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Preparation of Osmium Hydrazido Complexes by Interception of an Osmium(IV) Imido Intermediate

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Oxidation of polypyridyl Ru^{II} and Os^{II} aqua complexes leads to stable oxo complexes by sequential $1H^+/1e^-$ transfers (eq 1).[1]

$$[M^{II}(tpy)(bpy)(H_2O)]^{2+} \underset{+H^+/e^-}{\overset{-H^+/e^-}{\rightleftharpoons}} [M^{III}(tpy)(bpy)(OH)]^{2+} \underset{+H^+/e^-}{\overset{-H^+/e^-}{\rightleftharpoons}} [M^{IV}(tpy)(bpy)(O)]^{2+} \quad (1)$$

M = Ru, Os; tpy = 2,2′:6′,2″-terpyridine, bpy = 2,2′-bipyridine

Similarly, $Os(tpy)Cl_2NH_3$ undergoes a *chemically* reversible $3H^+/4e^-$ transfer to give the corresponding nitrido through an Os^{IV} intermediate (eq 2).[2] Oxidation of other Ru and Os ammine

$$Os^{II}(tpy)Cl_2NH_3 \underset{+3H^+/4e^-}{\overset{-3H^+/4e^-}{\rightleftharpoons}} [Os^{VI}(tpy)Cl_2(N)]^+ \quad (2)$$

complexes by two electrons is followed by rapid, complex disproportionation pathways and the appearance of the M^{II} nitrosyl as the exclusive product (eqs 3–5).[3] We report here that

$$[M^{II}(tpy)(bpy)(NH_3)]^{2+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [M^{III}(tpy)(bpy)(NH_3)]^{3+} \quad (3)$$

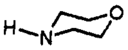
$$[M^{III}(tpy)(bpy)(NH_3)]^{3+} \xrightarrow{-2H^+/1e^-} [M^{IV}(tpy)(bpy)(NH)]^{2+} \quad (4)$$

$$3[M^{IV}(tpy)(bpy)(NH)]^{2+} + H_3O^+ \rightarrow 2[M^{II}(tpy)(bpy)(NH_3)]^{2+} + [M^{II}(tpy)(bpy)(NO)]^{3+} \quad (5)$$

the reactive Os^{IV} imido intermediate can be trapped in the presence of secondary amines to give a novel series of stable Os^{IV} and Os^{V} hydrazido(2–) complexes. In addition to being the first examples of terminal hydrazido coordination to osmium, these complexes exhibit electrochemical behavior which may be relevant to the N–N bond cleavage step in the functioning of nitrogenase enzymes.

Electrochemical measurements reveal that eq 3 (M = Os) is a one-electron process which is reversible and pH-independent ($E_{1/2}$ = +0.41 V)[4] over the range $0 \leq pH \leq 4.5$, while eq 4 is strongly pH-dependent and irreversible.[3] At pH ≥ 7, oxidation of Os^{III} to Os^{IV} occurs at *lower* potentials than oxidation of Os^{II} to Os^{III}. In the presence of a large excess of a secondary amine (0.5 M NHR_2 buffered to pH 7.0 with NaH_2PO_4), exhaustive oxidation of a solution 1.75 mM in $[Os(tpy)(bpy)(NH_3)](PF_6)_2$ (**1**) resulted in the transformation described by eq 6.[5] Chronocoulometry established the electron count to be 4.6–5.0 electrons.

$$[Os^{II}(tpy)(bpy)(NH_3)]^{2+} + NH_2R_2{}^+ \xrightarrow{-5H^+/5e^-} [Os^{V}(tpy)(bpy)(NNR_2)]^{3+} \quad (6)$$

$HNR_2 = HNEt_2$ (**a**),  (**b**)

From the electrolyzed solutions, the Os^{V} products (**3a** and **3b**) were isolated.[6,7] Exhaustive reduction of **3** at 0 V occurred with $n = 1.0 \pm 0.1$ and gave the corresponding Os^{IV} products (eq 7).

$$\underset{\mathbf{3}}{[Os^{V}(tpy)(bpy)(NNR_2)]^{3+}} \xrightarrow{+e^-} \underset{\mathbf{2}}{[Os^{IV}(tpy)(bpy)(NNR_2)]^{2+}} \quad (7)$$

Once isolated,[7,8] **2** was oxidized to **3** in aqueous and nonaqueous electrolytes with $n = 1.0 \pm 0.1$ (*vide infra*). Crystals suitable for X-ray diffraction were grown by vapor diffusion of diethyl ether into saturated acetonitrile solutions of **2**. The structure of **2a**, determined by X-ray crystallography,[9] is shown in Figure 1.

Multiple bonding between Os^{IV} and the hydrazido ligand is revealed by the Os–N_α distances of 1.89(1) Å in **2a** and 1.85(2) Å in **2b**. The Os–N(bpy) bond lengths *trans* to the hydrazido are short (2.05(1) Å for **2a**; 1.98(2) Å for **2b**) compared to those *cis* (2.14(1) Å for **2a**; 2.11(1) Å for **2b**. The complexes are diamagnetic,[10] and the Os–N_α–N_β bond angle of 137° (in **2a**, **2b**) suggests that two pairs of electrons are donated to the metal. This value is close to the Os–N–P angle of *trans*-$[Os(tpy)Cl_2NPPh_3](PF_6)$, in which the phosphoraminato ligand is a four-electron donor.[11] Moreover, the NNCC units of the hydrazido ligands are planar, suggesting a π interaction between nitrogens (N_α–N_β = 1.25(2) Å in **2a**; 1.40(2) Å in **2b**), with the π* component of this interaction donating electrons to Os^{IV}.

Cyclic voltammetry of compounds **2** and **3** indicates that the Os(V/IV) couple is reversible in acetonitrile and in aqueous solutions, where the wave is pH-independent.[12] Further *irreversible* oxidation (E_{pa} = +1.50 V for **2** in CH_3CN) gives a new product, which is currently under investigation.

Electrochemical properties of **2** in aqueous solution are pH- and scan rate-dependent. The data represented in Figures 2 and

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[1] (a) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436–444. (b) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845–1851.

[2] Pipes, D. W.; Bakir, M.; Vitols, S. E.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5507–5514.

[3] (a) Murphy, W. R.; Takeuchi, K. J.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1041–1053. (b) Coia, G. Work in progress.

[4] All potentials cited in this paper are vs the saturated sodium chloride calomel electrode (SSCE).

[5] In an earlier study under comparable conditions, we reported the formation of Os^{II} nitrosamine complexes which would be the six-electron oxidation products (Stershic, M. T.; Keefer, L. K.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 6884–6885). The present results call the initial observations into question, although it remains to be seen if the nitrosamines can be obtained by further oxidation of the hydrazidos.

[6] Addition of excess NH_4PF_6 resulted in the precipitation of yellow-orange solids (**3**). **3a** was redissolved in water and purified by cation exchange chromatography using Sephadex CM C-25 40-100 μ support and aqueous NH_4Cl as the eluent. **3b** was less stable in aqueous solution and was not isolated in pure form.

[7] Purity of the complexes was established by ^1H-NMR and elemental analysis.

[8] Addition of excess NH_4PF_6 resulted in the precipitation of dark green solids (**2**). **2a** and **2b** were both purified by cation exchange chromatography as described above.

[9] Crystals of **2a** and **2b** were triclinic and belonged to the $P\bar{1}$ space group, with $Z = 2$. X-ray diffraction data were collected using Mo Kα radiation, $\mu = 36.9$ cm^{-1}. For **2a**, $a = 9.004(1)$ Å, $b = 9.796(1)$ Å, $c = 20.710(2)$ Å; $V = 1816.7(7)$ Å^3; $\alpha = 88.78(2)°$, $\beta = 85.43(2)°$, $\gamma = 86.22(2)°$; $D_{calcd} = 1.749$ g cm^{-1}. Data were collected by an Enraf-Nonius CAD-4 diffractometer through a maximum $2\theta = 49.9°$, giving 6389 unique reflections. $R = 0.068$, $R_w = 0.075$. For **2b**, $a = 9.632(8)$ Å, $b = 21.229(9)$ Å, $c = 9.039(5)$ Å; $V = 1822.2(20)$ Å^3; $\alpha = 97.41(4)°$, $\beta = 94.28(5)°$, $\gamma = 85.07(5)°$; $Z = 2$; $D_{calcd} = 1.842$ g cm^{-1}. Data were collected by a Rigaku diffractometer through a maximum $2\theta = 45°$, giving 4782 unique reflections. $R = 0.079$, $R_w = 0.105$.

[10] Diamagnetism was established by ^1H-NMR. Temperature-dependent magnetic measurements of the Os(IV) and Os(V) complexes are currently in progress.

[11] Bakir, M.; White, P. S.; Dovletoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2835–2836.

[12] $E_{1/2}$ values for the **3a**/**2a** couple are +0.36 V in water and +0.59 V in acetonitrile. For **3b**/**2b**, the couple lies higher: +0.40 V in water; +0.67 V in acetonitrile. $E_{1/2}$ is defined as $(E_{pa} + E_{pc})/2$.

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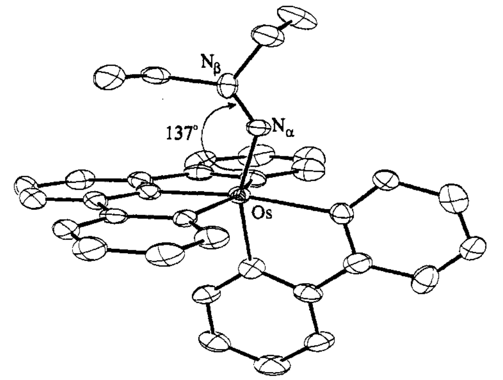


Figure 1. The structure of the cation in [Os(tpy)(bpy)NNEt$_2$](PF$_6$)$_2$ (**2a**) determined by X-ray crystallography.

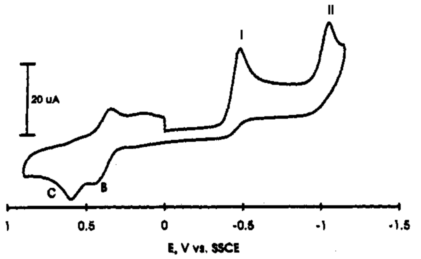


Figure 2. Cyclic voltammogram of **2a** at pH = 5.0 (2.5 mM in CH$_3$COONa buffer) showing both reduction Waves, I and II, and product Waves, B and C. The working electrode was a 2-mm glassy carbon disk, and the reference electrode was the SSCE.

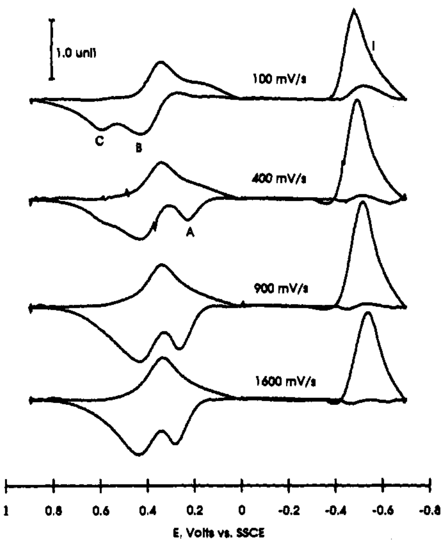
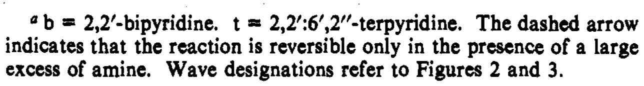


Figure 3. Background-subtracted cyclic voltammograms of **2a** at pH = 5.0. The product $i_f v^{-1/2}$ is plotted on the y-axis, where i_f is the faradaic current and v is the scan rate. Units are μA·s$^{1/2}$·mV$^{-1/2}$. Each sweep was initiated cathodically from 0 V.

Scheme 1. Summary of Electrochemical Properties of [Os(tpy)(bpy)NNEt$_2$](PF$_6$)$_2$ in Aqueous Solution[a]



[a] b = 2,2′-bipyridine. t = 2,2′:6′,2″-terpyridine. The dashed arrow indicates that the reaction is reversible only in the presence of a large excess of amine. Wave designations refer to Figures 2 and 3.

3 were taken at pH 5.0, where all of the electrochemical events identified in Scheme 1 are resolvable. The initial reduction (Wave I) appears to involve the transfer of two electrons and two protons, generating an Os^{II} dialkylhydrazine complex. Reduction of this species by two more electrons (Wave II, Figure 2) yields the ammine complex and free dialkylamine. The Os^{II} dialkylhydrazine complex can be reoxidized to give the starting complex (Wave A, Figure 3) at sufficiently high scan rates. Both E_{pc} for wave I and E_{pa} for wave A decrease as the pH is raised, consistent with Scheme 1. Below pH 6, Wave A can be observed only at higher scan rates, because the hydrazine complex decomposes to give **1**. We have not yet determined whether this process involves disproportionation (eq 8), or occurs intramolecularly (eq 9), as observed for MCp*Me$_3$(η^2-NH$_2$NH$_2$)$^+$ (M = Mo, W; Cp* = C$_5$Me$_5$).[13] In the latter case, the imido complex once formed would

$$2\mathrm{Os(tpy)(bpy)NH_2NR_2}^{2+} + \mathrm{H}^+ \rightarrow \mathrm{Os(tpy)(bpy)NNR_2}^{2+} + \mathrm{Os(tpy)(bpy)NH_3}^{2+} + \mathrm{H_2NR_2}^+ \quad (8)$$

$$[\mathrm{Os^{II}(tpy)(bpy)NH_2NR_2}]^{2+} + \mathrm{H}^+ \rightarrow [\mathrm{Os^{IV}(tpy)(bpy)NH}]^{2+} + \mathrm{H_2NR_2}^+ \quad (9)$$

be immediately reduced to **1** at the electrode. Decomposition of the hydrazine complex to **1** occurs very slowly at pH 9, but is rapid below pH 6. This is seen at the slower scan rates of Figure 3, where a reverse scan following reduction at Wave I shows the two-wave pattern for the reversible Os$^{III/II}$ couple (Wave B) and the irreversible Os$^{IV/III}$ couple (Wave C) of **1**. At pH < 2, disproportionation becomes quite rapid, and a single, four-electron reductive process is observed (eq 10) at the expense of Wave II.

The products of *bulk* reduction past the first wave also depend on pH. In neutral and basic solutions, reduction occurs with $n \approx 3$, giving **1** and an additional product, which is probably the hydrazine complex. At pH = 0.5 the reduction occurs with $n = 4.0 \pm 0.2$ and gives **1** quantitatively (eq 10).

$$[\mathrm{Os(tpy)(bpy)(NNR_2)}]^{2+} \xrightarrow{+5\mathrm{H}^+/4e^-} [\mathrm{Os(tpy)(bpy)(NH_3)}]^{2+} + \mathrm{NH_2R_2}^+ \quad (10)$$

The electron-transfer reactivity of these complexes may be relevant to the mechanisms of N$_2$ fixation. It demonstrates two distinct pathways for reduction of coordinated hydrazines to amines. The Os hydrazido complexes share important features with previous nitrogenase models based on molybdenum and tungsten[13,14] but differ in that (1) they are relatively electron deficient; (2) they are coordinatively rigid and saturated, with coordination number 6 for all oxidation states; and (3) the d^4 configuration forces a bent M–N$_\alpha$–N$_\beta$ structure instead of the more common linear geometry. In addition to guiding the reductive chemistry, these factors account for the hydrolytic stability of the complexes and the net chemical reversibility of N–N formation and cleavage: features which stand in contrast to other models.

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Supplementary Material Available: Complete crystallographic reports for **2a** and **2b** (46 pages); listing of observed and calculated structure factors for **2a** and **2b** (67 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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