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Effect of Nitro and Triethylphosphonium Substituents on the Photophysical and Photoredox Properties of Tris(2,2′-bipyridine)ruthenium(II) Complexes

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The mono- and disubstituted nitro and triethylphosphonium derivatives of 2,2′-bipyridine have been synthesized to probe by flash photolysis techniques possible chemical or radical mechanisms in the photoinduced reactions of the corresponding Ru(II) and Co(III) complexes. The monosubstituted derivatives form the tris complex whereas the disubstituted bipyridines, because of a severe reduction in basicity, form only the dihalobis(*X,X′*-bipyridine) metal complex. Cyclic voltammograms show that both substituents cause similar increases in the potential for oxidation of the corresponding Ru(II) complex, but the absorption and emission spectra of substituted Ru(II) complexes differ. The tris(4-(triethylphosphonio)-2,2′-bipyridine)ruthenium(II) has an emission maximum at 640 nm and an excited state lifetime of 760 ± 40 ns. No emission could be detected from either room-temperature or frozen (77 K) solutions of tris(4-nitro-2,2′-bipyridine)ruthenium(II). Resonance Raman spectra of the nitro-substituted Ru(II) complex show that a considerable portion of the charge transferred in the MLCT transition resides on the nitro substituent which is strongly coupled to the solvent medium. The lack of emission and the differences in the thermal and photochemical reactions—nucleophilic displacement of the NO_2 group—of 4-nitro-2,2′-bipyridine and the corresponding Ru(II) complex are attributed to this relaxation pathway. Quenching of $^*Ru(bpy)_3^{2+}$ and $^*Ru(Et_3Pbpy)_3^{5+}$ by $Et_3P(bpy)^+$ and $NO_2(bpy)$ occurs by a photoredox mechanism, but no indication of a chemical or radical mechanism is found following flash photolysis of $Ru(bpy)_3^{2+}$ in the presence of the Co(III) complexes of these ligands.

Introduction

Luminescence quenching and flash photolysis experiments have established the photoredox chemistry of the luminescent charge-transfer state of $Ru(bpy)_3^{2+}$, designated $^*Ru(bpy)_3^{2+}$.[2] In aqueous solution, the oxidation and reduction potentials, 0.84[2] and 0.77 V,[3] respectively, are sufficient to reduce or oxidize a wide variety of substrates and have led to a use of the complex as a probe of rapid electron-transfer reactions. Flash photolysis experiments in this and other laboratories, for example, have utilized oxidative quenching of $^*Ru(bpy)_3^{2+}$ by pyridine- and (polypyridine)cobalt(III) complexes to study redox reactions between these reagents.[2a,4] Because of the exothermicity of the redox quenching by these Co(III) complexes[2a] and/or the similarity of the ligands to methylviologen,[4] which forms a stable radical anion, evidence for a chemical or radical mechanism was sought. The results of these experiments—no transient absorbance attributable to the intermediate was detected—are, however, inconclusive.

Although intermediacy of a coordinated ligand radical anion is invoked as a possible explanation for deviations between calculated and observed rate constants, the bulk of the evidence is based on rate comparisons.[4,5] Direct experimental evidence for a ligand radical anion coordinated to Co(III) has been obtained, however, in pulse radiolytic reductions of (nitrobenzoato)pentaamminecobalt(III).[6] Hoffman and co-workers report that substitution of one or more NO_2 groups onto a benzoate ligand coordinated to $Co(NH_3)_5^{3+}$ reduces the rate of intramolecular electron transfer from $>10^7\ s^{-1}$ for (benzoato)pentaamminecobalt(III) to $2.6 \times 10^3\ s^{-1}$ for (*p*-nitrobenzoato)pentaamminecobalt(III). Apparently, substitution of the strong electron-withdrawing group—50–55% of the coordinated radical spin density resides on the NO_2 moiety[6]—stabilizes the ligand radical anion and reduces the intramolecular electron-transfer rate.

A transient absorbance observed in the γ-radiolysis of $Co(bpy)_3^{3+}$ has been characterized as an excited state of the reduced complex with a coordinated bipyridine radical anion, but as mentioned above, attempts to detect this intermediate in flash photolysis experiments have been unsuccessful. A possible explanation for the inability to detect this intermediate is the rapid rate of intramolecular electron transfer from the bound ligand radical to the Co(III) center.[2a,4] In view of the retarding effect of NO_2 groups on the rate of intramolecular electron transfer,[6] however, substitution of NO_2 and perhaps other strong electron-withdrawing substituents onto the periphery of the bipyridine ligand might be expected to stabilize and increase the lifetime of a coordinated bipyridine radical anion. If also substituted onto the periphery of $Ru(bpy)_3^{2+}$ where, in the excited state, the reducing electron resides in a ligand centered π^* orbital, strong electron-withdrawing groups could significantly modify the excited-state redox properties of the Ru(II) complex and subsequent thermal back-reactions.

So that the effect of strong electron-withdrawing groups on the photoinduced redox reactions between tris(polypyridine) complexes of Ru(II) and Co(III) could be explored, the ligands 4-nitro-2,2′-bipyridine ($NO_2(bpy)$), 4,4′-dinitro-2,2′-bipyridine ($(NO_2)_2bpy$), 4-(triethylphosphonio)-2,2′-bipyridine ($Et_3P(bpy)^+$), and 4,4′-bis(triethylphosphonio)-2,2′-bipyridine ($(Et_3P)_2(bpy)^{2+}$) were synthesized. The monosubstituted bipyridines formed the tris complexes whereas the disubstituted derivatives, under a variety of reaction conditions, formed only the dichlorobis(polypyridine) complex. Substitution of NO_2 onto the four positions of the bipyridine ring, in contrast to the effect induced by $P(Et)_3^+$, radically modifies the excited-state properties of the Ru(II) complex. The results of cyclic voltammetry, absorption, emission, and resonance Raman spectroscopy, lifetime measurements, emission quenching, and flash photolysis experiments are described. For comparison with previous experiments,[8] the results of quenching of the monosubstituted Ru(II) complexes by $Fe(H_2O)_6^{3+}$ are also described.

Experimental Section

Materials. The syntheses of $NO_2(bpy)$, $(NO_2)_2(bpy)$, $Et_3P(bpy)^+$, and $(Et_3P)_2(bpy)^{2+}$ have been previously described.[9] Ru-

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(1) (a) Queens College. (b) City College.

(2) (a) Berkoff, R.; Krist, K.; Gafney, H. D. *Inorg. Chem.* **1980**, *19*, 1. (b) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710. (c) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2159.

(3) Creutz, C.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 496.

(4) Leopold, K. R.; Haim, A. *Inorg. Chem.* **1978**, *17*, 1753.

(5) (a) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162. (b) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627. (c) Toma, H. E.; Creutz, C. *Ibid.* **1977**, *16*, 545.

(6) Simic, M. G.; Hoffman, M. Z.; Brezniak, N. V. *J. Am. Chem. Soc.* **1977**, *99*, 2166.

(7) (a) Baxendale, J. H.; Fiti, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1995. (b) Waltz, W. L.; Pearson, R. G. *J. Phys. Chem.* **1969**, *73*, 1941.

(8) Lin, C. T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

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$(bpy)_3Cl_2·3H_2O$ was prepared according to the procedure described by Palmer and Piper.[10] Absorption and emission spectra of samples twice recrystallized from distilled water were in excellent agreement with published spectra. The Ru(II) complexes of NO_2(bpy) and $Et_3P(bpy)^+$ were prepared by a procedure analogous to the preparation of $Ru(bpy)_3Cl_2$. A 0.262-g (1-mmol) sample of $RuCl_3·(1-3)H_2O$ (Alfa-Ventron) and 0.864 g (4 mmol) of NO_2(bpy) or 1.412 g (4 mmol) of $Et_3P(bpy)^+Br$ was added to 20 mL of ethanol and the solution refluxed for 72 h. The reaction mixture was filtered, 5 mL of a saturated aqueous solution of $NaClO_4$ was added to the hot filtrate, and the bright orange product precipitated on cooling. After recrystallization from distilled water, the yields of $[Ru(Et_3P(bpy))_3](ClO_4)_5·5H_2O$ and $[Ru(NO_2(bpy))_3](ClO_4)_2$ were 50 and 55%, respectively. Anal. Calcd for $[Ru(NO_2(bpy))_3](ClO_4)_2$: C, 39.87; H, 2.32; Cl, 7.85. Found: C, 39.75; H, 2.72; Cl, 8.35. Calcd for $[Ru(Et_3P(bpy))_3](ClO_4)_5·5H_2O$: C, 38.22; H, 5.04; Cl, 11.75. Found: C, 38.04; H, 4.78; Cl, 11.25.

Repeated attempts to prepare the tris Ru(II) complexes of $(NO_2)_2$(bpy) and $(Et_3P)_2(bpy)^{2+}$ failed. Regardless of whether a larger excess of the ligand was used or the reaction mixture was refluxed for a longer time, ca. 1 week, absorption spectra and elemental analysis indicated the formation of dichlorobis(4,4′-X-2,2′-bipyridine)ruthenium(II), which we infer to be the cis-configured compound due to similarity of the visible spectra to that of *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II).[9,31] In one experiment, a sample of dichlorobis(4,4′-dinitro-2,2′-bipyridine)ruthenium(II) isolated from a previous preparation was added to a fresh ethanol solution containing a 10-fold excess of $(NO_2)_2$(bpy) and refluxed. Spectra of the reaction mixture recorded after refluxing for 72 h gave no indication of the tris complex and, after filtering the cooled mixture, $Ru((NO_2)_2(bpy))_2Cl_2$ was quantitatively recovered.[11]

$Ru(Et_3P(bpy))_3^{6+}$ was prepared in situ by Cl_2 oxidation. Extensive Cl_2 bubbling of 10^{-5} M aqueous solutions of the complex caused a complete loss of optical density at the MLCT band maximum, but only 40–50% of the original optical density could be regenerated when a large excess of $NaNO_2$ or NaOH was added to the solution. So that possible discrepancies due to an irreversible change could be eliminated, Cl_2 oxidations of 10^{-4} M solutions of $Ru(Et_3P(bpy))_3^{5+}$ were monitored spectrally and limited to ca. 30% reaction. Under these conditions 96–99% of the original MLCT optical density could be regenerated when a 10-fold excess of $NaNO_2$ was added to the solution. Cl_2 bubbling does not oxidize $Ru(NO_2(bpy))_3^{2+}$, however, and a Ce(IV) procedure was used to prepare $Ru(NO_2(bpy))_3^{3+}$. To a 1 M HNO_3 solution containing 5×10^{-5} M $Ru(NO_2(bpy))_3^{2+}$ was added dropwise 1 M $(NH_4)_2Ce(NO_3)_6$ until spectra recorded during the addition showed a decline of ca. 30% in the MLCT band. The oxidation was limited to ≤30% because 90–95% of the initial MLCT absorbance could be regenerated when excess $NaNO_2$ was added. The extinction coefficients of the Ru(III) complexes were calculated from these partially oxidized solutions with the assumption of a 1:1 stoichiometry.

$[Co(bpy)_3](ClO_4)_3·3H_2O$ was prepared by procedures described in the literature[12] and recrystallized from distilled water containing 30% H_2O_2 to eliminate contamination by $[Co(bpy)_3](ClO_4)_2$.[2a] Thiocyanate analysis indicated that the amount of Co(II) in the recrystallized sample was less than 2%.[2a] The substituted analogue $[Co(NO_2(bpy))_3](ClO_4)_3$ was prepared in a similar manner. A 238-mg (0.25-mmol) sample of $CoCl_2·6H_2O$ and 700 mg (3.5 mmol) of NO_2(bpy) were dissolved in 20 mL of warm (60 °C) 95% ethanol and treated with 1 mL of 30% H_2O_2. Following the effervesence, a saturated solution of $NaClO_4$ was added and, on cooling, a yellowish brown precipitate was obtained. Since thiocyanate analysis of this precipitate indicated the presence of Co(II), the sample was twice recrystallized from distilled water containing 30% H_2O_2.[2a] Analysis after recrystallization indicated that the amount of Co(II) had been reduced to less than 2%.

Like that found with Ru(II), attempts to prepare tris Co(III) complexes with the disubstituted ligands by H_2O_2 oxidation also failed. Absorption spectra of the reaction mixtures suggested that the product is the dichlorobis(*X*,*X*′-bipyridine)cobalt(III) complex.

All other chemicals used in these experiments were reagent grade, and solutions were prepared with water distilled in a Corning distillation apparatus. Because of a slow thermal reaction with $Ru(NO_2(bpy))_3^{2+}$ (see below), all photochemical experiments were carried out with freshly prepared solutions deareated by N_2 bubbling and adjusted to an ionic strength of 1.0 M (0.33 M Na_2SO_4 and 0.0275 M $NaHSO_4$).

Photolysis Procedures. The steady-state and flash photolysis equipment used in these experiments has been previously described.[2a]

Lifetime measurements were performed in the laboratory of Professor Nicholas Turro at Columbia University. Excitation pulse durations were 3–5 ns, which introduced no significant error in the reported lifetimes. No attempt was made to resolve risetimes.

Physical Measurements. Cyclic voltammetry measurements employed a Princeton Applied Research system consisting of a Model 173 potentiostat and a Model 175 universal programmer. Millimolar solutions of the free ligands and the Ru(II) complexes (as ClO_4^- salts) were prepared in a 0.1 M acetonitrile solution of tetraethylammonium perchlorate. The acetonitrile used in these experiments was dried over calcium hydride and then distilled over P_2O_5. For the Ru(II) complexes, the working and auxiliary electrodes were platinum and platinum gauze, respectively. For the free ligands, a hanging-Hg drop was used as the working electrode. In all measurements, the reference electrode was a saturated calomel electrode (SCE). All measurements were made at a scan rate of 100 mV/s and under a nitrogen atmosphere.

Electronic absorption spectra were recorded on a Cary 14 spectrophotometer. Emission spectra were recorded on a Perkin-Elmer MPF-2A emission spectrophotometer equipped with a Hamamatsu R818 red-sensitive photomultiplier. For room-temperature emission spectra, solutions were contained in 1-cm × 1-cm quartz or Pyrex cells. For low-temperature spectra (77 K), solutions in 2-mm diameter Pyrex tubes were placed in a quartz Dewar filled with liquid N_2. Infrared spectra of the complexes were recorded on a Perkin-Elmer 237B spectrophotometer calibrated against polystyrene. A Beckman Expandomatic SS-2 pH meter, calibrated with standard buffers, was used for pH measurements.

Resonance Raman spectra were obtained with 457.9- or 488.0-nm lines of a Spectra Physics Model 164-08 argon ion laser. The Raman spectrophotometer employed a SPEX model 14018 double monochromator, an RCA C31034 photomultiplier, and Pacific Precision Instruments photon-counting equipment. Spectra were obtained with H_2O or ethanol solutions of the reagents in a glass capillary tube or a 3-mm square, flat-bottomed cell with 90° transverse excitation. Optical spectra were recorded before and after the Raman spectra to determine if any change in the reagent had occurred.

Results

Electrochemical Properties. Substitution of NO_2 or PEt_3^+ onto the four positions of the pyridine rings affects various physical parameters of the bipyridines and in turn the Ru(II) complexes. The four position is directly conjugated with the ring nitrogens, and the substituents decrease the pK_a for monoprotonation from 4.27 for the unsubstituted bipyridine to 3.25 ± 0.02 and 2.82 ± 0.01 for NO_2(bpy) and $Et_3P(bpy)^+$, respectively. A severe reduction in basicity occurs in the disubstituted analogues. The pK_a's for monoprotonation of $(NO_2)_2$(bpy) and $(Et_3P)_2(bpy)^{2+}$ are reduced to 0.06 ± 0.02 and 0.03 ± 0.02, respectively. This substantial decrease in ligand basicity may account, in part, for their inability to form the tris complex.

The data summarized in Table I illustrate the effect of these substituents on the spectra and redox potentials of the bipyridines and the Ru(II) complexes. In acetonitrile, the cyclic voltammograms of these bipyridines show two successive waves corresponding to the first and second reductions of the bipyridine π system. The potentials listed in Table I correspond to the first wave, a one-electron reduction of the molecule,[9,13] since photoredox quenching is a one-electron event. For both

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[9] Weiner, M. A.; Basu, A. *Inorg. Chem.* **1980**, *19*, 2797.

[10] Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864.

[11] Basu, A. Ph.D. Thesis, City University of New York, 1980.

[12] (a) Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3577. (b) Ellis, P.; Wilkins, R. G.; Williams, M. J. G. *Ibid.* **1957**, 4456. (c) Baker, B. R.; Basolo, F.; Newman, H. M. *J. Phys. Chem.* **1959**, *63*, 371. (d) Hogg, R.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 341.

[13] Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58*, 401.

Table I. Absorption and Emission Maxima and Redox Potentials of the Bipyridines and the Corresponding Ru(II) Complexes

substrate	abs max,[a] nm	emission max,[b] nm	potentials, V
bpy	233 (9.6), 281 (13.4)	434	−2.21[d]
$Et_3P(bpy)^+$	236 (9.2), 289 (9.6)	445	−1.67[d]
$NO_2(bpy)$	233 (18.0), 273 (8.0), 312 (3.9)		−1.55[d]
$Ru(bpy)_3{}^{2+}$	452 (13.2)	595	1.29 (70)[e]
$Ru(Et_3P(bpy))_3{}^{5+}$	466 (18.3)	628	1.52 (60)[e]
$Ru(NO_2(bpy))_3{}^{2+}$	486 (15.0)	680[c]	1.54 (80)[e]

[a] Molar extinction coefficients × 10^{-3} are indicated in parentheses. [b] Uncorrected emission maxima of aqueous solutions of the substrate. [c] Emission maximum found in the background of the resonance Raman spectrum of the complex when ionically bound to a dry porous glass matrix (Corning code 7930). [d] Potential of the first wave in cyclic voltammogram corresponding to $L + e^- \rightarrow L^-$. [e] Oxidation potentials measured in CH_3CN containing 0.1 M tetraethylammonium perchlorate. Peak separation of cathodic and aniodic waves in millivolts listed in parentheses.

the substituted and unsubstituted bipyridines, the reductions are irreversible; no indication of an anodic waves was apparent in the cyclic voltammograms. Both substituents lower the reduction potential, yet the NO_2 group, presumably because it is formally resonant with the bipyridine π system, exhibits a greater decrease in the reduction potential.

As expected, both substituents increase the oxidation potentials of the Ru(II) complexes: $RuL_3{}^{3+} + e^- \rightarrow RuL_3{}^{3+}$. The separation in anodic and cathodic peaks, 70 ± 10 mV, is slightly larger than the theoretical difference, 59 mV, but the ratio anodic to cathodic peak currents, ≥ 0.95, suggests that oxidations of these complexes are reversible. The values listed in Table I are $E_{1/2}$ values obtained by averaging the anodic and cathodic peaks. In these tris(polypyridine)ruthenium(II) complexes, where oxidation removes an electron from a metal t_{2g} orbital, the similarity of the $E_{1/2}$ values suggests that the effect induced at the metal center by NO_2 and $PEt_3{}^+$ is similar.

Absorption and Emission Spectra. The substituents also affect the transition energies as illustrated by the band maxima listed in Table I. Although slightly red shifted, the UV absorption spectrum of $Et_3P(bpy)^+$ closely resembles that of bpy where the two bands have been assigned to transitions between the π and π^* levels.[14] In $NO_2(bpy)$, however, the π–π^* transition energies increase relative to bpy and a new band at 312 nm appears as a low-energy shoulder on the π–π^* transition. Jones and co-workers have assigned this 312-nm shoulder to a n–π^* transition of the NO_2 group.[15]

The visible absorption spectra of the metal complexes are similar and dominated by the familiar MLCT band. The band is assigned to a t_2–π^* MLCT transition and, as indicated by the band maxima listed in Table I, the transition energy is sensitive to the substituent on the ligand periphery. Despite the positive charge on $PEt_3{}^+$, the NO_2 group, by exerting a greater withdrawing effect on the ring π system, causes a larger reduction in the MLCT transition energy. In general, these changes in transition energies and redox potentials are consistent with that expected for strong electron-withdrawing groups.[15] Unexpected, however, are the differences in the emission properties of the bipyridines and their corresponding Ru(II) complexes.

The maxima of single broad emission bands observed from room-temperature fluid solutions of bpy or $Et_3P(bpy)^+$ are listed in Table I. The emission is not quenched by O_2 and is attributed to fluorescence. In low-temperature, 77 K, 4:1 ethanol–methanol glasses, the band maxima are slightly red shifted, ≤ 3 nm, and a vibrational progression of three distinct peaks is resolved. When similar degassed room-temperature solutions or low-temperature glasses containing $NO_2(bpy)$ are excited at the absorption maxima of the molecule, however, no emission in the 350–800-nm region is detected.

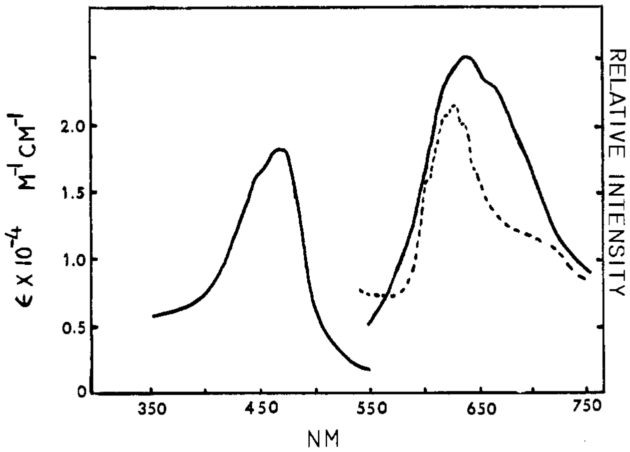

Figure 1. Absorption spectrum of $Ru(4\text{-}P(Et)_3{}^+(bpy))_3{}^{5+}$ in aqueous solution at room temperature (—) and emission spectra at room temperature (—) and at 77 K (- - -) in 4:1 EtOH–MeOH mixture; excitation wavelength was 466 nm.

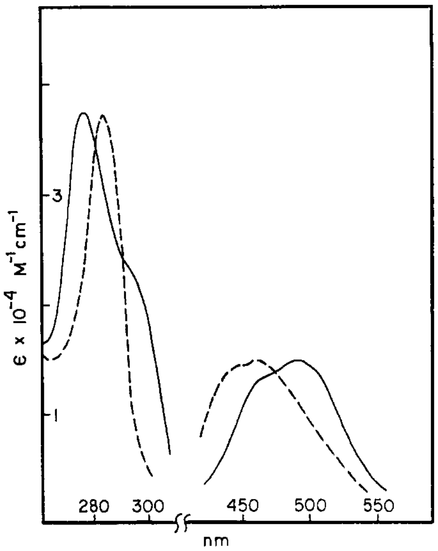

Figure 2. Absorption spectra of $Ru(4\text{-}NO_2(bpy))_3{}^{2+}$ (—) and the thermal reaction product (---) in 95% ethanol.

The emission properties of the Ru(II) complexes are also dependent upon the substituents attached to the bipyridine. An intense emission with a maximum at 640 ± 8 nm is observed from room-temperature fluid solution and low-temperature glasses containing $Ru(Et_3P(bpy))_3{}^{5+}$ (Figure 1). The excitation spectrum of the emission corresponds to the MLCT transition of the complex and, in fluid solution, the emission intensity is dependent on the O_2 concentration of the solution. Although shifts, ≤ 10 nm, occur in the band maximum, the emission spectra of $Ru(Et_3P(bpy))_3{}^{5+}$ in water, acetonitrile, 20% ethanol–water, or 95% ethanol are similar and closely resemble the emission of $Ru(bpy)_3{}^{2+}$.

No emission is detected in the 500–800 nm region when degassed room-temperature 10^{-5} M water, acetonitrile, or 20% ethanol–water solutions of $Ru(NO_2(bpy))_3{}^{2+}$ are excited at the MLCT maximum. Freezing these solutions to 77 K or preparing 4:1 methanol–ethanol glasses containing the complex failed to induce an emission. If the complex is dissolved in

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(14) (a) Henry, M. S.; Hoffman, M. Z. *J. Phys. Chem.* **1979**, *83*, 618. (b) Brinen, J. S.; Rosebrook, D. D.; Hirt, C. R. *Ibid.* **1963**, *67*, 2651. (c) Gondo, Y.; Kanda, Y. *Bull. Chem. Soc. Jpn.* **1975**, *38*, 1187.

(15) Jones, R. A.; Roney, B. D.; Sasse, W. H. F.; Wade, K. O. *J. Chem. Soc. B* **1967**, 106.

95% ethanol, however, a time-dependent emission with a maximum at 650 nm is observed. Repeating the experiment at both room temperature and 77 K with freshly prepared 95% ethanol solutions of the complex established that the complex is also nonluminescent in this solvent. Rather, absorption and emission spectra recorded periodically after preparation, Figure 2, confirm that the complex undergoes a reaction in 95% ethanol to form a luminescent product. After 12 h at room temperature, no further change occurs in the absorption spectrum or the emission intensity. At this point, the shoulder at 312 nm has disappeared and the product has absorption maxima at 460 nm, with a shoulder at 440 nm, and at 279 nm. The excitation spectrum of the 650 nm emission has a maximum at 460 nm and agrees with the final absorption spectrum of the solution. Lifetime measurements indicate that the product emission decays via first-order kinetics with a rate constant of $(2.36 \pm 0.06) \times 10^6$ s^{-1}.

So that it could be determined whether the reaction is thermal or photochemical, two 4-mL aliquots of 95% ethanol solutions of $Ru(NO_2(bpy))_3^{2+}$ were placed in a rotating cell holder in the emission spectrophotometer. Water from a Haake FK2 constant-temperature bath was pumped through the cell holder to thermostat the solutions to 25 ± 0.1 °C. One aliquot was continually exposed to 460 nm light from the spectrophotometer while the other was kept in the dark. Within experimental error, the emission intensity at 650 nm, recorded periodically over 8 h, from both the dark and exposed samples were identical and indicate that the reaction is thermal and not photochemically induced. So that the rate constant for the reaction at 25 °C could be obtained, the growth in emission intensity was monitored from 10^{-5}, 5×10^{-5}, and 10^{-4} M $Ru(NO_2(bpy))_3^{2+}$ solutions. At each concentration, plots of log of the intensity vs. time are linear and yield a first-order rate constant of $(1.36 \pm 0.04) \times 10^{-1}$ min^{-1}.

Resonance Raman Studies. Although essentially a vibrational technique, resonance enhanced Raman spectroscopy can detail the molecular vibrations which are coupled to the electronic transition.[16] So that the involvement of these substituents in the MLCT transitions could be determined, resonance Raman spectra of water and ethanol solutions of the Ru(II) complexes, Figure 3, were recorded. When excited with 457.9-nm radiation, the spectrum of $Ru(bpy)_3^{2+}$ consists of seven polarized, or totally symmetric, vibrations of the bipyridine ligands.[17] These vibrations are vibronically active in the MLCT transition and consistent with the generally accepted description of the electronic absorption with a maximum at 450 nm as an MLCT transition.

As shown in Figure 3, asymmetric substitution of one of the bipyridine rings in $Ru(Et_3P(bpy))_3^{5+}$ leads to a splitting of certain vibrational modes of the C–C and C–N skeleton. If the ligand is viewed as a pair of pyridine rings coupled at the 2,2′-position, replacing H by PEt_3^+ on only one pyridine moiety would explain the observed splittings. Since many of the Raman active modes involve C–H bends coupled with ring vibrations, the extent of the splittings is consistent with replacing H by $P(Et)_3^+$, which exerts a strong withdrawing effect principally through the σ-bond network.

The resonance Raman spectrum of aqueous solutions of $Ru(NO_2(bpy))_3^{2+}$ is similar to that of $Ru(Et_3P(bpy))_3^{5+}$ in that additional modes are observed when compared to the spectrum of $Ru(bpy)_3^{2+}$. Coupling with the NO_2 attached to the 4-position of one pyridine ring is again invoked to explain this feature of the spectrum. When excited at 488.0 nm, the most prominent feature of the spectrum is an intense band at 1359 cm^{-1}. By analogy to its appearance in the resonance Raman spectra of nitro substituted aromatics,[18] 1345 cm^{-1} in nitrobenzene, this band is assigned to the NO_2 symmetric stretch. The appearance of the NO_2 mode as the most intense in the resonance Raman spectrum indicates that in the MLCT transition significant electron density is shifted to the NO_2 group. If the MLCT state of the complex is viewed as a Ru(III) complex with a coordinated ligand radical anion, the resonance enhancement found with the $Ru(NO_2(bpy))_3^{2+}$ is consistent with the coordinated nitrobenzoato radical anion where ESR spectra show 50–55% of the radical spin density on the NO_2 moiety.[6]

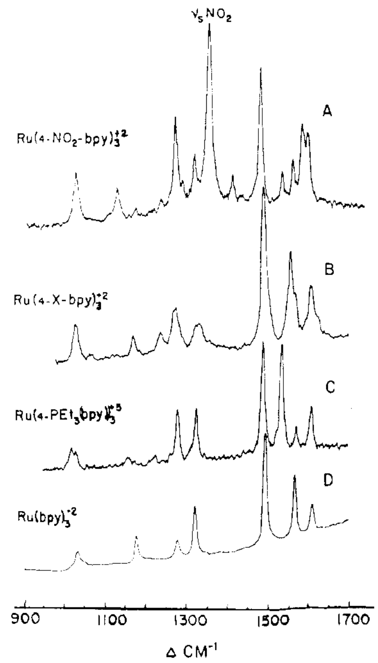

Figure 3. Resonance enhanced Raman spectra obtained from 457.9-nm excitation (B–D) and 514.5-nm excitation (A) from an argon ion laser. Spectral conditions: spectral slit width 5-cm^{-1}; scan rate 1 cm^{-1} s^{-1}; 1000 counts/s full scale; time constant 0.1 s.

Because of the relatively small amount of ligand available for these experiments, no attempt was made to isolate the product of the thermal reaction of $Ru(NO_2(bpy))_3^{2+}$ in 95% ethanol. An indication of what the reaction entails, however, is available from the absorption and resonance Raman spectra. The absorption spectrum of the product, which has an absorption maximum at 460 nm, indicates that the integrity of the complex is retained. When excited with 457.9-nm radiation, the resonance Raman spectrum of the product, Figure 3, shows that 1359-cm^{-1} band due to NO_2 is absent. The spectrum of the product does not show new modes but does retain the multiple-band pattern, indicating a new substituent in the 4-position. Since the reaction occurs in 95% ethanol and not in water, the new substituent is attributed to an ethoxy group. An ethoxy substituent, like $P(Et)_3^+$, would not couple with the aromatic π system and no new bands are expected.

Photochemical Studies. Since the differences in emission properties suggest difference in excited-state behavior, the Ru(II) complexes and, for comparison, the bipyridines were examined by flash photolysis. Aqueous or 95% ethanol solutions 10^{-4} M in bpy or 5×10^{-5} M in $Et_3P(bpy)^+$ and adjusted to an ionic strength of 1.0 M (aqueous 0.333 M Na_2SO_4 and 0.0275 M $NaHSO_4$; 95% ethanol, 1.0 M Et_4NCl) were exposed to a 245-J unfiltered flash. Spectra of the transients were obtained by monitoring their decay at a number of wavelengths from 300 to 600 nm and at each wavelength, measuring the absorbance at a fixed time, 200 μs, on the decay

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(16) Clark, R. J. H.; Stewart, B. *Struct. Bonding (Berlin)* **1979**, *36*, 1–80.

(17) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391.

(18) Behringer, J. "Raman Spectroscopy"; Szymanski, H. A., Ed.; Plenum Press: New York, 1967; Vol. 1, p 168.

trace. Both the transient spectra and decay rates are independent of the solvent, and the transient absorption maxima are 350 nm for bpy and 375 nm for $Et_3P(bpy)^+$. In solutions degassed by freeze–pump–thaw cycles or deaerated by N_2 bubbling, both transients decay by first-order kinetics. Plots of the log of the transient absorbance vs. time are linear and yield rate constants of $(2.2 \pm 0.5) \times 10^3$ s^{-1} and $(2.3 \pm 0.2) \times 10^3$ s^{-1} for bpy and $Et_3P(bpy)^+$, respectively. Saturating the solutions with O_2, however, increases the decay rate. Absorption spectra recorded before and after the flash photolysis of deareated or O_2 saturated solutions are identical <2% net chemical change in both substrates. The transient absorption spectrum and O_2 quenching are identical with previous results where the transient observed on flash photolysis of bpy has been attributed to the $^3(n \rightarrow \pi^*)$ state.[19] Since the absorption spectrum, O_2 quenching, and decay rate of the transient generated by flash photolysis of $Et_3P(bpy)^+$ are similar to those of bpy, this transient is also attributed to the $^3(n \rightarrow \pi^*)$ state.

Exposing 95% ethanol solutions 10^{-4} M in $NO_2(bpy)$ to an unfiltered 245-J flash generates a transient with an absorption maximum at 450 nm. This transient is independent of solution ionic strength, adjusted with Et_4NCl, and decays by first-order kinetics with a rate constant of $(6.67 \pm 0.03) \times 10^1$ s^{-1}. Saturating the solution with O_2 decreases the transient absorbance and increases the decay rate which, under these conditions, is pseudo first order with a rate constant of $(1.38 \pm 0.07) \times 10^3$ s^{-1}. Since absorption spectra recorded before and after these flash experiments indicated a net photochemical change, 95% ethanol solutions 7×10^{-5} M in $NO_2(bpy)$ were photolyzed with 312-nm light. Spectra recorded periodically during photolysis show a loss of the 312 nm shoulder, attributed to the $n-\pi^*$ transition of the NO_2 group[15] and a shift of the $\pi-\pi^*$ transition from 278 to 285 nm. The quantum yield of the reaction, determined by measuring the decline in absorbance at 312 nm, where the product does not absorb, is $(9.8 \pm 0.2) \times 10^{-4}$ in degassed 95% ethanol and $(5.2 \pm 0.2) \times 10^{-4}$ in air saturated 95% ethanol.

When degassed aqueous or alcoholic solutions 5×10^{-5} M in either $Ru(bpy)_3^{2+}$ or $Ru(Et_3P(bpy))_3^{5+}$ are exposed to unfiltered 245-J flashes, no transient absorbance is detected in the 550–800 nm region and absorption spectra recorded after the experiments are identical with the initial spectra. Similarly, no transient absorptions are detected when 5×10^{-5} M aqueous or alcoholic solutions of $Ru(NO_2(bpy))_3^{2+}$ are exposed to the flash; but in 95% ethanol, spectra recorded before and after the flash differ. The same spectral change occurs in unexposed aliquot, however, and the change is attributed to the previously described thermal reaction of $Ru(NO_2(bpy))_3^{2+}$ in 95% ethanol.

The Stern–Volmer constants, K_{SV}, and bimolecular rate constants, k_q, describing the quenching of $^*Ru(bpy)_3^{2+}$ and $^*Ru(Et_3P(bpy))_3^{5+}$ by the individual bipyridines, the Co(III) complexes, and $Fe(H_2O)_6^{3+}$ are listed in Table II. For each of the quenchers, Stern–Volmer plots, measured at the emission maxima of the Ru(II) complex, are linear and corrections for trivial effects were ≤5%. $Co(NO_2(bpy))_3^{3+}$, however, has a strong absorption band at 380 nm, $\epsilon = 7.6 \times 10^3$ M^{-1} cm^{-1}, which tails into the visible region, and corrections for trivial effects are somewhat larger, ≤10%. Bimolecular rate constants were calculated from the relation $K_{SV} = k_q t_o$, where t_o is the radiative lifetime of the excited Ru(II) complex. The lifetime of $^*Ru(bpy)_3^{2+}$ measured in aqueous solution at an ionic strength of 1.0 M (0.333 M Na_2SO_4 and 0.0275 M $NaHSO_4$) agrees with previous determinations and is taken to be 600 ± 20 ns.[2c] The lifetime of the MLCT state of $Ru(Et_3P(bpy))_3^{5+}$ was measured under the same conditions. Plots of the natural log of intensity vs. time are linear through 95% of the emitted light and yield a lifetime (the time required for the intensity to decrease to $1/e$ of the initial value) of 760 ± 40 ns.

Table II. Stern–Volmer Constants, Bimolecular Quenching Rate Constants, and the Rate Constants of the Thermal Back-Reactions[a]

reactants	$10^2 K_{SV}$, M^{-1}	$10^8 k_q$,[c] M^{-1} s^{-1}	k_{th}, M^{-1} s^{-1}
$Ru(bpy)_3^{2+}$–bpy	0.0025	0.042	no transient
$Ru(bpy)_3^{2+}$–$NO_2(bpy)$	15.7 ± 0.5	25.8 ± 1.2	no transient
$Ru(bpy)_3^{2+}$–$Et_3P(bpy)$	1.37 ± 0.02	2.25 ± 0.03	no transient
$Ru(bpy)_3^{2+}$–$Co(bpy)_3^{3+}$	11.5 ± 0.1	19.2 ± 1.5	$(1.33 \pm 0.27) \times 10^8$
$Ru(bpy)_3^{2+}$–$Co(NO_2(bpy))_3^{3+}$	5.4 ± 0.9	9.0 ± 1.4	no transient
$Ru(bpy)_3^{2+}$–$Fe(H_2O)_6^{3+}$[b]	20.5 ± 1.0	27.0 ± 1.3	$(4.0 \pm 0.2) \times 10^6$
$Ru(Et_3P(bpy))_3^{5+}$–bpy	0.002	0.04	no transient
$Ru(Et_3P(bpy))_3^{5+}$–$Et_3P(bpy)^+$	0.204	0.27	no transient
$Ru(Et_3P(bpy))_3^{5+}$–$NO_2(bpy)$	4.32 ± 0.05	5.70 ± 0.30	no transient
$Ru(Et_3P(bpy))_3^{5+}$–$Co(bpy)_3^{3+}$	1.40 ± 0.15	1.84 ± 0.18	$(2.15 \pm 0.15) \times 10^8$
$Ru(Et_3P(bpy))_3^{5+}$–$Co(NO_2(bpy))_3^{3+}$	0.50 ± 0.02	0.66 ± 0.04	no transient
$Ru(Et_3P(bpy))_3^{5+}$–$Fe(H_2O)_6^{3+}$[b]	11.0 ± 0.4	14.5 ± 0.6	$(1.85 \pm 0.20) \times 10^8$

[a] Ionic strength 1.0 M; 0.33 M Na_2SO_4 and 0.0275 M $NaHSO_4$. [b] Measured in 0.50 M H_2SO_4. [c] The lifetime of $^*Ru(bpy)_3^{2+}$ is taken as 600 ± 20 ns, and that for $^*Ru(Et_3P(bpy))_3^{5+}$ is 760 ± 40 ns.

Deareated aqueous solutions of each donor–quencher pair listed in Table II were photolyzed with 350 nm light to determine if quenching leads to an irreversible change. In each experiment, the initial concentration of the Ru(II) complex and the quenchers were 2×10^{-4} and 10^{-3} M, respectively. With the individual bipyridines or the Co(III) complexes as quenchers, spectra of $CHCl_3$ extracts of the photolyte indicate that the quantum yield for a net change in the bipyridines or aquation of the Co(III) complex is $\leq 5 \times 10^{-3}$. With $Fe(H_2O)_6^{3+}$ as a quencher, no Fe^{2+} was detected spectrally at 510 nm when the photolyte was treated with 1,10-phenanthroline, $\phi_{Fe(II)} \leq 10^{-3}$. These results establish the reversibility of the quenching reactions and that flash photolysis can be used as a relaxation technique to measure photoinduced redox events.[20]

Solutions containing 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ or $Ru(Et_3P(bpy))_3^{5+}$ and amounts of the individual quenchers ranging from 10^{-3} to 10^{-2} M were deareated by N_2 bubbling or degassed by freeze–pump–thaw cycles. Each solution was exposed to a 245-J flash and analyzed at various wavelengths from 550 to 850 nm. No transient absorbance, $\Delta A \geq 0.02$, persisting longer than 20 μs is detected in this spectral region when either bpy, $NO_2(bpy)$, or $Et_3P(bpy)^+$ is present as a quencher at a concentration of 5×10^{-3} M. Surprisingly, the same result is obtained when $Co(NO_2(bpy)_3)^{3+}$ is the quencher. No transient absorbance is detected at the absorption maxima of $Ru(bpy)_3^{3+}$, 675 nm, or $Ru(Et_3P(bpy))_3^{6+}$, 650 nm, even though the concentration of $Co(NO_2(bpy))_3^{3+}$, 10^{-3} M or 5×10^{-3} M, corresponds to ~83% quenching. Yet, with the presumably analogous quencher $Co(bpy)_3^{3+}$, transient absorbances at the absorption maxima of $Ru(bpy)_3^{3+}$ or $Ru(Et_3P(bpy))_3^{6+}$ are detected. In these experiments, where the

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[19] Harriman, A. *J. Photochem.* **1978**, *8*, 205.

[20] Young, R. C.; Keene, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468.

concentration of $Co(bpy)_3^{3+}$ is 10^{-3} M or 5×10^{-3} M, the amount of the Ru(III) complex generated is proportional to the concentration of $Co(bpy)_3^{3+}$ and independent of the number of times the solution is exposed to the flash.

As previously reported, the spectrum of the transient observed on flash photolysis of solutions containing 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} M $Co(bpy)_3^{3+}$ establishes $Ru(bpy)_3^{3+}$ as a product of the quenching reaction.[2a] Similarly, the spectrum of the transient generated by flash photolysis of 7.5×10^{-5} M $Ru(Et_3P(bpy))_3^{5+}$ and 10^{-3} M $Co(bpy)_3^{3+}$ establishes $Ru(Et_3P(bpy))_3^{6+}$ as the product of the quenching reaction. At each wavelength, plots of the reciprocal of the Ru(III) complex absorbance vs. time are linear through ≥80% reaction, and the rate constants for the reactions between the Ru(III) complexes and $Co(bpy)_3^{2+}$ are summarized in Table II.

Spectra of the transients generated by flash photolysis of solutions containing the Ru(II) complexes and $Fe(H_2O)_6^{3+}$ also establish the Ru(III) complexes as reaction products. With 7.5×10^{-5} M $Ru(Et_3P(bpy))_3^{5+}$ and 10^{-3} M $Fe(H_2O)_6^{3+}$, plots of the reciprocal of the $Ru(Et_3P(bpy))_3^{6+}$ absorbance vs. time are linear and the rate constant for the back-reaction is listed in Table II. When solutions containing 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ and the same concentration of $Fe(H_2O)_6^{3+}$ are exposed to the same energy flash, 245-J, and monitored at 675 nm; however, a two-component decay analogous to that previously reported is observed.[8] Although $Ru(bpy)_3^{2+}$ is the dominant absorbing species in the visible region, $Fe(H_2O)_6^{3+}$ does absorb in the UV region. Yet, filling the outer annulus of the flash cell with 0.162 M $K_3Fe(C_2O_4)_3$, which transmits $\lambda > 420$ nm, does not reduce the decay to a single component.[21] The initial component persists for ≤200 μs and is followed by a slower component which persists for several milliseconds. The slower component decays via second-order kinetics; plots of $1/A$ vs. time are linear and yield a rate constant, $(4.0 \pm 0.3) \times 10^6$ M^{-1} s^{-1}, which agrees with previous determinations. Subtracting the second-order component and extrapolating to $t = 0$ indicate that 20 ± 2% of the $Ru(bpy)_3^{3+}$ generated in the flash decays by the initial rapid process and 80 ± 2% decays by the second-order process.

Although $Ru(NO_2(bpy))_3^{2+}$ is nonluminescent under the conditions of these experiments, luminescence is not necessarily a criteria for photoredox behavior. Because of the rapid rate at which $Fe(H_2O)_6^{3+}$ quenches $^*Ru(bpy)_3^{2+}$ ($k_q = (2.70 \pm 0.13) \times 10^9$ M^{-1} s^{-1}) and the slow rate of the back-reaction solutions containing 7.5×10^{-5} M $Ru(NO_2(bpy))_3^{2+}$ and 5×10^{-3} M or 10^{-2} M $Fe(H_2O)_6^{3+}$ were examined for photoredox behavior by flash photolysis. However, no indication, $\Delta A \geq 0.02$, of $Ru(NO_2(bpy))_3^{3+}$ was obtained at the absorption maximum, 700 nm, of the complex.

These experiments were undertaken to obtain evidence for a chemical or radical electron-transfer mechanism, but no indication of an excited state of the Co(II) complex having a coordinated ligand radical anion was obtained. Degassed solutions containing 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} M $Co(NO_2(bpy))_3^{3+}$ were exposed to unfiltered 245-J flashes and analyzed at 568 nm, the isobestic point in the spectra of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$. Although Baxendale and Fiti have shown that an excited state of $Co(bpy)_3^{2+}$ having a coordinated bipyridine radical anion absorbs at this wavelength[7a] and König and Kremer report the extinction coefficient of the bipyridine radical anion to be ca. 3500 M^{-1} cm^{-1},[22] no transient absorbance, $\Delta A \geq 0.02$, lasting longer than 20 μs was detected.

Discussion

Both NO_2 and $P(Et)_3^+$ change the excited-state redox potentials of $Ru(bpy)_3^{2+}$ and the rates of the photoinduced electron-transfer reactions. Although both are strong electron-withdrawing groups when substituted onto the 4- or 4,4′-positions of bipyridine, their effect is critically dependent on the extent of their interactions with the σ and/or π systems of the bipyridine ring. Substituting $P(Et)_3^+$ polarizes principally the σ-bond network with a concurrent, but weaker, polarization of the π system. The nitro substituent, however, is formally resonant with the bipyridine ring and induces a substantially greater polarization of the π system. This difference is apparent in the physical properties of these substituted bipyridines and their corresponding metal complexes.

Relative to bpy, both substituents decrease the reduction potentials and the pK_a's of the bipyridine system.[23] Apparently, the severe reduction of the pK_a's of the disubstituted derivatives, $(NO_2)_2bpy$ and $(P(Et)_3)_2bpy^{2+}$, is sufficient to prevent the formation of the tris complexes of Ru(II) and Co(III). The difference between these substituents, however, is apparent in their spectral properties. The $P(Et)_3^+$ group slightly lowers $\pi-\pi^*$ transition energies, but otherwise the absorption and fluorescence spectra of bpy and $P(Et)_3(bpy)^+$ are essentially identical. Although phosphorescence is not observed from 4:1 methanol–ethanol glasses (77 K) containing either bpy or $P(Et)_3(bpy)^+$, the effect of $P(Et)_3^+$ on the triplet state is apparent from flash photolysis spectra. Flash photolysis of aqueous or 95% ethanol solutions of bpy generates a transient which has previously been assigned, because of its solvent dependence, to the $^3(n-\pi^*)$ state.[19] Since the transient generated by flash photolysis of aqueous solutions of $Et_3P(bpy)^+$ has a similar dependence on O_2 and decays, $k = (2.3 \pm 0.2) \times 10^3$ s^{-1}, at the same rate as the $^3(n-\pi^*)$ state of bpy, $k = (2.2 \pm 0.5) \times 10^3$ s^{-1}, this transient is also assigned to the $^3(n-\pi^*)$ state. Although symptomatic of triplet character,[24] O_2 sensitivity and decay rate are not necessarily indicative of orbital parentage. In view of the relatively slight effect of $P(Et)_3^+$ on the $\pi-\pi^*$ energies (Table I), however, assigning the transient generated on flash photolysis of $P(Et)_3bpy^+$ to a $^3(\pi-\pi^*)$ state would not appear to be consistent with the shift in the transient maximum from 350 nm for bpy to 375 nm for $P(Et)_3(bpy)^+$.

Being formally resonant with the ring π system, NO_2 causes extensive spectral changes. The lower energy $\pi \rightarrow \pi^*$ transition which has a maximum at 281 nm in bpy shifts to 273 nm, and an $n-\pi^*$ transition attributed to the NO_2 group has a maximum at 312 nm. Fluorescence or phosphorescence is not observed from either room-temperature solutions or 4:1 methanol–ethanol glasses (77 K) containing $NO_2(bpy)$. Flash photolysis of 95% ethanol solutions of $NO_2(bpy)$ generates a transient which has an absorption maximum at 450 nm. Because of its sensitivity to O_2, this transient is tentatively assigned as a triplet state.

Unlike bpy and $P(Et)_3(bpy)^+$ which are photochemically inert under the conditions of these experiments, $NO_2(bpy)$ undergoes a photochemical reaction in 95% ethanol. The spectral changes which occur during 312 nm photolysis—a loss of the 312 nm band characteristic of the NO_2 group and a shift of the $\pi-\pi^*$ transition from 273 to 281 nm—indicate a photodissociation of the NO_2 group. The quantum yield of this reaction decreases from $\phi^0 = (9.8 \pm 0.2) \times 10^{-4}$ in degassed 95% ethanol to $\phi = (5.2 \times 0.2) \times 10^{-4}$ in air-saturated 95% ethanol. Although this O_2 dependence is qualitatively similar to the O_2 dependence of the 450 nm transient, the value of the ratio $\phi^0/\phi = 1.9$ obtained from the steady-state photolyses differs from a value of 5.1 calculated from the rate constants measured in the flash experiments. Consequently, we assume that the O_2 dependence of the photochemical reaction indicates

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[21] Krist, K.; Gafney, H. D. *J. Phys. Chem.*, in press.

[22] König, E.; Kremer, S. *Chem. Phys. Lett.* **1970**, *5*, 87.

[23] Brandt, W. W.; Smith, G. F. *Anal. Chem.* **1949**, *21*, 1313.

[24] Parker, C. A. "Photoluminescence of Solutions"; Elsevier: New York, 1968; p 38.

an involvement of a triplet state, but we hesitate, because of the difference in the ratios, to specify the 450 nm transient as the reactive triplet state.

These substituents exert similar effects on the properties of the Ru(II) complexes. Relative to $Ru(bpy)_3^{2+}$, both substituents cause essentially identical increases in the potential of the $RuL_3^{n+} - RuL_3^{(n+1)+} + e^-$ couple. Since oxidation removes an electron from the metal-centered t_2 orbitals, the similarity of the oxidation potentials of $Ru(Et_3P(bpy))_3^{5+}$ and $Ru(NO_2(bpy))_3^{2+}$ indicates that the t_2 orbital energy is the same for both complexes. Therefore, the decrease in the t_2–π^* transition energy must be attributed to a decrease in the energy of the π^* (LUMO) orbital. Eaborn has pointed out that the difference between the electron-withdrawing effect of substituents on an aryl system favors NO_2 as the negative charge in the aryl system increases.[25] Since the electronic transition increases the electron density in the bipyridine π^* orbital, the NO_2 substituent will have a greater effect than $P(Et)_3^+$ on the excited-state properties.

Although shifted to longer wavelengths, the absorption and emission spectra of $Ru(Et_3P(bpy))_3^{5+}$ are analogous to those of $Ru(bpy)_3^{2+}$. In degassed aqueous solution, however, the lifetime of the $Ru(Et_3P(bpy))_3^{5+}$ MLCT state, 760 ± 40 ns, is longer than that of $^*Ru(bpy)_3^{2+}$, 600 ± 20 ns. Previous lifetime measurements have shown that, depending on their position of substitution on $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, alkyl and aryl substituents can increase the excited-state lifetime by apparently insulating the chromophore from the solvent.[8,26] The resonance Raman spectrum of aqueous solutions of $Ru(Et_3P(bpy))_3^{5+}$ shows that the asymmetry introduced by $P(Et)_3^+$ substitution splits the bpy ring vibrations, but vibrations characteristic of $P(Et)_3^+$ are not present in the spectrum. The $P(Et)_3^+$ group, because of its positive charge, most likely polarizes the excited state but is neither resonant with the ring π system nor vibronically coupled to the MLCT transition. The absence of these formal coupling mechanisms suggests that the bulky $P(Et)_3^+$ group, like an alkyl substituent, increases the $^*Ru(Et_3P(bpy))_3^{5+}$ lifetime by insulating the chromophore from the solvent.

In contrast, $Ru(NO_2(bpy))_3^{2+}$ is not luminescent; no emission is detected when room-temperature or frozen (77 K) degassed water, 20% ethanol, 95% ethanol, ethanol, and acetonitrile solutions of the complex are excited at the MLCT maximum or in the UV region. Analogous to $Ru(Et_3P(bpy))_3^{5+}$, the resonance Raman spectrum of aqueous solutions of $Ru(NO_2(bpy))_3^{2+}$, Figure 2 shows that the asymmetry of substitution in $NO_2(bpy)$ splits the symmetric bipyridine ring vibrations. Unlike the spectrum of $Ru(Et_3P(bpy))_3^{5+}$, where the substituent is not vibronically coupled to the MLCT transition, however, the prominent feature of the $Ru(NO_2(bpy))_3^{2+}$ spectrum is the 1359-cm^{-1} vibration which, by analogy to nitro-substituted aromatics, is attributed to the nitro symmetric stretch. The striking resonance enhancement of this vibration indicates that a substantial portion of the charge transferred in the MLCT transition is associated with the NO_2 group[16,17,27] and is consistent with an electron-withdrawing substituent which is formally resonant with the bpy π system. The NO_2 vibration is also dependent on the solvent medium. Changing from water to ethanol shifts this vibration from 1359 to 1353 cm^{-1} but has no effect, $\Delta\nu \leq 1$ cm^{-1}, on the symmetric bipyridine vibrations of $Ru(NO_2(bpy))_3^{2+}$ or $Ru(Et_3P(bpy))_3^{5+}$ and $Ru(bpy)_3^{2+}$. In addition to being coupled to the MLCT transition, this 6-cm^{-1} shift indicates that the NO_2 symmetric stretch is also coupled to the solvent medium. Since this represents a mechanism by which the electronic excitation energy can be vibrationally dissipated to the solvent medium, the absence of a charge-transfer emission from $^*Ru(NO_2(bpy))_3^{2+}$ is attributed a rapid vibronic radiationless deactivation of the excited state.

The deactivating mode introduced by substituting NO_2 onto the 4-position of $Ru(bpy)_3^{2+}$ suggests an explanation for the difference in the reactions of the complex, $Ru(NO_2(bpy))_3^{2+}$, and the ligand, NO_2bpy. Both the complex and the free ligand undergo reactions in 95% ethanol which absorption and resonance Raman spectra indicate is a displacement of the NO_2 group. With the complex the reaction is not photochemical but is thermally activated. With the ligand, the inverse is true; the reaction is not thermal but is photochemically activated. The O_2 dependence and flash photolysis experiments point to a triplet as the photoactive state in NO_2bpy. On complexation to Ru^{2+}, however, the lowest energy excited state would most likely be the MLCT state. Previous experiments have shown that the spin–orbit coupling of Ru^{2+} induces an efficient relaxation of bipyridine π^* states to the lower energy MLCT state.[26,28] If this is also true in $Ru(NO_2(bpy))_3^{2+}$, then a photochemical reaction would not occur because of the deactivation of the MLCT state by NO_2 coupling with the solvent. On the other hand, Maerker and Case point out that in 4,4′-dinitro-2,2′-bipyridine 1,1′-dioxide nucleophilic displacement of NO_2 is facilitated by the electron-withdrawing effect of the *N*-oxide moiety.[29] Since the positive charge on the Ru(II) ion would exert an effect similar to the *N*-oxide moiety, we propose that the metal ion labilizes the NO_2 group. The Ru(II) ion appears to exert a stronger labilizing effect, however, since reaction observed in these experiments occurs with a weaker base, EtOH, as compared to OEt^-.

NO_2 and $P(Et)_3^+$ also convert bipyridine from a molecule which does not quench to molecules which quench $Ru(bpy)_3^{2+}$ with bimolecular quenching rate constants, k_q, comparable to those of transition-metal complexes. With 23 000 cm^{-1} taken as the energy of the lowest triplet state of bpy,[19] the shifts in the absorption maxima and the triplet maxima detected by flash photolysis are not large enough to suggest that the lowest triplet states of $NO_2(bpy)$ and $Et_3P(bpy)^+$ are less than the energy of $^*Ru(bpy)_3^{2+}$, 16 300 cm^{-1}. This apparent endothermicity suggests that energy-transfer quenching of $^*Ru(bpy)_3^{2+}$ and $^*Ru(Et_3P(bpy))_3^{5+}$ by $NO_2(bpy)$ and $Et_3P(bpy)$ is unlikely. Rather, the correlation between rate and the reduction potentials of $NO_2(bpy)$ and $Et_3P(bpy)^+$ indicates photoredox quenching[8]: reaction 1 where L and L^- represent

$$^*Ru(bpy)_3^{2+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(bpy)_3^{3+} + L^- \qquad (1)$$

$NO_2(bpy)$ and $Et_3P(bpy)^+$ and their one-electron reduction products. Although the absorption spectra of L^- are expected to resemble bpy^-,[22] neither L^- or $Ru(bpy)_3^{3+}$ is detected following flash photolysis. At least with $NO_2(bpy)$, the products of reaction 1 are attractive and product separation, which most likely is necessary for detection, may not be competitive with the rate of the reverse reaction. With the assumption that the lack of detection reflects the reverse reaction, the detection limits of this flash equipment requires that $k_{-1} \geq 5 \times 10^9$ M^{-1} s^{-1}. Although rapid, the value of k_{-1} is consistent with the rate constants of reactions between $Ru(bpy)_3^{3+}$ and cationic radical species.[2b] Consequently, the inability to detect the products of reaction 1 does not necessarily preclude photoredox quenching. Establishing photoredox quenching by these substituted bipyridines, however, is crucial to the energetic

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(25) Bolt, R. W.; Dowden, B. F.; Eaborn, C. *J. Chem. Soc.* **1965**, 4994.

(26) Hager, G. D.; Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7037.

(27) Nishimura, Y.; Hirakawa, A.; Tsuboi, M. *Adv. Infrared Raman Spectrosc.* **1978**, *5*, 217.

(28) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841.

(29) Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745.

feasibility of a mechanism which postulates electron transfer to the coordinated ligand.

When $Ru(Et_3P(bpy))_3^{5+}$ is the donor ion, $NO_2(bpy)$ quenches ($K_{SV} = (4.32 \pm 0.05) \times 10^2$ M^{-1}) but $Et_3P(bpy)^+$ does not ($K_{SV} \leq 20.4$ M^{-1}). The higher charge of the complex, 5+ as compared to 2+ for $Ru(bpy)_3^{2+}$, makes the electrostatic work (w_{12} in ref 30) required to bring the ions together larger. In view of the solution ionic strength, 1.0 M, and the rate constants for quenching by $Co(bpy)_3^{3+}$ and $Co(NO_2(bpy))_3^{3+}$, however, electrostatic repulsion cannot account for the absence of quenching. If the reduction potentials of these bipyridines listed in Table I parallel the reversible reduction potentials, then the lack of quenching of $^*Ru(Et_3P(bpy))_3^{5+}$ by $Et_3P(bpy)^+$ reflects the decrease in $^*E°$ of $^*Ru(Et_3P(bpy))_3^{5+}$ and the corresponding decrease in the quenching reaction driving force.

With 0.84 V as the oxidation potential of $^*Ru(bpy)_3^{2+}$ and the thermodynamic cycles described by Sutin,[8] the oxidation potentials and emission maxima listed in Table I yield

$$^*Ru(Et_3P(bpy))_3^{5+} \rightarrow Ru(Et_3P(bpy))_3^{6+} + e^- \qquad ^*E° = 0.48 \text{ V} \tag{2}$$

Although emission is not detected from either room-temperature or frozen solutions of $Ru(NO_2(bpy))_3^{2+}$, a weak emission is detected when the complex is ionically bound to a porous glass matrix. The emission, which has a maximum at 680 nm, appears in the background of the resonance Raman spectrum of the complex within the glass when excited at 514.5 nm. Since the visible spectrum and resonance Raman spectrum of the complex within the glass are identical with the fluid solution spectra, this maximum is taken as the energy of $^*Ru(NO_2(bpy))_3^{2+}$ in fluid solution. This energy and the oxidation potential listed in Table I yield

$$^*Ru(NO_2(bpy))_3^{2+} \rightarrow Ru(NO_2(bpy))_3^{3+} + e^- \qquad ^*E° = 0.42 \text{ V} \tag{3}$$

Although somewhat larger, the changes in $^*E°$ are consistent with the effect of strong electron-withdrawing substituents.[8]

The intent of these experiments, however, was to use these electron-withdrawing substituents to retard the rate of intramolecular electron transfer and allow detection of a chemical or radical mechanism. Although quenching by these substituted bipyridines indicates the energetic feasibility of a chemical mechanism, no direct evidence confirming a coordinated ligand radical anion was obtained in these flash photolysis experiments. Monitoring deaerated solutions containing 7.5×10^{-5} M $Ru(bpy)_3^{2+}$ and 10^{-3} M $Co(NO_2(bpy))_3^{3+}$ at 568 nm, the $Ru(bpy)_3^{2+/3+}$ isobestic point, gave no indication of a coordinated radical intermediate after flash photolysis. Similarily, when deaerated solutions containing 7.5×10^{-5} M $Ru(Et_3P(bpy))_3^{5+}$ and 10^{-3} M $Co(NO_2(bpy))_3^{3+}$ are exposed to a flash and analyzed at 600 nm, the $Ru(Et_3P(bpy))_3^{5+/6+}$ isobestic point, no indication of a coordinated ligand radical was detected.

For a series of pentaamminecobalt(III) complexes with 4,4′-bipyridine analogues, Haim and Leopold note that the similarity between the rate of quenching by the ligand and the corresponding Co(III) complex implicates the ligand in the electron-transfer pathway.[4] Although limited to $NO_2(bpy)$ and $Co(NO_2(bpy))_3^{3+}$, the quenching rate constants listed in Table II show that the rate of reactivity of the ligand is similar to that of the Co(III) complex. The similarity of the rates is suggestive of a chemical mechanism, but drawing a firm conclusion is tenuous given the absence of detection of the proposed radical intermediate.

A somewhat surprising result of these experiments, which may be related to the question of the orbital pathway for electron transfer, is that the rate of quenching of these Ru(II) complexes by $NO_2(bpy)$ is similar to the rate of quenching by $Co(bpy)_3^{3+}$, and approximately three to four times larger than the rate of quenching by $Co(NO_2(bpy))_3^{3+}$. The difference in the rates of quenching may be due to the differences in the charges of $NO_2(bpy)$ and the Co(III) complexes, but electrostatic repulsion cannot account for the difference in the rates of quenching by the Co(III) complexes. If a radical mechanism prevails in these quenching reactions, the rate of photoinduced electron transfer to $Co(NO_2(bpy))_3^{3+}$ is expected to be larger than the rate of transfer to $Co(bpy)_3^{3+}$. Furthermore, the nitro group increases the potential for oxidation of the isoelectronic Fe(II) and Ru(II) polypyridine complexes by ~0.3 V relative to the unsubstituted analogue.[9] With the assumption that a similar increase also occurs in the oxidation potential of $Co(NO_2(bpy))_3^{2+}$ relative to $Co(bpy)_3^{2+}$, the driving force of the $Ru(bpy)_3^{3+}$–$Co(NO_2(bpy))_3^{2+}$ back-reaction is less than the driving force of the $Ru(bpy)_3^{3+}$–$Co(bpy)_3^{2+}$ back-reaction. Yet, the absence of a transient absorbance characteristic of $Ru(bpy)_3^{3+}$ following flash photolysis suggests that the rate constant for the $Co(NO_2(bpy))_3^{2+}$–$Ru(bpy)_3^{3+}$ back-reaction must be $\geq 3 \times 10^9$ M^{-1} s^{-1}, which is approximately 1 order of magnitude larger than the rate constant of the $Co(bpy)_3^{2+}$–$Ru(bpy)_3^{3+}$ reaction. A full understanding of these rates and the effect of the nitro substituent will have to await further experiments.

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Registry No. $[Ru(NO_2(bpy))_3](ClO_4)_2$, 73891-48-2; $[Ru(Et_3P(bpy))_3](ClO_4)_5$, 73891-50-6; $Ru(bpy)_3^{2+}$, 15158-62-0; $Co(bpy)_3^{3+}$, 19052-39-2; $Co(NO_2(bpy))_3^{3+}$, 80105-99-3; $Fe(H_2O)_6^{3+}$, 15377-81-8; bpy, 366-18-7; $Et_3P(bpy)^+$, 80105-69-7; $NO_2(bpy)$, 31860-68-1; $Ru(4\text{-}EtO\text{-}bpy)_3^{2+}$, 80106-00-9.

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(30) Haim, A.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 476.

(31) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190.