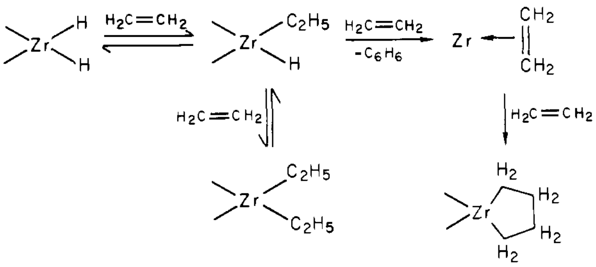

(40)

Conclusions

This work demonstrates that proper ligational adjustment can lead to thermally stable yet highly reactive actinide hydrocarbyls and hydrides. It is evident that such species have a rich and diverse chemistry. In placing this chemistry in perspective, there appear distinct similarities to main-group and early transition-metal[66b] reactivity patterns; there are also striking differences. In regard to the group 4B systems, differences in structure and reactivity appear to reflect the relative availability of metal formal oxidation states, the greater polarity of actinide–element bonds, the larger actinide ionic radii, and the commensurate increase in available coordination sites about the 5f ion. The actinide chemistry is by no means monolithic, and the observed chemical differences between the thorium and uranium arise from differences in accessible oxidation states as well as in metal–ligand bond polarity.

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Effects of Ligand Substituents on Excited-State Reactivity and Overall Photoredox Behavior for (Polypyridyl)ruthenium(II) Complexes. A Laser Flash Study with Potential Reductive Quenchers

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Abstract: This paper reports results of a study of the quenching of excited states of RuL_3^{2+} ruthenium complexes and subsequent reactions occurring with potential reductants—amines, aromatic ethers, *p*-hydroquinone, and water. The ligands, L, contain electron-withdrawing carboxy ester groups in the meta (5,5′) (**1**) or para (4,4′) (**2**) positions of the bipyridine ring; this substitution produces anodic shifts in both the 2+/+ and 3+/2+ electrochemical potentials for the complexes, rendering them easier to reduce but more difficult to oxidize. Both laser flash and conventional spectroscopic techniques have been used to monitor the primary quencher products. Thus the photoreduction of one complex (**1**) with triethylamine can be shown to consist of two components, a primary photoprocess and a subsequent dark reaction, while for **2** only the first process is observed. The reduced complexes, RuL_3^+, produced in the reaction are relatively stable in dry, deaerated solutions but can be observed to react rapidly with both oxygen and water. The reaction of reduced **1** with water produces a relatively stable product which appears to be a ligand (probably carboxy ester)-protonated species, RuL_3H^{2+}; this product yields hydrogen and the starting complex **1** upon treatment with colloidal platinum. Excited states of **1** are also quenched by aromatic ethers and hydroquinone in processes giving transients having spectra similar to that of reduced **1**; no permanent chemistry is observed with these quenchers and rapid first-order decay of the transient is observed. A reaction of excited **1** with water is also observed; this reaction ($k = 1 \times 10^7$ M^{-1} s^{-1}) gives a short-lived transient ($\tau = 250$ ns) which is apparently not a redox product but more likely an adduct or ligand-protonated species.

Introduction

A large number of investigations with polypyridyl complexes of ruthenium(II), osmium(II), iridium(III), and chromium(III) have shown that excited states of these complexes can be both oxidized and reduced by a variety of reagents.[3-21] The well-characterized spectroscopic properties[22-26] of these complexes and their one-electron redox products have facilitated study of processes

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where simple electron transfer quenching occurs. Since electron transfer quenching often occurs with high efficiency and can result in efficient conversion of excitation energy through high-energy product formation, there has been considerable interest in coupling ensuing reactions with these processes to achieve net chemical change. Various approaches have included the use of scavengers,[27-33] quenchers whose redox products undergo rapid reactions with solvent or other reagents,[18,34] organized assemblies,[35-38] and/or highly reactive colloidal or heterogeneous catalysts;[29-33,39-42] in addition, a number of studies have focused on tuning of the photoredox behavior of these complexes by modifying the net charge on the complex[43-45] or by adjusting ligand substituents.[18,34,46]

In several cases of quenching, photoreactions, and net photoredox conversion for these complexes, both the primary photoprocess and ensuing reactions involve only simple one-electron-transfer processes. However, in a number of cases there is evidence that primary or competitive reactions involving other types of interactions may be of importance. For example, in the well-studied system involving interaction of excited Ru(bpy)$_3^{2+}$ with cobalt(III) complexes,[3,39,47,50] it is clear that rapid unimolecular decomposition of the labile Co(II) complex permits net photoconversion to occur. In recently reported cases, such as the quenching of Ru(bpy)$_3^{2+*}$ by inorganic ions (Hg^{2+},[51] Ti^{3+},[52] and Ag^{+} [53-55]), it is clear that the reduced metal ion can undergo a variety of rapid reactions not involving electron transfer in competition with the normally observed back-electron-transfer process. In several cases the net chemical change observed is potentially useful. In the case of Hg^{2+} reduction, for example, dimerization of the initial product to yield Hg$_2^{2+}$ results in a survival time for Ru(bpy)$_3^{3+}$ on the scale of minutes without the use of other sacrificial reagents.[51] In contrast, for Ti^{3+} reduction, rapid reaction of Ti^{2+} with water has been suggested to prevent back electron transfer.[52] The question of solvent—particularly water—interaction with excited states of these complexes or primary products of their photoreactions remains an area of active investigation. Interest in these reactions and interactions is due in part to questions concerning the mechanisms of catalyst involvement in transition-metal complex mediated water redox processes and also to the observation of strong solvent effects on the lifetimes and properties of metal complex charge transfer and ligand field excited states. Several studies have focused on pronounced changes in acid–base properties which occur at ligand sites upon excitation of these transition-metal complexes in aqueous solutions,[45,56] other studies have indicated that reaction with water or solute anions can occur at the metal center following excitation and in some cases, partial labilization of a bipyridine-type ligand.[57,61] While in a few cases stable monodentate complexes have been isolated or clearly indicated to be formed,[59] their lability[58,60] renders their intermediacy or precise structure difficult to establish in many photoreactions. The question of reaction of water or other ions with excited metal complexes or their primary photoproducts remains an extremely important one since, for several systems, it is likely that protonated or deprotonated species or other adducts are key intermediates in sequences leading to water splitting or other useful chemical conversions.[62-64]

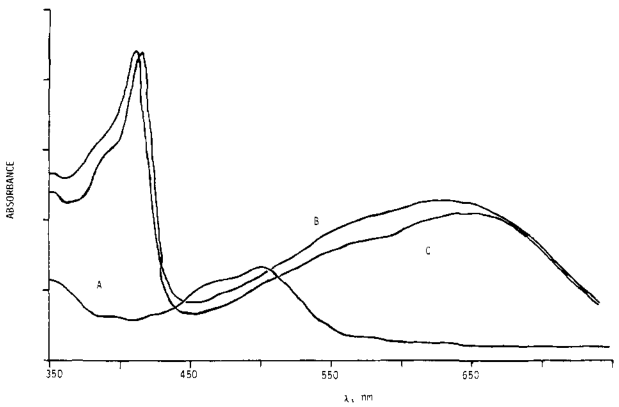

Figure 1. Absorption spectra of starting complex **1** (A) and its reduction products in acetonitrile (B) and acetonitrile–water (C).

The present study deals with excited-state quenching processes and ensuing reactions occurring with RuL$_3^{2+}$ ruthenium(II) complexes in which 2,2′-bipyridine ligands have been substituted with electron-withdrawing carboxy ester groups in the meta (5,5′) and para (4,4′) positions. We have used laser flash and conventional spectroscopic techniques to examine the reactions of these excited complexes with potential reductants ranging from tertiary

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amines to water. Results of our study indicate that quenching can occur by net electron transfer reduction as well as by interactions not involving electron transfer at all. Not surprisingly, our experiments indicate that readily observable reactions subsequent to the primary quenching process play a dominant role in determining the overall chemical change occurring. A key result of these studies is the finding that ligand substituents not only play a major role in controlling reactivity but also provide a specific site for solvent interactions.

Experimental Section

Materials. Ruthenium complexes **1** and **2** were prepared as described previously[34] with the exception that ethanol replaced the 2-propanol in the synthesis of the meta (5,5′) dicarbethoxy complex (**1**). Spectrograde acetonitrile was distilled from anhydrous P_2O_5 and stored over molecular sieves prior to use. Triethylamine was purified by distillation. *p*-Benzoquinone was purified by vacuum sublimation. All other chemicals used were reagent grade (Fluka).

Physical Measurements. Time-correlated experiments were performed by using laser flash photolysis techniques. The double-frequency pulse (530 nm) of a JK neodymium Yag laser (pulse width 15 ns, energy output 400 mJ) was used as an exciting source. The details of the optical and detection systems have been described elsewhere.[65,66] The temporal behavior of the transients formed was recorded with two Tektronix transient digitizers (R-7912) in tandem, both coupled to a PDP 11/04 computer.

Absorption spectra were recorded on a Cary 14 spectrometer or a Perkin-Elmer 576ST spectrophotometer. Luminescence excitation and emission spectra were recorded on a Perkin-Elmer MPF-4 spectrometer. Conventional flash photolysis experiments were performed as previously described.[4,5]

Results and Discussion

Photoreduction of (Dicarbethoxybipyridyl)ruthenium(II) Complexes by Amines. The major excited substrate employed in these studies has been the complex RuL_3^{2+}, where L = 5,5′-dicarbethoxy-2,2′-bipyridine (**1**). This complex, similarly to its previously investigated[34,67] para-substituted counterpart $RuL'_3{}^{2+}$, where L′ = 4,4′-bis[(propyloxy)carbonyl]-2,2′-bipyridine (**2**), has reduction potentials for both the 3+/2+ (1.63 V vs. SCE) and 2+/+ (−0.65 V vs. SCE in acetonitrile) cathodically shifted compared to those for $Ru(bpy)_3{}^{2+}$ (**3**). The shift in the latter potential is pronounced enough in the case of **1** to make its excited state potentially subject to reductive quenching by a number of reagents not reactive toward **2** or **3**. Red shifts in the absorption and emission spectra of **1** indicate a slightly lower excited-state energy for **1*** such that excited-state redox potentials $E^{3+/2+*} = -0.28$ V and $E^{2+*/+} = 1.26$ V can be estimated.[5,20,21]

Irradiation of **1** in the presence of amines such as triethylamine in dry deaerated aprotic solvents leads to luminescence quenching ($k_q = 1.2 \times 10^8\ M^{-1}\ s^{-1}$) and to formation of a permanent photoproduct whose spectrum is shown in Figure 1. This behavior is similar to that observed upon irradiation of **2** under similar conditions,[67] and from ESR and electrochemical evidence it can be concluded that the spectrum is that of the one-electron-reduction product of **1**, RuL_3^+.[34] Previously, we ascribed photoreduction of **1** and **2** by amines such as triethylamine to the mechanism given by eq 1–4.[34] For **2** the highest quantum yield

$$RuL_3^{2+} \xrightarrow{h\nu} RuL_3^{2+*} \qquad (1)$$

$$RuL_3^{2+*} + :NEt_3 \rightarrow RuL_3^{+} + \cdot\overset{+}{N}Et_3 \qquad (2)$$

$$\cdot\overset{+}{N}Et_3 + :NEt_3 \rightarrow CH_3\dot{C}H\ddot{N}Et_2 + \overset{+}{H}NEt_3 \qquad (3)$$

$$CH_3\dot{C}H\ddot{N}Et_2 + RuL_3^{2+} \rightarrow CH_3CH{=}\overset{+}{N}Et_2 + RuL_3 \qquad (4)$$

for metal complex reduction obtained is 0.35 in dry acetonitrile; in current studies with **1** we obtain $\phi_{Red} = 0.49$ with triethylamine

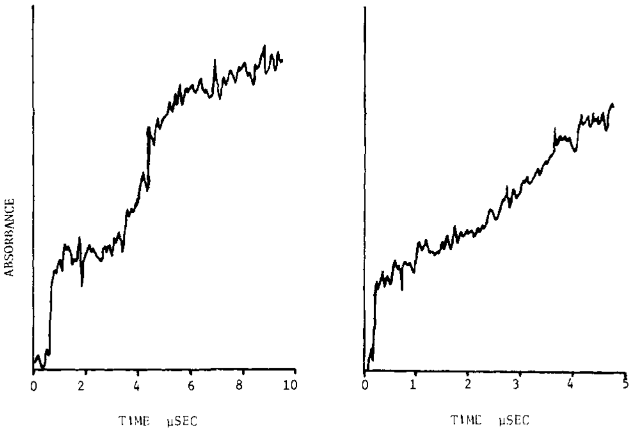

Figure 2. Temporal behavior observed at 600 nm following laser flash excitation of **1** in triethylamine–acetonitrile. Shown are traces on two time scales for the first flash on replicate samples.

and $\phi_{Red} = 0.52$ for diisopropylamine in dry degassed acetonitrile. Since the mechanism given by eq 1–4 predicts a limiting quantum yield of 2 for photoreduction, a question of fundamental importance is the source of the observed inefficiency in the overall process. Previous studies[68,69] have suggested that net electron transfer quenching efficiencies (eq 2) are often much lower than unity such that some quenching can simply produce a net result of nonradiative decay (eq 5). A second source of inefficiency

$$RuL_3^{2+*} + :NEt_3 \rightarrow RuL_3^{2+} + :NEt_3 \qquad (5)$$

could be the failure of radicals such as $CH_3\dot{C}HNEt_2$ (**4**) to participate in the dark reduction of the metal complex (eq 4). Previous studies[70,71] have suggested that **4** is a strong reductant having a potential $E^{+/0}$ in the range −1.0 V vs. SCE; however, this value represents an approximation since the "true" potential would be very difficult to obtain, considering the instability of both **4** and its oxidation product.

In the present study we have examined the time dependence of the production of RuL_3^+ following laser flash excitation of **1** and **2** in the presence of triethylamine in dry degassed acetonitrile. Figure 2 shows the buildup of reduced **1** at 600 nm as a function of time. For both **1** and **2** it was found that there is no decay of the long-wavelength-absorbing product following the laser flash. This indicates that there is no back-reaction of the "free ions" formed in eq 2 for either of the complexes. The temporal characteristics of reduced species following the initial rapid formation are different for reactions of **1** and **2** with triethylamine. For **2** the product is stable but there appears to be no further detectable reaction up to milliseconds after the laser pulse. In contrast, there are clearly two components in the buildup of reduced species for **1** as shown in Figure 2. The second component, which occurs on the microsecond time scale under the conditions employed, is evidently the dark reduction described by eq 4. Using only data from the initial flash, in each case, we found that over several replications with **1**, roughly equal amounts of product are generated in the "fast" and "slow" steps. The second step gives a reasonable linear plot of $1/A_{600}$ vs. time, indicating a second-order process following approximate equal-concentration kinetics.

The secondary product generation indicated in Figure 2 is attributed to reaction 4. Considering the quantum yield of ~0.5 to be due to equal contributions from reactions 2 and 4, the concentrations of RuL_3^{2+} and imine radical **4** after the photoreaction (eq 2) and proton-transfer steps (eq 3) from an initial concentration of [**1**] = 8×10^{-5} M should be 6×10^{-5} and 2×10^{-5} M, respectively. Using these concentrations and assuming

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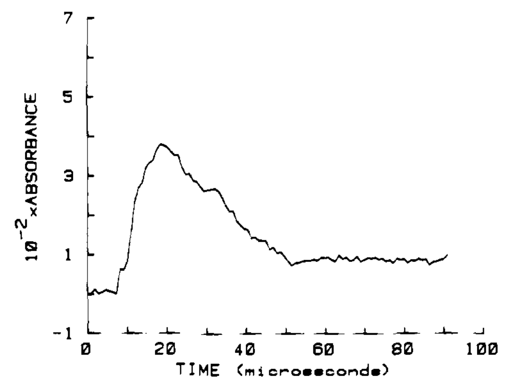

Figure 3. Temporal behavior observed at 600 nm following laser flash excitation of **1** in triethylamine–water–acetonitrile.

$k_4 = 10^{10}$ M^{-1} s^{-1} (diffusion controlled), we calculate that the observed lifetime for the reaction should be several microseconds in good agreement with the observed grow-in time for the second component of product formation. Thus it appears reasonable that radical **4** is a more powerful reductant than reduced **1** but perhaps a less powerful reductant than reduced **2**, putting the potential for the couple in the range $-0.92\ \mathrm{V} \leq E^{+/0} < -0.65$ V.[72]

These results suggest that the overall inefficiency in photoreduction of **1** by amines lies primarily in the initial quenching step. Thus under the present conditions, the quantum yields indicate the yield of "free" ions via eq 2 appears to be only in the range 0.2–0.3 and the remaining fraction of the excited states decays via a net reaction (eq 5) of nonradiative decay. The still lower yield of reduction products from **2** can be attributed to inefficiency in reaction 4; although reaction 4 may account for some reduction of **2**, it must occur at a much slower rate since we were unable to observe it on the time scale accessible in these experiments.[72] As pointed out previously, low efficiencies in the generation of free ions (eq 2) remain a serious barrier to practical employment of light-induced electron-transfer reactions. The precise sensitivity of these reactions to solvent effects and to structural features in both substrate and quencher remain to a large extent undefined.

As indicated previously, the product formed from irradiation of **1** in the presence of triethylamine is stable in dry, degassed acetonitrile solution. The absorption spectrum of this solution, as well as the ESR spectrum,[34] suggest this is best described as a ruthenium(II) complex in which one of the ligands has been reduced to a radical anion. The electronic spectrum produced (Figure 1) is strikingly similar to that of reduced methylviologen in both the visible and ultraviolet regions. Not surprisingly, we find that the reduced product from **1** is quite reactive toward oxygen and water. For example, admission of air to dry solutions does not suppress formation of the transient absorbing at 600 nm; however, the product, stable under the same conditions in the absence of air, is observed to decay with a lifetime of ca. 3 ms, regenerating the starting complex **1**.[73]

Addition of water also results in rapid reaction of the initial product formed in eq 1–4. Once again (Figure 3), there is a rapid buildup of product absorbing at 600 nm and a subsequent decay. From a measured transient lifetime of 2.85×10^{-5} s (600 nm) at [$\mathrm{H_2O}$] = 1.4 M we obtain a rate constant $k = 2.5 \times 10^4$ M^{-1} s^{-1} for reaction of the reduced complex with water.

The reaction of reduced **1** with water is evidently quite different from the corresponding reaction previously studied with reduced **2**. In the latter case the reaction was found to result in regeneration of the starting complex together with some decomposition. As Figure 1 indicates, a product having a slightly red-shifted but generally similar spectrum to that produced in anhydrous acetonitrile is obtained when steady-state photolysis of **1** with triethylamine is carried out in the presence of moderate amounts of water. The same end product is observed in laser flash experiments. This suggests that the net reaction with water is simply a protonation (or hydration) of the reduced species (eq 6) rather

$$\mathrm{RuL_3^+} + \underset{(\mathrm{H_2O})}{\mathrm{H^+}} \rightarrow \mathrm{RuL_3H^{2+}} \tag{6}$$

than a redox process. Since reduced **1** and **2** are much more reactive toward water than reduced **3** even though reduced **3** is obviously a more powerful reductant and potentially more reactive, the most likely explanation is that modification of ligand structure to include carboxy ester groups in **1** and **2** provides a site for water (proton) attack. Although definitive evidence is not available, these results together with the spectral similarity of reduced **1** and its reaction product with water suggest protonation of an oxygen of the ligand carboxy ester group is the initial step in reaction with water. The observation of protonation is reasonable considering the fact that reduced **1** is best described as a ruthenium(II) ligand radical anion. Radical anions of aromatic hydrocarbons and especially carbonyl compounds are well known to undergo protonation even in the presence of relatively poor proton donors.[75]

The carboxy ester complexes are labile to ester hydrolysis in triethylamine–water solutions in the dark. Net hydrolysis is quite slow compared with photoreduction and the reaction of reduced **1** with water and thus it does not play a role in the present results. The fact that prolonged irradiation does not at all enhance hydrolysis over the dark process suggests that reaction 6 does not promote hydrolysis. In fact, reduced **1** is more stable in triethylamine–water–acetonitrile solutions than **1** toward hydrolysis. This is not unreasonable in view of the most prominent structural contributor for the reduced, protonated ester ligand, $-\dot{\mathrm{C}}(\mathrm{OH})\mathrm{OEt}$, which should be relatively unreactive toward nucleophiles at the ester carbon and suffer only reversible deprotonation upon prolonged treatment with aqueous base.

In previous studies we have found that irradiation of **2** in the presence of triethylamine and water with a platinum catalyst leads to production of molecular hydrogen.[76] In similar studies with complex **1** it was found that no hydrogen could be detected.[77] Given the probable mechanism for hydrogen production, it is reasonable that at the high pH (~12) involved the reduced complexes from **1**, $\mathrm{RuL_3^+}$ or $\mathrm{RuL_3H^{2+}}$, are not sufficiently powerful to reduce protons. Although it is not possible to measure the reducing potential for $\mathrm{RuL_3H^{2+}}$, it appears reasonable that it should be only slightly lower than that of $\mathrm{RuL_3^+}$. Thus it would be expected that reduction of **1** at lower pHs in the presence of water and a reactive catalyst should result in hydrogen production by reaction 7. To test this possibility we used the disodium salt

$$2\mathrm{RuL_3H^{2+}} \xrightarrow{\text{catalyst}} 2\mathrm{RuL_3^{2+}} + \mathrm{H_2} \tag{7}$$

of ethylenediaminetetraacetic acid (EDTA) as a reducant for **1** in a 4:1 mixture of water–acetonitrile buffered to pH 4.7 with a Carbowax-supported platinum catalyst which has been shown highly reactive for hydrogen generation in other studies.[40] Although quenching of the excited state of **1** by EDTA is incomplete at the concentrations used ($K_{\mathrm{SV}} = 20$), moderate evolution (1 mL of $\mathrm{H_2}$/(L of sample/h)) of hydrogen was obtained when these solutions were irradiated. Although a quantum yield was not measured for this process, the amount of hydrogen produced was clearly lower by at least 1 order of magnitude from the most reactive systems studied with this catalyst.[78,79] Thus while these studies clearly indicate reaction 7 occurs, the results indicate that the system, at least with EDTA as a reductant, is not an optimal one for hydrogen generation.

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(72) Since we are unable to follow accurately reactions occurring on a time scale longer than milliseconds, we cannot rule out the occurrence of a much slower reduction of **2** by the imine radical **4**.

(73) Since the solubility of oxygen in most nondeareated organic solvents is ca. 0.003 M,[74] the observation of a lifetime on the millisecond time scale suggests reaction of reduced **1** with $\mathrm{O_2}$ is slower than diffusion controlled.

(74) Murov, S. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 89.

(75) Hoijtink, G. J.; Van Schooten, J.; de Boer, E.; Aalbersbert, W. I. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 895–909.

(76) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 4007–4009.

(77) DeLaive, P. J., unpublished results.

(78) Kiwi, J.; Grätzel, M. *Nature (London)* **1979**, *281*, 657.

(79) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214–7217.

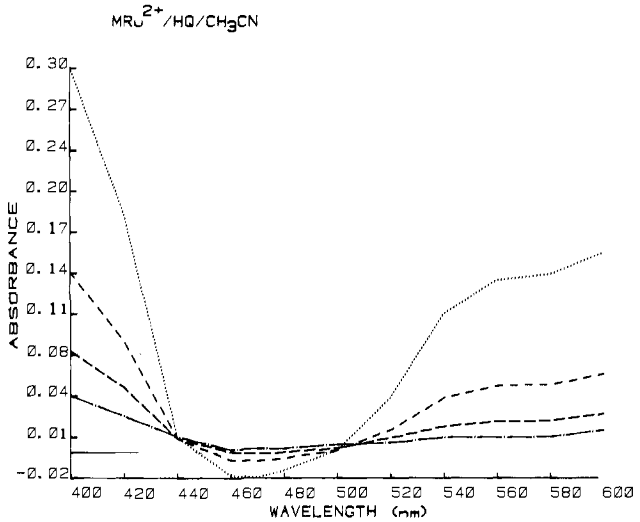


Figure 4. Transient absorption spectra obtained following laser flash excitation of **1**-hydroquinone in acetonitrile.

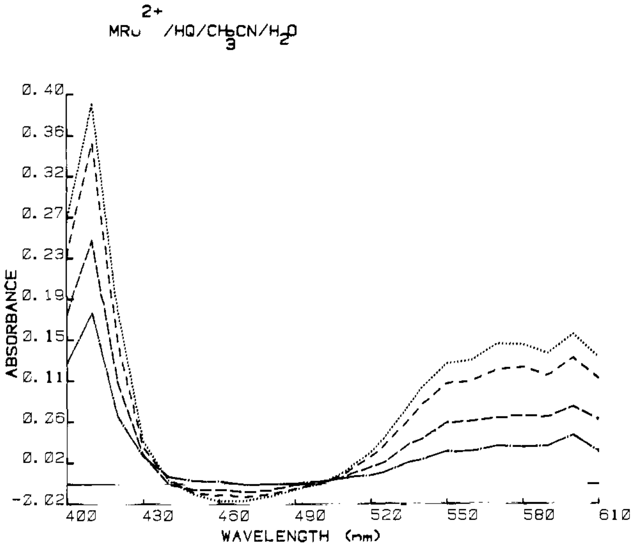
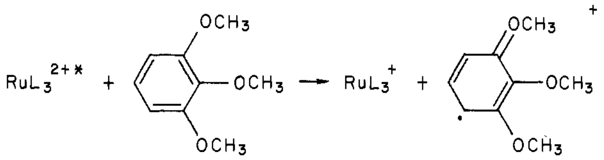


Figure 5. Transient absorption spectra obtained following laser flash excitation of **1**-hydroquinone in acetonitrile–water.

Photoreaction of Complex 1 with Other Reagents. The cathodically shifted potentials of **1** suggest that it should be possible to obtain photoreduction with a variety of reductants not measurably reactive toward excited states of **2** and **3**. Not surprisingly, we have found that a number of aromatic ethers and hydroquinone quench the luminescence of **1** in reactions which evidently involve net electron transfer. We have investigated the transient behavior with these oxygen-containing quenchers and have found that while quenching occurs in each case, the type of transient and transient lifetime are quite dependent on the quencher.

A number of di- and trimethoxybenzenes having oxidation potentials in the range 1.12–1.5 V (vs. SCE in acetonitrile) have been found to quench the luminescence of **1** with rate constants 2–3 orders of magnitude below diffusion controlled.[80] Clearly, considering the potentials involved, it is reasonable that quenching could involve net electron transfer from the ether to excited **1**. For the case of 1,2,3-trimethoxybenzene it was found that laser flash excitation of **1** at 530 nm in the presence of 0.8 M quencher resulted in essentially complete luminescence quenching with concurrent spectral changes consistent with reduction of **1** as indicated by eq 8. The transient spectrum produced, although



(8)

very similar to that of RuL_3^+ shown in Figure 1, was quite short-lived and showed a clean first-order decay with $k = (1.4 \pm 0.2) \times 10^7\ s^{-1}$ (correlation coefficients >0.99 for each trace). The observation of first- rather than second-order decay of the transient indicates that in this case "free" ionic products are not formed. This could be attributed to the occurrence of back-reaction while the product ions in eq 8 are within an effective cage[81,82] or to decay of an exciplex, $RuL_3^+\cdots Q^+$.[83] The lifetime of the transient in this case (100 ns) is clearly too short to make this substrate–quencher combination an attractive one for obtaining net useful chemistry although high concentrations of reactive scavengers might enable the net production of one of the products.

In similar experiments *p*-hydroquinone was found to react with excited **1** to give similar transient spectra but with a much longer transient lifetime. Figures 4 and 5 show transient spectra obtained following laser flash excitation of **1** with hydroquinone in the absence and the presence of water, respectively. As with the ethers, the transient spectra generated are clearly indicative of an excited-state electron-transfer process to generate reduced complex and oxidized quencher (eq 9). Initially, it was thought that this

$$RuL_3^{2+*} + QH_2 \rightarrow RuL_3^+ + QH\cdot + H^+ \qquad (9)$$

reaction might offer the possibility of forming one-half of a useful two-component system for accomplishing water splitting since we and others have found several cases where similar metal complexes are oxidized photochemically by quinones to produce oxidized substrate and reduced quinone as permanent products by the sequence given by eq 10–12.[85] Since a similar sequence can be

$$S^* + Q \rightarrow S^+ + Q^- \qquad (10)$$

$$Q^-\cdot + H^+ \rightarrow \cdot QH \qquad (11)$$

$$2\cdot QH\cdot \rightarrow QH_2 + Q \qquad (12)$$

written following eq 9, it is obviously possible to conceive a system in which S^+ and RuL_3^+ (or RuL_3H^{2+} in the presence of water) are used to effect separately the oxidation and reduction of water, respectively, while the Q, QH_2 system acts as a shuttle similar to its role in photosynthesis.

In the present case the initial findings are somewhat disappointing since even with highly purified QH_2 as quencher, we observe a rapid decay of the product RuL_3^+, although the initial efficiency of product formation (eq 9) appears to approach unity in both dry and aqueous acetonitrile solutions. The decay of RuL_3^+ in this case is first order and we have established that it is due to minute amounts of quinone impurity in the starting hydroquinone. Thus in separate experiments we have measured the rate constant for oxidation of RuL_3^+ by quinone to be $3.5 \times 10^9\ M^{-1}\ s^{-1}$. This indicates that even an impurity of 0.01% quinone (virtually impossible to exclude, even with highly purified hydroquinone) the "natural" back-reaction, even if diffusion controlled, will be overwhelmed by destruction of RuL_3^+ by quinone

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(80) Foreman, T. K.; Sobol, W., unpublished results.

(81) That the short lifetime was not due to reactions of reduced **1** with an impurity present in the quencher was checked by conducting flash experiments with varying quencher concentration (no change in γ was observed) and by generating reduced **1** by Et_3N (1 M) reduction of **1** in the presence of 0.05 M 1,2,3-trimethoxybenzene; the buildup of reduced **1** was not suppressed under these conditions.

(82) The first-order lifetime of the **1**-1,2,3-trimethoxybenzene transient is solvent dependent (acetonitrile, 87 ns; *N,N*-dimethylformamide, 33 ns; dimethyl sulfoxide, 21 ns), as would be predicted for a cage process. This reaction is currently under investigation.

(83) Several fairly analogous excited donor–acceptor systems giving exciplex emission have been found to give transients having spectra similar to those of the radical ions with rapid first-order decay.[84]

(84) Peters, K., private communication.

(85) Schmehl, R. H., unpublished results.

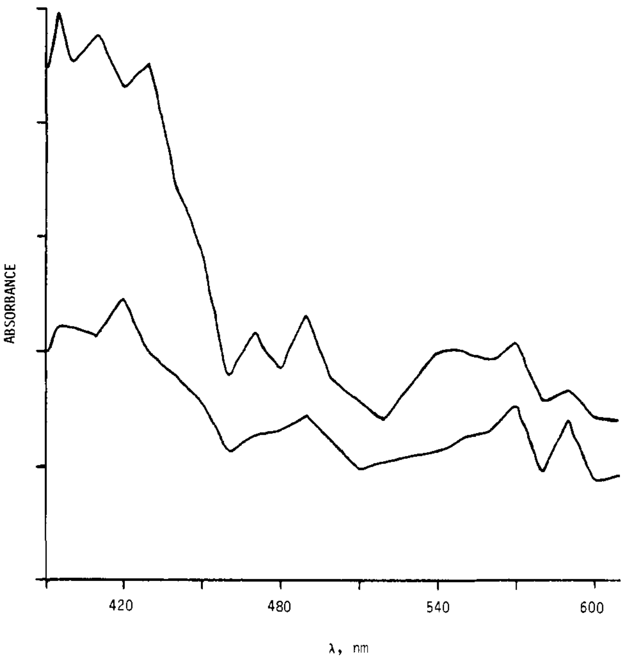

Figure 6. Transient absorption spectra obtained following laser flash excitation of **1** in water–acetonitrile.

impurity. This emphasizes the difficulty in finding a suitable relay to function on both sides of a two-absorber system not employing sacrificial reagents. Thus while for many quinone derivatives the hydroquinone formed in the "anodic" half-reaction does not hinder the buildup of oxidized substrate, it is clear that it will be difficult to find a system in which a reduced substrate is not oxidized by the quinone produced in the "cathodic" half-reaction.

Photoreaction of 1 with Water. The observation that excited states of **1** are reactive toward a number of oxygen-containing substrates prompted us to examine its potential reactivity with water. Through laser flash investigation we find that water both quenches the luminescence of **1** and results in a transient product formation even though no permanent chemical change occurs.[86] The excited-state quenching constant for water in acetonitrile is $k = 1 \times 10^7\ M^{-1}\ s^{-1}$; a transient is produced following the quenching which has the spectrum given in Figure 6. The short-lived transient[87] decays via first-order kinetics and shows general absorption in the visible range. While the spectrum produced is not sufficiently resolved to give any definitive structural information, the lack of congruence between it and that of the RuL_3^+ produced by the other quenchers makes it clear that the quenching is *not* a redox process. Since there appears to be little or no net decomposition upon irradiation of a pure water–acetonitrile solution of **1**, it appears that the photoreaction does not likely involve gross reorganization or decomposition of the complex such as might be expected by water attack at a metal–ligand center.[57–61] It appears much more reasonable that a reversible water attack on the ligand is the origin of the quenching; here again a reasonable possibility appears that the enhanced ligand basicity in the CT excited state can result in a protonation either at a ligand carbon or, more likely, at the oxygen of a carboxy ester group. In parallel with the reduced species, the analogy can be drawn between the charge-transfer excited state and a metal-oxidized ligand radical anion; although interaction with the solvent can furnish a path for nonradiative decay via transient product formation, the interaction does not result in any permanent chemical conversion.

Summary

The results of the present study demonstrate that ligand substituents can produce a variety of effects on the photoreactions of these ruthenium complexes both by "tuning" the redox and excited-state properties of the complex and by providing specific sites for interaction of the complex with solvent or other reagents. The laser flash examination of the complex photoreduction with tertiary amines has demonstrated clearly the occurrence of a mechanism previously suggested by indirect kinetic and ESR spectroscopic evidence; direct observation of the various steps in the process and their importance permit an evaluation of inefficiencies in the overall conversion and sources of energy wastage. The observations made with different oxygen compounds as quencher–reductants for these ruthenium(II) complexes suggest that the range of photoredox reactions available for metal complexes of this or related families should be greatly expandable; while no net chemical conversion occurs in the specific cases examined, it is reasonable to expect that suitable oxygen or other heteroatom-based reductants can be found which lead to net reductive quenching processes analogous to those obtained with amines. Finally, the interactions of both the excited metal complexes and their reduction products with water in nonredox processes occurring at ligand sites suggest the existence of a rich chemistry initiated through ligand-based interactions that has been hitherto unexplored.

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(86) In neutral aqueous solutions hydrolysis of **1** is extremely slow.

(87) The transient lifetime is 250 ns.

Reactivity of Lanthanide Metals with Unsaturated Hydrocarbons: Terminal Alkyne Reactions[1]

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Abstract: The reactions of ytterbium, samarium, and erbium metal vapor with neutral unsaturated hydrocarbons containing acidic hydrogen have been investigated by cocondensation of the metals with 1-hexyne at 77 K followed by isolation and physical and chemical characterization of the organolanthanide products at room temperature. For ytterbium, oxidative addition of the terminal C–H bond of the alkyne is facile, and divalent alkynide hydride complexes are the primary products. Samarium and erbium react with 1-hexyne to form trivalent alkynide hydrides. The catalytic activity of these alkynide hydrides in hydrogenation reactions is also described.

During the past few years we have been investigating[3–8] the low-valent chemistry of the lanthanide elements in efforts to demonstrate experimentally that these metals have a more extensive chemistry than is found in their traditional, ionic, trivalent

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