similar reaction stoichiometry but reacts via a radical-based mechanism.[25] The effect of the substrate alkyl group structure on the reaction rates for this complex is the opposite of that observed for $Ni^{I}(OEiBC)^{-}$. Additionally, $Ni(tmc)^{+}$ does not react with tosylates.[25c] One might expect that the differences in mechanism arise from the different steric demands of tmc and OEiBC. The *N*-methyl groups adjacent to the metal in tmc could create too much steric congestion for nickel(I) to function effectively as a nucleophile. The nickel in OEiBC should be relatively unhindered. Pletcher has shown, however, that the reactivity order tertiary > secondary > primary still holds for a relatively unhindered nickel(I) tetraaza macrocyclic complex.[24a] (Strangely, this paper proposes a nucleophilic mechanism.[26]) Thus, it would appear that radical-based mechanisms are characteristic of nickel(I) tetraaza macrocyclic complexes.

The reactivity of $Ni^{I}(OEiBC)^{-}$ more closely resembles that of several low-valent tetrapyrrole complexes. Fe(I)[20] and Rh(II)[22b] porphyrins and Co(I)[35] corrins have been reported to react by nucleophilic mechanisms. The reactivity of the nickel complex still differs in several important respects. $Ni(OEiBC)^{-}$ is the only one of these complexes that does not form a stable, isolable alkyl complex. Aside from Co(I), the others react at rates several orders of magnitude lower than the nickel(I) complex. With the exception of $RFe^{III}(P)$, the alkyl complexes obtained are reduced at potentials negative of the couple for the parent, nonalkylated metal complex. Apparently, paramagnetic alkylmetal complexes are reduced at potentials positive of the parent couple while diamagnetic alkylmetal complexes are reduced at more negative potentials. Effective electrocatalysis requires a potential negative of the alkylmetal complex couple.[21] Rhodium porphyrin and cobalt porphyrin mediated electrocatalysis must therefore be run at potentials negative of that required for formation of the intermediate alkyl complex.

It is clear from the above discussion that $Ni^{I}(OEiBC)^{-}$ is particularly well suited to mediate electrocatalysis. It reacts rapidly, is an effective mediator at the potential of the Ni^{II}/Ni^{I} couple, and does not have long-lived (inert) alkyl intermediates that tie up the catalyst and slow the reaction.

Biological Significance of the Reactivity of $Ni^{I}(OEiBC)^{-}$. Investigations of the mechanism of methyl coenzyme M reductase are at a relatively early stage. Some evidence suggests that the nickel in F_{430} is redox active during the catalytic cycle.[9] Given what is known about the cofactors required for the reaction and the makeup of the enzyme, it is difficult to conceive a plausible mechanism for the reductive cleavage of *S*-methyl coenzyme M to methane that does not actively involve the nickel. Information about the reactivity of low-valent nickel complexes will be quite useful in defining the range of possible mechanisms for the enzyme. Therefore, the most important result of our investigation is the discovery that Ni^{I} can react by a two-electron nucleophilic pathway. Only radical-based mechanisms were established for nickel(I) prior to our study.

Nickel is not a particularly common element in biological systems. Its presence in these systems invites one to speculate about the reasons that it has been selected for this chemistry. Assuming that methylnickel F_{430} is an important intermediate in methanogenesis, our results suggest that nickel combines several desirable properties for the chemistry of interest. We have shown that $Ni^{I}(OEiBC)^{-}$ (and presumably by extention the nickel(I) form of F_{430}) is an extremely reactive nucleophile. It may in fact be sufficiently reactive that *S*-methyl coenzyme M can alkylate it. This substrate is unlikely to be reactive in radical-based mechanisms. When the system is poised at the potential required for reduction to nickel(I), the alkylnickel complex, once formed, will be readily reduced and cleaved.[55] This will not occur with the other biologically significant low-valent metal complex of sufficient nucleophilicity that reaction with *S*-methyl coenzyme M is a possibility. The alkyl complexes of vitamin B_{12} are too stable. In fact, the role of B_{12} has been described as being a reversible radical carrier.[56] An overly stable intermediate is not a desirable feature for rapid catalysis. Finally, a potential disadvantage of strong nucleophiles is that they are often strong bases. Protonation of this key intermediate would not be desirable. The sluggishness of the methyl tosylate reaction with $Ni^{I}(OEiBC)^{-}$ suggests that the latter is a rather soft base. Thus, nickel(I) may combine the properties of being a very strong nucleophile with being a weak base toward the proton.

Acknowledgment. We thank the Camille and Henry Dreyfus Foundation (Young Faculty Grant to A.M.S.), the Research Corp., and the National Institutes of Health (Grant No. GM33882) for support of this research. We also thank James Hoglen and Professor Thomas Hollocher for their assistance with GC and GC-MS analyses.

(55) It has not yet been established that the reduction potential of alkylnickel(III) complexes is invariably positive of the Ni^{II}/Ni^{I} couple.
(56) Halpern, J. *Science* **1985**, *227*, 869.

Redox-Coupled Linkage Isomerizations with η^2-Coordinated Anilines

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received February 1, 1988*

Abstract: In solution, the complex $[Os(NH_3)_5(PhNH_2)]^{2+}$ undergoes a linkage isomerization from its nitrogen-bound form to one in which the metal center engages the aromatic ring. Upon one-electron oxidation this η^2-coordinated species reverts to the nitrogen isomer. Through the utilization of this facile redox change, isomerization rates and the related thermodynamic parameters were determined for both valences of osmium, and comparisons are made with the results obtained in a similar investigation of the sterically encumbered *N,N*-dimethylaniline derivative.

Our interest in the chemistry of electron-rich metal centers containing saturated auxiliary ligands[1] has recently focused on the reactivity of pentaammineosmium(II) with unsaturated organic molecules.[2] Because of the great tendency for osmium(II) to back-bond,[1] many of these complexes feature coordination modes that differ from the corresponding osmium(III) analogues. Thus, aldehydes and ketones, which coordinate through the oxygen to

(1) Taube, H. *Pure Appl. Chem.* **1979**, *51*, 901.
(2) Harman, W. D. Ph.D. Thesis, Stanford University, 1987. Also see: Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101.

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pentaammineosmium(III), rapidly isomerize to adopt η^2-coordination upon the one-electron reduction of the metal.[3,4] In a similar fashion the sterically hindered O-bound 2,2-dimethylpropiophenone ligand isomerizes to form a stable η^2-arene complex on osmium(II).[4]

In the course of investigating the reactivity of pentaammineosmium(II) with substituted benzenes, we observed an unexpected isomerization of aniline in the complex $[Os(NH_3)_5(PhNH_2)]^{2+}$ from nitrogen to the aromatic ring. Upon oxidation, the π-bound ligand reverts to the N-bound form. Through utilization of this facile redox change, we hoped to determine isomerization rates for both valence states of osmium and ultimately the corresponding thermodynamic parameters. To assess the effects of steric encumbrance, we included the *N,N*-dimethylaniline derivative in our study.

Experimental Section

^{1}H NMR spectra were recorded on a Varian XL-400 spectrometer and are reported as ppm shifts from tetramethylsilane. Electrochemical experiments were performed under anaerobic conditions with a PAR Model 173 potentiostat driven by a Model 175 universal programmer. Cyclic voltammograms taken at fast scan rates (1–100 V/s) were recorded on a Tektronix single-beam storage oscilloscope. All voltammograms, unless otherwise noted, were measured from +1.0 to −1.5 V in a standard three-electrode cell[5] and are reported vs the normal hydrogen electrode. The reference electrode was calibrated with the ferrocene/ferrocenium couple ($E^\circ \equiv +0.55$ V (NHE)) as measured in situ.

First-order rate constants in the range 1.0–1000 s^{-1} were determined through cyclic voltammetry using the method of Nicholson and Shain.[6] Other rate constants were obtained through a plot of ln [A] vs time[7] where the decay of [A] was measured by cyclic voltammetry utilizing an in situ electroactive standard. Specific rates associated with the N $\rightleftarrows$ π isomerizations of $[Os(NH_3)_5(PhNH_2)](TFMS)_2$ in acetone-d_6 and DMSO-d_6 were determined with the method outlined by Espenson[7] for a reversible first-order reaction.

Reagents. The syntheses of the compounds $[Os(NH_3)_5(N\text{-}PhNH_2)](TFMS)_2$[8] (**1**), $[Os(NH_3)_5(\eta^2\text{-}PhNR_2)](TFMS)_2$[8] (**3**), and $[Os(NH_3)_5(CH_3CN)](TFMS)_2$[4] (TFMS$^-$ ≡ $CF_3SO_3^-$; R ≡ CH_3) have been described previously. $[Os(NH_3)_5(py)](TFMS)_2$ (py = pyridine) was prepared from the tetramethylbenzene precursor complex[9] as described by Cordone.[10] Acetone was purified by vacuum distillation over B_2O_3[11] and Et_2O and 1,2-dimethoxyethane (DME) by distillation over NaK alloy.[12] *N,N*-Dimethylacetamide (DMA) and *N*-methylpyrrolidinone (NMP) were dried over BaO and refluxed from triphenylsilyl chloride.[13] The amides were then refluxed with CaH_2 for 24 h and redistilled to remove traces of HCl. Aniline and *N,N*-dimethylaniline were refluxed over CaH_2 for 24 h and distilled. DMSO was dried over molecular sieves. NaTFMS was recrystallized three times from acetone and Et_2O, and tetrabutylammonium hexafluorophosphate (TBAH), from methanol and water. All solvents were deoxygenated and all reactions carried out under argon in a Vacuum Atmospheres Co. glovebox.

Preparation of $[Os(NH_3)_5(\eta^2\text{-}PhNH_2)](TFMS)_2$ (2). A total of 50 mg of **1** was dissolved in 2.0 mL of DMSO, and the resulting solution allowed to stand for 5 h. The addition of 10 mL of Et_2O resulted in the formation of an orange-red oil, which was separated from the ether layer and redissolved in 1.0 mL of acetone. When Et_2O was added to this solution, a reddish precipitate formed, which was collected and washed with Et_2O.

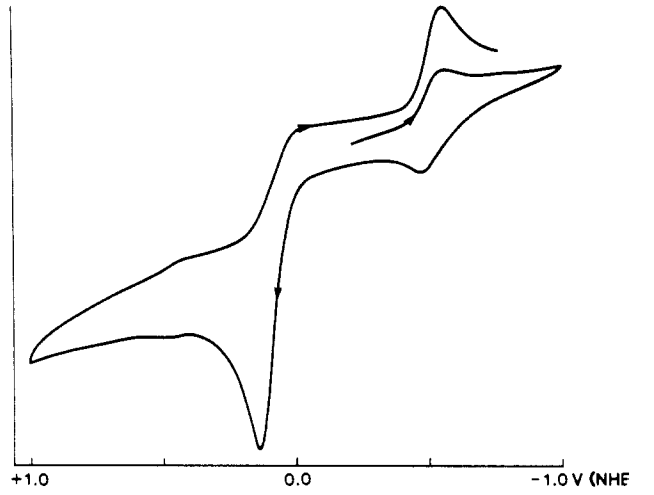

Figure 1. Cyclic voltammogram of $[Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{2+}$ recorded in acetone at 100 mV/s.

On the basis of cyclic voltammetry, we conclude that approximately 90% of the aniline complex is converted to the η^2 isomer by this procedure. E_{pa} = +0.13 V (NHE; 100 mV/s; 1 M TBAH in acetone). ^{1}H NMR: 6.40 (2 H, m); 5.58 (1 H, d); 5.32 (1 H, t); 5.10 (1 H, d), 4.98 (2 H, b); 4.75 (3 H, b); 3.58 (12 H, b).

Results

I. Aniline. When pentaammineosmium(II) is generated in a DME solution of aniline,[8] a yellow-orange precipitate appears corresponding to the nitrogen-bound pentaammine(aniline)osmium(II) complex **1**. The ^{1}H NMR spectrum of this material in acetone-d_6 confirms this stoichiometry, showing resonances for both *cis*- and *trans*-ammines (3.78 (12 H, b) and 3.90 (3 H, b) ppm, respectively) and aniline, the latter appearing slightly downfield from those of the free ligand.[14] A cyclic voltammogram of **1**[15] features a reversible couple with $E_{1/2}$ = −0.54 V. This potential is similar to that found for other $[Os(NH_3)_5L]^{3+/2+}$ redox couples in which L is not a π acceptor[16] (e.g. NH_3, H_2O, DME). Over time, both NMR and cyclic voltammetry indicate the formation of a new species in solution. In contrast to that observed for **1**, the ^{1}H NMR spectrum of this new material (**2**) features five inequivalent aromatic proton resonances ranging from 6.4 to 5.1 ppm, the chemical shifts bearing close resemblance to those observed for $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$.[17] The cyclic voltammogram of **2** is also similar to the benzene analogue, displaying a chemically irreversible oxidation wave at 0.13 V on initial anodic scan (v = 100 mV/s)[15] (Figure 1). Subsequent scanning reveals that, upon oxidation, **2** reverts back to the oxidized form of the nitrogen-bound aniline complex (**1**). On the basis of these findings, compound **2** is assigned to be an isomer of **1** in which the metal is coordinated η^2 to the arene ring.[18]

A fresh acetone-d_6 solution saturated with **1** was monitored over a 10-h period by ^{1}H NMR. During this time, an equilibrium was established between **1** and **2**, slightly favoring the nitrogen-bound isomer (**1**).

$$[Os(NH_3)_5(N\text{-}PhNH_2)]^{2+} \rightleftarrows [Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{2+}$$

$$K_{eq} = 0.50 \pm 0.05$$

When this system is treated as reversible first order, specific rates for the N → π and π → N isomerizations are calculated to be $k_1 = (2.3 \pm 0.4) \times 10^{-5}$ s^{-1} and $k_{-1} = (4.6 \pm 0.4) \times 10^{-5}$ s^{-1}, respectively. From the equilibrium constant, the free energy

(3) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223–8227.
(4) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.
(5) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980; p 23. Unless otherwise noted, cyclic voltammograms are recorded at 100 mV/s in a 1 M solution of NaTFMS using a Pt^0 working electrode.
(6) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. Also see: Reference 5, pp 452–454.
(7) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 12, 42.
(8) Harman, W. D.; Sekine, M.; Taube, H., accepted for publication in *J. Am. Chem. Soc.*
(9) Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917.
(10) Cordone, R. Ph.D. Thesis, Stanford University, 1988.
(11) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.
(12) Purchased from Aldrich Chemical Co. as an 80% K^0 alloy.
(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Oxford: New York, 1980.
(14) ^{1}H NMR of **1** in acetone-d_6: 7.32 (t, 2 H), 7.02 (t, 1 H), 7.05 (d, 2 H), 7.04 (b, 2 H), 3.78 (b, 12 H), 3.90 (b, 3 H).
(15) Cyclic voltammogram recorded in a 1 M TBAH acetone solution.
(16) Gulens, J.; Page, J. A. *J. Electroanal. Chem., Interfacial Electrochem.* **1974**, *55*, 239. Also see: Reference 2.
(17) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883.
(18) The similarity found between the NMR spectra of **2** and **3** suggests that the former complex exists as the 2,3 η^2 isomer.

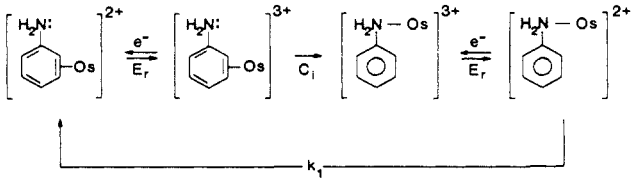

Figure 2. Redox-induced linkage isomerization for the complex $[Os(NH_3)_5(PhNH_2)]^{2+}$.

of isomerization at 20 °C is calculated to be $\Delta G^\circ = 0.40 \pm 0.05$ kcal/mol. Substitution by solvent acetone was not observed over a 10-h period. Taking into account the substitution-inert nature of $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2CO)]^{2+}$,[3] we conclude that both N $\rightleftarrows$ π isomerizations are intramolecular.

When the experiment is repeated in DMSO-d_6, an equilibrium is established in which the η^2-bound isomer dominates ($K_{eq} = 9 \pm 1$). Evaluation as a reversible first-order reaction yields N $\rightarrow$ π and $\pi \rightarrow$ N specific rates of $(2.0 \pm 0.2) \times 10^{-4}$ and $(2.2 \pm 0.2) \times 10^{-5}$ s^{-1}, respectively, which correspond to a free energy for N $\rightarrow$ π isomerization of $\Delta G^\circ = -1.3 \pm 0.1$ kcal/mol at 20 °C. Thus, a difference of 1.7 kcal/mol can be attributed to solvent effects alone for this system.

The voltammetric oxidation of **2** at 100 mV/s can be treated as a reversible electrochemical reaction followed by an irreversible chemical one (Figure 1).[19] Variation of the scan rate in this regime produces the expected shift in $E_{p,a}$ for an E_rC_i system operating in the pure kinetic limit.[20] Fast scan rates (20–100 V/s) reveal that the oxidized product $[Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{3+}$ isomerizes to the nitrogen-bound isomer at a rate of $k_{-2} = (1.8 \pm 0.5) \times 10^2$ s^{-1}. Knowledge of this specific rate leads to an accurate determination of $E_{1/2} = 0.16 \pm 0.02$ V in acetone[21] for the $[Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{3+/2+}$ couple. Similar results are obtained when the electrochemistry is investigated in NMP.[22] In short, the combined actions of metal oxidation followed by reduction induce the quantitative conversion of the π-bound aniline complex to the nitrogen analogue (Figure 2).

Consideration of the redox potentials for both η^1 and η^2 isomers along with the N $\rightarrow$ π isomerization energy for osmium(II) yields the corresponding isomerization energy for osmium(III) in acetone.

$$[Os(NH_3)_5(N\text{-}PhNH_2)]^{3+} + e^- = [Os(NH_3)_5(N\text{-}PhNH_2)]^{2+} \quad (-0.54\text{ V})(-F)$$

$$[Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{2+} = [Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{3+} + e^- \quad -(0.16\text{ V})(-F)$$

$$[Os(NH_3)_5(N\text{-}PhNH_2)]^{2+} = [Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{2+} \quad 0.40\text{ kcal/mol}$$

$$[Os(NH_3)_5(N\text{-}PhNH_2)]^{3+} = [Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{3+} \quad \Delta G^\circ = +16.5\text{ kcal/mol}$$

A standard free energy of 16.5 ± 0.7 kcal/mol at 20 °C corresponds to an equilibrium constant of 4×10^{-13} for

$$[Os(NH_3)_5(N\text{-}PhNH_2)]^{3+} \rightleftarrows [Os(NH_3)_5(\eta^2\text{-}PhNH_2)]^{3+}$$

This value together with that of k_{-2} leads to a specific rate of $k_2 = 8 \times 10^{-11}$ s^{-1} ($pk_2 = 10.1 \pm 0.6$) for N $\rightarrow$ π isomerization on osmium(III). These results are summarized in Figure 6.

II. *N,N*-Dimethylaniline. In contrast to the behavior observed for aniline, *N,N*-dimethylaniline coordinates to Os(II) exclusively at the arene. Homonuclear decoupling experiments reported in a separate publication[8] conclusively show that the metal occupies the 2,3 η^2 position and is static on the NMR time scale. A high correlation exists for the ^1H NMR ring resonances of **3** and **2**, suggesting that aniline is coordinated analogously.

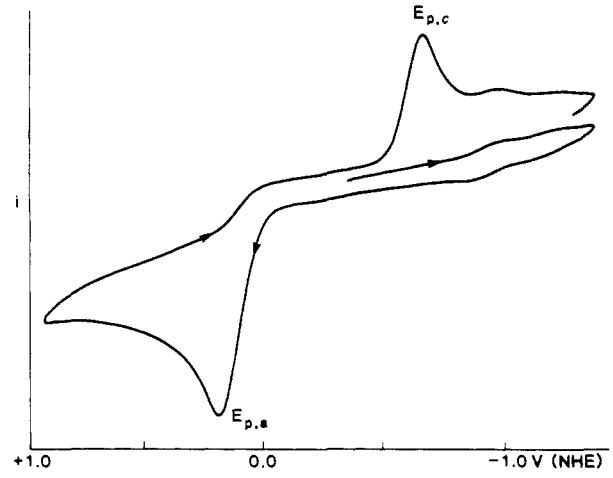

Figure 3. Cyclic voltammogram of $[Os(NH_3)_5(\eta^2\text{-}PhNR_2)]^{2+}$ recorded in acetone at 100 mV/s.

As is the case for the parent complex **2**, oxidation of **3** results in the rapid $\pi \rightarrow$ N isomerization of the organic ligand: A cyclic voltammogram recorded in acetone at 100 mV/s (Figure 3) shows an irreversible oxidation wave at $E_{p,a} = +0.16 \pm 0.02$ V. The subsequent cathodic scan reveals an irreversible reduction wave at $E_{p,c} = -0.40 \pm 0.02$ V, which is absent prior to oxidation. The potential of this peak is consistent with that for **1** and, hence, indicates the formation of a nitrogen-bound Os(III) species, which isomerizes upon reduction.

Repeated scanning fails to produce any of the substitution-inert solvent complex $[Os(NH_3)_5(\eta^2\text{-}(CH_3)_2CO)]^{2+}$. On the basis of this observation, we consider the N $\rightarrow$ π isomerization on osmium(II) to be intramolecular, as in the case of aniline. In light of the inert nature of pentaammineosmium(III) complexes,[23] the absence of substitution suggests an intramolecular process is operating for Os(III) as well. Cyclic voltammograms of **3** recorded in NMP and CH_3CN further support this conclusion.

At scan rates above 5 V/s, both the oxidation of **3** and the subsequent reduction of $[Os(NH_3)_5(N\text{-}PhNR_2)]^{3+}$ begin to appear chemically reversible. When the method of Nicholson and Shain[6] is used, specific rates of $k_1 = 8.3 \pm 2.0$ s^{-1} and $k_{-2} = 3.7 \pm 0.9$ s^{-1} can be extracted for the corresponding isomerizations in acetone.

$$[Os(NH_3)_5(N\text{-}PhNR_2)]^{2+} \xrightarrow{k_1} [Os(NH_3)_5(\eta^2\text{-}PhNR_2)]^{2+}$$

$$[Os(NH_3)_5(\eta^2\text{-}PhNR_2)]^{3+} \xrightarrow{k_{-2}} [Os(NH_3)_5(N\text{-}PhNR_2)]^{3+}$$

Both $E_{p,a}$ and $E_{p,c}$ in Figure 3 show the expected scan rate dependence at slow scan rates (≤100 mV/s) for an E_rC_i reaction operating in the pure kinetic limit.[20] Adjustment of the corresponding redox potentials for these coupled chemical reactions yields $E_{1/2}$ values of +0.14 ± 0.02 and −0.38 ± 0.02 V for the π- and N-bound species, respectively.

An important difference between the nitrogen- and π-bound isomers of the pentaammine(aniline)osmium(II) systems lies in their ability to act as reducing agents: Coordination of aniline at the nitrogen position greatly stabilizes Os(III) relative to the arene, which is a much weaker Lewis base. In contrast, the divalent metal center requires the η^2-coordination geometry in order to back-bond effectively. As a result, the osmium(III/II) redox potentials differ by more than 0.5 V for these isomers, with the N-bound isomer showing the greater reducing power. By allowing a solution of **3** to react with a homogeneous oxidant, {O}, having a potential between these values, we hoped to oxidize the N isomer selectively. Provided that the *direct* oxidation of the

(19) See: Reference 5, pp 429–465.
(20) See: Reference 5, pp 452–3.
(21) From the slow-scan data, values of $E_{p,a}$ measured at 20, 50, and 100 mV/s are averaged to determine $E_{1/2}$. Bard and Faulkner define the condition $kRT/nFv > 5$ for pure kinetic control, where v is the scan rate and k the specific rate for the coupled chemical reaction. This condition is met for $v \leq 100$ mV/s, and hence $E_{1/2}$ can be determined as described in ref 20.
(22) In NMP: $E_{1/2} = -0.02$ V; $k_{-2} = 4.5 \times 10^2$ s^{-1}.
(23) Taube, H. *Proc. R. Aust. Chem. Inst.* **1975**, *42*, 139.

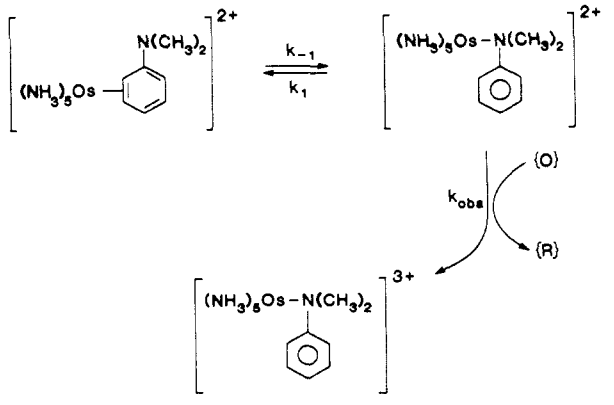

Figure 4. Homogeneous oxidation of $[Os(NH_3)_5(PhNR_2)]^{2+}$.

Table I. Kinetic Data for the Homogeneous Oxidation of $[Os(NH_3)_5(PhNR_2)]^{2+}$

redox couple: {O} + e⁻ = {R}	$E_{1/2}$, V	[{O}],[a] mM	[{R}],[a] mM	$k_{obsd} \times 10^5$, s^{-1}
$[Os(NH_3)_5(CH_3CN)]^{3+/2+}$	−0.30	3.0	4.8	2.0 ± 0.2
$[Os(NH_3)_5(CH_3CN)]^{3+/2+}$	−0.30	21	18	2.1 ± 0.2
$[Os(NH_3)_5(py)]^{3+/2+}$	−0.42	2.8	2.5	1.2 ± 0.2

[a] The initial concentration of $[Os(NH_3)_5(PhNR_2)]^{2+}$ is approximately equal to that of {O}.

arene isomer is avoided, the observed rate of oxidation for **3** should be a direct reflection of the specific rate of $\pi \rightarrow$ N isomerization (k_{-1}) on Os(II) (Figure 4). If electron transfer from the nitrogen isomer is substantially faster than the reverse isomerization (k_1), k_{obsd} will be independent of both concentration and potential of {O} and, hence, will be equal to the specific rate of isomerization, k_{-1}.

A series of experiments were performed in which an acetone solution of **3** was treated with an oxidant, {O}, in varying concentration and reduction potential. An equivalent amount of the reduced form of {O}, {R}, was included in order to suppress the direct oxidation of the π-bound isomer (see Table I). The rate of oxidation was monitored electrochemically over a period of several hours, and the results are shown in Figure 5 and Table I. When $[Os(NH_3)_5(CH_3CN)]^{3+}$ was used as the oxidant, a first-order decay was observed in which the reaction rate remained virtually constant for different concentrations. On the basis of these data, the specific rate, k_{-1}, for the $\pi \rightarrow$ N isomerization on osmium(II) is assigned the average value of $(2.0 \pm 0.2) \times 10^{-5}$ s^{-1}, a specific rate that is comfortably above that reported for solvent substitution.[2] When the weaker oxidant $[Os(NH_3)_5(py)]^{3+}$ is used, the observed rate decreases slightly, an observation that suggests that a limited amount of back-reaction occurs with the more potent reducing agent.

$$[Os(NH_3)_5(py)]^{2+} + [Os(NH_3)_5(N\text{-}PhNR_2)]^{3+} \rightarrow [Os(NH_3)_5(py)]^{3+} + [Os(NH_3)_5(N\text{-}PhNR_2)]^{2+}$$

The ratio of k_1 to k_{-1} leads to the free energy of N $\rightarrow \pi$ isomerization for *N,N*-dimethylaniline on Os(II): At 20 °C, the arene isomer is favored by 7.6 kcal/mol. When this value is considered along with the reduction potentials for the two isomers, the corresponding free energy for Os(III) is also derived.

$$[Os(NH_3)_5(N\text{-}PhNR_2)]^{3+} + e^- = [Os(NH_3)_5(N\text{-}PhNR_2)]^{2+} \quad (-0.38\ V)(-F)$$

$$[Os(NH_3)_5(\eta^2\text{-}PhNR_2)]^{2+} = [Os(NH_3)_5(\eta^2\text{-}PhNR_2)]^{3+} + e^- \quad -(0.14\ V)(-F)$$

$$[Os(NH_3)_5(N\text{-}PhNR_2)]^{2+} = [Os(NH_3)_5(\eta^2\text{-}PhNR_2)]^{2+} \quad -7.5\ kcal/mol$$

$$[Os(NH_3)_5(N\text{-}PhNR_2)]^{3+} = [Os(NH_3)_5(\eta^2\text{-}PhNR_2)]^{3+} \quad \Delta G^\circ = 4.5 \pm 0.4\ kcal/mol$$

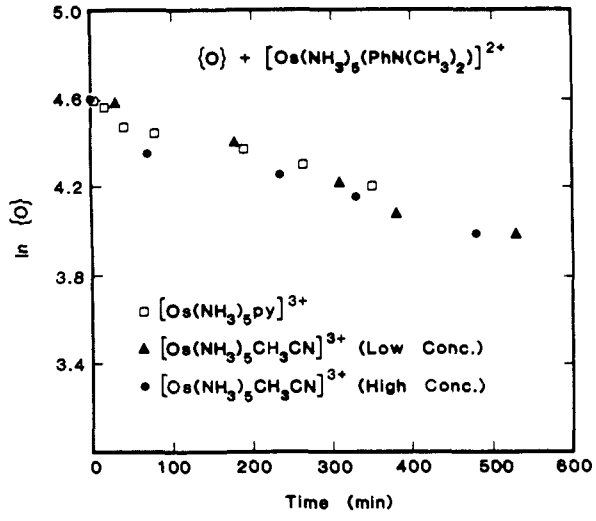

Figure 5. Kinetic data for the homogeneous oxidation of $[Os(NH_3)_5(PhNR_2)]^{2+}$.

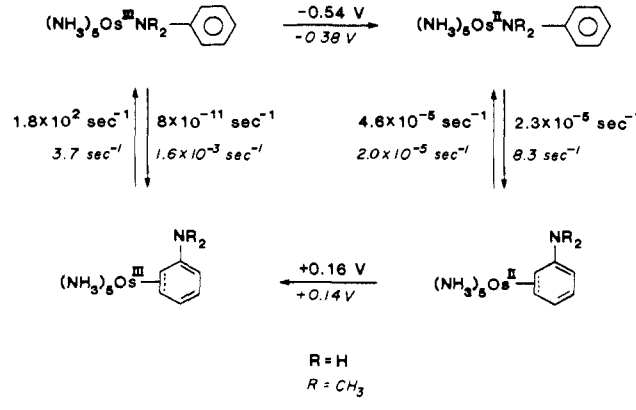

Figure 6. Comparison of linkage isomerization processes for aniline and *N,N*-dimethylaniline.

At 20 °C this corresponds to a equilibrium quotient of 2.3×10^3 for

$$[Os(NH_3)_5(\eta^2\text{-}PhNR_2)]^{3+} \rightleftarrows [Os(NH_3)_5(N\text{-}PhNR_2)]^{3+}$$

On combining this value with k_{-2}, we calculate for k_2 a specific rate of $k_2 = 1.6 \times 10^{-3}$ s^{-1} ($pk_2 = 2.79 \pm 0.3$) for N $\rightarrow \pi$ isomerization on Os(III). These results are summarized in Figure 6.

Discussion

Relative to most organometallic complexes, a metallopentaammine would be considered sterically encumbered. For the methylated aniline complex, **3**, these steric effects are striking: Relative to arene coordination, the replacement of the amine protons by methyl groups destabilizes the nitrogen-bound isomer by 8.0 kcal/mol when coordinated to Os(II) and 12.1 kcal/mol for the trivalent species. This greater sensitivity of Os(III) to amine substituents is also manifested in the reduction potentials of the nitrogen isomers: $E_{1/2}$ values differ by 160 mV for aniline and *N,N*-dimethylaniline, whereas for the arene species these values are virtually equivalent. The relative preference of Os(III) for the unsubstituted aniline nitrogen can be directly expressed by combining the two nitrogen–isomer half-reactions.

$$[Os(NH_3)_5(N\text{-}PhNR_2)]^{3+} + e^- = [Os(NH_3)_5(N\text{-}PhNR_2)]^{2+} \quad (-0.38\ V)(-F)$$

$$[Os(NH_3)_5(N\text{-}PhNH_2)]^{2+} = [Os(NH_3)_5(N\text{-}PhNH_2)]^{3+} + e^- \quad -(-0.54\ V)(-F)$$

$$[Os(NH_3)_5(N\text{-}PhNR_2)]^{3+} + [Os(NH_3)_5(N\text{-}PhNH_2)]^{2+} = [Os(NH_3)_5(N\text{-}PhNH_2)]^{3+} + [Os(NH_3)_5(N\text{-}PhNR_2)]^{2+} \quad \Delta G^\circ = -3.7\ kcal/mol$$

Similar findings have been reported in the case of pentaammineruthenium: Equilibrium studies have shown that the Ru(III) metal center is more sensitive to amine substituents than the divalent analogue.[24] As with ruthenium,[25] the coordination sphere for Os(II) probably does not contract significantly upon oxidation, since the valence electron resides in a nonbonding orbital. Hence, the increased stability of the trivalent metal center with aniline cannot be ascribed to an *increase* in steric effects upon oxidation. Rather, we feel this enhancement arises from the better σ-donating properties of the unsubstituted ligand; although dimethylaniline is slightly more basic than its parent,[26] the methyl groups apparently prevent the nitrogen from achieving its optimum bond distance.

The 8.0 kcal/mol decrease in the N → π isomerization energy of $[Os(NH_3)_5(PhNR_2)]^{2+}$, attributable to the methyl groups, is reflected in the rate of this isomerization as well. A rate of 8.3 s^{-1} corresponds to a decrease of 7.5 kcal/mol in the free energy of activation[27] ($\Delta G^{\ddagger}$ = 15.9 kcal/mol) compared to that for aniline ($\Delta G^{\ddagger}$ = 23.4 kcal/mol). On osmium(III) the findings are similar; in this case the difference in N → π isomerization rates corresponds to a 9.8 kcal/mol change in the free energy of activation. Given that these processes are intramolecular, the rate-determining step for this rearrangement for either valence state is most certainly the cleavage of the Os–N bond, the strength of which would be profoundly affected by the methyl groups. In pleasing contrast to this are the rates for π → N isomerization; these rates are virtually independent of the steric constraint, which implies that the rate-determining step occurs prior to the coordination of nitrogen.

A second point concerns the reversal of relative isomerization rates upon oxidation. For both complexes, the rate of N → π isomerization on Os(III) is significantly slower than that for the corresponding divalent species, reflecting the enhancement of the metal–nitrogen bond strength for the higher oxidation state. This is in contrast to the π → N isomerizations for which the converse statement is true. A comparison of these rates suggests that the metal–arene bond strength is greater for Os(II), a result that is readily attributable to metal π-back-bonding.

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Photochemistry of Diplatinum(III,III) Pyrophosphite Complexes. Efficient Photochemical Reduction of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ in Methanol

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Abstract: UV–vis irradiation of $[Pt_2(pop)_4X_2]^{4-}$ [pop = $P_2O_5H_2^{2-}$; X = Cl, Br, SCN, I, Im (ImH = imidazole)] in methanol leads to reduction to $[Pt_2(pop)_4]^{4-}$ with nearly quantitative yield (over 92%). Upon ligand-to-metal charge-transfer [σ_x → d_σ*] excitation, the quantum yield (ϕ_r) for the reduction of $[Pt_2(pop)_4X_2]^{4-}$ decreases with X_2 = $(CH_3)(I)$ > $(SCN)_2$ > I_2 > Im_2 > Cl_2 > Br_2. The ϕ_r values are wavelength dependent, being higher with σ_x → d_σ* excitation than that with d_π → d_σ*. Flash photolysis experiments indicate that the primary step of the photoreactions is the homolytic breakage of the Pt–X bond, $[Pt_2(pop)_4X_2]^{4-}$ → $[Pt^{III}Pt^{III}(pop)_4X]^{4-}$ + •X.

The photochemistry of binuclear metal–metal-bonded Rh(II) and Pt(III) complexes remains relatively unexplored despite the extensive structural and spectroscopic work reported on this class of compounds.[2,3] Our interest in photochemical studies of diplatinum(III,III) pyrophosphite complexes, $[Pt_2(pop)_4X_2]^{4-}$ (pop = $P_2O_5H_2^{2-}$; X = Cl, Br, SCN, I, Im), arose as a result of previous works.[4-9] Both spectroscopic and X-ray structural data showed that the Pt–Pt bond in these Pt(III) complexes contains substantial charge-transfer character,[4-7] indicating the possibility of having redox occur upon ligand-to-metal [X → Pt(III)] charge-transfer excitation. Recent work has shown that the intensely luminescent $[Pt_2(pop)_4]^{4-}$ complex possesses rich photochemistry;[10-17] in

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