However, as discussed by Juris et al.,[2] the ΔE_1 value really defines the effective barrier between two states, not the thermodynamic energy difference. Equations 2 and 3 describe the minimal decay

$$^3\mathrm{CT} \xrightarrow{k_a} {}^3\mathrm{d{-}d} \tag{2a}$$

$$^3\mathrm{d{-}d} \xrightarrow{k_{-a}} {}^3\mathrm{CT} \tag{2b}$$

$$^3\mathrm{d{-}d} \xrightarrow{k_b} \mathrm{GS} \tag{3}$$

scheme that allows for deactivation via a ^{3}d–d state, where the k_b step represents decay to the ground state (GS). Since the ^{3}d–d state is a short-lived state that is populated via a thermally activated process, it can be regarded as a steady-state species, in which case the rate constant for decay through this channel can be written as

$$k = k_a \frac{k_b}{k_{-a} + k_b} \tag{4}$$

Limiting cases of eq 4 have been discussed by Juris et al.[2] Case I behavior obtains when $k_b \gg k_{-a}$. In this limit, the rate constant for the relaxation process in question is effectively k_a. As can be seen from Table II, the ΔE_1 processes all have frequency factors of the order of 10^{13} s^{-1}, which are consistent with a simple barrier crossing (case I) process. Accordingly, ΔE_1 is taken to be the barrier associated with crossing from the ^{3}CT to the short-lived ^{3}d–d state. As with 2,2′-bipyridine complexes,[28] this barrier is enhanced by phenyl substituents located para to the donor nitrogens, but in the case of the trpy systems, the bulk of the effect appears to associated with substitution at the 4′-position.

A second thermally activated decay channel can also be resolved for the 4,4′-dpt and the tsite complexes, where the onset of deactivation via the ^{3}d–d state is displaced to higher energy. A low barrier and a much reduced frequency factor are associated with this channel. The magnitude of the frequency factor A_2 is consistent with internal conversion between nested energy surfaces, where the Franck–Condon factors for surface crossing are unfavorable. Additional low-lying ^{3}CT states are known to occur in polyimine complexes of ruthenium(II),[29] and there is evidence that they, too, facilitate relaxation from the emitting state.[2,30] Therefore, the ΔE_2 process is attributed to relaxation via a neighboring ^{3}CT state. Equations analogous to eqs 2 and 3 can be written for this process as well, but a somewhat different kinetic model is appropriate. In view of the fact that a series of nested surfaces are involved and in view of the proximity of the two excited states, we assume that repopulation of the emitting ^{3}CT state is more facile than relaxation to the ground state; i.e., $k_{-a} \gg k_b$. In this limit, the two ^{3}CT states are thermally equilibrated, and

$$k_2 \approx k_b k_a / k_{-a} \tag{5}$$

(Note that this is a limiting case of eq 4, but eq 5 may be valid even if the steady-state assumption is inappropriate.) According to this model, the low frequency factor is associated with intersystem crossing from the proximal ^{3}CT state to the ground state. In line with this interpretation, A_2 is of the order of k_0.

One of the assumptions in our analysis is that direct intersystem crossing from the lowest energy ^{3}CT state to the ground state is a temperature-independent process. The plateau regions in the plots presented in Figure 3 are consistent with this model. Below 20 K, however, Agnew et al. have shown that k_0 is also a temperature-dependent quantity.[31]

Acknowledgment. We wish to acknowledge Jon R. Kirchhoff, who carried out some initial studies of Ru(tsite)$_2^{2+}$. This research was supported by Grant CHE-8719638.

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Emission and Photochemical Reactivity in Fluorescent Arene Complexes of Cyclopentadienylruthenium(II). Requirements for an Emissive CpRu(arene)$^+$ Complex

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The syntheses and characterization of five new compounds that contain the CpRu$^+$ (Cp = η^5-C_5H_5) moiety bound to a highly fluorescent arene ligand are reported. Nonemissive complexes of the highly emissive laser dyes coumarin-7 (3-(2′-Benzimidazolyl)-7-(*N*,*N*-diethylamino)coumarin) and coumarin-30 (3-(2′-*N*-methylbenzimidazolyl)-7-(*N*,*N*-diethylamino)coumarin) in which the CpRu$^+$ group binds the dye benzimidazolyl arene ring were prepared and are compared to the structurally analogous, emissive complex of coumarin-6. Isomeric complexes of 9-phenylanthracene in which either the end anthracene ring or the substituent phenyl group is bound by the CpRu$^+$ moiety were prepared for comparison to the structurally analogous complexes of rubrene (5,6,11,12-tetraphenylnaphthacene). Room-temperature emission from fluid solutions of these [CpRu(η^6-arene)]$^+$ complexes is only observed when the metal complex exhibits its lowest energy singlet absorption band at $\lambda_{max} \geq 480$ nm. Reaction and emission quantum yields for the CpRu$^+$ complexes of coumarin-6, rubrene, and 9-phenylanthracene are reported and used to elucidate the electronic and structural requirements for emission from these compounds.

Introduction

For the past several years, our group has been studying various aspects of the thermal and photochemistry of the arene complexes of iron, ruthenium, and osmium. Most recently, our efforts in this area have turned towards the use of highly fluorescent arenes as the arene ligand in [CpRu(η^6-arene)]$^+$ (Cp = η^5-C_5H_5) complexes. The emission associated with these ligands is very sensitive to changes that result from binding ruthenium to the arene π-system, making it an excellent spectroscopic probe of subtle changes in ruthenium–arene bonding. Consequently, we decided to investigate compounds of this type in the hope that they might yield spectroscopic evidence for reaction intermediates proposed to occur during the thermal[1] and photochemical[2] displacement

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of arene from [CpRu(η^6-arene)]$^+$ complexes in acetonitrile solution. Although we had previously prepared CpRu$^+$ complexes of emissive arenes, including azulene, chrysene, anthracene, and pyrene,[1] we did not observe room-temperature emission from fluid solutions of any CpRu(η^6-arene)$^+$ complexes until we prepared the complexes of the laser dye coumarin-6[3] and the polyaromatic hydrocarbon rubrene (5,6,11,12-teraphenylnaphthacene),[4] which emit intensely in fluid solution. We became interested in understanding why only very specific arene ligands could retain their fluorescence in the corresponding CpRu(η^6-arene)$^+$ complexes. Room-temperature emission in transition-metal compounds is relatively rare, and delineation of the requirements for emission in the [CpRu(η^6-arene)]$^+$ complexes could be useful in suggesting rational pathways to the preparation of other emissive organometallic compounds. We wish to report emission and reaction quantum yield data as well as reactivity and structural studies for a series of CpRu$^+$ complexes of highly fluorescent arenes. These studies suggest the structural and electronic requirements for emission in ruthenium–arene complexes.

Experimental Section

All solvents were of spectroscopic grade and were used without further purification. Coumarin laser dyes were obtained from the Eastman Kodak Co. Rubrene and 9-phenylanthracene were obtained from the Aldrich Chemical Co. Room-temperature UV–vis spectra of the compounds were obtained with a Cary 17D spectrometer. Emission and excitation profiles were recorded on a Spex F112x spectrofluorometer. Standard 1D, ^{1}H NMR spectra were obtained on an IBM Bruker 200-MHz spectrometer and 2-D, COSY ^{1}H NMR spectra were obtained on an IBM Bruker 300-MHz spectrometer.

Synthesis of Compounds. [CpRu(CH$_3$CN)$_3$]PF$_6$ and some previously described laser dye complexes have been reported.[1,3,4] The new complexes of coumarin-30, coumarin-7,9-phenylanthracene, and rubrene were synthesized by stirring the appropriate arene with 1 equiv of [CpRu(CH$_3$CN)$_3$]PF$_6$ in degassed 1,2-dichloroethane or acetone. The reaction products were purified by column chromatography followed by recrystallization. The details of these synthetic procedures are given in the supplementary material.

[CpRu(coumarin-7)]PF$_6$. The complex was prepared in 32% yield by refluxing the starting materials in 1,2-dichloromethane for 23 h followed by column chromatography using diatomaceous earth. ^{1}H NMR (acetonitrile-d_3): δ 8.85 (s, 1 H, H$_4$), 7.61 (d, 1 H, H$_5$, J = 9.1 Hz), 6.95 (m, 2 H, protons ortho to the nitrogen substituents on the bound benzimidazolyl arene ring), 6.81 (d of d, 1 H, H$_6$, J = 9.1 Hz), 6.59 (weakly coupled d, 1 H, H$_8$), 5.80 (m, 2 H, protons meta to the nitrogen substituents on the bound benzimidazolyl arene ring), 4.97 (s, 5 H, Cp), 3.50 (q, 4 H, ethyl CH$_2$, J = 7.1 Hz), 1.20 (t, 6 H, ethyl CH$_3$, J = 7.1 Hz). UV–vis data (dichloromethane solution): λ_{max} = 474 nm (ϵ_{max} = 76000 M^{-1} cm^{-1}). Anal. Calcd for C$_{25}$H$_{24}$N$_3$O$_2$RuPF$_6$: C, 46.59; H, 3.75; N, 6.52. Found: C, 46.37; H, 4.00; N, 6.37.

[CpRu(coumarin-30)]PF$_6$. The complex was prepared in 91% yield in the same manner as the coumarin-7 complex. ^{1}H NMR (acetonitrile-d_3): δ 8.12 (s, 1 H, H$_4$), 7.50 (d, 2 H, H$_5$, J = 8.98 Hz), 6.95 (d of m, protons ortho to the nitrogen substituents on the bound benzimidazolyl arene ring, J = 25 Hz), 6.78 (d of d, 1 H, H$_6$, J = 8.98 Hz), 6.60 (d, 1 H, H$_8$, J = 2.38 Hz), 5.88 (m, 2 H, protons para to the nitrogen substituents on the bound benimidazolyl arene ring), 5.03 (s, 5 H, Cp), 3.64 (s, 3 H, CH$_3$ from the *N*-methylbenzimidazolyl group), 3.50 (q, 4 H, CH$_2$ from amino ethyl groups, J = 7.09 Hz), 1.20 (t, 6 H, CH$_3$ from amino ethyl groups, J = 7.07 Hz). UV–vis data (dichloromethane solution): λ_{max} = 437 nm (ϵ_{max} = 35000 M^{-1} cm^{-1}). Anal. Calcd for C$_{26}$H$_{26}$N$_3$O$_2$RuPF$_6$: C, 47.42; H, 3.98; N, 6.38. Found: C, 47.36; H, 4.12; N, 6.47.

[CpRu(9-phenylanthracene)]PF$_6$ (Anthracene-Bound Isomer). The complex was prepared in 78% yield by stirring the starting materials in 1,2-dichloroethane at room temperature for 2.5 h followed by column chromatography using diatomaceous earth. ^{1}H NMR (acetone-d_6): δ 8.72 (s, 1 H, H$_{10}$), 8.04 (d, 1 H, H$_8$, J = 8.5 Hz), 7.68 (m, 5 H, phenyl group), 7.67 (d, 1 H, H$_1$, J = 6.1 Hz), 7.48 (m, 3 H, H$_{5,6,7}$), 6.83 (d, 1 H, H$_4$, J = 6.3 Hz), 6.64 (t, 1 H, H$_2$, J = 5.8 Hz), 6.49 (t, 1 H, H$_3$, J = 5.7 Hz), 5.16 (s, 5 H, Cp). UV–vis data: λ_{max} = 486 nm (ϵ_{max} = 3400 M^{-1} cm^{-1}). Anal. Calcd for C$_{25}$H$_{19}$RuPF$_6$: C, 53.10; H, 3.39. Found: C, 53.20; H, 3.24.

[CpRu(9-phenylanthracene)]PF$_6$ (Phenyl-Bound Isomer). The complex was prepared in 23% yield by refluxing the starting materials for 4 days in acetone followed by column chromatography using alumina. ^{1}H NMR (acetone-d_6): δ 9.12 (d, 1 H, unbound anthracene ring proton adjacent to the phenyl bound CpRu$^+$ group, J = 8.92 Hz), 8.86 (s, 1 H, H$_{10}$), 8.23 (m, 2 H, unbound anthracene ring), 7.9 (m, 2 H, unbound anthracene ring), 7.67 (d, 1 H, unbound anthracene ring, J = 7.50 Hz), 7.57 (m, 2 H, unbound anthracene ring), 6.77 (m, 4 H, bound phenyl ring), 6.66 (m, 1 H, bound phenyl ring), 5.73 (s, 5 H, Cp). UV–vis data (acetonitrile solution): λ_{max} = 397 nm (ϵ_{max} = 7000 M^{-1} cm^{-1}), λ_{max} = 379 nm (ϵ_{max} = 7900 M^{-1} cm^{-1}), λ_{max} = 360 nm (ϵ_{max} = 5300 M^{-1} cm^{-1}). Anal. Calcd for C$_{19}$H$_{15}$RuPF$_6$: C, 53.10; H, 3.39. Found: C, 53.22; H, 3.46.

[(CpRu)$_2$(rubrene)](PF$_6$)$_2$. The complex was prepared in 51% yield in the same manner as the coumarin-7 complex. ^{1}H NMR (acetone-d_6): δ 9.02 (d, 2 H, bay protons on naphthacene rings adjacent to metal bearing phenyl groups, J = 9.16 Hz), 7.67 (m, 2 H, unbound naphthacene ring), 7.59 (d, 1 H, unbound naphthacene ring, J = 9.03 Hz), 7.36 (m, 9 H, unbound naphthacene and phenyl rings), 7.16 (d of d, 4 H, unbound phenyl rings, J = 7.1 Hz), 6.30 (m, 4 H, bound phenyl rings), 6.21 (m, 6 H, bound phenyl rings), 5.39 (s, 10 H, Cp). UV–vis data (acetonitrile solution): λ_{max} = 574 nm (ϵ_{max} = 13000 M^{-1} cm^{-1}), λ_{max} = 535 nm (ϵ_{max} = 12000 M^{-1} cm^{-1}). Anal. Calcd for C$_{52}$H$_{38}$RuP$_2$F$_{12}$: C, 54.08; H, 3.32. Found: C, 54.00; H, 3.66.

Emission Quantum Yields. The emission quantum yield for [CpRu(coumarin-6)]$^+$ was determined at 298 K in dichloromethane solution with the comparative method of Demas and Crosby.[5] Coumarin-6 in acetonitrile at 298 K was used as the standard (ϕ_r = 0.63).[6] [CpRu(coumarin-6)]$^+$ solutions were prepared with the same absorbance as the coumarin-6 samples at the excitation wavelength (absorbance ~ 0.05). [CpRu(rubrene)]$^+$ (phenyl-bound isomer) was determined at 298 K in dichloromethane solution by the same procedure, except that rubrene in dichloromethane was used as the standard. (ϕ_r = 0.94).[7]

Reaction Quantum Yields. Quantum yields were measured for the photochemical release of arene from the [CpRu(η^6-arene)]$^+$ complexes in acetonitrile solutions. Monochromatic light was obtained from the output of a 75-W medium-pressure mercury vapor lamp with the appropriate interference filter (Oriel). The monochromatic light beam was then passed into a sealed quartz cell. All solutions were stirred during photolysis. Samples of [CpRu(9-phenylanthracene)]$^+$ and [CpRu(rubrene)]$^+$ (phenyl-bound isomers) were degassed by bubbling them with N$_2$ for 5 min to insure clean photolysis; the quantum yield for [CpRu(coumarin-6)]$^+$ was determined in nondegassed acetonitrile as the photoreaction proceeded cleanly without degassing. [CpRu(9-phenylanthracene)]$^+$ and [CpRu(coumarin-6)]$^+$ were irradiated at 365 nm, and [CpRu(rubrene)]$^+$ was irradiated at 313 nm. Quantum yields are based on the stoichiometry of eq 1. The procedure for determining the

$$[\mathrm{CpRu}(\eta^6\text{-arene})]^+ \xrightarrow[\mathrm{CH_3CN}]{h\nu} [\mathrm{CpRu}(\mathrm{CH_3CN})_3]^+ + \text{arene} \qquad (1)$$

quantum yield for each compound involved measuring the differential absorbance of the sample (at 411, 520, and 580 nm, respectively, for the complexes of 9-phenylanthracene, coumarin-6, and rubrene) as a function of photolysis time for two independently prepared solutions. The data for a given solution were corrected for incomplete light absorption and inner filter effects.[8] Actinometric measurements were made periodically with an Aberchrome 540 actinometer.[9] Quantum yields were calculated as the average of all the data obtained for each compound (a minimum of five data points).

Results and Discussion

Structural Determination. We have prepared CpRu$^+$ complexes of a wide variety of different fluorescent arenes. Many of the fluorescent arenes we have used as π-ligands are polyaromatic systems, containing two or more aromatic rings to which the CpRu$^+$ moiety can potentially coordinate. Because the electronic transitions of these polyaromatic molecules that produce the fluorescence are localized on particular arene rings, all the benzenoid rings do not contribute equally to the spectroscopic characteristics of the molecule. Consequently, it is very important to know unambiguously which aromatic ring the CpRu$^+$ group

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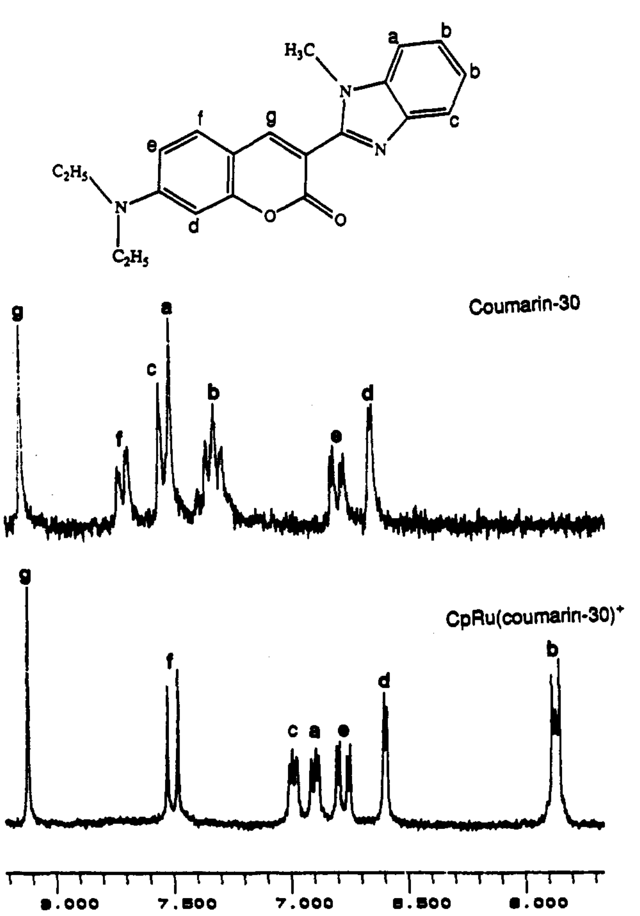

Figure 1. ^1H NMR spectra of the ring protons of coumarin-30 (above) and [CpRu(coumarin-30)]PF_6 (below).

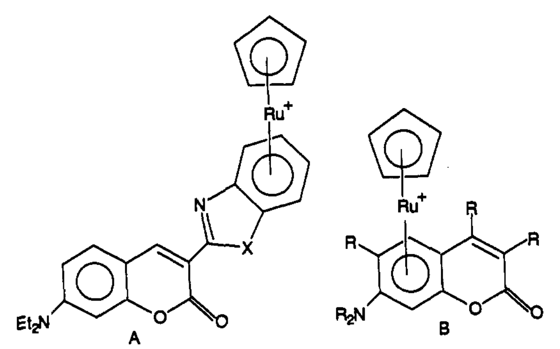

Figure 2. (A) Proposed structures of [CpRu(coumarin-6)]$^+$, [CpRu(coumarin-7)]$^+$, and [CpRu(coumarin-30]$^+$; X = S, N-H, and N-CH_3, respectively. (B) Proposed structures of coumarin laser dye complexes in which the dye contains only a single arene ring; R = H or CH_3.

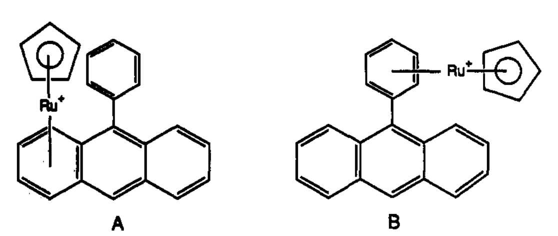

Figure 3. Proposed structures of the anthracene-bound isomer (A) and the phenyl-bound isomer (B) of [CpRu(9-phenylanthracene)]PF_6.

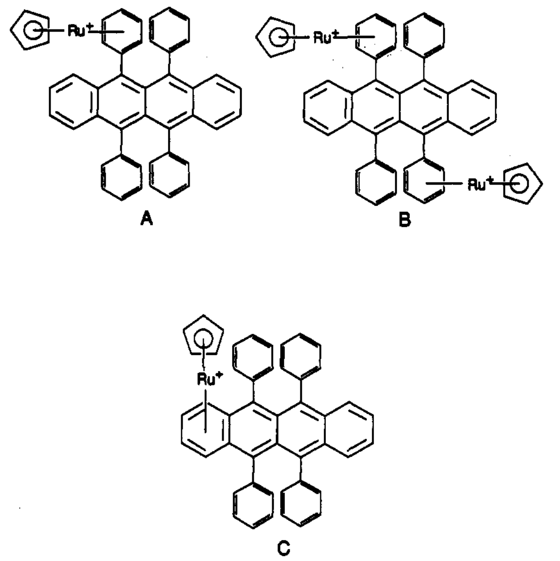

Figure 4. Proposed structures of (A) [CpRu(rubrene)]$^+$ (phenyl-bound isomer), (B) [$(CpRu)_2$(rubrene)]$^{+2}$, and (C) [CpRu(rubrene)]$^+$ (naphthacene-bound isomer).

binds in any given complex in order to understand its spectroscopic properties.

^1H NMR spectroscopy was used to elucidate the structures of the newly synthesized, fluorescent-arene complexes. Complexation of an arene ring with the CpRu$^+$ group characteristically shifts the arene proton resonances upfield,[10-12] permitting the following type of analysis: Figure 1 depicts the aromatic ring proton resonances of the laser dye coumarin-30 and its corresponding CpRu$^+$ complex. The individual proton resonances of the free dye and the metal complex are assigned on the basis of 2-D COSY ^1H NMR spectra (assignments of the proton NMR spectra of the other compounds were made on a similar basis; detailed assignments are given in the Experimental Section as compound characterization data). The COSY experiment confirms that the protons on the benzimidazolyl ring (labeled a, b, and c in Figure 1) are only coupled to each other and the protons on the coumarin arene ring (labeled e, f, and d in Figure 1) are similarly coupled only to each other. Examination of the ring proton resonances in Figure 1 shows that the chemical shift of the coumarin arene ring protons shift only slightly upon formation of the CpRu$^+$ complex. All four protons of the benzimidazolyl ring, on the other hand, shift significantly upfield in the metal complex, clearly indicating that the CpRu$^+$ moiety binds the benzimidazolyl arene ring in [CpRu(coumarin-30)]$^+$, as is depicted in Figure 2A. Coumarin-7 is structurally analogous to coumarin-30, and analysis of the ^1H NMR spectra of [CpRu(coumarin-7)]$^+$ in the manner outlined above indicates that it also contains the CpRu$^+$ group bound to the benzimidazolyl arene ring.

Reaction of [CpRu$(CH_3CN)_3$]$^+$ with 9-phenylanthracene can yield two different "ring-binding" isomers, one in which the CpRu$^+$ binds the end ring of the anthracene core, as depicted in Figure 3A, and one in which the CpRu$^+$ binds the substituent phenyl arene ring, as shown in Figure 3B. The anthracene bound isomer forms quantitatively and rapidly at room temperature from the 9-phenylanthracene/[CpRu$(CH_3CN)_3$]$^+$ reaction mixture as a kinetic product; prolonged refluxing of the reaction mixture in acetone results in the gradual conversion of the kinetic product to the more thermodynamically stable phenyl-bound isomer. This reactivity is identical with that observed between [CpRu$(CH_3CN)_3$]$^+$ and rubrene (5,6,11,12-tetraphenylnaphthacene), which is structurally very similar to 9-phenylanthracene. A detailed discussion of the kinetics and reaction mechanisms underlying this arene ring complexation selectivity has been published.[4]

The isomeric complexes of [CpRu(9-phenylanthracene)]$^+$ can also be structurally characterized by ^1H NMR spectroscopy. The NMR spectra of the 9-phenylanthracene complexes are analogous to those of the previously reported complexes of rubrene.[4] The

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(10) The upfield shift in aromatic ring proton resonances incurred upon binding a CpRu$^+$ group to the ring has been well established experimentally[11] as well as on theoretical grounds for related compounds.[12]

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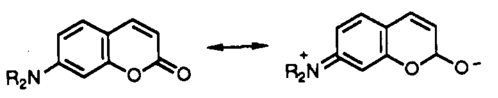
^{1}H NMR spectra of the anthracene-bound isomer and phenyl-bound isomer are quite different and can be easily differentiated. Binding the CpRu$^+$ group to the end anthracene ring has a strong net shielding effect on the four end ring protons and spreads them out into four well-resolved resonances at δ 7.67, 6.83, 6.64, and 6.49. In the phenyl-bound isomer, on the other hand, the most upfield aromatic proton resonance is a multiplet that integrates as five hydrogens, which we assign to the bound 9-phenyl ring. The ^{1}H NMR of the phenyl-bound isomer also exhibits a conspicuous doublet that is shifted unusually far downfield (δ 9.12) which we assign to the anthracene end ring proton that is adjacent to the phenyl-bound CpRu$^+$ group. A similar, highly deshielded doublet is also observed in the analogous phenyl-bound isomer of [CpRu(rubrene)]$^+$ (see Figure 4A). The reactivity of the two isomers also consistent with their structural assignment. The anthracene-bound isomer is thermally unstable in acetonitrile; like [CpRu(anthracene)]PF$_6$,[1] it rapidly undergoes dissociation of the bound arene in acetonitrile to yield [CpRu(CH$_3$CN)$_3$]$^+$ and free arene. The phenyl-bound isomer, on the other hand, is quite stable in acetonitrile solutions that are protected from light. This behavior is also observed in the previously characterized isomers of [CpRu(rubrene)]PF$_6$.[4]

^{1}H NMR spectroscopy again was useful in elucidating the structure of the multiply metallated rubrene complex. The ^{1}H NMR spectrum of the bismetalated rubrene complex is analogous to that of the monometalated, phenyl-bound complex.[4] A singlet that integrates as 10 hydrogens is due to the two chemically equivalent Cp groups in the complex. The furthest upfield resonances in the spectrum are multiplets that integrate as 10 hydrogens. A 2-D COSY spectrum indicates that these multiplets are coupled only to each other; we assign them as the signals from two chemically equivalent phenyl groups bearing the CpRu$^+$ moiety. There is also a doublet shifted far downfield, like that observed in the phenyl-bound monometalated isomer, that integrates as two hydrogens and arises from the end naphthacene ring protons adjacent to the two bound phenyl rings. There are three structural isomers possible for a bimetallic, phenyl-bound complex of rubrene; the CpRu$^+$ groups could be arranged vicinally, geminally, or diagonally on the rubrene substrate. ^{1}H NMR indicates that a single isomer is isolated from the synthetic reaction but cannot distinguish between the different isomers as they have similar symmetry. We tentatively propose the diagonally substituted structure depicted in Figure 4B for the bimetallic rubrene complex as it offers the least amount of steric strain.

Spectroscopic Properties of Coumarin Laser Dye Complexes. One of the families of fluorescent arenes that we have had the most success with in these studies has been the 7-aminocoumarin laser dyes. We have previously reported the synthesis and characterization of the CpRu$^+$ complexes of a variety of differently substituted coumarin laser dyes.[3] Complexes of the general structure depicted in Figure 2B, corresponding to complexes of the dyes coumarin-1, coumarin-2, coumarin-311, coumarin-314, coumarin-334, coumarin-337, and coumarin-338, are nonemissive. The loss of the intense emission of the laser dye upon formation of complexes of this type can be understood by considering the nature of the electronic transitions that give rise to the laser dye fluorescence.

In the ground state, the 7-aminocoumarin chromophore is primarily described by resonance form A, while the first singlet excited state is primarily described by the polar resonance form B.[13-15] When excited to its first singlet excited state, the 7-aminocoumarin chromophore undergoes an intramolecular charge transfer (ICT) of an electron from a nonbonding orbital centered on the nitrogen to a π^* orbital associated with the pyrone ring, giving rise to an extremely intense absorption band in the visible region ($\epsilon \sim 10^4$ M^{-1} cm^{-1}). Complexation of the main coumarin arene ring by a CpRu$^+$ group localizes the arene π electrons into metal–arene bonds, making the π electrons far less mobile in the metal complex than they are in the free dye. It is far more difficult for the metal-complexed coumarin chromophore to reorganize to the stabilized, polar form in the emissive ICT excited state. The electronic spectra of these complexes support this, as the intense ICT absorption band of the laser dye completely disappears upon complexation of the main coumarin arene ring by the CpRu$^+$ group, and the emission associated with the ICT transition also disappears.[3]



A B

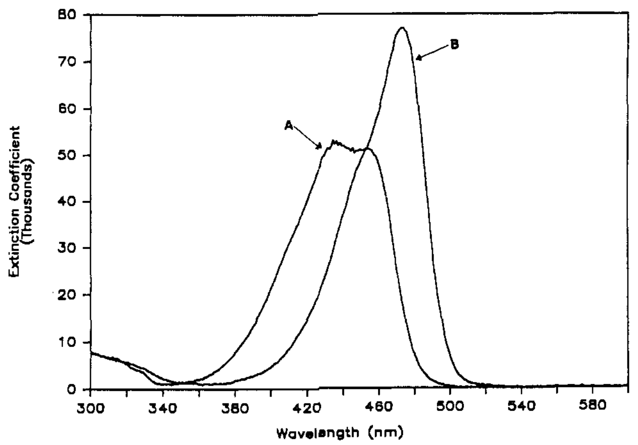


Figure 5. UV-visible absorption spectra of coumarin-7 (A) and [CpRu(coumarin-7)]PF$_6$ (B) recorded at room temperature as dichloromethane solutions.

Complexation of a coumarin lase dye containing an additional arene ring to which the CpRu$^+$ can coordinate yields a product that exhibits very different behavior. Reaction of the laser dye coumarin-6 with [CpRu(CH$_3$CN)$_3$]$^+$ yields a complex in which the CpRu$^+$ is no longer bound to the main coumarin arene ring but rather is bound to the substituent benzothiazolyl arene ring, as depicted in Figure 2A. In a complex of this type, the ruthenium no longer strongly interacts with the orbitals involved in the emissive electronic transitions of the dye, which are localized in the coumarin–arene ring. Consequently, this complex exhibits dye-localized electronic transitions very similar to those observed in the free dye. While complexes in which the CpRu$^+$ binds the main coumarin arene ring exhibit neither the intense ICT absorption band nor the corresponding emission band characteristic of the free dye, the complex of coumarin-6 exhibits both an intense ICT absorption band and a corresponding emission band in fluid solution at room temperature.[3]

The new complexes of coumarin-30 and coumarin-7 are analogous to the previously reported [CpRu(coumarin-6)]$^+$ complex. The two new complexes differ from the coumarin-6 complex in that the sulfur atom of the coumarin-6 benzothioazolyl group is replaced by a N–H or N–CH$_3$ group, respectively, to form the benzimidazolyl group of coumarin-7 and coumarin-30. Because the CpRu$^+$ group is not bound to the main coumarin arene ring in [CpRu(coumarin-30)]$^+$ and [CpRu(coumarin-7)]$^+$, the Ru does not interfere strongly with the laser dye chromophore, and consequently the complexes are expected to retain the intense ICT transition characteristic of the free dye. The UV–vis spectra of these complexes support this expectation. Figure 5 illustrates the UV–vis spectra of coumarin-7 (Figure 5A) and [CpRu(coumarin-7)]$^+$ (Figure 5B). These spectra are analogous to those previously reported for coumarin-6 and its corresponding CpRu$^+$ complex.[3] Although the coumarin chromophore is not perturbed strongly enough to remove the ICT absorption band from the UV–vis spectrum, the CpRu$^+$ group does shift the dye-centered transition to longer wavelength and increases its intensity. Both of these effects likely result from the inductive influence the electropositive CpRu$^+$ group exerts on the chromophore. This

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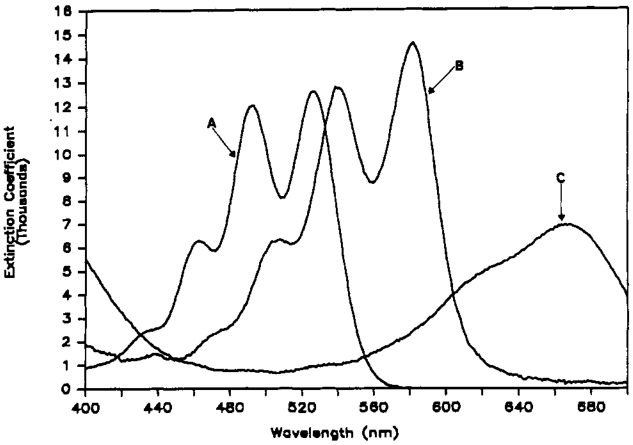

Figure 6. UV-visible absorption spectra of (A) rubrene, (B) $[(CpRu)_2(rubrene)]^{+2}$, and (C) $[CpRu(rubrene)]^+$ (phenyl-bound isomer) recorded at room temperature as dichloromethane solutions.

effect stabilizes the polar excited state, red shifts the absorption band, and produces a larger electronic dipole moment change in the electronic transition, which results in enhanced oscillator strength for the transition.

Replacement of the sulfur atom with an amino group causes the ICT absorption band of the free dye to shift to higher energy, from 457 nm in coumarin-6 to 414 and 434 nm, respectively, in coumarin-30 and coumarin-7. The ICT bands of the CpRu$^+$ complexes of coumarin-30 and coumarin-7 are also shifted to higher energy relative to $[CpRu(coumarin\text{-}6)]^+$, by 46 and 10 nm, respectively. Even though $[CpRu(coumarin\text{-}30)]^+$ and $[CpRu(coumarin\text{-}7)]^+$ are very similar to $[CpRu(coumarin\text{-}6)]^+$ in both structure and electronic absorption spectra, the complexes of coumarin-30 and coumarin-7 do *not* exhibit significant room-temperature emission in fluid solution as does the coumarin-6 complex. These observations suggest that emissive [CpRu(laser dye)]$^+$ complexes should retain a dye-localized lowest excited state. The ICT lowest singlet transition that characterizes the 7-aminocoumarin laser dyes is retained in the complexes of coumarin-6, coumarin-7, and coumarin-30, but the fluorescence associated with that transition is only observed in the coumarin-6 complex. Because the structures of all three complexes are nearly identical, it is unlikely that geometric structure causes the loss of emission in complexes of coumarin-30 and coumarin-7. The main spectroscopic difference between these three similar complexes is the energy of their ICT transitions, suggesting that the energy of the fluorescent transitions localized in the arene ligand has an important influence on the emissivity of the corresponding metal–arene complex.

Spectroscopic Properties of Phenylacene Complexes. To gain insight into the factors that influence the spectroscopic behavior of [CpRu(arene)]$^+$ complexes, we studied the complexes of the two fluorescent phenylacenes, rubrene and 9-phenylanthracene. The phenylacenes are analogous to coumarin-6, coumarin-7, and coumarin-30, discussed above, as they contain arene rings that are strongly associated with the fluorescent chromophore as well as arene rings that interact relatively weakly with the fluorescent chromophore. For instance, rubrene (5,6,11,12-tetraphenylnaphthacene) exhibits an electronic absorption spectrum in the visible region with well-developed vibrational structure and a corresponding intense, structured emission. Multiple substitution of naphthacene with phenyl groups to yield rubrene leaves the vibrational structure of the naphthacene lowest singlet–singlet absorption band essentially unchanged, confirming that the fluorescent electronic transitions of rubrene are localized in the naphthacene core. However, the substituent phenyl groups do produce a significant red shift of the naphthacene-centered transitions, indicating that a small degree of interaction between a perpendicular π-systems occurs.[16] In the phenylacenes, the substituent phenyl groups are analogous to the substituent benzothiazolyl and benzimidazolyl arene rings in coumarin-6, coumarin-7, and coumarin-30. These arene rings are also weakly interactive with the emissive chromophore. The acene arene rings are direct analogues of the main arene ring of the coumarin chromophore where the fluorescent transitions are localized.

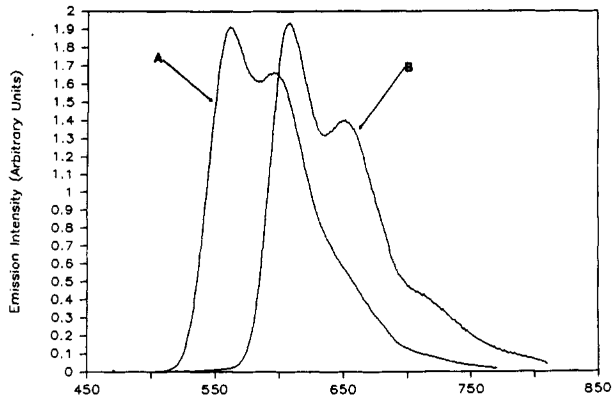

Figure 7. Emission spectra of (A) rubrene and (B) $[(CpRu)_2(rubrene)]^{+2}$ recorded at room temperature as dichloromethane solutions.

Reaction of rubrene with 1 equiv of $[CpRu(CH_3CN)_3]^+$ at room temperature yields a complex in which the CpRu$^+$ group is bound to the end ring of the naphthacene moiety, as depicted in Figure 4C. This complex is analogous to the laser dye complexes in which the CpRu$^+$ binds the main coumarin arene ring: the Ru is bound directly to the main rubrene chromophore. Figure 6 illustrates the visible absorption spectra of rubrene (Figure 6A) and the naphthacene-bound isomer of $[CpRu(rubrene)]^+$ (Figure 6C). These absorption spectra indicate that the CpRu$^+$ group strongly interfers with the rubrene chromophore. The structured $^1(\pi\text{–}\pi^*)$ transitions localized in the naphthacene core are completely lost upon formation of the naphthacene bound complex. Instead of the intense, structured absorption band characteristic of free rubrene, the naphthacene-bound isomer exhibits a weaker, unstructured absorption band at ~660 nm. It is not surprising that the emission associated with the structured $^1(\pi\text{–}\pi^*)$ transitions in rubrene is also not observed in the naphthacene-bound CpRu$^+$ complex. Emission spectra (λ_{ex} = 460 nm) of a dichloromethane solution of rubrene recorded at regular intervals following the addition of $[CpRu(CH_3CN)_3]^+$ indicate that the rubrene emission rapidly decays as the metal complex forms until, after ~ 30 minutes, the free rubrene emission is barely detectable. No new emission bands are observed to grow in as the reaction proceeds. The previously reported complex $[Cp^*Ru(rubrene)]^+$ (naphthacene-bound isomer; Cp* = η^5-pentamethylcyclopentadienyl)[7] exhibits analogous spectroscopic characteristics.

Although the room-temperature reaction of rubrene with 1 equiv of $[CpRu(CH_3CN)_3]^+$ produces a complex that has lost the spectroscopic characteristics of the arene ligand, the reaction of rubrene with 2 equiv of the CpRu$^+$ reagent yields a product with entirely different properties. Refluxing rubrene with 2 equiv of $[CpRu(CH_3CN)_3]^+$ yields the complex depicted in Figure 4B, in which no CpRu$^+$ groups are bound to the naphthacene core of the molecule. Rather, a CpRu$^+$ group is bound to two of the substituent phenyl groups on the naphthacene core. This molecule is analogous to the laser dye complexes depicted in Figure 2A, in which the CpRu$^+$ group is bound to an arene ring that is not directly involved in the fluorescent electronic transitions localized in the ligand. By analogy with the coumarin laser dye complexes, this bimetallic rubrene complex retains the spectroscopic characteristics of the uncomplexed arene. The visible absorption spectrum of $[(CpRu)_2(rubrene)]^{2+}$ depicted in Figure 6B shows that the bimetallic complex exhibits a structured absorption band that is essentially identical in shape with the absorption band of free rubrene. As in the case of the coumarin laser dye complexes, the CpRu$^+$ moiety weakly perturbs the naphthacene-centered, $^1(\pi\text{–}\pi^*)$ transitions, shifts them to longer wavelength, and increases their intensity slightly. The inductive effect of the CpRu$^+$ is

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Table I. Emission and Reaction Quantum Yields for $[CpRu(\eta^6\text{-arene})]^+$ Complexes

complex	$\phi_{emission}$[a]	$\phi_{reaction}$[b]
$[CpRu(benzene)]^+$	$\leq 10^{-4}$[c]	0.40 (4)[d]
$[CpRu(coumarin\text{-}6)]^+$	0.07 (1)	0.075 (8)
$[CpRu(rubrene)]^+$ (phenyl-bound isomer)	0.024 (2)	0.0018 (2)
$[CpRu(9\text{-}phenylanthracene)]^+$ (phenyl-bound isomer)	$\leq 10^{-4}$[c]	0.048 (5)

[a] Emission quantum yields are measured for dichloromethane solutions of the compounds. [b] Reaction quantum yields are measured for the displacement of arene from the compounds of acetonitrile solution to yield $[CpRu(CH_3CN)_3]^+$ and free arene. [c] Quantum yield is below our detection limit. [d] Data taken from ref 17.

somewhat less pronounced on the rubrene complex than the coumarin laser dye complexes because the ICT transition in the coumarin dyes involes a much larger electronic dipole moment change than the π–π^* transitions of rubrene. In addition to retaining the structured $^1(\pi$–$\pi^*)$ absorption band characteristic of rubrene, $[(CpRu)_2(rubrene)]^{2+}$ also retains the structured emission associated with those transitions. Figure 7 illustrates the emission spectra of rubrene (Figure 7A) and $[(CpRu)_2(rubrene)]^{+2}$ (Figure 7B). Again, the shape of the emission bands of the metal complex are identical with those of rubrene, suggesting that they arise from transitions that are primarily localized in the rubrene chromophore, but are shifted to longer wavelength. The previously, reported monometalated, phenyl-bound $[CpRu(rubrene)]^+$ complex, illustrated in Figure 4A, is structurally and spectroscopically analogous to the bimetallic complex; it exhibits structured and absorption and emission bands that are slightly red-shifted with respect to the bands of free rubrene. A tetrametalated complex of rubrene in which each of the four substituent phenyl groups is coordinated to a Cp^*Ru^+ has also been reported to exhibit structured, red-shifted absorption and emission bands that are localized on the rubrene chromophore.[7]

The $CpRu^+$ complexes of 9-phenylanthracene (see Figure 3) are structurally analogous to the phenyl-bound complexes of rubrene discussed above. Like the rubrene complex, where the $CpRu^+$ group is bound to the substituent phenyl group of 9-phenylanthracene rather than to the anthracene core, the complex retains the electronic transitions that are localized on the anthracene moiety. The phenyl-bound isomer of $[CpRu(9\text{-}phenylanthracene)]^+$ exhibits an absorption band with well-defined vibrational structure that is red-shifted by ~13 nm from the similarly shaped absorption band characteristic of uncomlexed 9-phenylanthracene. In contrast, the $CpRu^+$ group of the anthracene-bound isomer strongly disrupts the $^1(\pi$–$\pi^*)$ transitions localized in the anthracene core, and consequently the complex exhibits a relatively weak, unstructured MLCT absorption band at 486 nm instead of the structured absorption band characteristic of the anthracene core.

As the phenyl-bound complexes of rubrene and 9-phenylanthracene are analogous in structure and differ spectroscopically primarily in the energy of the acene-centered $^1(\pi$–$\pi^*)$ electronic transitions, they provide an excellent model with which to examine the effect of the energy of the ligand-centered bands on the complex emissivity. The phenyl-bound complex of 9-phenylanthracene does not exhibit observable emission at room temperature in fluid solution. As for the complexes of coumarin-6, coumarin-7, and coumarin-30, raising the energy of the ligand-localized electronic transitions results in a loss of emission in the metal complex.

Photochemical Reactivity. The $[CpRu(\eta^6\text{-arene})]^+$ complexes undergo a very characteristic photochemical reaction. Upon photolysis in acetonitrile, the bound arene ring is very readily replaced by three acetonitrile ligands to yield $[CpRu(CH_3CN)_3]^+$ and free arene.[17] Quantum yields for the photochemical displacement of arene and for emission from some $[CpRu(\eta^6\text{-arene})]^+$ complexes are listed in Table I. In general, the photochemical

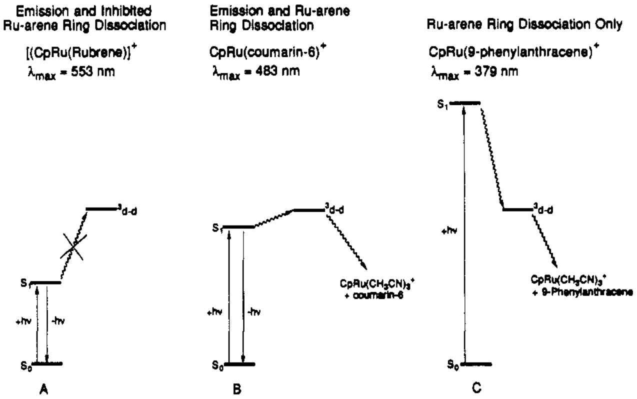

Figure 8. Qualitative state diagram indicating the relative energies of the fluorescent S_1 state and the reactive a^3E_1 state in (A) $[CpRu(rubrene)]^+$ (phenyl-bound isomer), (B) $[CpRu(coumarin\text{-}6)]^+$, and (C) $[CpRu(9\text{-}phenylanthracene)]^+$ (phenyl-bound isomer).

reaction is facile, as even the emissive $[CpRu(coumarin\text{-}6)]^+$ complex generates free coumarin-6 when photolyzed in acetonitrile. The efficiency of photochemical displacement of arene from the $CpRu^+$ complex decreases in the order benzene > coumarin-6 > 9-phenylanthracene ≫ rubrene. The emissive $CpRu^+$ complexes of rubrene are unusual because the photochemical displacement of rubrene is inefficient. The phenyl-bound isomer of $[CpRu(rubrene)]PF_6$ exhibits a quantum yield for arene labilization in acetonitrile that is ~230 times smaller than that for the photochemical labilization of benzene.[17]

Discussion

The inverse relationship between emission and photochemical reactivity observed in these different $[CpRu(arene)]^+$ complexes can be understood by considering the important electronic transitions that characterize the compounds. The situation in these $[CpRu(arene)]^+$ complexes is similar in some regards to one present in binuclear Rh and Ir complexes[18,19] and in substituted ruthenium bypyridine complexes.[20] A qualitative Jablonski diagram illustrating the pertinent excited states in $[CpRu(9\text{-}phenylanthracene)]^+$ (phenyl-bound isomer), $[CpRu(coumarin\text{-}6)]^+$, and $[CpRu(rubrene)]^+$ (phenyl-bound isomer) is shown in Figure 8. In most of the previously studied $[CpRu(arene)]^+$ complexes, the $CpRu^+$ group is bound directly to the main chromophore of the aromatic substrate. Complexes of this type characteristically exhibit relatively weak metal-to-ligand charge-transfer (MLCT) transitions upon excitation to the lowest singlet excited state, S_1.[11] The complexes discussed in this study are fundamentally different in that the $CpRu^+$ group is not bound directly to the main chromophore of the aromatic substrate. The electronic spectra of these complexes (vide supra) indicate that the lowest singlet state is the arene-localized π–π^* state (for the rubrene and 9-phenylanthracene complexes) or ICT state (for the complexes of coumarin-6, coumarin-7, and coumarin-30). Because the emission spectra of the rubrene and coumarin-6 complexes are almost identical in shape with the fluorescence spectra of the uncoordinated arenes, the emission of these metal complexes is assigned to an arene-centered fluorescence. This assignment is consistent with the short emission lifetime (τ = 11.6 (5) ns) that has been measured for the analogous phenyl bound $[(CpRu^*)_4(rubrene)]^{+4}$ complex.[7]

Another important excited state in these complexes is the triplet d–d state (a^3E_1), which previous studies in our group have implicated as the excited state that leads to the loss of the bound arene ring in the photochemical reaction.[21] The energy of this

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d–d excited state depends upon the splitting of the Ru d orbitals caused by the ligand field arising from the Cp and arene ligands.[22] The differences in the ligand field produced by the different types of arene rings bound to the CpRu$^+$ moiety are relatively small and the energy of the d–d a^{3}E$_1$ state is relatively insensitive to the nature of the arene ligand. In comparison, the energy of the lowest ligand-localized singlet state of the complex is sensitive to the nature of the arene ligand. These effects result in the distribution of the energy levels depicted in Figure 8. The reactive a^{3}E$_1$ states of all the complexes are at roughly the same energy while the arene-localized first singlet state varies from relatively low energy for the rubrene complex to intermediate energy for the coumarin-6 complex to relatively high energy for the 9-phenylanthracene complex.

There are two main factors that influence the efficiency of the photochemical arene labilization reaction in these [CpRu(η^6-arene)]$^+$ complexes. The first factor is the relative ease with which the metal complex crosses from the first excited singlet state, S$_1$, to the reactive triplet excited state, a^{3}E$_1$. In turn, the ease of S$_1$ → a^{3}E$_1$ intersystem crossing depends primarily on the energy match between the states as per the energy gap law,[23] other factors being equal. As there is a high density of ligand states isoenergetic with the upper triplet state, the crossing to a^{3}E$_1$ may occur through initial thermal population of an upper ligand triplet state. Once the reactive excited state is populated, a second factor, the rate of the arene displacement reaction, becomes important. Recent experiments in our group have demonstrated that arene rings with high degrees of aromaticity such as benzene or the phenyl substituents on rubrene and 9-phenylanthracene form significantly more thermodynamically stable CpRu$^+$ complexes than arene rings in which the aromaticity is compromised by extended conjugation such as the rings in anthracene and naphthacene.[4] Consequently, the Ru–arene bonds in [CpRu(benzene)]$^+$ should be stronger than those in the CpRu$^+$ complex of coumarin-6, in which the bound arene ring is conjugated to the CN double bond in the benzothiazolyl group, and a corresponding inhibition effect for the photochemical labilization of benzene over coumarin-6 would be expected. The influence of the S$_1$ energy on the efficiency of the photochemical labilization of arene can be analyzed separately from the influence of ruthenium–arene bond strength by comparing CpRu$^+$ complexes that have similar types of arene rings bound to them but exhibit different S$_1$ energies.[24]

Comparison of the phenyl-bound isomers of [CpRu(9-phenylanthracene)]$^+$ and [CpRu(rubrene)]$^+$ permits analysis of the effect of the excited state energies on photochemical behavior because the bound arene rings in these complexes are extremely similar, acene-substituent phenyl groups. The rubrene complex exhibits a relatively long wavelength absorption band, corresponding to a low-energy S$_1$ state. The S$_1$ state in [CpRu(rubrene)]$^+$ probably lies well below the energy of the reactive a^{3}E$_1$ state, as is depicted in Figure 8A. The S$_1$ → a^{3}E$_1$ intersystem crossing required for the photochemical displacement of rubrene from the complex will be an energetically "uphill" process and, consequently, will be relatively unfavorable and slow. This is consistent with the small reaction quantum yield that is observed for the phenyl bound rubrene complexes.

In the complex of 9-phenylanthracene, the situation is reversed. [CpRu(9-phenylanthracene)]$^+$ exhibits a relatively short wavelength absorption band, corresponding to an S$_1$ state that lies higher in energy than the reactive triplet state, as shown in Figure 8C. For this complex the S → a^{3}E$_1$ crossing is an energetically "downhill" process, and is expected to be favorable and rapid.[25] Our experimental data support this, as the quantum yield for arene loss from the 9-phenylanthracene complex is 27 times larger than that from the structurally analogous rubrene complex. This model also suggests an explanation for the emissivity of these complexes. Because the *photochemical* deactivation of S$_1$ in [CpRu(rubrene)]$^+$ is inhibited, the complex is able to competitively lose energy by emission from S$_1$. In contrast, the photochemical reaction pathway of the [CpRu(9-phenylanthracene)]$^+$ complex is a facile, energetically favorable process that occurs essentially to the exclusion of any loss of excitation energy by fluorescence. The complexes of coumarin-30 and coumarin-7, which are not depicted in Figure 8, are analogous to [CpRu(9-phenylanthracene)]$^+$; they also exhibit relatively short wavelength absorption bands, are photochemically reactive, and are nonemissive.

The complex of coumarin-6 provides an example of a system that is intermediate between the complexes of 9-phenylanthracene and rubrene. While the complex of 9-phenylanthracene is unable to relax efficiently through fluorescence and the rubrene complex is unable to relax efficiently through arene displacement, the complex of coumarin-6 exhibits both fluorescence and photochemical reactivity. This behavior arises from the position of the energy levels in the complex. [CpRu(coumarin-6)]$^+$ exhibits an absorption band that is intermediate beteen the bands observed in the complexes of 9-phenylanthracene and rubrene. Consequently S$_1$ in the coumarin-6 complex is between the S$_1$ energies of the phenylacene complexes. We propose that S$_1$ is slightly lower in energy than the reactive a^{3}E$_1$ state, as depicted in Figure 8B. This arrangement of energy levels makes the S$_1$ → a^{3}E$_1$ intersystem crossing required for photochemical reaction a somewhat energetically unfavorable process and explains the inhibited reactive quantum yield relative to that of a complex like [CpRu(benzene)]$^+$ in which the S$_1$ → a^{3}E$_1$ crossing is very energetically "downhill" and favorable. This hypothesis is also consistent with the observation of room-temperature emission from [CpRu(coumarin-6)]$^+$. Relaxation through the photochemical reaction pathway for the coumarin-6 complex is inhibited enough to allow competitive deactivation through fluorescence. The coumarin-6 complex is an interesting example of a [CpRu(arene)]$^+$ complex in which the energy levels are balanced to permit both efficient photochemical reactivity and fluorescence. We intend to direct future efforts to study this system further as it offers the chance to measure the rate of Ru–arene bond cleavage via fluorescence measurements.

Conclusions

There are two main requirements for preparing [CpRu(η^6-arene)]$^+$ complexes that will exhibit room-temperature fluorescence in fluid solution. First, the complex should have an arene-localized lowest singlet excited state. This requirement is generally met if the CpRu$^+$ group is *not* bound to an arene ring in which the electronic transitions of the ligand are localized. Violation of this requirement explains why previously prepared CpRu$^+$ complexes of highly fluorescent aromatic ligands such as anthracene, chrysene, and pyrene fail to emit. Each of these ligands offer only aromatic rings with strong participation in the chromophore. The second requirement for an emissive [CpRu(arene)]$^+$ complex is that the absorption energy of the arene-centered, lowest singlet excited state cannot be much higher than ~20700 cm^{-1} (the value observed for [CpRu(coumarin-6)]$^+$. Raising the energy of S$_1$ higher than this value increases the energetic favorability of intersystem crossing to the reactive a^{3}E$_1$ state, which leads to excited-state deactivation through displacement of the arene ring. The energy of S$_1$ required for an emissive [CpRu(η^6-arene)]$^+$ complex is quite critical. In

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[22] A quantitative measurement of the energy of the a^{3}E$_1$ state in these complexes is not possible as the weak a^{3}E$_1$ ← ^{1}A$_1$ transition is obscured by other absorption bands in the LF region. However, a weak band corresponding to this transition occurs in the analogous complex [CpRu(hexamethylbenzene)]$^+$ at 26300 cm^{-1} (ϵ = 8 M^{-1} cm^{-1}).[21]

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[24] It is more difficult to measure the effect of ruthenium–arene bond strength on the reaction quantum yield because complexes with weaker metal–arene bonds often undergo thermal arene displacement in acetonitrile. Work is in progress to characterize suitable compounds to permit an investigation of the bond energy contribution to the photochemical reactivity of these complexes.

[25] In complexes with relatively high energy S$_1$ states like [CpRu(benzene)]$^+$ or the phenyl-bound isomer of [CpRu(9-phenylanthracene)]$^+$, there will be a relatively large energy gap between S$_1$ and a^{3}E$_1$. Intersystem crossing in these complexes probably occurs initially from S$_1$ to some upper triplet state, T$_n$, which then undergoes rapid thermal degradation to a^{3}E$_1$.

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[CpRu(coumarin-7)]$^+$, for instance, S_1 is only 440 cm^{-1} higher in energy ($\Delta\lambda_{max}$ = 9 nm) than in the coumarin-6 complex, but this change is sufficient to shut down the ligand-localized emission in the coumarin-7 complex. When ligand-centered emission *is* observed from a ruthenium complex, it is always much less intense than that of the corresponding uncomplexed arene. This decrease in fluorescence efficiency probably results from intersystem crossing within the dye manifold induced by the heavy ruthenium atom.

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Supplementary Material Available: Procedures for synthesizing [CpRu(coumarin-7)]PF_6, [CpRu(coumarin-30)]PF_6, [CpRu(9-phenylanthracene)]PF_6 (phenyl-bound and anthracene-bound isomers), and $[(CpRu)_2(rubrene)](PF_6)_2$ (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Three New Compounds Containing M_3S_4 (M = Mo, W) Cores Prepared from $M_3S_7X_4$ (M = Mo, W; X = Cl, Br) Starting Materials

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$Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot OPEt_3$ (**1**), $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ (**2**), and $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ (**3**) were prepared by reacting triethylphosphine with $Mo_3S_7Cl_4$, $Mo_3S_7Br_4$, and $W_3S_7Br_4$, respectively, in THF at room temperature. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 13.290 (2) Å, b = 18.282 (4) Å, c = 17.934 (4) Å, β = 93.95 (2)°, V = 4347 (3) Å^3, and Z = 4. Compounds **2** and **3** are isostructural and crystallize in the triclinic space group $P\bar{1}$. For **2**, a = 12.908 (4) Å, b = 18.299 (6) Å, c = 12.153 (4) Å, α = 98.26 (2)°, β = 116.69 (2)°, γ = 77.21 (2)°, V = 2498 (3) Å^3, and Z = 2. For **3**, a = 12.925 (4) Å, b = 18.318 (6) Å, c = 12.141 (4) Å, α = 98.41 (3)°, β = 116.51 (3)°, γ = 77.00 (3)°, V = 2503 (2) Å^3, and Z = 2. All three compounds belong to the B_1, M_3X_{13} structure family. An explanation for the formation of the Et_2HPO ligand in **2** and **3** is proposed.

Introduction

Much attention has recently been directed toward trinuclear transition-metal clusters. The discovery of new methods of synthesis has contributed to the rapid evolution of this field. Solution methods using mononuclear starting materials have been widely used to prepare molybdenum and tungsten trinuclear clusters with a variety of ligands.[1-6] Other methods involve ligand substitution on a preformed M_3 core with preservation of the triangular structure.[7-12] Recently, the synthesis and characterization of polymeric trimers having the formula $M_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3X_2X_{4/2}$ or, more simply, $M_3S_7X_4$ (M = Mo, W; X = Cl, Br) opened new routes for preparing substituted trimers.[13,14] Several new compounds have been prepared by utilizing $Mo_3S_7X_4$ as the starting material. For example, Federov et al. prepared $Mo_3S_7X_4\cdot 2PPh_3$ (X = Cl, Br) by reacting $Mo_3S_7X_4$ with PPh_3 in CH_3CN.[15] Saito et al. reported the synthesis of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_n(MeOH)_{5-n}$ (n = 3, 4) from $Mo_3S_7Cl_4$ reacted with PEt_3 in THF.[16] In this laboratory, $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)(H_2O)_2\cdot 3THF$ and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(PPh_3)(dmpe)_3]Cl\cdot 2MeOH$ were prepared by using this type of synthetic method.[17] So far only two compounds have been prepared by methods that make use of tungsten trinuclear polymeric starting materials, and only one of these contained substituted phosphines. They are $[W_6S_8(PEt_3)_6]$[18] and $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(H_2O)_3]^{2-}$.[19] We report here the syntheses and crystal structures of three new compounds that further exemplify the use of molybdenum and tungsten trinuclear chalcogenide halides as excellent synthons for trinuclear, triangular clusters of the M_3S_4 type having phosphine ligands in the outer coordination sites.

Experimental Section

Materials and Methods. All experiments were carried out under an argon atmosphere by using standard vacuum-line and Schlenk techniques. Solvents were distilled under nitrogen over the appropriate drying agents. Chemicals were obtained from the following sources: sulfur (precipitated grade), Fisher; triethylphosphine, S_2Cl_2, molybdenum (100-mesh powder), and tungsten (100-mesh powder), Strem. They were used without further purification. $Mo_3S_7Cl_4$, $Mo_3S_7Br_4$, and $W_3S_7Br_4$ were prepared

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