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Preparation of Osmium(II) Nitrosyls by Direct Oxidation of Osmium(VI) Nitrides

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One of the most dramatic examples of multielectron chemistry is the reversible interconversion of nitrosyl and ammine in polypyridyl complexes of ruthenium and osmium, eq 1,[2−9] where bpy is 2,2′-bipyridine and tpy is 2,2′:6′,2″-terpyridine.

$$[M(bpy)_2(py)(NO)]^{3+} \underset{-6e^-,-5H^+,+H_2O}{\overset{+6e^-,+5H^+,-H_2O}{\rightleftharpoons}} [M(bpy)_2(py)(NH_3)]^{2+} \quad (1)$$

In this overall 6-electron change there is evidence for a series of one-electron intermediates beginning with $[M^{II}(bpy)_2(py)(NO^0)]^{2+}$ on reduction and $[M^{III}(bpy)_2(py)(NH_3)]^{3+}$ on oxidation. In the more electron rich ammine $[Os^{II}(tpy)(Cl)_2(NH_3)]$,[4] reversible oxidation of bound ammonia occurs in a net 4-electron change to give the corresponding nitride with evidence for intervening intermediates of Os^{III}, Os^{IV}, and Os^{V}, eq 2. The

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

nitride does not undergo further electrochemical oxidation to the nitrosyl at pH ≤ 12, and the corresponding nitrosyl has previously been inaccessible. We report here a novel reaction which provides access to the nitrosyl by oxygen atom transfer with a formal 4-electron change at the metal,

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + ONMe_3 \rightarrow [Os^{II}(tpy)(Cl)_2(NO)]^+ + NMe_3 \quad (3)$$

We showed recently that there are *trans* (**1a**) and *cis* (**1b**) isomers of the d^2 nitride, $[Os(tpy)(Cl)_2(N)]^+$.[10] Rapid addition of $ONMe_3$ to a stirred acetonitrile solution containing *trans*-**1a** (magenta) or *cis*-**1b** (tan) results in immediate conversion to *trans*-$[Os(tpy)(Cl)_2(NO)]^+$ (**2a**) (blue) or *cis*-$[Os(tpy)(Cl)_2(NO)]^+$ (**2b**) (orange), eq 3. These reactions do not occur upon addition of triphenylphosphine oxide, pyridine *N*-oxide, or $[Ru(bpy)_2(py)(O)]^{2+}$ over a period of days.

The N−O stretching frequencies in compounds **2**, 1865 (*trans*) and 1889 cm^{-1} (*cis*), are decreased by ca. 500 cm^{-1} compared to the nitrosonium cation[11] but increased relative to $[Os(NO)(Cl)_4]^-$ (1822 cm^{-1}).[12] In both isomers of **2**, the nitrosyl resists attack by nucleophilic reagents such as hydroxide, amines, and phosphines, consistent with the low-energy N−O stretch. We are unable to reverse the oxygenation reaction by oxygen atom transfer to PPh_3 or $[Ru(NH_3)_5(OH_2)]^{2+}$ or to decompose the nitrosyl ligands by attack of N_3^-. Even at pH ≥ 12, there is no evidence for the onset of a nitro/nitrosyl equilibrium analogous to reaction 4, where the two forms are present in equal amounts at pH 4.[13]

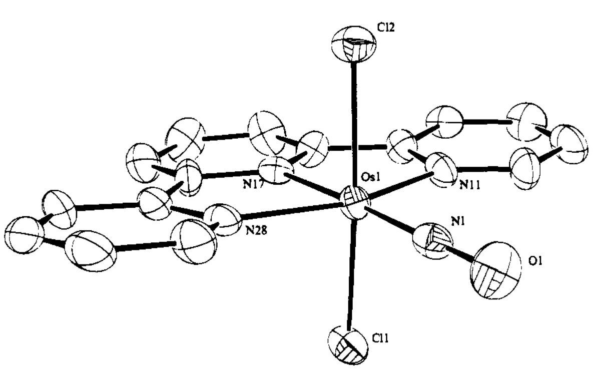

Figure 1. ORTEP diagram of the cation in *trans*-$[Os(tpy)Cl_2(NO)][BF_4]$. Pertinent bond lengths (Å) and angles (degree) for *trans*-$[Os(tpy)(Cl)_2(NO)][BF_4]$: Os−N(1) = 1.704 (14), N−O = 1.188 (19), Os−N(11) = 2.066 (11), Os−Cl(1) = 2.361 (4), Os−N(17) = 2.017 (12), Os−Cl(2) = 2.358 (4), Os−N(28) = 2.073 (11); Os−N−O = 176.6 (10), N(1)−Os−N(11) = 100.0 (5), Cl(1)−Os−Cl(2) = 173.80 (16), N(1)−Os−N(17) = 175.3 (5), Cl(1)−Os−N(11) = 89.1 (4), N(1)−Os−N(28) = 103.4 (5), Cl(1)−Os−N(17) = 85.8 (4), N(1)−Os−Cl(1) = 89.9 (4), Cl(1)−Os−N(28) = 90.8 (4), N(1)−Os−Cl(2) = 96.1 (4), Cl(2)−Os−N(11) = 88.3 (4), N(11)−Os−N(17) = 78.3 (5), Cl(2)−Os−N(17) = 88.2 (4), N(11)−Os−N(28) = 156.7 (5), Cl(2)−Os−N(28) = 89.3 (4), N(17)−Os−N(28) = 78.4 (5).

$$[Ru(bpy)_2(py)(NO)]^{3+} + H_2O \rightleftharpoons [Ru(bpy)_2(py)(NO_2)]^+ + 2H^+ \quad (4)$$

The molecular structure of *trans*-$[Os(tpy)(Cl)_2(NO)][BF_4]$ has been determined by X-ray crystallography,[14] and the cation is shown in Figure 1. The N−O bond (1.188(19) Å) is 0.13 Å longer than that in NO^+ (1.06 Å),[11] and the nitrosyl ligand is essentially linear (Os−N−O = 176.6(10)°). The Os−N bond in the nitrosyl (1.704(14) Å) is longer than the Os−N (nitride) bond in *trans*-$[Os(tpy)Cl_2(N)]Cl$ (1.663(7) Å)[4] but still provides clear evidence for multiple bonding. The Os−N bond is ca. *0.2 Å shorter* in *trans*-$[Os(tpy)Cl_2(NO)]^+$ than that in $[Os(NO)Cl_4]^-$ (1.89(2) Å),[12] while the N−O bond is ca. *0.2 Å longer*, illustrating the dramatic effect of binding a pyridyl ligand trans to the nitrosyl. The Os−O distance is nearly the same in the two ions (2.79(3) Å).

There are important features in the redox chemistry of the nitrosyls. In water it is only possible to study the *cis* isomer because of rapid *trans* → *cis* isomerization.[10] Cyclic voltammograms of *cis*-$[Os(tpy)Cl_2(NH_3)]$, *cis*-$[Os(tpy)Cl_2(N)]^+$, and *cis*-$[Os(tpy)Cl_2(NO)]^+$ at pH 0.04 (HCl) are shown in Figure 2. These waves are strongly pH dependent.[4] Upon reduction

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[14] Crystals of *trans*-$[Os(tpy)(Cl)_2(NO)][BF_4]$ were grown by vapor diffusion of ether into a concentrated acetonitrile solution of the salt. They are monoclinic, of space group $P2_1/c$, with $a = 8.8545$ (11) Å, $b = 9.3559$ (11) Å, $c = 23.058$ (5) Å, $\beta = 97.479$ (14)°, $V = 1893.9$ (5) Å^3, $Z = 4$, FW = 614.48, $d_{calc} = 2.155$ Mg m^{-3}, and $\mu = 7.07$ mm^{-1}. Data were collected on a Rigaku AFC6/S diffractometer with Mo Kα radiation and a graphite monochromator and the $\theta/2\theta$ scan mode. A total of 3344 unique reflections were measured, with 2203 having $I > 2.5\sigma(I)$ used in the structure refinement by full-matrix least-squares techniques (277 parameters). Final $R_f = 0.053$, $R_w = 0.059$. Full details can be found in the supplementary material. Software package used was NRCVAX: Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

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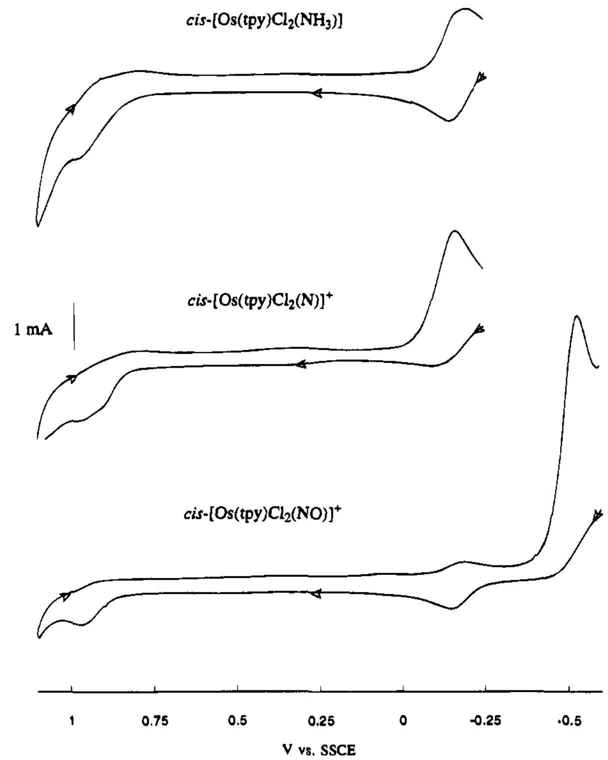

Figure 2. Cyclic voltammograms at 200 mV/s of *cis*-[Os(tpy)(Cl)$_2$(NH$_3$)] (top), *cis*-[Os(tpy)(Cl)$_2$(N)]$^+$ (middle), and *cis*-[Os(tpy)(Cl)$_2$(NO)]$^+$ (bottom) vs SSCE in aqueous HCl at pH 0.04 at a 1 cm diameter glassy carbon electrode.

of the nitride ($E_{p,c} = -0.17$ V) or nitrosyl ($E_{p,c} = -0.5$ V), the ammine complex ($E_{1/2}(\mathrm{Os}^{\mathrm{III/II}}) = -0.17$; $E_{1/2}(\mathrm{Os}^{\mathrm{IV/III}}) = 0.96$ V) is observed, and reoxidation results only in the nitride, even under basic conditions. Controlled potential electrolysis of *cis*-[Os(tpy)(Cl)$_2$(NO)]Cl in 1 M HCl at −0.5 V vs SSCE results in transfer of 5.8 ± 0.3 electrons/mol to give the corresponding ammine *cis*-[Os(tpy)(Cl)$_2$(NH$_3$)] (**3**), which has been reported previously.[4,15] Once formed, **3** is oxidized by 1.0 ± 0.1 electrons/mol to *cis*-[Os(tpy)(Cl)$_2$(NH$_3$)]$^+$ at $E_{1/2} = -0.17$ V, consistent with previous results although the product was misformulated as *trans* rather than *cis* in earlier work.[4,10] The Os(III) ammine undergoes further, quasireversible oxidation to *cis*-[Os$^{\mathrm{VI}}$(tpy)(Cl)$_2$(NH$_3$)]$^{2+}$ at 0.96 V at pH 0.04. On the longer time scale of electrolysis, it is unstable with respect to disproportionation, and net 3-electron oxidation occurs to give the Os(VI) nitride:[4]

$$cis\text{-}[\mathrm{Os}^{\mathrm{III}}(\mathrm{tpy})(\mathrm{Cl})_2(\mathrm{NH}_3)]^+ \underset{+3e^-,+3H^+}{\overset{-3e^-,-3H^+}{\rightleftharpoons}} cis\text{-}[\mathrm{Os}^{\mathrm{VI}}(\mathrm{tpy})(\mathrm{Cl})_2(\mathrm{N})]^+ \quad (5)$$

There is no evidence for formation of *cis*-[Os(tpy)(Cl)$_2$(NO)]$^+$ by oxidation of *cis*-[Os(tpy)(Cl)$_2$(NH$_3$)] at pH ≤ 12.5. This behavior is in contrast to the 5-electron, irreversible interconversion between nitrosyl and ammine in reaction 1.

The difference in oxidative behavior between [Ru(bpy)$_2$(py)(NH$_3$)]$^{2+}$ and *cis*-[Os(tpy)(Cl)$_2$(NH$_3$)] is significant. It is attributable to the more electron rich environment at the metal in the osmium complex. In [Os(tpy)(Cl)$_2$(NH$_3$)], 4-electron oxidation and proton loss occur to give a nitride which is relatively electron rich and stabilized by Os−N multiple bonding.[16] In acidic solution, further oxidation of [Os$^{\mathrm{VI}}$(tpy)(Cl)$_2$(N)]$^+$ to [Os$^{\mathrm{VII}}$(tpy)Cl$_2$(N)]$^{2+}$ does not occur to the solvent limit of ~1.2 V.

The metal is more electron deficient in the ruthenium complex. Oxidation and proton loss at Ru$^{\mathrm{IV}}$, Ru$^{\mathrm{V}}$, or Ru$^{\mathrm{VI}}$ must leave the nitrogen atom susceptible to attack by water, e.g.,[9]

$$[\mathrm{Ru}^{\mathrm{VI}}(\mathrm{bpy})_2(\mathrm{py})(\mathrm{N})]^{3+} + \mathrm{H_2O} \rightarrow [\mathrm{Ru}^{\mathrm{IV}}(\mathrm{bpy})_2(\mathrm{py})(\mathrm{NOH})]^{2+} + \mathrm{H}^+ \quad (6)$$

$$[\mathrm{Ru}^{\mathrm{V}}(\mathrm{bpy})_2(\mathrm{py})(\mathrm{N})]^{2+} + \mathrm{H_2O} \rightarrow [\mathrm{Ru}^{\mathrm{III}}(\mathrm{bpy})_2(\mathrm{py})(\mathrm{NH_2O})]^{2+} \quad (7)$$

With the N−O bond formed, further oxidation can occur with loss of protons to give the nitrosyl, e.g.,

$$[\mathrm{Ru}^{\mathrm{IV}}(\mathrm{bpy})_2(\mathrm{py})(\mathrm{NOH})]^{2+} \xrightarrow[-\mathrm{H}^+]{-2e^-} [\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_2(\mathrm{py})(\mathrm{NO})]^{3+} \quad (8)$$

While we have been unable to find a precedent for oxidation of the nitrido ligand to nitrosyl, it has been reported previously that Mo(N)(dtc)$_3$ and Re(N)(Cl)$_2$(L)$_3$ undergo reactions with S$_8$ and S$_2$Cl$_2$, respectively, to afford the corresponding thionitrosyls.[17] In the nitride to nitrosyl oxidation, there is no evidence for intermediate formation and oxygen atom transfer from the *N*-oxide may be synchronous. When phosphines are added to the nitrides, oxidation and phosphoraminato formation occur, reaction 9.[10,18] Reactions 3 and 9 demonstrate a remarkable

$$[\mathrm{Os}^{\mathrm{VI}}(\mathrm{tpy})(\mathrm{Cl})_2(\mathrm{N})]^+ + \mathrm{PR}_3 \rightarrow [\mathrm{Os}^{\mathrm{IV}}(\mathrm{tpy})(\mathrm{Cl})_2(\mathrm{NPR}_3)]^+ \quad (9)$$

versatility of the nitride ligand in its ability to mediate multiple electron transfer either to or from external reagents.

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Supplementary Material Available: Details of experimental preparation, NMR, IR, UV-vis, and analytical data for all compounds; details of the crystallographic analysis of *trans*-[Os(tpy)Cl$_2$(NO)][BF$_4$]; a fully labeled ORTEP[19] diagram; tables of atomic coordinates, isotropic thermal parameters, and bond lengths and angles (11 pages); listing of calculated and observed structure factors (11 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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