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Ion-Pairing Effects in the Photochemistry of the Cyclopentadienyl(η^6-benzene)osmium(II) Cation. Synthesis and Reactions of a Synthetically Useful Intermediate: The Cyclopentadienyltris(acetonitrile)osmium(II) Cation

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Previously, we investigated the photochemistry of the thermally inert, low-spin d^6 [CpM(arene)]$^+$ complexes with simple arene ligands[1-8] (M = Ru, Fe; Cp = η^5-cyclopentadienyl; arene = η^6-arene). Photolytic arene displacement has considerable synthetic utility[1-19] and provides mechanistic insight.[8,19-25] Extending this chemistry to osmium has long been a goal of our group because few general methods are available for the preparation of complexes that contain the CpOs$^+$ group. Moreover, recent[26-29] investigations of CpRu$^+$ coumarin laser dye complexes suggest that the corresponding Os complexes will have higher thermal stability and attractive photochemical and photophysical properties.

We now report that the photochemical displacement of the η^6-benzene ligand from [CpOs(η^6-benzene)]$^+$ [30,31] in acetonitrile affords the tris(acetonitrile) complex [CpOs(CH_3CN)$_3$]$^+$ in useful synthetic quantities. As in the case of the Ru analog, "CpOstris" is a useful synthetic intermediate for CpOsL$_3^+$ complexes. Previous excursions along this synthetic route failed because the photoreaction displays a significant anion dependence that limits the quantum efficiency and a secondary photochemical reaction of the tris complex produces a dramatic inner filter effect that precludes high conversions. The proposed sequence of reactions is shown below:

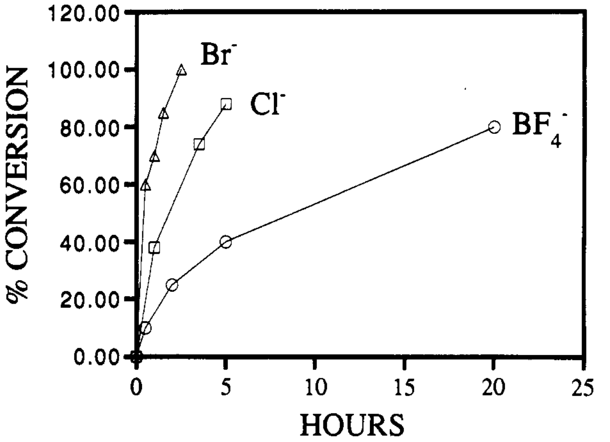

Figure 1. Percent conversion of [CpOs(η^6-benzene)]$^+$ to [CpOs(CH_3CN)$_3$]$^+$ vs photolysis time in the presence of BF_4^- (○), Cl^- (△), and BF_4^- plus Br^- (□).

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

$$\mathrm{CpOs(CH_3CN)_3}^+ \xrightarrow{h\nu} \text{inner filter absorber} \qquad (2)$$

We reduced these unfavorable effects in separate experiments by **increasing** the quantum efficiency of step 1 and by **reducing** the efficiency of step 2. The first method gave results of mechanistic interest, while the second method was synthetically important.

Previous mechanistic investigations of Fe and Ru chemistry[8,19-25] suggested that the quantum yield for arene release from [CpOs(η^6-benzene)]$^+$ would increase upon addition of nucleophilic anions to the reaction mixture. Figure 1 shows a plot of percent conversion of the starting material to product vs reaction time for the photolysis of [CpOs(η^6-benzene)]BF_4, [CpOs(η^6-benzene)]Cl, and [CpOs(η^6-benzene)]BF_4 with bromide. The photochemical reactivity of [CpOs(η^6-benzene)]$^+$ is strongly enhanced by the addition of halides. Unfortunately, these methods do not lead to a useful synthesis of [CpOs(CH_3CN)$_3$]$^+$ because of scaleup problems and, at high conversions, CpOs(CH_3CN)$_2$X (X = Cl, Br) and osmocene are also formed. However, a successful synthesis of CpOs(CH_3CN)$_3$$PF_6$ was realized by reducing the efficiency of step 2 by adding a chemically inert, light absorber. In this regard, biphenyl was particularly effective at enhancing the percent conversion by protecting [CpOs(CH_3CN)$_3$]$^+$ from secondary photolysis at 254 nm. In contrast to the halide promoted reactions, scaleup of this reaction was possible. Photolysis of 0.50 g of [CpOs(η^6-benzene)]PF_6 and 1.5 g of biphenyl in 300 mL of degassed acetonitrile with a 450-W Hg/vapor lamp in an immersion photolysis apparatus at 15 °C gave 0.49 g of CpOs(CH_3CN)$_3$$PF_6$ (90%).[32]

The synthetic utility of [CpRu(CH_3CN)$_3$]$^+$ suggests similar reactions with [CpOs(CH_3CN)$_3$]$^+$. In preliminary studies, we have observed that [CpOs(CH_3CN)$_3$]$^+$ reacts readily with a wide

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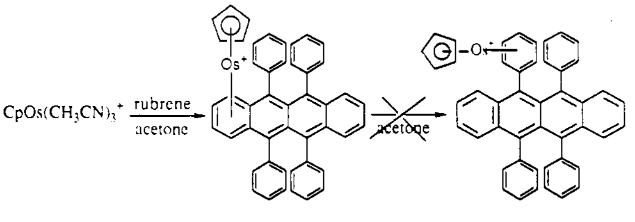
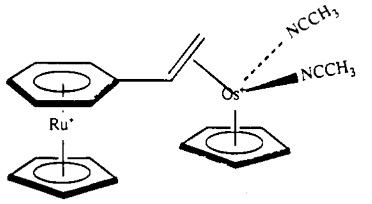
variety of ligands, including arenes, phosphines, polypyrazolylborates, CO, and NO, thereby demonstrating the utility of $[CpOs(CH_3CN)_3]^+$ as a synthon for $CpOsL_3{}^+$ complexes.[33] While many of these reactions are analogs of ruthenium, significant differences in reactivity and stability between the metals are also apparent. **In particular, $[CpOs(CH_3CN)_3]^+$ shows a marked propensity to form products that are only kinetically stable or are reaction intermediates in the corresponding ruthenium chemistry.**

For example, in the reaction of $[CpRu(CH_3CN)_3]^+$ with rubrene, Koefod et al.[27] demonstrated that kinetic and thermodynamic isomers could be synthesized. The kinetic isomer with $CpRu^+$ bound to an end naphthacene ring is produced in methylene chloride while the thermodynamic isomer with the metal bound to a phenyl ring was formed by refluxing the kinetic product in acetone.



The reaction between $[CpOs(CH_3CN)_3]^+$ and rubrene in refluxing acetone solution produced *only* the napthacene bound isomer.[34] Even extended reaction times in refluxing acetone did not initiate isomerization of the osmium complex to the phenyl bound isomer.

The osmium and ruthenium tris complexes display even more striking differences in their reactions with styrene.[35] $[CpRu(CH_3CN)_3]^+$ reacts quantitatively with 1 equiv of styrene in acetone to give the η^6-bound arene complex, ($[CpRu(\eta^6\text{-styrene})]^+$). The corresponding reaction of $[CpOs(CH_3CN)_3]^+$ gives exclusively the η^2-bound olefin complex, ($[CpOs(\eta^2\text{-styrene})(CH_3CN)_2]^+$). Even prolonged reaction times at room temperature do not give $[CpOs(\eta^6\text{-styrene})]^+$. Further, reactions of $[CpOs(CH_3CN)_3]^+$ with $[CpRu(\eta^6\text{-styrene})]^+$ and $[CpRu(CH_3CN)_3]^+$ with $[CpOs(\eta^2\text{-styrene})(CH_3CN)_2]^+$ gave identical products, formulated as $[(CpRu)(\eta^6{:}\eta^2\text{-}\mu\text{-}C_6H_5CH{=}CH_2)(CpOs(CH_3CN)_2)]^{2+}$:



As a final exhibit of selectivity, a solution that contains both $[CpRu(CH_3CN)_3]^+$ and $[CpOs(CH_3CN)_3]^+$ reacts with styrene to give **exclusively** $[(CpRu)(\eta^6{:}\eta^2\text{-}\mu\text{-}C_6H_5CH{=}CH_2)(CpOs(CH_3CN)_2)]^{2+}$.

Table I. Quantum Yield Data[a] for Photolysis of $[CpOs(\eta^6\text{-benzene})]PF_6$ in Acetonitrile at 313 nm with Added Amounts of (TBA)Br

[TBABr], M	quantum yield	[TBABr], M	quantum yield
0.0	0.012	0.074	0.33
0.014	0.10	0.44	0.73
0.022	0.14		

[a] Quantum yield data were measured for the appearance of $[CpOs(CH_3CN)_3]^+$ for photolysis at 313 nm by monitoring the increase in the absorbance at 430–380 nm. To minimize the inner filter effects caused by $[CpOs(CH_3CN)_3]^+$, total conversion was limited to 5%. Quantum yields are ±10%.

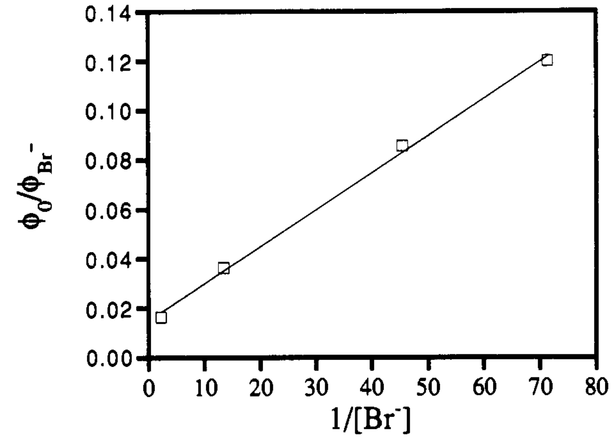


Figure 2. Plot of Φ_0/Φ_{Br} vs $1/[Br^-]$ for the photolysis of $[CpOs(\eta^6\text{-benzene})]^+$ in acetonitrile. Slope = 0.0015; intercept = 0.015.

In addition to this synthetic chemistry, the mechanism of arene displacement from $[CpOs(\eta^6\text{-benzene})]^+$ is also of interest. Quantum yields were measured for the photolysis of $[CpOs(\eta^6\text{-benzene})]PF_6$ in neat acetonitrile and in the presence of bromide. Results are given in Table I.

An arene release quantum yield of 0.012 was determined for $[CpOs(\eta^6\text{-benzene})]PF_6$ in acetonitrile. This value is 60 and 34 times smaller than the quantum yields determined for the analogous iron and ruthenium complexes,[22] respectively. The bromide dependence of the quantum yield for photolysis of $[CpOs(\eta^6\text{-benzene})]^+$ in acetonitrile is substantial. At our highest concentration of (TBA)Br (0.44 M) the quantum yield is 60 times the value determined in the absence of bromide. A Stern–Volmer plot (Figure 2)[36] of Φ_0/Φ_{Br} vs $1/[Br^-]$ is linear, with a slope of 0.0015 and an intercept of 0.015. Several mechanisms can explain the $[Br^-]$ dependence of the arene release quantum yield, but the most likely mechanism for this reaction involves ground-state ion pairing of bromide with $[CpOs(\eta^6\text{-benzene})]^+$ (Scheme I).

This mechanism features two ground-state absorbers in solution, the free ion and the ion pair $[CpOs(\eta^6\text{-benzene})^+\cdots Br^-]$. Each species produces a reactive excited state that either nonradiatively decays back to starting material or reacts to form $[CpOs(CH_3CN)_3]^+$. The large increase of the quantum yield with $[Br^-]$ suggests that arene release from the ion-paired excited state to form $[CpOs(CH_3CN)_3]^+$ must be extremely efficient. The details of the mathematical analysis cannot be given here, but if unit efficiency is assumed for the ion pair, a value of 10 M^{-1} is obtained for the ion pairing formation constant (K_a). Typical literature values[37] of ion pairing constants for some comparable bromide salts in acetonitrile are $(CH_3)_4NBr$ (K_a = 37 M^{-1}) and Et_4NBr (K_a = 4.7 M^{-1}). These values suggest that 10 M^{-1} is a reasonable value for K_a for the $[CpOs(\eta^6\text{-benzene})^+\cdots Br^-]$ ion pair, and that

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(32) $CpOs(CH_3CN)_3PF_6$ was separated from the biphenyl by reducing the photolyte volume followed by addition of diethyl ether to precipitate the product as light yellow needles. Elution down a short alumina column with acetonitrile produced an analytically pure sample. Anal. Calcd for $C_{11}H_{14}N_3OsPF_6$: C, 25.24; H, 2.70, N, 8.03. Found: C, 25.41; H, 2.81, N, 7.89. ^1H NMR (200 MHz, acetone-d_6): δ 4.664 (s, C_5H_5); 2.697 (s, CH_3CN). CV of $[CpOs(CH_3CN)_3]PF_6$ in $CH_3CN/(TBA)PF_6$ (TBA = tetrabutylammonium) exhibits a reversible, one-electron oxidation at $E°$ = +0.83 V vs Ag/AgCl.

(33) The syntheses of CpOs complexes from $[CpOs(CH_3CN)_3]PF_6$ will be reported.

(34) $[CpOs(rubrene)]PF_6$ is obtained as a blue-green powder in 72% yield. Anal. Calcd for $C_{47}H_{33}OsPF_6$: C, 60.50; H, 3.57. Found: C, 59.93; H, 3.97. ^1H NMR (200 MHz, CD_2Cl_2): δ 5.602 (s, C_5H_5, 5H), 6.565 (m, 2H, bound naphthacene ring, $H_{2,3}$), 6.8–7.4 (m, unbound rings and $H_{1,4}$ on bound naphthacene ring). Visible spectrum: λ_{max} = 660 nm, ϵ_{max} = 6,600 $M^{-1}cm^{-1}$.

(35) Reactions with styrene were monitored with ^1H NMR spectroscopy. Peak positions of the various species generated are included as supplementary material.

(36) The derivation of the Stern–Volmer equation for the ion pairing mechanism is given in the supplementary material.

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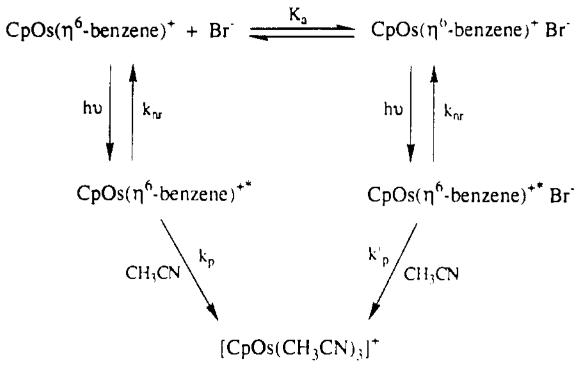
Scheme I. Ion-Pairing Mechanism for Photolysis of $[CpOs(\eta^6\text{-benzene})]^+$ with Bromide



the quantum yield for arene release from the ion pair must approach 1. The participation of anion assistance in the photochemical removal of arene ligands is well documented;[22-25] however, this system is unique in that a significant effect is observed in the highly polar solvent acetonitrile. For $[CpFe(arene)]^+$ complexes, the only significant ion-pairing dependence was observed either in the lower dielectric methylene chloride[22,24] or in mixtures of methylene chloride and nitrile solvents.[25] Further studies that address these mechanistic issues are planned.

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Supplementary Material Available: Text giving ^{1}H NMR data for $[CpRu(\eta^6\text{-styrene})]^+$, $[CpOs(\eta^2\text{-styrene})(CH_3CN)_2]^+$, and $[(CpRu)(\eta^6{:}\eta^2\text{-}\mu\text{-}C_6H_5CH{=}CH_2)(CpOs(CH_3CN)_2)]^{2+}$ and the derivation of the Stern–Volmer equations for Scheme I (2 pages). Ordering information is given on any current masthead page.