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Photochemistry of Hetero-Tris-Chelated Ruthenium(II) Polypyridine Complexes in Dichloromethane†

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The results of an investigation of the photochemical and photophysical properties of a series of complexes of the type $[RuL_2L']Cl_2$ are reported, where L and L′ are bipyridine, phenanthroline, and methyl and phenyl derivatives of those ligands. All measurements were conducted in CH_2Cl_2. Luminescence lifetime and quantum yield data indicate that the ligand which accepts the electron in the localized MLCT excited state plays a significant role in the excited-state decay. HPLC analysis of the organic photoproducts from mixed-ligand complexes shows that flexible bipyridyl ligands are preferentially photolabilized, consistent with a dissociative mechanism involving an open-ended bipyridine in the transition state.

Introduction

The tris(bipyridyl)ruthenium(II) ion has played a role in a wide variety of photophysical and photochemical investigations over the past two decades. Those investigations have been the subject of a number of recent reviews.[2-9] Furthermore, $[Ru(bpy)_3]^{2+}$ continues to be utilized as an excited-state redox reagent,[10] as a probe of microheterogeneous environments,[11] and as a photomediator in various solar energy conversion schemes.[12] While taking advantage of the various desirable exicted-state properties of $[Ru(bpy)_3]^{2+}$, many workers have seen fit to ignore the fact that the compound undergoes photodecomposition in water,[13-15] albeit slowly ($\phi = 0.003$ in 0.1 M HCl at 70 °C).[14]

While it is true that studies utilizing $[Ru(bpy)_3]^{2+}$ have added considerably to our fundamental knowledge of excited-state energy-transfer and electron-transfer processes and that $[Ru(bpy)_3]^{2+}$ has served well as a model compound in solar energy conversion schemes, the inherent photolability of $[Ru(bpy)_3]^{2+}$ is a drawback in certain applications. The problem is most severe in applications involving $[Ru(bpy)_3]^{2+}$ as a mediator for solar energy conversion, since the necessity to replenish $[Ru(bpy)_3]^{2+}$ could render such schemes unattractive for economical and technical reasons.

We have undertaken a study of the effect of ligand substituents on the excited-state properties of a series of $[Ru(diimine)_3]^{2+}$ complexes. Our goal was to design a more robust complex while retaining the desirable photoredox properties that have stimulated so much interest in the past. In the process we have also demonstrated once again that, in addition to minimizing photodecomposition, ligand modifications provide the opportunity to "tune" the excited-state properties—energy, lifetime, and decay mode—to optimize the desired processes and to minimize the undesirable energy-wasting and resource-wasting processes. Although the primary aim of our work was to design a complex that would be more inert to photodecomposition than is $[Ru(bpy)_3]^{2+}$, our results also provide a number of examples of the effects of ligand substituents on the photophysics as well as on the photochemistry of $[Ru(diimine)_3]^{2+}$ complexes.

We have used CH_2Cl_2 exclusively as the solvent for the work reported herein. Previous reports[13,14,16-19] have documented that the photochemical decomposition of $[Ru(bpy)_3]^{2+}$ in dichloromethane is more facile ($\phi = 0.07$–0.10 at 25 °C)[16,19] than it is in water ($\phi < 10^{-5}$ at 25 °C).[14] Furthermore, the reaction is "cleaner" in CH_2Cl_2 than it is in H_2O, occurring with good isosbestic points throughout the course of the reaction in CH_2Cl_2,[16-18] whereas a long-lived intermediate is observed in dilute aqueous acid.[13-15] Isosbestic points have been reported[20] for photolysis in 2 M aqueous acid, but the quantum yield remains small.

Experimental Section

Materials. Reagent grade chemicals were used in all synthetic work. The solvents used in all photochemical and photophysical experiments and as HPLC mobile phases were all Omnisolve grade supplied by MCB.

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Photochemical quantum yields and luminescence lifetimes and quantum yields were determined for solutions that were deoxygenated by bubbling with chromous-scrubbed, dried argon; the solutions were thermostated at 25 °C and were magnetically stirred. A few lifetime determinations were performed with CH_2Cl_2 that had been distilled under argon from calcium hydride, stored in vacuo over 3A molecular sieves, and vacuum-transferred to the sample cell and freeze–pump–thaw-degassed just prior to use. Results obtained with solvent purified in this manner were indistinguishable from data obtained with argon-saturated Omnisolve grade solvent taken directly from the bottle.

Synthesis of *cis*-RuL_2Cl_2. In order to prepare the mixed-ligand complexes, the appropriate *cis*-dichlorobis(diimine)ruthenium(II) precursors were synthesized by an adaptation of the method of Bosnich and Dwyer.[21] In each case the *cis*-RuL_2Cl_2 complex was synthesized by preparing a mixture of 55 mmol of the appropriate diimine ligand (G. F. Smith Chemical Co.) and 30 mmol of $RuCl_3 \cdot 3H_2O$ (Alfa) in 250 mL of DMF. (The 8% deficiency of ligand vis a vis the stoichiometric 2:1 mole ratio minimizes formation of $[RuL_3]^{2+}$ at this stage.) This mixture was refluxed for 1.5 h and then transferred to a beaker and heated for about 2 h until the volume was reduced to 90 mL. Then 250 mL of acetone was added and the mixture was cooled in an ice bath. The resulting dark purple microcrystals were collected by filtration, and a second crop was collected after placing the mother liquor in the freezer overnight. The crude crystals were washed with water and recrystallized by dissolving them in 1200 mL of 50% ethanol/water, adding 112 g of LiCl, reducing the volume until the boiling point reached 96 °C (approximately 650 mL), cooling slowly to room temperature, filtering, washing with H_2O, and drying in vacuo at room temperature. Yield: 55–60%.

Synthesis of $[RuL_2L']Cl_2$. Samples of the mixed-ligand complexes, $[RuL_2L']Cl_2$, were prepared in a manner similar to that described by Crosby and Elfring.[22] A mixture of 1 mmol of RuL_2Cl_2 and 1.2 mmol of the appropriate ligand, L′, was refluxed overnight in 75 mL of 75% ethanol/water. The resulting red-orange mixture was rotary-evaporated, washed with ether to remove excess ligand, and dissolved in 10 mL of hot methanol, and the new mixture was filtered. The insoluble dark purple residue (probably unreacted RuL_2Cl_2) was discarded, and the methanol solution was further purified by chromatography on a Sephadex LH-20 column with methanol as the eluent. The orange band was collected, and the solvent was rotary-evaporated. The resulting solid was dissolved in 5 mL of hot H_2O, a few drops of saturated LiCl were added, and the mixture was refrigerated overnight. Orange crystals were then collected by filtration, washed with cold water, and dried in vacuo at room temperature. The constitution of the mixed-ligand complexes was verified by proton NMR spectroscopy (JEOL Model FX-90Q).

Luminescence. Luminescence spectra were recorded on an SLM Model 8000 spectrofluorometer. The spectra were corrected for variation in instrument response as a function of wavelength. Luminescence quantum yields (442-nm excitation) were determined by the modified Parker–Rees method[23] using an aqueous solution of $[Ru(bpy)_3]Cl_2$ as a reference with a quantum yield of 0.042.[13]

Photolysis. A helium–cadmium laser (Liconix Model 4240) with a nominal continuous output of 40 mW at 442 nm was used as a photolysis source. The incident laser intensity was measured daily by ferrioxalate actinometry.[24] Photochemical quantum yields were determined for optically dilute (ca. 10^{-5} M) solutions by directing the laser beam into the sample compartment of the SLM spectrofluorometer and utilizing the SLM emission optics to monitor the disappearance of the luminescence of the starting material with time during the course of the photolysis.[14]

Lifetimes. Luminescence lifetimes were determined by using the 337-nm output of a pulsed nitrogen laser (Laser Science, Inc., Model VSL-337) as the excitation source. The emission optics of the SLM spectrofluorometer were used to monitor the luminescence decay of the sample following each laser pulse, with the output of the photomultiplier fed into a Stanford Research Systems gated boxcar integrator through a 50-Ω terminating resistor. The resulting signal-averaged decay curves were fit to a single exponential with the use of software provided by SRS.

Photoproduct Analysis. HPLC analysis was used to characterize the organic photoproducts from hetero-tris-chelated samples. A 25–30-mg sample of the desired mixed-ligand complex was dissolved in 50 mL of CH_2Cl_2 in a capped 100-mL Ehrlenmeyer flask. This solution was photolyzed exhaustively at room temperature with the He–Cd laser. Typically this photolysis required a few hours, but the actual reaction time varied considerably depending on the photolability of each sample (see Table I). The progress of the reaction was monitored by visually noting the penetration depth of the laser beam. The optical density of the starting solution at the irradiation wavelength (442 nm) was much larger than that of the photoproducts, so the laser beam penetrated only about 1 mm initially, whereas it could be seen to penetrate several centimeters as the reaction went to completion. The reaction mixture turned from orange to deep purple. After photolysis was complete, the flask was uncapped and the solvent was allowed to evaporate overnight at room temperature under a gentle stream of air. [Note: We have observed that evaporation under more vigorous conditions (i.e. heat or vacuum) leads to loss of bipyridine from the product mixture due to bipyridine's relatively high vapor pressure.] Following evaporation of the solvent, the organic photoproducts were extracted by stirring the solid for 1–2 h with several 20-mL aliquots of ether. The ether extracts were dried under a gentle stream of air at room temperature, and the solid was taken up in methanol and analyzed by reversed-phase HPLC using a Varian Model 5000 chromatograph equipped with a MCH-5-N-CAP column and variable-wavelength UV detector. The mobile phase consisted of a mixture of methanol and water containing 1% tetraethylammonium chloride. The methanol:water ratio in the mobile phase was varied depending upon which pair of ligands were being separated and analyzed. The details of the HPLC procedure are to be published elsewhere.

Table I. Excited-State Properties of Argon-Saturated CH_2Cl_2 Solutions at 25 °C[a]

sample	luminescence lifetime, ns	luminescence quantum yield	photochemical quantum yield
$[Ru(bpy)_3]Cl_2$	731	0.123	0.084
$[Ru(bpy)_2(phen)]Cl_2$	450	0.079	0.079
$[Ru(phen)_2(bpy)]Cl_2$	387	0.042	0.069
$[Ru(phen)_3]Cl_2$	182	0.021	0.008
$[Ru(bpy)_2(Me_2bpy)]Cl_2$	918	0.183	0.033
$[Ru(Me_2bpy)_2(bpy)]Cl_2$	1008	0.136	0.014
$[Ru(phen)_2(Me_2bpy)]Cl_2$	1089	0.130	0.017
$[Ru(bpy)_2(Ph_2bpy)]Cl_2$	1447	0.440	0.028
$[Ru(Ph_2bpy)_2(bpy)]Cl_2$	1360	0.401	0.011
$[Ru(Ph_2bpy)_3]Cl_2$	1370	0.480	0.004
$[Ru(phen)_2(Ph_2bpy)]Cl_2$	1523	0.302	0.031
$[Ru(bpy)_2(Me\text{-}phen)]Cl_2$	675	0.120	0.032
$[Ru(phen)_2(Me\text{-}phen)]Cl_2$	316	0.032	0.018

[a] Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; Ph_2bpy = 4,4′-diphenyl-2,2′-bipyridine; Me-phen = 4-methyl-1,10-phenanthroline. Estimated error limits: lifetimes ±5%, quantum yields ±10–20%; based on standard deviations of replicate measurements.

Results

General Information. The luminescence lifetimes and quantum yields and photochemical quantum yields for the various $[Ru(diimine)_3]Cl_2$ complexes involved in this study are summarized in Table I. Whereas a considerable amount has been published on the photochemical and photophysical processes of $[Ru(bpy)_3]^{2+}$ and related complexes in solvents such as water,[13-15,25-28] acetonitrile,[18,29-31] and dimethylformamide,[31-33] little has been published[16-19,30,34] for these compounds in dichloromethane. Nevertheless, the trends reported in Table I for $[RuL_2L']Cl_2$ in CH_2Cl_2 (e.g. decreasing lifetime as phenanthroline replaces bipyridine in the coordination sphere and increasing lifetime as methyl- or

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Table II. Excited-State Decay Parameters Calculated from Data in Table I

sample	$10^{-3}k_r$, s^{-1}	$10^{-3}k_{nr}$, s^{-1}	$10^{-3}k_p$, s^{-1}
$[Ru(bpy)_3]Cl_2$	168	1085	115
$[Ru(bpy)_2(phen)]Cl_2$	176	1871	176
$[Ru(phen)_2(bpy)]Cl_2$	109	2297	178
$[Ru(phen)_3]Cl_2$	115	5333	46
$[Ru(bpy)_2(Me_2bpy)]Cl_2$	199	854	36
$[Ru(Me_2bpy)_2(bpy)]Cl_2$	135	843	14
$[Ru(phen)_2(Me_2bpy)]Cl_2$	119	783	16
$[Ru(bpy)_2(Ph_2bpy)]Cl_2$	304	368	19
$[Ru(Ph_2bpy)_2(bpy)]Cl_2$	295	432	8
$[Ru(Ph_2bpy)_3]Cl_2$	350	377	3
$[Ru(phen)_2(Ph_2bpy)]Cl_2$	198	438	20
$[Ru(bpy)_2(Me\text{-}phen)]Cl_2$	178	1256	47
$[Ru(phen)_2(Me\text{-}phen)]Cl_2$	101	3006	57

Table III. Product Analysis following Exhaustive Photolysis at 442 nm in CH_2Cl_2 at Room Temperature

sample	photoproduct distribn
$[Ru(bpy)_3]Cl_2$	100% bpy
$[Ru(bpy)_2(phen)]Cl_2$	100% bpy
$[Ru(phen)_2(bpy)]Cl_2$	100% bpy
$[Ru(phen)_3]Cl_2$	100% phen
$[Ru(bpy)_2(Me_2bpy)]Cl_2$	100% bpy
$[Ru(Me_2bpy)_2(bpy)]Cl_2$	100% bpy
$[Ru(phen)_2(Me_2bpy)]Cl_2$	100% Me_2bpy
$[Ru(bpy)_2(Ph_2bpy)]Cl_2$	24% bpy
$[Ru(Ph_2bpy)_2(bpy)]Cl_2$	13% bpy
$[Ru(Ph_2bpy)_3]Cl_2$	100% Ph_2bpy

phenyl-substituted ligands are incorporated) reproduce similar trends observed in other organic solvents. The enhanced photolability of the halide and thiocyanate salts in CH_2Cl_2 has been attributed[16,19] to ion pairing in this solvent.

Since all the complexes studied are both luminescent and photoactive in solution at 25 °C, the data from Table I could be used to calculate the rate constants for the three fundamental processes involved in excited-state decay—radiative decay, nonradiative decay, and photodecomposition. The details of those calculations have been outlined elsewhere.[9,13,16,30,35] The rate constants are summarized in Table II.

Table III shows the product distribution determined by HPLC analysis of the organic photoproducts. The *cis*-$Ru(bpy)_2X_2$ photoproduct ($X = Cl^-$, Br^-, or NCS^-) has been characterized previously.[16,17,30] Our spectral studies indicate that analogous ruthenium-containing photoproducts are obtained for all complexes included in this study. The presence of clean isosbestic points throughout the course of all reactions (our observations and ref 16 and 17) mitigates against long-lived intermediates such as RuL_2ClS^+. No evidence of secondary photolysis has been observed.

The $[Ru(bpy)_{3-n}(phen)_n]^{2+}$ Series. The first four lines in each table represent the series of compounds $[Ru(bpy)_{3-n}(phen)_n]Cl_2$ where n = 0, 1, 2, or 3. As has been previously reported for other organic solvent systems,[11] and for the PF_6^- salts in CH_2Cl_2,[19] the lifetime decreases monotonically as the number of phenanthroline ligands increases. On the other hand, in water, the lifetime for this series of complexes has been observed[27] to increase as n increases. The UV–visible absorption spectra[27] of the mixed-ligand complexes appear to be composites of the parent homo-tris-chelated complexes.

A dissociative mechanism involving a monodentate bipyridyl ligand has been proposed for the photodecomposition[7,9,13-16,29,36,37] and photoracemization[28] of $[Ru(bpy)_3]^{2+}$. Such a mechanism would predict that rigid phenanthroline ligands should be less labile than bipyridine. Since only one ligand is lost in the photoanation reaction, this mechanism would lead one to expect the photochemical quantum yield to remain relatively constant when bipyridine is in the coordination sphere and to decrease precipitously when three phenanthroline ligands are coordinated. That effect was observed for this series, as the photochemical quantum yield for $[Ru(phen)_3]Cl_2$ was an order of magnitude smaller than for the other members of the series. However, the effect is overshadowed somewhat by the fact that the luminescence lifetime and quantum yield also decrease for this series as the number of phenanthroline ligands increases.

It could be argued that the decrease in photochemical quantum yield observed as the number of coordinated phenanthrolines increases is merely a reflection of the decrease in excited-state lifetime due to an increase in the nonradiative rate constant for phenanthroline-containing complexes. In that case, if the photochemical rate constant were to remain unchanged, the photochemical quantum yield would be expected to decrease for the mixed bpy–phen complexes, since the photodecomposition process could not compete as efficiently with radiationless decay back to the ground state of the starting material. In fact, the kinetic data in Table II for this series show that although k_{nr} does increase by about a factor of 2 for the mixed bpy–phen complexes relative to $[Ru(bpy)_3]Cl_2$, the photochemical rate constant also doubles; hence, these cancel one another and the photochemical quantum yield remains essentially unchanged. The large drop in photochemical quantum yield upon going to $[Ru(phen)_3]Cl_2$ is attributable to a decrease in k_p as well as to a somewhat larger increase in k_{nr}.

No free phenanthroline was detected following photolysis of either of the mixed-ligand complexes in this series (see Table III). However, a stoichiometric amount of phenanthroline was observed following photolysis of $[Ru(phen)_3]Cl_2$, thus verifying that our analytical technique was sensitive to phenanthroline. Preferential loss of the more flexible ligand—bipyridine in this case—is consistent with the proposed[9,13,14,29,36-38] dissociative mechanism involving monodentate or orthometalated bipyridine.

Another notable feature of the data in Table II for this series is the fact that the photochemical and nonradiative decay rate constants, k_p and k_{nr}, for $[Ru(bpy)_2(phen)]Cl_2$ and $[Ru(phen)_2(bpy)]Cl_2$ are more similar to k_p and k_{nr} for $[Ru(bpy)_3]Cl_2$ than to the corresponding parameters for $[Ru(phen)_3]Cl_2$. Thus, it appears that bipyridine dominates the nonradiative decay processes in these complexes (photodecomposition being considered a mode of nonradiative decay for the purposes of this discussion). The fact that bipyridine dominates the nonradiative decay of the mixed-ligand complexes is also consistent with an excited-state model in which the excited electron is localized primarily on the bipyridine.[36]

Excitation localization in hetero-tris-diimine systems was proposed by Watts and Van Houten[39] for π–π^* excited states of rhodium(III) complexes. Electron localization in MLCT excited states of tris(diimine)ruthenium(II) complexes was first suggested by Dallinger, Woodruff, and co-workers[40,41] on the basis of time-resolved resonance Raman data and by Carlin and DeArmond.[42,43] Further experimental confirmation of excited-state localization has been provided by additional excited-state resonance Raman,[36,44] transient absorption,[45] transient circular dichroism,[46]

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and picosecond Raman scattering data.[47] Additional details of this "localized-orbital model" have been provided recently by Myrick et al.[48] Krausz[49] has disputed this interpretation for homo tris chelates of ruthenium(II).

Complexes Containing Me_2bpy. Data for three complexes containing 4,4'-dimethyl-2,2'-bipyridine are included in the tables. The data in Table I for these complexes show that all three have lifetimes of about 1 μs and luminescence quantum yields of about 0.15. For the $[Ru(bpy)_{3-n}(Me_2bpy)_n]^{2+}$ series in water, lifetimes of 470, 385, and 335 ns (n = 1–3, respectively) have been reported.[44] We could reproduce those results for aqueous solutions of the compounds we synthesized. Nevertheless, our lifetime data for these same complexes in CH_2Cl_2 show the opposite trend—i.e., increasing lifetime upon methyl substitution. The converse effect was observed for the $[Ru(bpy)_{3-n}(phen)_n]^{2+}$ series in which the lifetime increases in water as n increases,[9,27] and the lifetime decreases in CH_2Cl_2 as n increases.[19] Also in contrast to those of the $[Ru(bpy)_{3-n}(phen)_n]^{2+}$ series, the UV–visible absorption spectra[31,50] of mixed-ligand complexes containing Me_2bpy are alike.

The photochemical quantum yield decreases as the number of Me_2bpy ligands increases. Kinetic analysis of these results (Table II) shows that the nonradiative rate constant is relatively invariant over this series and that k_{nr} for the complexes in this second series is smaller than that observed for any of the members of the first series.

From these data it is clear that Me_2bpy is dominating the nonradiative excited-state decay process for these complexes in CH_2Cl_2. This is somewhat surprising, given the reports based on excited-state Raman measurements in H_2O[50] and CH_3CN[44] that the MLCT excited electron is localized on bipyridine in $[Ru(bpy)_2(Me_2bpy)]^{2+}$ and that the ligand of localization is mixed in $[Ru(Me_2bpy)_2(bpy)]^{2+}$. We intend to investigate this further in order to resolve this issue.

The lifetime and quantum yield results for $[Ru(phen)_2(Me_2bpy)]Cl_2$ and $[Ru(bpy)_2(Me_2bpy)]Cl_2$ in Table I are remarkably consistent. On the basis of these data, it appears that the electron may be localized on the Me_2bpy ligand in $[Ru(phen)_2(Me_2bpy)]^{2+}$. Table III shows that, as expected, no free phenanthroline was observed following photolysis of $[Ru(phen)_2(Me_2bpy)]Cl_2$.

Complexes Containing Ph_2bpy. Data for four complexes containing 4,4'-diphenyl-2,2'-bipyridine are included in the tables. The luminescence quantum yields and lifetimes for these complexes are all greater than those of any other complexes included in this study. Whereas the inclusion of one or more Me_2bpy ligands led to a lifetime in the 1-μs range regardless of whether the other ligand or ligands were phenanthroline or bipyridine, the incorporation of one or more Ph_2bpy ligands further increases the lifetime to the 1.4-μs range. The excited-state resonance Raman spectra[38] of $[Ru(bpy)_2(Ph_2bpy)]^{2+}$ and $[Ru(Ph_2bpy)_2(bpy)]^{2+}$ show that the excited electron resides exclusively on the Ph_2bpy ligand in these complexes. In the UV–visible absorption spectra[31] of this series, the π–π^* and MLCT bands are observed to shift to lower energy as the number of Ph_2bpy ligands increases.

For the members of this series, the photochemical quantum yield is observed to decrease as the number of coordinated Ph_2bpy ligands increases. Examination of the data in Table II shows that this decrease in photochemical quantum yield can be attributed directly to a decrease in the rate constant for photoanation as the number of Ph_2bpy ligands increases. On this basis, one might expect that bipyridine would be preferentially photolabilized from mixed-ligand complexes containing both bpy and Ph_2bpy. However, our data in Table III show that Ph_2bpy is the predominant photoproduct. In contrast to our results, a recent report[37] by De Cola et al. contains the suggestion that "photochemistry takes place by preferential detachment of bpy in the[se] mixed ligand complexes" and furthermore that their photoproduct analysis "confirms the above conclusion".

A number of differences exist between our experimental procedure and those of ref 37. We performed our experiments in argon-saturated CH_2Cl_2 whereas De Cola et al. used "O_2-equilibrated"[37] CH_2Cl_2. They used the iodide salts of the ruthenium complexes and added 0.01 M benzyltriethylammonium chloride, whereas we used the chloride salts of the ruthenium complexes with no additional anion. We photolyzed with the 442-nm line of a He–Cd laser with an output of 30–40 mW (ca. 3×10^{-9} einstein s^{-1} as determined by ferrioxalate actinometry), whereas they used a tungsten lamp and a 462-nm interference filter but the incident intensity is not stated explicitly. Finally, the analytical procedure used by De Cola et al. differs considerably from ours. Given the number of significant differences in procedure, any attempt to rationalize the differences between our results and those of ref 37 would be purely speculative. The possibilities include the following: kinetic effects with the more labile bipyridyl ligand being displaced in O_2-equilibrated samples where the lifetime is shorter; steric effects when the larger iodide anion is present; effects stemming from the fact that we performed exhaustive photolysis using a relatively intense light source. In an attempt to reproduce the results of De Cola et al., we have found[51] that broad-band irradiation of air-equilibrated samples with a xenon lamp gives a larger percentage of bpy labilization than that reported in Table III.

Complexes Containing 4-Me-phen. Two complexes containing a substituted phenanthroline ligand (4-methylphenanthroline) were studied. They were $[Ru(bpy)_2(Me\text{-}phen)]Cl_2$ and $[Ru(phen)_2(Me\text{-}phen)]Cl_2$. The effect of methyl substitution on a phenanthroline ligand is demonstrated by comparing the data for $[Ru(bpy)_2(Me\text{-}phen)]Cl_2$ with the data for $[Ru(bpy)_2(phen)]Cl_2$ and by comparing the data for $[Ru(phen)_2(Me\text{-}phen)]Cl_2$ with the data for $[Ru(phen)_3]Cl_2$. The data in Table I show that the lifetimes of the Me-phen complexes are longer than those of the unsubstituted analogues. The data in Table II show that the increased lifetimes are attributable to a decrease in k_{nr} upon methyl substitution. The UV–visible spectrum of $[Ru(bpy)_2(Me\text{-}phen)]Cl_2$ appears to be dominated by transitions involving the Me-phen ligand. The absorption spectrum of $[Ru(phen)_2(Me\text{-}phen)]Cl_2$ is virtually identical with the spectrum of $[Ru(phen)_3]Cl_2$. Attempts to characterize the photoproducts from complexes containing Me-phen were unsuccessful.

Discussion

The fact that the excited-state decay processes in tris(diimine)ruthenium(II) complexes are sensitive to the nature of the ligands has been well documented in the past. Two goals of photomediator design that have been addressed in the present study are (1) minimizing the resource-wasting photodecomposition of the ruthenium complex and (2) minimizing the energy-wasting nonradiative decay of the excited state. The photodecomposition quantum yield of $[Ru(phen)_3]Cl_2$ is an order of magnitude smaller than that of $[Ru(bpy)_3]Cl_2$ in CH_2Cl_2; however, this is accompanied by a 5-fold decrease in the lifetime in this solvent. Nevertheless, in water the lifetime of $[Ru(phen)_3]^{2+}$ is almost twice as long[52–55] as that of $[Ru(bpy)_3]^{2+}$. Among the complexes included in this study, $[Ru(Ph_2bpy)_3]^{2+}$ appears promising as a photomediator. Compared to those of $[Ru(bpy)_3]^{2+}$, the photodecomposition quantum yield of $[Ru(Ph_2bpy)_3]^{2+}$ is a factor of 20 smaller, the lifetime is almost twice as long, and the luminescence quantum yield is 4 times larger. In water, the lifetime increases by only 10%[52] for $[Ru(Ph_2bpy)_3]^{2+}$ compared to $[Ru(bpy)_3]^{2+}$. A drawback of phenyl substitution is that it shifts the excited state to lower energy. Methyl substitution on bipyridine

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also serves to inhibit photodecomposition and to enhance the excited-state lifetime in CH_2Cl_2, although the effects are not as pronounced as for phenyl substitution. An advantage of methyl substitution is that it does not significantly perturb the excited-state energy.

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Registry No. $[Ru(bpy)_3]Cl_2$, 14323-06-9; $[Ru(bpy)_2(phen)]Cl_2$, 60828-36-6; $[Ru(phen)_2(bpy)]Cl_2$, 60828-37-7; $[Ru(phen)_3]Cl_2$, 23570-43-6; $[Ru(bpy)_2(Me_2bpy)]Cl_2$, 77461-13-3; $[Ru(Me_2bpy)_2(bpy)]Cl_2$, 119998-53-7; $[Ru(phen)_2(Me_2bpy)]Cl_2$, 119998-54-8; $[Ru(bpy)_2(Ph_2bpy)]Cl_2$, 77494-67-8; $[Ru(Ph_2bpy)_2(bpy)]Cl_2$, 119998-55-9; $[Ru(Ph_2bpy)_3]Cl_2$, 31790-57-5; $[Ru(phen)_2(Ph_2bpy)]Cl_2$, 119998-56-0; $[Ru(bpy)_2(Me\text{-}phen)]Cl_2$, 119998-57-1; $[Ru(phen)_2(Me\text{-}phen)]Cl_2$, 119998-58-2; bpy, 366-18-7; phen, 66-71-7; Me_2bpy, 1134-35-6; Ph_2bpy, 6153-92-0.

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Preparation, Photochemistry, and Electronic Structures of Coumarin Laser Dye Complexes of Cyclopentadienylruthenium(II)

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The syntheses and characterization of six new compounds that contain the $CpRu^+$ ($Cp = \eta^5\text{-}C_5H_5$) moiety bound to a substituted coumarin laser dye are reported. The complexes prepared are of the general form $[CpRu(\eta^6\text{-laser dye})]PF_6$, where laser dye = coumarin-1 (7-(diethylamino)-4-methylcoumarin), coumarin-2 (4,6-dimethyl-7-(ethylamino)coumarin), coumarin-6 (3-(2-benzothiazolyl)-7-(diethylamino)coumarin), coumarin-311 (7-(dimethylamino)-4-methylcoumarin), coumarin-334 (10-acetyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one), or coumarin-338 (2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylic acid 1,1-dimethylethyl ester). The structures of all of the new complexes except the complex of coumarin-6 were determined by ^1H and ^{13}C NMR spectroscopy and contain the $CpRu^+$ group bound to the benzenoid moiety of the coumarin system. The $CpRu^+$ group binds to the benzothiazole group of the coumarin-6 compound. Photolysis of the complexes in CH_3CN solutions results in the formation of $CpRu(CH_3CN)_3^+$ and the free dye. The complexes of the dyes other than coumarin-6 exhibit low-lying MLCT bands and are not emissive. The coumarin-6 complex retains the low-lying intramolecular charge-transfer band present in the free dye and emits in fluid solution at room temperature with $\lambda_{max} = 532$ nm and $\Phi = 0.11 \pm 0.02$. The laser dye centered emission band of the complex is red-shifted 25 nm with respect to the free coumarin-6 emission.

Introduction

For the past several years, our group has investigated the arene photosubstitution reactions of $[CpM(arene)]^+$ complexes (M = Ru, Fe; Cp = η^5-cyclopentadienyl, arene = η^6-arene). The photochemical release of the arene from the metal in these complexes occurs via nucleophilic attack of the medium on the distorted a^3E_1 ligand field excited state in an associative or associative-interchange mechanism.[1,2] Kinetic data for related thermal arene displacement reactions of $CpRu(anthracene)PF_6$[3] are consistent with two possible mechanisms.[4] Differentiation of these mechanisms depends on the kinetic properties of a proposed "slipped ring" η^4-arene complex reaction intermediate. At the time of these original studies, a spectroscopic probe sensitive to $\eta^6 \rightarrow \eta^4$ coordination changes was not available. Recently, we became interested in the possibility that either the UV–vis spectral bands or the emissive properties of a strongly absorbing arene might serve as the sensitive probe. To this end we have synthesized $CpRu^+$ complexes of substituted coumarin laser dyes, which appeared ideal for these studies. These new laser dye complexes exhibit strong electronic transitions that respond to arene coordination changes in both absorption and emission spectroscopic experiments.

Experimental Section

Dichloromethane and acetonitrile were of spectroscopic grade and were used without further purification. Laser dyes were obtained from the Eastman Kodak Co. All other reagents were reagent grade and were used as received. Room-temperature UV–vis spectra of the compounds were obtained (acetonitrile solution) with a Cary 17D spectrometer. Emission and excitation profiles were recorded on a Spex F112X spectrofluorometer. NMR spectra were obtained on an IBM Bruker 200-MHz spectrometer (^1H) and an IBM Bruker 300-MHz spectrometer (^{13}C). IR spectra were obtained (dichloromethane solution) for the compounds with a Perkin-Elmer 1710 FT spectrophotometer.

Synthesis of $[CpRu(laser\ dye)]PF_6$ Compounds. The starting materials $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $[CpRu(CH_3CN)_3]PF_6$ were prepared by literature procedures.[5,6]

$[CpRu(coum\text{-}1)]PF_6$. To a degassed flask containing 100.0 mg (0.230 mmol) of $[CpRu(CH_3CN)_3]PF_6$ and 53.3 mg (0.230 mmol) of the laser dye coumarin-1 (7-(diethylamino)-4-methylcoumarin) was added 25 mL of N_2-degassed 1,2-dichloroethane. The solution immediately assumed an intense golden brown hue. The solution was bubbled with N_2 for another 5 min and then was stirred for 2 h. The solvent was removed by rotary evaporation to yield a dark yellow residue, which was redissolved in acetone and adsorbed on a short diatomaceous earth column. The column was allowed to equilibrate for 1 h and then was eluted with pentane to remove excess coumarin-1. The washed product was stripped off the column with acetone and then sent through a short alumina column. Evaporation of the eluate followed by recrystallization from acetone–ether yielded 59.0 mg (0.109 mmol) of light yellow $[CpRu(coum\text{-}1)]PF_6$ (47% yield). ^1H NMR (methylene-d_2 chloride): δ 6.47 (d, aryl H (bound ring), 1 H, $J = 6.6$ Hz), 6.33 (s, aryl H (bound ring), 1 H), 6.13 (s, aryl H_3 (unbound ring), 1 H), 5.72 (d, aryl H (bound ring), 1 H, $J = 6.6$ Hz), 5.10 (s, Cp, 5 H), 3.37 (q, ethyl CH_2, 4 H, $J = 7.18$ Hz), 2.46 (s, aryl CH_3, 3 H), 1.23 (t, ethyl CH_3, 6 H, $J = 7.20$ Hz). Anal. Calcd for $C_{19}H_{22}NO_2RuPF_6$: C, 42.07; H, 4.09; N, 2.58. Found: C, 42.15; H, 4.03; N, 2.70. IR data (cm^{-1}): 1765 s, 1631 m, 1569 s, 1513 w.

$[CpRu(coum\text{-}2)]PF_6$. The coumarin-2 complex was prepared by the same method used to obtain $[CpRu(coum\text{-}1)]PF_6$, except coumarin-2

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