Mechanistic aspects of the photochemistry of [CpM(η^6-arene)]$^+$ complexes of Fe, Ru and Os

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ABSTRACT The photochemical displacement of η^6-arenes from CpM(η^6-arene)$^+$ complexes (M=Fe, Ru, Os) involves excitation to produce reactive, d-d excited states. The reactivity of these complexes decreases in the order Fe > Ru >Os for simple methyl substituted arenes. The quantum yields of these photoreactions indicate a significant associative component in the mechanism of arene release. The quantum yields for Fe complexes can be varied by 10^5 by changing the steric hindrance, the solvent nucleophilicity and the nature of the counterion. The synthesis, photochemical and photophysical properties of CpRu(η^6-arene)$^+$ complexes (arene = rubrene, 9-phenylanthracene, coumarin laser dyes) have been investigated. In several cases (rubrene, 9-phenylanthracene) emissive and non-emissive isomers are produced. CpRu(η^6-arene)$^+$ complexes that exhibit fluid solution emission have metal complexation of a pendant rather than "chromophore" arene ring. Photochemical arene decomplexation and emission quantum yields for the CpRu$^+$ complexes of substitued coumarins, rubrene, and 9-phenylanthracene show that the reaction and emission quantum yields are inversely related. When the photo-active d-d states are below the emissive arene chromophore in energy, arene displacement is observed; when the arene localized chromophore energy is lowest, emission from the complex is observed.

INTRODUCTION

During the last fifteen years, we have investigated the photochemistry of the substitutionally inert, low-spin d^6 [CpM(arene)]$^+$ complexes with simple arene ligands[1-8] (M = Fe, Ru, Os; Cp = η^5-cyclopentadienyl; arene = η^6-arene). These reactions have considerable synthetic utility[1-8] and provide mechanistic insight[8-13] into the photochemical release of arene ligands. In this paper, we shall discuss the basic photochemistry of these compounds, the mechanism of photochemical arene release and the design and synthesis of metal arene of complexes that contain CpRu$^+$ bound to highly functionalized, emissive arenes, such as coumarin-338 (Figure 1)[14-18]. In these highly function-

Coumarin-338

Figure 1.

alized compounds, interactions among the chromophores modify the properties of the isolated laser dye and M-arene functionalities.

EXPERIMENTAL
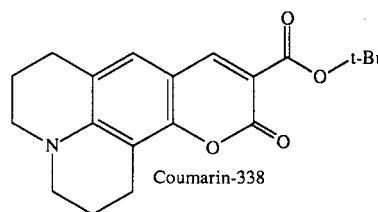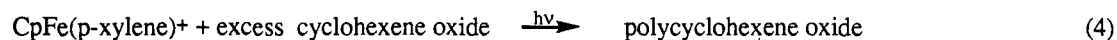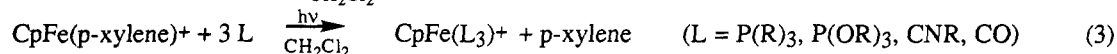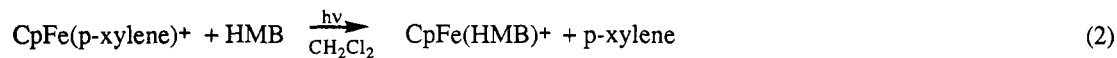
The previously reported [CpM(arene)]$^+$ complexes of iron, ruthenium and osmium with arene = benzene and methyl, ethyl and chloro substituted benzene were synthesized by standard methods[10,11,14-18]. The synthesis and chacterization of 9-phenylanthracene, rubrene and coumarin complexes of CpRu$^+$ have also been previously reported[14-17]. Electronic spectroscopy and photochemical experiments were conducted by standard techniques described in the literature[1-18].

PHOTOCHEMISTRY OF [CpM(arene)]$^+$ COMPLEXES (M = Fe, Ru, Os)

In acetonitrile or tetrahydrofuran solutions, [CpFe(arene)]$^+$ complexes undergo a photochemical disproportionation reaction that gives solvated Fe^{2+}, ferrocene and free arene (Eqn 1)[19]. It has been shown that the putative intermediate in this reaction (CpFe(NCCH$_3$)$_3^+$) is unstable with respect to solvolysis and ligand redistribution occurs to give the final products. At low temperatures, CpFe(NCCH$_3$)$_3^+$ is trapped by ligands to yield CpFeL$_n$(NCCH$_3$)$_{(3-n)}^+$ complexes[4]. In less nucleophilic solvents (CH$_2$Cl$_2$), arene exchange reactions can also be observed if the entering arene is more electron

rich than the complexed one (Eqn 2)[1]. Substitution reactions that yield CpFe(L)$_3^+$ are also readily observed upon photolysis of CH$_2$Cl$_2$ solutions (Eqn 3)[1]. Recently, the electrophilic properties of the photo-intermediate in CH$_2$Cl$_2$ have been used to effect the polymerization of epoxides (Eqn 4)[20,21].

$$2 \; CpFe(benzene)^+ + 6 \; CH_3CN \xrightarrow{\;h\nu\;} Fe(NCCH_3)_6^{2+} + FeCp_2 + benzene \qquad (1)$$

$$CpFe(p\text{-}xylene)^+ + HMB \xrightarrow[CH_2Cl_2]{h\nu} CpFe(HMB)^+ + p\text{-}xylene \qquad (2)$$

$$CpFe(p\text{-}xylene)^+ + 3 \; L \xrightarrow[CH_2Cl_2]{h\nu} CpFe(L_3)^+ + p\text{-}xylene \qquad (L = P(R)_3, P(OR)_3, CNR, CO) \qquad (3)$$

$$CpFe(p\text{-}xylene)^+ + excess \; cyclohexene \; oxide \xrightarrow{\;h\nu\;} polycyclohexene \; oxide \qquad (4)$$

The chemistry of the ruthenium analogs shows interesting differences compared with the corresponding iron complexes; in particular, no arene replacement or exchange is observed in CH$_2$Cl$_2$ solutions. However, photolyses in acetonitrile produce rapid and quantitative conversion to the tris acetonitrile complex (Eqn 5)[3]. This complex and the Cp* (pentamethylcyclopentadienyl) analog have been extensively utilized in synthetic reactions to introduce the CpRu$^+$ moiety into a variety of molecules[22-28].

$$CpRu(benzene)^+ + 3 \; CH_3CN \xrightarrow{\;h\nu\;} CpRu(NCCH_3)_3^+ + benzene \qquad (5)$$

In some of our most recent work, we have begun to develop the chemistry of the osmium derivative[18]. The photochemical displacement of arene from CpOs(benzene)$^+$ is particularly slow under most conditions, but high yields of arene displacement products are obtained from acetonitrile solutions that contain either biphenyl or halide ions. The nature of the halide promoted reactions will be discussed; they exhibit a dramatic nucleophilic component that results from ion-pairing of the halide ion with CpOs(benzene)$^+$ to produce photochemically reactive ion pairs.

ELECTRONIC STRUCTURE

An investigation of the electronic structure of [CpM(arene)]$^+$ complexes with spectroscopically transparent arenes (300nm - 700nm) provided a basis for understanding the photochemistry of the compounds[8-13]. The putative excited state implicated in the photochemical M-arene displacement reactions is the metal localized a^{3}E$_1$ (LF) excited state that is populated by excitation of the singlet $a_1(d_{z^2})^2 \longrightarrow a_1(d_{z^2})^1 e_1(d_{xz}, d_{yz})^1$ excitation, followed by rapid intersystem crossing to the triplet. From preliminary quenching experiments[11], we have estimated the reactive state to be at 15,400 cm^{-1} (650nm) for Fe and at 22,200 cm^{-1} (450nm) for Ru. The chemical reactivity that is expected for this state is illustrated in Figure 3. Population of $e_1(d_{xz}, d_{yz})$ should considerably weaken the strong (>50kcal/mole) M-arene bond, while depopulation of $a_1(d_{z^2})$ generates a "hole" in the equitoral belt between the Cp and arene ligand that could allow nucleophilic attack of the excited state. These ideas are quite consistent with X-ray structural data and reactivity studies obtained for compounds that have $a_1(d_{z^2})$ singly occupied (d^5 compounds, FeCp$_2^+$, RuCp$_2^+$) and for compounds that have $e_1(d_{xz}, d_{yz})$ singly occupied (d^7 compounds, CpFe(arene)). Comparison of the d^7 and d^5 compounds relative to d^6 compounds suggest that population of d_{xz}, d_{yz} in the d^7 compounds significantly lengthens the M-arene bonds while depopulation of d_{z^2} in the d^5 complex RuCp$_2^+$ makes it very susceptible to nucleophilic attack[29-30]. We have investigated these mechanistic ideas by changing the nucleophilicity of the solvent and with substituent effects to vary the bond strength and steric hindrance around the M-arene bond[10-13]. We suggested that changes in the strength of M-arene bond should exhibit a linear free energy relationship (Eqn 6).
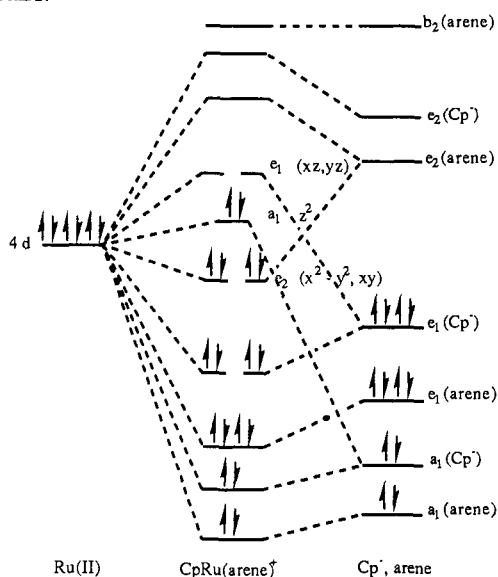
Figure 2. Qualitative MO Diagram
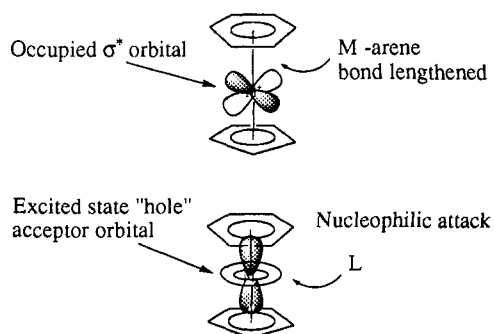
Figure 3. Orbital Orientations

$$\log(\phi/(1 - \phi)) = n \; \sigma \; \rho + \log(k_p^\circ/k_{nr}^\circ) \qquad (6)$$

k_p° and k_{nr}° are the rates of photochemical product formation and non-radiative decay for arene = benzene; n = # of substituents; σ = Hammett substituent constant and ρ = reaction constant. We predict a plot of $\log(\phi/(1 - \phi))$ vs n σ should be a straight line if only electronic effects are important. Deviations from linearity are due to the added effects of steric hindrance. Figure 4 shows a plot of this equation for quantum yields of methyl- and chloro- substituted iron (solid squares) and ruthenium (open squares) complexes in acetonitrile solutions. Notice that a good linear correlation exists for both cases, with the ruthenium quantum yields significantly lower than those of the corresponding iron compound in every case. Additionally, the points labeled HEB (hexaethylbenzene) for iron and 1,3,5-(t-bu) benzene for ruthenium deviate significantly below the appropriate least squares line. This deviation results from steric protection of the excited state from nucleophilic attack of acetonitrile. The effect is most dramatic in the less nucleophilic solvent CH_2Cl_2 where the iron compounds are less reactive, but the ruthenium systems are completely unreactive .
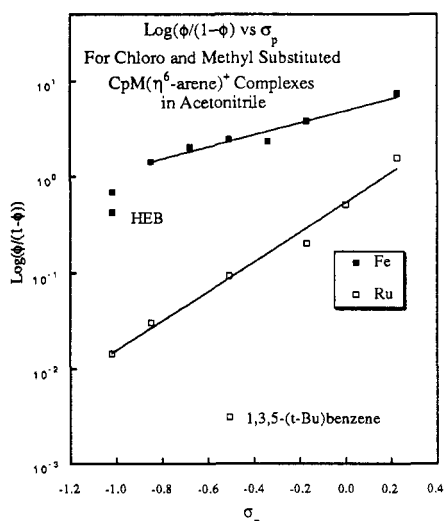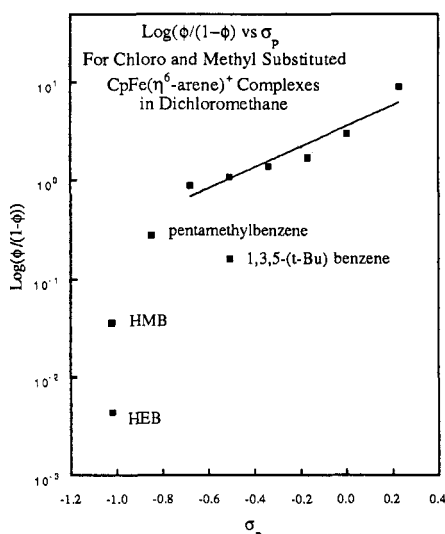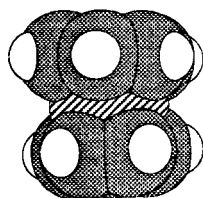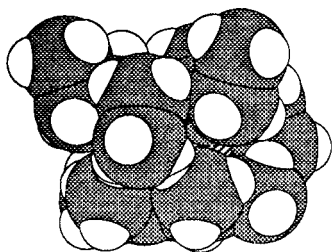

Figure 4.

Figure 5

Figure 6. Space filling model of CpFe(benzene)+

Figure 7. Space filling model of Cp*Fe(HEB)+

Table 1. Medium Effects on the Arene Release Quantum Yields For Hindered CpFe(arene)⁺ Complexes

Complex	Solvent	Anion	Quantum Yield
CpFe(HMB)⁺	CH_3CN	BF_4^-	0.41(1)
CpFe(HEB)⁺	CH_3CN	BF_4^-	0.30(1)
CpFe(HMB)⁺	CH_2Cl_2	BF_4^-	0.035(2)
Cp*Fe(TOL)⁺	CH_2Cl_2	BF_4^-	0.007(2)
CpFe(HEB)⁺	CH_2Cl_2	BF_4^-	0.0044(2)
CpFe(HEB)⁺	CH_2Cl_2	PF_6^- AsF_6^- SbF_6^- BPh_4^-	0.00087(5)
Cp*Fe(HMB)⁺	CH_2Cl_2	PF_6^-	0.00002(2)

HMB = hexamethylbenzene; HEB = hexaethylbenzene; TOL = toluene

Figure 5 shows the dramatic fall-off of the hexa-substituted HMB and HEB iron compounds, that are one and two orders of magnitude slower than predicted on the basis of electronic effects. Table 1 presents data for several severely hindered iron compounds that indicate a significant counterion dependence on the quantum yield in the poorly nucleophilic solvent CH_2Cl_2. Figures 6 and 7 illustrate the severe steric hindrance in the "equitorial band" of the complex. All of the data presented suggest that the arene release mechanisms in these CpFe(arene)+ and CpRu(arene)+ complexes are consistent with the mechanism presented in Figure 8. A recent paper suggests that Ru(arene)$_2^{2+}$ complexes also react photochemically via this mechanism[31].
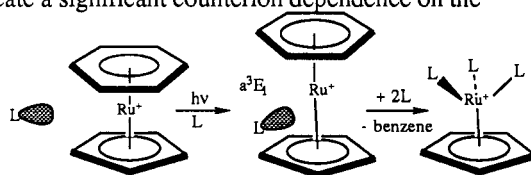

Figure 8. Mechanism of arene release

Photolysis of CpOs(benzene)+ in acetonitrile in the presence of different anions gives dramatic confirmation of the importance of ion-pairing as a contributing factor in arene release reactions in CpM(arene)+ photochemistry[18]. Essentially no conversion is observed for $A^- = PF_6^-$ while rapid conversion results when Cl- or Br- are present (Figure 9). If the ion-pair and the free ion each can give product upon excitation, Eqn. 7 may be derived from the mechanism in Figure 10.

$$(\phi_o/\phi_{obs}) = \phi_o \, (1 + [Br^-] \, K_{ip}) / (\phi_o + ([Br^-] \, K_{ip} \, \phi_{Br^-})) \tag{7}$$

A least squares fit of the quantum yield data for the photolysis of CpOs(benzene)+ in acetonitrile in the presence of different concentrations of Br- gives $\phi_o = 0.01200(1)$, $\phi_{Br^-} = 0.89(7)$ and $K_{ip} = 7.9(7)M^{-1}$. These parameters are quite reasonable for this system. This model suggests that the CpOs(benzene)+ Br- ion pair is nearly 75 times more reactive than CpOs(benzene)+ with respect to arene release
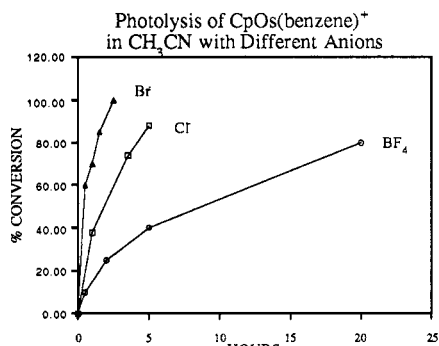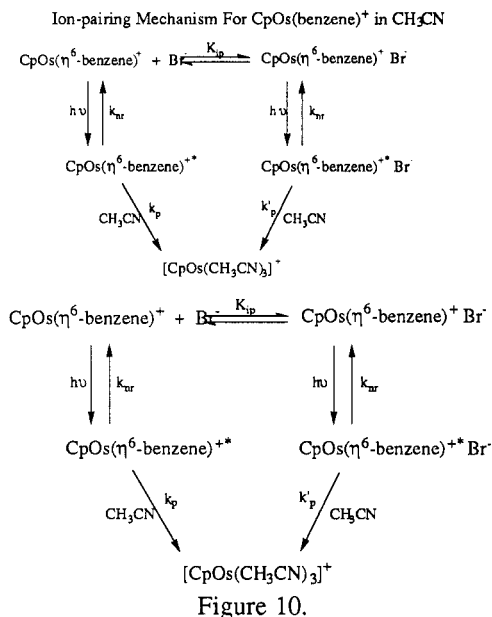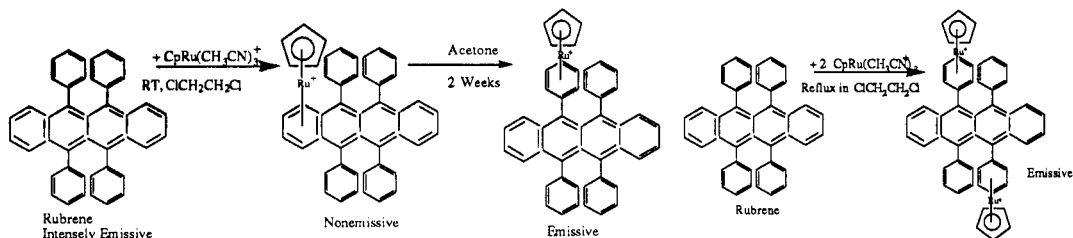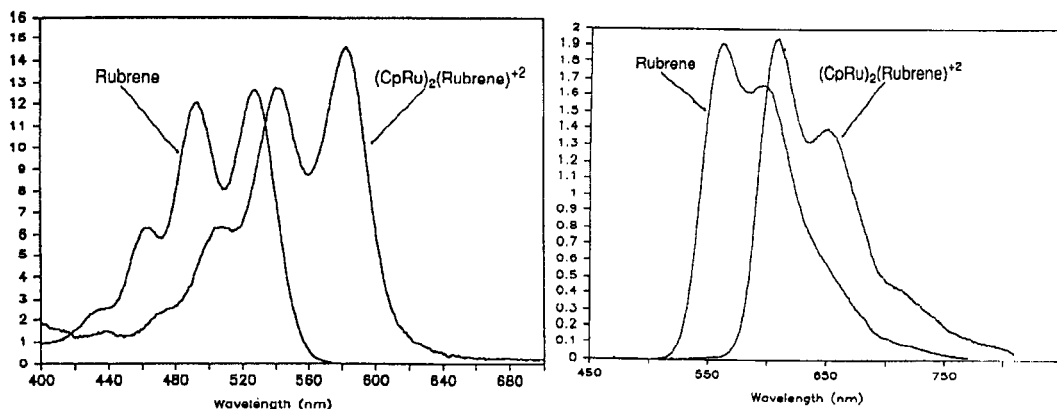

Figure 9.

Figure 10.

COMPLEXES OF EMISSIVE ARENES

Photochemical production of synthetically useful quantities of CpRu(NCCH$_3$)$_3^+$ have enabled us to synthesize CpRu(arene)+ complexes with emissive arenes[14-17,24]. These synthetic reactions are quite

Figure 11. Synthesis of two isomers of (CpRu)(rubrene)+   Figure 12. Synthesis of (CpRu)$_2$(rubrene)$^{2+}$

general, allowing a wide range of highly functionalized CpRu(arene)⁺ complexes to be produced. For example, two isomeric complexes of rubrene are produced by stirring the arene in either dichloroethane or acetone with one equivalent of CpRu(NCCH₃)₃⁺ (Figure 11). The disubstituted compound can also be produced in high yield in refluxing dichloroethane (Figure 12). The availability of these compounds has allowed us to address the question of how metal complexation changes the emission properties of the arene. The phenyl bound compounds are emissive and exhibit a moderate red shift in the band position while acene complexation quenches the emissive behavior of the complexes and gives a much larger red shift of the arene absorption. Considerable differences are also observed in the thermal and photochemical stabilities of the isomers. Acene bound isomers are much less thermally stable than phenyl isomers. Treatment with acetonitrile decomplexes the arene from the acene isomer within minutes or hours depending on the exact complex.

Figures 13 and 14. Absorption (left) and emission spectra of rubrene and (CpRu)₂(rubrene)²⁺

The phenyl isomers are stable indefinitely in acetonitrile but the CpRu⁺ group may be removed photochemically from the arene in some cases (vide infra). The absorption and emission spectra of uncomplexed rubrene and the (CpRu)₂(rubrene)²⁺ complex are shown in Figures 13 and 14. In both cases the spectrum of the complex is red shifted but retains the vibronic structure of the uncomplexed arene. Similar isomeric complexes of 9-phenyl anthracene (9-pa) have also been synthesized . The UV-VIS spectra of the phenyl and anthracene bound complexes are shown in Figure 15. Again, the phenyl bound isomer exhibits a moderate red shift in the spectrum and retains some vibronic structure while the anthracene complexed isomer band is red shifted to a larger degree and the vibronic structure is replaced with a broad, featureless absorption envelope. The colors and absorption maxima for these complexes are summarized in Table 2.
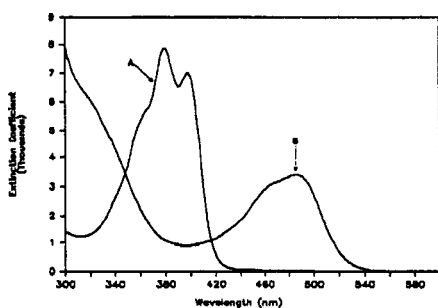
Table 2. CpRu⁺ Complexes of Rubrene and 9-phenylanthracene (9-pa)

Complex (binding mode)	Color	λmax
rubrene	red	520nm
(CpRu)(rubrene)⁺ (η⁶-napth isomer)	blue-green	660nm
(CpRu)(rubrene)⁺ (η⁶-Ph)	purple	553nm
(CpRu)₂(rubrene)²⁺ (η⁶-Ph)	purple	574nm
9-phenylanthracene	yellow	384nm
CpRu(9-pa)⁺ (η⁶-Anth)	orange	486nm
CpRu(9-pa)⁺ (η⁶-Ph)	yellow	397nm

Figure 15. Absorption spectra of CpRu(9–pa)⁺ . A is the η⁶-anthracene isomer; B is the η⁶-phenyl isomer

The synthesis[17] of coumarin derivatives has also been successful in yielding a variety of new compounds with variable photophysical and photochemical properties. Treatment of coumarin-6 with $CpRu(NCCH_3)_3^+$ first gives an intermediate species with an emission band at 555nm. This transient species has an IR spectrum that suggests the benzthiazole nitrogen and the ketonic oxygen of the lactone are coordinated to the ruthenium. Over time, this species rearranges to a η^6 complex with the ruthenium coordinated to the benthiazole arene group (Figure 16). This complex is also emissive.
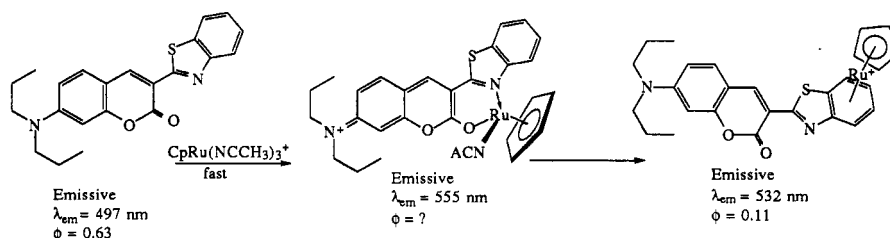

Figure 16

The absorption spectra of free coumarin-6 and the $CpRu(coumarin-6)^+$ complex are shown in Figure 17. As in the case of the rubrene and 9-pa pendant arene group complexes, the spectrum of $CpRu(coumarin-6)^+$ is moderately red shifted from the free dye molecule. The coumarin-6 complex is interesting in that it exhibits both emission and photochemical release of arene in acetonitrile solution. The related coumarin-30 complex (Figure 18) shows the arene release reaction but is non-emissive.
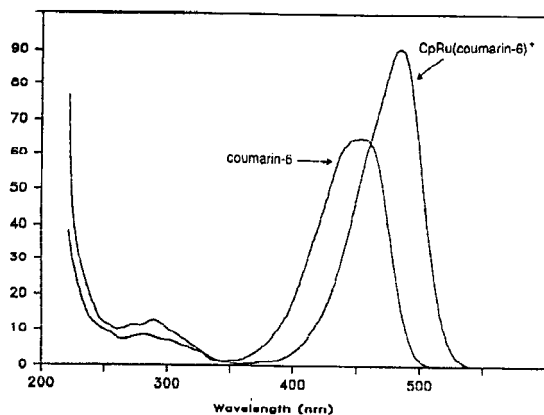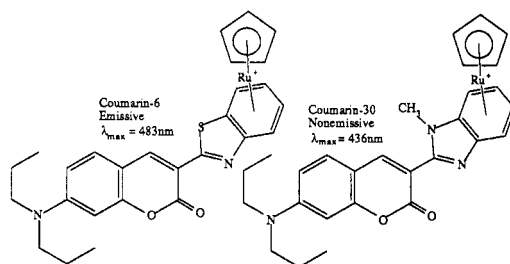

Figure 17. Absorption spectra of coumarin-6 and $CpRu(coumarin-6)^+$

Figure 18

DISCUSSION OF EMISSIVE ARENE COMPLEXES

The basic energetics of the emissive arene complexes of rubrene, 9-pa and coumarin-6 are shown in Figure 19. The inverse relationship between emission quantum yield and arene release suggests that the position of the photoactive ^3dd state ($^3E_1$) and the emitting state of the arene ligand is important. We suggest that when the emitting arene state is shifted higher in energy than the relatively arene insensitive ^3dd state, rapid internal conversion from the ligand excited states to ^3dd occurs and photochemical release of arene is observed. This case is observed for the phenyl bound $CpRu(9-pa)^+$ complex. When the energy of ^3dd is well above the emitting arene state, efficient

Figure 19. State diagram

ligand emission from the shifted chromophore is observed. This case is observed for the phenyl bound $CpRu(rubrene)^+$ complex. The intermediate case ($CpRu(coumarin-6)^+$) has ^3dd slightly above the emitting arene state, but it is close enough to be thermally populated. In this, case we predict and observe both modes of excited state deactivation. Further, we predict that both processes should show a marked temperature dependence. Future experiments are planned to experimentally verify this prediction.
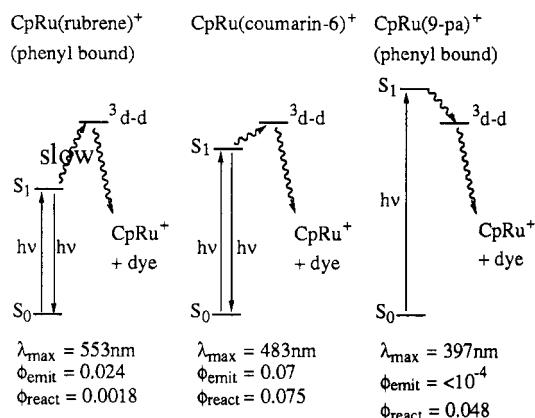
Another point of interest is the effect of M-arene binding mode on the emissive properties of the complex. In complexes that have the metal bound directly to the main π-system of the ligand chromophore (as in the η^6-acene CpRu(rubrene)⁺ and η^6-anthracene CpRu(9–pa)⁺ isomer) rearomatization of the ligand π-system after it supplies the 6 π electrons needed for η^6-arene coordination causes large spectral shifts and renders the complex non-emissive, even though the relative ^{3}dd - ligand state energetics are favorable. The nature of the featureless absorption bands observed for these complexes may be due to a MLCT band rather than the shifted ligand-localized band. More detailed spectroscopic experiments will be required to answer this intriguing question.

CONCLUSIONS

We have shown that the photoactive CpM(arene)⁺ dd excited states have dissociative character, but the M-arene bond is not completely broken in the lowest excited state. The arene release reactions for these compounds show dramatic substituent and medium effects. These effects are consistent with an arene release mechanism that has considerable associative character. The arene release reactions have been developed into useful synthetic procedures for the metals of the iron triad. Emissive arene complexes can be prepared that have emission spectra red shifted relative to the free arene. In general, emissive complexes are obtained when the emitting state of the free arene is below ^{3}dd and the arene is bound through the metal via a pendant group rather than the main π-system of the ligand chromophore. The observation of emission or arene release in these complexes is ultimately controled by the relative positions of ^{3}dd and the emitting arene state.

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