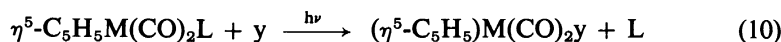
2) those with lowest energy MLCT absorptions, emission lifetimes in the range 15–40 μsec and much smaller, λ_{irr} dependent Φ_{L} values.

Since the properties of the first group are closely analogous to those of the piperidine complex it was concluded that these complexes have lowest energy LF states and the latter have lowest energy MLCT states.¹³ These are respectively analogous to the "reactive" and "unreactive" categories of the Ru(II) complexes described above, and their photochemical and photophysical behaviors can be explained by simple excited state models analogous to Figure 7.

The failure to see significant CO photolabilization for any of these complexes has an important connotation regarding the reactivity of the MLCT excited states. The MLCT state involves transference of electron density from the d_{π} orbitals of the metal. Given the importance of d_{π} - p_{π} back bonding to the metal-CO bonding, one might expect the carbonyl group to be more labile in the MLCT state than in the ground state. Such an explanation has been invoked in other cases,⁵² but this effect is apparently insufficient to give significant lability in the present example.

4. $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{py-x})$ (M = Re or Mn)

The electronic spectra of the $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{py-x})$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{py-x})$ derivatives display MLCT absorptions in the visible range which are markedly sensitive to the nature of x and to the solvent medium.²² Photolysis of these complexes in *isooctane* solution and in the presence of various trapping agents leads to ligand substitution:



where M = Re or Mn and y is a nucleophile such as 1-pentene, piperidine or a substituted pyridine. Quantum yields were essentially independent of the identity of the trapping agents but were quite dependent on the central metal atom and substituent -x. Notably, the manganese complexes are quite photoactive regardless of x, including those substituents which lead to very long wavelength absorptions (Table 4). Among the rhenium analogs, high photoactivity is seen for the NH_3 complex and those py-x complexes with the higher energy MLCT absorptions. In contrast, Φ_L is very small when x is strongly electron withdrawing. The rhenium photochemistry is qualitatively consistent with that of the Ru(II) and W(0) complexes discussed above and excited state models of the type illustrated in Figure 7 can be invoked to rationalize this behavior. Again, those systems which are found photoactive are considered to have a lowest energy LF state and the photoinactive systems to have a lowest MLCT state (Figure 7b). The high reactivity of the Mn(I) complexes regardless of the nature of x was attributed²² to these systems having much lower energy LF states and the excited state order described in Figure 7a.

5. $\text{Fe}(\text{CN})_5\text{py-x}^{3-}$

Several authors^{20,21,53} have pointed out the strong similarities between the bonding and spectral behavior of the pentacyanoferrate(II) systems $\text{Fe}(\text{CN})_5\text{L}^{3-}$ and those of the pentaammineruthenium(II) analogs $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$. The similarities are evident in comparing the MLCT spectra of the Ru(II) and Fe(II)

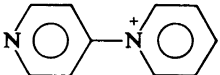
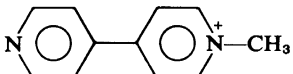
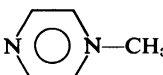
Table 4. Representative photosubstitution quantum yields for $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{L}^a$

L	$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}$		$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{L}$	
	λ_{max} (MLCT) nm	Φ_{L}^b mol einstein ⁻¹	λ_{max} (MLCT) nm	Φ_{L}^b mol einstein ⁻¹
NH ₃	—	—	320 ^c	0.34 ^d
piperidine	455, 380 ^e	0.16	—	—
py-4-Me	—	—	430, 380	0.30
py	495, 412	0.37 ^e	445, 393	0.11
py-3-Br	—	—	475, 415	0.013
py-3,5-Cl ₂	555, 470	0.40	505, 435	0.005
py-4-COCH ₃	640, 525	0.25 ^f	555, 480	< 10 ⁻⁴² ^g
py-4-CHO	670, 555	0.25 ^h	—	—

^a Data from Reference 22.^b Quantum yields for eq. (10) in *isooctane* solution, 25°C, 0.25 M y, where y = 1-pentene except where noted and where $\lambda_{\text{irr}} = 436$ nm except where noted.^c LF band.^d y = py; $\lambda_{\text{irr}} = 313$ nm.^e $\lambda_{\text{irr}} = 405$ nm.^f $\lambda_{\text{irr}} = 550$ nm.^g y = py.^h $\lambda_{\text{irr}} = 633$ nm.

complexes in Table 1 and additional strong analogies are seen with the pentacarbonyltungsten(0) species $\text{W}(\text{CO})_5\text{L}$. Thus, it is likely that the similarities between the properties of these complexes are the result of analogous symmetries (C_{4v}) and electronic configurations (low spin d^6) and a fortuitous match of ligand field strengths and optical electronegativities.

Table 5. Quantum yields for photosubstitution reactions of $\text{Fe}(\text{CN})_5\text{L}^{3-}$ in aqueous solution^a

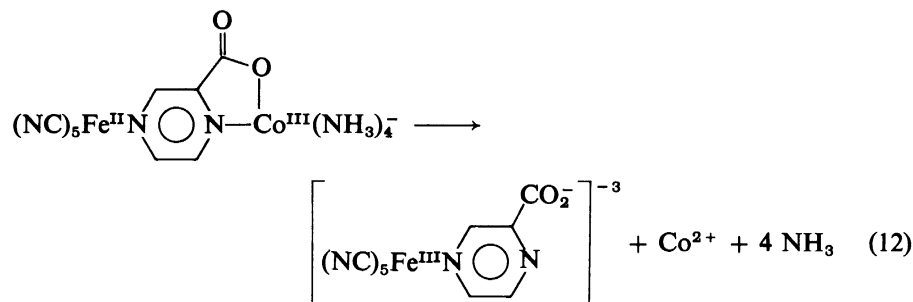
L	λ_{max} (CT) nm	λ_{irr} nm	Φ_{L}^b mol einstein ⁻¹
pyridine	362	365	0.23
py-4-CONH ₂	435	436	0.41
pyrazine	452	365	0.15
		436	0.39
py-4-COCH ₃	478	436	0.19
	483	436	0.04
			
	520	546	0.02
			
	660	365	0.01
		436	0.02
		577	0.003

^a Data from Reference 21.^b Quantum yields for eq. (11) in 250° aqueous solution, y = py except for L = py in which case y = H₂O.

Photolysis of aqueous $\text{Fe}(\text{CN})_5\text{py-x}^{3-}$ leads to photolabilization of the unique ligand:



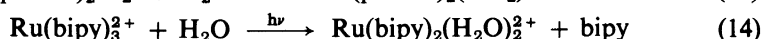
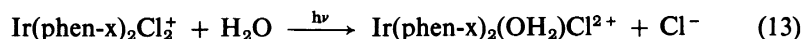
where y is a trapping agent such as another pyridine. Quantum yields are summarized in Table 5. The pattern is consistent with those seen for the Ru(II), W(0) and Re(I) systems. This similarity includes the λ_{irr} dependent Φ_{L} values for the "unreactive" methyl pyrazinium complex. Again a model such as Figure 7 was offered in explanation.²¹ Notably, MLCT excitation of a pyrazine bridged binuclear complex of $\text{Fe}(\text{CN})_5^{3-}$ leads to a photoredox reaction⁵⁴ (eq. 12)) in



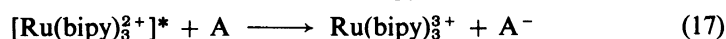
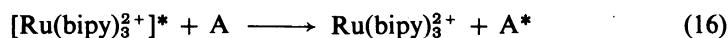
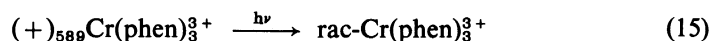
analogy to the photoredox behavior seen in eq. (7).⁵⁰

B. Polypyridyl and phenanthroline complexes

As was noted in Section II, substituent effects on polypyridyl and phenanthroline complexes have been the subject of considerable spectroscopic interest. Photochemical studies on these complexes have been more limited. However, the fact that these systems are often luminescent in fluid solution ensures that this will continue to be an active area of photochemical interest. A full gamut of excited state chemical processes have been noted for these complexes. Ligand photosubstitution has been reported both for halide ligands³⁸ (eq. (13)) and for bipyridines⁵⁵ (eq. (14)).



Racemization of optically active tris complexes,⁵⁶ energy transfer,^{6,57} and electron transfer^{6,57} to and from other substrates (A) have all been reported (eqs. (15–17)).



Thus, given the scope of photoreactions possible and the demonstrated effects of substituents on the spectral properties, the opportunities here for substituent tuning of photochemical properties appear exceedingly rich.

1. $\text{Ir}(\text{phen-x})_2\text{Cl}_2^+$

The nature of the lowest excited states of $\text{Ir}(\text{phen})_2\text{Cl}_2^+$ has been the subject of some controversy. Earlier work by Crosby and co-workers^{2a} assigned the emission in low temperature glasses as MLCT and according to the postulate by Crosby,^{2b} the emitting state is considered to be the lowest energy state or one in Boltzmann equilibrium with the lowest state. There is general agreement³⁸⁻⁴¹ that the low temperature emission is from a MLCT state but there is some question as to whether this state is indeed the lowest energy state or whether a LF state occurs below this.³⁹ Methyl substitution changes the excited states sufficiently that the low temperature emission from $\text{Ir}(\text{phen-5,6-(CH}_3)_2)\cdot\text{Cl}_2^+$ is assigned as $\pi,\pi^*\text{IL}$,²⁶ although there again is controversy as to whether a LF state occurs at a lower energy.³⁸⁻⁴¹

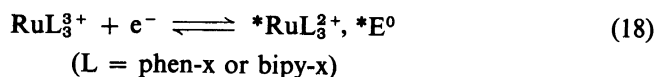
Continuous photolysis of $\text{Ir}(\text{phen})_2\text{Cl}_2$ or $\text{Ir}(\text{phen-5,6-(CH}_3)_2)\text{Cl}_2^+$ in aqueous solution gives only chloride photoaquation (eq. (13)). In both cases the quantum yields ($\Phi_{\text{Cl}} = 0.05$ and $0.09 \text{ mol einstein}^{-1}$ respectively at 25°) are independent of λ_{irr} over the range 254–405 nm, suggesting that initial excitation is followed by efficient internal conversion to a common state precursor to the substitution reaction. The photoreactivity of both complexes is considerably suppressed in dimethylformamide solution.

Ballardini *et al.*³⁸ have argued that a LF triplet state must be the reacting state in each of these systems, but have maintained⁴⁰ that the LF state is reached by thermal back population from the lowest energy MLCT or $\pi,\pi^*\text{IL}$ states respectively. In this context, the solvent dependence of Φ_{Cl} might be argued to result from a wider gap between the reactive state and the lowest energy state induced by the organic solvent. This argument is consistent with the MLCT assignment for the lowest state of $\text{Ir}(\text{phen})_2\text{Cl}_2^+$ since MLCT states are markedly solvent dependent. However, since neither LF nor IL states are particularly affected by the solvent media, the argument is not applicable to the virtually identical solvent behavior of Φ_{Cl} for $\text{Ir}(\text{phen-5,6-(CH}_3)_2)\text{Cl}_2^+$. There are numerous possible interpretations of the photochemical solvent effect, but one consistent with the behavior of both systems would be direct involvement of solvent in the rate determining reaction pathway from the reactive LF state.

Aside from the controversial emission studies,³⁸⁻⁴¹ the evidence that the lowest states of $\text{Ir}(\text{phen-x})_2\text{Cl}_2^+$ are other than LF in character is not compelling. The quantum yields compare respectably with those for chloride aquation from aqueous $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$ ($0.15 \text{ mol einstein}^{-1}$)⁵⁸ and the temperature effects ($E_a \simeq 4 \text{ kcal mol}^{-1}$) are similar to those seen for photoaquation from systems clearly having a lowest energy LF state.^{6,59} Nonetheless, there appears to be no doubt that among the lowest energy excited states of the $\text{Ir}(\text{phen-x})_2\text{Cl}_2^+$ complexes three types, LF, MLCT and IL, are energetically close. Thus, these systems should be well suited for excited state tuning experiments by phenanthroline substituents.

2. Ru(bipy-x)₃²⁺ and Ru(phen-x)₃²⁺

For these systems, substituent effects have been exploited by Sutin, Creutz, and co-workers to evaluate bimolecular quenching mechanisms of the MLCT excited states.³³ From emission and electrochemical data, these workers calculated reduction potentials *E⁰ for the reduction of RuL₃³⁺ to the Ru(II) excited state [RuL₃²⁺]* (eq. (18)).



These potentials were calculated using *E⁰ = -0.84 V for the tris(2,2'-bipyridine) complex⁶⁰ and adding the corresponding *ΔG⁰ to the sum of the ΔG⁰ values for reactions (19) and (20). The ΔG⁰ value for eq. (19) was assumed equal



to the differences in the emission maxima of *Ru(bipy)₃²⁺ and *RuL₃²⁺, an assumption requiring identical Franck-Condon contributions and entropy changes in the two emission processes. The *E⁰ values thus calculated are quite sensitive to x, varying from -1.11 V for L = phen-3,4,7,8-(CH₃)₄ to -0.67 V for L = phen-5-NO₂ (Table 6). However, the bulk of this effect can be attributed

Table 6. Comparison of reduction potentials *E⁰ for RuL₃³⁺/**RuL₃²⁺* to rate constants (k_q) for the quenching of *RuL₃²⁺ by various quenchers (Q)^a in aqueous solution

L	*E ⁰ (V)	k _q for various Q		
		Cr(III) (10 ⁷ l mol ⁻¹ s ⁻¹)	Fe(III) (10 ⁹ l mol ⁻¹ s ⁻¹)	Eu(III) (10 ⁶ l mol ⁻¹ s ⁻¹)
bipy-4,4'-(CH ₃) ₂	-0.94	1.0	2.9	~5
bipy-4,4'-(C ₆ H ₅) ₂	-0.85			
bipy	-0.84	1.2	2.7	≤0.8
phen-3,4,7,8-(CH ₃) ₄	-1.11		3.4	
phen-3,5,6,8-(CH ₃) ₄	-1.04		2.5	
phen-4,7-(CH ₃) ₂	-1.01	1.3	3.0	21
phen-5,6-(CH ₃) ₂	-0.93	1.4	2.6	7.5
phen-4,7-(C ₆ H ₅) ₂	-0.90			
phen-5-CH ₃	-0.90	1.3	2.6	4.2
phen-5-C ₆ H ₅	-0.87		2.7	
phen	-0.87	1.4	2.8	~1
phen-5-Cl	-0.77	1.2	2.3	≤0.5
phen-5-Br	-0.76	1.3	2.3	≤0.5
phen-5-NO ₂	-0.67			

^a Data from Reference 33.

to differences in the ground state potentials for the Ru(bipy)₃²⁺/RuL₃³⁺ couple (eq. (20)) since the emission energies from *RuL₃²⁺ (and hence ΔG⁰ for eq. (19)) are relatively insensitive to ligand substituents.

A related way to calculate ${}^*E^0$ would be from the relationship ${}^*E^0 = E^0 - E(h\nu)$. The value $E(h\nu)$ is the approximate free energy difference (in volts) between the ground and excited states calculated from the average of singlet-triplet absorption and emission energies with entropy changes other than due to the multiplicity change ($R \ln 3$) neglected.^{60b} Thus, if $E(h\nu)$ is essentially independent of ligand substituents, then ${}^*E^0$ would have a simple linear dependence on ground state reduction potential E^0 (eq. (21)) in the same medium.

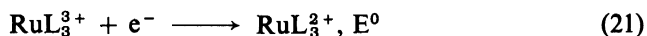
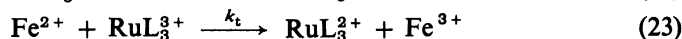
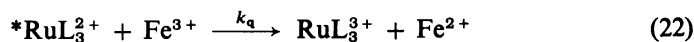


Table 6 compares the ${}^*E^0$ values to the rate constants for bimolecular quenching of the various ${}^*\text{RuL}_3^{2+}$ by Cr^{3+} , Fe^{3+} , and Eu^{3+} . Previously, flash photolysis studies⁶⁰ demonstrated that quenching of ${}^*\text{Ru}(\text{bipy})_3^{2+}$ by Fe^{3+} can be interpreted in terms of an electron transfer scheme such as eqs. (22) and (23)



(where k_q is the bimolecular rate constant for excited state quenching and k_t is the bimolecular rate constant for thermal relaxation to the initial reaction components). Despite the electron transfer nature of the quenching by Fe^{3+} , the magnitude of k_q is only marginally dependent on the ligand substituents. Presumably this weak correlation with the ${}^*E^0$ values is the consequence of k_q approaching the diffusion controlled limit. In contrast, the back electron transfer rate constants k_t are markedly dependent on x and correlate with the differences in the ground state reduction potentials, E^0 . Those Ru(III) ions with the more positive potentials react with Fe^{2+} more rapidly. The photostationary ratios $[\text{RuL}_3^{3+}]/[\text{RuL}_3^{2+}]$ depend upon the relative rates of reactions 22 and 23. Thus the marked sensitivity of k_t to ligand substituents and comparative insensitivity of k_q combine to make these ratios dependent on the nature of the substituent x . Under conditions of identical irradiation intensity and initial Fe^{3+} concentration, $\text{RuL}_3^{3+}/\text{RuL}_3^{2+}$ photostationary ratios are larger for electron donating substituents than for electron withdrawing substituents.

Unlike the k_q value for Fe^{3+} , the rate constants for Eu(III) quenching of ${}^*\text{RuL}_3^{2+}$ vary by several orders of magnitude as L changes. The k_q values follow the ${}^*E^0$ values in a trend indicative of electron transfer quenching, and flash photolysis experiments confirm the formation of Eu^{2+} as a transient intermediate. In contrast, quenching by Cr^{3+} shows virtually no sensitivity to the nature of L despite the fact that these k_q values are considerably slower than the diffusion controlled limit. Given the relative insensitivity of the emission maxima to L, an energy transfer pathway (eq. (16)) is suggested. Energy transfer from ${}^*\text{Ru}(\text{bipy})_3^{2+}$ to Cr(III) complexes has been reported previously.^{57,61}

The above discussion leads to the conclusion that, especially in those cases where the quenching rate constants are much smaller than the diffusion controlled limit, ligand substituent effects on k_q may differentiate electron transfer

and energy transfer mechanisms. In this context it was noted³³ that the rate constants for quenching of $*\text{RuL}_3^{2+}$ by O_2 , although close to the diffusion limit, do show a weak dependence on $*E^0$. This observation led to the speculation³³ that the quenching which leads to the formation of singlet oxygen⁶² may proceed by an initial electron transfer path to give Ru(III) plus the superoxide ion O_2^- , followed by a thermal reaction to regenerate Ru(II) and to give singlet oxygen.

C. Summary

A consistent theme of this review is that relatively subtle modifications of ligand properties may have dramatic effects on both photochemical and photophysical properties of metal complexes. Such substituent effects are most likely to be major when a system has two or more excited states of different orbital parentages closely grouped energetically, especially if these states are the lowest energy excited states of the complex. The different sensitivities of the various excited state energies to the ligand substituents then allow the *tuning* of photochemical and photophysical behavior to give desired properties. Since ground and excited state redox potentials are also functions of ligand substituents, it is clear that not only the orbital parentage of the lowest state but also the very reactivities of these states can be tuned in this manner. The principal focus of the quantitative studies of ligand substituent effects on metal complex photochemistry has been the pyridyl, bipyridyl, and phenanthroline complexes described in this review. However, it is clear that other organometallic and metal organic complexes have vast potential for the exploration of these types of studies.

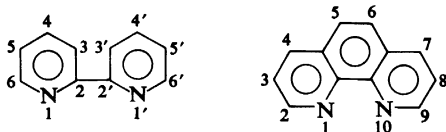
IV. Acknowledgment

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