

Intramolecular, Oxidatively Induced Substitution on a Coordinated Terpyridyl Ligand

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In recent experiments, we demonstrated that in the Os–hydrazido complexes, *trans*-[Os^{VI}(L₃)(Cl)₂(NN(CH₂)₄O)]²⁺ (L₃ = 2,2':6',2''-terpyridine or tris(1-pyrazolyl)-methane and N(CH₂)₄O[−] = morpholide), there are four interconvertible oxidation states with Os(VI), Os(V), Os(IV), and Os(III) accessible within the solvent limit in CH₃CN.¹ Examples of Os(VI), Os(V), and Os(IV) have been characterized by X-ray crystallography.² We report here a remarkable reaction between *trans*-[Os^{VI}(tpy)(Cl)₂(NN(CH₂)₄O)]²⁺ (**1**) and a series of nitrogen and oxygen bases to give ring-substituted products. One example, *trans*-[Os^{VI}(4'-O(CH₂)₄Ntpy)(Cl)₂(NN(CH₂)₄O)]²⁺ (**2**), has been characterized crystallographically. An extraordinary electrophilic substituent effect of Os(VI) on the tpy ligand and the ability of Os(VI) to undergo reversible intramolecular Os(VI) → IV) electron transfer appear to play essential roles in these reactions.

When **1** and HN(CH₂)₄O are mixed in CH₃CN, a rapid reaction occurs as shown by a change in color from light brown to bright blue. With the addition of HN(CH₂)₄O new spectral features are observed at λ_{max} 624, ~400, and 344 nm (Supporting Information Figure 1). Cyclic voltammetry at the end of the reaction (Figure 1A) reveals two sets of waves, one set for **2** with waves at E_{1/2} = +0.78 V, +0.09V, and −0.48V for the Os(VI/V), Os(V/IV), and Os(IV/III) couples and another set for *trans*-[Os^V(tpy)(Cl)₂(NN(CH₂)₄O)]⁺ with E_{1/2} for the Os(VI/V) and Os(V/IV) couples at +0.98 and 0.00 V, respectively, in 0.1 M TBAH/CH₃CN (TBAH = tetra-*n*-butylammonium hexafluorophosphate). The cyclic voltammogram of *trans*-[Os^V(tpy)(Cl)₂(NN(CH₂)₄O)]⁺ is shown in Figure 1B for comparison. From relative peak heights, the product ratio of the unsubstituted Os(V):**2** is 2:1.

Crystals of **2**(PF₆)₂ were grown by a slow diffusion of Et₂O with a stream of argon into a solution containing the salt prepared by electrochemical oxidation of *trans*-[Os^V(tpy)(Cl)₂(NN(CH₂)₄O)]⁺ at E_{app} = 1.2 V followed by incremental additions of HN(CH₂)₄O. The resulting salt was characterized by X-ray crystallography,³ elemental analysis,⁴ UV–visible spectroscopy,⁵ and cyclic voltammetry.

The structure of **2** is illustrated in Figure 2. It reveals that

(1) Huynh, M. H. V.; El-Samanody, E.-S.; Demadis, K. D.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* 1999, 121, 1403. (b) Huynh, M. H. V.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* 1999, 121, 4530.

(2) Huynh, M. H. V.; El-Samanody, E.-S.; White, P. S.; Meyer, T. J. *Inorg. Chem.* 1999, 38, 3760.

(3) Crystals of *trans*-[Os^{VI}(4'-O(CH₂)₄Ntpy)(Cl)₂(NN(CH₂)₄O)](PF₆)₂ were grown by vapor diffusion of Et₂O into a CH₃CN solution of the salt. They are monoclinic, space group P2₁/c, with a = 8.4693(5) Å, b = 20.2029(11) Å, c = 18.6137(10) Å, β = 94.768(1)°, V = 3173.9(3) Å³, Z = 4, fw = 969.52, d_{calc} = 2.029 g/cm³, and μ = 4.39 mm^{−1}. 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 19 361 reflections were collected, and 5609 of them are unique; 4149 reflections with I > 2.5σ(I) were used in the structure refinement by full-matrix least-squares techniques (433 parameters). Absorption corrections were made by using SADABS. Final R_p = 4.1%, R_w = 3.1%, GoF = 1.08 (R = 4.7%, R_w = 6.5%, for all reflections). NRCVAX was used as the software package. Full details can be found in the Supporting Information.

(4) Elemental analysis: Anal. Calcd for OsC₂₃H₂₆Cl₂N₆O₂P₂F₁₂·0.2(*n*-Bu₄N)(PF₆) (MW 1047.02). C, 30.06; H, 3.20; N, 8.29. Found: C, 30.42; H, 3.19; N, 8.51.

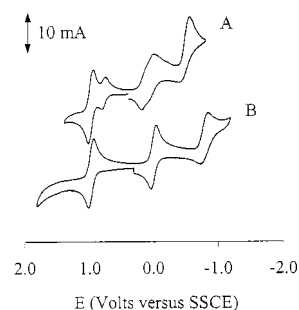


Figure 1. A: Cyclic voltammogram after mixing *trans*-[Os^{VI}(tpy)(Cl)₂(NN(CH₂)₄O)](PF₆)₂, 3.8 × 10^{−3} M, and morpholine, 1.3 × 10^{−3} M, in 0.1 M TBAH/CH₃CN versus SSCE. B: Cyclic voltammogram of *trans*-[Os^V(tpy)(Cl)₂(NN(CH₂)₄O)](PF₆) as in A, showing the chemically reversible waves for the Os(VI/V), Os(V/IV) and Os(IV/III) couples at E_{1/2} = +0.98 V, 0.00 V, and −0.79 V (E_{1/2} = (E_{p,a} + E_{p,c})/2).

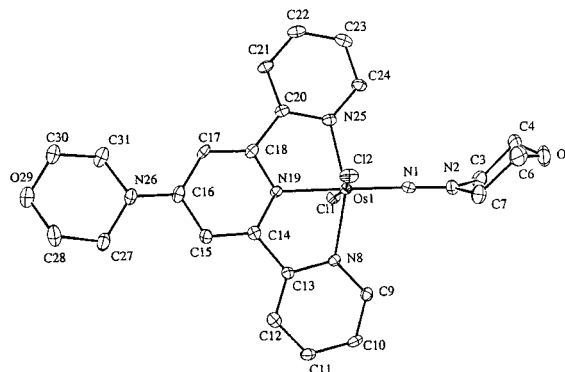
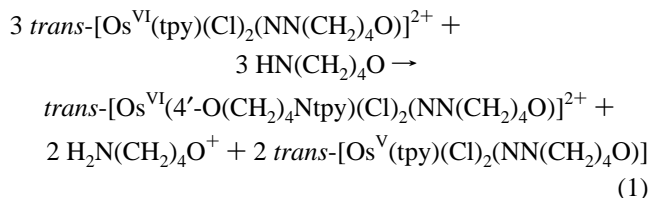


Figure 2. ORTEP diagram (30% ellipsoids) and labeling scheme for the cation in *trans*-[Os^{VI}(4'-O(CH₂)₄Ntpy)(Cl)₂(NN(CH₂)₄O)](PF₆)₂.

morpholide substitution has occurred at the 4'-position of the tpy ligand. Based on ∠N(26)–C(16)–C(15) = 120.6(5)°, sp² hybridization at C(4')-position of the tpy ligand is unchanged in the adduct. The Os–N(tpy) bond lengths range from 1.988(4) to 2.077(5) Å with the shortest Os–N bond *trans* to the hydrazido ligand. The Os–N(hydrazido) bond length of 1.778(4) Å, N–N(hydrazido) length of 1.237(6) Å, and ∠Os(1)–N(1)–N(2) = 172.5(4)° are all consistent with an Os(VI)–hydrazido complex.²

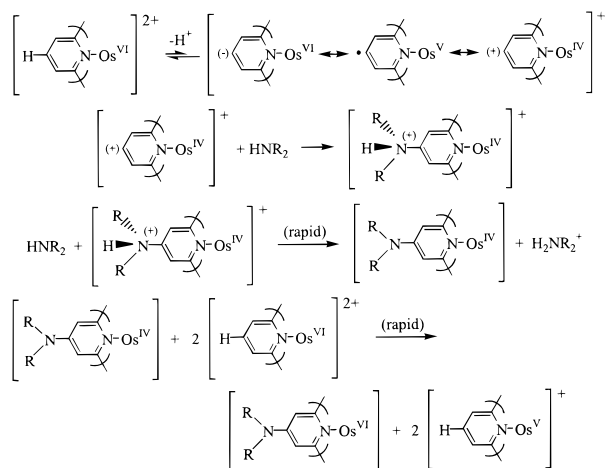
As shown by relative peak heights in cyclic voltammograms and by coulometric measurements, two molecules of unsubstituted Os(V) are formed for each molecule of **2**. Coulometry past the Os(VI/V) wave for **2** at E_{app} = 0.88 V occurred with n = 0 and oxidation at E_{app} = 1.20 V with n = 2/3. Based on these results, the stoichiometry of the reaction is



Good pseudo-first-order kinetics were obtained when the reaction was monitored by UV–visible spectrophotometry at 25.0 ± 0.1 °C in CH₃CN with an excess of HN(CH₂)₄O. A plot of

(5) UV–visible spectrum of *trans*-[Os^{VI}(4'-O(CH₂)₄Ntpy)(Cl)₂(NN(CH₂)₄O)](PF₆)₂ (**2**) in CH₃CN (λ_{max}, nm (ε, M^{−1} cm^{−1}): 624 (8.60 × 10³); 344 (1.46 × 10⁴); 308 (2.28 × 10⁴); 282 (3.06 × 10⁴); 240 (3.52 × 10⁴); 218 (4.27 × 10⁴).

Scheme 1



k_{obs} versus $[\text{HN}(\text{CH}_2)_4\text{O}]^2$ (Supporting Information, Figure 1) is linear consistent with the rate law

$$-d[\text{Os}^{\text{VI}}(\text{NNR}_2)^{2+}]/dt = k[\text{Os}^{\text{VI}}(\text{NNR}_2)^{2+}][\text{HNR}_2]^2 = k_{\text{obs}}[\text{Os}^{\text{VI}}(\text{NNR}_2)^{2+}]$$

with $k_{\text{obs}} = k[\text{HNR}_2]^2$ and $k = (2.15 \pm 0.04) \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$. Under these conditions, with excess morpholine, there is a slower following reaction in which morpholine reduces **2** to *trans*- $[\text{Os}^{\text{V}}(4'\text{-O}(\text{CH}_2)_4\text{Ntpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$.

A nucleophilic substitution mechanism, reminiscent of the Chichibabin⁶ and vicarious substitution reactions,⁷ is consistent with most of the available data. However, such reactions require vigorous conditions and are known to occur only when a very strong base is present and usually at elevated temperatures. Since the reaction described above occurs at room temperature and in a weakly basic solution, it may proceed via a mechanism initiated by deprotonation followed by internal electron transfer as summarized in Scheme 1.

An experimental fact in support of this mechanism is the observation that all of the aromatic protons of the tpy ligand, which appear at 7.97–8.63 ppm in the ¹H NMR spectrum, undergo exchange in CD₃CN with added D₂O.⁸ The key features in the mechanism proposed are the extraordinary electrophilic influence of Os(VI) as a substituent on the tpy ligand and the accessibility of reversible Os(VI → IV) intramolecular electron transfer.

The formation of the monosubstituted Os(VI)–hydrazido complex in eq 1 can be driven essentially to completion by oxidation of unsubstituted Os(V) to **1** followed by incremental additions of HN(CH₂)₄O and repeating this procedure in the same solution three times. Further addition of HN(CH₂)₄O to **2** followed by incremental electrolysis causes stepwise addition of a second and then third amine molecule to the tpy ligand to give *trans*- $[\text{Os}^{\text{VI}}(4,4'\text{-O}(\text{CH}_2)_4\text{N}_2\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$ and *trans*- $[\text{Os}^{\text{VI}}(4,4',4''\text{-O}(\text{CH}_2)_4\text{N}_3\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$.⁹ These products remain to be characterized structurally, but the subsequent additions presumably occur at the 4' and 4''-positions of the tpy rings.

The preparation of a large number of tpy ligands substituted at the 4'-position has been previously described by Constable.¹⁰

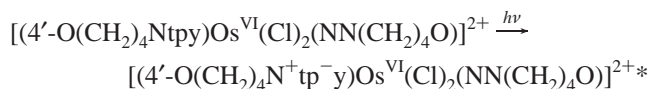
(6) McGill, C. K.; Rappa, A. *Adv. Heterocycl. Chem.* **1988**, *44*, 1.

(7) Makosza, M.; Stalinski, K. *Polish J. Chem.* **1999**, *73*, 151.

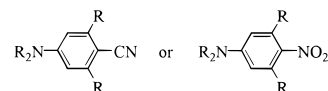
(8) All of the aromatic protons of the tpy ligand from 7.97 to 8.63 ppm undergo exchange in CD₃CN with added D₂O. No change occurs to the NMR spectrum when an equivalent amount of H₂O is added. When approximately equal amounts of H₂O (pH = 6.34) and D₂O (pH = 8.47) are added, the resonances for the most acidic protons at the 4, 4', 4'', 6, and 6'' positions from 8.4 to 8.63 ppm undergo exchange. Upon addition of incremental amounts of D₂O, the twin doublet resonances at 8.15–8.27 ppm for the 3' and 5' protons exchange followed by the resonances at 7.97–8.11 ppm for the 3, 3', 5, and 5'' protons.

The chemistry described here appears to be quite general and may provide another route to substituted tpy ligands. A variety of N-bases react with **1** to give colored adducts: H₂N(C₆H₅) (~540 nm), HN=S(C₆H₅)₂ (628 nm), HN=C(C₆H₅)₂ (594 nm), HN(CH₂)₄CH₂ (638 nm), HN(C₂H₅)₂ (624 nm), and H₂N(*t*-C₄H₉) (590 nm).¹¹ For some nucleophiles, electron transfer occurs rather than ring attack. For example, reaction of **1** with KOH, NaOCH₃, P(C₆H₅)₃, HP(C₆H₅)₂, (C₂H₅)₂S, and (C₆H₅)₂S results in reduction of **1** to *trans*- $[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$ or to *cis*- $[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})(\text{NCCH}_3)(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$.¹² Adducts are also formed with $[n\text{-}(\text{C}_4\text{H}_9)_4\text{N}][\text{CH}_3\text{CO}_2]$ (580 nm) and K[*t*-C₄H₉O] (~550 nm). Reactions with aromatic tertiary amines take a different course and are currently under investigation.

These reactions are remarkable in that they involve displacement of an aromatic C–H bond by a nucleophile in a polar organic solvent under mild conditions. The influence of the metal as a “substituent” also plays an important role in the electronic structure of the complexes. The intense ($\epsilon = 8.60 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), low-energy absorption band at 624 nm in **2** appears to originate from an intraligand charge-transfer absorption



with the Os^{VI}–hydrazido group acting as an electron-withdrawing substituent analogous to –NO₂ or –CN in¹³



Upon reduction to Os(V), this band is shifted to 452 nm consistent with a decrease in the electron-withdrawing character of the “Os-substituent”.

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Supporting Information Available: Tables containing crystal data, atomic coordinates, isotropic thermal parameters, bond distances and angles, packing diagrams, and figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(9) The UV–visible spectrum of *trans*- $[\text{Os}^{\text{VI}}(4, 4'\text{-O}(\text{CH}_2)_4\text{N}_2\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$ in CH₃CN (λ_{max} , nm (ϵ , M⁻¹ cm⁻¹) includes bands at 626 (5.61 × 10³); 372 (8.32 × 10³); 282 (2.47 × 10⁴); 236 (3.24 × 10⁴); 216 (4.28 × 10⁴) and for *trans*- $[\text{Os}^{\text{VI}}(4,4',4''\text{-O}(\text{CH}_2)_4\text{N}_3\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$ in CH₃CN (λ_{max} , nm (ϵ , M⁻¹ cm⁻¹) at 608 (1.83 × 10³); 384 (7.79 × 10³); 294 (1.65 × 10⁴); 238 (3.48 × 10⁴); 216 (4.38 × 10⁴).

(10) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Thompson, A. M. W. C. *Inorg. Chem.* **1995**, *34*, 2759.

(11) $E_{1/2}$ values for the Os(VI/V), Os(V/IV), and Os(IV/III) couples of the ring-substituted products from reactions between *trans*- $[\text{Os}^{\text{VI}}(\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$ and nitrogen bases (V (±2 mV) versus SSCE) are: H₂N(C₆H₅) (0.568, 0.163, and –0.514), HN=S(C₆H₅)₂ (0.754, 0.137, and –0.597), HN=C(C₆H₅)₂ (0.775, 0.155, and –0.502), HN(CH₂)₄CH₂ (0.760, 0.157, and –0.580), HN(C₂H₅)₂ (0.760, 0.143, and –0.532), and H₂N(*t*-C₄H₉) (0.776, 0.114, and –0.587). $E_{1/2}$ values for the products of reactions with oxygen bases are $[n\text{-}(\text{C}_4\text{H}_9)_4\text{N}][\text{CH}_3\text{CO}_2]$ (0.766, 0.136, and –0.616) and K[*t*-C₄H₉O] (0.790, 0.135, and –0.590).

(12) Reduction of *trans*- $[\text{Os}^{\text{V}}(\text{tpy})(\text{Cl})_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$ in CH₃CN by tertiary phosphines forms *cis*-Os(IV) followed by isomerization and solvolysis to give *cis*- $[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})(\text{NCCH}_3)(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$ which undergoes further solvolysis to give *cis*- $[\text{Os}^{\text{IV}}(\text{tpy})(\text{NCCH}_3)_2(\text{NN}(\text{CH}_2)_4\text{O})]^{2+}$. The details will be presented in a later paper.

(13) (a) Makosza, M.; Stalinski, K. *Polish J. of Chem.* **1999**, *73*(1), 151 and references therein. (b) Carrol, F. H. *Perspectives on Structure and Mechanism in Organic Chemistry*; Brooks/Cole: New York, 1998; pp 522–538 and references therein.