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Cyclometalated Complexes of Ruthenium. 3. Spectral, Electrochemical, and Two-Dimensional Proton NMR of $[Ru(bpy)_2(\text{cyclometalating ligand})]^+$

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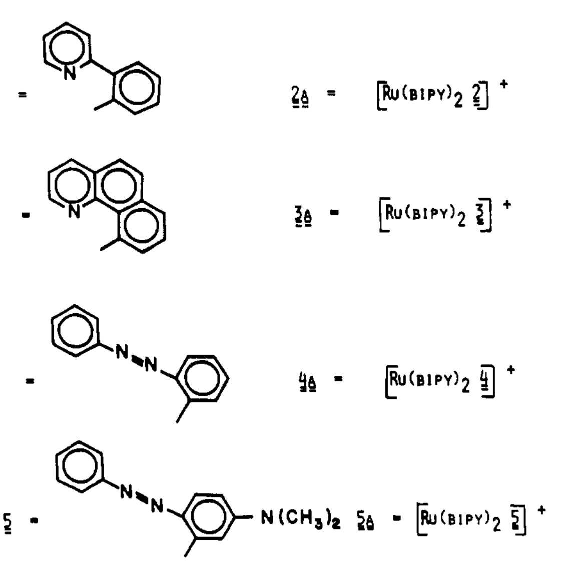
Cyclometalated complexes of ruthenium(II), $[Ru(bpy)_2(L)]^+$, where L = 2-(3-nitrophenyl)pyridine, phenylpyridine, benzo[*h*]quinoline, azobenzene, and *p*-(dimethylamino)azobenzene, have been prepared and characterized by two-dimensional proton NMR (HDCOSY) spectra and by cyclic voltammetry. Excited-state behavior of the complexes of the first three listed ligands has been investigated by absorption and emission spectroscopy and the photochemical stability of these species monitored. A substantial decrease is found in oxidation potential (the oxidations are metal-centered, with the electron coming from a t_2 orbital) in going from a dication (e.g. $[Ru(bpy)_3]^{2+}$) containing bidentate nitrogen donors only to our monocation containing a cyclometalated anion. This decrease undoubtedly results from both the ion charge decrease and the replacement of a σ-donor/π-acceptor nitrogen by a much stronger σ-donor carbanion. The one-electron reduction of $[Ru(bpy)_3]^{2+}$ results in $[Ru(bpy)_2(bpy^-)]^+$. The subsequent reduction of this (unstable) species may be compared to the *first* reduction of our monocation species, as the presence of the cyclometalating anion shifts the reduction potential (of a coordinated bpy) to a more negative value than that caused by the negative diimine anion formed in the first reduction step of $[Ru(bpy)_3]^{2+}$. Absorption bands of our new species found in the visible region (450–550 nm) are assigned as metal-to-ligand transitions (MLCT), the lower energy one associated with the bpy ligand and the higher energy one associated with the carbon-bonded anion. All three complexes emit in a glass at 77 K, the emission apparently primarily from the MCLT excited triplet associated with the bpy ligand. Temperature dependence of the emission intensities and lifetimes is discussed as is evidence for photoanation or very rapid nonradiative decay for different species.

Introduction

In previous papers we have reported the preparation and two-dimensional proton NMR study[1] of a cyclometalated complex of ruthenium(II), **1a**, its unique spectral and electrochemical properties, and its X-ray structure.[2] Now, in addition to the cyclometalating ligand **1**, the cyclometalating ligands **2–5** have yielded ruthenium(II) complex cations **2a–5a**. We report here their preparation, spectral and electrochemical properties, and two-dimensional proton NMR spectra. These examples of a new type of d^6 complex, containing both polypyridine and cyclometalating aromatics, are of interest because of their significant photophysics and photochemistry and since they contribute to our knowledge and understanding of the purely polypyridine complexes.



Experimental Section

A. Preparation of Compounds. $[Ru(bpy)_2(1)]BF_4 \cdot {}^1/_2CH_2Cl_2$, (4-Nitro-2-(2-pyridyl)phenyl)bis(2,2′-bipyridine)ruthenium(II) Tetrafluoroborate (1a). This complex was prepared in low yield (ca. 10%) by a previously described procedure.[1] The perchlorate salt of this complex ion was also prepared by an analogous procedure using bis(acetone)bis(2,2′-bipyridine)ruthenium(II) perchlorate as starting material.

$[Ru(bpy)_2(2)]PF_6 \cdot {}^1/_2CH_2Cl_2$, (2-(2-Pyridyl)phenyl)bis(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate (2a). This complex was prepared from $[Ru(bpy)_2(MeOCH_2CH_2OMe)](PF_6)_2$ (20 mL, 5.0 × 10^{-2} M) (which was prepared according to the procedure of Connor, Meyer, and Sullivan[3]) and 2-phenylpyridine (308 mg, 1.98 mmol) by stirring and refluxing these materials in dimethoxyethane solution under dry nitrogen for 3 h. Then, triethylamine was added and the mixture refluxed for another 36 h. The solvent was removed by rotary evaporation and the product chromatographed on an alumina column. Elution with 1:1 acetonitrile/toluene yielded unreacted ligand first. The first intense dark reddish band contained the desired product, which was recrystallized from dichloromethane/ether, washed with ether, and dried in vacuo (yield 9%). Anal. Calcd for $[RuC_{31}H_{24}N_5]PF_6 \cdot {}^1/_2CH_2Cl_2$: C, 50.12; H, 3.34; N, 9.28. Found: C, 51.66; H, 3.36; N, 9.57.

$[Ru(bpy)_2(3)]PF_6 \cdot {}^1/_2CH_2Cl_2$, (Benzo[*h*]quinolin-10-yl)bis(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate (3a). This complex was prepared (in low yield, 8%) from the ligand benzo[*h*]quinoline and the same starting ruthenium complex as for **2a**, by following the same procedure as described for **2a**. Anal. Calcd for $[RuC_{33}H_{24}N_5]PF_6 \cdot {}^1/_2CH_2Cl_2$: C, 51.66; H, 3.36; N, 8.99. Found: C, 51.42; H, 3.21; N, 8.83.

$[Ru(bpy)_2(4)PF_6] \cdot {}^1/_2CH_2Cl_2$, (2-(Phenylazo)phenyl)bis(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate (4a). This compound was prepared (in low yield, 7%) from the ligand azobenzene and the same starting ruthenium compound as for **2a** by following the same procedure as described for **2a**. Anal. Calcd for $[RuC_{32}H_{25}N_6]PF_6 \cdot {}^1/_2CH_2Cl_2$: C, 49.92; H, 3.48; N, 10.75. Found: C, 50.83; H, 3.48; N, 10.96.

$[Ru(bpy)_2(5)]PF_6 \cdot {}^1/_2CH_2$, (5-(Dimethylamino)-2-(phenylazo)phenyl)bis(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate (5a). This compound was also prepared (in low yield, 7%) from the ligand *p*-(dimethylamino)azobenzene and the same starting ruthenium compound as for **2a**, by using the same procedure as described for **2a**. Anal. Calcd for $[RuC_{34}H_{30}N_7]PF_9 \cdot {}^1/_2CH_2Cl_2$: C, 50.23; H, 3.92; N, 11.89. Found: C, 51.29; H, 3.98; N, 11.88. The evidence, from NMR results, that the phenyl ring bearing the dimethylamino group is the ring attached by an aromatic carbon to the ruthenium will be detailed in the section dealing with NMR results.

B. NMR Experiments. The homodecoupled COSY (HDCOSY) spectra were acquired with 2048 × 512 data matrices resulting in 1024 × 1024 transforms after zero-filling in F1 and with the absolute-value spectra. Spectra were acquired by using a 1024-Hz spectral window.

The HDCOSY experiment uses a 180° refocusing pulse between the preparation and mixing pulses to produce a spectrum in which the ho-

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monuclear coupling is collapsed in the F1 domain. There is a fixed delay between the preparation and mixing pulses set to half the normal acquisition time. The refocusing pulse follows an incremented delay. A 45° mixing pulse is necessary, and the 180° refocusing pulse must be carefully calibrated. All three pulses and the receiver reference phase are cycled so that only the coherence-transfer echo is detected. A Gaussian window function was used in both domains.

All spectra were taken in Me_2SO-d_6 on a sample prepared by dissolving 20 mg of the compound in 0.5 mL of 100 atom% Me_2SO-d_6. Spectra were acquired at 400.133 MHz on a Bruker WH-400 spectrometer.

C. Electrochemistry. Electrochemical measurements were made on dilute (5×10^{-4} M) dichloromethane solutions (0.1 M in tetrabutylammonium perchlorate, TBAP, supporting electrolyte) by using a three-electrode system. A platinum-wire working electrode and counter electrode were used, along with a pseudoreference electrode of silver-wire–dichloromethane solution that is 0.1 M in TBAP.[4] The potentials of the pseudoreference electrode vs. the saturated sodium chloride calomel electrode (SCE) were measured at the end of each run. The reason for using the silver-wire pseudoreference was to avoid contamination of the main body of the electrolyte with water from an SCE electrode or other contaminants. The waveform generators and potentiostats for the cyclic voltammetry experiments were a Pine Instrument Company, Model RDE for slower scan rates and a Princeton Applied Research Model 174A polarographic analyzer for fast scans. Cyclic voltammograms were recorded on a Hewlett-Packard Model 7044A X-Y recorder.

D. Absorption and Emission Spectra. Absorption spectra were recorded on a Cary 14 spectrometer. The emission spectra were recorded on an SLM-4800S spectrofluorometer and are corrected for photomultiplier response. The relative emission intensities were determined for each sample in a 6 mm i.d. Pyrex tube after several freeze/pump/thaw degassing cycles. The temperature was maintained by adjusting the flow of precooled nitrogen gas. The sample temperature was monitored with a copper/constantan thermocouple.

The relative quantum yields were converted into absolute quantum yields by using $Ru(bpy)_3^{2+}$ as the standard. The lifetime of $Ru(bpy)_3^{2+}$ over the temperature range of 77–250 K has been evaluated.[5] The emission quantum yield for this complex was then determined at 120 K from the lifetime and radiative rate constant. This procedure may introduce some systematic error so that quantitative arguments are best based upon the temperature dependence of the emission lifetime.

E. Photochemistry. The photoanation progress was monitored by absorption spectroscopy with a Cary 14 spectrometer. A locally constructed cell holder allowed for sample stirring, temperature control, and right-angle irradiation. The sample temperature was maintained at 23 ± 1 °C as measured by a copper/constantan thermocouple.

Results and Discussion

NMR. The detailed analysis of the 2D HDCOSY spectrum for $[Ru(bpy)_2(\mathbf{1})]^+$ has already been published,[1] and assignments of all 23 protons were made for this complex. In a similar way the 2D HDCOSY spectra of the other four cyclometalated compounds reported herein were analyzed and, with the aid of several independent decoupling experiments, all proton assignments made. These specific assignments are available elsewhere.[6]

The aryl protons of the cyclometalating ligand 2-phenylpyridine in $[Ru(bpy)_2(\mathbf{2})]^+$ are shifted strongly upfield when compared to the corresponding protons in $[Ru(bpy)_2(\mathbf{1})]^+$, where the nitro derivative is the ligand. This is expected, as the electron-withdrawing nitro group deshields the aryl ring. The 24 protons in the benzo[*h*]quinoline complex, $[Ru(bpy)_2(\mathbf{3})]^+$, have all been assigned assuming a similar geometry to that found[1,2] for $[Ru(bpy)_2(\mathbf{1})]^+$. All 25 protons in the azobenzene complex cation $[Ru(bpy)_2(\mathbf{4})]^+$ have been separately assigned, since it turns out that it is possible to distinguish between protons in the phenyl group that is supposedly "free to rotate". However, since these "free" phenyl protons are distinguishable, it does suggest that there is some preferred conformation of this group in the molecule. No temperature-dependent studies were made, however, to support this idea.

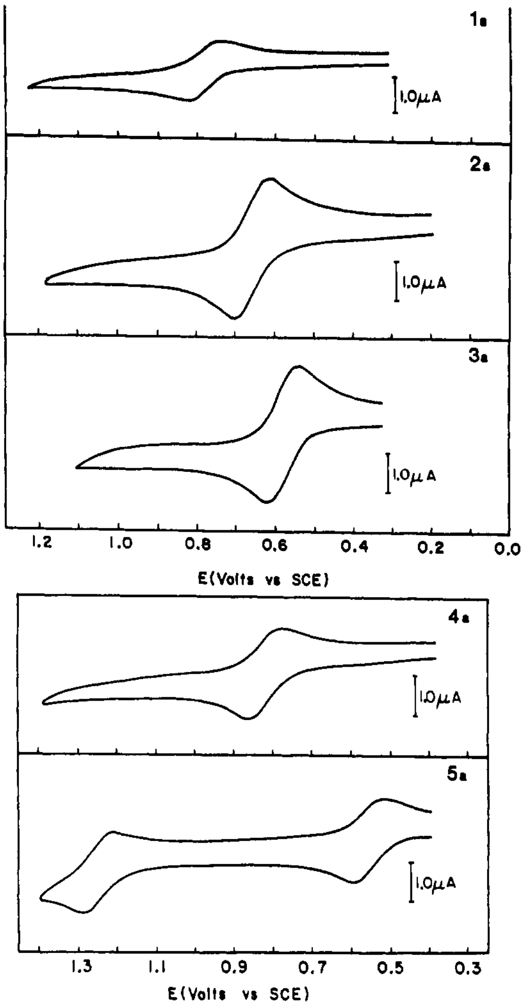

Figure 1. Cyclic voltammograms of the five indicated complexes in dichloromethane (0.1 M TBAP).

On the other hand, with the complex containing the *p*-(dimethylamino)azobenzene, $[Ru(bpy)_2(\mathbf{5})]^+$, the peaks appearing between 6.8 and 7.0 ppm are all coupled to themselves and integration of these peaks corresponds to five protons. Thus, the free phenyl group appears in this molecule to actually be in free rotation and it is clear from the NMR spectrum that the Ru–C bond comes from the substituted phenyl ring. The other prominent feature of the NMR spectrum is a substantial upfield shift of the aryl protons in the cyclometallated ring. This shift is expected owing to the presence of the strongly electron-donating dimethylamino group.

Electrochemistry. Cyclic voltammograms for the oxidation of **1a**–**5a** in dichloromethane containing 0.1 M TBAP as supporting electrolyte are presented in Figure 1. Reversible (at least quasi-reversible) one-electron oxidation for all the complexes were observed within the electrochemical window (voltage range) of the solvent used. The $E_{1/2}$ values (vs. SCE) for the oxidations, tabulated in Table I, were deduced by averaging peak potentials for the oxidation and reduction waves. The sweep rate was varied between 100 and 200 mV/s without significant change in ΔE_p ($=E_p(\mathrm{ox}) - E_p(\mathrm{red})$), which is approximately 70 mV for most of the voltammograms. In contrast to oxidations, irreversible and quasi-reversible behavior was observed in the cyclic voltammograms for reductions, and E_{peak} values are presented in Table I. Full characterization of the irreversible reduction waves was not attempted. In general, reductions occur at very negative voltages, and in our solvent and supporting electrolyte (0.1 M TBAP) it was possible to observe only one reduction wave for compounds **1a**, **2a**, and **3a** and two reduction waves for compounds **4a** and **5a** (Table I). For comparison purposes, the potentials for several

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Table I. Oxidation–Reduction Potentials of the Cyclometalated Ruthenium Complexes and Selected Diimine Analogues (Scan Rate 200 mV s^{-1})

no.	complex	$E_{1/2}$(ox) vs. SCE, V	E_{peak}(red) vs. SCE, V
1a	$[\text{Ru(bpy)}_2(\mathbf{1})]^+$	0.78	−1.23
2a	$[\text{Ru(bpy)}_2(\mathbf{2})]^+$	0.66	−1.65
3a	$[\text{Ru(bpy)}_2(\mathbf{3})]^+$	0.58	−1.57
4a	$[\text{Ru(bpy)}_2(\mathbf{4})]^+$	0.82	(−1.32)[b]; −1.56[c]
5a	$[\text{Ru(bpy)}_2(\mathbf{5})]^+$	0.56; 1.25[a]	(−1.42)[b]; −1.58[c]
6	$[\text{Ru(bpy)}_3]^{2+}$[d]	1.354	−1.332; −1.517; −1.764
7	$[\text{Ru(bpy)}_2(4'\text{-NO}_2\text{-bpy})]^{2+}$[e]	1.365	(0.56)[i]; −1.17; 1.53
8	$[\text{Ru(bpy)}_2\text{Cl}_2]$[f]	0.31	
9	$[\text{Ru(bpy)}_2\text{pyCl}]^+$[g]	0.77	
10	$[\text{Ru(bpy)}_2(\text{2-arylazopy})]^{2+}$[h]	1.603	(−0.520); −1.258

[a] Most likely the oxidation of ligand **5**, containing the electron-donating dimethylamino group. [b] These values most likely represent the reduction of the azo group. [c] $\Delta E_p \sim 140$ and 170 mV, for these second, quasi-reversible reductions, respectively. [d] In CH_3CN, 0.1 M (TBA)BF_4; ref 4. [e] In CH_3CN, 0.1 M TBAP; ref 8. [f] In CH_3CN, 0.1 M TEAP; ref 9. [g] In CH_3CN, 0.1 M (TBA)PF_6; ref 10. [h] In CH_3CN, 0.1 M TEAP; ref 11. [i] The reduction of the nitro group.

Table II. LUMO's of the Ligands and Their Anions Calculated by CNDO/S Molecular Orbital Calculations[6]

ligand	LUMO, eV	ligand	LUMO, eV
bpy	−1.205	$\mathbf{3}^-$	+1.696
1	−1.893	**4**	−0.377;[a] −1.463
$\mathbf{1}^-$	+1.793	$\mathbf{4}^-$	+1.598
2	−1.220	**5**	−1.524
$\mathbf{2}^-$	+2.387	$\mathbf{5}^-$	+1.677
3	−1.533		

[a] Localized principally in the azo group.

diimine ruthenium analogues of the cyclometalated complexes also are given in Table I.

The substantial decrease in the oxidation potential on going from a dication (containing bidentate nitrogen donors only) to our monocation (containing one cyclometalated anion) undoubtedly results from both the decrease in positive charge on the ion and the replacement of a π-acceptor nitrogen by a much stronger σ-donor carbanion. The oxidations are metal-centered, the electron being removed from a metal t_2 orbital, and therefore the lowered oxidation potentials observed in our compounds are expected on the basis of the destabilization of the t_2 orbitals. Furthermore, the relative σ-donor strengths of the cyclometalated ligands should be reflected in these oxidation potentials. This leads to the order of ligands, based on their ability to destabilize t_2 electrons, **5** > **3** > **2** > **1** > **4** (see Table I and note that the oxidation at 1.25 V for **5a** is attributed to the oxidation of ligand **5**, which possesses the electron-donating dimethylamino group). It is not surprising that the oxidation potential value for the noncyclometalated monocation $[\text{Ru(bpy)}_2\text{py(Cl)}]^+$, of 0.77 V, fits better with the values for our monocations and would place the chloride ion just about equal to ligand **1** in its ability to destabilize t_2 electrons.

Whereas the oxidations are metal-centered, based on the electronic spectra of the complexes as well as the calculations, the observed reductions most probably are ligand-centered. For the cyclometalating ligands the LUMO's are expected, both from CNDO/S molecular orbital calculations (Table II) (detailed elsewhere[6]) and from $\pi^* \leftarrow \pi$ transitions observed (vide infra) in the UV region, to be at higher energies than for 2,2′-bipyridine. For the free 2,2′-bipyridine, two reductions, at -2.21 and -2.46 V (CH_3CN, 0.1 M TEAP vs. SCE), are observed.[7] That is, there is one electrochemically accessible LUMO giving rise to the two successive reductions. Therefore, the reduction potentials for the cyclometalating ligands should be even more negative, and we could not observe them in our solvent with its approximate +1.7 to −1.7 V electrochemical window. Now when any of the ligands coordinate to the metal, thereby shifting some of their electron density onto the metal, their reduction potentials must shift to more positive values. Thus, for $[\text{Ru(bpy)}_3]^{2+}$ the values −1.33, −1.52, and −1.76 V (Table I) have been observed,[4] where the first value represents the reduction

$$[\text{Ru(bpy)}_3]^{2+} + e^- \rightleftarrows [\text{Ru(bpy)}_2(\text{bpy}^-)]^+$$

Since only one reduction potential is found for each of the cyclometalated species **1**–**3** in our observation range, it most likely represents the reduction

$$[\text{Ru(bpy)}_2(\text{L})]^+ + e^- \rightarrow [\text{Ru(bpy)(bpy}^-)\text{L}] \qquad (1)$$

Since the cyclometalated complexes and their analogous diimine complexes differ by one charge unit, it is more appropriate to contrast the reduction potential values for $[\text{Ru(bpy)}_2(\text{L})]^+$ with the *second* reduction potential value (of −1.52 V)[2] for $[\text{Ru(bpy)}_3]^{2+}$, which represents the reduction

$$[\text{Ru(bpy)}_2(\text{bpy}^-)] + e^- \rightarrow [\text{Ru(bpy)(bpy}^-)_2] \qquad (2)$$

That is, reductions 1 and 2 should be comparable, and the observed reduction potentials (Table I) bear this out. Furthermore, the data from Table I allow a comparison of reduction potentials in analogous complexes $[\text{Ru(bpy)}_2(\text{diimine})]^{2+}$ and $[\text{Ru(bpy)}_2(\text{l})]^+$, where the three diimine ligands and three cyclometalating ligands are analogues. Thus, the dications **6**, **7**, and **10** have their cyclometalated monocation counterparts in compounds **2**, **1**, and **4**, respectively (see Table I). As we go from dication to monocation (i.e. from diimne to cyclometalated ligand), the reduction potential values go from −1.52 to −1.65, from −1.17 to −1.23, and from −1.26 to −1.56 V, respectively. In other words, the presence of the cyclometalating anion shifts the reduction potential of a coordinated bpy ligand to a more negative value than does the presence of a negative diimine anion (formed in the first reduction step). This is not unexpected since the inductive effect of the carbanion on the other 2,2′-bipyridine ligands is more localized and direct (the σ bond is stronger) than that of a bipyridine anion. However, one should be cautious in comparing potential values of reversible waves with an irreversible system because the causes of irreversibility are not known.

Finally, it must be stated that the foregoing electrochemical studies have been preliminary and not definitive. Because the causes of slow kinetics are not known, there is no theoretical basis for correlations between irreversible waves and spectroscopic knowledge. Nevertheless, it is possible to address the question of how electron transfer occurs, to the metal or ligand, if electrochemical data is used to support conclusions based on electronic spectra and CNDO/S MO calculations.

Excited-State Behavior. Several bands are apparent in the absorption spectra of **1a**–**3a**. Those bands occurring in the 250–320-nm region may be reasonably assigned as intraligand transitions due to their similarity to those in the absorption spectra of the free ligands.

The bands occurring in the visible region (450–550 nm) are assigned as metal-to-ligand charge-transfer transitions (MLCT). This assignment is based upon the large extinction coefficients related to these transitions and their similarity to MLCT transitions in related Ru(II) complexes.[11] The energetics of MLCT transitions are best discussed in terms of the relative energies of the metal-centered t_2 orbital and the π^* orbital of the ligands.

For **2a**, two intense absorptions are observed at 550 and 495 nm (Figure 2). The former band can be assigned as an MLCT transition associated with the bpy ligands. The large bathochromic shift of this absorption band (relative to that of Ru(bpy)_3^{2+}) is

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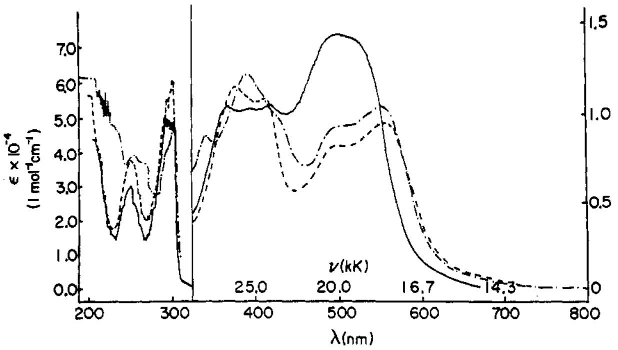

Figure 2. UV–visible absorption spectra of $[Ru(bpy)_2(\mathbf{1})]^+$ (—), $[Ru(bpy)_2(\mathbf{2})]^+$ (---), and $[Ru(bpy)_2(\mathbf{3})]^+$ (-··-) in methanol solutions at room temperature.

related to the much lower oxidation potential of the t_2 d electrons (Table I). This dramatic lowering of the oxidation potential is due, as explained above, to the increased electron density around the metal atom as the nitrogen-bonded neutral ligand is replaced by a carbon-bonded anion. The second band, located at 495 nm, is also assigned as an MLCT transition but now associated with the phenylpyridine ligand. The hypsochromic shift is related to the higher reduction potential of this ligand relative to that of bpy (vide supra).

The introduction of a nitro substituent has two effects: the electron density around the metal atom decreases and the phenylpyridine ligand becomes a much better π acceptor, i.e. has a lower π^* orbital. The decreased electron density stabilizes the t_2 metal-centered orbitals, which is confirmed by the increased oxidation potential. This induces a hypsochromic shift in the MLCT associated with the bpy ligands. On the basis of the oxidation potentials, the hypsochromic shift is expected to be 40–50 nm, in agreement with the spectra.

For the MLCT transition associated with the phenylpyridine ligand, both effects are important and tend to offset one another. A hypsochromic shift is expected due to the stabilization of the t_2 orbitals. However, the lower reduction potential of the ligand due to the presence of the nitro substituent offsets the expected hypsochromic shift. The end result is little variation in the wavelength maximum of this transition, so that both MLCT transitions (associated with bpy and **1** + H) occur at nearly identical energies.

All three complexes emit in a glass (4:1 EtOH/MeOH) at 77 K. The emission appears to be primarily from the MLCT excited triplet state associated with the bpy ligand. Certainly, in the cases of **2a** and **3a**, the substantial bathochromic shift in this emission (relative to that of either $Ru(bpy)_3^{2+}$ or **1a**) dictates this assignment. In the case of **1a**, the emitting state could be assigned as an MLCT state associated with either bpy or **1** + H. However, on the basis of the previous two examples, the emission is most likely to be from the bpy MLCT excited state.

The temperature dependence of the emission intensity and lifetime was evaluated in an EtOH/MeOH (4:1) solution. The results for **1a** have been reported previously,[2] and the pertinent results are reproduced in Table III. Unfortunately, the emission from either **2a** or **3a** was too weak for a similar analysis. Indeed, both complexes displayed emission only below 140 K, indicating a very small activation energy for one or more nonradiative processes.

Table III. Comparison of Photophysical Properties of $[Ru(bpy)_2(\mathbf{1})]^+$ and $[Ru(bpy)_3]^{2+}$

	$[Ru(bpy)_2(\mathbf{1})]^+$		$[Ru(bpy)_3]^{2+\,a}$	
abs max, nm	495^b		452	
emission				
λ_{max}, nm	682^c		583	
τ, ns	878		5200	
temp dependence	L^d	Q^d	L^d	Q^d
$k^{c\,e}$	1.2×10^6	1.2×10^{-1}	3.9×10^5	7.9
$k^c{}_0{}^e$	2.6×10^{11}	6.7×10^6	1.9×10^{14}	1.6×10^9
ΔE, cm^{-1}	956	1404	3859	3951

[a] Much of this data has been reported previously (see ref 1 of our previous paper[2]), but the reported values were evaluated as a check on procedures. These values agree with those in the literature. [b] In methanol, room temperature. [c] In 4:1, ethanol/methanol at 77 K. [d] L = based upon lifetime measurements; Q = based upon intensity measurements. [e] Units: L, s^{-1}; Q, unitless.

The temperature dependence of the emission intensity and lifetime for **1a** clearly indicates thermal population of a higher lying state that results in a very rapid nonradiative decay. For $Ru(bpy)_3^{2+}$, a similar behavior has been noted and ascribed to thermal population of a ligand field state.[12] Indeed, population of this state results in a photoanation reaction. In contrast, no photoanation of **1a** accompanies population of the higher lying state. Furthermore, simple ligand field arguments indicate that **1a** should have a ligand field state at substantially higher energies than that of $Ru(bpy)_3^{2+}$. Consequently, this higher state has been assigned as an MLCT state with substantial singlet character.[2] Recently, Meyer and co-workers have suggested such an MLCT should indeed exist and would provide a mechanism for rapid decay of the triplet MLCT excited state.[13]

For **2a** and **3a**, no qualitative results are available, but certainly both excited species undergo very rapid nonradiative decay above 140 K. This indicates a small barrier for this decay process. These two complexes are also completely photostable in CH_2Cl_2 (0.01 M tetrabutylammonium chloride). Under these conditions, $Ru(bpy)_3^{2+}$ undergoes photoanation with a quantum yield of 0.03. Thus, the qualitative behavior is similar to that of **1a**, and we suggest that the rapid nonradiative decay is due to thermal population of a higher lying MLCT state containing substantial singlet character. The major difference between **1a** and **2a** or **3a** is the small activation barrier for population of this state. At present, the factors responsible for this lower barrier are unknown.

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Registry No. (**1a**)(BF_4), 101810-31-5; (**2a**)(PF_6), 101810-32-6; (**3a**)(PF_6), 101810-33-7; (**4a**)(PF_6), 101810-35-9; (**5a**)(PF_6), 101810-37-1; $[Ru(bpy)_2(MeOCH_2CH_2OMe)](PF_6)_2$, 69365-50-0.

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