

Synthesis, Characterization, and Electrochemistry of New Tetra- and Pentaamminesmium(II) Complexes Containing Unsaturated Ligands

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Herein we describe the preparation, characterization, and electrochemistry of a series of new tetra- and pentaamminesmium(II) complexes containing unsaturated ligands, L = methyl acrylate, acrylamide, acrylonitrile, propionitrile, and methyl benzoate. The compounds were prepared by ligand substitution using either dihydrogen ($[\text{Os}^{\text{III}}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})]^{2+}$) or trifluoromethanesulfonate ($[\text{Os}^{\text{III}}(\text{NH}_3)_5(\text{OTf})]^{2+}$) salts as starting materials, in acetone solution. For the pentaamine compounds, reduction was effected by Zn/Hg amalgam. With the exception of the nitrile ligands, which coordinate through the nitrogen atom, all other ligands show η^2 -binding to the metal center. Contrary to expectation, for none of the "acryl" complexes was linkage isomerization accompanying electron transfer observed.

Introduction

The organometallic chemistry of the osmium amines has received much attention during recent years.¹ The stability of a great number of organometallic osmium(II) complexes is attributable to the strong tendency osmium has for back-bonding interactions. In many cases, the mono-electron oxidations for the Os(II) complexes take place at potentials of less than 1 V, and the resultant species have enough kinetic stability to be characterizable.

The Os(II)-pentaamine unit, $[\text{Os}(\text{NH}_3)_5]^{2+}$, has received special attention.¹ Although it has a simple composition, it has opened a new subfield of organometallic chemistry, in showing an unprecedented affinity for certain unsaturated ligands.^{2,3}

Some of the effects observed for the osmium pentaamine compounds extend to the chemistry of the tetraamine analogues. For example $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})]^{2+}$ can be prepared by a procedure similar to that described for the pentaamine dihydrogen complex.⁵ Furthermore, $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})]^{2+}$ was found to be quite reactive with strong π -acid ligands proving it to be good starting material for the synthetic work. When two labile positions are open, new reaction opportunities arise. Herein we describe the preparation and electrochemical behavior of new osmium(II) ammine complexes, which has led to some novel results and conclusions.

Glossary of Numbered Species: $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCO}_2\text{-CH}_3)((\text{CH}_3)_2\text{C}=\text{O})]^{2+}$ (1), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCONH}_2)((\text{CH}_3)_2\text{C}=\text{O})]^{2+}$ (2), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCO}_2\text{H})(\text{H}_2\text{O})]^{2+}$ (3), $[\text{Os}(\text{NH}_3)_4(\eta^2, \eta^1\text{-}(\text{CH}_2=\text{CHCO}_2\text{H})_2)]^{2+}$ (4), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_2=\text{CHCN})]^{2+}$ (5), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_3\text{CH}_2\text{-CN})]^{2+}$ (6), $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-CH}_2=\text{CHCO}_2\text{CH}_3)]^{2+}$ (7), $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-methyl benzoate})]^{2+}$ (8), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-}((\text{CH}_3)_2\text{C}=\text{O}))]^{2+}$ (9). The numbers refer to the cations but can also be applied to the salts; for example, 1 $(\text{PF}_6)_2$ = the hexafluorophosphate salt of 1.

Glossary of Most Used Abbreviations: OTF = trifluoromethanesulfonate; TBA = tetrabutylammonium; DME = dimethoxyethane; DMSO = dimethyl sulfoxide; SCE = saturated calomel electrode; SHE = standard hydrogen electrode.

Experimental Section

Equipment. ¹H NMR spectra were obtained on Varian XL-400 (400 MHz) and Gemini (200 MHz) spectrometers in acetone-*d*₆ solutions using TMS as internal standard.

Electrochemical experiments were performed under nitrogen by using a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded using a platinum or glassy-carbon working electrode, a Pt⁰ counter electrode, and either a SCE (0.243 V vs SHE) or a gold button immersed in a 0.50 M NaOTf/DME solution, which was calibrated with the ferrocenium/ferrocene couple ($E_{1/2}$ = 0.55 V vs SHE). The ionic strength was kept constant using either LiOTf or (TBA)PF₆. All potentials are reported vs SHE.

Microanalyses were done by Desert Analytics, Inc.

Materials and Reagents. Osmium tetroxide (Nat. Colonial Metal, Inc), hydrazine (98%, Aldrich), trifluoromethanesulfonic acid (98%, Aldrich), methyl acrylate (99%, Aldrich), acrylamide (97%, Aldrich), acrylonitrile (99%, Aldrich), propionitrile (99%, Aldrich), and methyl benzoate (99%, Aldrich) were used as supplied.

Synthesis. (Dihydrogen)tetraamminesmium(II) bis(tetraphenylborate), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})](\text{B}(\text{C}_6\text{H}_5)_4)_2$, was prepared by the procedure of Li and Taube.⁴ The PF₆⁻ salt is readily prepared by dissolving the $\text{B}(\text{C}_6\text{H}_5)_4^-$ salt in acetone and adding an equivalent amount of TlPF₆. After removal of the TlB(C₆H₅)₄ formed, ether is added to the filtrate and the off-white solid recovered.

(Methyl acrylate)(acetone)tetraamminesmium(II) Bis(hexafluorophosphate), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCO}_2\text{CH}_3)((\text{CH}_3)_2\text{C}=\text{O})](\text{PF}_6)_2$ (1). $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})](\text{B}(\text{C}_6\text{H}_5)_4)_2$ (296 mg, 3.2×10^{-4} mol) and methyl acrylate (574 mg, 6.7×10^{-3} mol) were dissolved in 10 mL of acetone. After 4 h, 223 mg (6.4×10^{-4} mol) of TlPF₆ dissolved in 2 mL of acetone was added to the solution. After removal of the TlB(C₆H₅)₄ which precipitated, 100 mL of ether was added to the filtrate. The yellow solid which formed was collected, washed with ether, and dried under vacuum. The yield was 50%. The compound was further purified by dissolving it in 20 mL of deionized water and passing the solution through a Sephadex SP-C-25 cationic-exchange resin. After the column was washed several times with deionized water, the complex was eluted with a 0.5 M lithium trifluoromethanesulfonate solution. Most of the solvent was removed under vacuum, and 2 mL of a 0.4 M NaB(C₆H₅)₄ solution was added. The light yellow solid was separated, washed several times with water, and dried under vacuum. The complex was then dissolved in acetone, and an acetone solution containing an equivalent amount of TlPF₆ was added. The white solid was removed by filtration and ether was added to the filtrate, yielding a yellow solid. This was recovered, collected on a medium-porosity frit, washed with ether, and dried under vacuum. The yield is 20%. Anal. Calcd for OsC₇H₂₄O₃N₄P₂F₁₂: C, 12.15; H, 3.47; N, 8.09. Found: C, 11.52; H, 3.20; N, 8.60. ¹H NMR data in acetone-*d*₆, δ (ppm): 3.92 (12H, s, broad, 4NH₃), 3.60 (3H, s, sharp, CO₂-CH₃), 3.5–4.4 (3H, m, (CH₂=CH-). Cyclic voltammetry: $E_{1/2}$ = 0.65 V vs SHE, 0.50 M LiOTf aqueous solution, 100 mV/s; switching potentials $E_{\lambda\text{a}}$ = +1.24 V, $E_{\lambda\text{c}}$ = -0.16 V (SHE).

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(Acrylamide)(acetone)tetraammineosmium(II) Bis(hexafluorophosphate), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCONH}_2)((\text{CH}_3)_2\text{C}=\text{O})](\text{PF}_6)_2$ (2). The procedure is the same as that described for 1 above. Anal. Calcd for $\text{OsC}_6\text{H}_{23}\text{N}_5\text{O}_3\text{P}_2\text{F}_{12}$: C, 10.63; H, 3.40; N, 10.34. Found: C, 9.86; H, 3.18; N, 10.91. $^1\text{H NMR}$ data in acetone- d_6 , δ (ppm): 3.7–5.0 (m, 15H, 4NH₃ + olefinic protons), 7–7.4 (s, broad, 2H). Cyclic voltammetry: $E_{1/2} = 0.56$ V vs SHE, 0.50 M LiOTf aqueous solution, 100 mV/s; switching potentials $E_{\lambda a} = +0.90$ V, $E_{\lambda c} = -0.20$ V (SHE).

(Acrylonitrile)(dihydrogen)tetraammineosmium(II) Bis(hexafluorophosphate), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_2=\text{CHCN})](\text{PF}_6)_2$ (5). $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})](\text{B}(\text{C}_6\text{H}_5)_4)_2$ (306 mg, 3.3×10^{-4} mol) and acrylonitrile (180 mg, 3.3×10^{-3} mol) was dissolved in 10 mL of acetone. The color of the solution changed slowly from light yellow to orange within 4 h, whereupon 3 mL of a 0.22 M of TlPF₆ solution in acetone was added to the system. After removal of the white solid, the filtrate was concentrated, and 100 mL of ether was added. The resulting orange solid was collected on a medium-porosity frit, washed with ether, and dried under vacuum. The yield is 72%. Anal. Calcd for $\text{OsC}_3\text{H}_{17}\text{N}_5\text{P}_2\text{F}_{12}$: C, 5.97; H, 2.82; N, 11.60. Found: C, 6.38; H, 2.82; N, 11.42. $^1\text{H NMR}$ data in acetone- d_6 , δ (ppm): 3.85 (s, broad, 12H, 4NH₃), 6.45–6.55 (m) (3H, ABC system), –6.89 (s, 2H, $\eta^2\text{-H}_2$). Cyclic voltammetry: E_{pa} at 0.60, 0.88, and 1.04 V vs SHE, all irreversible waves, 0.1 M HOTf/0.4 M LiOTf, aqueous solution; switching potentials $E_{\lambda a} = +1.10$ V, $E_{\lambda c} = +0.04$ V (SHE).

(Propionitrile)(dihydrogen)tetraammineosmium(II) Bis(hexafluorophosphate), $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_2\text{CH}_2\text{CN})](\text{PF}_6)_2$ (6). The procedure is the same as described for 5. Anal. Calcd for $\text{OsC}_3\text{H}_{19}\text{N}_5\text{P}_2\text{F}_{12}$: C, 5.95; H, 3.14; N, 11.56. Found: C, 6.29; H, 3.12; N, 11.59. $^1\text{H NMR}$ data in acetone- d_6 , δ (ppm): 3.79 (s, broad, 12H, NH₃), 3.14 (quartet, 2H, –CH₂–), 1.41 (triplet, 3H, CH₃–), –7.64 (s, 2H, $\eta^2\text{-H}_2$). Cyclic voltammetry: E_{pa} at 0.44, 0.77, and 0.94 V vs SHE, all waves irreversible, 0.1 M HOTf/0.4 M LiOTf, aqueous solution; switching potentials $E_{\lambda a} = +1.10$ V, $E_{\lambda c} = +0.04$ V (SHE).

(Methyl acrylate)pentaammineosmium(II) Bis(trifluoromethanesulfonate), $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-CH}_2=\text{CHCO}_2\text{CH}_3)](\text{OTf})_2$ (7). $[\text{Os}(\text{NH}_3)_5(\text{OTf})](\text{OFT})_2$ (72 mg, 1×10^{-4} mol) and methyl acrylate (84 mg, 1×10^{-3} mol) were dissolved in ca. 3 mL of anhydrous methanol, and ≈ 1 g of Zn/Hg amalgam was added. The mixture was stirred for 1.5 h, during which there was a slow change of the color of the solution from light yellow to an intense yellow. It is important not to extend the reaction time, otherwise there is reduction of the methyl acrylate. After removal of the Zn/Hg amalgam by filtration, 40 mL of ethyl ether was added. A yellow solid was collected in a medium-porosity frit, washed with ether, and dried under vacuum. The yield is 63%. Anal. Calcd for $\text{OsC}_6\text{H}_{21}\text{N}_5\text{O}_8\text{S}_2\text{F}_6$: C, 10.93; H, 3.19; N, 10.62. Found: C, 10.89; H, 3.17; N, 10.32. $^1\text{H NMR}$ data in acetone- d_6 , δ (ppm): 3.64 (s, 3H, –CO₂–CH₃), 3.76 (s, broad, 12H, 4 cis-NH₃), 3.93 and 4.37 (m, 3H, olefinic H), 5.10 (s, broad, 3H, trans-NH₃). Cyclic voltammetry: $E_{1/2} = 0.87$ V vs SHE, 1 M (TBA)PF₆-acetone solution; switching potentials $E_{\lambda a} = +1.20$ V, $E_{\lambda c} = -1.00$ V (SHE).

(Methyl benzoate)pentaammineosmium(II) Bis(trifluoromethanesulfonate), $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-methyl benzoate})](\text{OTf})_2$ (8). $[\text{Os}(\text{NH}_3)_5(\text{OTf})](\text{OFT})_2$ (74 mg, 1×10^{-4} mol) and methyl benzoate (150 mg, 1×10^{-3} mol) were dissolved in ca. 3 mL of methanol, and ≈ 1 g of Zn/Hg amalgam was added. The mixture was stirred for 1.5 h; during this time, the color of the solution changed from light yellow to brown. After the Zn/Hg was removed by filtration, 10 mL of ether/CH₂Cl₂ (3:1 v/v) was added. A brown solid was collected, washed with ether, and dried under vacuum. The yield is 58%. Anal. Calcd for $\text{OsC}_{10}\text{H}_{23}\text{N}_5\text{O}_8\text{S}_2\text{F}_6$: C, 16.93; H, 3.24; N, 9.87. Found: C, 16.01; H, 2.99; N, 9.38. $^1\text{H NMR}$ data in acetone- d_6 , δ (ppm): 3.62 (s, broad, 12H, 4 cis-NH₃), 3.79 (s, 3H –CO₂CH₃), 4.84 (s, broad, 3H, trans-NH₃), 6.95 (s, broad, 5H, ring protons). Cyclic voltammetry: $E_{pc} = -0.36$ V and $E_{pa} = 0.49$ V vs SHE, irreversible waves, 1 M (TBA)PF₆-acetone solution; switching potentials: $E_{\lambda a} = +0.90$ V, $E_{\lambda c} = -0.62$ V (SHE).

Results and Discussion

Characterization of the Complexes. The mode of coordination of osmium(II) amines to unsaturated ligands is often readily revealed by the $^1\text{H NMR}$ spectrum. Coordination in the η^2 -mode causes an upfield shift of ≈ 2 ppm for the olefinic proton signals, relative to those of the free ligand. That is what we observe in the $^1\text{H NMR}$ spectrum of the compounds 1–4, 7, and 8. The $^1\text{H NMR}$ spectra of 1–3⁶ are consistent with only one

Table 1. Chemical Shifts for the Dihydrogen Ligand for the Compounds $[\text{Os}^{\text{II}}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-L}_1)]^{2+}$ in Acetone- d_6 ^a

$\delta(\eta^2\text{-H}_2)^a$	L ₁	$\delta(\eta^2\text{-H}_2)^a$	L ₁
–6.89	CH ₂ =CHCN*	–10.78	Cl [–]
–7.64	CH ₃ –CH ₂ CN*	–11.29	Br [–]
–7.80	CH ₃ CN	–11.35	D ₂ O
–7.44	pyridine	–11.37	(CD ₃) ₂ CO
–7.43	imidazole	–11.60	I [–]

^a In ppm; an asterisk indicates data from this work.

Table 2. Electrochemical Data for the Osmium(II) Ammine Complexes

no.	compd	$E_{1/2}$, V vs SHE	conditions
1	$[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCO}_2\text{CH}_3)(\text{H}_2\text{O})]^{2+}$	0.65 ^a	<i>d</i>
2	$[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCONH}_2)(\text{H}_2\text{O})]^{2+}$	0.56 ^a	<i>d</i>
3	$[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCO}_2\text{H})(\text{H}_2\text{O})]^{2+}$	0.69 ^{a,c}	<i>d</i>
4	$[\text{Os}(\text{NH}_3)_4(\eta^2, \eta^1\text{-CH}_2=\text{CHCO}_2\text{H})]^{2+}$	0.59 ^{a,c}	<i>d</i>
5	$[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_2=\text{CHCN})]^{2+}$	(0.60, 0.88, 1.04) ^b	<i>e</i>
6	$[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_2\text{CH}_2\text{CN})]^{2+}$	(0.44, 0.77, 0.94) ^b	<i>e</i>
7	$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-CH}_2=\text{CHCO}_2\text{CH}_3)]^{2+}$	0.87 ^a	<i>f</i>
8	$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-methyl benzoate})]^{2+}$	(0.49, –0.36) ^b	<i>f</i>

^a Reversible wave. ^b E_{pa} , irreversible wave. ^c Reference 6. ^d 0.50 M LiOTf/H₂O. ^e 0.4 M LiOTf/0.1 M HOTf. ^f 1 M TBAPF₆/acetone.

unsaturated ligand being coordinated in the η^2 mode. The $^1\text{H NMR}$ spectrum of 2 in acetone- d_6 shows multiplets characteristic of the olefinic protons in an ABC system over the range of 3.7 to 5.0 ppm, overlapping with the ammine peak at 4 ppm. These signals integrate to 15 protons, and it is clear that the metal center is η^2 bound through the alkene group of the acrylamide ligand. The amide proton signals appear as broad peaks between 7 and 7.4 ppm, integrating for two protons. Compound 4 has been shown to be quite interesting in the sense that it exhibits two kinds of binding, η^2 and η^1 , to the acrylic acid ligand.⁶

The acrylonitrile complex, 5, shows a different kind of coordination. Its $^1\text{H NMR}$ spectrum shows a broad and intense peak at 3.85 ppm, integrating for 12 protons and assigned to the four ammine ligands. Two sets of multiplets at 6.45 and 6.55 ppm are attributed to the three olefinic protons in an ABC system. These values are very close to the corresponding signals of the free ligand, indicating that the coordination to the metal center is through the nitrogen of the nitrile group. This conclusion is supported by the chemical shift of the dihydrogen ligand ($\eta^2\text{-H}_2$). The value of –6.89 ppm found for complex 5 is in line with the trend reported by Li and Taube⁴ as seen in Table 1. The same considerations also apply to the propionitrile complex, 6. The chemical shift for the $\eta^2\text{-H}_2$ ligand is very sensitive to the ligand in the trans position.⁴

All tetraammine compounds herein described have the trans configuration of the ammine ligands. For the pentaammine complexes, 7 and 8, the separations between the trans and cis ammine peaks are 1.34 and 1.22, respectively. The large separation indicates $\eta^2\text{-}\pi$ binding.⁷ The broad peak at 6.95 ppm that appears in the $^1\text{H NMR}$ spectrum of compound 8, corresponding to the absorption of the ring protons, indicates fluxional behavior of the $[\text{Os}(\text{NH}_3)_3]^{2+}$ moiety, consistent with a $\eta^2\text{-}\pi$ binding as previously reported in the literature.²

Electrochemistry of the Complexes. Table 2 summarizes the electrochemical data for the osmium(II) ammine complexes prepared. The compounds 1–4 and 7 have simple electrochemical responses. Their cyclic voltammograms show only one reversible wave assigned to the general mono-electron reaction: $\text{Os}^{\text{II}}\text{A}_m\text{L}_n \rightarrow \text{Os}^{\text{III}}\text{A}_m\text{L}_n + e^-$ (A = NH₃, L = unsaturated ligand, $m = 4$ or 5 and $n = 1$ or 2). It is interesting to compare the redox potential for the compounds 1–6 with the corresponding $E_{1/2}$ (1.5 V vs

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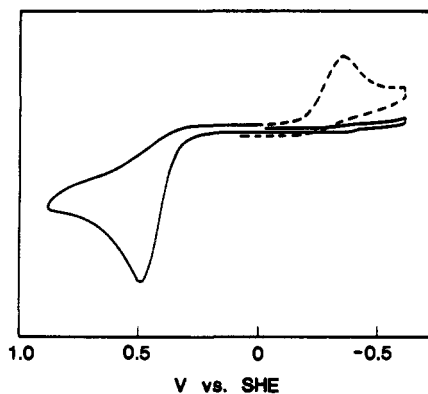
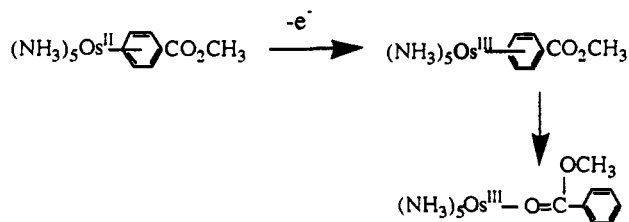


Figure 1. Cyclic voltammogram of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-methyl benzoate})]^{2+}$ (5×10^{-3} M). Conditions: 1 M (TBA)PF₆-acetone; 100 mV/s; initial cathodic scan; dashed line = 2nd scanning.

Scheme 1



SHE) for the bis(ethylene)tetraammineosmium(II) complex, $[\text{Os}(\text{NH}_3)_4(\eta^2, \eta^2\text{-(C}_2\text{H}_4)_2)]^{2+}$.⁶ The large difference observed between these values clearly illustrates the effect of a second η^2 coordination to the metal center.

In most of the compounds prepared, the geometry of the unsaturated ligand appears to be appropriate for linkage isomerization following electron transfer. Moreover the site alternate to η^2 attachment is polar and would be expected to be favored in the 3+ state. While the phenomenon is rarely observed in classic organometallic chemistry because of the high redox potentials usually required to remove one electron from the complexes, coupled with instability of the product, a number of examples have been reported for pentaammineosmium systems, $[\text{Os}(\text{NH}_3)_5\text{L}]^{2+/3+}$. Most of the reactions take place on the time scale of the cyclic voltammetry, and in most cases L is an aromatic function with a polar group attached, for example, anilines,⁸ *tert*-butyl phenyl ketone,⁹ diphenylacetylene,¹⁰ and 2,6-lutidine.¹¹ The exceptions to an aromatic function serving as an alternate site involve 1,2 shifts as observed in the $[\text{Os}(\text{NH}_3)_5(\text{acetone})]^{3+/2+}$ and $[\text{Ru}(\text{NH}_3)_5\text{DMSO}]^{3+/2+}$ systems.¹²

In accord with this general tendency, among the compounds in Table 2, only the methyl benzoate complex, $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-methyl benzoate})]^{2+}$ (**8**), exhibits linkage isomerization coupled to the monoelectron oxidation as seen in Figure 1. The cyclic voltammogram of **8** in a 1 M (TBA)PF₆ acetone solution shows one anodic wave at +0.49 V vs SHE and one cathodic process at -0.36 V, 100 mV/s. It should be emphasized that the cathodic wave is observed only after the first scan. The overall reaction given by Scheme 1.

Upon oxidation **8** undergoes rapid linkage isomerization from η^2 to η^1 on osmium(III). When the resulting complex, $[\text{Os}(\text{NH}_3)_5(\eta^1\text{-methyl benzoate})]^{3+}$, is subsequently reduced, the terminally coordinated methyl benzoate reverts to the η^2 - π bound form. The peak potentials and the breadth of anodic and cathodic waves show a scan rate dependence, the cathodic wave shifting toward

negative potentials as the scan rate is increased. Both oxidation and reduction processes remained totally irreversible in the range 0.01–100 V/s, suggesting a very rapid isomerization reaction. To discard a possible electrochemical irreversibility due to cell resistance, cyclic voltammograms of the standard ferrocene (FcCp₂) and also of compound **7** were run over the same scan range; both showed very good reversible features. Furthermore we should emphasize the high concentration of the electrolyte (1 M (TBA)PF₆) used to minimize cell resistance problems. Consequently, we can classify the overall process as an E_iC_i type under the Nicholson and Shain formalism.¹³ Unfortunately Nicholson and Shain schemes offer no theoretical treatment to determine the value of the rate constant of isomerization for an E_iC_i reaction.

For a more rigorous test of the kinetic stability toward linkage isomerization we have oxidized each of the compounds shown in Table 2 with an equivalent amount of Ag⁺. For the entries 1–7 no linkage isomerization reactions were observed within 24 h. Whether the failure of $[\text{Os}(\text{NH}_3)_n]^{3+}$ ($n = 4$ or 5) to relocate to the polar site is a consequence of an equilibrium barrier or kinetic inertia is not known. The outcome, in either event is surprising.

The value of E_{pc} of -0.36 V vs SHE registered for the monoelectron reaction of the ester complex seems remarkably high for a σ donor oxygen ligand. Thus, E_{pc} for $[\text{Os}(\text{NH}_3)_5(\eta^1\text{-(CH}_3)_2\text{CO})]^{3+/2+}$ is reported as -0.45 V, and the η^1 -acetone can be considered to have some capacity for back-donation.⁹ For $[\text{Os}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+/2+}$, E_{pc} is in the range of -0.73 V.¹⁴ The comparisons suggest that the ester itself functions as a π acid, perhaps by conjugation of carbonyl with the aromatic ring. Presumably benzoic acid could function in a similar way, but the measurement of the corresponding redox potential is vitiated by the rapid dissociation of the proton.

The cyclic voltammograms of **8** in a 0.5 M LIOTF aqueous solution is similar to the one in acetone, with an anodic wave at +0.40 V vs SHE and a cathodic one at -0.30 V, both irreversible, ruling out a possible solvent substitution on the CV time scale when compared to $E_{1/2}$ of -0.73 V for the $[\text{Os}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+/2+}$ ion complex.¹⁴

Electrochemistry of the Osmium(II) Tetraammine Dihydrogen Nitrile Complexes. Figure 2a shows the cyclic voltammogram of compound **9** in a 0.75 M (TBA)PF₆ dry acetonitrile solution at 100 mV/s. The η^1 -acetone ligand is labile under the conditions of the experiment, the species studied being $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_3\text{CN})]^{2+}$. The wave A at +0.9 V vs SHE is assigned to the 1e⁻ oxidation to the Os(III) form. When the resulting complex, $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_3\text{CN})]^{3+}$, is subjected to more positive potentials, a second irreversible anodic wave of greater amplitude appears at +1.4 V (wave B). Similar behavior was observed in the electrochemistry of the pentaammine(dihydrogen)osmium(II) complex,⁵ the second wave being attributed to the bis(electron) oxidation of the η^2 -H₂ ligand. Repeated scanning leads to the formation of the bis(acetonitrile) complex, $[\text{Os}(\text{NH}_3)_4(\eta^1, \eta^1\text{-(CH}_3\text{CN})_2)]^{3+}$, as indicated by the appearance of the reversible couple at +0.26 V (wave C). $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_3\text{CN})]^{3+}$ acts as an efficient reducing agent for the acetone that came out as a product of the dissociation of the $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-(CH}_3)_2\text{C=O})]^{2+}$ ion, producing isopropyl alcohol (L₁) and the corresponding complex, $[\text{Os}(\text{NH}_3)_4(\eta^1\text{-CH}_3\text{CN})(\eta^1\text{-(CH}_3)_2\text{CH(OH)})]^{3+}$, which undergoes reduction at $E_{\text{pc}} = +0.04$ V (wave D). The formation of the isopropyl alcohol is fast in the sense that the wave D can be seen even when the scanning direction is reversed before the beginning of the second oxidation process (wave B), as shown in Figure 2b. The overall reactions are summarized in Scheme 2.

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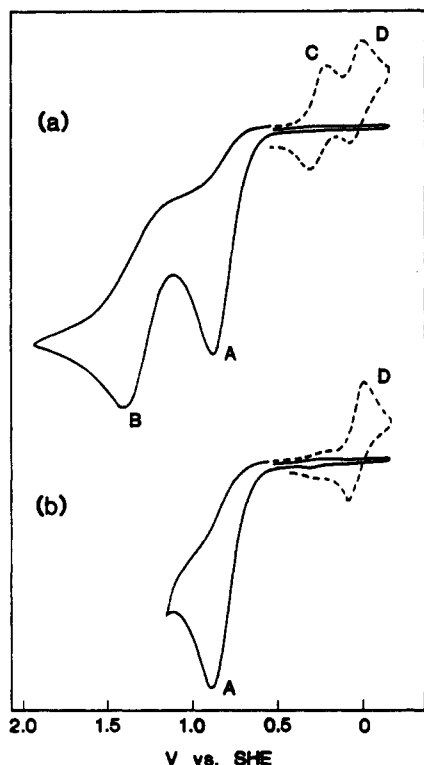
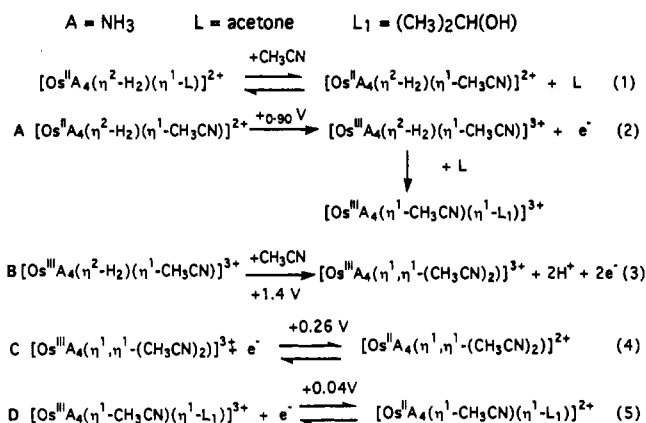


Figure 2. (a) Cyclic voltammogram of $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-acetone})]^{2+}$ (5×10^{-3} M). Conditions: 0.75 M (TBA)PF₆-acetonitrile solution, 100 mV/s; initial cathodic scan; dashed line = 2nd scanning. (b) Same as (a) except reversing the scanning after the first anodic wave.

Scheme 2



It should be emphasized that the waves C and D are not seen in the first cathodic scan, +0.50 to -0.10 V, so they are the property of species formed by oxidation. Wave D has its intensity increased when extra amounts of acetone are added to the solution, substantiating the formation of the isopropyl alcohol complex. It should be emphasized that since $[\text{Os}^{\text{III}}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{CH}_3\text{CN})]^{3+}$ is partially consumed by the reaction with acetone, wave B integrates in fact for less than 2e⁻.

The fact that the product of reduction of acetone enters the coordination sphere of the metal as already noted in the early work⁵ merits comment. It implies intimate contact with the metal center in the act of reduction, the isopropyl alcohol occupying the position vacated by H₂ (H⁺H⁻). The experiment of ref 5 was done with $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-H}_2)](\text{OTf})_2$, acetone being added to the medium. We have repeated this kind of experiment with the tetraammine by dissolving $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-acetone})](\text{PF}_6)_2$ (1.0×10^{-2} M) in CD₃CN, containing 1.0 M (CH₃)₂CO, and treating it with an equivalent of [FeCp₂](OTf) solid. The blue color of the oxidizing agent is discharged within minutes, and the ¹H NMR spectrum taken after 20 min shows that 15% of the

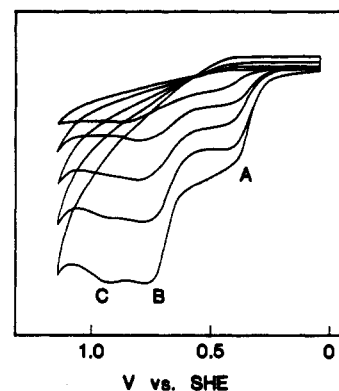
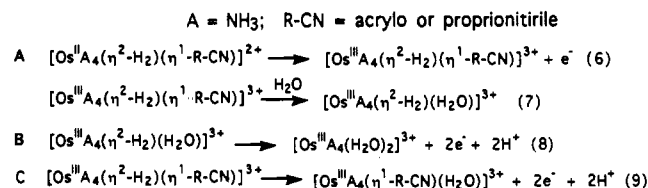


Figure 3. Cyclic voltammogram of $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_3\text{CH}_2\text{-CN})]^{2+}$ (5×10^{-3} M). Conditions: 0.10 M HOTF/0.40 M LiOTf aqueous solution; scan rates 10, 20, 50, 100, and 200 mV/s; initial anodic scan.

Scheme 3



expected product, isopropyl alcohol, appears free in solution.¹⁵ The remainder is NMR silent, presumably because it remains bound to the paramagnetic Os(III) product.

Because in dried CD₃CN there is no ready source of protons, the outcome of the tracer experiment is demanded by simple stoichiometry. As a more rigorous test of intimate details of the mechanism of reduction of coordinated H₂, the oxidation of $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})]^{2+}$ by [FeCp₂](OTf) in a 0.10 M HOTF aqueous solution containing acetone (1.1 M) was carried out. In contrast to the oxidation of $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{CH}_3\text{CN})]^{2+}$ in CH₃CN, that in water is so rapid that it was conducted as a titration. Moreover, a bis(electron) change is observed as reported for the similar oxidation without added acetone.¹⁶ Were an $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})]^{3+}$ or the corresponding isopropyl species intercepted by reduction of H₂ by acetone, a mono(electron) change on the metal would be observed. Ferrocenium ion is incapable of oxidizing $[\text{Os}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ in acid solution.

The cyclic voltammogram of the acrylonitrile complex, $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_2=\text{CHCN})]^{2+}$ (5), in a 0.40 M LiOTf/0.10 M HOTF aqueous solution shows three irreversible anodic waves as described in Table 2. The trace is characteristic of a dihydrogen complex with one oxidation wave that integrates for one electron at +0.60 V vs SHE, corresponding to the following mono(electron) reaction: $[\text{Os}^{\text{II}}(\eta^2\text{-H}_2)(\eta^1\text{-acrylonitrile})]^{2+} \rightarrow [\text{Os}^{\text{III}}(\eta^2\text{-H}_2)(\eta^1\text{-acrylonitrile})]^{3+} + \text{e}^-$. At more positive potentials, additional waves are observed at +0.88 and +1.04 V vs SHE, not necessarily of equal amplitude, which integrate for two electrons. Similar behavior was observed for $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\eta^1\text{-CH}_3\text{CH}_2\text{CN})]^{2+}$, (6), and we can conclude that nitrile(η¹)-to-olefin(η²) rearrangement in the 3+ state is not the cause of the behavior. The propionitrile complex gives rise to a mono(electron) oxidation at +0.44 V vs SHE (wave A, Figure 3) and two more waves at +0.77 (B) and +0.94 V (C) vs SHE, together integrating for two electrons. Of the three other possibilities which have occurred to us, replacement of the nitrile by water, (η¹)-to-nitrile(η²) isomerization, and trans-to-cis isomerization, the most likely appears to be the first. The electrochemical response as a function of scan rate is consistent with this hypothesis. At the slowest scan rate, the wave at the higher potential is barely noticeable,

(15) ¹H NMR data for isopropyl alcohol in CD₃CN, δ (ppm): 3.3, m, 1H. The doublet is masked by the solvent peak at 1.93 ppm.

(16) Li, Zai-Wei; Yeh, A.; Taube, H. *J. Am. Chem. Soc.* 1993, 115, 10384.

while that at lower potential it is augmented indicating that the conversion of **5** in the 3+ state to $[\text{Os}^{\text{III}}(\text{NH}_3)_4(\eta^2\text{-H}_2)(\text{H}_2\text{O})]^{3+}$ is almost complete by the time the second stage of oxidation begins (Scheme 3). Even though this appears to be the most likely alternative, the high lability of an Os(III) species to substitution at first sight is unexpected. The labilization of the π -acid ligand by another is well documented in the chemistry of Ru(II).¹⁷ There are many indications in the behavior of Os(III) amines for a considerable degree of back-bonding, including

(17) Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1976**, *15*, 3070.

the high kinetic stability (and perhaps equilibrium stability) of the η^2 -acrylic acid complex to rearrange to the η^1 -form and to resist aquation as described in related work.⁶

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