molar volumes of the products than the reactants would increase these values by approximately 2 kJ mol^{-1}. A simple angular overlap calculation[32-34] leads to 67 and 59 kJ mol^{-1}, respectively. This is surprisingly good agreement with experimental observation for such a crude calculation,[32,35] but more importantly, the AOM calculation supports the inference of a very slightly stronger Cr–NH$_3$ bond in Cr(NH$_3$)$_6^{3+}$ than in Cr(NH$_3$)$_5$Cl^{2+}. Our experimental values are also very close to the mean value of ΔBDE $\cong$ 39.7 kJ mol^{-1} reported for Co(NH$_3$)$_6^{3+}$ based on conventional thermodynamic measurements.[36]

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(32) The small difference in calculated bond energies arises from the contribution of off diagonal elements (σ only) in the secular determinant. Matrix elements were calculated by using tables from Douglas and Hollingsworth[33] and using AOM parameters tabulated by Vanquickenborne and Ceulemans.[34] Note that the Cr–NH$_3$ bond is stronger than the Cr–OH$_2$ bond both in the theoretical calculation and in the experimental measurement.

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(34) Vanquickenborne, L. G.; Ceulemans, A. *Coord. Chem. Rev.* **1983**, *100*, 157.

(35) Note that the assumption that $\Delta H_1 \cong \Delta H_2$ is probably not accurate to the level of a few 10's of kJ mol$^-$ found for the differences between the calculated and experimental values of ΔBDE. Similarly, the neglect of electron correlation effects must lead to significant errors in this application of the angular overlap model. It must also be observed that $\Phi(\Delta H_r)$ is determined as the difference between two very large numbers. For example, for Cr(NH$_3$)$_5$Cl^{2+}, $\Phi(\Delta H_r) \cong -(0.028 \pm 0.01) \times 21.636 \times 10^3$ cm^{-1}. Even if the uncertainty in Φ is negligible, the net uncertainty in ΔH_r is at least 30%.

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Common Emissive Intermediates in the Thermal and Photochemical Reactions of Nonemissive Cyclopentadienylruthenium(II) Complexes of Coumarin Laser Dyes

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Fluorescent intermediates are observed in the reaction of [CpRu(CH$_3$CN)$_3$]$^+$ (Cp = η^5-C$_5$H$_5$) with five highly emissive 7-aminocoumarin laser dyes (laser dye = coumarin-334 (10-acetyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one), 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), coumarin-314 (2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylic acid ethyl ester), coumarin-337 (2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-nitrile), and coumarin-6 (3-(2-benzothiazolyl)-7-(diethylamino)coumarin). The intermediates exhibit intense, dye-centered absorption and emission bands that are red-shifted 27–79 nm with respect to the free laser dye bands. Similar intermediates are observed when the corresponding nonemissive [CpRu(η^6-laser dye)]$^+$ complexes of coumarin-314, coumarin-338, and coumarin-334 are photolyzed in dichloromethane. IR spectral studies suggest that the intermediates contain the laser dye bound to the ruthenium through ligating substituent groups present in the dyes. Both the thermally and photochemically generated intermediates are metastable. The photochemically generated intermediate decays to give free laser dye, while the thermally generated intermediate decays to the [CpRu(η^6-dye)]$^+$ complex. This behavior is proposed to result from the relative ability of the differing ancillary ligands present in the thermal and photochemical reactions to stabilize energetic CpRu$^+$ reaction intermediates.

Introduction

Recently, we have been studying compounds of the form CpRu(arene)$^+$ (Cp = η^5-C$_5$H$_5$; arene = η^6-arene) that contain the CpRu$^+$ group bound to fluorescent arene ligands such as the 7-aminocoumarin laser dyes. The perturbation of luminescence properties by intermolecular interaction is a well-known phenomenon. Previous studies in our group have demonstrated that the intense emission of these laser dyes is sensitive to changes in the binding of the CpRu$^+$ moiety to the chromophore.[1] This sensitivity to binding is a useful spectroscopic probe for the study of CpRu$^+$–π-ligand chemistry. A major goal of our research is to exploit this spectroscopic sensitivity to detect intermediate species such as a η^4-arene intermediate proposed to occur in the photochemical release of bound arene from [CpRu(arene)]$^+$ in acetonitrile.[2] Toward this goal, we wish to report the observation and spectroscopic characterization of reaction intermediates that occur during both the thermal complexation reaction and the photochemical decomplexation reaction of CpRu$^+$ complexes of certain 7-aminocoumarin laser dyes.

Experimental Section

Dichloromethane was distilled over P$_2$O$_5$. Acetone and acetonitrile were of spectroscopic grade and were used without further purification. Laser dyes were obtained from the Eastman Kodak Co. Room-temperature UV–vis spectra of the compounds were obtained with a Cary 17D spectrometer. Rapid-scan UV–vis absorption spectra were collected with a Tracor Northern TN-6500 diode-array apparatus. Emission and excitation profiles were recorded with a Spex F112x spectrofluorometer. ^{1}H NMR spectra were obtained with an IBM Bruker 200-MHz spectrometer. IR spectra (Mattson Sirius 100 mid-IR spectrometer (120 scans)) of dilute solutions (dichloromethane, 2 × 10^{-4} M) were obtained of the CpRu–laser dye intermediates with a demountable cell modified with a 0.5-cm Teflon spacer to allow a sufficient path length.

Synthesis of Compounds. [CpRu(CH$_3$CN)$_3$]PF$_6$ and the laser dye complexes [CpRu(coumarin-1)]PF$_6$, [CpRu(coumarin-2)]PF$_6$, [CpRu(coumarin-311)]PF$_6$, [CpRu(coumarin-344)]PF$_6$, [CpRu(coumarin-6)]PF$_6$, and [CpRu(coumarin-388)]PF$_6$ were prepared as previously described.[1]

[CpRu(coumarin-334)]AsF$_6$. The AsF$_6^-$ salt was prepared in the same manner as the PF$_6^-$ salt with the exception that [CpRu(CH$_3$CN)$_3$]AsF$_6$ was used in place of [CpRu(CH$_3$CN)$_3$]PF$_6$. The NMR, IR, and UV–vis spectra of the cation are identical with those of the PF$_6^-$ compound, and this AsF$_6^-$ salt was used without further characterization.

[CpRu(coumarin-314)]AsF$_6$. A 20-mL volume of N$_2$-degassed 1,2-dichloroethane was added to a degassed flask containing 99.9 mg (0.209 mmol) of [CpRu(CH$_3$CN)$_3$]AsF$_6$ and 68.0 mg (0.217 mmol) of coumarin-314 (2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizine-10-carboxylic acid ethyl ester). The resulting red orange solution was stirred for 3 h. The solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane, and the solution was eluted on a short diatomaceous earth column. Elution with dichloromethane removed the product and left a dark brown impurity on the column. Evaporation of the eluant followed by recrystallization from acetone–ether and washing with ether to remove excess free laser dye yielded 135 mg (0.202 mmol) of dark yellow [CpRu(coumarin-314)]-

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(1) Koefod, R. S.; Mann, K. R. *Inorg. Chem.* **1989**, *28*, 2285.

(2) Schrenk, J. L.; McNair, A. M.; McCormick, F. B.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501.

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AsF_6 (97% yield). ^1H NMR (dichloromethane-d_2): δ 8.59 (s, H_4 (unbound pyrone ring), 1 H), 6.31 (s, H_5 (bound arene ring), 1 H), 5.09 (s, Cp, 5 H), 3.43 (q, ethyl CH_2, 2 H, $J = 7.0$ Hz), 3.26 (m, alkyl CH_2, 3 H), 2.9 (broad m, alkyl CH_2, 3 H), 1.39 (t, ethyl CH_3, 3 H, $J = 7.2$ Hz). Anal. Calcd for $C_{23}H_{24}NO_4AsF_6$: C, 41.33; H, 3.62; N, 2.10. Found: C, 41.16; H, 3.80; N, 2.18. IR data (cm^{-1}): 1784 s, 1718 m, 1618 m, 1561 s, 1522 m.

[CpRu(coumarin-337)]PF$_6$. A 30-mL volume of N_2-degassed acetone was added to a degassed flask containing 75.6 mg (0.174 mmol) of $[CpRu(CH_3CN)_3]AsF_6$ and 46.6 mg (0.175 mmol) of coumarin-337 (2,3,6,7-tetrahydro-11-oxo-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]-quinolizine-10-nitrile). The mixture was refluxed under a slow N_2 purge for 2 h, and then the solvent was removed by rotary evaporation leaving an orange solid. Dichloromethane was added to the orange solid, and the solution was eluted on a short diatomaceous earth column. Elution with dichloromethane removed unreacted laser dye and left the relatively insoluble orange solid at the top of the column. The orange product was stripped off the column by eluting with acetone. Recrystallization of the orange product from acetone–ether followed by either washing yielded 83 mg (0.144 mmol) of orange $[CpRu(coumarin\text{-}337)]PF_6$ (83% yield). ^1H NMR (acetone-d_6): δ 8.87 (s, H_4 (unbound pyrone ring), 1 H), 6.60 (s, H_5 (bound arene ring), 1 H), 5.45 (s, Cp, 5 H), 3.5 (m, alkyl CH_2, 2 H), 3.4 (m, alkyl CH_2, 2 H), 2.8 (broad m, alkyl CH_2, 6 H), 2.2 (m, alkyl CH_2, 2 H). Anal. Calcd for $C_{21}H_{19}N_2O_2PF_6$: C, 43.68; H, 3.32; N, 4.85. Found: C, 43.64; H, 3.28; N, 4.97. IR data (cm^{-1}): 1763 s, 1613 m, 1562 m, 1522 w.

Results and Discussion

Absorption and Emission Spectra of [CpRu(coumarin-334)]$^+$. Previously, we reported the synthesis and UV–vis spectral characteristics of $[CpRu(coumarin\text{-}334)]PF_6$.[1] Reaction of coumarin-334 with $[CpRu(CH_3CN)_3]PF_6$ in 1,2-dichloroethane yields a brick red solid that exhibits relatively weak absorption bands at 450 and 500 nm, which we originally assigned to metal-to-ligand charge-transfer transitions (reaction 1); none of the other laser dye complexes we reported exhibited this weak pair of bands in the visible region of the spectrum. Since that report, we have discovered that these weak absorption bands are due to minute amounts of intensely absorbing impurities. When $[CpRu(coumarin\text{-}334)]PF_6$ is synthesized in refluxing acetone instead of at room temperature in dichloroethane, the resulting product is a yellow solid that does not exhibit the weak absorption bands at 450 and 500 nm but is otherwise identical with the brick red $[CpRu(coumarin\text{-}334)]PF_6$ product reported previously in its UV, IR, and ^1H NMR spectra (reaction 2). The 450-nm band in the impure brick red product is likely due to free coumarin-334 present as an impurity, as coumarin-334 has its intense intramolecular charge-transfer (ICT) absorption λ_{max} at 450 nm. The 500-nm band, on the other hand, has a more interesting origin. In addition to possessing the weak absorption band at 500 nm, solutions of the impure, brick red $[CpRu(coumarin\text{-}334)]PF_6$ (0.1 mM in dichloromethane) also exhibit a unique emission band that is not observed in any of the other laser dye complexes previously reported.[1] Excitation of the sample at 500 nm results in the observation of a structured emission (λ_{max} = 530, 564, 610 nm) band that gradually decays. The 500-nm absorption band also decays on this time scale. The η^6-bound laser dye complex is ruled out as the source of this structured emission band because samples of the pure, yellow $[CpRu(coumarin\text{-}334)]PF_6$ product that have been protected from light do not exhibit this structured emission. This suggested that the unusual absorption and emission bands observed from the impure samples of $[CpRu(coumarin\text{-}334)]^+$ might arise from small amounts of a metastable complex, which is formed during the synthetic reaction between $[CpRu(CH_3CN)_3]^+$ and coumarin-334. We have extensively studied and characterized the nature of these emissive intermediates.

$$[CpRu(CH_3CN)_3]^+ \xrightarrow[\text{dichloroethane}]{\text{coumarin-334}} [CpRu(\eta^6\text{-coumarin-334})]^+ + nCH_3CN + \text{“500-nm absorber”} \quad (1)$$

$$[CpRu(CH_3CN)_3]^+ \xrightarrow[\text{acetone, }\Delta]{\text{coumarin-334}} [CpRu(\eta^6\text{-coumarin-334})]^+ + 3CH_3CN \quad (2)$$

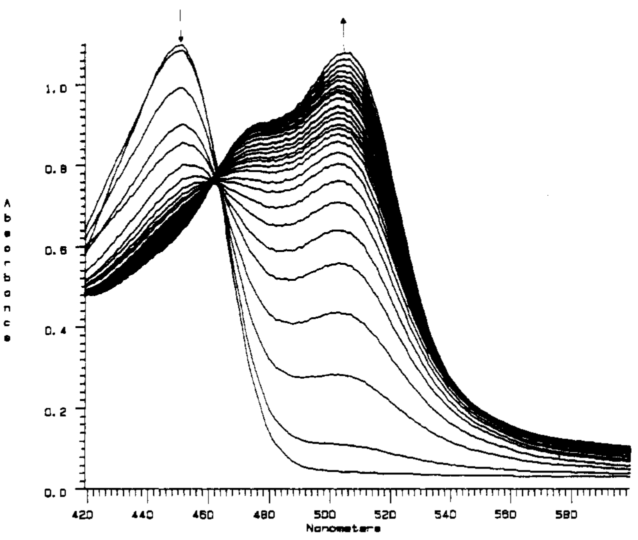

Figure 1. Visible absorption spectra of a 2 × 10^{-5} M dichloromethane solution of coumarin-334 recorded at approximately 1-s intervals following the addition of 4 equiv of $[CpRu(CH_3CN)_3]PF_6$ dissolved in 50 μL of dichloromethane.

Thermal Generation of an Emissive Intermediate. The reaction between coumarin-334 and $[CpRu(CH_3CN)_3]^+$ was monitored with a rapid-scan diode-array absorption spectrometer to seek spectroscopic evidence for intermediates that might form during complexation of the laser dye by the $CpRu^+$ moiety. Figure 1 shows the changes in the visible absorption spectra of a dichloromethane solution of coumarin-334 (0.02 mM)) following the addition of 4 equiv of $[CpRu(CH_3CN)_3]PF_6$; spectra were recorded at ~1-s intervals. Addition of the $[CpRu(CH_3CN)_3]^+$ starting material to the dye solution results in a rapid decrease in the free-dye ICT absorption band at 450 nm and a concomitant growth of a new absorption band at 502 nm with a shoulder at approximately 470 nm. Following the generation reaction, the new 502-nm absorption band very gradually decreases in intensity until it is almost unobservable (not shown in Figure 1). This latter change is consistent with the conversion of the intermediate species to the η^6-bound coumarin-334 complex (reaction 3), which does not exhibit strong absorption bands in this region of the spectrum. The rate of this process is greatly enhanced by the addition of a small amount of acetone to the reaction mixture (reaction 4).

$$[CpRu(CH_3CN)_3]^+ \xrightarrow[CH_2Cl_2\text{, fast}]{\text{coumarin-334}} \text{“502-nm absorber”} \xrightarrow[\text{slow}]{} [CpRu(\eta^6\text{-coumarin-334})]^+ \quad (3)$$

$$\text{“502-nm absorber”} \xrightarrow[\text{acetone}]{\text{fast}} [CpRu(\eta^6\text{-coumarin-334})]^+ \quad (4)$$

This rate enhancement is consistent with the conversion of the intermediate to the arene-bound dye complex, as recent kinetic studies in our laboratory indicate complexation of arene rings by $[CpRu(CH_3CN)_3]^+$ is greatly accelerated in the presence of acetone.[3] Addition of a small amount of acetonitrile to the reaction mixture, on the other hand, results in the decomposition of the intermediate back to free dye, as evidenced by the reappearance of the coumarin-334 ICT band at 450 nm (reaction 5).

$$\text{“502-nm absorber”} \xrightarrow[CH_3CN]{\text{fast}} [CpRu(CH_3CN)_3]^+ + \text{coumarin-334} \quad (5)$$

An emission spectrum taken of the solution following generation of the intermediate (λ_{ex} = 500 nm) exhibits a structured band with maxima identical with those observed in the emission spectrum of impure samples of $[CpRu(coumarin\text{-}334)]PF_6$. The emission band of the reaction mixture decays on the same time

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(3) Koefod, R. S.; Mann, K. R. *J. Am. Chem. Soc.* **1990**, *112*, 7287.

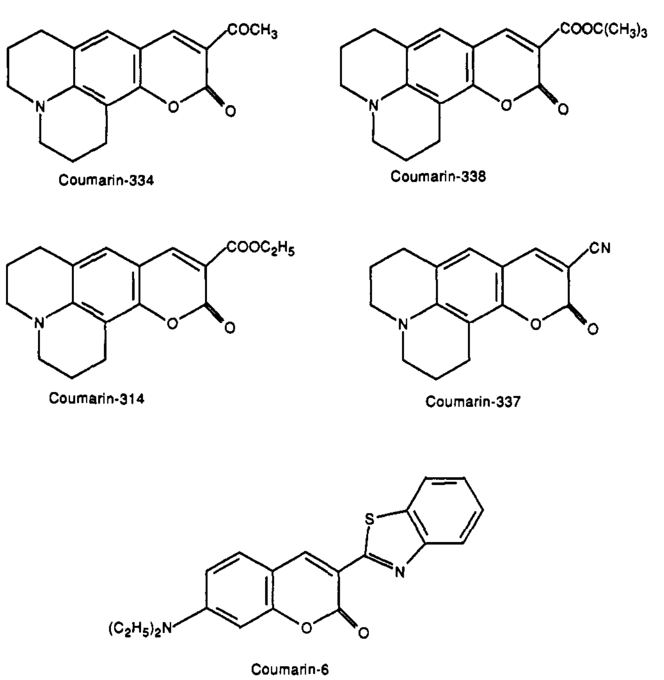

Figure 2. Structures of 3-substituted 7-aminocoumarin laser dyes.

scale as the decay of the 500-nm absorption band. These experiments clearly demonstrate that prior to the complexation of coumarin-334 by $[CpRu(CH_3CN)_3]^+$ in dichloromethane to form the nonemissive, arene-coordinated $[CpRu(coumarin\text{-}334)]^+$ complex, an emissive reaction intermediate is formed. The presence of the weak 500-nm absorption band observed in previously reported samples of the laser dye complex was clearly due to the presence of small amounts of this species.

It is interesting to note that the absorption due to the thermally generated intermediate is very intense; it is similar in intensity to the free-dye absorption, which has an extinction coefficient of approximately 50000 M^{-1} cm^{-1}. The absorption of the η^6-bound laser dye complex in this region is extremely weak, having an extinction coefficient at 500 nm of ~5 M^{-1} cm^{-1}. This suggests that the electronic transitions of the emissive intermediate are primarily centered on the intensely absorbing laser dye ligand and are only slightly perturbed by the metal. Behavior of this type is not consistent with a $CpRu^+$ group bound to the arene ring of the 7-aminocoumarin chromophore, which strongly interferes with the intense dye ICT transition.[1] The structure of the intermediate permits the strong ICT absorption and emission characteristics of the dye chromophore to be retained. We have observed similar behavior for the $CpRu^+$ complex of the laser dye coumarin-6 (see Figure 2), in which the $CpRu^+$ group is bound in an η^6-fashion to the benzothiazolyl arene ring instead of the arene ring of the coumarin chromophore. In this complex, the ruthenium does not interfere strongly with the main coumarin chromophore, and consequently the complex exhibits a slightly red-shifted, extremely intense, dye-centered ICT absorption band and a correspondingly red-shifted emission.[1]

Our observation of an emissive reaction intermediate in the complexation of coumarin-334 by $[CpRu(CH_3CN)_3]^+$ led us to search for similar intermediates in the synthetic reactions of other $[CpRu(\eta^6\text{-coumarin laser dye})]^+$ complexes. Investigation of a variety of differently substituted laser dyes revealed four additional dyes laser dyes that formed emissive intermediates upon reaction with $[CpRu(CH_3CN)_3]^+$: coumarin-6, coumarin-337, coumarin-314, and coumarin-338 (see Figure 2). These dyes share a common structural feature; they contain a potentially ligating functional group in the 3-position of the coumarin backbone. Coumarin-338 and coumarin-314 are analogous to coumarin-334 in that they are substituted with carbonyl groups in the 3-position. Coumarin-337 is substituted with a nitrile functionality, and coumarin-6, with a benzothiazolyl group containing a potentially ligating nitrogen atom.

Table I. UV-Vis Absorption and Emission Data (λ_{max}, nm) for Substituted Coumarin Laser Dyes and Their Complexes

	free dye		thermal intermediate[a]	
	abs	em	abs	em
coumarin-6	464	497	523	555
coumarin-337	446	478	473	507
coumarin-338	432	467	489	517
			465 (sh)	554 (sh)
				600 (vw sh)
coumarin-314	434	469	492	521
			462 (sh)	557 (sh)
				600 (vw sh)
coumarin-334	450	485	502	564
			471 (sh)	530 (sh)
				610 (vw sh)

[a] Intermediate generated by addition of $[CpRu(CH_3CN)_3]PF_6$ to a CH_2Cl_2 solution of the dye.

All five of these dyes exhibit similar behavior when they react with $[CpRu(CH_3CN)_3]^+$. Addition of excess $[CpRu(CH_3CN)_3]^+$ to dichloromethane solutions of these dyes results in the rapid replacement of the intense free-dye absorption and emission bands with new intense absorption and emission bands at longer wavelength. These red-shifted absorption and emission bands then slowly decay as the intermediate converts to the η^6-dye complex. The positions of the absorption and emission maxima of these intermediates, along with spectral data for the free dyes, are summarized in Table I. It is interesting to note that while the intermediates formed from coumarin-337 and coumarin-6 exhibit only a single absorption and emission band, the three 3-acyl laser dyes yield intermediates that exhibit three distinct features in their absorption and emission spectra. In the intermediates derived from coumarin-314 and coumarin-338, which are substituted with ester groups in the 3-position, the main emission band occurs at ~520 nm and exhibits a shoulder with varying intensity at ~555 nm. The intermediate derived from coumarin-334, which is substituted with an acetyl group rather than an ester group, exhibits a similar band system with the maximum band and shoulder reversed; it is characterized by an intense emission band at 564 nm that has a shoulder at ~530 nm that also varies from being very weak in intensity to being moderate in intensity from experiment to experiment. The factors that govern the relative intensity of these intermediate absorption and emission shoulders during the reaction of the laser dyes with $[CpRu(CH_3CN)_3]^+$ remain unclear, but it is clear that this shoulder represents a minor contribution to the intermediate spectra and that it arises independently from the major absorption and emission bands of the intermediate. This suggests that the 3-acyl coumarin laser dyes form two distinct intermediates during their reaction with $[CpRu(CH_3CN)_3]^+$ in dichloromethane, one of which predominates with the ester-substituted dyes and the other of which is formed preferentially by the acetyl-substituted dye (vide infra). The intensely absorbing ICT chromophore of the laser dye is very sensitive to the mode of complexation by the $CpRu^+$ group, and the different electronic transitions observed in the intermediate solutions may arise from complexes in which the $CpRu^+$ group is bound differently to the dye, causing small perturbations of the dye-centered emission and absorption characteristics. The three 3-acyl coumarin laser dye intermediates also exhibit a very weak shoulder in their emission spectra at ~600–610 nm, which is probably due to weak vibrational structure of the main emission band.

Coumarin laser dyes that do not have basic groups substituted in the 3-position exhibit very different spectral changes in the course of their complexation by $CpRu^+$. Addition of excess $[CpRu(CH_3CN)_3]^+$ to dichloromethane solutions of dyes lacking a nucleophilic 3-substituent (e.g., coumarin-1, coumarin-2, and coumarin-311) results in a very slow disappearance of the free-dye ICT absorption band; no new absorption or emission bands are observed in the ICT wavelength region as the reaction proceeds to the η^6-arene complex.

Photochemical Generation of an Emissive Intermediate. As discussed previously, the intermediate responsible for the structured

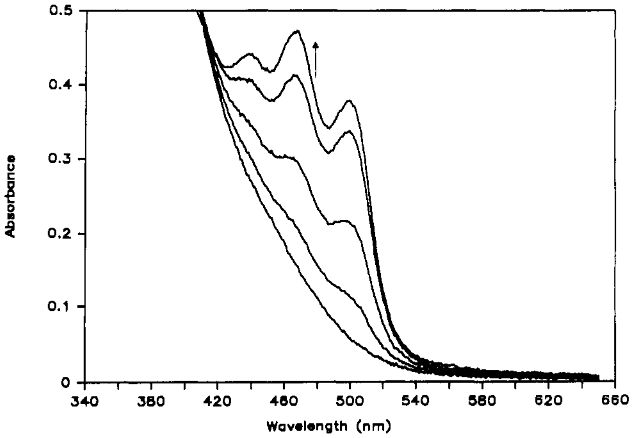

Figure 3. UV–vis spectra recorded during the photolysis ($\lambda > 250$ nm) of a 3×10^{-4} M solution of [CpRu(coumarin-334)]PF_6 in dichloromethane. Absorption bands characteristic of the intermediate at 438, 468, and 500 nm grow in intensity as the photolysis proceeds. Spectra are recorded at approximately 5-min intervals.

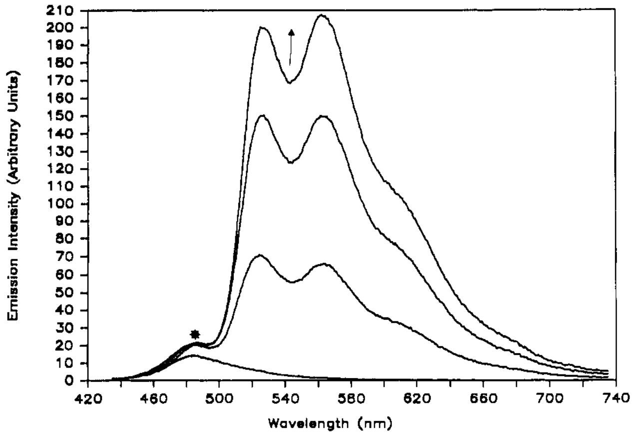

Figure 4. Emission spectra ($\lambda_{ex} = 415$ nm) recorded during the photolysis ($\lambda > 250$ nm) of a 3×10^{-4} M solution of [CpRu(coumarin-334)]PF_6 in dichloromethane. Emission bands characteristic of the intermediate at 526 and 562 nm grow in intensity as the photolysis proceeds. The starred, weak emission band at 485 nm is due to a small amount of free coumarin-334 as an impurity.

emission observed from mixtures of coumarin-334 and [CpRu$(CH_3CN)_3]^+$ in dichloromethane is not present in carefully purified samples of [CpRu(coumarin-334)]PF_6 that have also been protected from light. However, a structured emission can be generated by photolysis of dichloromethane solutions of the complex ($\lambda > 250$ nm; reaction 6). There is a rapid growth period for

$$[\mathrm{CpRu}(\eta^6\text{-coumarin-334})]^+ \xrightarrow[\mathrm{CH_2Cl_2}]{h\nu} \text{"emissive intermediate"} \qquad (6)$$

the formation of the intermediate by photolysis; surprisingly, the intensity of the intermediate emission increases for several minutes following photolysis of the solution.[4] Changes in the absorption spectrum also occur on this time scale. We have monitored the photochemical generation of this emissive species by emission, excitation, and absorption spectroscopy. Figure 3 illustrates the changes in the absorption spectrum of a solution of [CpRu(coumarin-334)]$^+$ that occur upon photolysis, and Figures 4 and 5 show the concomitant changes that occur in the solution's emission and excitation profiles, respectively. The emission spectrum of the photogenerated intermediate is mirrored by both the absorption and excitation spectra, indicating that the species responsible for the changes in the solution's visible absorption spectrum is also the source of the solution's structured emission. Furthermore, the changes in the absorption spectra suggest a smooth conversion of the η^6-bound coumarin-334 complex to a new species that is *not* free coumarin-334.

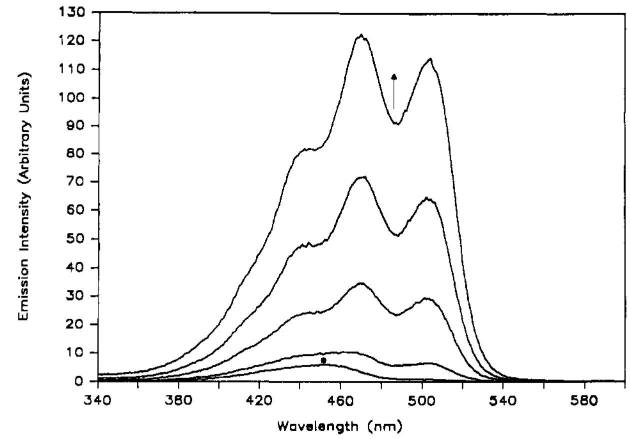

Figure 5. Excitation profile of emitted light at 660 nm recorded during the photolysis ($\lambda > 250$ nm) of a 3×10^{-4} M solution of [CpRu(coumarin-334)]PF_6 in dichloromethane. Excitation bands characteristic of the intermediate at 442, 466, and 501 nm grow in intensity as the photolysis proceeds. The starred, weak excitation band at 450 nm is due to a small amount of free coumarin-334 as an impurity.

As a control experiment, the photolysis of a dichloromethane solution of free coumarin-334 did not give rise to the intense, structured emission observed when solutions of the η^6-ruthenium complex were photolyzed under the same conditions. Furthermore, the photodecomposition products of the 7-aminocoumarin laser dyes have been investigated[5-7] and have not been reported to emit in the region where we observe the structured emission from the photoproduct of [CpRu(coumarin-334)]$^+$. Because the η^6-laser dye complex, the free laser dye, and photodecomposition products of the uncomplexed laser dye can all be ruled out as the source of the structured emission bands observed for solutions of [CpRu(coumarin-334)]$^+$, we suggest that the chemical species responsible for this unusual emission is a photochemically generated, CpRu$^+$–laser dye complex with a binding mode different from η^6-coordination through the dye arene ring. Attractive, tentative structures are η^4-arene coordination or coordination through the δ lactone and acyl oxygen.

The emission and absorption spectra of the photogenerated intermediate from [CpRu(coumarin-334)]$^+$ have maxima nearly identical with those of the intermediate generated thermally from coumarin-334 and [CpRu$(CH_3CN)_3]^+$. The spectra of the photochemically and thermally generated intermediates differ primarily in the relative intensity of the higher energy absorption and emission bands. The thermally generated intermediate exhibits a shoulder on the main 502-nm absorption band at 471 nm, while the photochemically generated intermediate exhibits a well-defined band at 468 nm, which is slightly more intense than the 500-nm band. This again suggests that the 468-nm band and the 500-nm band arise from chemically distinct intermediate species that are produced in different quantities by the photochemical and thermal reactions. The photochemically generated intermediate also exhibits weak absorption and emission shoulders at 438 and ~610 nm, respectively, as does the thermally generated intermediate.

Photochemical generation of the intermediate species from dichloromethane solutions of [CpRu(coumarin-334)]$^+$ does not exceed ~10% conversion. Prolonged photolysis of the solution

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(4) Apparently, the "emissive intermediate" is not the initially photogenerated product in the photolysis of [CpRu(coumarin-334)]$^+$ in dichloromethane. It is possible that a "slipped-ring", [CpRu(η^4-dye)$(CH_2Cl_2)]^+$ complex is the initially photogenerated reaction product. It is generated more quickly than it can react to form the observed emissive intermediate.

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(7) Winters, B. H.; Mandelberg, H. I.; Mohr, W. B. *Appl. Phys. Lett.* **1974**, *25*, 723.

Table II. IR Carbonyl Bands (cm^{-1}) for Substituted Coumarin Laser Dyes and Their Complexes

	free dye		thermal intermediate[a]		[CpRu(η^6-dye)]$^+$	
	δ-lactone	3-acyl	δ-lactone	3-acyl	δ-lactone	3-acyl
coumarin-6	1709	*b*	1643	*b*	1709	*b*
coumarin-337	1719	*b*	1719	*b*	1763	*b*
coumarin-314	1750 1726[c]	1692	1572	1661	1784	1718
coumarin-338	1747	1687	1580	1665	1783	1713
coumarin-334	1713	1663	1570	1659	1767	1700

[a] Intermediate generated by addition of [CpRu(CH$_3$CN)$_3$]PF$_6$ to a CH$_2$Cl$_2$ solution of the dye. [b] Not applicable. [c] The band is split by Fermi resonance, which is a common phenomenon for α-pyrone type carbonyls.

results in the decomposition of both the intermediate and the η^6-complex spectral bands. Initial attempts to obtain an IR spectrum of the intermediate by photolysis of a dilute solution of [CpRu(η^6-coumarin-334)]$^+$ followed by FT-IR analysis in a manner directly analogous to that used to obtain the UV–vis and emission spectra of the photogenerated intermediate did not result in any observable change in the solution IR spectrum, further suggesting that photolysis of the solution converted only a small percentage of the complex to the intermediate.

In a manner similar to that for the thermally generated intermediate, the photochemically generated intermediate is metastable, and we followed its thermal decay by visible absorption spectroscopy. Absorption spectra of a dichloromethane solution of [CpRu(coumarin-334)]$^+$ that was previously photolyzed to generate the intermediate were recorded over a 12-h period. These spectra exhibit an isosbestic decrease in the absorption maxima at 468 and 500 nm with a concomitant increase in free coumarin-334 absorption maximum at 450 nm, indicating that the photochemically generated intermediate species thermally decomposes to liberate free coumarin-334 in solution (reaction 7).

$$\text{“emissive intermediate”} \xrightarrow[\text{(12 h)}]{\text{slow}} \text{coumarin-334} + \text{undetermined Ru-containing products} \quad (7)$$

The rate of the intermediate decay to free laser dye was measured by monitoring the decay of the intermediate absorption maximum at 500 nm. A plot of ln ($A - A_f$) vs time for a room-temperature solution of [CpRu(coumarin-334)]PF$_6$ (0.2 mM in dichloromethane) that had initially been photolyzed for 5 min is linear over at least 3 half-lives and yields a rate constant $k_{obsd} = 1.6 \times 10^{-5}$ s^{-1} ($t_{1/2}$ = 12 h). The rate of this process increases significantly if the solvent contains small amounts of water, acetonitrile, acetone, or tetrabutyl ammonium salts. Indeed, in the presence of 0.02 M tetrabutylammonium hexafluorophosphate the intermediate cannot be generated photochemically. This suggests the possibility that the counterion and/or other potentially coordinating species play an important role in the thermal decomposition of the intermediate.

To explore this possibility, we prepared [CpRu(coumarin-334)]AsF$_6$. The [CpRu(η^6-coumarin-334)]$^+$ cation in the AsF$_6^-$ salt is spectroscopically identical with the PF$_6^-$ compound. Previous studies in our laboratory and elsewhere have shown that AsF$_6^-$ is a more weakly nucleophilic anion than PF$_6^-$ as measured by its ability to assist the photochemical displacement of arene from [CpM(arene)]$^+$ complexes (M = Ru, Fe).[8] We theorized that if a decrease in the nucleophilicity of the medium kinetically stabilized the CpRu–coumarin-334 intermediate, an increase in the intermediate lifetime would be observed for the AsF$_6^-$ compound over the PF$_6^-$ compound.

A solution of the intermediate generated photochemically from a dilute dichloromethane solution (0.2 mM) of the AsF$_6^-$ compound under otherwise identical conditions does not decay measurably over 48 h. However, at higher concentration, the enhanced stability of the intermediate generated from the AsF$_6^-$ complex is lost, preventing detectable amounts of the intermediate from forming at the concentrations required for NMR analysis. These data indicate that the intermediate is very sensitive to the presence of other coordinating species in solution. Consequently, even very poorly nucleophilic species such as the PF$_6^-$ or AsF$_6^-$ counterion can effectively displace the laser dye from the metal center and allow the intermediate to be generated only in dilute solutions. At higher concentrations, an increase in the extent of ion pairing facilitates the displacement of the laser dye from the intermediate by a coordinating counterion.

The emissive intermediate can also be photochemically generated from the [CpRu(η^6-dye)]$^+$ complexes of the other two 3-acyl-7-aminocoumarin laser dyes. Photolysis of dichloromethane solutions of [CpRu(coumarin-338)]$^+$ and [CpRu(coumarin-314)]$^+$ results in the appearance of emission bands that are shifted by $\leq$3 nm from the bands of the thermally generated intermediates. The emissive intermediate cannot be photogenerated from the [CpRu(η^6-dye)]$^+$ complexes of the 3-cyano and 3-benzothiazolyl dyes. No new emission bands are observed during photolysis of these compounds, and prolonged photolysis results in decomposition of the solution.

Structural Characterization of the Intermediate by IR Spectroscopy. Because both the photochemical and thermal generation of the intermediate can only be realized in relatively dilute solutions ($\sim 10^{-4}$ M), it is not feasible to study the intermediate generation by NMR spectroscopy, nor have we been able to grow crystals of the intermediate to permit X-ray structural characterization. IR spectroscopy offered attractive possibilities, but the low yield of photochemical production of the intermediate prevented its analysis by IR spectroscopy. The thermal generation of the intermediate, however, is readily amenable to IR spectral analysis.

When an excess of [CpRu(CH$_3$CN)$_3$]$^+$ is added to a dilute dichloromethane solution of a 3-acyl-7-aminocoumarin laser dye, two sets of spectral changes on different time scales are observed in a series of solution IR spectra. The long time scale changes (24 h) after addition of the CpRu$^+$ starting material show bands due to the η^6-dye complex beginning to grow in, confirming that the ultimate product of the reaction is the η^6-arene bound Ru–dye complex. The faster, initial spectral change (5 min) observed upon addition of excess [CpRu(CH$_3$CN)$_3$]$^+$ to the free-dye solution shifts the δ-lactone and 3-acyl carbonyl bands. The positions of the carbonyl IR bands of the coumarin laser dyes and their corresponding intermediates and [CpRu(η^6-dye)]$^+$ complexes are listed in Table II. Both carbonyl bands almost completely disappear upon addition of 3 equiv of [CpRu(CH$_3$CN)$_3$]PF$_6$ to a solution ($\sim 5 \times 10^{-4}$ M) of the ester-substituted dyes coumarin-314 and coumarin-338. The IR spectrum of the resulting intermediate solution consists of two new IR bands as well as other bands that are at essentially in the same position as the carbon–carbon double-bond vibration bands of the free dye. The two new bands in the intermediate IR spectra are shifted to lower energy with respect to the carbonyl bands of the free dye and are not observed in the IR spectra of the η^6-dye complexes. Consistent with the visible absorption studies, these observations suggest that under these conditions the free dye is almost quantitatively converted to a new species in which the carbonyl groups are bonded to the metal.

The more intense of these two new bands we assign to the δ-lactone carbonyl band and the less intense to the 3-acyl group because the δ-lactone band is much more intense than the acyl band in the free dyes and in the [CpRu(η^6-dye)]$^+$ complexes. The

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(8) Schrenk, J. L.; Palazzotto, M. C.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 4047.

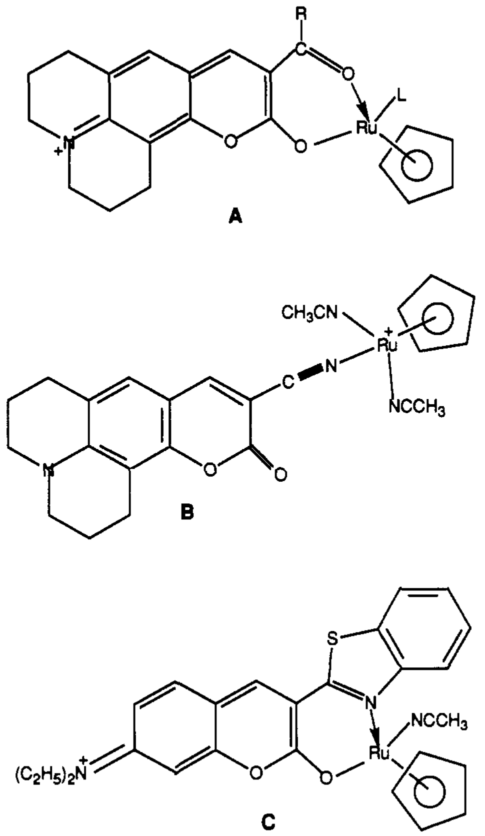
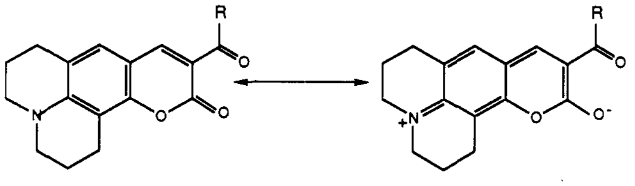


Figure 6. (A) Proposed structure of the intermediate generated from the 3-acyl-7-aminocoumarin laser dyes. The ancillary ligand, designated "L", is probably acetonitrile in the thermally generated intermediate and either dichloromethane or a coordinating counterion in the photochemically generated intermediate. (B) Proposed stucture of the intermediate generated from coumarin-337. (C) Proposed structure of the intermediate generated from coumarin-6.

δ-lactone bands of coumarin-338 and coumarin-314 shift 167 and 178 cm^{-1}, respectively, to lower energy upon formation of the intermediate, indicating that there is a very strong interaction between the δ-lactone carbonyl and the metal center. The shift of the 3-ester carbonyl band is considerably smaller. The ester bands of coumarin-338 and coumarin-314 shift to lower energy by 22 and 31 cm^{-1}, respectively. In support of these assignments, the 3-acyl-7-aminocoumarin laser dyes have a resonance form that enables the carbonyl groups to assume a form not unlike that of acetylacetonate. Thus, we suggest that the predominant emissive ruthenium intermediates derived from the 3-ester-substituted dyes coumarin-338 and coumarin-314 consist of a laser dye that chelates the ruthenium center through its carbonyl groups in enolate fashion, as is depicted in Figure 6A.



In contrast to the behavior of the 3-ester-substituted dyes, the 3-carbonyl band of coumarin-334 does not change significantly upon formation of the intermediate, shifting only 4 cm^{-1} lower in energy. The δ-lactone carbonyl, however, behaves much as it does in the other two 3-acyl dyes, disappearing upon formation of the intermediate and being replaced by a new, intense band shifted 143 cm^{-1} lower in energy. These IR data indicate that the ruthenium in the coumarin-334 intermediate is not chelated by both dye carbonyl groups but rather binds to the laser dye primarily through the δ-lactone carbonyl in monodentate fashion. This is consistent with the absorption and emission spectra of these intermediates discussed above. The electronic spectra of these three intermediates reflect contributions from two distinct species, one of which is produced predominantly by the 3-ester dyes and the other of which is generated predominantly by the 3-acetyl dye. Consequently, we assign the absorption band occurring at ~489–502 nm to the primarily monodentate, δ-lactone carbonyl bound dye intermediate and the ~462–471-nm band to the chelating dye intermediate.

Coumarin-337 is unlike the three 3-acyl coumarin laser dyes in that its 3-substituent (a CN group) is not able to easily adopt a conformation that would permit the dye to act as a chelating ligand. In light of this, it is interesting to note that the δ-lactone band of free coumarin-337 does *not* disappear or shift in any way upon addition of an excess of $[CpRu(CH_3CN)_3]^+$ to form the intermediate. Indeed, none of the IR bands of coumarin-337 undergo any significant shift with the single exception of the 3-nitrile band at 2224 cm^{-1}, which completely disappears upon formation of the intermediate.[9] The IR spectrum of the coumarin-337 intermediate, therefore, clearly demonstrates that this dye interacts with the metal strongly through the nitrile group, as depicted in Figure 6B, and not through the δ-lactone carbonyl.

These observations together with our inability to generate intermediates from coumarin laser dyes that lack a basic 3-substituent indicate that the coumarin laser dyes are reluctant to coordinate through the δ-lactone carbonyl unless a nucleophilic group in the 3-position assists the interaction by permitting a chelation effect. This may explain the small but distinct 4-cm^{-1} red shift of the 3-acetyl band that occurs upon formation of the coumarin-334 intermediate. Even though it does not form the relatively strong acyl–metal bond that occurs in the chelated intermediates, coumarin-334 probably does exhibit a very weak bonding interaction between the ruthenium and the acetyl carbonyl, which assists the formation of the δ-lactone carbonyl–metal bond.

The behavior of the coumarin-6 intermediate also supports this hypothesis. Coumarin-6 does not contain a carbonyl group substituted to the coumarin backbone that can chelate the metal, but the 3-benzothiazolyl substituent is available such that the C–N double bond assumes the same "acac-like" conformation that the 3-acyl groups assume. Thus, the benzothiazolyl nitrogen can potentially bind the metal center concurrently with the δ-lactone carbonyl, as is shown in Figure 6C, through a stabilizing chelation effect. This, in fact, is experimentally observed; IR spectra indicate that the δ-lactone carbonyl band of free coumarin-6 completely disappears upon formation of the intermediate, confirming that coumarin-6 binds through its δ-lactone carbonyl in the intermediate.

Discussion

The behavior of these unusual, emissive intermediates is interesting in light of previous studies that have been published concerning the photochemistry of transition-metal–arene complexes. The photochemical reactivity of $[CpRu(\eta^6\text{-arene})]^+$ complexes has been well established.[10] $[CpRu(\eta^6\text{-arene})]^+$ complexes readily undergo photochemical displacement of the arene ring in the presence of good nucleophiles such as acetonitrile. Studies from our group have established that the excited state that leads to loss of arene in these compounds is probably the distorted a^3E_1 state.[11] The distortion in the metal–ring breathing mode of the complex results in a net lengthening of the metal–arene bond in the excited state and enhances the steric accessibility of the metal center to nucleophilic attack. The $[CpRu(\eta^6\text{-laser dye})]^+$ complexes we report here are typical in this respect; photolysis of acetonitrile solutions of the complexes results in rapid accumulation of uncomplexed laser dye in solution.[1] However,

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(9) A new nitrile band is not observed in the coumarin-337 intermediate, but this is not surprising because the ν(CN) stretches of metal–nitrile complexes are often quite weak. For example, the nitrile bands of $[CpRu(CH_3CN)_3]^+$ are not detectable in the IR spectra at the concentrations used to study the dye intermediates.

(10) Moriarty, R. M.; Gill, U. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157.

(11) McNair, A. M.; Schrenk, J. L.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 2633.

the experiments outlined here indicate that certain of these [CpRu(η^6-laser dye)]$^+$ complexes exhibit very different behavior depending on whether they are photolyzed in a relatively non-nucleophilic medium such as dichloromethane or in a nucleophilic medium like acetonitrile. By carrying out photolyses in the absence of good nucleophiles, it is possible to trap the laser dye between its fully η^6-bound state and its completely unbound state as a weakly complexed intermediate.

The fact that the photochemically generated intermediates thermally decay to give free dye while the thermally generated intermediates decay to give the η^6-dye complex indicates that the intermediates generated from these two pathways are not identical. However, our observations that the photochemically and thermally derived intermediates exhibit essentially identical absorption and emission spectra argues that the structures of the two intermediates must be very similar. Because the emission and electronic absorption characteristics of both intermediates are centered on the dye ligand, it follows that the electronic transitions of the dye are perturbed in a manner nearly identical with that of the two intermediates. The perturbation of the dye absorption and emission properties results primarily from its interaction with the CpRu$^+$ moiety, and it is therefore reasonable to assume that the dye binds the ruthenium center the same way in the thermally and photochemically generated intermediates. On the basis of IR spectra, we propose the structure depicted in Figure 6A (vide supra) for the dyes that contain a 3-acyl substituent. The remaining ambiguity in the intermediate's structure is the identity of the ancillary ligand, designated "L" in Figure 6.

The formation of the thermally generated intermediates probably involves the replacement of two acetonitrile ligands by the chelating coumarin dye ligand and leaves an acetonitrile as the most likely ancillary ligand. In contrast, during the photochemical generation of the intermediate, there is no acetonitrile present to serve as a ligand. Consequently, the ancillary ligand in the photochemically generated intermediate is probably either a molecule of the dichloromethane solvent or perhaps the counterion (PF_6^-).

Differences in the ancillary ligand may explain the differing reactivity of the two species. In the strict sense, the emissive species we observe in these reactions are probably more likely shunts rather than intermediates because it is unlikely that dye chelates could proceed directly to the η^6-complex. The coumarin arene ring in a ruthenium–dye chelate would be held at a great enough distance from the ruthenium center to prevent any facile "walk over" of the ruthenium from the carbonyl groups to the arene ring; rather, the dye probably first dissociates from the chelate shunt and then subsequently undergoes complexation of its arene ring to form the more thermodynamically stable η^6-arene complex. The nature of the ancillary ligand would have an important influence on this process. For the formation of the η^6-complex to proceed successfully from the shunt, the CpRu$^+$ moiety must be stabilized following the dissociation of the dye. Acetonitrile is a very good ligand and effectively stabilizes the CpRu$^+$ group after the chelate collapses but before the η^6-complex is formed. Dichloromethane and the PF_6^- counterion, on the other hand, are very poor ligands. Consequently, upon dissociation of the laser dye from the photochemically generated intermediate, the poorly nucleophilic species present are inadequate to stabilize the CpRu$^+$ moiety. In this case the [CpRu(S)$_3$]$^+$ species decomposes before complexation of the laser dye arene ring can occur.

The photochemical behavior of the [CpRu(η^6-dye)]$^+$ complexes in acetone solution supports this model as well. Photolysis of a dry, degassed acetone solution of [CpRu(coumarin-334)]$^+$ results in the slow and irreversible conversion of the complex to free laser dye. If the ruthenium-containing product of this photodecomplexation reaction was a stable [CpRu(acetone)$_3$]$^+$ complex, the photolyzed solution of free coumarin-334 would be expected to be rapidly complexed by the CpRu$^+$ group to re-form the η^6-complex because the more weakly basic acetone ligands yield a far more reactive species than the tris(acetonitrile) complex. The free coumarin-334 is not, in fact, thermally recomplexed when the photolyzed sample is left in the dark. The ruthenium-containing product of the photoreaction has decomposed to a species that is not able to complex the dye. Because acetone cannot effectively stabilize the CpRu$^+$ moiety, it is even less likely that far poorer nucleophiles such as dichloromethane or PF_6^- will be able to prevent the decomposition of CpRu$^+$ following dissociation of the dye from the photogenerated intermediate.

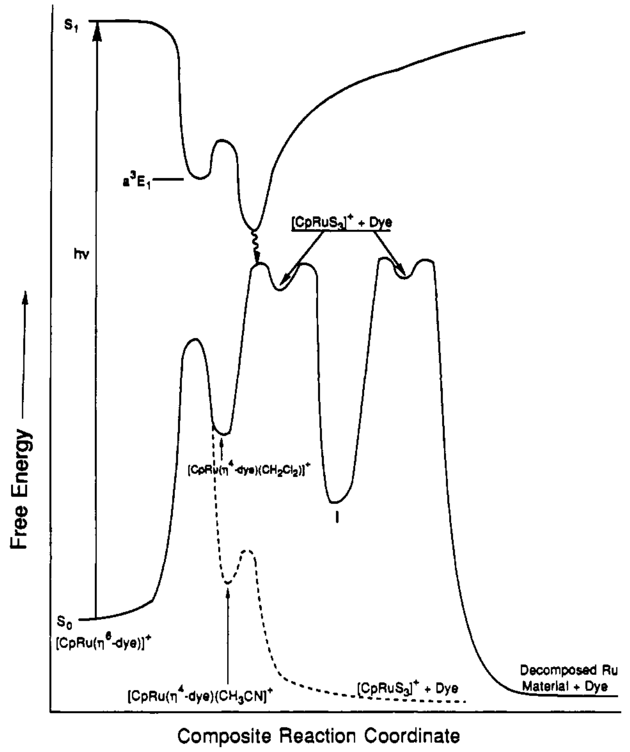

Figure 7. Qualitative ground- and excited-state reaction coordinate diagram for the displacement of laser dye from an η^6-CpRu$^+$ complex of a 3-acyl-7-aminocoumarin laser dye. The solid line and the dashed line represent the reaction coordinates in dichloromethane and acetonitrile solution, respectively. The CpRu(S)$_3$$^+$ + dye "state" appears twice on the reaction coordinate diagram because I is actually a shunt species that does not lie directly on the CpRu(η^6-dye)$^+$ $\rightarrow$ CpRu(S)$_3$$^+$ + dye coordinate.

The observation of similar intermediates in both the thermal complexation reactions of the laser dyes by CpRu$^+$ and in the photochemistry of the η^6-dye–metal complex suggests that these two processes share a common parentage. A likely candidate for this common parentage is the "slipped-ring" η^4-arene complex, which has been proposed to occur in both the thermal[12] and photochemical[2] arene decomplexation reactions of [CpRu(η^6-arene)]$^+$ complexes as well as in the thermal arene complexation reactions of [CpRu(CH$_3$CN)$_3$]PF$_6$.[3] The implication of a common branching point in both the complexation and decomplexation reactions of the laser dyes together with the behavior of the intermediates outlined above suggests the qualitative reaction coordinate diagram depicted in Figure 7.

Thermal displacement of the dye from [CpRu(η^6-laser dye)]$^+$ complexes does not occur to any appreciable extent in dichloromethane and occurs relatively slowly in acetonitrile, indicating that there is a fairly high-energy barrier toward formation of the η^4-slipped-ring state as the ground state S$_0$ reaction path is traversed in either dichloromethane or acetonitrile solution. The chief difference in the reaction paths followed in dichloromethane (solid line in Figure 7) and acetonitrile (dashed line in Figure 7) is in the free energy of solvated [CpRu(η^4-arene)S]$^+$ and [CpRuS$_3$]$^+$ species that are generated as the decomplexation reaction proceeds. Acetonitrile is a good σ-donor and π-acceptor that stabilizes these species very effectively. Dichloromethane, on the other hand, is a very poor ligand that is unable to confer stability. Consequently, the free energy contribution from the

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(12) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519.

$[CpRu(\eta^4\text{-arene})S]^+$ and $[CpRuS_3]^+$ intermediates that are generated as the reaction coordinate in Figure 7 is crossed will be much larger in dichloromethane than in acetonitrile, giving rise to the energy gap between these solvated intermediates in the two solvents. The dichloromethane-solvated $[CpRuS_3]^+$ product is a high-energy species that either rapidly complexes the dye arene ring to form the η^4-slipped-ring intermediate, complexes the dye carbonyl groups to form the emissive intermediate (designated "I" in Figure 7), or simply decomposes to an unknown, unreactive ruthenium species with the irreversible liberation of free dye in solution.

This scheme is consistent with the observed generation of a metastable, carbonyl-complexed intermediate during complexation of the dye in dichloromethane solution even though the source of $CpRu^+$ in our experiments was the tris(acetonitrile) adduct. Recent kinetic studies in our laboratory of the complexation of arenes by $[CpRu(CH_3CN)_3]^+$ indicate that the tris(acetonitrile) adduct is quite inert and that the reactive species in these reactions is the "unsaturated" $[CpRu(CH_3CN)_2(S)]^+$ solvate in which an acetonitrile ligand has been replaced by a solvent molecule.[3]

Traversing the excited-state reaction coordinate involves the initial population of the lowest singlet state, S_1, of the η^6-complex and subsequent rapid intersystem crossing to the distorted a^3E_1 state. Distortion of the triplet state to form the slipped-ring, η^4-arene complex channels the molecule into an excited-state funnel from which it readily back-intersystem crosses and relaxes to the ground-state potential surfaces that lead to the characteristic reactions previously discussed.

Conclusions

An emissive intermediate is observed in the photolysis of the η^6-$CpRu^+$ complexes of 3-acyl-7-aminocoumarin laser dyes in noncoordinating media. The perturbed, dye-centered emission observed from the intermediate indicates that the $CpRu^+$ moiety is bound to the dye in the intermediate but is not bound to the dye arene ring as this complexation mode would be expected to completely quench the dye emission. The observation that the intermediate is only observed from 3-substituted coumarin laser dyes and consideration of the IR spectra of the intermediates suggests that they consist of the laser dye coordinating the $CpRu^+$ group through its two carbonyl groups. The ability to observe the intermediate in both the thermal complexation and photochemical decomplexation of laser dye suggests that these two processes occur through a common transition state that may be a "slipped-ring" complex of reduced arene hapticity. In the future we intend to pursue the synthesis and isolation of other transition-metal–laser dye complexes that retain the emissivity of the free laser dye.

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Notes

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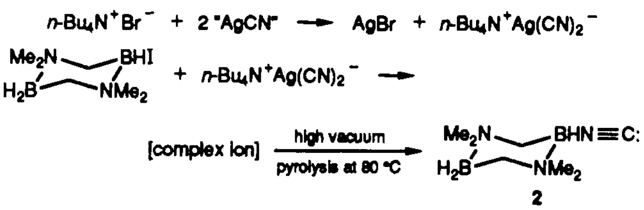
Borane Isonitriles and Carboxylates. Synthesis and Characterization of the 2-Carboxylic Acid Derivative of 1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratacyclohexane

Norman E. Miller

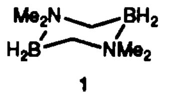
Received October 16, 1990

Carboxylic acid substitution onto boranes is a desirable transformation because it provides a means of conjugating borane moieties to organic structures or vice versa. Bringing about such substitution has been difficult, and a general route for substituting intact nonpolyhedral boranes has not existed. The first carboxylate derivative of a borane is the carbonyl adduct of borane $BH_3 \cdot C{\equiv}O$,[1] which can be considered the anhydride of the acid $H_3O^+BH_3CO_2H^-$, known only as the divalent salt ion $BH_3CO_2^{2-}$, and derivatives.[2] Carboxylate substitutions onto $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ ions proceed via hydration of the anhydride carbonyl derivatives. The B_{10}–bis(carbonyl) is obtained by displacement of the nitrogen in $B_{10}H_8(N_2)_2$ inner salt, and the B_{12}–bis(carboxylic acid), by carbonylation of the crystalline, hydrated acid of $B_{12}H_{12}^{2-}$ under pressure at elevated temperature.[3] More recently, carboxylic acid derivatives of nominally BH_3 adducts were made by the two-stage hydrolysis of nitrilium salts of preformed cyanoboranes.[4]

Scheme I



Bringing about carboxylate substitution on 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (**1**) is an objective



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of long standing. This ring system has been shown[5] to be robust enough to withstand reasonable chemical processing. Once obtained, the carboxylate and other functions to which it could be converted would be capable of being conjugated to organic structures of interest.

A method is reported here to convert a B–I substituent to a $B{-}CO_2H$ function on extant borane derivatives. It began with the development of a new cyaniding reagent to make isonitrilo-substituted boranes.

Exchange of isonitrile for iodide in Me_3NBH_2I is reported by Vidal and Ryschkewitsch[6] using silver cyanide to form a complex

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