the ESR spectrum was recorded at increasing temperatures (−40 to +25 °C). After the experiment, the mother solution was evaporated to dryness at 25 °C. No phosphine oxide was detected.

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Registry No. **1**, 21576-91-0; **3a**, 103437-84-9; **3b**, 103437-86-1; **4a**, 103437-89-4; **4b**, 103437-87-2; $[Fe(NO)_2(PPh_3)_3]^+$, 103437-88-3; $Fe(NO)_2dppe$, 15683-28-0; $[Fe(NO)(dppe)_2]^+PF_6^-$, 52194-32-8; $Fe(NO)_2(PPh_3)_2$, 14056-98-5.

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Effect of Arene Methylation on Photochemical Arene Replacement Reactions of $[(\eta^5\text{-}C_5(CH_3)_5)M(\eta^6\text{-arene})]^+$ (M = Fe, Ru) Complexes

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The quantum yields (ϕ) for the photochemical arene release from $[Cp^*M(\eta^6\text{-arene})]^+$ complexes ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) have been measured for M = Fe(II) and Ru(II) in acetonitrile solutions at room temperature. (Fe: arene = toluene ($\phi = 0.007$), hexamethylbenzene ($\phi = 0.00002$). Ru: arene = benzene ($\phi = 0.19$), mesitylene ($\phi = 0.025$), hexamethylbenzene ($\phi = 0.0019$).) For both M = Fe and Ru, permethylation of the cyclopentadienyl ligand decreases the arene release quantum yields as compared to those of the analogous cyclopentadienyl compounds. For M = Fe, the decreases are factors of 113 and 20 500, respectively, for arene = toluene and hexamethylbenzene. The very large decrease observed for the (pentamethylcyclopentadienyl)(hexamethylbenzene)iron complex is consistent with an important steric blocking effect of the five pentamethylcyclopentadienyl methyl groups. For the three (pentamethylcyclopentadienyl)ruthenium compounds studied, decreases are more modest relative to the cyclopentadienyl compounds (1.8, 3.4, and 7.4 for M = Ru, where arene = benzene, mesitylene, and hexamethylbenzene). In this case, a linear correlation persists between $\log(\phi/(1-\phi))$ and σ_p, the Hammett parameter for methyl substituents. The linearity of the $\log(\phi/(1-\phi))$ vs. σ_p plot indicates that steric effects are not present to hinder the participation of acetonitrile in the transition state of the highly methylated Ru complexes studied. The increase in the Hammett ρ parameter from +1.38 to +2.05 upon cyclopentadienyl methylation of the Ru complexes suggests a slight increase in negative charge occurs at the arene in the arene release transition state of the pentamethylcyclopentadienyl complexes relative to the cyclopentadienyl complexes.

Introduction

A recent investigation of the mechanism of photochemical arene release from $[CpM(\eta^6\text{-arene})]^+$ complexes ($Cp = \eta^5$-cyclopentadienyl; M = Fe, Ru; arene = alkyl- or Cl-substituted benzenes) revealed electronic and steric inhibition of the arene release quantum yield for alkyl arene substituents.[1] The electronic effect exists for complexes of both metals but was slightly more important for the ruthenium compounds. The steric effect that results either from a high degree of arene methylation (five or six methyl groups) or from very bulky (ethyl or *tert*-butyl) arene substituents protects the excited metal center from nucleophilic attack. This steric effect is much more pronounced in the iron complexes. We have now extended our studies to the η^5-pentamethylcyclopentadienyl (Cp*) complexes of iron and ruthenium. These studies show that the decreases in the arene replacement quantum yields that occur on permethylation of the cyclopentadienyl ring in the ruthenium complexes result from an electronic effect, while the larger decreases observed for the iron systems result from a steric effect.

Experimental Section

General Considerations. All solvents were of spectroscopic grade and were used without further purification unless otherwise noted.

Dichloromethane and acetonitrile were dried over activated alumina or activated 4-Å molecular sieves prior to use. NH_4PF_6 was purchased from Pennwalt Inc. $Ru_3(CO)_{12}$ was purchased from Strem Chemicals. All other reagents were purchased as reagent grade and used as received. UV–visible spectra were obtained on either a Cary 17D or a Hewlett-Packard 8450 A spectrophotometer. ^1H NMR spectra were obtained for acetone-d_6 solutions of the compounds with a Varian CFT 20 spectrometer equipped with a proton accessory.

Synthesis of $[Cp^*Fe(\eta^6\text{-arene})]PF_6$ Compounds. $[Cp^*Fe(CO)_3]PF_6$ was synthesized by the method of Catheline and Astruc.[2] $[Cp^*Fe(\eta^6\text{-HMB})]PF_6$ (HMB = hexamethylbenzene) was synthesized by the method of Hamon et al.,[3] with the improvement suggested by Roman[4] for the corresponding Cp complexes.

$[Cp^*Fe(\eta^6\text{-tol})]PF_6$ (tol = toluene) was obtained by metal atom techniques[5] as a gift of the 3M Co. The complete details of the synthesis and characterization of this compound will be reported later.

Synthesis of $[Cp^*Ru(\eta^6\text{-arene})]PF_6$ Compounds. $[(C_6H_6)RuCl_2]_2$,[6] $(n\text{-Bu})_3Sn(C_5(CH_3)_5)$,[7] and $[Cp^*Ru(CO)_2]_2$[8] were prepared by literature procedures.

$[Cp^*Ru(\eta^6\text{-}C_6H_6)]PF_6$. (a) Method I. A sample of 0.9577 g (1.915 mmol) of $[(C_6H_6)RuCl_2]_2$ was placed under nitrogen in 75–100 mL of freshly distilled acetonitrile. Approximately 2 mL (~3.4 mmol) of $(n\text{-Bu})_3Sn(C_5(CH_3)_5)$ was then added, and the solution was refluxed for 18.5 h. The resultant solution was dark red-brown. The solvent was removed under vacuum to leave a dark oily residue. Distilled water (~500 mL) was added to this residue, and the mixture was filtered to give a pale yellow filtrate. Excess NH_4PF_6 was added, causing precipitation of a brown solid, which was collected by filtration. Elution of the brown solid through a short alumina column with acetone gave a mixture of yellow $(n\text{-Bu})_3SnCl$ and a white solid. Two recrystallizations from acetone/ether gave 0.5456 g (1.188 mmol) of white microcrystalline $[Cp^*Ru(\eta^6\text{-}C_6H_6)]PF_6$ (31% yield). Mp: 310–313 °C dec. ^1H NMR (solvent acetone-d_6): δ 606 (s, C_6H_6, 6 H), 2.08 (s, Cp*, 15 H). Anal. Calcd for $C_{16}H_{21}RuPF_6$: C, 41.83; H, 4.61. Found: C, 42.01; H, 4.67.

(b) Method II. A stirred solution of 0.363 g (0.621 mmol) of $[Cp^*Ru(CO)_2]_2$ in 30 mL of dry dichloromethane was cooled in an ice bath. A solution of 0.33 mL (6.44 mmol) of Br_2 dissolved in 10 mL of dry, degassed dichloromethane was slowly added by cannula. After the solution was stirred for an additional 40 min, the solvent was evaporated

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under vacuum. To the resulting dark green solid were added 1.0 g (7.5 mmol) of $AlCl_3$ and 75 mL of dry benzene. The mixture was refluxed for 20 h under nitrogen. After removal of the benzene under vacuum, 100 mL of H_2O/ice was carefully added. The aqueous solution was treated with NH_4OH, and the mixture was filtered into an excess of solid NH_4PF_6. The resulting precipitate was filtered out to yield 0.247 g (0.538 mmol) (43% yield) of crude $[Cp^*Ru(\eta^6\text{-}C_6H_6)]PF_6$. Purification of the crude solid (see method I) gave 0.156 g (0.340 mmol) of white microcrystalline powder.

$[Cp^*Ru(CH_3CN)_3]PF_6$. $[Cp^*Ru(CH_3CN)_3]PF_6$ was prepared by irradiating a solution of 0.2616 g (0.570 mmol) of $[Cp^*Ru(\eta^6\text{-}C_6H_6)]PF_6$ and 150 mL of CH_3CN in a quartz water-jacketed cell. The cell was stoppered, and the solution was bubbled with N_2 for $1\frac{1}{2}$ h. The stirred solution was irradiated with the output of a 400-W Ace Hanovia medium-pressure Hg lamp for 20 h. After irradiation, the solution was transferred under N_2 to another flask, and the solution was taken to dryness under vacuum. The golden-yellow product was washed with diethyl ether and collected under N_2 to give 0.2546 g (0.505 mmol) of air-sensitive $[Cp^*Ru(CH_3CN)_3]PF_6$ (89% yield). ^1H NMR (acetonitrile-d_3): δ 1.97 (s, CH_3CN, 9 H), 1.60 (s, Cp*, 15 H). UV-vis data: $\lambda_{max} = 370$ nm ($\epsilon_{370} = 1287$ M^{-1} cm^{-1}), $\lambda_{max} = 317$ nm ($\epsilon_{317} = 870$ M^{-1} cm^{-1}).

$[Cp^*Ru(\eta^6\text{-mes})]PF_6$ (mes = Mesitylene). A 60.4-mg (0.120-mmol) sample of $[Cp^*Ru(CH_3CN)_3]PF_6$ was added to a N_2-degassed solution of 2 mL (14.4 mmol) of mesitylene and 15 mL of $ClCH_2CH_2Cl$. The solution was stirred for 18 h and then refluxed for 2 h. Evaporation of the solvent yielded a residue, which was washed with ether to remove the excess mesitylene. This residue was dissolved in acetone and the solution sent through a short alumina column to remove the brown impurities. Evaporation of the solvent yielded 48.7 mg (0.0971 mmol) of white $[Cp^*Ru(\eta^6\text{-mes})]PF_6$ (81% yield). Mp: 329–331 °C dec. ^1H NMR (acetone-d_6): δ 5.82 (s, aromatic, 3 H), 2.24 (s, aromatic CH_3, 9 H), 1.95 (s, Cp*, 15 H). Anal. Calcd for $C_{19}H_{27}RuPF_6$: C, 45.51; H, 5.43. Found: C, 45.39; H, 5.40.

$[Cp^*Ru(\eta^6\text{-HMB})]PF_6$. A 74.5-mg (0.148-mmol) sample of $[Cp^*Ru(CH_3CN)_3]PF_6$ was added to a thoroughly degassed mixture of 0.519 g (3.20 mmol) of hexamethylbenzene in 20 mL of acetone. The solution was degassed for an additional 10 min with nitrogen and heated gently for 26.5 h. The solvent was removed, and the light brown solid was washed three times with 30-mL portions of hexane and two times with 40-mL portions of ether to remove excess hexamethylbenzene. The residue was then dissolved in acetone and the solution eluted through a short alumina column. After removal of the solvent, the product was recrystallized twice from acetone/ether to give 51.7 mg (0.0951 mmol) of white $[Cp^*Ru(\eta^6\text{-HMB})]PF_6$ (64% yield). Mp: 322–326 °C dec. ^1H NMR (acetonitrile-d_3): δ 2.07 (s, η^6-HMB, 18 H), 1.63 (s, Cp*, 15 H). Anal. Calcd for $C_{22}H_{33}RuPF_6$: C, 48.61; H, 6.12. Found: C, 47.34; H, 5.94.

Compound Purification. The samples used for quantum yield measurements were further purified by dissolving them in dichloromethane (Fe) or acetone (Ru) and passing the solutions down a short alumina column. The solutions were then evaporated to yield microcrystalline powders. All operations were carried out in the dark for the Fe compounds.

General Photolysis Procedures. Monochromatic light was obtained from the output of a 100-W medium-pressure mercury lamp with the appropriate interference filter (Oriel). The monochromatic light beam was then passed into sealed (vacuum stopcocks) quartz cells that were held in a cell holder consisting of an insulated copper block mounted on a magnetic stirrer.

Quantum Yield Measurement Procedure for $[Cp^*Fe(\eta^6\text{-arene})]PF_6$ Salts. Quantum yields for the $[Cp^*Fe(\eta^6\text{-arene})]PF_6$ complexes were determined in CH_3CN solutions by monitoring the formation of air-sensitive $[Cp^*Fe(CH_3CN)_3]PF_6$ according to the reaction

$$[Cp^*Fe(\eta^6\text{-arene})]PF_6 + 3CH_3CN \xrightarrow{h\nu} [Cp^*Fe(CH_3CN)_3]PF_6 + \text{arene} \quad (1)$$

This procedure supplants the one developed[1,9] for the Cp compounds based on the formation of $[Fe(phen)_3]^{2+}$. Two-hundredths molar solutions were carefully degassed with four or five freeze–pump–thaw cycles (10^{-4} mmHg). The toluene complex was irradiated with 436-nm light, while the hexamethylbenzene complex was irradiated with broad-band Pyrex-filtered light (cutoff $\lambda = 271$ nm, absorbance = 2). Actinometry was carried out as previously reported,[1] with the exception that neutral density filters were used during photolysis of $[CpFe(\eta^6\text{-}p\text{-xylene})]BF_4$ to attenuate the lamp intensity for the Pyrex-filtered light.

Table I. Electronic Absorption Spectra[a] of $[Cp^*M(\eta^6\text{-arene})]PF_6$ Complexes

complex	λ_{max} (ϵ_{max})[b]
$[Cp^*Ru(\eta^6\text{-}C_6H_6)]PF_6$	321 (221)[c]
$[Cp^*Ru(\eta^6\text{-mes})]PF_6$	326 (195)[c]
$[Cp^*Ru(\eta^6\text{-HMB})]PF_6$	324 (251)[c]
$[Cp^*Fe(\eta^6\text{-tol})]PF_6$	384 (115), 448 (96)
$[Cp^*Fe(\eta^6\text{-HMB})]PF_6$	406 (107), 460 (88)[c]

[a] All spectra were determined in acetonitrile solution at 25 °C. [b] Wavelength (λ) in nm; extinction coefficient (ϵ) in M^{-1} cm^{-1}; ±10%. [c] Shoulder.

The molar absorptivity ($\lambda_{max} = 540$ nm; $\epsilon_{max} = 510$ M^{-1} cm^{-1}) of $[Cp^*Fe(CH_3CN)_3]PF_6$ was determined by exhaustive photolysis of a degassed solution of $[Cp^*Fe(CO)_3]PF_6$ in CH_3CN with Pyrex-filtered light. The solution was freeze–pump–thaw-degassed periodically to remove the CO generated by the photolysis. Spectra were taken before and after the degas cycles to confirm no loss of solvent had occurred.

Quantum yields were not determined for CH_2Cl_2 solutions of $[Cp^*Fe(\eta^6\text{-arene})]PF_6$ because no spectroscopic technique with adequate sensitivity for the detection of arene release under these conditions currently exists. Photolyses were followed by ^1H NMR.

Quantum Yield Measurement Procedures for $[Cp^*Ru(\eta^6\text{-arene})]PF_6$ Complexes. Quantum yields ($\lambda_{irr} = 313$ nm) were measured for degassed, stirred solutions of the $[Cp^*Ru(\eta^6\text{-arene})]^+$ complexes. The appearance of $[Cp^*Ru(CH_3CN)_3]^+$ was conveniently monitored as previously described[1] for the generation of $[CpRu(CH_3CN)_3]^+$. Quantum yields are based on the stoichiometry of eq 2. For the permethylated species the

$$[Cp^*Ru(\eta^6\text{-arene})]^+ \xrightarrow[CH_3CN]{h\nu} [Cp^*Ru(CH_3CN)_3]^+ + \text{arene} \quad (2)$$

reaction is monitored at 370 nm (λ_{max} of $[Cp^*Ru(CH_3CN)_3]PF_6$). The procedure for determining the quantum yield for each compound involved the measurement of the absorption spectrum (280–600 nm) as a function of photolysis time (five to eight data points) for one to three independently prepared solutions. The data for a given solution were corrected for incomplete light absorption and inner-filter effects.[10] Actinometric measurements were made periodically with the Reineckate[11] actinometer. Quantum yields were calculated as the average of all the data obtained for each compound (a minimum of five data points).

Thermal Control Reactions. Solutions of the Fe and Ru compounds stored in the dark at 25 °C were monitored by UV-visible spectroscopy. No dark reactions were found for any of the compounds on the photolysis time scales.

Results

Electronic Absorption Spectra. Previously,[1] we have identified the photoactive excited state in $[CpM(\eta^6\text{-arene})]^+$ complexes (M = Fe, Ru) as the distorted a^3E_1 ligand field (LF) state. In the cyclopentadienyl (Cp) compounds, this state is produced by rapid nonradiative decay and intersystem crossing from the $^1E_2$ and a^1E_1 LF excited states reached on absorption. Spectral data for the LF region of the electronic absorption spectra of the permethylated cyclopentadienyl (Cp*) compounds are given in Table I. Both the peak positions and extinction coefficients of the Cp* compounds are nearly identical with those of the corresponding Cp compounds. The close spectral correspondence between the Cp* and Cp complexes of a given arene and metal is consistent with the assignment of the Cp* complex spectra as metal-centered absorptions.

Photochemical Reactions. Irradiations of the $[Cp^*Ru(\eta^6\text{-arene})]^+$ complexes (arene = benzene, mesitylene, hexamethylbenzene) at 313 nm (a region of LF absorption) in dichloromethane solutions give no detectable reactions; however, acetonitrile solutions of all the complexes are photosensitive, yielding $[Cp^*Ru(CH_3CN)_3]^+$ as the only metal-containing product. These reactions are analogous to the reactions exhibited by the previously studied $[CpRu(\eta^6\text{-arene})]^+$ complexes.[1,12] The quantum yields for CH_3CN solutions of the substituted complexes are given in Table II. The magnitude of the quantum yield decreases with an increase in alkyl substitution of the arene, and the quantum

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Table II. Substituent Effects on the Arene Release Quantum Yield[a,b] for $[\mathrm{CpM}(\eta^6\text{-arene})]\mathrm{PF_6}$ and $[\mathrm{Cp^*M}(\eta^6\text{-arene})]\mathrm{PF_6}$ Complexes

metal	arene	Cp[c]	Cp*
Ru	benzene	0.34 (1)	0.19 (1)
Ru	mesitylene	0.085 (4)	0.025 (2)
Ru	hexamethylbenzene	0.014 (1)	0.0019 (4)
Fe	toluene	0.79 (4)	0.007 (1)
Fe	hexamethylbenzene	0.41 (1)	0.00002 (1)

[a] The number in parentheses is the estimated standard deviation in the last significant digit. [b] Measured for $\mathrm{CH_3CN}$ solutions. [c] These values have been reported previously; see ref 1.

yields for the Cp* complexes are smaller than those previously determined[1] for the corresponding Cp compounds.

In contrast to the similarities of the photochemical behavior exhibited by the Cp and Cp*Ru complexes, the photochemical reactions of the $[\mathrm{Cp^*Fe}(\eta^6\text{-arene})]^+$ complexes are substantially different from those of the CpFe complexes previously studied. Both the products produced and the quantum efficiencies for the observed reactions are affected. Although the permethylated cyclopentadienyl Fe complexes photochemically release arene in $\mathrm{CH_3CN}$ solutions, they do not undergo Fe–Cp* bond breakage as do the $[\mathrm{CpFe}(\eta^6\text{-arene})]^+$ complexes:

$$2[\mathrm{CpFe}(\eta^6\text{-arene})]^+ \xrightarrow[\mathrm{CH_3CN}]{h\nu} \mathrm{FeCp_2} + \mathrm{Fe(CH_3CN)_6}^{2+} + 2\,\text{arene} \tag{3}$$

$$[\mathrm{CpFe}(\eta^6\text{-arene})]^+ \xrightarrow[\mathrm{CH_3CN,\ phen}]{h\nu} \mathrm{Fe(phen)_3}^{2+} + \mathrm{Cp^*} + \text{arene} \tag{4}$$

In the Cp compounds, reactions 3 and 4 have been shown to proceed through the thermally unstable $[\mathrm{CpFe(CH_3CN)_3}]^+$ complex,[13,14] while $[\mathrm{Cp^*Fe(CH_3CN)_3}]^+$ generated (reaction 5) is indefinitely stable under vacuum at room temperature:

$$[\mathrm{Cp^*Fe}(\eta^6\text{-arene})]^+ \xrightarrow{h\nu} [\mathrm{Cp^*Fe(CH_3CN)_3}^+] + \text{arene} \tag{5}$$

The quantum yields based on reaction 5 for irradiations into the LF bands at ~400 nm are given in Table II. These quantum yields are *dramatically* lower than those exhibited by the analogous CpFe, CpRu, or Cp*Ru complexes and will be discussed below.

The photolyses of the Cp*Fe complexes in dichloromethane solutions also take a course different from those of the Cp complexes. The photolyses of degassed $[\mathrm{Cp^*Fe}(\eta^6\text{-arene})]\mathrm{PF_6}$ (arene = toluene, HMB) in dichloromethane were followed by ^{1}H NMR. Photolysis with the full lamp spectrum (100-W Hg lamp) of $[\mathrm{Cp^*Fe}(\eta^6\text{-toluene})]\mathrm{PF_6}$ yielded no changes in the ^{1}H NMR spectrum in the first 0.5 h; however, after approximately 20 h the peaks in the spectrum had broadened considerably and about 25% of the arene was present as free arene. Further photolysis led to the production of insoluble yellow products. No $\mathrm{FeCp^*_2}$ or Fe(II) (products that would result from Fe–Cp* bond cleavage) was observed in these solutions. The quantum yield under these conditions is extremely low, much smaller than the quantum yield observed for an otherwise identical acetonitrile solution (80% conversion to $[\mathrm{Cp^*Fe(CH_3CN)_3}]\mathrm{PF_6}$ in only 4 h). Photolyses of the hexamethylbenzene complex in dichloromethane solutions gave results similar to those obtained for the toluene complex, but only after 5 days of photolysis. In summary, both Cp*Fe complexes are photoactive in dichloromethane solutions, but the quantum yields for the arene release process are much lower than those listed in Table II for acetonitrile solutions and the nature of the Fe-containing photoproducts has not been determined at this time.

Discussion

Photophysical Model. The quantum yields for the Cp* complexes studied here will be interpreted within the framework of a photophysical model applicable to mixed-ring low-spin d^6-transition-metal systems that has been discussed in detail previously.[1] Briefly, the model relates ϕ (the quantum yield for product formation) to k_p (the rate of product formation from the lowest triplet excited state) and k_nr (the rate of nonradiative decay from the lowest triplet excited state) with the additional assumption that $\phi_\mathrm{isc} \approx 1$:

$$\phi = k_\mathrm{p}/(k_\mathrm{p} + k_\mathrm{nr}) \tag{6}$$

Rearrangement of eq 6 allows the ratio of k_p to k_nr to be derived:

$$k_\mathrm{p}/k_\mathrm{nr} = \phi/(1 - \phi) \tag{7}$$

Variations of ϕ with the degree of arene methylation were previously assumed to be variations in the rate constant k_p and not variations in excited-state lifetimes. This assumption was justified by arene deuteration studies for the Cp complexes and is also expected to hold for the Cp* complexes.

Arene ring methylation decreases the quantum yield for arene release in Cp compounds through both steric and electronic effects. The relative importance of these effects was determined by treating the ratio $k_\mathrm{p}/k_\mathrm{nr}$ as an empirical rate parameter that was correlated with the Hammett σ_p parameter (eq 8), where $k_{0,\mathrm{p}}/k_{0,\mathrm{nr}} = \phi_0/(1 - \phi_0)$ for the unsubstituted (benzene) complexes. A straight line

$$\log\,(\phi/(1 - \phi)) = \log\,(k_\mathrm{p}/k_\mathrm{nr}) = n\sigma_\mathrm{p} + \log\,(k_{0,\mathrm{p}}/k_{0,\mathrm{nr}}) \tag{8}$$

obtained for plots of log $(\phi/(1 - \phi))$ vs. $n\sigma_\mathrm{p}$ (where n is the number of arene methyl substituents and $\sigma_\mathrm{p} = -0.17$ for methyl) was taken as an indication that only electronic effects determine ϕ and $k_\mathrm{p}/k_\mathrm{nr}$. Deviations (large decreases in $k_\mathrm{p}/k_\mathrm{nr}$) from linear behavior for these plots were interpreted as due to decreases in k_p caused by significant steric effects.

Quantum Yield Variations with Methylation. (a) Ru Complexes. The steric and electronic requirements of the arene release reaction in the Ru systems are obtained through comparison of the quantum yield data for the pentamethylcyclopentadienyl Ru complexes with those of their nonmethylated analogues (Table II). Although each Cp* complex shows a decrease in quantum yield for arene replacement relative to the Cp analogue, the $[\mathrm{Cp^*Ru}(\eta^6\text{-arene})]^+$ compounds maintain the linearity[15] of the log $(\phi/(1 - \phi))$ vs. σ_p plots previously observed for the Cp complexes of Fe and Ru when studied in $\mathrm{CH_3CN}$ solutions. The lack of significant deviations from linearity for the log $(\phi/(1 - \phi))$ vs. $n\sigma_\mathrm{p}$ plot even for the highly methylated $[\mathrm{Cp^*Ru}(\eta^6\text{-HMB})]^+$ complex indicates that steric blockage of acetonitrile does *not* significantly affect the quantum yield for arene release. Only electronic effects are significant in determining the quantum yield of arene release in the $[\mathrm{Cp^*Ru}(\eta^6\text{-arene})]^+$ systems.

The slightly larger ρ value found for the Cp* system ($\rho = +2.05$) relative to the Cp value ($\rho = +1.38$) coincides with the expected increase in the covalency of the Cp*–Ru–arene bonds in comparison to the Cp–Ru–arene bonds.

(b) Fe Complexes. Although LF irradiation of $[\mathrm{Cp^*Fe}(\eta^6\text{-arene})]\mathrm{PF_6}$ complexes at ~400 nm in dichloromethane or acetonitrile leads to release of the arene as in the Cp analogues previously studied, permethylation of the cyclopentadienyl ring *dramatically* lowers the quantum yield for arene release. Quantum yields for the $[\mathrm{Cp^*Fe}(\eta^6\text{-arene})]\mathrm{PF_6}$ compounds are given in Table II. In Figure 1, a typical photolysis of $[\mathrm{Cp^*Fe}(\eta^6\text{-tol})]\mathrm{PF_6}$ in acetonitrile followed by UV-vis spectroscopy is presented. The decrease in the quantum yield between the toluene and the hexamethylbenzene permethylcyclopentadienyl complexes of Fe ($\phi_\mathrm{tol} = 0.007$, $\phi_\mathrm{HMB} = 0.000\,02$) is more pronounced than for either the parent $[\mathrm{CpFe}(\eta^6\text{-arene})]^+$ species ($\phi_\mathrm{tol} = 0.79$, $\phi_\mathrm{HMB} = 0.41$) or the corresponding $[\mathrm{Cp^*Ru}(\eta^6\text{-arene})]^+$ species. Permethylation of the Cp ligand decreases the photochemical arene release from the Fe–toluene complex by a factor of 113 and from the Fe–hexamethylbenzene complex by a factor of 20 500. The large decrease in the arene release quantum yields markedly

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(15) The plot of log $(\phi/(1 - \phi))$ vs. σ_p for the Cp* ruthenium complexes of benzene, mesitylene, and hexamethylbenzene is linear with least-squares slope = +2.05 and intercept = −0.60.

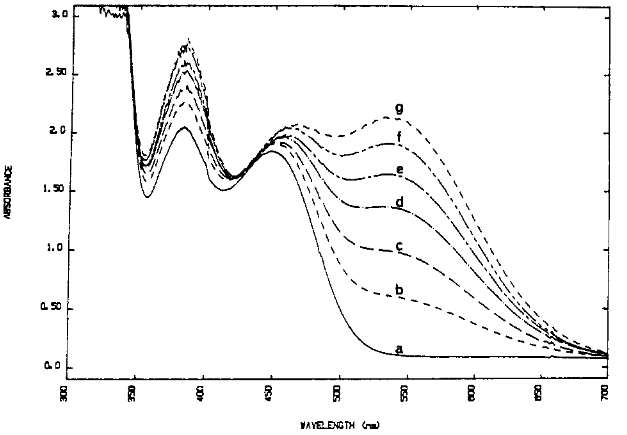

Figure 1. Absorption spectra obtained during the Pyrex-filtered photolysis of $[Cp^*Fe(\eta^6\text{-tol})]PF_6$ in degassed CH_3CN solution: (a) initial spectrum; (b–g) obtained at 5-min photolysis intervals.

contrasts the ruthenium complex results and is too large to be solely the result of electronic effects if the addition of a methyl group to the cyclopentadienyl ring produces an electronic effect of magnitude similar to that of a methyl substituent on the arene ligand. For example, eq 8 predicts a quantum yield of 0.30 for arene release for $[Cp^*Fe(\eta^6\text{-HMB})]^+$ based on 11 methyl substituents. The experimentally determined quantum yield is actually 15 000 times smaller. As in the case of $[CpFe(\eta^6\text{-arene})]^+$ complexes with highly substituted or bulky arenes (i.e., hexamethylbenzene and hexaethylbenzene, or 1,3,5-tri-*tert*-butylbenzene in CH_2Cl_2 solutions), steric effects rather than electronic effects dominate the quantum yield for arene release.[1] The large steric effect is also consistent with the difference in quantum yields between the $[Cp^*Fe(\eta^6\text{-tol})]^+$ and $[Cp^*Fe(\eta^6\text{-HMB}$ complexes, which amounts to a factor of 350 as compared to the case of their cyclopentadienyl analogues, whose quantum yields differ by only a factor of 2.

Proposed Photochemical Arene Release Mechanism. We propose a detailed mechanism (Figure 2) for these reactions that is consistent with both the Cp and the Cp* data for both metals in CH_2Cl_2 and CH_3CN solutions. For both solvents and metals the mechanism features photochemical excitation and rapid excited-state relaxation to ultimately form the distorted a^3E_1 LF state. Enhanced excited-state reactivity results from the characteristics of the a^3E_1 LF excited state. This excited-state features a "hole" in a low-lying d orbital that increases its susceptibility toward nucleophilic attack relative to the ground state and population of a σ^* M–arene orbital that lengthens and weakens the M–arene bond. Previous work[16] has shown that the Fe–arene bond lengthens upon population of the $e_1\sigma^*$ orbital set in the d^7 radical species $[CpFe(\eta^6\text{-}C_6Et_6)]$.

Although the a^3E_1 excited state lifetime appears to be rather short, this does not preclude interactions between the excited state and the first solvation sphere of the complex. The rate-limiting attack on the *excited* metal center by either a solvent molecule or an anion in the first solvation sphere is facilitated in the sterically hindered Ru complexes relative to the hindered Fe complexes because of the larger ring-to-ring spacing present in the Ru compounds. For example, in a structurally characterized Fe compound,[16] the spacing is only 3.23 Å as compared with 3.50 Å in a similar Ru compound.[17] The M–arene bond lengthening in the a^3E_1 excited state is also expected to be more important for the Ru systems than for the Fe systems,[18] further increasing the relative steric protection of the Fe complex a^3E_1 excited state

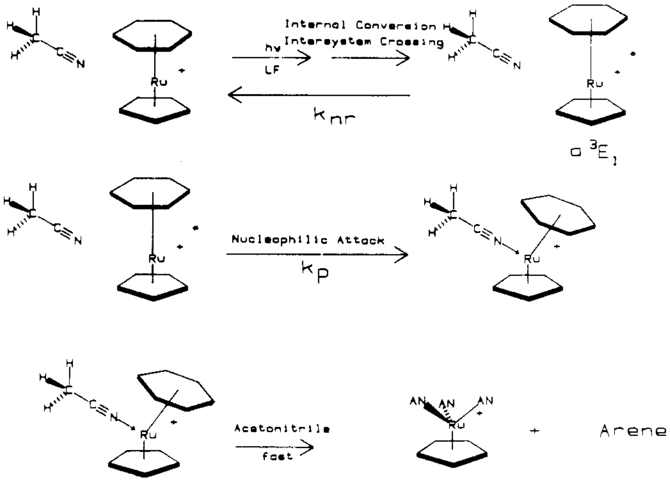

Figure 2. Detailed mechanism for the attack of acetonitrile on the a^3E_1 LF excited state of $[CpM(\eta^6\text{-arene})]^+$ and $[Cp^*M(\eta^6\text{-arene})]^+$ complexes. Ring substituents are omitted for clarity.

from nucleophilic attack. This analysis leads us to conclude that the Ru systems exhibit excited states similar to those of Fe, but ones that are more accessible to nucleophilic attack even with 11 methyl groups in place. Thus, *electronic* substituent effects still dominate the quantum yields for the Cp*Ru complexes and the log $(\phi/(1 - \phi))$ vs. σ_p straight-line plot persists with only a small change in slope while the Cp*Fe complexes are dominated by the *steric* influence of the substituents.

In solutions that are more weakly nucleophilic than CH_3CN (i.e., CH_2Cl_2), the quantum yields for arene release are very small for the Cp*Fe complexes and essentially zero for the Cp*Ru complexes. These results are consistent with the previous arguments if the strength of the nucleophile is an important factor in overcoming the steric effects of arene methylation. The accumulated data suggest that the weaker nucleophile CH_2Cl_2 is less able to penetrate the steric protection of the metal center afforded by methylation than is CH_3CN. The strength of the nucleophile in overcoming the steric protection was also found to be important in cases where the counterion acts as the nucleophilic agent in the arene release reactions.

Conclusions

We have studied the photochemical arene replacement reactions of $[Cp^*M(\eta^6\text{-arene})]^+$ (M = Fe, Ru) in CH_2Cl_2 and CH_3CN solutions. In CH_2Cl_2 solutions the Fe complexes exhibit the photochemical arene release reaction, but with very low quantum efficiency; the Ru complexes are stable under these conditions. In CH_3CN solution, complexes of both metals photochemically release the arene and yield the corresponding $[Cp^*M(CH_3CN)_3]^+$ complex. The two Fe complexes studied exhibit extremely low quantum yields for arene release in CH_3CN due to efficient steric protection of the Fe-localized LF excited state from acetonitrile attack. The Ru complexes studied exhibit a small decrease in arene release quantum yield relative to the Cp analogues but maintain a linear log $(\phi/(1 - \phi))$ vs. σ_p plot. The linearity of this plot indicates that steric factors are not important determining factors for the arene release quantum efficiency of the Ru complexes.

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Registry No. $[Cp^*Ru(\eta^6\text{-}C_6H_6)]PF_6$, 99631-48-8; $[Cp^*Ru(\eta^6\text{-mes})]PF_6$, 99617-75-1; $[Cp^*Ru(\eta^6\text{-HMB})]PF_6$, 99617-77-3; $[Cp^*Fe(\eta^6\text{-tol})]PF_6$, 103619-51-8; $[Cp^*Fe(\eta^6\text{-HMB})]PF_6$, 71713-57-0; $[(C_6H_6)RuCl_2]_2$, 37366-09-9; $(n\text{-Bu})_3Sn(C_5(CH_3)_5)$, 69382-50-9; $[Cp^*Ru(CO)_2]_2$, 70669-56-6; $[Cp^*Ru(CH_3CN)_3]PF_6$, 99604-67-8; benzene, 71-43-2; mesitylene, 108-67-8; hexamethylbenzene, 87-85-4.

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(17) McCormick, F. B., private communication, 1985.

(18) The σ^* antibonding level in the Ru complex a^3E_1 excited state is relatively more antibonding than the analogous level in the Fe complex. This should result in more lengthening of the Ru–arene bond relative to that of the Fe–arene bond.