Preparation and Reactions of $[CpOs(CH_3CN)_3]^+$. A Useful Synthetic Intermediate for the Preparation of $CpOsL_3$ Compounds

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A photochemical synthesis of $[CpOs(CH_3CN)_3]^+$ is reported (Cp = η^5-cyclopentadienyl). Photolysis of $[CpOs(Bz)]^+$ (Bz = η^6-benzene) in acetonitrile solution gives $[CpOs(CH_3CN)_3]^+$, but only 30% conversion is achieved before significant photochemically induced decomposition of $[CpOs(CH_3CN)_3]^+$ occurs. Photolysis of acetonitrile solutions of $[CpOs(Bz)]^+$ that contain biphenyl eliminates this side reaction and allows the high-yield preparation of $[CpOs(CH_3CN)_3]^+$. Quantum yields for the photodearylation reaction are identical in the presence or absence of biphenyl, suggesting that biphenyl acts as a passive filter, slowing the photochemical decomposition of $[CpOs(CH_3CN)_3]^+$. $[CpOs(CH_3CN)_3]^+$ reacts with arenes, CO, and polypyrazolylborate ligands, providing a high-yield route to $CpOsL_3$ compounds under mild conditions. Compounds that were synthesized and fully characterized include $[CpOs(\eta^6\text{-anthracene})]PF_6$, $[CpOs(\eta^6\text{-rubrene})]PF_6$, $CpOs(BPz_4)$ (BPz_4^- = tetrakis(1-pyrazolyl)borate), $CpOs(HBPz_3)$ ($HBPz_3^-$ = hydrotris(1-pyrazolyl)borate), $[CpOs(CH_3CN)_2CO]PF_6$, and $CpOs(CO)_2Br$. ^1H NMR evidence for an additional species ($[(CpOs)(CpOs(CH_3CN))(\mu\text{-}\eta^6,\eta^4\text{-anth})]^{2+}$) that contains an η^6 and an η^4 $CpOs^+$ group is presented. Intriguing differences between the reactivity of $[CpOs(CH_3CN)_3]^+$ and $[CpRu(CH_3CN)_3]^+$ with rubrene are observed, with the osmium complex showing a remarkable kinetic preference for the naphthacene backbone relative to the pendant phenyl rings.

Introduction

Complexes containing the $CpFe^+$ and $CpRu^+$ fragments are ubiquitous in organometallic chemistry. In comparison, the chemistry of the $CpOs^+$ group is limited to a small number of compounds, principally carbonyl and phosphine derivatives.[1] A versatile preparative route for $CpOs^{II}L_3$ complexes would have considerable utility. Given the wealth of information available for the $CpFeL_3$ and $CpRuL_3$ compounds, the preparation of analogous $CpOsL_3$ compounds would make it possible to compare the physical properties and chemical reactivity of $CpML_3$ complexes of the iron triad. Additionally, $CpOsL_3$ compounds are expected to exhibit increased kinetic stability relative to the analogous iron and ruthenium compounds.[2]

The preparation of $CpOsL_3$ compounds that do not contain CO or phosphines has suffered from the lack of a general means of introducing the $CpOs^+$ group. A notable exception[1a] is the use of $(C_5Me_5)_2Os_2Br_4$ as a precursor to high-valent $(C_5Me_5)OsL_x$ complexes. In contrast, a wide variety of $CpRuL_3$ compounds have been prepared by reacting $[CpRu(CH_3CN)_3]^+$ (readily prepared by the photolysis of $[CpRu(Bz)]^+$ in acetonitrile solution) with the desired ligand.[3] It is likely that the analogous osmium complex would be an equally useful synthon for $CpOsL_3$ complexes. Unfortunately, previously unpublished work[4] from our group demonstrates that this direct approach does not provide a feasible synthetic route to $[CpOs(CH_3CN)_3]^+$. The direct photolysis of $[CpOs(Bz)]^+$ produces $[CpOs(CH_3CN)_3]^+$, but only limited conversion accompanied by extensive decomposition is achieved.

In this work, we demonstrate that $[CpOs(CH_3CN)_3]^+$ can be conveniently prepared by photolyzing $[CpOs(Bz)]^+$ in acetonitrile solutions that contain biphenyl.[5] An investigation of the mechanism of biphenyl assistance is presented. We also show that $[CpOs(CH_3CN)_3]^+$ reacts with arene, CO, and polypyrazolylborate ligands under mild conditions to give a number of previously unavailable complexes, demonstrating the utility of $[CpOs(CH_3CN)_3]^+$ as a synthon for $CpOsL_3$ complexes. The reactivity of $[CpOs(CH_3CN)_3]^+$ with arene ligands in particular shows intriguing differences with the analogous ruthenium compounds.

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Experimental Section

General Considerations. All synthetic procedures were carried out under a N_2 atmosphere unless otherwise noted. Solvents used were of spectroscopic grade and were used without further purification except where noted. The preparation of $[CpOs(Bz)]PF_6$ was reported previously.[5] ^1H NMR spectra were recorded on IBM AC-200 and IBM AC-300 spectrometers. Chemical shifts are relative to $(CH_3)_4Si$. Electronic spectra were recorded with a Cary 17D spectrometer. Quantum yield data were acquired with a Tracor Northern TN-6500 diode array apparatus. Elemental analyses were performed by MHW Laboratories. $KH(pz)_3$ and $KB(pz)_4$ were purchased from Strem Chemicals. Rubrene was purchased from Eastman-Kodak. OsO_4 (Mallinckrodt) was donated by the University of Minnesota Chemical Recycling Program.

Compound Synthesis. $[CpOs(CH_3CN)_3]PF_6$. $[CpOs(Bz)]PF_6$ (0.5 g) and biphenyl (1.5 g) were added to an immersion photolysis apparatus equipped with a stir bar. The apparatus was purged with N_2, and 300 mL of freshly distilled acetonitrile was added via syringe. The solution was purged with N_2 and then photolyzed for 14 h with a 450 W mercury vapor lamp under a slow N_2 purge. It is essential that the reactions be kept at or below 15 °C during the photolysis. The resultant light yellow solution was reduced to a volume of ca. 10 mL via rotary evaporation. Addition of diethyl ether and cooling for several hours at 0 °C precipitated the product as light yellow needles, which were filtered and washed with diethyl ether (0.42 g yield). A second crop was obtained by evaporating the solution to dryness and washing the resulting solid with hexane to remove the biphenyl, leaving behind an additional 70 mg of $[CpOs(CH_3CN)_3]PF_6$ (overall yield 89%). A sample of $[CpOs(CH_3CN)_3]PF_6$ gave an acceptable elemental analysis after eluting with acetonitrile down a short alumina (neutral, Brockman Activity I) column. 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, 8.89. ^1H NMR (200 MHz, d_6-acetone): 4.66 (s, C_5H_5, 5H), 2.697 (s, CH_3CN, 9H).

$[CpOs(P(OCH_3))_3]BF_4$. A solution was prepared by dissolving 24 mg of $[CpOs(Bz)]BF_4$ and 1 mL of $P(OCH_3)_3$ in 10 mL of dichloromethane. This solution was placed in a quartz test tube and irradiated with an Oriel 100 mercury vapor lamp for 4.5 h. After irradiation, the solvent was removed by rotary evaporation. The oil remaining was washed with ether to remove unreacted trimethyl phosphite. This residue was dissolved in acetone and eluted through a short alumina column. $[CpOs(P(OCH_3)_3)_3]BF_4$ (22.6 mg, 55% yield) was recovered as a white crystalline material upon evaporation of the solvent. Mp: 259−261 °C with decomposition. Anal. Calcd for $C_{14}H_3BF_4O_3OsP_3$: C, 23.54; H, 4.52. Found: C, 23.52; H, 4.60. ^1H NMR (d_6-acetone): 5.48 (q, Cp, 5H, $J_{H-P} = 0.8$ Hz), 3.69 (m, CH_3, 27H).

$[CpOs(P(OCH_2CH_3)_3)_3]BF_4$. A solution was prepared by dissolving 31 mg of $[CpOs(Bz)]BF_4$ and 1 mL of $P(OCH_2CH_3)_3$ in 10 mL of dichloromethane. This solution was placed in a quartz test tube and irradiated with an Oriel 100 W mercury vapor lamp for 4 h. After photolysis, the solvent was evaporated and the residue was washed with ether to remove unreacted triethyl phosphite. The product was dissolved in acetone and eluted down a short alumina column. Removal of the solvent by rotary evaporation followed by crystallization from acetone/hexane afforded 31 mg of white crystalline $[CpOs(P(OCH_2CH_3)_3)_3]BF_4$ (50% yield). Mp: 233−235 °C with decomposition. Anal. Calcd for $C_{23}H_{50}BF_4O_9OsP_3$: C, 32.87; H, 6.00. Found: C, 32.63; H, 5.98. ^1H NMR (d_6-acetone): 5.39 (q, Cp, 5H, $J_{H-P} = 0.8$ Hz), 4.09 (m, CH_2, 18H), 1.31 (t, CH_3, 27H, $J_{H-P} = 7.0$ Hz).

$[CpOs(\eta^6\text{-anthracene})]PF_6$. Anthracene (50 mg, 0.28 mmol) was dissolved in 20 mL of acetone, and the solution was purged with nitrogen for 15 min. $[CpOs(CH_3CN)_3]PF_6$ (50 mg, 0.10 mmol) was added, and the solution was stirred for 4 h. The resulting brownish yellow solution was passed down a short alumina column, leaving some dark brown material at the top of the column and a light yellow solution. The volume of the solution was reduced to approximately 5 mL by rotary evaporation, and diethyl ether was added, precipitating the product, which was filtered and washed with diethyl ether, leaving a light yellow powder (35 mg, 61% yield). Anal. Calcd for $C_{19}H_{15}OsPF_6$: C, 39.44; H, 2.62. Found: C, 39.16; H, 2.56. ^1H NMR (200 MHz, d_6-acetone): 5.43 (s, Cp, 5H), 6.62 (d of d, $H^{2,3}$, 2H, $J_{vic} = 4.2$ Hz, $J_{allylic} = 2.1$ Hz), 7.41 (d of d, $H^{6,7}$, 2H, $J_{vic} = 6.9$ Hz, $J_{allylic} = 3.0$ Hz), 7.66 (d of d, $H^{1,4}$, 2H, $J_{vic} = 4.2$ Hz, $J_{allylic} = 2.1$ Hz), 7.84 (d of d, $H^{5,8}$, 2H, $J_{vic} = 6.9$ Hz, $J_{allylic} = 3.0$ Hz), 8.37 (s, $H^{9,10}$, 2H).

$[CpOs(\eta^6\text{-rubrene})]PF_6$. Rubrene (50 mg, 0.096 mmol) was dissolved in 20 mL of acetone, and the solution was purged with nitrogen for 15 min. $[CpOs(CH_3CN)_3]PF_6$ (50 mg, 0.096 mmol) was added, giving an instant change in color from the bright orange-red of the free rubrene to a brownish color. The solution was stirred for 4 h, during which time the color of the solution changed to green. The acetone was removed under reduced pressure, leaving a dark residue, which was dissolved in dichloromethane and passed down a short column of diatomaceous earth. Addition of hexane precipitated the product as a blue green powder, which was filtered and washed with diethyl ether (68 mg, 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): 5.60 (s, C_5H_5, 5H), 6.57 (m, 2H, bound naphthacene ring, $H^{2,3}$), 6.8−7.4 (m, unbound rings and $H^{1,4}$ on bound naphthacene ring).

$CpOs(BPz_4)$. $KB(Pz)_4$ (30 mg, 0.11 mmol) was dissolved in 20 mL of acetonitrile, and the solution was purged with nitrogen for 15 min. $[CpOs(CH_3CN)_3]PF_6$ (50 mg, 0.10 mmol) was added, and the solution was refluxed for 3 h. The acetonitrile was removed via rotary evaporation, and the resulting brownish yellow solid was washed with diethyl ether until the ether extracts were colorless. The washings were combined, and the diethyl ether was removed, leaving a bright yellow powder. The product was recrystallized from CH_2Cl_2/hexane, giving yellow microcrystals (36 mg, 71% yield). Anal. Calcd for $C_{17}H_{17}BN_8Os$: C, 38.20; H, 3.21; N, 20.97. Found: C, 38.07; H, 3.39; N, 20.76. ^1H NMR (200 MHz, d_6-acetone): 4.58 (s, C_5H_5), 6.12 (s, bound H^4, 3H), 6.66 (s, unbound H^4, 1H), 7.765 (d, bound H^3, 3H, $J = 3.0$ Hz), 7.90 (s, unbound H^5, 1H), 8.12 (d, unbound H^3, 1H, $J = 1.8$ Hz), 8.17 (apparent s, bound H^5, 3H).

$CpOs(HBPz_3)$. $[CpOs(CH_3CN)_3]PF_6$ (88 mg, 0.17 mmol) was reacted with $K[HB(Pz)_3]$ (48.0 mg, 0.19 mmol) in the same manner as for $CpOs(BPz_4)$. The product was collected as a light yellow powder (59 mg, 75% yield). Anal. Calcd for $C_{14}H_{15}BN_6Os$: C, 35.90; H, 3.23; N, 17.95. Found: C, 36.06; H, 3.36; N, 17.82. ^1H NMR (200 MHz, d_6-acetone): 4.51 (s, C_5H_5), 6.09 (t, H^4, 3H, $J = 3$ Hz), 7.74 (d, H^3, 2H, $J = 3$ Hz), 8.03 (apparent s, H^5, 3H).

$[CpOs(CH_3CN)_2CO]PF_6$. $[CpOs(CH_3CN)_3]PF_6$ (150 mg, 0.287 mmol) was dissolved in 25 mL of freshly distilled acetonitrile, and the solution was purged with nitrogen for 20 min. The nitrogen was replaced with carbon monoxide, and the solution was refluxed for 12 h under a slow CO purge. The solution was then passed through a short alumina column, giving a light yellow solution. The volume of the solution was reduced to approximately 5 mL under reduced pressure, and diethyl ether was added until the solution turned cloudy. Cooling at 0 °C precipitated the product, which was filtered and washed with diethyl ether, giving a brownish yellow powder (110 mg, 75% yield). IR (CH_2Cl_2): $\nu_{CO} = 1979\ cm^{-1}$. ^1H NMR (200 MHz, d_6-acetone): 5.59 (C_5H_5, 5H), 2.83 (CH_3CN, 6H).

$CpOs(CO)_2Br$. $[CpOs(CH_3CN)_2CO]PF_6$ (40 mg, 0.074 mmol) and LiBr (6.8 mg, 0.077 mmol) were added to a quartz tube equipped with a stir bar and sealed with a serum stopper. Acetone (10 mL, freshly distilled from B_2O_3) was added via syringe, and the solution was purged with CO. The solution was photolyzed for 2 h and then passed down a short alumina column to remove the $LiPF_6$. The acetone was removed, and the residue was recrystallized from CH_2Cl_2/hexane to give a light yellow powder (27 mg, 88% yield). IR and ^1H NMR were identical with previously reported results.[1f]

NMR Experiments. Monitoring the photolysis of $[CpOs(Bz)]PF_6$ by ^1H NMR was accomplished by adding a 5 mg sample of $[CpOs(Bz)]PF_6$ to a quartz NMR tube equipped with a rubber septum. The

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solution was bubble degassed and photolyzed with the unfiltered output of a 75 W, high-pressure, Hg/Xe arc lamp. A typical procedure for monitoring the reaction of $[CpOs(CH_3CN)_3]^+$ with various ligands by ^{1}H NMR is as follows. $[CpOs(CH_3CN)_3]PF_6$ (5 mg, 0.0096 mmol) and $[CpOs(rubrene)]PF_6$ (5 mg, 0.0054 mmol) were added to an NMR tube which was connected to a vacuum line by an Ace NMR tube tip-off manifold. d_6-Acetone (dried over B_2O_3 and freeze−pump−thaw degassed) was distilled into the NMR tube, which was sealed under vacuum.

Photochemical Experiments. Synthetic scale photolyses were accomplished with a 450 W medium-pressure Hg lamp in an immersion well. Temperatures at or below 20 °C were maintained during photolyses by circulating tap water through the jacket of the well and a copper coil immersed in 50 gal of ice water.

Quantum yield measurements were made with monochromatic light (313 nm) obtained by filtering the output of a 1000 W Hg/Xe lamp with the appropriate interference filter (Oriel). To filter out infrared radiation, the beam was initially passed through a Corning 7-40 filter immersed in a circulating water bath. The commercially available compound Aberchrome 540 was used as the actinometer.[6] A solution of the actinometer in toluene was photolyzed at the appropriate wavelength, and the appearance of the product was monitored at 494 nm. The resulting measurements showed that the lamp was very stable and provided highly reproducible light intensities. Typically, the flux at 313 nm was 1.6×10^{-7} einsteins/min.

A typical quantum yield determination is as follows. $[CpOs(Bz)]PF_6$ (22 mg) was introduced into a 1 cm quartz cell equipped with a stir bar. The cell was connected to a vacuum line, and acetonitrile (approximately 2 mL, dried over P_2O_5 and freeze−pump−thaw degassed) was distilled into the cell, giving a typical $[CpOs(Bz)]PF_6$ concentration of 0.019 M. The sample was stirred and thermostated at a temperature of 20 °C (±2 °C). Quantum yields were determined for the appearance of $[CpOs(CH_3CN)_3]^+$, the concentration of which was measured by integrating the visible spectrum from 380−430 nm. Due to the large inner-filter effect caused by the $[CpOs(CH_3CN)_3]^+$, overall conversion was limited to 5%. A minimum of 6 data points were acquired for each sample.

Electrochemical Measurements. All electrochemical experiments were performed with a BAS 100 electrochemical analyzer. Electrochemical measurements were performed at ambient temperatures with a normal three-electrode configuration consisting of a highly polished glassy-carbon-disk working electrode, a Ag/AgCl reference electrode containing 1.0 M KCl, and a platinum wire auxiliary electrode. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of the supporting electrolyte. Acetonitrile was distilled from P_2O_5 under N_2, and the supporting electrolyte tetrabutylammonium hexafluorophosphate ($TBA^+PF_6^-$) was used without further purification. Electrolyte solutions were introduced into the electrochemical cell through a short column of activated (heated at 200 °C) alumina. The working compartment of the cell was bubbled with solvent-saturated argon to deoxygenate the solution. Potentials are reported versus aqueous Ag/AgCl and are not corrected for the junction potential. A standard electrochemical current convention is used (anodic currents are negative). To allow future corrections[7] and the correlation of these data with other workers, we have measured the $E^{\circ\prime}$ for a ferrocenium/ferrocene couple under conditions identical to those used for the compounds under study. In 0.1 M $TBA^+PF_6^-/CH_3CN$, $E^{\circ\prime}$ is equal to +0.50 V. No *iR* compensation was used.

Spectroelectrochemical Experiments. UV−visible spectral changes accompanying thin-layer bulk electrolyses were measured with a flow-through spectroelectrochemical thin-layer cell, as described previously.[8] Bulk electrolyses were controlled by a BAS 100 electrochemical analyzer.

Results and Discussion

Synthesis and Characterization of $[CpOs(CH_3CN)_3]PF_6$. When the photolysis (unfiltered output from a high-pressure 75 W Hg/Xe arc lamp) of a sample of $[CpOs(Bz)]PF_6$ in CD_3CN is monitored by ^{1}H NMR, the disappearance of the $[CpOs(Bz)]^+$ peaks at 6.09 and 5.62 ppm (Bz and Cp resonances, respectively) and the appearance of a new resonance at 4.62 ppm, the cyclopentadienyl resonance for $[CpOs(CD_3CN)_3]^+$ (vide supra), are observed. Unfortunately, after approximately 35% conversion to product the solution begins to darken and the conversion rate slows. Extended photolysis (40 h) never leads to greater than 80% conversion. No improvement in the percent conversion was realized when the acetonitrile was rigorously dried and degassed. The chemical yield was even worse on a preparative scale, where no more than 30% conversion was achieved. The reaction slows because the dark material formed as a reaction byproduct has an intense absorption band in the UV and acts as an efficient inner filter. Less than complete photochemical conversion of $[CpOs(Bz)]^+$ to $[CpOs(CH_3CN)_3]^+$ is not synthetically useful because separation of these complexes is not feasible.

It is likely (and is demonstrated conclusively, vide infra) that the dark impurity is formed by the photochemical decomposition of $[CpOs(CH_3CN)_3]^+$. This assumption is supported by the lack of any observed darkening of a photolyzed solution of $[CpOs(Bz)]^+$ until after a significant amount of $[CpOs(CH_3CN)_3]^+$ has been formed (approximately 30% conversion), suggesting that decomposition begins when the concentration of $[CpOs(CH_3CN)_3]^+$ is large enough to compete with the starting material as an effective absorber. The proposed sequence is shown in reactions 1 and 2. To circumvent the inner-filter effect, it is necessary either to increase the quantum efficiency of reaction 1 or to reduce the efficiency of reaction 2 or both.

$$[CpOsBz]^+ \xrightarrow[CH_3CN]{h\nu} [CpOs(CH_3CN)_3]^+ + Bz \qquad (1)$$

$$[CpOs(CH_3CN)_3]^+ \xrightarrow{h\nu} \text{decomposition} \qquad (2)$$

Over the last decade, considerable effort by our group[4] has gone into investigating routes to circumvent this inner-filter effect. For example, alternatives to acetonitrile have been investigated. Photolysis of $[CpOs(Bz)]^+$ in the presence of phosphite ligands leads to efficient displacement of benzene to form $[CpOs(P(OR)_3)_3]^+$ complexes[4a] (see Experimental Section). These complexes were isolated and fully characterized for R = CH_3 and CH_2CH_3. The preparation of these complexes indicates that efficient photochemical arene displacement is possible given a sufficiently strong nucleophile, but the high stability of the phosphite complexes precludes the use of these compounds as $CpOsL_3$ synthons. Other ligands which were investigated and gave unsatisfactory results include benzonitrile[4c] and trimethylamine.[4b]

A second possible alternative is to replace benzene with a more labile arene ligand. Fused arenes, such as naphthalene (naph), have been shown to form less stable metal complexes than benzenenoid arenes.[3d] With this in mind, we tried to prepare $[(\eta^6\text{-naph})OsCl_2]_x$ as a precursor to $[CpOs(\eta^6\text{-naph})]^+$ with the expectation that naphthalene would be more easily replaced by acetonitrile than benzene, essentially raising the efficiency of reaction 1. Replacing the 1,3-cyclohexadiene used in the preparation of $[BzOsCl_2]_x$ with dihydronaphthalene gave no identifiable products rather than the expected $[(\eta^6\text{-naph})OsCl_2]_x$.[4c,d]

A third possibility was to exploit the significant counterion assistance observed in the photodearylation reactions of $[CpFe(arene)]^+$ complexes.[3b,3e,9] It was observed that nucleophilic ions substantially enhanced the quantum yield for arene displacement in dichloromethane solution.[9] Extending this chemistry to osmium did show that bromide ion significantly increases the quantum yield for reaction 1, but side reactions

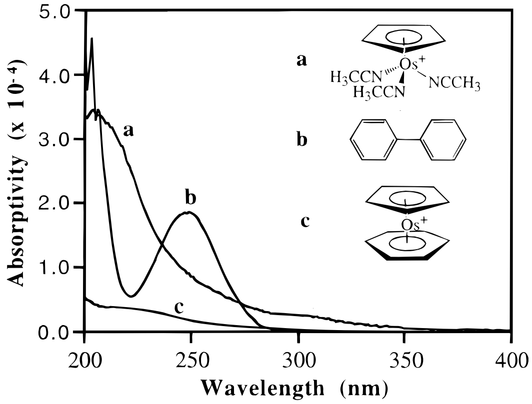

Figure 1. Electronic spectra of (a) $[CpOs(CH_3CN)_3]PF_6$, (b) biphenyl, and (c) $[CpOs(Bz)]PF_6$ in acetonitrile solution.

of an unknown nature along with difficulties in removing the bromide made it impossible to exploit this effect synthetically.[4,5]

A fourth possible method for bypassing the inner-filter effect we investigated involves the use of a triplet sensitizer to generate the reactive excited state of $[CpOs(Bz)]^+$. This has been shown to be possible for $[CpFe(arene)]^+$ complexes.[3b] To investigate this possibility, d_3-acetonitrile solutions of $[CpOs(Bz)]^+$ and biphenyl or anthracene were irradiated by using a Hg/Xe arc lamp. The progress of the reaction was monitored by ^1H NMR. For both solutions it did not appear that the rate of conversion had increased appreciably versus the rate observed in the absence of the sensitizers (this was quantitatively demonstrated for biphenyl, vide infra), but extended photolysis gave almost 100% conversion to $[CpOs(CH_3CN)_3]^+$. Biphenyl was found to be particularly effective due to its high solubility in acetonitrile. It was possible to scale this reaction up to 0.50 g of $[CpOs(Bz)]PF_6$. Photolysis (14 h) of an acetonitrile solution which was 0.0035 M in $[CpOs(Bz)]PF_6$ and 0.02 M in biphenyl with a 450 W Hg/vapor lamp in an immersion photolysis apparatus gave almost quantitative (89% isolated yield) conversion to $[CpOs(CH_3CN)_3]PF_6$.

The high-intensity light source combined with the immersion photolysis apparatus was necessary to drive the reaction to completion. This is in contrast to the relatively simple preparation of $[CpRu(CH_3CN)_3]^+$ by external photolysis of an acetonitrile solution of $[CpRu(Bz)]PF_6$.[3a] Capturing the entire lamp output in the osmium case is necessary for several reasons. First, the quantum yield for arene displacement from $[CpOs(Bz)]^+$ is 40 times less than for $[CpRu(Bz)]^+$ (vide infra). Second, the biphenyl has an intense absorbance band in the UV, allowing it to act as an inner filter for the $[CpOs(Bz)]^+$. Finally, $[CpOs(CH_3CN)_3]^+$ is itself an effective inner filter, having an absorptivity approximately an order of magnitude greater than that of $[CpOs(Bz)]^+$ at wavelengths less than 350 nm. Figure 1 shows the UV−vis spectra of the three compounds of interest plotted in units of absorptivity. In the preparative reaction, the concentration of biphenyl is 5 times that of $[CpOs(Bz)]^+$.

The large amount of heat generated by the 450 W lamp in the immersion well apparatus caused an additional synthetic problem. During January in Minnesota, when this synthesis was first accomplished, tap water at about 5 °C was available; this cold water allowed the photolyzed solution of $[CpOs(Bz)]^+$ to be maintained between 10−15 °C, producing excellent results. During the summer, with the tap water temperature at ca. 20 °C, the reaction behaved as it did with no biphenyl present, i.e., low conversion accompanied by extensive decomposition. Photolysis of acetonitrile solutions of $[CpOs(Bz)]^+$ thermostated at ca. 5 °C without biphenyl also led to significant decomposition. The temperature dependence is surprising as photochemical reactions do not typically show any great temperature dependence.[3b,10]

The $[CpOs(CH_3CN)_3]^+$ is easily separated from the biphenyl by reducing the volume of the acetonitrile photolysis mixture and adding a large amount of diethyl ether, precipitating the product as light yellow needles or powder. A sample gave an acceptable elemental analysis after chromatography on alumina. ^1H NMR shows the Cp proton resonances at 4.66 ppm and the acetonitrile resonance at 2.70 ppm in d_6-acetone (in CD_3CN only free acetonitrile is observed due to rapid exchange of bound acetonitriles with solvent). In the solid state and in acetonitrile solution $[CpOs(CH_3CN)_3]PF_6$ is only moderately air sensitive and can be stored at −15 °C for weeks with only minimal decomposition. The solid appears to be indefinitely stable under an inert atmosphere. It is significantly less stable in acetone and dichloromethane solutions, rapidly decomposing to an unidentified dark material. The greater instability of $[CpOs(CH_3CN)_3]^+$ versus the analogous ruthenium complex is probably due to the greater sensitivity of osmium to oxidation. The cyclic voltammogram (CV) of $[CpOs(CH_3CN)_3]PF_6$ in acetonitrile solution exhibits a reversible, one-electron process at $E° = +0.83$ V versus Ag/AgCl. In comparison, the CV of $[CpRu(CH_3CN)_3]^+$ shows a quasi-reversible oxidation at +1.04 V versus Ag/AgCl.

Effect of Biphenyl. To investigate the role of biphenyl in the displacement of benzene from $[CpOs(Bz)]^+$, quantum yields were measured for the photolysis of $[CpOs(Bz)]PF_6$ in neat acetonitrile and in the presence of biphenyl.

Quantum yield data were measured for the appearance of $[CpOs(CH_3CN)_3]^+$ for photolysis at 313 nm by monitoring the increase in the integrated absorbance between 430−380 nm. A quantum yield of 0.012(2) was determined for $[CpOs(Bz)]PF_6$ in acetonitrile. This value is 60 and 34 times smaller than the quantum yields determined for benzene displacement from the analogous iron and ruthenium complexes, respectively.[3b] The decrease in the efficiency of the reaction in the heavier members of the iron triad is probably due to a combination of greater metal−arene bond strength and more efficient nonradiative decay pathways.

The quantum yield for reaction 1 was determined in a solution which was 0.167 M in biphenyl. This gave a value of 0.013(2), identical, within experimental error, to the value determined in the absence of biphenyl. Biphenyl does not affect the quantum yield for reaction 1.

The absence of any effect by biphenyl on the quantum yield for reaction 1 was surprising because it eliminates direct interactions between either $[CpOs(Bz)]^+$ or $[CpOs(CH_3CN)_3]^+$ and biphenyl. As suggested previously, the assistance of the biphenyl can be either to increase the efficiency of the photodearylation of $[CpOs(Bz)]^+$ or to prevent the decomposition of $[CpOs(CH_3CN)_3]^+$. The former possibility is eliminated by the quantum yield data, since biphenyl has no effect on the efficiency of reaction 1. Biphenyl could prevent the decomposition of $[CpOs(CH_3CN)_3]^+$ by several possible mechanisms: ground and/or excited state complexation, energy transfer, or passive filtering. Ground state complexation is ruled out because no change in the ^1H NMR spectrum of $[CpOs(CH_3CN)_3]^+$ is observed in the presence of biphenyl in acetonitrile solution. Deactivation of the excited state of $[CpOs(CH_3CN)_3]^+$ via direct energy transfer, is ruled out by the lack of variation in the absorption spectrum of $[CpOs(CH_3CN)_3]^+$ in the presence of biphenyl. The passive filter hypothesis was confirmed by photolyzing two samples of $[CpOs(Bz)]^+$, one with the unfiltered output of a 75 W Hg/Xe lamp (254 and 313 nm) and the other with light from the same source that was passed through a solution of biphenyl, which had an absorbance of approximately 4 at 250 nm. The unfiltered solution swiftly turned dark brown in color, and ^{1}H NMR indicated that after 30% of the $[CpOs(Bz)]^+$ had been converted to $[CpOs(CH_3CN)_3]^+$, further photolysis did not increase the concentration of $[CpOs(CH_3CN)_3]^+$, but the $[CpOs(Bz)]^+$ was slowly depleted. In comparison, the sample photolyzed with the biphenyl filter showed quantitative conversion of $[CpOs(Bz)]^+$ to $[CpOs(CH_3CN)_3]^+$ with no observed darkening of the solution. Furthermore, photolysis of $[CpOs(CH_3CN)_3]^+$ with the biphenyl filter resulted in virtually no decomposition of the sample while unfiltered photolysis gave rapid decomposition. These experiments indicate that the dark color is the product of a photochemical reaction of $[CpOs(CH_3CN)_3]^+$ and that light of wavelengths longer than approximately 280 nm will not cause decomposition of $[CpOs(CH_3CN)_3]^+$. The identity of the decomposition products is as yet undetermined. The experiments also suggest that a solution of biphenyl in acetonitrile would make a perfectly acceptable external filter solution, but in practice, commercially available immersion apparatus do not allow for a filter solution between the lamp and photolysis solution.

Figure 1 shows the absorption spectra of $[CpOs(Bz)]^+$, $[CpOs(CH_3CN)_3]^+$, and biphenyl plotted in units of absorptivity. An interesting feature to note is that the absorption maximum of biphenyl is centered at 250 nm, where it absorbs the bulk of the 254 nm light from quartz-filtered medium/high-pressure Hg vapor lamps. Concentrations of biphenyl approximately 5 times greater then the osmium complex are used in the synthesis, so even at 100% conversion the biphenyl absorbs at least 90% of the 254 nm light. We believe that biphenyl acts as a filter for the high-energy 254 nm light, which causes the decomposition of $[CpOs(CH_3CN)_3]^+$. Population of lower energy excited states of $[CpOs(CH_3CN)_3]^+$ from longer wavelength photolysis does not lead to decomposition.

The wavelength dependent photochemical reactivity we observe for $[CpOs(CH_3CN)_3]^+$ has precedence in studies of the photochemistry of $[Ru(NH_3)_6]^{2+}$. Ford et al.[11] have shown that high-energy photolysis leads to oxidation of the metal while low-energy excitation gives ligand substitution. The electronic spectrum of $[CpOs(CH_3CN)_3]^+$ is analogous to that of $[Ru(NH_3)_6]^{2+}$, exhibiting weak, low-energy shoulders at 375 and 310 nm on an intense UV absorption. Ligand substitution from population of lower energy (LF) excited states would result in no net reaction for $[CpOs(CH_3CN)_3]^+$ in acetonitrile. A charge transfer (CT) process occurring from the higher energy excited state results in irreversible oxidation of the osmium with the concomitant reduction of solvent or other species in solution. Either the Os(III) products or the organic products resulting from reduction of solvent could account for the intense color of the decomposition products. Thermal equilibration between the CT and LF manifolds may also account for the temperature dependence of the photochemistry. At higher temperatures sufficient energy is available to populate the CT state from the LF state, leading to photodecomposition. Further work will be needed to establish this. It is also noteworthy that this behavior is not observed in the preparation of $[CpRu(CH_3CN)_3]^+$ from $[CpRu(Bz)]^+$, presumably due to the considerably greater oxidation potential of ruthenium(II) compared to osmium(II).

Synthesis of $CpOsL_3$ and $CpOs(arene)^+$ Complexes. The production of gram quantities of $[CpOs(CH_3CN)_3]^+$ allowed us to investigate it as a convenient synthon for $CpOsL_3$ and $[CpOs(arene)]^+$ complexes. We found that $[CpOs(CH_3CN)_3]^+$ reacts readily with a wide variety of ligands, including arenes, polypyrazolylborates, and CO. These reactions are summarized in Figure 2.

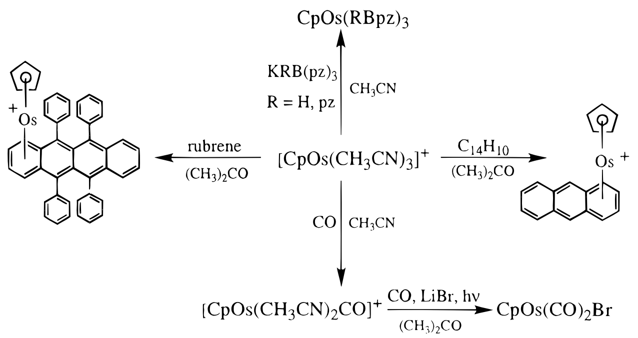

Figure 2. Preparation of $CpOsL_3$ complexes from $[CpOs(CH_3CN)_3]^+$.

Previous studies[3,4] of the properties and reactivity of $[CpRu(arene)]^+$ complexes suggested that reactions of $[CpOs(CH_3CN)_3]^+$ with arene ligands might also have synthetic utility. In this regard, an interesting pattern of similarities and differences in the reactivity of $[CpRu(CH_3CN)_3]^+$ and $[CpOs(CH_3CN)_3]^+$ with arene ligands is observed.

$[CpRu(CH_3CN)_3]^+$ reacts rapidly with a wide variety of arenes to form the η^6-bound metal−arene complexes. In reactions with fused polycyclic aromatics, $[CpOs(CH_3CN)_3]^+$ behaves much like $[CpRu(CH_3CN)_3]^+$. For instance, $[CpOs(CH_3CN)_3]PF_6$ reacts rapidly with anthracene to give $[CpOs(\eta^6\text{-anth})]PF_6$. This compound was isolated as a light yellow powder and fully characterized. As in the ruthenium analogue,[3d] the metal binds to an end ring, leaving the middle ring and other end ring uncomplexed. Similarly, $[CpOs(\eta^6\text{-anth})]^+$ reacts rapidly with acetonitrile to give free anthracene and $[CpOs(CH_3CN)_3]^+$. Significant differences in the reactivity of $[CpOs(CH_3CN)_3]^+$ and $[CpRu(CH_3CN)_3]^+$ are observed in their behavior toward benzenoid aromatic rings. Whereas $[CpRu(CH_3CN)_3]^+$ reacts rapidly with benzene and alkylated benzenes to give the $[CpRu(\eta^6\text{-arene})]^+$ complexes,[3b] we have been unable to prepare the analogous complexes with osmium. Refluxing $[CpOs(CH_3CN)_3]^+$ with mesitylene in acetone did not yield an isolable product. The reaction of $[CpOs(CH_3CN)_3]^+$ with benzene was monitored over several months by preparing a sealed NMR tube of $[CpOs(CH_3CN)_3]^+$ with 5 equivalents of benzene in d_6-acetone. No $[CpOs(Bz)]^+$ was formed. Slow decomposition of the $[CpOs(CH_3CN)_3]^+$ was observed.

To investigate the competition between the complexation of $[CpOs(CH_3CN)_3]^+$ by conjugated and unconjugated arenes, the reactivity of $[CpOs(CH_3CN)_3]^+$ with the laser dye rubrene was investigated. Rubrene (5,6,11,12-tetraphenylnaphthacene) contains three chemically distinct types of arene binding sites, two in the naphthacene backbone and the pendant phenyl rings. Previous work by Koefod[3i] demonstrated that two isomers (one kinetically determined and one thermodynamically) could be synthesized by reaction of rubrene with 1 equiv of $[CpRu(CH_3CN)_3]^+$. The kinetic product, produced by combining the reactants in dichloromethane, contains the $CpRu^+$ group bound to an end ring of the naphthacene backbone. The thermodynamically preferred isomer, in which the metal is bound to a phenyl ring, was formed by refluxing the kinetic product in acetone. The reaction of $[CpOs(CH_3CN)_3]^+$ and rubrene in refluxing acetone solution produced *only* the naphthacene-bound isomer. The compound was characterized by ^{1}H NMR and electronic spectroscopy. The ^{1}H NMR spectrum is complex. In addition to the Cp resonance, an easily assignable feature is a doublet of doublets at 6.27 ppm, which integrates as 2 protons compared to the Cp resonance. This signal is assigned to

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(11) Ford, P. C. *Adv. Chem. Ser.* **1977**, *168*, 73.

hydrogens 2 and 3 on the rubrene ring complexed by the CpOs group. These resonances exhibit the characteristic upfield shift of the protons on the ring bound to the metal. As in the analogous ruthenium complex, the remaining naphthacene and phenyl resonances are consistent with C_s symmetry and appear as complicated multiplets, with the exception that the signal for $H^{1,4}$ is also observable in the ruthenium complex. The UV−vis spectrum of $[CpOs(\eta^6\text{-rubrene})]^+$ exhibits an intense absorption band (λ_{max} = 660 nm, ϵ_{max} = 6,600 M^{-1} cm^{-1}) giving the complex a blue-green color. The UV−vis spectrum supports the structural assignment of the complex to the naphthacene, bound isomer. The analogous ruthenium complex has an almost identical absorption band (λ_{max} = 660 nm, ϵ_{max} = 7000 M^{-1} cm^{-1}) that was assigned to a metal-to-arene charge transfer transition.[3i,j] Although the naphthacene-bound isomer of $[CpOs(\eta^6\text{-rubrene})]^+$ is spectroscopically similar to the Ru analogue, refluxing the osmium complex did not initiate isomerization to the phenyl-bound isomer. Extended reaction times resulted in decomposition of the starting material to unidentifiable products. Given that the naphthacene-bound isomer is thermodynamically less stable than the phenyl-bound isomer, our inability to prepare the phenyl-bound isomer must be a consequence of either a relatively greater kinetic stability of the naphthacene-bound isomer or a greater activation barrier for formation of the phenyl-bound isomer than is observed for ruthenium.[3i] In an attempt to destabilize the naphthacene-bound isomer, a sample of $[CpOs(\eta^6\text{-rubrene})]^+$ was sealed in an NMR tube in d_6-acetone with approximately 5 equiv of acetonitrile. ^1H NMR indicated that $[CpOs(rubrene)]^+$ reacted with the acetonitrile after several hours, producing $[CpOs(CH_3CN)_3]^+$ and free rubrene. Unfortunately, no isomerization reaction was observed when the sample was heated.

Reacting a second equivalent of $[CpOs(CH_3CN)_3]^+$ with $[CpOs(\eta^6\text{-rubrene})]^+$ is a second possible route to the phenyl-bound isomer. For ruthenium, this reaction produced dimetalated species in which both metals are complexed to pendant phenyl groups.[3j] Reaction of $[CpOs(CH_3CN)_3]^+$ with $[CpOs(\eta^6\text{-rubrene})]^+$ produced interesting results. Monitoring the reaction by ^1H NMR shows that the starting material is rapidly depleted as the color of the solution changes from blue-green to a reddish-orange. The ^1H NMR spectrum of the final product is shown in Figure 3.

The four Cp resonances observed in Figure 3 indicate that the second osmium is also complexed to the rubrene. Addition of acetonitrile to the solution immediately regenerates $[CpOs(\eta^6\text{-rubrene})]^+$, indicating that the second metal is only loosely bound to the rubrene. The phenyl-bound ruthenium complexes of rubrene are completely inert to thermal substitution by acetonitrile,[3i] and the osmium analogue should be even more stable. It is unlikely that the coordination site of the second $CpOs^+$ is a phenyl ring. The NMR spectrum shown in Figure 3 is also inconsistent with a phenyl-bound metal. The ^1H NMR spectrum of the phenyl-bound ruthenium complex has a resonance shifted downfield to approximately 9 ppm, assigned to the proton bound to the naphthacene backbone, which is proximate to the ruthenium bound to the pendant phenyl ring. A similar resonance is not exhibited by the osmium complex. Singlets at 2.8 and 2.9 ppm (not shown in Figure 3; assigned to bound acetonitrile resonances) and the multiplet at 4.96 ppm are also inconsistent with a phenyl-bound metal. An alternative possibility is that both metals are bound to the naphthacene portion of rubrene, as shown in Figure 3. It was noted by Clar[12] that fused aromatics systems such as the naphthacene portion of rubrene are best formulated as containing a single, fully aromatic π-system which is diluted through conjugation with the other three rings. It should be possible for a $[CpOs(CH_3CN)]^+$ group to coordinate in η^4 fashion to the localized π-system on a ring not occupied by the η^6-coordinated metal. Two isomers are possible, depending on whether the second metal binds endo or exo to the first. The ^1H NMR is consistent with the presence of both of these isomers in approximately a 2:1 ratio. The region of the spectrum where the Cp proton resonances appear, approximately 5.5 ppm, shows two pairs of peaks in approximately this ratio. Each pair of peaks can be assigned to the η^6-bound $CpOs^+$ and the η^4-bound $CpOs(CH_3CN)^+$ of either the exo or endo isomer (there is no way to conclusively assign the Cp resonances to either the η^4- or η^6-bound $CpOs^+$ groups). Other features in the ^1H NMR support this assignment. The two peaks at 2.8−2.9 ppm, which are also in a 2:1 ratio, are assigned to the acetonitrile ligands of the exo and endo η^4-coordinated $CpOs(CH_3CN)^+$ groups. The multiplet at 5 ppm in Figure 3 is readily interpreted as two overlapping doublets of doublets in an approximately 2:1 ratio, the same ratio observed for the Cp resonances. These are assigned to $H^{2,3}$ of the exo and endo isomers. Coordination of the second osmium apparently shifts the naphthacene resonances to a higher field relative to the monometalated complex. It is not possible to discern whether the exo or endo isomer predominates solely by NMR, but steric considerations suggest that the exo isomer would be more stable. Attempts to convert the bimetalated compound into a phenyl-bound rubrene complex by refluxing it in acetone were unsuccessful.

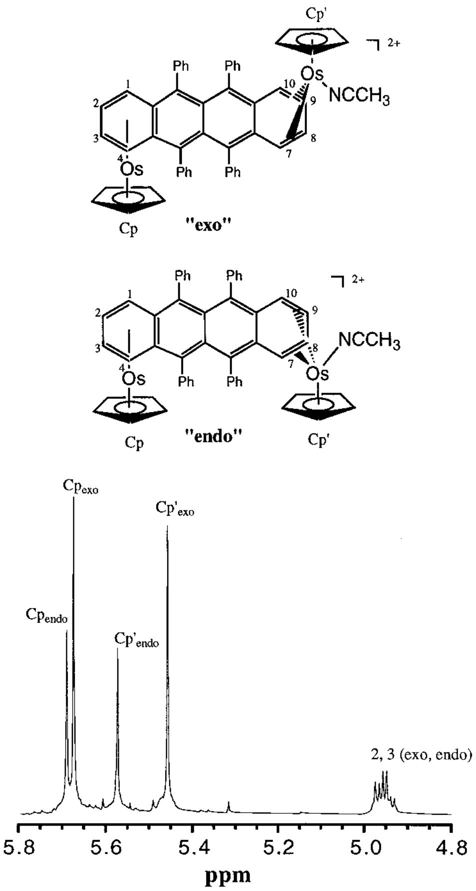

Figure 3. ^1H NMR spectra and proposed structures of *endo*- and *exo*-$[(CpOs)(CpOs(CH_3CN))(\mu\text{-}\eta^6,\eta^4\text{-rubrene})]^{2+}$ formed by reaction of $[CpOs(\eta^6\text{-rubrene})]PF_6$ with $[CpOs(CH_3CN)_3]PF_6$ in d_6-acetone after 24 h.

To determine whether the formation of dimetalated η^6,η^4 compounds with conjugated arenes could occur with compounds other than rubrene, $[CpOs(CH_3CN)_3]^+$ was added to an NMR

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[12] Clar, E. *The Aromatic Sextet*; Wiley: London, 1972.

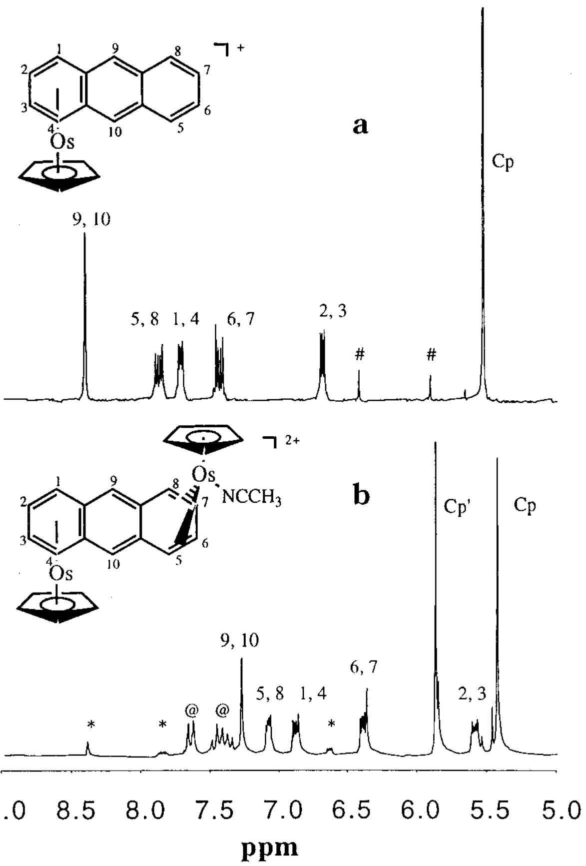

Figure 4. ^{1}H NMR spectrum and proposed structure of (a) [CpOs(η^6-anth)]PF_6 in d_6-acetone and (b) *exo*-[(CpOs)(CpOs(CH_3CN))(μ-η^6,η^4-anth)]$^{2+}$ formed by reaction of [CpOs(anth)]PF_6 with $[CpOs(CH_3CN)_3]PF_6$ in d_6-acetone after 24 h. In spectrum a, peaks marked with a pound sign (#) are due to [CpOs(Bz)]PF_6. In spectrum b, peaks marked with an asterisk (*) are due to unreacted [CpOs(η^6-anth)]PF_6; those marked with an "at" symbol (@) are from a biphenyl impurity.

tube sample of [CpOs(η^6-anth)]$^+$. The resulting ^{1}H NMR spectrum is shown in Figure 4. The spectrum is consistent with the formulation of the product as *exo*-[(CpOs)(CpOs(CH_3CN)(μ-η^6,η^4-anth)]$^{2+}$. Only two Cp resonances are observed, indicating that only one of the two possible isomers is present. Again, steric considerations predict that the single isomer is the one in which the metals are exo, as shown in Figure 4. As with the monometalated anthracene complex, the anthracene protons appear as a singlet for $H^{9,10}$ and 4 doublets of doublets for the protons on the end rings. These peaks are shifted considerably upfield of the peaks for the monometalated complex, consistent with the additional electron density added to the anthracene by the second metal. The appearance of four signals for the protons on the end rings of anthracene supports the formulation of the complex as the asymmetric η^4,η^6-bimetalated complex. This is in contrast to the recently reported symmetrical [(Cp*Ru)$_2$(μ-η^6,η^6-anth)]$^{2+}$ complex in which only two signals are observed for the protons on the end rings (protons 1−8).[13] As with the bimetalated rubrene complex, the bimetalated anthracene complex was not isolable due to the lability of the η^4-bound osmium; reflux of an acetone solution of $[CpOs(CH_3CN)_3]^+$ and [CpOs(η^6-anth)]$^+$ also did not give any identifiable products.

The inability to prepare the phenyl-bound isomer of [CpOs(rubrene)]$^+$ indicates significant differences between the reactivity of $[CpOs(CH_3CN)_3]^+$ and $[CpRu(CH_3CN)_3]^+$. Kinetic studies[3i] carried out on the reaction of $[CpRu(CH_3CN)_3]^+$ with arenes in acetone solution led to the conclusion that exchange of acetone for acetonitrile in the inner-coordination sphere of the metal forms the reactive complexes. The data indicated that displacement of acetone ligands by the arene formed a transition state in which the arene is bound in either η^4 or η^2 fashion to the metal. It is likely that the greater kinetic barrier in the osmium case arises from the diminished tendency for $[CpOs(CH_3CN)_3]^+$ to exchange acetone for acetonitrile. The ^{1}H NMR of $[CpRu(CH_3CN)_3]^+$ in d_6-acetone exhibits a small peak assigned to $[CpRu(CH_3CN)_2((CD_3)_2CO)]^+$. No analogous peak is observed for $[CpOs(CH_3CN)_3]^+$. Other factors may also contribute to differences in the energy of the proposed transition state: the loss in aromatic stabilization in the aromatic ring upon partial complexation to the metal and the metal−arene bond strength in the transition state. Further work will be necessary to establish the mechanism for Os−arene bond formation.

CO Complexes. Due to the considerable interest in $[CpOs(CO)_{(3-x)}L_x]^+$ compounds ($x = 0, 1, 2$), we investigated the reaction of $[CpOs(CH_3CN)_3]^+$ with CO. The available synthetic routes for the preparation of $CpOs(CO)_2X$ complexes are somewhat inconvenient because of starting materials which must be prepared under extreme conditions (high temperature and pressure).[1f,g] The preliminary investigations reported here indicate that $[CpOs(CH_3CN)_3]^+$ provides a synthon for the high-yield preparation of carbonyl complexes under mild conditions.

Refluxing $[CpOs(CH_3CN)_3]^+$ in acetonitrile under a CO atmosphere gives quantitative conversion to $[CpOs(CH_3CN)_2CO]^+$. The IR spectrum shows a single CO stretch at 1979 cm^{-1}. ^{1}H NMR shows a Cp proton resonance at 5.59 ppm, shifted 0.93 ppm downfield from $[CpOs(CH_3CN)_3]^+$. The bound acetonitrile resonance appears at 2.83 ppm and, unlike $[CpOs(CH_3CN)_3]^+$, $[CpOs(CH_3CN)_2CO]^+$ does not appear to undergo any exchange with the CD_3CN solvent. The reluctance of the acetonitrile ligands to undergo thermal exchange was observed in several other reactions attempted with this complex, i.e., refluxing $[CpOs(CH_3CN)_2CO]^+$ with [CpOs(η^6-rubrene)]$^+$ with the hope of forming a stable η^4-bound complex resulted in no reaction. Similarly, no reaction was observed between $[CpOs(CH_3CN)_2CO]^+$ and $KB(Pz)_4$.

Even though $[CpOs(CH_3CN)_2CO]^+$ does not react thermally with CO, the synthesis of the previously reported compound $CpOs(CO)_2Br$[1f] was achieved photochemically from the monocarbonyl. Photolysis of an acetone solution of $[CpOs(CH_3CN)_2CO]^+$ and LiBr under a CO atmosphere gives $CpOs(CO)_2Br$ in excellent yield, but it was necessary to rigorously dry the solvent to avoid the formation of $[CpOs(CO)_2H_2O]^+$. For synthetic reasons it would be more desirable to synthesize $[CpOs(CO)_2CH_3CN]^+$, but no reaction was observed when $[CpOs(CH_3CN)_2CO]^+$ was photolyzed in acetone under a CO atmosphere without bromide present. ^{1}H NMR indicates that $[CpOs(CH_3CN)_2CO]^+$ undergoes an initial, thermal reaction with bromide to form $CpOs(CH_3CN)(CO)Br$. Substitution of CO for acetonitrile might then occur with the assistance of the bromide. Bromide has been observed to exert a cis-labilizing effect in CO substitution of $M(CO)_5Br$ complexes.[14]

Pyrazolylborate Complexes. Since the synthesis of the first polypyrazolylborate ligands by Trofimenko,[15] a wide range of transition metal complexes including these ligands have been prepared.[16] McNair et al.[3c] synthesized several neutral complexes of the type $CpRu(RB(pz)_3)$ by combining [CpRu(CH_3-

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(13) Koelle, U.; Wang, M. H. *Organometallics* **1990**, *9*, 195.

(14) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole Pub.: Monterey, CA, 1985; p 115.

(15) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842.

(16) (a) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419. (b) Santos, I.; Marques, N. *New J. Chem.* **1995**, *19*, 551. (c) Shaver, A. *J. Organomet. Chem. Libr.* **1977**, *3*, 157.

$CN)_3]^+$ with the potassium salt of the polypyrazolylborate ligand. Electrochemical studies of these mixed ligand complexes revealed quasi-reversible, one-electron oxidations.

The osmium analogues of two of these complexes were easily prepared by combining $KHB(pz)_3$ or $KB(pz)_4$ with $[CpOs(CH_3CN)_3]^+$ in refluxing acetonitrile. $CpOsHB(pz)_3$ and $CpOsB(pz)_4$ were isolated as mildly air sensitive, bright yellow microcrystalline compounds. An attempt to synthesize $CpOsHB(3,5\text{-}Me_2pz)_3$ failed, apparently due to the highly air sensitive nature of this compound. The ^1H NMR spectra of the $HB(pz)_3^-$ and $B(pz)_4^-$ compounds are consistent with an η^5-coordinated Cp ligand and a tridentate polypyrazolylborate ligand. The ^1H NMR spectrum of $CpOsHB(pz)_3$ consists of a singlet at 4.51 ppm, assigned to the Cp ring, a triplet at 6.09 ppm, a doublet at 7.74 ppm, and a singlet at 8.04 ppm. The latter three peaks can be assigned to the coordinated pyrazole groups. The triplet is assigned to H^5. By comparison to the analogous ruthenium complex[3c] the doublet is assigned to H^3 and the singlet to H^5. The ^1H NMR of $CpOsBPz_4$ is similar to that of the $HBPz_3$ complex with the addition of the resonances for the uncoordinated pyrazole group.

The previous electrochemical studies[3c] of the ruthenium polypyrazolylborate complexes showed reversible behavior even in acetonitrile solution. Similar results were obtained for $CpOsHB(pz)_3$. The CV of $CpOsHB(pz)_3$ in acetonitrile/$TBA^+PF_6^-$ exhibits a one-electron anodic process with $E° = +0.065$ V. The process is highly reversible with $i_{p,c}/i_{p,a} = 0.99$ and is shifted 0.288 V negative from the analogous ruthenium complex.[3c] This shift is consistent with the expected increase in ease of oxidation upon changing from a second- to a third-row metal. Figure 5 shows the changes observed in the UV−visible region during the spectroelectrochemical oxidation of $CpOsHB(pz)_3$.

Conclusions

Photolysis of $[CpOs(Bz)]^+$ in the presence of biphenyl provides a convenient, high-yield synthesis of the useful synthetic intermediate $[CpOs(CH_3CN)_3]^+$. Biphenyl acts as a passive filter of the short-wavelength output of the photolysis source and protects the $[CpOs(CH_3CN)_3]^+$ from photochemical decomposition.

$[CpOs(CH_3CN)_3]^+$ reacts with a variety of different ligands, including arenes, polypyrazolylborates, and CO, to provide convenient, high-yield preparations of new $CpOsL_3$ complexes. In reactions with arenes, $[CpOs(CH_3CN)_3]^+$ shows a strong tendency to give kinetic products that have $CpOs^+$ bound to highly conjugated arenes or complexes with less than η^6 coordination. Of particular importance is the observation of the η^4-bound $[CpOs(CH_3CN)]^+$ group in the bimetalated rubrene and anthracene complexes. Complexes with reduced hapticities have been proposed as intermediates in the complexation and decomplexation of arenes to iron and ruthenium, but have not been observed in those systems. This is the first of many expected examples in which putative CpM^+ containing intermediates postulated for iron and ruthenium chemistry will be isolable or observable for the analogous osmium case. Of particular interest is the development of synthetic routes to the thermodynamically stable $[CpOs(arene)]^+$ complexes for arene ligands such as the pendant phenyls on rubrene or oligothiophenes[17] with unique photophysical properties, including room temperature emission.[18]

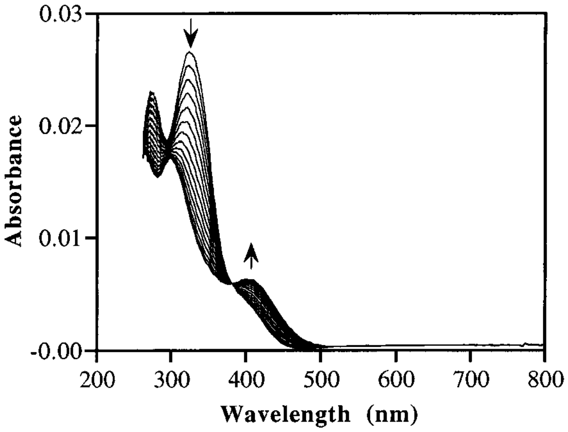

Figure 5. Changes observed in the UV−visible spectrum of $CpOsHB(pz)_3$ during electrolysis at +200 mV vs Pt psuedoreference. Arrows show the direction of the spectral changes.

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Supporting Information Available: Cyclic voltammograms of 1.0 mM $[CpOs(CH_3CN)_3]PF_6$ and 0.1 mM $CpOsHB(pz)_3$ in 0.1 M $TBA^+PF_6^-/CH_3CN$ (1 page). Ordering information is given on any current masthead page.

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(18) Graf, D. D.; Mann, K. R. Unpublished results.