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Synthesis, Characterization, and Photochemistry of Bis(arene) and Acetonitrile Complexes of Osmium(II)

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Osmium complexes of arenes, acetonitrile, and chloride have been studied. The yield has been significantly increased for the synthesis of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$, an excellent starting material for the synthesis of Os−benzene complexes. Reactivity studies with this complex show that one chloride is displaced by Ag^+ in acetonitrile to give $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ but both chlorides are displaced by Ag^+ in acetone to give $[(\eta^6\text{-}C_6H_6)Os(acetone)_3]^{2+}$. The acetone ligands of the latter complex can be displaced by acetonitrile to give $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ and by other arenes (1,3,5-triethylbenzene, hexamethylbenzene, durene, naphthalene) to give $[(\eta^6\text{-}C_6H_6)Os(arene)]^{2+}$ complexes. Studies of thermal ligand exchange with the $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_{3-x}Cl_x]^{(2-x)+}$ complexes indicate that chloride enhances the rate of thermal acetonitrile exchange. Photolysis of $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ and $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ in acetonitrile results in loss of benzene to produce the new complexes $[Os(NCCH_3)_6]^{2+}$ and $[Os(NCCH_3)_5Cl]^+$ in high yield. Photolysis of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ initially results in the formation of $Os(NCCH_3)_4Cl_2$, which subsequently undergoes photochemical loss of chloride to give $[Os(NCCH_3)_5Cl]Cl$. Examination of this reaction by ^1H NMR spectroscopy indicates that the *cis* isomer of $Os(NCCH_3)_4Cl_2$ is produced. The photolysis of $[(\eta^6\text{-}C_6H_6)Os(P(Ph)_3)(NCCH_3)Cl]^+$ in acetonitrile also leads to release of benzene to form the *cis* product. Electrochemical data acquired for the new acetonitrile complexes ($[Os(NCCH_3)_6]^{2+}$, $[Os(NCCH_3)_5Cl]^+$, and $Os(NCCH_3)_4Cl_2$) show highly reversible, one-electron oxidations with the potential a linear function of the stoichiometry. The osmium complexes are about 0.5 V easier to oxidize than the corresponding ruthenium analogs.

Introduction

Previously, we described the photochemical arene replacement reactions of $[CpM(arene)]^+$ complexes (Cp = η^5-cyclopentadienyl; arene = η^6-arene; M = Fe, Ru, Os). Quantitative studies of these reactions have provided information about the photoactive state and the mechanism of arene displacement.[1] Photochemical arene displacement also provides an excellent synthetic route to $[CpM(L)_3]^+$ complexes because three metal coordination sites are opened upon arene release.[2] A particularly useful compound for synthetic chemistry is $[CpRu(NCCH_3)_3]^+$, which has labile acetonitrile ligands.[3] This complex is produced by the photolysis[4] of $[CpRu(\eta^6\text{-}C_6H_6)]^+$ in $NCCH_3$ (eq 1).

$$CpRu(\eta^6\text{–}C_6H_6)^+ \xrightarrow[CH_3CN]{h\nu} CpRu(CH_3CN)_3^+ + C_6H_6 \qquad (1)$$

Until we recently reported the synthesis of $[CpOs(NCCH_3)_3]^+$ and demonstrated its utility as a synthon for $CpOsL_3^+$ complexes,[5] general, high-yield synthetic routes to organometallic osmium complexes of this type were not available. Similar complexes with an arene in place of the Cp ligand have also been largely neglected because synthetic methods to overcome the common problems of long reaction times and low yields are not available. These problems are symptoms of stronger Os−L bonds and higher ligand substitution activation energies in comparison with the case of ruthenium analogs. The relatively few reports in the literature of osmium−arene compounds point out important differences between the chemistry of osmium compounds and the corresponding chemistry of analogous ruthenium compounds. For example, the important starting materials of the general formula $(arene)MCl_2$ in the case of ruthenium, when arene = *p*-cymene,[6] mesitylene,[6] or hexamethylbenzene,[7] behave as neutral dimeric complexes that are soluble in low-polarity solvents (chloroform). The benzene complex is polymeric, but is soluble in nucleophilic solvents such as acetonitrile.[8] All these ruthenium compounds are synthesized in high yields (>80%) and show similar reactivities. In contrast, the chemistry of the osmium analogs is variable. $[(p\text{-cymene})OsCl_2]_2$[9] (reaction 2 with α -phellandrine in place of cyclohexadiene) is prepared in 80% yield and has properties similar to those of the Ru complex. The preparation of $[(HMB)OsCl_2]_2$ has also been reported.[10] More strikingly, 1,3,5-trimethyl-1,4-cyclohexadiene in reaction 2 produces $[(Mes)_3Os_4Cl_9]$ rather than $[(Mes)OsCl_2]_2$.[7] This compound reacts with nucleophiles (DMSO, CO) to give clean, high-yield conversion to $(Mes)OsCl_2L$. Reaction with COT^{2-} produces the neutral complex (Mes)Os(COT).


(2)

Yields of the parent complex, $[(\eta^6\text{-}C_6H_6)OsCl_2]_2$[9,10] (via variations of reaction 2), are less than 50%. Facile replacement

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of the chlorides of $[(\eta^6\text{-}C_6H_6)OsCl_2]_2$ occurs in aqueous solution because it is partially ionized. In acetonitrile solution, no ionization occurs[11] and chloride displacement requires the addition of Ag^+. Addition of the appropriate ligand to an aqueous solution of $[(\eta^6\text{-}C_6H_6)OsCl_2]_2$ produces $[(\eta^6\text{-}C_6H_6)Os(L)_3]^{2+}$ (L = NH_3, H_2O) and $[(\eta^6\text{-}C_6H_6)Os(L)_2Cl]^+$ (L = ethylenediamine, isonicotinamide, pyridine, imidazole) complexes but in reported yields of less than 21%[11] (based on $OsCl_6^{2-}$). The preparation of $[(\eta^6\text{-}C_6H_6)OsI_2]_2$ from $[(\eta^6\text{-}C_6H_6)OsCl_2]_2$ by direct halide exchange has been reported.[12] The iodo-bridged dimer was used as starting material for the synthesis of $(\eta^6\text{-}C_6H_6)OsI_2L$ (L = PPh_3, $P(OMe)_3$) complexes.[7b,13] These complexes are interesting because they have characteristics of both organometallic compounds and classic, Werner type coordination complexes. Taube reports kinetic and thermodynamic data for substitution reactions of these compounds.[11] Ludi, et al.[14] have measured the solvent exchange rates for $[(\eta^6\text{-}C_6H_6)M(H_2O)_3]^{2+}$ (M = Ru, Os) in aqueous solution, demonstrating that the π-bound arene has a *trans*-labilizing effect on the water ligands. In one of the few reports of arene−osmium photochemistry, Taube notes that $[(\eta^6\text{-}C_6H_6)OsCl_2]_2$ is photosensitive in H_2O and $NCCH_3$ solutions, leading to loss of coordinated arene, but no mention was made of the metal-containing products.[11] In this paper, we describe the synthesis of new complexes of the form $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_{3-x}Cl_x]^{(2-x)+}$ and their photochemical benzene displacement reactions in acetonitrile.

Experimental Section

General Considerations. All synthetic procedures were carried out under an inert N_2 atmosphere unless otherwise noted. Solvents were of spectroscopic grade and were used without further purification except for acetonitrile which was distilled from P_2O_5 under nitrogen prior to use. ^1H NMR spectra were recorded on IBM AC-200 and JEOL 90 FXQ spectrometers. Chemical shifts are relative to $(CH_3)_4Si$. Elemental analyses were performed by MHW Laboratories. $(NH_4)_2OsCl_6$ was prepared from OsO_4 by a literature procedure.[15]

Compound Synthesis. $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$. $(NH_4)_2OsCl_6$ (4.0 g, 9.11 mmol) was stirred in 75 mL of water for 15 min. A solution of $NaB(Ph)_4$ (5.36 g, 0.01822 mmol) in 20 mL of water was added to the $(NH_4)_2OsCl_6$ slurry over 5 min to give a sticky white precipitate of $NH_4B(Ph)_4$. The solution was stirred for 2 h and filtered, giving a light yellow filtrate. As excess NH_4^+ is usually present (and appears to cause complications in subsequent reactions), $NaB(Ph)_4$ was added to the filtrate, and if more precipitate was observed, an additional 0.5 g of $NaB(Ph)_4$ was added, followed by stirring and filtration. This procedure was repeated until no precipitate was observed. The filtrate was reduced to a sticky, dark red solid by rotary evaporation at approximately 40 °C (higher temperatures cause decomposition). The Na_2OsCl_6 was transferred to a 100 mL round-bottom flask and dissolved in 30 mL of 95% ethanol. The solution was then purged with N_2 for 30 min. 1,3-Cyclohexadiene (8 mL, 10 times excess) was added, and the solution was refluxed for 48 h, during which time a light yellow precipitate formed. The product was filtered off and washed with cold ethanol and diethyl ether to give 3.01 g of light yellow powder. The product was refluxed for 12 h in acetonitrile. The hot solution was filtered, and diethyl ether was added to precipitate the dark yellow, microcrystalline $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ (1.8 g, 52.0% yield).

$[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]PF_6$. $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ (0.150 g, 0.39 mmol) was dissolved in 15 mL of acetonitrile to give a yellow solution. When $AgPF_6$ (0.100 g, 0.39 mmol) was added, AgCl precipitated. The solution was stirred for 2 h and filtered, and the filtrated was concentrated by rotary evaporation. Addition of diethyl ether precipitated the product as a brownish-yellow powder. Purification was effected by dissolving the product in acetone and followed by filtering. The acetone was removed under reduced pressure to leave a yellow oil that was dissolved in acetonitrile. After 1 h of stirring, the product was precipitated as a light yellow powder upon the addition of diethyl ether (0.151 g, 72% yield). Anal. Calcd for $C_{10}H_{12}N_2ClF_6POs$: C, 22.62; H, 2.28; N, 5.28. Found: C, 22.87; H, 2.47; N, 5.49. ^1H NMR (200 MHz, CD_3NO_2): δ 6.16 (s, C_6H_6, 6 H), 2.0 (s, $NCCH_3$, 6 H).

$[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3](PF_6)_2$. $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ (0.100 g, 0.262 mmol) and $AgPF_6$ (0.132 g, 0.522 mmol) were added to 20 mL of acetone, and the mixture was stirred for 3 h. The AgCl was filtered off to give a brownish yellow solution. The acetone was removed via rotary evaporation, the resulting yellow oil was dissolved in acetonitrile, and the solution was sparged with N_2 and refluxed for 3 h. The resulting solution was concentrated by rotary evaporation and the product precipitated with diethyl ether. The compound was purified by elution down a short alumina column with acetonitrile. Addition of diethyl ether to the acetonitrile solution precipitated the product as a pale yellow powder (0.100 g, 57% yield). Anal. Calcd for $C_{12}H_{15}N_3F_{12}P_2Os$: C, 21.15; H, 2.22; N, 6.17 Found: C, 21.46; H, 2.28; N, 6.28. ^1H NMR (200 MHz, CD_3CN): δ 6.27 (s, C_6H_6, 6 H), 2.66 (s, $NCCH_3$, 9 H).

$[(\eta^6\text{-}C_6H_6)Os(P(Ph)_3)(NCCH_3)Cl]PF_6$. $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ (0.100 g, 0.263 mmol) and $P(Ph)_3$ (0.069 g, 0.263 mmol) were dissolved in 15 mL of acetone, and the mixture was stirred for 15 min. $AgPF_6$ (0.066 g, 0.263 mmol) was added, and the resulting light yellow solution was stirred for 3 h. The solution was passed through a short column of diatomaceous earth to remove AgCl. The acetone was removed by rotary evaporation, and the residue was dissolved in methylene chloride. Addition of hexanes precipitated the light yellow, microcrystalline product (0.070 g, 35% yield). Anal. Calcd for $C_{26}H_{24}NClF_6OsP_2$: C, 41.52; H, 3.22; N, 1.86. Found: C, 41.70; H, 3.06; N, 1.87. ^1H NMR (90 MHz, $CDCl_3$): δ 7.49 (d, $P(Ph)_3$, 15 H, J = 6.0 Hz), 5.84 (d, C_6H_6, 6 H, J = 0.6 Hz), 2.14 (d, $NCCH_3$, 3 H, J = 1.61 Hz).

$[CpOs(\eta^6\text{-}C_6H_6)]PF_6$. $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ (0.500 g, 0.0013 mol) and TlCp (0.390 g, 0.0014 mol) were added to a 100 mL round-bottom flask under N_2 purge. A 40 mL portion of freshly distilled acetonitrile was added via syringe, and the solution was stirred for 4 h. The precipitated TlCl was filtered off, and the light yellow filtrate was evaporated to dryness by rotary evaporation. The residue was dissolved in water, and the solution was filtered. The product was precipitated by adding an excess of NH_4PF_6 and cooling the solution in an ice bath. The $[CpOs(\eta^6\text{-}C_6H_6)]PF_6$ was redissolved in acetonitrile, and the solution was passed through a short alumina column. The product was then precipitated with diethyl ether and filtered off to give a pure white powder (0.55 g, 88% yield). ^1H NMR (200 MHz, CD_3CN): δ 5.65 (s, C_5H_5, 5 H), 6.12 (s, C_6H_6, 6 H).

$[Os(NCCH_3)_6](PF_6)_2$. $[(\eta^6\text{-}C_6H_6)_2Os](PF_6)_2$ (70 mg, 0.11 mmol) and $NCCH_3$ (15 mL) were placed in a quartz tube. The solution was freeze−pump−thaw-degassed and photolyzed with a 175 W mercury vapor lamp for 72 h. The solution was then concentrated and passed down a short alumina column. The product was precipitated with diethyl ether, filtered off, and washed with diethyl ether, yielding a pure white powder (65 mg, 80% yield). Anal. Calcd for $C_{12}H_{18}OsN_6P_2F_{12}$: C, 19.84; H, 2.50; N, 11.57. Found: C, 20.02; H, 2.39; N, 11.53. ^1H NMR (200 MHz, CD_3CN): δ 2.71 (s, $NCCH_3$). FAB-MS: *m/e* = 583 ($[Os(NCCH_3)_6PF_6]^+$), 438 ($[Os(NCCH_3)_6]^{2+}$).

$[Os(NCCH_3)_5Cl]PF_6$. This compound was prepared analogously to $[Os(NCCH_3)_6](PF_6)_2$ with $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl](PF_6)$ substituted for $[(\eta^6\text{-}C_6H_6)_2Os](PF_6)_2$. The compound was isolated as a white powder in 70% yield. Anal. Calcd for $C_{12}H_{15}OsN_5ClPF_6$: C, 20.86; H, 2.54; N, 12.16. Found: C, 21.14; H, 2.63; N, 12.16. ^1H NMR (200 MHz, CD_3CN): δ 2.74 (s, *cis*-$NCCH_3$, 12 H), 2.81 (s, *trans*-$NCCH_3$, 3 H). FAB-MS: *m/e* = 429 ($[Os(NCCH_3)_5Cl]^+$).

$[(\eta^6\text{-}C_6H_6)Os(HMB)](PF_6)_2$. $AgPF_6$ (0.1503 mg, 0.301 mmol) was added to a solution of 50 mg (0.131 mmol) of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ in 15 mL of acetone. After the solution was a stirred for 20 min, the precipitated silver chloride was filtered off to leave a light yellow solution. The acetone was removed by rotary evaporation to yield a light yellow oil. Trifluoroacetic acid (5mL) and an excess of hexam-

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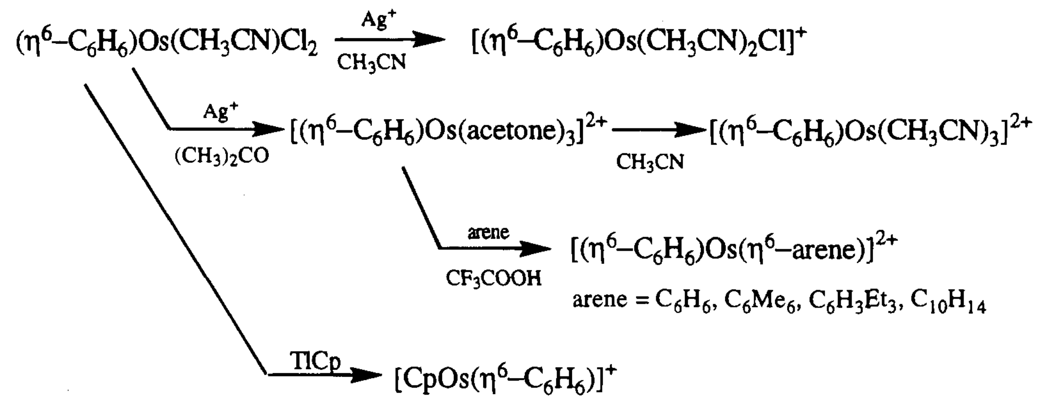
Scheme 1



ethylbenzene (0.2011 g) were added, and the solution was refluxed for 2.5 h to give a brownish yellow solution. The trifluoroacetic acid was removed by rotary evaporation, and a small amount of water was added. The solution was then filtered into an aqueous solution of ammonium hexafluorophosphate to give an off-white precipitate. The product was recrystallized from acetone/diethyl ether to yield 63 mg of white powder (59% yield). Anal. Calcd for $C_{18}H_{24}OsP_2F_{12}$: C, 30.01; H, 3.36. Found: C, 29.77; H, 3.52. ^{1}H NMR (200 MHz, CD_3CN): δ 2.54 (s, C_6Me_6, 18 H), 6.68 (s, C_6H_6, 6 H).

[(η^6-C_6H_6)Os(1,3,5-triethylbenzene)](PF_6)$_2$. (η^6-C_6H_6)Os($NCCH_3$)Cl_2 (125 mg , 0.329 mmol), $AgPF_6$ (187 mg, 0.740 mmol), and 1,3,5-triethylbenzene (2 times excess) were treated the same as above to give 0.2155 g (81% yield) of white powder. Anal. Calcd for $C_{18}H_{24}OsP_2F_{12}$: C, 30.01; H, 3.36. Found: C, 30.03; H, 3.70. ^{1}H NMR (200 MHz, CD_3CN): δ 1.27 (t, $C_6H_3(CH_2CH_3)_3$, 9 H, J = 7.4 Hz), 2.71 (q, $C_6H_3(CH_2CH_3)_3$, 6 H), 6.92 (s, C_6H_6, 6 H), 7.06 (s, $C_6H_3(CH_2CH_3)_3$, 3 H).

[(η^6-C_6H_6)Os(durene)](PF_6)$_2$. (η^6-C_6H_6)Os($NCCH_3$)Cl_2 (50 mg , 0.132 mmol), $AgPF_6$ (75 mg, 0.300 mmol), and durene (100 mg) were treated the same as above to give 88.5 g (87% yield) of white powder. ^{1}H NMR (200 MHz, CD_3CN): δ 2.46 (s, $C_6H_2(CH_3)4$, 12 H), 6.85 (s, C_6H_6, 6 H), 7.12 (s, $C_6H_2(CH_3)_4$, 2 H).

[(η^6-C_6H_6)Os(naph)](PF_6)$_2$. [(η^6-C_6H_6)Os($NCCH_3$)Cl_2] (50 mg, 0.132 mmol), $AgPF_6$ (67 mg, 0.263 mmol), and naphthalene (10 times excess) were treated the same as above to give 48 mg (53% yield) of a light yellow powder. Anal. Calcd for $C_{16}H_{14}OsP_2F_{12}$: C, 27.99; H, 2.06. Found: C, 28.08; H, 2.26. ^{1}H NMR (90 MHz, acetone-d_6): δ 8.44 (d of d, $H_{5,8}$, 2 H, J_{allylic} = 4.6 Hz, J_{vic} = 2.5 Hz), 8.17 (s, $H_{1,2,3,4}$, 4 H), 7.56 (d of d, $H_{6,7}$, 2 H, J_{allylic} = 4.6 Hz, J_{vic} = 2.5 Hz), 7.12 (s, C_6H_6, 6H).

[Ru($NCCH_3$)$_6$](PF_6)$_2$.[14] [(η^6-C_6H_6)Ru($NCCH_3$)$_3$](PF_6)$_2$ (80 mg) and acetonitrile (15 mL) were added to a quartz tube equipped with a magnetic stir bar and serum stopper. The solution was purged with nitrogen and photolyzed for a total of 36 h with a medium-pressure, 175 W mercury vapor lamp. During the course of the photolysis, the initial yellow color of the solution bleached. The volume of the solution was reduced by rotary evaporation, and diethyl ether was added to precipitate the product . Filtration was followed by washing with diethyl ether to give 45 mg of colorless powder. ^{1}H NMR (200 MHz, CD_3CN): δ 2.48 (s, $NCCH_3$).

[Ru($NCCH_3$)$_5$Cl](PF_6). [(η^6-C_6H_6)Ru($NCCH_3$)$_2$Cl](PF_6) (50 mg) and acetonitrile (10 mL) were added to a quartz tube equipped with a magnetic stir bar and serum stopper. The solution was purged with nitrogen and photolyzed for a total of 6 h with a medium-pressure, 175 W mercury vapor lamp. The volume of the solution was reduced by rotary evaporation, and diethyl ether was added, precipitating the product, which was filtered off and washed with more diethyl ether to give 40 mg of colorless powder. ^{1}H NMR (200 MHz, acetone-d_6): δ 2.62 (s, *cis*-$NCCH_3$, 12 H), 2.83 (s, *trans*-$NCCH_3$, 3 H).

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; propylene carbonate (Burdick and Jackson) and supporting electrolytes tetrabutylammonium hexafluorophosphate ($TBA^+PF_6^-$) and tetrabutylammonium tetrafluoroborate ($TBA^+BF_4^-$) were used without further purification. Electrolyte solutions were introduced into the electrochemical cell through a short column of activated 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 and the correlation of these data with those of other workers, we have measured $E^{\circ\prime}$ for the ferrocenium/ferrocene couple under conditions identical to those used for the compounds under study.[16] In 0.1 M $TBA^+PF_6^-/CH_3CN$, $E^{\circ\prime}$ = +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.[17] Bulk electrolyses were controlled by a BAS 100 electrochemical analyzer.

Results

Synthesis of [(η^6-C_6H_6)Os($NCCH_3$)$_{3-x}$$Cl_x$]$^{(2-x)+}$ and (η^6-C_6H_6)Os(arene)$^{2+}$ Compounds. The reaction of $OsCl_6^{2-}$ with 1,4-cyclohexadiene in refluxing ethanol yields a yellow powder which is a ca. 50/50 mixture of two compounds. Refluxing the mixture in acetonitrile yields a yellow solution and a light yellow, insoluble solid. The acetonitrile-soluble material is (η^6-C_6H_6)Os($NCCH_3$)Cl_2 and was isolated in approximately 50% yield. The insoluble material was unreactive in refluxing acetonitrile (one week) and was insoluble in all common solvents. No further attempts to characterize this material were made.

Scheme 1 summarizes the preparation of (η^6-C_6H_6)OsL_3 complexes from (η^6-C_6H_6)Os($NCCH_3$)Cl_2. Reaction of this complex with TlCp in acetonitrile solution affords a direct, high-yield synthesis of [CpOs(η^6-C_6H_6)]$^+$. In the presence of Ag^+, the chlorides can be exchanged for other ligands. (η^6-C_6H_6)Os($NCCH_3$)Cl_2 reacts with $AgPF_6$ in acetonitrile to give [(η^6-C_6H_6)Os($NCCH_3$)$_2$Cl]PF_6 (contrary to a previous report that identified this material as [(η^6-C_6H_6)Os($NCCH_3$)$_3$](PF_6)$_2$).[11] This new compound was characterized by ^{1}H NMR and elemental analysis. Surprisingly, even in the presence of an excess of Ag^+, only a single chloride is removed in acetonitrile solution; however, both chlorides are removed from (η^6-C_6H_6)Os($NCCH_3$)Cl_2 with 2 equiv of Ag^+ in acetone solution to produce

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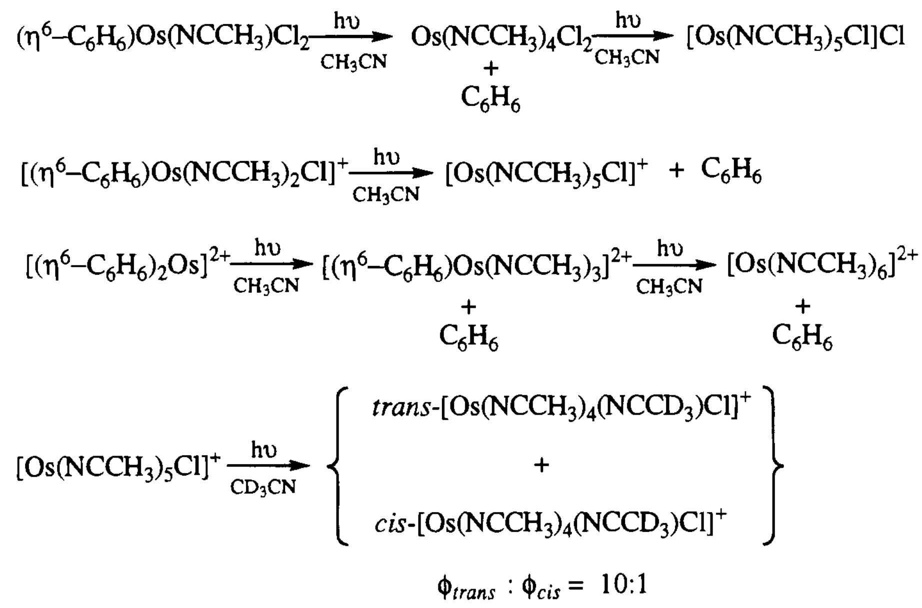
Scheme 2



$$(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2 \xrightarrow[CH_3CN]{h\nu} \underset{C_6H_6}{\overset{}{Os(NCCH_3)_4Cl_2 +}} \xrightarrow[CH_3CN]{h\nu} [Os(NCCH_3)_5Cl]Cl$$

$$[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+ \xrightarrow[CH_3CN]{h\nu} [Os(NCCH_3)_5Cl]^+ + C_6H_6$$

$$[(\eta^6\text{-}C_6H_6)_2Os]^{2+} \xrightarrow[CH_3CN]{h\nu} \underset{C_6H_6}{[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+} +} \xrightarrow[CH_3CN]{h\nu} \underset{C_6H_6}{[Os(NCCH_3)_6]^{2+} +}$$

$$[Os(NCCH_3)_5Cl]^+ \xrightarrow[CD_3CN]{h\nu} \left\{ \begin{array}{c} trans\text{-}[Os(NCCH_3)_4(NCCD_3)Cl]^+ \\ + \\ cis\text{-}[Os(NCCH_3)_4(NCCD_3)Cl]^+ \end{array} \right\}$$

$$\phi_{trans} : \phi_{cis} = 10{:}1$$

a slightly air-sensitive yellow oil.[18] Refluxing the yellow oil in acetonitrile gives facile conversion to $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3](PF_6)_2$, which was characterized by ^1H NMR and elemental analysis. The reaction of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ with triphenylphosphine and $AgPF_6$ in acetone solution produces $[(\eta^6\text{-}C_6H_6)Os(P(Ph)_3)(NCCH_3)Cl]PF_6$.

In reactions similar to those reported by Bennett[19] for the synthesis of $[Ru(arene)_2]^{2+}$ compounds, $[(\eta^6\text{-}C_6H_6)Os(acetone)_3]^{2+}$ reacts readily with arenes (benzene, hexamethylbenzene, 1,3,5-triethylbenzene, naphthalene) in trifluoroacetic acid, to give $[(\eta^6\text{-}C_6H_6)Os(arene)]^{2+}$ complexes. All of the bis(arene) complexes are colorless, thermally stable complexes with the exception of $[(\eta^6\text{-}C_6H_6)Os(naph)]^{2+}$, which is light yellow and decomposes in acetonitrile with loss of naphthalene to form $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$.

Thermal Ligand Substitution Reactivity of $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_{3-x}Cl_x]^{(2x-1)+}$ Compounds. Our experience with the solubility of ionizable organometallic compounds in acetonitrile suggested that the high solubility of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ might be due to partial ionization in this solvent. To investigate this possibility, aliquots of $[C_6H_5CH_2NEt_3]Cl$ solution were added to a solution of $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ in CD_3CN. As chloride was added, the benzene proton resonance from the monochloride at 6.12 ppm decreased in intensity proportionally as the dichloride benzene resonance at 5.99 ppm increased. The separate, sharp peaks observed throughout the experiment suggest that exchange is slow on the NMR time scale ($<10^3$ s^{-1}). The addition of a single equivalent of chloride completely converted $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ to $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$, indicating that the equilibrium in acetonitrile solution greatly favors the neutral dichloro species. The reason for the high solubility of the neutral complex in acetonitrile remains a mystery.

Qualitative assessments of the rate of exchange of bound acetonitriles for CD_3CN for $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ and $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ were made by ^1H NMR. The ^1H NMR of $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ acetonitrile-d_3 shows rapid and complete replacement of the bound acetonitriles for solvent. In comparison, the identical experiment performed with $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ shows virtually no exchange over several days; however, solvent exchange is observed when the solution is photolyzed (vide infra).

Photochemical Reactivity. Scheme 2 shows photochemical reactions of arene–osmium and acetonitrile–osmium complexes in acetonitrile solution. All the compounds studied exhibited photochemical arene displacement reactions in acetonitrile solutions. Photolysis of $[(\eta^6\text{-}C_6H_6)Os(acetone)_3]^{2+}$, $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$, or $[(\eta^6\text{-}C_6H_6)_2Os]^{2+}$ gives clean conversion to $[Os(NCCH_3)_6]^{2+}$. $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ is observed by ^1H NMR as an intermediate in the photolysis of $[(\eta^6\text{-}C_6H_6)_2Os]^{2+}$. The homoleptic osmium–acetonitrile compound was characterized by elemental analysis and FAB-MS. As expected, the ^1H NMR shows a single acetonitrile resonance at 2.71 ppm. Photolysis of $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ in acetonitrile produces $[Os(NCCH_3)_5Cl]^+$. The ^1H NMR exhibits two resonances at 2.74 and 2.81 ppm in a 4:1 ratio, respectively, corresponding to the acetonitrile ligands *cis* and *trans* to the chloride. Both of the new octahedral osmium complexes are remarkably inert to thermal ligand substitution. No detectable exchange of bound acetonitrile for solvent was detected by ^1H NMR of CD_3CN solutions of either compound. Slow exchange of bound acetonitrile with solvent was observed by ^1H NMR when CD_3CN solutions of both complexes were photolyzed. During the photolysis of $[Os(NCCH_3)_5Cl]^+$, the resonance for the *trans* acetonitrile decreases in intensity at a rate approximately 2.5 times faster than those of *cis*, indicating that *either* excited state loss of the *trans* acetonitrile occurs with a quantum yield 10 times larger than that of a *cis* acetonitrile *or* rapid equilibration of a putative five-coordinate intermediate preferentially yields the *trans* product.

The photochemical behavior of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ in acetonitrile was more complex. The final product of the photolysis has a ^1H NMR spectrum identical with that of $[Os(NCCH_3)_5Cl]^+$, indicating that a chloride is displaced in addition to the benzene ligand. In order to determine the sequence of ligand loss, the progress of the reaction was monitored by cyclic voltammetry and ^1H NMR spectroscopy. Figure 1 shows the changes in the cyclic voltammogram observed during the photolysis of an acetonitrile solution of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$. The initial scan shows only the quasi-reversible oxidation of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$. During the photolysis, three new processes are observed. A reversible

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(18) This yellow oil was not characterized, but further reactions with the material suggest it is likely to contain the $[(\eta^6\text{-}C_6H_6)Os(acetone)_3]^{2+}$ cation.

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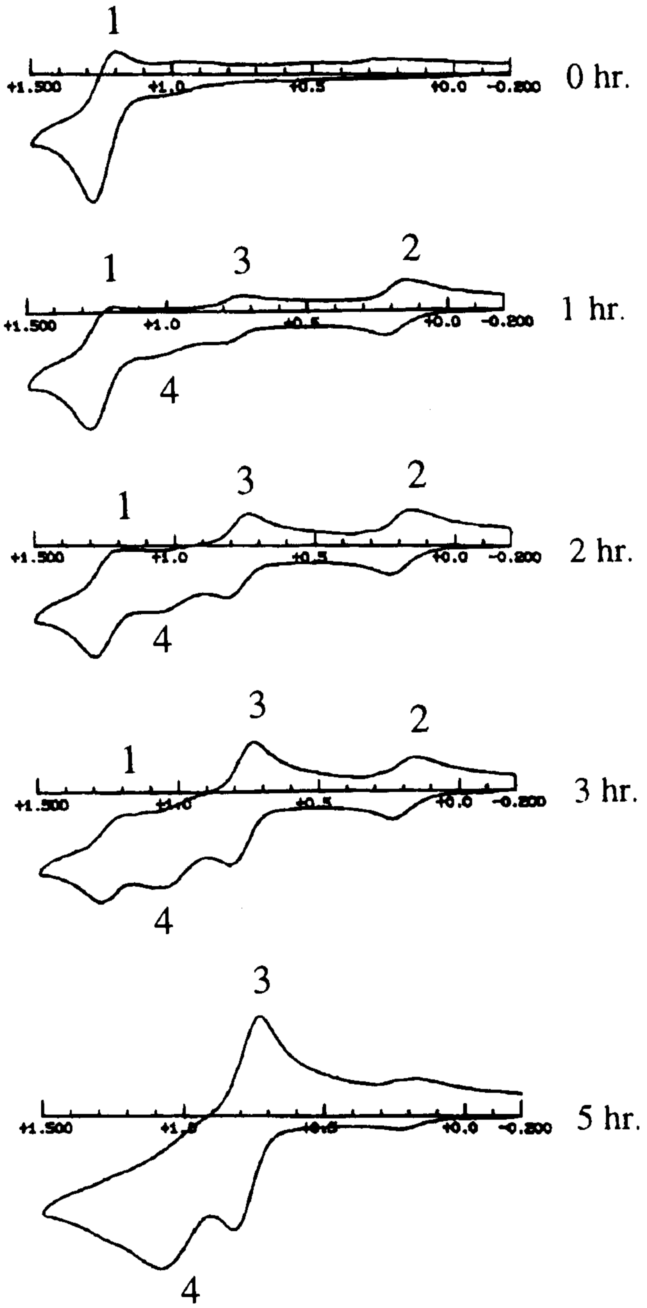

Figure 1. Cyclic voltammograms taken during the photolysis of a 2 mmol solution of (η^6-C_6H_6)Os($NCCH_3$)Cl_2 in CH_3CN/$TBA^+PF_6^-$. Peak assignments: 1 = (η^6-C_6H_6)Os($NCCH_3$)Cl_2; 2 = Os$(NCCH_3)_4Cl_2$; 3 = [Os$(NCCH_3)_5$Cl$]^+$; 4 = Cl^-.

oxidation at +192 mV that grows in and subsequently dies away is assigned to Os$(NCCH_3)_4Cl_2$ (vide supra), which is apparently unstable under these reaction conditions. When the solution containing Os$(NCCH_3)_4Cl_2$ was protected from light for 1 h, no visible decrease in the concentration of Os$(NCCH_3)_4Cl_2$ was observed, indicating that the chloride is displaced via a second photochemical process on this time scale. The final products of the photolysis exhibit a reversible oxidation at +772 mV, identical to that of [Os$(NCCH_3)_5$Cl$]^+$, and an irreversible oxidation at +1000 mV that increases in intensity when chloride ([$C_6H_5CH_2NEt_3$]Cl) is added to the solution. The overall reaction is shown in Scheme 2. The initial reaction is the photochemical displacement of benzene from (η^6-C_6H_6)-Os($NCCH_3$)Cl_2 to form *cis*-Os$(NCCH_3)_4Cl_2$, which loses chloride by a secondary photochemical reaction that produces [Os$(NCCH_3)_5$Cl]Cl.

Table 1. Electrochemical Data[a]

complex	$E°$ (V)	$E_{p,a} - E_{p,c}$ (V)	$i_{p,c/ip,a}$	$E°_{calc}$[f] (V)
(η^6-C_6H_6)Os$(Cl)_2NCCH_3$	1.248[b]	0.119	0.66	
[Os$(NCCH_3)_6]^{2+}$	1.383	0.119	0.94	1.42
[Os$(NCCH_3)_5$Cl$]^+$	0.772	0.073	0.99	0.84
cis-Os$(NCCH_3)_4Cl_2$	0.194	0.064	0.99	0.26
[Ru$(NCCH_3)_5$Cl$]^+$	1.301	0.069	0.93	1.24
[Ru$(NCCH_3)_6]^{2+}$ [c,d]	1.83			1.82
Ru$(NCCH_3)_4Cl_2$[e]	0.84			

[a] Data recorded in $NCCH_3$/$TBA^+PF_6^-$ at a scan rate of 150 mV/s and referenced to Ag/AgCl unless otherwise noted. [b] Scan rate is 500 mV/s. [c] Data taken from ref 14. [d] Data acquired in trifluoromethanesulfonic acid. [e] Data taken from ref 28. [f] $E°$ values calculated from ligand additivity parameters described in ref 30.

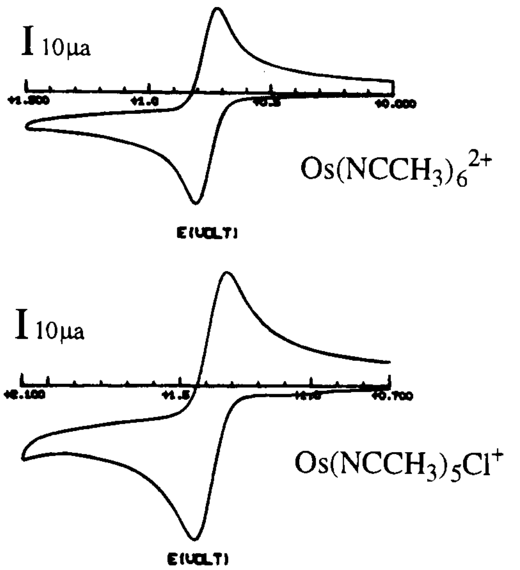

Figure 2. Cyclic voltammograms of 2 mM solutions of [Os$(NCCH_3)_6]^{2+}$ and [Os$(NCCH_3)_5$Cl$]^+$ in CH_3CN/$TBA^+PF_6^-$. Vertical bars indicate the current scale.

The photolysis of (η^6-C_6H_6)Os($NCCH_3$)Cl_2 was also monitored by ^1H NMR spectroscopy in order to determine which isomer of Os$(NCCH_3)_4Cl_2$ forms in the reaction. The two isomers can be discerned by ^1H NMR. For the *trans* isomer, all four acetonitriles are equivalent and should give only a single ^1H NMR resonance. For the *cis* isomer, the two acetonitriles *cis* and *trans* to the chloride should produce two ^1H NMR peaks of equal intensity. During the photolysis of (η^6-C_6H_6)Os($NCCH_3$)Cl_2 in acetonitrile, two peaks of equal intensity grow in at 2.770 and 2.906 ppm and subsequently die away, indicating that Os$(NCCH_3)_4Cl_2$ forms as the *cis* isomer. To confirm that the *cis* isomer formed when the benzene ring was displaced, the photolysis of [(η^6-C_6H_6)Os(P$(Ph)_3$)(Cl)($NCCH_3$)$]^+$ in acetonitrile was also investigated. During the photolysis, three new acetonitrile resonances grow in at 2.62, 2.46, and 2.33 ppm in a 1:2:1 ratio, respectively. These peaks are consistent with the formation of *cis*-[Os$(NCCH_3)_4$(P$(Ph)_3$)Cl$]^+$that has two equivalent acetonitrile ligands *cis* to both triphenylphosphine and chloride. These acetonitrile ligands account for the larger peak. The two smaller peaks are assigned to the remaining acetonitriles *trans* to chloride and *trans* to the phosphine ligand.

Electrochemistry and UV−Vis Spectroelectrochemistry. The electrochemical data are tabulated in Table 1. None of the complexes investigated exhibited any reductive processes to the solvent limit (−2.0 V). The [Os$(NCCH_3)_{6-x}$Cl$_x]^{(2-x)+}$ complexes all show reversible one-electron oxidations. The cyclic voltammograms for [Os$(NCCH_3)_6]^{2+}$and [Os$(NCCH_3)_5$Cl$]^+$ are shown in Figure 2. Although we did not isolate Os$(NCCH_3)_4Cl_2$, electrochemical data for this compound were acquired by monitoring the photolysis of (η^6-C_6H_6)Os($NCCH_3$)Cl_2.

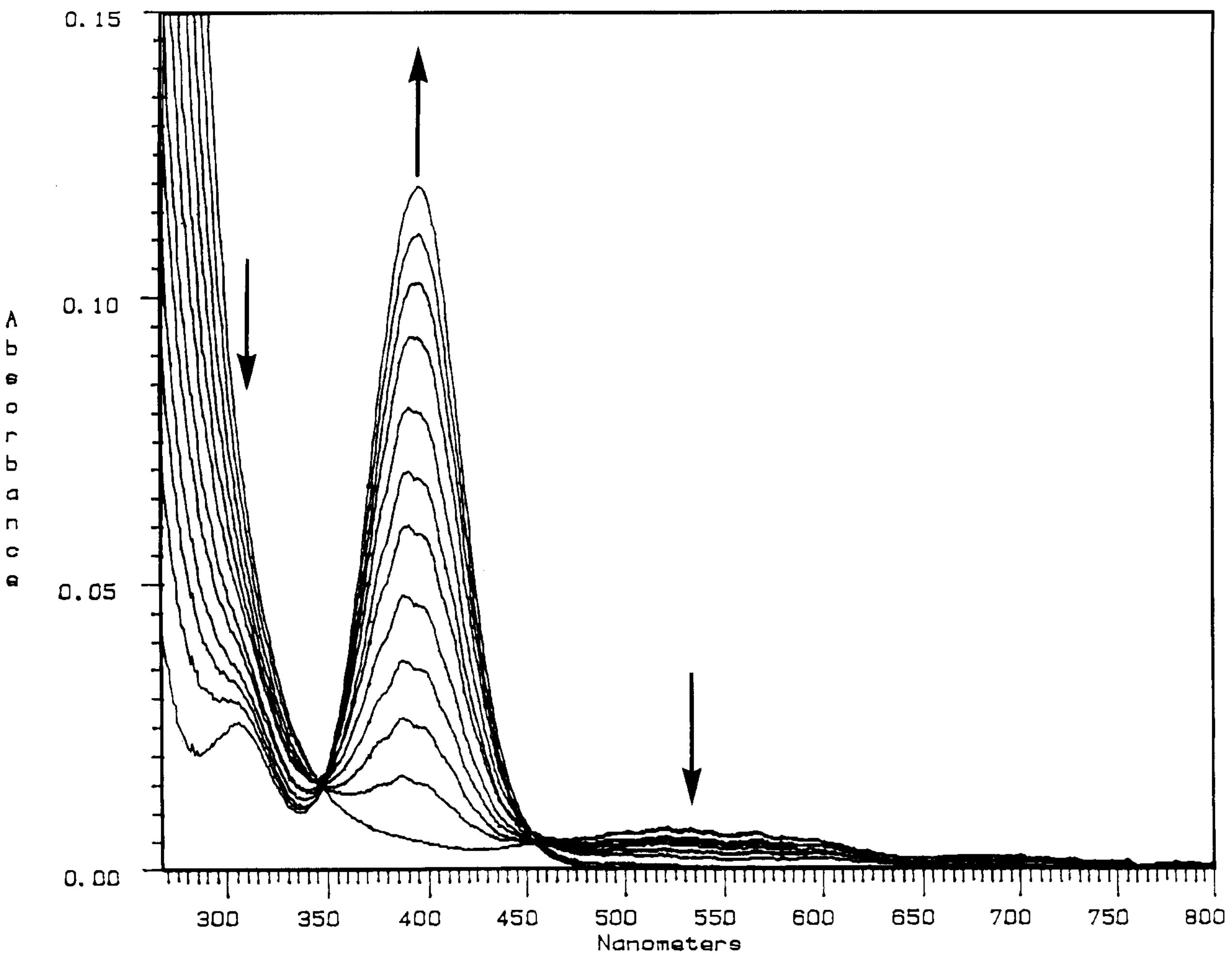

Figure 3. UV–visible spectral changes observed during the oxidation of a solution of $[Os(NCCH_3)_5Cl]^+$ in $CH_3CN/TBA^+PF_6^-$ at +0.800V vs the Pt pseudoreference electrode in the thin-layer spectroelectrochemical cell. The arrows indicate the direction of change.

$[Os(NCCH_3)_6]^{2+}$ is the most difficult to oxidize with an $E°$ of +1383 mV. $[Os(NCCH_3)_5Cl]^+$ and $Os(NCCH_3)_4Cl_2$ are much easier to oxidize, with $E°$'s of 772 and 194 mV, respectively.

UV–vis spectroelectrochemical data for the one-electron oxidations of $[Os(NCCH_3)_6]^{2+}$ and $[Os(NCCH_3)_5Cl]^+$ are shown in Figure 3. In both experiments, isosbestic points are maintained throughout the electrolysis, indicating clean conversion of starting material to product. The initial spectrum for each complex exhibits a featureless tail of an intense UV band. Oxidation of $[Os(NCCH_3)_6]^{2+}$ produces minor changes in the electronic spectrum, principally a shift of the UV tail to higher energies. Oxidation of $[Os(NCCH_3)_5Cl]^+$ produces a similar shift in the UV tail along with the appearance of a new peak at 390 nm.

Discussion

Synthesis and Thermal Reactivity. The synthesis of even the simple osmium complexes reported here required strict attention to detail because of the unexpected richness of the chemistry. The literature preparation of $[(\eta^6\text{-}C_6H_6)OsCl_2]_2$ produced an invariant ca. 1:1 mixture of the desired material and an insoluble, unreactive yellow powder. We suspect that this material might be the benzene analog of $[(Mes)_3Os_4(Cl)_9]$, the compound isolated from the reaction of $OsCl_6^{2-}$ with 1,3,5-trimethylcyclohexadiene. This tetrameric mesitylene osmium complex was soluble only in DMSO and other nucleophilic solvents. The insoluble byproduct formed in the reaction of $OsCl_6^{2-}$ with cyclohexadiene has similar properties but is even less reactive. It is possible that the lower steric bulk of the benzene ring, relative to mesitylene, allows the formation of higher order oligomers or polymers that are even less reactive than the mesitylene tetramer. Similar behavior is observed with the analogous ruthenium compounds. For instance, $[(C_6Me_6)RuCl_2]_2$ is dimeric while $[(\eta^6\text{-}C_6H_6)RuCl_2]_x$ is polymeric. In contrast to the osmium compounds, the polymeric ruthenium complexes can be broken up by reaction with nucleophilic solvents such as acetonitrile.

The 52% yield of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ (based on $OsCl_6^{2-}$) is not particularly impressive, although it offers a 2-fold improvement over that reported in the literature. The use of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ as the starting material for further synthetic reactions in place of the uncleaved dimer produces higher yields with fewer impurities. Of particular importance is the direct, high-yield route to $[CpOs(\eta^6\text{-}C_6H_6)]^+$, which is the starting material for the preparation of the synthetically useful $[CpOs(NCCH_3)_3]^+$ complex[5]. Several new $(\eta^6\text{-}C_6H_6)OsL_3^{n+}$ complexes have been synthesized from $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ via removal of one or both chlorides by reaction with silver ion in the presence of the desired ligand.

The ligand substitution reactivity of the $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_{3-x}Cl_x]^{(2-x)+}$ complexes is interesting. Although the neutral $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ complex is soluble in acetonitrile, it does not ionize to any significant extent. Chloride exchange between $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ and $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ in acetonitrile solution is slow on the NMR time scale. Additionally, the monochloro complex is quantitatively converted to the dichloro complex by the addition of a single equivalent of chloride. The stability of the dichloro complex in acetonitrile is probably due both to the strength of the osmium−chloride bond and to the poor solvating ability of acetonitrile for chloride.[11] The stability of the osmium−chloride bonds in acetonitrile solution allowed Ag^+ to abstract only the first Cl^- ion. In contrast, both chlorides are displaced in acetone solution due to the greater activity of silver cation in acetone relative to acetonitrile.

Qualitative investigations of the relative rates of ligand substitution for the $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ and $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ complexes also revealed some interesting differences. At room temperature, the latter complex exchanges bound acetonitrile for either solvent (in CD_3CN) or chloride too rapidly to observe any intermediate species by ^1H NMR. In comparison, under similar conditions, $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ is thermally unreactive with either CD_3CN or chloride. These marked differences in the rates of ligand substitution might be attributable to an effect similar to the *cis*-labilizing effect observed in the substitution reactions of octahedral metal−carbonyl compounds.[20] Further work will be needed to establish this point.

Photochemistry. The photochemistry of the new octahedral osmium−acetonitrile complexes was examined both for synthetic utility and as a probe of the differences and similarities between these compounds and classical coordination complexes. In particular, the photochemistry we report here will be considered in the context of two models that have been used to predict the leaving ligand in photochemically initiated ligand substitution reactions of octahedral coordination complexes.

The photochemical reactivity of new octahedral osmium compounds is summarized in Scheme 2. The following features need to be considered: (1) Photolysis of $[Os(NCCH_3)_5Cl]^+$ in CD_3CN solution results only in the exchange of acetonitrile with no evidence of loss of chloride to give $[Os(NCCH_3)_6]^{2+}$. (2) For the same compound, the acetonitrile *trans* to the chloride in $[Os(NCCH_3)_5Cl]^+$ is exchanged considerably more efficiently (approximately 10-fold) than the *cis* acetonitriles. (3) *cis*-$Os(NCCH_3)_4Cl_2$ undergoes rapid chloride loss to produce $[Os(NCCH_3)_5Cl]^+$. The reactivity observed for $[Os(NCCH_3)_5Cl]^+$ is consistent with the qualitative rules for photochemical ligand loss proposed by Adamson.[21] Ligand loss is predicted on the axis of an octahedral complex with the lowest average ligand field strength, and the stronger field ligand on the weak-field axis is labilized. For $[Os(NCCH_3)_5Cl]^+$ the axis containing the chloride is the weak-field axis and the acetonitrile *trans* to the chloride, being higher in the spectrochemical series, should be labilized. By the same analysis, photolysis of *cis*-$Os(NCCH_3)_4Cl_2$ is predicted to result in the exchange of the acetonitrile ligands *trans* to chloride. The observed reactivity differs substantially from this prediction. The only photochemical reaction of *cis*-$Os(NCCH_3)_4Cl_2$ that we could observe is facile loss of chloride to produce $[Os(NCCH_3)_5Cl]^+$. It is possible that acetonitrile exchange also occurs, but this could not be observed as the reaction was carried out in acetonitrile as the solvent. The photochemical reactivities of $[Os(NCCH_3)_5Cl]^+$ and *cis*-$Os(NCCH_3)_4Cl_2$ exhibit distinctly different patterns. The former complex shows no loss of chloride, while the latter complex undergoes chloride exchange rapidly.

A more quantitative AOM-based model proposed by Vanquickenborne has more successfully predicted the photochemical reactivity of transition metal complexes,[22] particularly for complexes of low-spin d^6 metals. This model utilizes the ligand AOM σ- and π-bonding parameters to estimate relative metal−ligand excited state bond energies (I^*). The ligand with the lowest value of I^* is predicted to be preferentially labilized in the photogenerated excited state. A difficulty in applying this model to the acetonitrile−osmium complexes is the lack (to our knowledge) of reliable AOM bonding parameters for acetonitrile. Estimates for these parameters were obtained with the method suggested by Hoggard et al.[23] Values of π_L for acetonitrile were estimated from the energy of the lowest lying MLCT band of $Ru(Bipy)_2L_2$ complexes ($L = Cl^-, NCCH_3$).[24−25] σ_L can be calculated from π_L and $10Dq$. A lower limit of 30 000 cm^{-1} for $10Dq$(acetonitrile) was estimated from the lack of any observable d−d transitions in the electronic spectrum of $[Os(NCCH_3)_6]^{2+}$. Although the assumptions made to calculate the bonding parameters undoubtedly introduce significant error, the relative magnitudes of the bonding parameters for acetonitrile and chloride are probably reasonable. The values of I^* calculated for $[Os(NCCH_3)_5Cl]^+$ and $Os(NCCH_3)_4Cl_2$ are given in Table 2. The calculated values of I^* clearly predict that excited state chloride loss should be favored over acetonitrile loss for both osmium compounds and the acetonitrile *trans* to chloride is labilized preferentially to those in the *cis* positions. The AOM approach correctly predicts loss of chloride for $Os(NCCH_3)_4Cl_2$ as well as correctly predicting the enhanced reactivity of the *trans* acetonitrile relative to the *cis* for $[Os(NCCH_3)_5Cl]^+$. Unfortunately, the model also predicts that chloride loss should be the dominant reaction mode for $[Os(NCCH_3)_5Cl]^+$, a reaction that was not observed.

Table 2. Calculated Values of I^* (cm^{-1})[a]

complex	I^* (Cl)	I^* ($NCCH_3$(ax))[b]	I^* ($NCCH_3$(eq))
$[Os(NCCH_3)_5Cl]^+$	7 700	15 100	19 700
cis-$Os(NCCH_3)_4Cl_2$	8 200	23 000	15 600

[a] $\sigma_{Cl} = 6200\ cm^{-1}$, $\pi_{Cl} = 470\ cm^{-1}$. $\sigma_{NCCH3} = 6900\ cm^{-1}$, $\pi_{NCCH3} = -2350\ cm^{-1}$. [b] The axial designation refers to the unique axis.

Theoretically, the AOM approach should be more applicable to these compounds as Adamson's rules have, in general, not been reliable when applied to d^6 metal complexes. The AOM approach has been reliably applied to d^6 metal complexes, and it is surprising that only mixed agreement has been obtained with these osmium complexes. Although AOM calculations occasionally give ambiguous results when calculated values of I^* for two ligands are nearly equivalent, whenever the calculations show differences in I^* as large as those shown in Table 2, the correct reactivity is predicted. The only significant difference between the reactions studied here and those for which the AOM model has been successfully applied is that the successful predictions were made for aqueous solution reactions. Given that acetonitrile can only weakly solvate halides,[11] perhaps excited state loss of chloride occurs but the chloride never escapes from the solvent cage. Rapid recombination with the osmium then regenerates the starting material. Future photochemical experiments in CH_3CN/H_2O mixtures could answer this question.

Unlike other studies of photochemical arene displacement reactions, our results provide information about the stereochemistry of arene release. There are several reports in the literature concerning the mechanism for photochemical arene displacement for ruthenium complexes.[26,27] Work from our group and others indicates that photochemical arene displacement occurs via a photogenerated excited state in which the arene−metal bond has been considerably weakened. Nucleophilic attack by

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solvent or anion on the excited state causes the arene to undergo an η^6 to η^4 hapticity change. In subsequent fast steps the arene is completely replaced by solvent. No stereochemical studies of arene release have been reported, since the majority of the mechanistic data have been acquired for $[CpM(arene)]^+$ complexes. An exception is a study of the photolysis of $[(\eta^6\text{-}C_6H_6)Ru(L)_3]^{2+}$ (L = H_2O, NH_3) in aqueous solution.[26] In this report, quantum yield data for arene release were consistent with the mechanisms proposed for $[CpM(arene)]^+$, but no information concerning product stereochemistry was available because the final photolysis products were always $[Ru(H_2O)_6]^{2+}$. Steric considerations of $[CpM(arene)]^+$ complexes suggest that nucleophilic displacement of the arene must occur via "front side" attack along the "equatorial" region of the metal because the Cp ring blocks back side attack on the *trans* arene trigonal face. If arene release from $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ occurs by a similar mechanism, the *cis* orientation of the chlorides in the arene complex should be retained in the product to produce *cis*-$Os(NCCH_3)_4Cl_2$, the isomer observed experimentally. Although it is possible that the *trans* isomer forms first and rapidly isomerizes to the *cis* isomer, the lack of ^{1}H NMR evidence for the intermediacy of the *trans* isomer during the photolysis of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ makes this possibility unlikely. Additional confirmation that the *trans* isomer is *not* involved is provided by the formation of the *cis* isomer of $[Os(NCCH_3)_4P(Ph)_3Cl]^+$when $[(\eta^6\text{-}C_6H_6)Os(P(Ph)_3)(NCCH_3)Cl]^+$ is photolyzed. Again, no ^{1}H NMR peaks attributable to the *trans* isomer were observed during the photolysis.

Electrochemistry and Spectroelectrochemistry. Recently Heath and Duff[28,29] reported electrochemical and electronic spectral data for a series of mixed nitrile–halide complexes of the formula $[Ru(NCR)_{6-x}X_x]^z$ ($x = 0-6$; R = CH_3, C_6H_5). The potential where these ruthenium(II) complexes oxidize was demonstrated to be a linear function of the stoichiometry. UV–vis spectra of the complexes show that the halide to metal charge transfer bands are also linearly dependent on the oxidation potential. The systematic variation in the Ru(III/II) potential has been put into a larger context by Lever's[30] recent description of the electrochemical ligand parameter, E_L, based on the observed change in the potential of the Ru(III/II) couple as a function of the bound ligands. Comparison with electrochemical data sets for other metals demonstrates that the E_L values are useful for predicting redox potentials for a variety of metals in a wide range of oxidation states. The electrochemical data presented here provide an opportunity to test Lever's model with osmium–nitrile complexes not represented in his data set. The electrochemical data for these compounds are shown in Table 1. The CV's shown in Figure 1 for $Os(NCCH_3)_4Cl_2$ and in Figure 2 for $[Os(NCCH_3)_6]^{2+}$ and $[Os(NCCH_3)_5Cl]^+$ demonstrate the highly reversible nature of these processes. The average potential shift of 595 mV for the successive replacement of an acetonitrile by a chloride for the three osmium complexes is nearly identical to the 590 mV shift reported for the series of $[Ru(NCCH_3)_{6-x}Cl_x]^z$ ($x = 2-6$) complexes.

The E°_{calc} values were calculated for $[Os(NCCH_3)_{6-x}Cl_x]^{(2-x)+}$ complexes by using the equations

$$E^\circ_{calc} = (6 - x)E_L(NCCH_3) + xE_L(Cl) - 0.40\ V$$

$$E_L(NCCH_3) = 0.34\ V$$

$$E_L(Cl) = -0.24\ V$$

$E_L(NCCH_3)$ and $E_L(Cl)$ are the ligand additivity parameters for acetonitrile and chloride, respectively. The −0.40 V term is necessary to convert from the ruthenium electrochemical data set, for which all the E_L values were derived, to the osmium data set. In all cases the calculated values are in good agreement with the experimental data. These calculations also serve as an additional confirmation of the identity of *cis*-$Os(NCCH_3)_4Cl_2$.

For the changes observed in the UV–vis spectroelectrochemistry of $[Os(NCCH_3)_6]^{2+}$ and $[Os(NCCH_3)_5Cl]^+$ during oxidation, we tentatively assign the intense UV band observed for the Os(II) species to a metal-to-nitrile charge transfer transition. The 390 nm band that appears when $[Os(NCCH_3)_5Cl]^+$ is oxidized to the low-spin d^5 $[Os(NCCH_3)_5Cl]^{2+}$ species is assigned to a Cl-to-Os(III) charge transfer transition. Studies of similar Ru compounds support this assignment.[28] Unfortunately, the position of the charge transfer band for the analogous ruthenium complex is not reported. Extrapolation of the available data yields a value of 472 nm, significantly lower in energy than the value for the osmium complex and consistent with the less positive Ru(III/II) redox couple for the ruthenium complex.

Conclusions

Advances have been made to understand the chemistry of monomeric benzene–osmium compounds. The yield has been significantly increased for the synthesis of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$, a convenient starting material for the synthesis of Os–benzene complexes. Reactivity studies with this complex show that one chloride is displaced by Ag^+ in acetonitrile to give $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ and both chlorides are displaced by Ag^+ in acetone to give $[(\eta^6\text{-}C_6H_6)Os(acetone)_3]^{2+}$. The acetone ligands of the latter complex are displaced by acetonitrile to give $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ and by other arenes to give $[(\eta^6\text{-}C_6H_6)Os(arene)]^{2+}$ complexes. Studies of thermal ligand substitution with the $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_{3-x}Cl_x]^{(2-x)+}$ complexes indicate that chloride ligands enhance the rate of thermal acetonitrile exchange. Photolyses of $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_3]^{2+}$ and $[(\eta^6\text{-}C_6H_6)Os(NCCH_3)_2Cl]^+$ in acetonitrile result in loss of benzene to produce the new complexes $[Os(NCCH_3)_6]^{2+}$ and $[Os(NCCH_3)_5Cl]^+$ in high yield. Photolysis of $(\eta^6\text{-}C_6H_6)Os(NCCH_3)Cl_2$ in acetonitrile initially results in the formation of $Os(NCCH_3)_4Cl_2$, which subsequently undergoes photochemical loss of chloride to give $[Os(NCCH_3)_5Cl]Cl$. Examination of this reaction by ^{1}H NMR spectroscopy indicates that the *cis* isomer of $Os(NCCH_3)_4Cl_2$ is produced. Electrochemical data acquired for $[Os(NCCH_3)_6]^{2+}$, $[Os(NCCH_3)_5Cl]^+$, and $Os(NCCH_3)_4Cl_2$ show highly reversible, one-electron oxidations with the potential a linear function of the stoichiometry. Future work in this area will concentrate on the synthetic and mechanistic aspects of the photochemistry of these osmium complexes. The photochemical lability of the acetonitrile ligands should provide a general route to a wide variety of new osmium compounds.

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Supplementary Material Available: A figure showing UV–vis changes during oxidation of $[Os(NCCH_3)_6]^{2+}$ in $NCCH_3/TBA^+PF_6^-$ (1 page). Ordering information is given on any current masthead page.

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