

## Oxo-Like Reactivity of High Oxidation State Osmium Hydrazido Complexes

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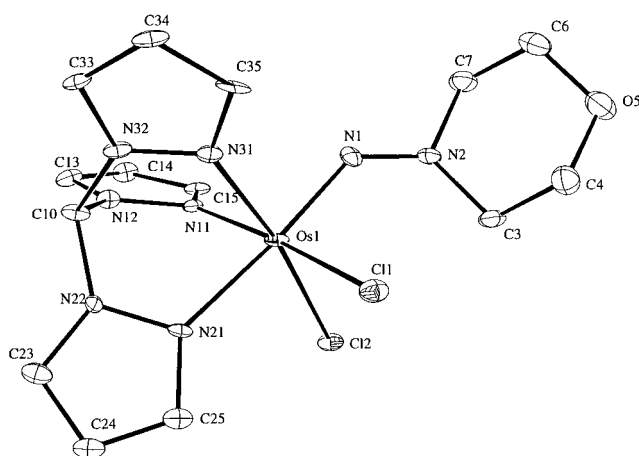
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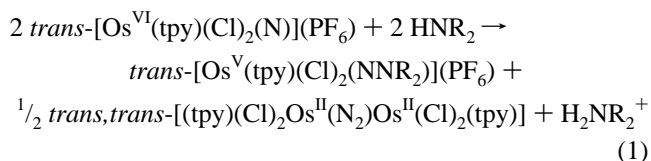
There is an extensive oxidation chemistry associated with high oxidation state Ru(IV), Ru(V), and Ru(VI) oxo complexes. It includes oxidation of phosphines to phosphine oxides,<sup>1</sup> sulfides to sulfoxides,<sup>2</sup> alcohols to aldehydes and ketones,<sup>3</sup> and olefin epoxidation.<sup>4</sup> We report here the preparation of a family of novel, high oxidation state Os(V) hydrazido complexes, which have a related redox chemistry and reactivity, but based on an Os=N interaction rather than the Ru=O interaction in the oxo complexes. High oxidation state hydrazido complexes have also been proposed as key intermediates in biological<sup>5</sup> and abiological<sup>6</sup> nitrogen fixation.

The salt *trans*-[Os<sup>VI</sup>(tpy)(Cl)<sub>2</sub>(N)](PF<sub>6</sub>)<sup>7</sup> (**1**, tpy = 2,2':6',2''-terpyridine) undergoes rapid reactions with the secondary amines, morpholine (HN(CH<sub>2</sub>)<sub>4</sub>O) and piperidine (HN(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>), in CH<sub>3</sub>CN under argon to give a precipitate of *trans,trans*-[(tpy)(Cl)<sub>2</sub>Os<sup>II</sup>(N<sub>2</sub>)Os<sup>II</sup>(Cl)<sub>2</sub>(tpy)]<sup>8</sup> and a brown solution. Evaporation of the solution to dryness and recrystallization from CH<sub>3</sub>CN/Et<sub>2</sub>O give the brown solid, *trans*-[Os<sup>V</sup>(tpy)(Cl)<sub>2</sub>(NNR<sub>2</sub>)](PF<sub>6</sub>) (NR<sub>2</sub> = morpholide, **2a**; NR<sub>2</sub> = piperidide, **2b**), by the net reaction in eq 1.<sup>9</sup>

There is an equivalent reactivity between [Os<sup>VI</sup>(tpm)(Cl)<sub>2</sub>(N)](PF<sub>6</sub>) (**3**, tpm = tris(1-pyrazolyl)methane) and morpholine. The reaction product, [Os<sup>V</sup>(tpm)(Cl)<sub>2</sub>(NNR<sub>2</sub>)]<sup>+</sup> (NR<sub>2</sub> = morpholide,



**Figure 1.** ORTEP diagram (30% ellipsoids) and labeling scheme for the cation in [Os<sup>V</sup>(tpm)(Cl)<sub>2</sub>(NNR<sub>2</sub>)](PF<sub>6</sub>) (NR<sub>2</sub> = morpholide, **4a**). Important features: Os(1)–N(1) 1.909(8) Å, N(1)–N(2) 1.321(12) Å, Os(1)–Cl(1) 2.3872(24) Å, Os(1)–Cl(2) 2.4036(22) Å, Os(1)–N(11) 2.046(7) Å, Os(1)–N(21) 2.075(7) Å, Os(1)–N(31) 2.064(8) Å, ∠Os(1)–N(1)–N(2) 134.9(6)°.



**4a**), has been isolated and characterized by X-ray crystallography (Figure 1).<sup>10</sup> The structure shows that the distorted octahedral arrangement of ligands around the Os atom in the parent nitrido complex is retained in the hydrazido product. The Os–N(tpm) bond lengths range from 2.046(7) to 2.075(7) Å with the longest Os–N bond *trans* to the hydrazido ligand. The Os–N(hydrazido) bond length is rather short at 1.909(8) Å, the N(1)–N(2) bond length is 1.321(12) Å, and ∠Os–N(1)–N(2) is 134.9(6)°. These features point to a *trans* effect by the hydrazido ligand and Os–N(hydrazido) multiple bonding. There are structural similarities with the Os(IV) hydrazido complex, [Os<sup>IV</sup>(tpy)(bpy)(NNR<sub>2</sub>)]<sup>2+</sup> (NR<sub>2</sub> = morpholide).<sup>11</sup>

These complexes have an extensive redox chemistry. For **2a**, in 0.1 M TBAH/CH<sub>3</sub>CN (TBAH = [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>](PF<sub>6</sub>)), chemically reversible waves appear for an Os(VI/V) couple at *E*<sub>1/2</sub> = +0.98 V, for Os(V/IV) at *E*<sub>1/2</sub> = 0.00 V, and for Os(IV/III) at *E*<sub>1/2</sub> = –0.79 V versus SSCE, Figure 2. A pH-dependence study of **2a** in 1:1 (v/v) H<sub>2</sub>O:CH<sub>3</sub>CN mixtures (0.1 M TBAH) reveals that the Os(VI/V) couple is pH-independent from pH 0.50 to pH 7.78 with *E*<sub>1/2</sub> = +0.81 V versus SSCE. The Os(V/IV) couple is

(9) The salts reported here gave satisfactory elemental analyses and were characterized by infrared and UV–vis spectroscopies as well as by cyclic voltammetry. Full details can be found in the Supporting Information.

(10) Crystals of [Os<sup>V</sup>(tpm)(Cl)<sub>2</sub>(NNR<sub>2</sub>)](PF<sub>6</sub>)·3CH<sub>3</sub>CN were grown by vapor diffusion of Et<sub>2</sub>O into a CH<sub>3</sub>CN solution of the salt. They are monoclinic, space group *P*2<sub>1</sub>/*a*, with *a* = 14.8348(7) Å, *b* = 11.7758(6) Å, *c* = 17.3115(9) Å, β = 93.432(1)°, *V* = 3018.8(3) Å<sup>3</sup>, *Z* = 4, *FW* = 843.57, *d*<sub>calc</sub> = 1.856 g/cm<sup>3</sup>, and μ = 4.53 mm<sup>–1</sup>. Intensity data were collected at –100 °C on a Siemens CCD SMART diffractometer with Mo Kα radiation and a graphite monochromator by using the ω scan mode. A total of 25 208 reflections were collected, and 5335 of them are unique. A total of 3840 reflections with *I* > 2.5σ(*I*) were used in the structure refinement by full-matrix least-squares techniques (379 parameters). Absorption corrections were made by using SADABS. Final *R* = 4.5%, *R*<sub>w</sub> = 5.2%, *GOF* = 2.02 (*R* = 6.1%, *R*<sub>w</sub> = 5.2%, for all reflections). NRCVAX was used as the software package. Full details can be found in the Supporting Information.

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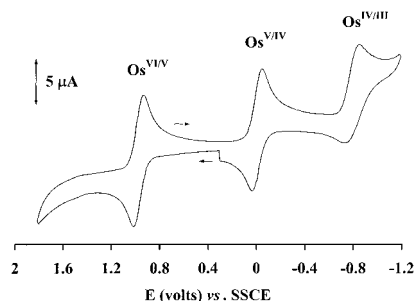
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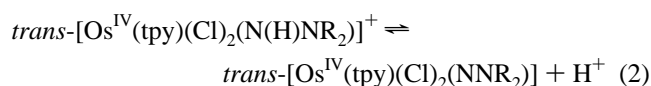
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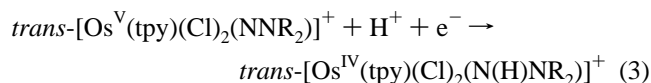
**Figure 2.** Cyclic voltammogram of  $trans\text{-}[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2(\text{NNR}_2)](\text{PF}_6)$  ( $\text{NR}_2 = \text{morpholide}$ , **2a**) in  $\text{CH}_3\text{CN}$ –0.1 M TBAH versus SSCE, showing chemically reversible waves for the  $\text{Os}(\text{VI}/\text{V})$ ,  $\text{Os}(\text{V}/\text{IV})$ , and  $\text{Os}(\text{IV}/\text{III})$  couples ( $E_{1/2} = (E_{\text{p,a}} + E_{\text{p,c}})/2$ ).

pH-dependent from pH 0.50 to pH 3.21 and pH-independent at higher pH values (Figure 1 in the Supporting Information).<sup>12</sup> From these data,  $\text{p}K_{\text{a}} = 3.20 \pm 0.04$  for the equilibrium in eq 2.

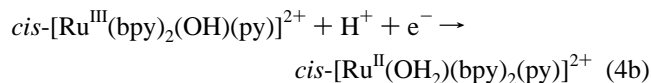
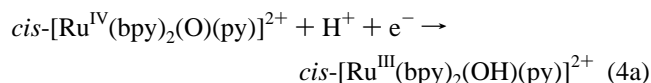


Further, irreversible multielectron, multiproton reduction of  $\text{Os}(\text{V})$  occurs from  $E_{\text{p,c}} = -0.45$  V to  $E_{\text{p,c}} = -0.87$  V versus SSCE from pH 0 to pH 8 to give  $trans\text{-}[\text{Os}^{\text{II}}(\text{tpy})(\text{Cl})_2(\text{NH}_3)]$  as shown by coulometry ( $n = 3$ ) and the appearance of a characteristic wave for the ammine product,  $E_{1/2}(\text{III}/\text{II}) = -0.18$  V.<sup>13a,b</sup> By analogy with earlier results on the reduction of  $[\text{Os}^{\text{IV}}(\text{tpy})(\text{bpy})(\text{NNR}_2)]^{2+}$ ,<sup>11b</sup> 3-electron, 2-proton reduction at pH 10.5 occurs at  $E_{\text{p,c}} = -1.00$  V presumably to give a hydrazine complex which is, as yet, uncharacterized,  $trans\text{-}[\text{Os}^{\text{II}}(\text{tpy})(\text{Cl})_2(\text{NH}_2\text{NR}_2)]$ . It is pseudostable and reoxidized at  $E_{\text{p,a}} = 0.25$  V to give  $trans\text{-}[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2(\text{NNR}_2)]$ .

The pH-dependent electrochemistry of the  $\text{Os}(\text{V}/\text{IV})$  couple,



is shared by typical  $\text{Ru}^{\text{IV}}=\text{O}$  couples. An example is<sup>14</sup>

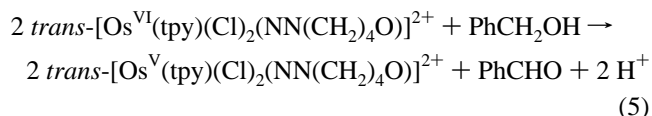


The hydrazido complexes also display “oxo-like” reactivity. In 0.1 M TBAH/ $\text{CH}_3\text{CN}$ , electrogenerated  $trans\text{-}[\text{Os}^{\text{VI}}(\text{tpy})(\text{Cl})_2-$

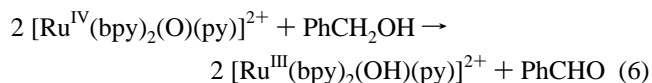
(12) In the  $\text{p}K_{\text{a}}$  measurements, buffer solutions from pH 1.0 to pH 8.0 ( $\mu = 0.1$  M) were prepared from  $\text{HNO}_3$  (pH 1–2), KHP (pH 3–6),  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ , (pH 7–8) before each run. Since  $trans\text{-}[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^+$  is not soluble in  $\text{H}_2\text{O}$ , a mixture of 1:1 (v/v)  $\text{CH}_3\text{CN}$ – $\text{H}_2\text{O}$  was used as the solvent in the electrochemical experiments. The pH values reported are those measured in the mixed solvents. The difference in measured pH values between the aqueous and mixed solvent was 0.1 pH unit or less. The  $E_{1/2}$ –pH (versus SSCE) plot is illustrated in Figure 1 in the Supporting Information.

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$(\text{NNR}_2)]^{2+}$  ( $\text{NR}_2 = \text{morpholide}$ ) reacts with benzyl alcohol to give  $trans\text{-}[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2(\text{NNR}_2)]^+$  and benzaldehyde. The latter was identified by GC–MS. The net reaction is

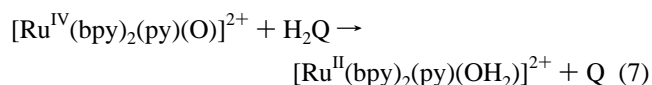


It is analogous to the oxidation of benzyl alcohol by  $\text{Ru}^{\text{IV}}=\text{O}$ .<sup>3a</sup>

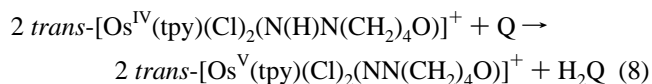


The kinetics of the reaction in eq 5 are first order in both  $\text{PhCH}_2\text{OH}$  and  $trans\text{-}[\text{Os}^{\text{VI}}(\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$  with  $k(25^\circ\text{C}, \text{CH}_3\text{CN}) = (1.80 \pm 0.07) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . For the reaction in eq 6,  $k(25^\circ\text{C}, 0.1 \text{ M HClO}_4) = 2.4 \text{ M}^{-1} \text{ s}^{-1}$ .

$\text{Ru}^{\text{IV}}=\text{O}$  is reduced by hydroquinone ( $\text{H}_2\text{Q}$ ),



with  $k(20^\circ\text{C}) = (1.111 \pm 0.010) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  in  $\text{H}_2\text{O}$  (pH  $1.16 \pm 0.02$ ,  $\mu = 0.1$  M) and  $\Delta G^\circ = -0.87$  eV.<sup>15</sup> Similarly, but in reverse,  $\text{Os}^{\text{IV}}$  is oxidized by quinone to  $\text{Os}^{\text{V}}$  ( $\Delta G^\circ = -0.045$  eV) in a reaction first order in each. From measurements with  $[\text{Q}]$  from  $3.51 \times 10^{-5}$  to  $1.75 \times 10^{-4}$  M,  $k(25^\circ\text{C}) = 55.1 \pm 1.7 \text{ M}^{-1} \text{ s}^{-1}$  in 1:1 (v/v)  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  (pH 1.0,  $\mu = 0.1$  M).



These results are significant in pointing to a parallel between the redox chemistries of  $\text{Ru}^{\text{IV}}=\text{O}$  complexes and this new family of high oxidation state Os hydrazido complexes. Continued evolution of this chemistry could lead to a new class of  $\text{Os}=\text{N}$ -based redox reagents for stoichiometric and catalytic organic oxidations.

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**Supporting Information Available:** Text giving experimental procedures for the preparation and characterization of the compounds, tables containing crystal data, atomic coordinates, isotropic thermal parameters, bond distances and angles, packing diagrams, and Supplementary Figure 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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