energy absorptions (E_{abs} (eV)) versus the difference in redox potentials between the metal-based oxidation (Os(II)/(III)) and first bridging-ligand-based reduction (BL/BL^-) ($\Delta E_{1/2} = E_{1/2}(Os^{II/III}) - E_{1/2}(BL/BL^-)$) should be linear if the same $d\pi-\pi^*$ MLCT orbitals are involved in both the optical and electrochemical processes. A plot of E_{abs} (eV) vs $\Delta E_{1/2}$ (V) for the three bimetallic complexes reported herein as well as for the previously reported monometallic complexes[7] $[Os(bpy)_3]^{2+}$, $[Os(bpy)_2(dpp)]^{2+}$, $[Os(bpy)_2(dpq)]^{2+}$, and $[Os(bpy)_2(dpb)]^{2+}$ yielded a linear least-squares analysis of

$$E_{abs} = 1.0395\Delta E_{1/2} + 0.4710 \qquad r = 0.995$$

where r is the correlation coefficient. Analysis of the equation shows that the slope is nearly equal to unity, as was to be expected,[7,39,41,42] and supports our assertion that the lowest energy absorptions are indeed MLCT in character. Continuing study of these complexes and their higher order polymetallic derivatives will be the subject of a forthcoming report.

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Reduction of $[Os(NH_3)_5(\eta^1\text{-}CH_3CN)]^{2+}$ to $[Os(NH_3)_5(\eta^2\text{-}CH_3CH{=}NH_2)]^{3+}$

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The reduction of $[Os(NH_3)_5(CH_3CN)](O_3SCF_3)_3$ or of $[Os(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$ in acetonitrile by zinc amalgam yields a product of composition corresponding to the formula $[Os(NH_3)_5(\eta^2\text{-}CH_3CH{=}NH_2)](O_3SCF_3)_3$ (**4**). Proton NMR spectroscopy shows a large splitting between cis and trans ammines and for the heteroligand shows a pattern consistent with the structure proposed. In particular three equivalent protons and one other proton are not exchangeable with deuterium in methanol-d_4 while two protons, inequivalent as observed in acetonitrile-d_3, are. Although some **4** is formed also in dried CH_3CN, the yield is much increased when a small amount of water is added. Compound **4** is quite stable in solution in DME, but when Proton Sponge (1,8-bis(dimethylamine)naphthalene) is added, deprotonation to produce $[Os(NH_3)_5(CH_3CH{=}NH)]^{2+}$ takes place, which then disproportionates to yield the acetonitrile complex as one of the products. The value of pK_a for the corresponding protonation–deprotonation equilibrium quotient, $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2C{=}NH_2)]^{3+} = [Os(NH_3)_5(\eta^1\text{-}(CH_3)_2C{=}NH)]^{2+} + H^+$, for the more stable analogue derived from acetone in water at room temperature was measured as 10.3 ± 0.2.

Introduction

Earlier work has shown that when acetone binds to $Os(NH_3)_5^{2+}$, the η^2-mode is strongly favored.[1,2] Moreover, since it appears that $[Os(NH_3)_5(\eta^2\text{-acetone})]^{2+}$ is the most stable η^2-acetone complex to have been prepared, it is expected that imines would also bind to $Os(NH_3)_5^{2+}$ in like fashion. Although other examples of this type of binding have been reported,[3] in the few examples from these laboratories, η^1-binding of imines to $Os(NH_3)_5^{2+}$ prevails.[4] This is also the case for acetonitrile,[5,6] and again there are several examples of η^2-binding, to other metal centers, even of unactivated nitriles.[7]

In continuing the investigation of the osmium ammine nitriles, we have discovered conditions under which the reduction of $[Os(NH_3)_5(CH_3CN)]^{3+}$ or of $[Os(NH_3)_5(O_3SCF_3)]^{2+}$ in the presence of acetonitrile takes a course different from that reported.[5,6] On the basis of evidence to be presented herein, we infer that an η^2-iminium adduct of $[Os(NH_3)_5]^{2+}$ is produced.

Experimental Section

Materials. Molecular sieve (3 Å) was obtained from Aldrich and activated by heating at 200 °C for 20 h under vacuum before use. Acetonitrile was purified by refluxing it over P_2O_5, after which it was distilled from anhydrous K_2CO_3. For the driest solvent, the resulting liquid was stored over molecular sieve and dispensed as needed.

Zinc amalgam was prepared from the granular form (30 mesh), this being first activated by pretreatment with 3 M HCl for 20 min, after which it was left in contact with saturated $HgCl_2(aq)$ for 30 min. The solid was washed thoroughly with water, washed with acetone and diethyl ether, and then was dried at 150 °C under vacuum for 20 h. Sodium trifluoromethanesulfonate was purchased from Alfa Chemical and was dried at 150 °C under vacuum. Acetonitrile-d_3 was obtained from Aldrich and dried over activated molecular sieve. No trace of water was observed by ^1H NMR spectroscopy. Acetone was purified by vacuum distillation over B_2O_3.[8] Ether was obtained from Aldrich (Sure Seal) and dried over NaH when necessary. All other chemicals were purchased from Aldrich and used as obtained. Buffer solutions were made up according to literature specifications.[9]

All solvents were deoxygenated by purging with dry argon, and reactions were carried out under argon atmosphere in a Vacuum Atmospheres Corp. glovebox.

Instrumentation. ^1H NMR spectra were obtained on Varian XL-400 (400-MHz) and Gemini (200-MHz) spectrometers. Internal references were used when estimating reaction yields. Electrochemical measurements were made under argon; as apparatus a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer was used. Cyclic voltammograms were recorded with a Pt^0 working electrode (1 mm^2), a Pt^0 counter electrode, and a reference that was calibrated with the ferrocenium/ferrocene couple (0.545 V vs NHE). All potentials are reported vs this couple. UV–vis spectra were recorded in quartz cells at room temperature on a Hewlett-Packard Model 8452A diode array spectrophotometer.

Preparation of Compounds. $[Os(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$ (**1**) was prepared as described in the literature.[10]

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$[Os(NH_3)_5(\eta^1\text{-}CH_3CN)](O_3SCF_3)_3$ (2) was obtained by the method described by Lay et al.[5] and also by a modified method herewith outlined. Compound 1 (500 mg) was dissolved in 25 mL of acetonitrile, and the solution was left for 12 h at room temperature, whereupon a white solid precipitated. This was separated, and 100 mL of ether was added to the filtrate to induce further precipitation. The yield of product exceeded 80%.

$[Os(NH_3)_5(\eta^1\text{-}CH_3CN)](PF_6)_2$ (3). Zinc amalgam (6 g) was added to a solution of compound 2, 130 mg in 3 mL of H_2O. The solution, initially colorless, quickly turned light yellow. It was kept for 15 min and then passed through a frit, and saturated KPF_6 was added. A light yellow precipitate formed; this was collected on a frit and dried. The dried solid was dissolved in 10 mL of acetone, and the solution was, filtered to remove undissolved impurities. Ether (100 mL) was added to the filtrate to precipitate a light yellow powder which was collected on a frit. ^1H NMR (acetone-d_6): δ 3.78 (3 H), 3.62 (12 H), 2.97 (3 H). ^1H NMR (acetonitrile-d_3): δ 3.09 (br, 3 H, trans NH_3), 2.97 (br, 12 H, cis NH_3), 2.91 (s, 3 H, CH_3). ^1H NMR (D_2O): δ 2.74 (s, CH_3). $E_f = 0.24$ V (reversible in DME, 0.5 N NaOTf). The triflate salt was also prepared in this case following the literature method.[5]

$[Os(NH_3)_5(\eta^2\text{-}CH_3CH{=}NH_2)](O_3SCF_3)_3$ (4). Compound 2 (260 mg) dissolved in a mixture of 10 mL of CH_3CN and 60 mg of H_2O was reduced by zinc amalgam (6 g) for 21 h, during which time the originally colorless solution became yellow, and a finely divided precipitate formed. It was kept in suspension by agitation, and the liquid was withdrawn from the metal by a pipet. It was passed through a frit to collect the product, and the filtrate was evaporated to reduce the volume to precipitate a powder which added to the yield of 4. The remaining solution contained 2. The solid was dissolved in acetone (10 mL), and the solution was filtered through a coarse frit. Ether was added to the filtrate, and the resulting solid was collected on a frit. This solid was dissolved in acetonitrile, and the solution was passed through a fine frit to remove $Zn(OH)_2$. The yellow filtrate was condensed by evaporation to precipitate a solid which was again dissolved in acetonitrile and recrystallized by adding ether. Total yield: 64%. ^1H NMR (acetonitrile-d_3): δ 7.3 (br, 1 H, NH), 7.2 (br, 1 H, NH), 5.51 (m, 1 H, CH), 5.15 (br, 3 H, trans NH_3), 3.78 (br, 12 H, cis NH_3), 1.77 (d, 3 H, CH_3). ^1H NMR (acetone-d_6): δ 8.10 (br, 1 H, NH), 8.05 (br, 1 H, NH), 5.86 (m, 1 H, CH), 5.85 (br, 3 H, trans NH_3), 4.4 (br, 12 H, cis NH_3), 1.97 (d, 3 H, CH_3). ^1H NMR (methanol-d_4): δ 5.24 (q, 1 H, CH), 4.60 (br, 3 H, trans NH_3), 3.00 (br, 12 H, cis NH_3), 1.74 (d, 3 H, CH_3). ^1H NMR (D_2O): δ 5.35 (br, 3 H, trans NH_3), 5.15 (q, 1 H, CH, $J = 5.6$ Hz), 3.92 (br, 12 H, cis NH_3), 1.56 (d, 3 H, CH_3). Anal. Calcd for $C_5H_{21}N_6OsS_3F_9O_9$: C, 7.83; H, 2.76; N, 10.96. Found: C, 7.88; H, 2.76; N, 10.36.

$[Os(NH_3)_5((CH_3)_2C{=}NH)](O_3SCF_3)_2$ (5) was synthesized by the literature method.[4]

$[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2C{=}NH_2)](O_3SCF_3)_3$ (6). To 4.3 mg of 5 in acetonitrile-d_3 (530 mg) was added ca. 5 mg of HO_3SCF_3 cautiously. The color of the solution changed promptly from orange to light yellow. This process was also monitored by cyclic voltammetry and ^1H NMR spectroscopy. No attempt was made to separate a solid. ^1H NMR (acetonitrile-d_3): δ 7.22 (br, 2 H, NH_2), 4.95 (br, 3 H, trans NH_3), 3.63 (br, 12 H, cis NH_3), 1.69 (s, 6 H, CH_3).

Results

In earlier work on the preparation of $[Os(NH_3)_5(CH_3CN)]^{2+}$, magnesium was used as a reducing agent, acting on $[Os(NH_3)_5(O_3SCF_3)](O_3SCF_3)_2$[5] dissolved in spectrophotometric grade CH_3CN containing some HO_3SCF_3 or on $[Os(NH_3)_5(CH_3CN)](O_3SCF_3)_3$[6] dissolved in acetone. In either case, the solid product separated was found to have CH_3CN bound to Os(II) in the orthodox manner and no evidence was obtained for the alternative reaction route involving reduction of CH_3CN, which we have encountered on using zinc amalgam as reducing agent.

Most of the evidence supporting the formulation of the new cation as containing $[CH_3CH{=}NH_2]^+$ bound to $[Os(NH_3)_5]^{2+}$ in the η^2-mode is summarized in the preparative section. Elemental analysis of 4 is consistent with the formula $[Os(NH_3)_5(CH_3CHNH_2)](O_3SCF_3)_3$, indicating that the cation carries a 3+ charge. Proton NMR spectroscopy of 4 dissolved in acetonitrile-d_3 shows three ammine protons at $\delta = 5.15$ and twelve at 3.78. The large splitting indicates that the heteroligand is bound in the η^2 mode, the only reasonable possibility when a double bond exists between C and N, and the nitrogen bears two protons. Three equivalent protons ($\delta = 1.77$ in acetonitrile-d_3) are retained in methanol-d_4 as solvent and are assigned to CH_3; the single proton at $\delta = 5.51$ is retained in methanol-d_4 and is assigned to CH. In acetonitrile, single protons are observed at $\delta = 7.3$ and at $\delta = 7.2$. These signals are broad, are lost in methanol-d_4, and are assigned to N–H. Their inequivalence shows that NH_2 is not free to rotate about the C–N bond.

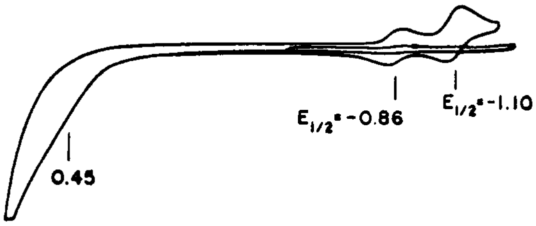

Figure 1. Cyclic voltammogram for the iminium complex $[Os(NH_3)_5(\eta^2\text{-}CH_3CHNH_2)]^{3+}$. Conditions: concentration of the compound ~10 mM in D_2O; supporting electrolyte, 1 M NaO_3SCF_3; room temperature; sweep rate, 200 mV s^{-1}. The reference for the values of $E_{1/2}$ is the ferrocenium/ferrocene complex ($E°$ vs NHE = 0.545).

Though the acetonitrile used as solvent in the first experiments was purportedly dry, the cation of 4 was observed in the product mixture but in variable yield in attempts at replication. The fact that the product heteroligand contains three more hydrogen atoms than does CH_3CN suggested that the variability was caused by variations in water content. A large increase in yield to 60% was observed on reducing $[Os(NH_3)_5(CH_3CN)]^{3+}$ in 10 mL of CH_3CN containing 0.06 mL of H_2O (not necessarily the optimum composition). Under the conditions of the preparation of 3 with D_2O as solvent, the yield of the cation of 4 was less than 1%, as determined by ^1H NMR spectroscopy in the product solution.

Remarkably, even the protons of the metal coordination sphere can be called on for reaction. When $[Os(NH_3)_5(O_3SCF_3)]^{2+}$ is reduced in dried (kept over molecular sieve) acetonitrile-d_3, after 6 h 4 was recovered in 8% yield. The CH peak at $\delta = 5.51$ and the NH peaks at $\delta = 7.2$ and 7.3 appeared in the ^1H NMR spectrum, but no signal at $\delta = 1.99$, corresponding to CH_3. That the source of the three protons is not residual H_2O in the solvent is indicated by an experiment in which the reduction of $[Os(NH_3)_5(CH_3CN)]^{2+}$ (compound 3) by zinc amalgam was attempted. No trace of 4 was observed after the same interval of time had elapsed. The ammine proton acidity of $[Os(NH_3)_5(CH_3CN)]^{3+}$ is expected to be much greater than that of $[Os(NH_3)_5(CH_3CN)]^{2+}$, and it is not surprising that the former, but not the latter species, can supply protons.

In Figure 1, the electrochemical behavior of 4 dissolved in D_2O is shown. There is no electrochemical response between −1.35 and −0.05 V. Above 0.15 V, an oxidizing current sets in, without the appearance of a well-defined wave. When the potential sweep is carried to 0.45 V and reversed, a reversible reduction wave appears at $E_{1/2} = -1.10$ V (the corresponding trace is not shown in Figure 1), which, by reference to earlier work,[4] we assign to $[Os(NH_3)_5(\eta^1\text{-}CH_3CH{=}NH)]^{3+/2+}$. When osmium is oxidized to the 3+ state, it is expected that a proton will be lost from $[CH_3CH{=}NH_2]^+$ and that the resulting imine will adopt the η^1-configuration. When the oxidation is carried beyond 0.45 V, an additional reversible peak appears, now at $E_{1/2} = -0.86$ (see Figure 1), which we assign to the $[Os(NH_3)_5(CH_3CN)]^{3+/2+}$ couple.

Though the success of the preparative method with water as the source of protons shows that $[Os(NH_3)_5(\eta^2\text{-}CH_3CH{=}NH_2)]^{3+}$ can coexist with low concentrations of OH^-, we find that it can be deprotonated. We observed that when Proton Sponge in considerable excess was added to a solution of 4 in DME (0.5 N NaO_3SCF_3), the peak in cyclic voltammetry which we ascribe to the $[Os(NH_3)_5(CH_3CH{=}NH)]^{3+/2+}$ couple gradually decreased and that which we ascribe to $[Os(NH_3)_5(CH_3CN)]^{3+/2+}$ gradually increased in amplitude ($t_{1/2} \sim 2$ h), even though the oxidation sweep was not carried to potentials positive enough to generate the nitrile complex electrochemically. Other unidentified peaks also appeared; earlier work[4] has shown that the complex $[Os(NH_3)_5(CH_3CH{=}NH)]^{2+}$ (7) is unstable to disproportionation.

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The electrochemical behavior shows that one product is the acetonitrile complex; another may be the ethylamine complex, but this has not been proven.

We set out to measure the deprotonation equilibrium between an η^2-iminium complex and chose to measure the corresponding imine complex equilibrium quotient for the imine derived from acetone, earlier work[4] having shown that this is much more stable than 7.

$$[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2C{=}NH_2)]^{3+} = [Os(NH_3)_5(\eta^1\text{-}(CH_3)_2C{=}NH)]^{2+} + H^+ \quad (1)$$

To this end, we recorded the absorption spectrum of **5** in a series of aqueous buffer solutions covering the range pH = 13 to pH = 0. In each of these extremes, the absorption is independent of pH over a range. In 0.1 M NaOH, **5** shows an absorption maximum at 212 nm ($\epsilon = 3.6 \times 10^4$ M^{-1} cm^{-1}) but at pH = 8 and lower, there is no significant absorption in this wavelength region. Measurements at room temperature in the intermediate pH range yielded for the pK_a of the acid $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2C{=}NH_2)]^{3+}$ the value of 10.3 ± 0.2.

Discussion

There are only a few examples of complexes in which an iminium cation, at least singly protonated on the nitrogen, is bound to a metal atom.[11] Our review of the literature suggests that in no case has the iminium ligand been generated by protonation of the imine nor has an equilibrium of the type represented by (1) been reported. Our work with the imine derived from acetone sets only a lower limit on the pK_a for reaction 2. The pK_a value for reaction 2 will be increased over that for reaction 1 by the pK for (3) (the sum of reactions 1 and 3 is reaction 2).

$$[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2C{=}NH_2)]^{3+} \rightarrow [Os(NH_3)_5(\eta^2\text{-}(CH_3)_2C{=}NH)]^{2+} + H^+ \quad (2)$$

$$[Os(NH_3)_5(\eta^1\text{-}(CH_3)_2C{=}NH)]^{2+} = [Os(NH_3)_5(\eta^2\text{-}(CH_3)_2C{=}NH)]^{2+} \quad (3)$$

The high proton affinity of an η^2-bound imine suggests that conversion of such imines to η^2-iminium derivatives by the action of carbonium ion donors can be realized.

Not understood is the difference in the action of the reducing agent Mg(0) ion on the one hand and zinc amalgam on the other. A possibility is that Mg rapidly scavenges protons, so that the reduction to imine, which requires protons, is disfavored. Nor is it at all clear why the yield of the iminium adduct is much reduced when the reaction medium changes from almost pure acetonitrile to water. It is unlikely that this behavior is attributable to a lower driving force for the reaction in water compared to acetonitrile. The 2e reduction of the acetonitrile complex to the iminium is represented by the equation

$$Zn + 3H_2O + [Os(NH_3)_5(CH_3CN)]^{2+} = Zn(OH)_2 + [Os(NH_3)_5(CH_3{-}CH{=}NH_2)]^{3+} + OH^-$$

The activity of the solids is unaffected by a change in solvent. Both because water is a reactant and because the ionic products are expected to be stabilized relative to the ionic reactant when water replaces acetonitrile as the solvent, the driving force is expected to be greater in water. It seems rather certain that the effect of the solvent change on the chemistry is a matter of mechanism rather than equilibrium stability.

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MLCT-dd Energy Gap in Pyridyl-Pyrimidine and Bis(pyridine) Complexes of Ruthenium(II)

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The photophysical and photochemical properties of a series of 2-(2′-pyridyl)pyrimidine and bis(pyridine) polypyridyl complexes of ruthenium(II) are described. The temperature dependences of the emission decay were fit to the equation $1/\tau(T) = k_1 + k_2 \exp(-\Delta E_2/RT)$. The values of k_1 ranged from 7.1×10^5 to 8.7×10^6 s^{-1}, k_2 ranged from 9×10^6 to 3×10^{17} s^{-1}, and ΔE_2 ranged from 428 to 4776 cm^{-1}. A plot of ln k_2 vs ΔE_2, known as a Barclay-Butler plot, was linear with a slope of 2.9×10^{-3} cm and a y intercept of 5.9. The study demonstrates the usefulness of excited-state parameters for assessing the photolability and/or stability of ruthenium(II) pyridyl complexes. It has also led to the design of the photostable core "$[Ru(bpy)(bpz)]^{2+}$" which may be of value in the design of molecular assemblies.

Introduction

A number of studies on the properties of polypyridyl complexes, in our work[1-4] and the work of others,[5-13] have focused attention on the problem of photosubstitution. The mechanism of the reaction is thought to involve ligand loss and formation of a five-coordinate intermediate.[7] There is evidence that photosubstitution follows a general pattern based on the energy gap between the ^{3}MLCT state and the ground state.[2] In a recent study, the logarithm of the quantum yield for photosubstitution was found

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