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Reactivity of Osmium(VI) Nitrides with the Azide Ion

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An extensive redox reactivity is emerging for nitrido complexes of Os(VI). With *trans*-$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+$, **1** (tpy = 2,2′:6′,2″-terpyridine), as the example, reactions that have been uncovered include one-electron reduction to form $\mathrm{Os^{II}(N_2)Os^{II}}$ dimers[1]

$$2[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+ \xrightarrow{2e^-} \mathrm{(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)} \qquad (1)$$

reversible $4e^-/3H^+$ reduction to $\mathrm{Os^{II}}$ ammines[2]

$$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+ \underset{-4e^-/-3H^+}{\overset{4e^-/3H^+}{\rightleftharpoons}} \mathrm{Os^{II}(tpy)(Cl)_2(NH_3)} \qquad (2)$$

oxo transfer from $\mathrm{O{=}NMe_3}$ to give $\mathrm{Os^{II}}$ nitrosyls[3]

$$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+ + \mathrm{O{=}NMe_3} \rightarrow [\mathrm{Os^{II}(tpy)(Cl)_2(NO)}]^+ + \mathrm{NMe_3} \qquad (3)$$

and nucleophilic attack by $\mathrm{PR_3}$ to give $\mathrm{Os^{IV}}$ phosphoraniminates[4]

$$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+ + \mathrm{PR_3} \rightarrow [\mathrm{Os^{IV}(tpy)(Cl)_2(NPR_3)}]^+ \qquad (4)$$

We report here that an extensive chemistry exists between **1** or $[\mathrm{Os^{VI}(tpm)(Cl)_2(N)}]^+$, **2** (tpm = tris(1-pyrazolyl)methane), and the azide ion ($\mathrm{N_3^-}$), including formation of terminally bound $\mathrm{N_2}$, $\mathrm{Os^{II}}$ thionitrosyls, or $\mathrm{Os^{III}}$ tetrazoles and electron transfer to give an $\mathrm{Os^{II}(N_2)Os^{II}}$ dimer.[5]

Reaction between stoichiometric or excess $\mathrm{[PPN]N_3}$ ($\mathrm{PPN^+}$ = bis(triphenylphosphoranylidene)ammonium cation) and $[\mathrm{Os^{VI}(tpm)(Cl)_2(N)}]^+$ in $\mathrm{H_2O}$, $\mathrm{CH_3OH}$, $\mathrm{CH_2Cl_2}$, or $\mathrm{CH_3CN}$ occurs within seconds to give $\mathrm{Os^{II}(tpm)(Cl)_2(N_2)}$ (**2a**), eq 5, for which

$$\underset{\mathbf{2}}{[\mathrm{Os^{VI}(tpm)(Cl)_2(N)}]^+} + \mathrm{N_3^-} \rightarrow \underset{\mathbf{2a}}{\mathrm{Os^{II}(tpm)(Cl)_2(N_2)}} + \mathrm{N_2} \qquad (5)$$

an intense $\nu(\mathrm{N{\equiv}N})$ band appears at 2068 cm^{-1} in KBr ($\nu(^{15}\mathrm{N{\equiv}}^{14}\mathrm{N})$ at 2032 cm^{-1}). $E_{1/2}$ for the $\mathrm{Os^{III/II}}$ couple is chemically reversible at a scan rate of 200 mV/s with $E_{1/2} = -0.27$ V (in 0.1 M $\mathrm{N}(n\text{-}\mathrm{Bu_4})(\mathrm{PF_6})$, vs SSCE, in DMSO), but oxidation with excess $\mathrm{Ce^{IV}}$ in $\mathrm{H_2O}$ or $\mathrm{CH_3CN}$ occurs with loss of $\mathrm{N_2}$ to give $[\mathrm{Os^{III}(tpm)(Cl)_2(L)}]^+$ (L = $\mathrm{CH_3CN}$ (**2b**) or $\mathrm{H_2O}$ (**2c**)).[6] Reduction of **2** with cobaltocene ($\mathrm{Co(Cp)_2}$) in $\mathrm{CH_2Cl_2}$ gives $\mathrm{(tpm)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpm)}$ (**2d**). In cyclic voltammograms of **2d** in DMSO,

$$\underset{\mathbf{2}}{2[\mathrm{Os^{VI}(tpm)(Cl)_2(N)}]^+} + 2\mathrm{Co(Cp)_2} \rightarrow \underset{\mathbf{2d}}{\mathrm{(tpm)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpm)}} + 2\mathrm{Co(Cp)_2}^+ \qquad (6)$$

chemically reversible $\mathrm{Os^{III}{-}Os^{II}/Os^{II}{-}Os^{II}}$ and $\mathrm{Os^{III}{-}Os^{III}/Os^{III}{-}Os^{II}}$ couples appear at $E_{1/2} = +0.04$ V and $+0.67$ V vs SSCE ($\Delta E_{1/2} = 0.63$ V) at a scan rate of 200 mV/s. **2d** undergoes oxidation by ferrocenium salts to give the mixed-valence form **2e**, eq 7, for which an intense $\nu(\mathrm{N{\equiv}N})$ stretch appears at 2029 cm^{-1} in KBr ($\nu(^{15}\mathrm{N{\equiv}}^{15}\mathrm{N})$ at 1965 cm^{-1}).

$$\underset{\mathbf{2d}}{\mathrm{(tpm)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpm)}} \xrightarrow{-e^-} \underset{\mathbf{2e}}{[\mathrm{(tpm)(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2(tpm)}]^+} \qquad (7)$$

With **1**, the reaction chemistry with $\mathrm{N_3^-}$ is highly solvent dependent. In $\mathrm{CH_3CN}$, a reaction occurs with stoichiometric $\mathrm{N_3^-}$ within seconds to give a mixture of products. The minor product is *trans*-$\mathrm{Os^{II}(tpy)(Cl)_2(N_2)}$ (**1a**) with $\nu(\mathrm{N{\equiv}N})$ at 2097 cm^{-1} in KBr ($\nu(^{15}\mathrm{N{\equiv}}^{14}\mathrm{N})$ at 2062 cm^{-1}). The major product is *trans*-$\mathrm{Os^{II}(tpy)(Cl)_2(NCCH_3)}$ (**1b**), which forms by solvation of **1a**. In nonpolar solvents such as acetone or $\mathrm{CH_2Cl_2}$, electron transfer occurs from $\mathrm{N_3^-}$ to **1** to give *trans,trans*-$\mathrm{(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)}$ cleanly.[1a] In $\mathrm{H_2O}$ with 2 equiv of $\mathrm{N_3^-}$, the final product is the azido complex *cis*-$\mathrm{Os^{III}(tpy)(Cl)_2(N_3)}$ (**1c**). Detailed mechanistic information is not available, but its formation can be rationalized by initial *trans* → *cis* isomerization of *trans*-$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+$,[8] followed by attack of $\mathrm{N_3^-}$ on the nitrido ligand to give $\mathrm{Os^{II}{-}N_2}$. Substitution of coordinated $\mathrm{N_2}$ by $\mathrm{N_3^-}$ and final air oxidation result in **1c**.

In $\mathrm{CH_3CN}$ with $\mathrm{N_3^-}$ in excess, the reaction takes a different course. Initial $\mathrm{N_3^-}$ attack on **1** and solvolysis give *trans*-$\mathrm{Os^{II}(tpy)(Cl)_2(NCCH_3)}$ (**1b**) (see above). It undergoes reaction with a second $\mathrm{N_3^-}$ by a [3+2] cycloaddition with bound $\mathrm{CH_3CN}$[9] followed by air oxidation to give *trans*-$\mathrm{Os^{III}(tpy)(Cl)_2}$(5-$\mathrm{CH_3}$-tetrazolate) (**1d**, Figure 1). The $\mathrm{N^2}$-bound isomer shown in **1d**, which is the final product, is favored on steric grounds.[10] Presumably it forms by linkage isomerization of the initially

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[1] (a) Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1997**, *36*, 5678. (b) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4605. (c) Che, C.-M.; Lam, H.-W.; Tong, W.-F.; Lai, T.-F.; Lau, T.-C. *J. Chem. Soc., Chem. Commun.* **1989**, 1883.

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

[3] Williams, D. S.; White, P. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 823.

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[5] The compounds and salts reported here gave satisfactory elemental analyses and were characterized by infrared and UV−vis spectroscopies and by cyclic voltammetry (see Supporting Information).

[6] Oxidation of $\mathrm{Os^{II}(tpm)(Cl)_2(N_2)}$ with ferrocenium salts in $\mathrm{CH_3CN}$ proceeds with formation of the mixed-valence dimer $[\mathrm{(tpm)(Cl)_2Os^{III}(N_2)Os^{II}(Cl)_2(tpm)}]^+$ by a process which is currently under investigation. Taube et al. have reported formation of $[\mathrm{(NH_3)_5Os^{III}(N_2)Os^{II}(NH_3)_5}]^{5+}$ after partial oxidation of $\mathrm{Os^{II}(NH_3)_5(N_2)^{2+}}$.[7]

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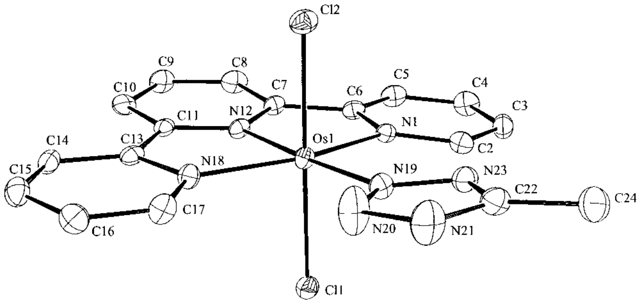


Figure 1. ORTEP diagram (30% ellipsoids) of *trans*-$Os^{III}(tpy)(Cl)_2$(5-CH_3-tetrazolate) with its labeling scheme. Important metric features: Os(1)−Cl(1) 2.345(2) Å, Os(1)−Cl(2) 2.343(2) Å, Os(1)−N(19) 2.093(5) Å, Os(1)−N(1) 2.087(5) Å, Os(1)−N(12) 1.990(5) Å, Os(1)−N(18) 2.085(5) Å, Cl(1)−Os(1)-Cl(2) 178.86(6)°, N(1)−Os(1)-N(18) 158.5(2)°.

formed N^1-bound isomer although we have no evidence for an intermediate. Isomerization has been observed in related reactions.[10] It was shown independently that a reaction occurs between $Os^{II}(tpy)(Cl)_2(NCCH_3)$ and N_3^- in the presence of air to give the same product. $E_{1/2}$ values for the $Os^{III/II}$ and $Os^{IV/III}$ couples are −0.26 and +1.01 V, respectively (in 0.1 M (^{n}Bu$_4$N)(PF_6), vs SSCE, in DMSO). The crystal structure of **1d**[11] (Figure 1) reveals that the *trans* geometry of the starting nitrido is retained. The 5-CH_3-tetrazolato ring is coplanar with tpy. N−N and C−N bond lengths within the tetrazolato ring range from 1.321(9) to 1.345(9) Å consistent with extensive electronic delocalization.[12] *To our knowledge, this is the first Os−tetrazolato complex which has been isolated and structurally characterized.*

Reaction between **1** or **2** and N_3^- in the presence of CS_2 in acetone gives the thionitrosyls *trans*-$[Os^{II}(tpy)(Cl)_2(NS)](SCN)$ (**1e**) and $[Os^{II}(tpm)(Cl)_2(NS)](SCN)$ (**2f**), e.g.

$$\underset{\mathbf{1}}{[Os^{VI}(tpy)(Cl)_2(N)]^+} + N_3^- + CS_2 \rightarrow \underset{\mathbf{1e}}{[Os^{II}(tpy)(Cl)_2(NS)]^+} + SCN^- + N_2 \quad (8)$$

In acetone neither **1** nor **2** is reactive with CS_2 or S_8 separately. Reaction between N_3^- and CS_2 is known to occur to give the 5-thio-1,2,3,4-thiatriazolato ring anion, which decomposes to give $^-$SCN, N_2, and S^0.[13]

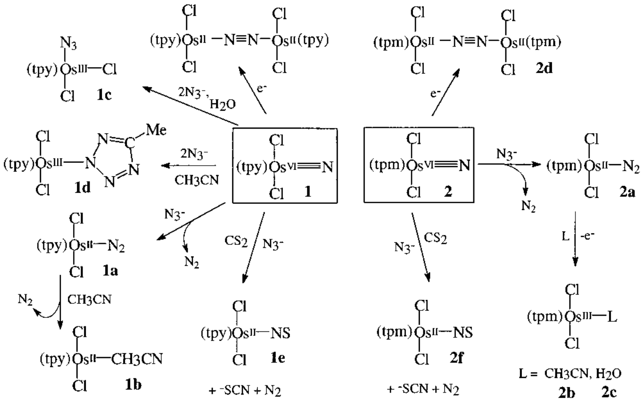
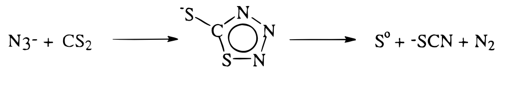
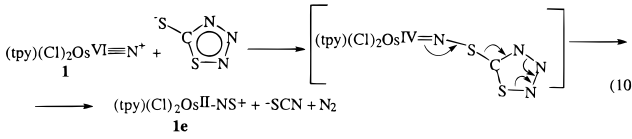


Figure 2. Reactivity of *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ (**1**) and $[Os^{VI}(tpm)(Cl)_2(N)]^+$ (**2**) with N_3^-.



(9)

Presumably, in the presence of **1** or **2**, nucleophilic attack on $Os^{VI}\equiv N$ by the thiolato portion of the ring takes place with sulfur atom transfer although we have no mechanistic information. Nucleophilic attack would be accompanied by reduction of Os^{VI} to Os^{II} and formation of the thionitrosyl



(10)

In the structurally characterized **1e**, the Os−N(S) bond distance is 1.834(7) Å, ∠Os−N−S is 178.5(5)°, and the N−S bond distance is 1.459(8) Å.[14]

These initial results reveal an extensive and novel reactivity chemistry between Os^{VI} nitrides and N_3^- which is summarized in Figure 2.

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Supporting Information Available: Text presenting experimental procedures for the preparation of the compounds and their spectroscopic characterization, a listing of details of the crystallographic analysis of *trans*-$Os^{III}(tpy)(Cl)_2$(5-CH_3-tetrazolate)·DMF (**1d**), and tables of atomic coordinates, isotropic thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

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(11) Crystals of *trans*-$Os^{III}(tpy)(Cl)_2$(5-CH_3-tetrazolate)·DMF were grown by vapor diffusion of Et_2O into a DMF solution of the compound. They are monoclinic, space group *C*2/*c*, with a = 22.321(5) Å, b = 13.146(2) Å, c = 14.549(5) Å, β = 105.37(2)°, V = 4116(2) Å^3, Z = 8, fw = 604.47, d_{calc} = 1.951 g/cm^3, and μ = 6.47 mm^{-1}. Intensity data were collected at −100 °C on a Rigaku diffractometer in the ω scan mode. A total of 3625 unique reflections were measured, with 2860 having $I > 2.5\sigma(I)$ used in structure refinement by full-matrix least-squares techniques (266 parameters). Absorption corrections were made. Final R = 3.0%, R_w = 3.7%, GoF = 1.21 (R = 5.1%, R_w = 4.1% for all reflections). NRCVAX was used as the software package. A disordered DMF molecule was found in the lattice, and its disorder was modeled successfully.

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(14) Relevant metric features: Os−Cl (mean) 2.363(2) Å, Os−N(S) 1.834(7) Å, N−S 1.459(8) Å, Os−N(tpy) 2.032(7)−2.084(7) Å. Details will be published in: Demadis, K. D.; Meyer, T. J.; White, P. S. Submitted for publication.