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Redox Chemistry of Morpholine-based Os(VI)−Hydrazido Complexes: *trans*-[$Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+}$

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The oxidations of benzyl alcohol, PPh_3, and the sulfides (SEt_2 and SPh_2) (Ph = phenyl and Et = ethyl) by the Os(VI)−hydrazido complex *trans*-[$Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine and $O(CH_2)_4N^-$ = morpholide) have been investigated in CH_3CN solution by UV−visible monitoring and product analysis by gas chromatography−mass spectrometry. For benzyl alcohol and the sulfides, the rate law for the formation of the Os(V)−hydrazido complex, *trans*-[$Os^{V}(tpy)(Cl)_2(NN(CH_2)_4O)]^{+}$, is first order in both *trans*-[$Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+}$ and reductant, with k_{benzyl} (25.0 ± 0.1 °C, CH_3CN) = $(1.80 \pm 0.07) \times 10^{-4}$ M^{-1} s^{-1}, $k(SEt_2) = (1.33 \pm 0.02) \times 10^{-1}$ M^{-1} s^{-1}, and $k(SPh_2) = (1.12 \pm 0.05) \times 10^{-1}$ M^{-1} s^{-1}. Reduction of *trans*-[$Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+}$ by PPh_3 is rapid and accompanied by isomerization and solvolysis to give the Os(IV)−hydrazido product, *cis*-[$Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)]^{2+}$, and $OPPh_3$. This reaction presumably occurs by net double Cl-atom transfer to PPh_3 to give Cl_2PPh_3 that subsequently undergoes hydrolysis by trace H_2O to give the final product, $OPPh_3$. In the X-ray crystal structure of the Os(IV)−hydrazido complex, the Os−N−N angle of 130.9(5)° and the Os−N bond length of 1.971(7) Å are consistent with an Os−N double bond.

Introduction

Earlier, we reported an extensive electron-transfer chemistry based on the Os(VI/V), Os(V/IV), and Os(IV/III) couples of Os(VI)−hydrazido complexes such as *trans*-[$Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+}$ (**1**).[1] Examples of Os(VI)−, Os(V)−, and Os(IV)−hydrazido complexes were structurally characterized,[2] and the features of their structural properties were rationalized by a molecular orbital model.[3] We also identified a novel series of reactions of **1** in which nucleophilic substitution accompanied by internal electron transfer occurs at the 4′-position of the tpy ligand.[4] In this paper, we report on an extension of the electron-transfer chemistry to net hydride transfer and comproportionation and provide further information about the redox chemistry of **1**.

Experimental Section

The following complexes and salts appear in this study: *trans*-[$Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)_2$ (**1**), *cis*-[$Os^{VI}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)_3$ (**2**), *cis*-[$Os^{VI}(tpy)(NCCH_3)_2(NN(CH_2)_4O)](PF_6)_4$ (**3**), *trans*-[$Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (**4**), *trans*-[$Os^{V}(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)$ (**5**), *cis*-[$Os^{V}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)_2$ (**6**), *trans*-[$Os^{IV}(tpy)(Cl)_2(N(H)N(CH_2)_4O)](PF_6)$ (**7**), *cis*-[$Os^{IV}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)$ (**8**), and *cis*-[$Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)](PF_6)_2$ (**9**).

Abbreviations and formulas used in the text include the following: tpy = 2,2′:6′,2″-terpyridine, TBAH = $[Bu_4N](PF_6)$ = tetrabutylammonium hexafluorophosphate, Ph = phenyl, and Et = ethyl.

Materials. House-distilled water was purified with a Barnstead E-Pure deionization system. High purity acetonitrile was used as received from Burdick and Jackson. Osmium tetraoxide (>99%) was purchased from Pressure Chemical Company. Deuteriated solvents were purchased from Cambridge Isotope Laboratories and used as received. TBAH was recrystallized three times from boiling ethanol and dried under vacuum at 120 °C for 2 days. Other chemicals employed in the preparation of compounds were reagent grade and used without further purification.

Instrumentation and Measurement. Fourier transform IR (FTIR), ^1H NMR, UV−visible (UV−vis), and near-IR spectra, elemental analyses, cyclic voltammetric data, and kinetic studies by UV−vis monitoring were obtained in a similar procedure.[3]

For all kinetic studies, the solvents were either CH_3CN or CH_3CN/H_2O mixtures and the temperature was maintained at 25.0 ± 0.1 °C by use of a Lauda RM6 circulating water bath. In each experiment, an excess of organic substrate was used to obtain pseudo-first-order kinetics. For the reaction between **1** and benzyl alcohol, the concentration of Os(VI) was 1.10×10^{-4} M and the concentration of benzyl alcohol was varied from 3.95×10^{-2} to 2.77×10^{-1} M. For the reaction between **1** and sulfide (SPh_2 or SEt_2), the concentration of Os(VI) was 5.25×10^{-4} M and the concentration of sulfide was varied from 1.06×10^{-3} to 8.86×10^{-2} M.

Product Analysis. Organic products from the oxidation reactions were analyzed by use of a Hewlett-Packard 5890 Series II gas chromatograph with a 12 m × 0.2 mm × 0.33 μm HP-1 column (cross-linked methyl silicone gum) and a Hewlett-Packard 5971A mass selective detector, interfaced with an HP Vectra PC computer system. PhCHO, Ph_2SO, and Et_2SO were analyzed by using calibration curves. A typical product analysis is described below.

For preparation of the calibration curves, CH_3CN solutions of benzyl alcohol, benzaldehyde, and chlorobenzene (the internal standard) were quantitatively prepared and extracted into hexane before injection into

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(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.

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

(3) Huynh, M. H. V.; El-Samanody, E.-S.; Demadis, K. D.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 3075.

(4) (a) Huynh, M. H. V.; Lee, D. G.; White, P. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 10446. (b) Huynh, M. H. V.; Lee, D. G.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2001**, *40*, 3842.

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the gas chromatograph. Plots of mole ratios (mole of organic compound/mole of internal standard = MR) vs area ratios (area of organic compound/area of internal standard = AR) are illustrated in Figures 1 and 2 in Supporting Information. The calibration data are tabulated in Table 1 of Supporting Information.

The oxidations of benzyl alcohol by **1**, **2**, and **3** were conducted in CH_3CN under an Ar atmosphere. Each Os(VI)−hydrazido complex (15−20 mg) was electrochemically generated under Ar in 3 mL of acetonitrile solution containing 0.1 M TBAH as a supporting electrolyte. An excess amount of benzyl alcohol (50−200 equiv) in 1 mL of CH_3CN was added to initiate the reaction. The reaction mixture was degassed with Ar for 30 s and stirred under an Ar atmosphere for an additional 10 h. The extent of reaction was monitored by following the appearance of the corresponding Os(V)−hydrazido complex with UV−vis spectroscopy. At the end of the reaction, a 1.0 mL aliquot of the reaction solution was added to a small vial containing chlorobenzene dissolved in 2.0 mL of hexane, and the mixture was diluted to 10 mL with hexane. The mixture was stirred for $^1/_2$ h under an Ar atmosphere. The hexane layer was injected into the gas chromatograph (GC), and the amount of product was determined with the calibration curve described above.

Synthesis and Characterization. The following complexes and compounds were prepared by literature procedures: *trans*-$[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)_2$ (**1**),[3] *trans*-$[Os^{VI}(tpy)(Cl)_2(N)](PF_6)$ (**4**),[5] *trans*-$[Os^{IV}(tpy)(Cl)_2(N(H)N(CH_2)_4O)](PF_6)$ (**7**),[6] and *trans*-$[Os^{V}(tpy)(Cl)_2(NN(CH_2)_4O)](PF_6)$ (**5**).[1]

***cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)](PF_6)_2$ (9).** The cation of **9** was formed from a stoichiometric reaction between **1** and 1 equiv of PPh_3 in CH_3CN. Crystals of **9** were grown by a slow diffusion of Et_2O into a CH_3CN solution containing **9**. Anal. Calcd for $OsC_{23}H_{25}N_7OP_2F_{12}\cdot H_2O$: C, 30.24; H, 3.20; N, 10.73. Found: C, 30.57; H, 3.19; N, 10.85. UV−vis data (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 421 (1.09×10^4); 314 (2.94×10^4); 318 (3.18×10^4); 320 (3.48×10^4); and 204 (4.84×10^4). Cyclic voltammetry data: $E_{1/2} = 1.52$ (Os(VI/V)), $E_{1/2} = 0.95$ (Os(V/IV)), and $E_{1/2} = -0.36$ (Os(IV/III)) V vs SSCE in 0.1 M TBAH/CH_3CN. IR (cm^{-1}, KBr disk): ν_{N-N} 1384.

***cis*-$[Os^{V}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)_2$ (6).** The cation of **6** was electrochemically generated from **5** by a two-step electrolysis in 0.1 M TBAH/CH_3CN, a one-electron reduction at $E_{app} = -0.29$ V (reduction to Os(IV) is accompanied by solvolysis and loss of one Cl^- ligand to form **8**[6]) followed by another one-electron oxidation at $E_{app} = 0.64$ V (vs SSCE). The product was isolated and fully characterized by the use of cyclic voltammetry, X-ray crystallography, and UV−vis and IR spectroscopies.[3]

***cis*-$[Os^{VI}(tpy)(Cl)(NCCH_3)(NN(CH_2)_4O)](PF_6)_3$ (2).** The cation of **2** was electrochemically generated from **5** by a two-step electrolysis in 0.1 M TBAH/CH_3CN: a one-electron reduction at $E_{app} = -0.29$ V (reduction to Os(IV) is accompanied by solvolysis and loss of one Cl^- ligand to form **8**[7]) followed by a two-electron oxidation at $E_{app} = 1.42$ V (vs SSCE). Cyclic voltammetry data: $E_{1/2} = 1.30$ (Os(VI/V)), $E_{1/2} = 0.44$ (Os(V/IV), and $E_{1/2} = -0.51$ (Os(IV/III)) V vs SSCE in 0.1 M TBAH/CH_3CN.

***cis*-$[Os^{VI}(tpy)(NCCH_3)_2(NN(CH_2)_4O)](PF_6)_4$ (3).** The cation of **3** was electrochemically generated from **9** by electrolysis in 0.1 M TBAH/CH_3CN at $E_{app} = 1.66$ V (vs SSCE).

X-ray Structural Determinations. Crystal data, intensity collection information, and structure refinement parameters for the structure of **9** are listed in Table 1. The structure was solved by direct methods. The non-hydrogen atoms were located in subsequent difference Fourier maps. Empirical absorption corrections were applied with SADABS. The ORTEP plotting program was used to generate the structure shown in Figure 1.[8] Hydrogen atoms were included in calculated positions with thermal parameters derived from the atom to which they were bonded. All computations were performed by using the NRCVAX suite of programs.[9] Atomic-scattering factors were taken from a standard source[10] and corrected for anomalous dispersion. The final positional parameters along with their standard deviations as estimates from the inverse matrix, tables of hydrogen atom parameters, anisotropic thermal parameters, and observed/calculated structure amplitudes for **9** are available as Supporting Information. Selected bond lengths and angles for the cation are listed in Tables 2 and 3, respectively.

Table 1. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for *cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)](PF_6)_2$

salt	**9**	collectn temp (°C)	−100
formula	$OsC_{25}H_{28}N_{8O}P_2F_{12}$	abs coeff, μ, (mm^{-1})	4.09
mol wt	936.67	$F(000)$	1822.89
a (Å)	8.9778(8)	$2\theta_{max}$ (deg)	50.0
b (Å)	28.592(3)	total reflns	23 330
c (Å)	13.3963(12)	unique reflns	5802
β (Å)	107.755(2)	refined reflns	4580
V (Å^3)	3275.0(5)	merging R value	0.047
Z	4	number of params	442
cryst syst	monoclinic	R (%)[a]	0.046
space group	$P2_1/n$	R_w (%)[b]	0.053
cryst size (mm)	0.25 × 0.20 × 0.05	GOF[c]	0.000
d_{calcd} (g cm^{-3})	1.900	deepest hole (e Å^{-3})	−1.760
diffractometer	Siemens CCD Smart	highest peak (e Å^{-3})	2.420
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)	σ	0.001

[a] $R = \sum(|F_o - F_c|)/\sum|F_o|$. [b] $R_w = [\sum(w|F_o - F_c|)^2/\sum w(F_o)^2]^{1/2}$. [c] GOF $= [\sum w(F_o - F_c)^2/(\text{no. of reflections} - \text{no. of parameters})]^{1/2}$.

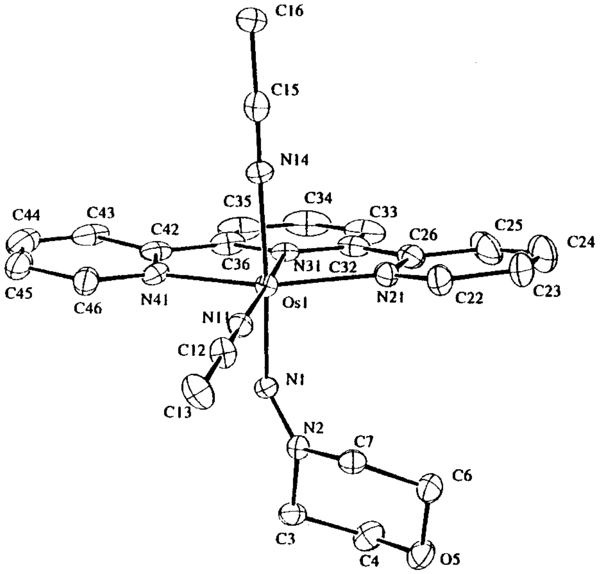

Figure 1. ORTEP diagrams (30% ellipsoids) and labeling scheme for the cation of **9**.

Results

Organic Product Analysis and Stoichiometry. The amount of benzaldehyde obtained from the oxidation of benzyl alcohol was determined quantitatively by gas chromatography−mass spectrometry (GC-MS) as described above. The yield of benzaldehyde obtained for the three hydrazido complexes was 92−95% based on the amount of Os(VI)−hydrazido present with the alcohol in excess. The product analysis for sulfide

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(5) (a) Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4598. (b) Pipes, D. W.; Bakir, M.; Vitols, S. E.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5507.

(6) Huynh, M. H. V.; White, P. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 4530.

(7) Huynh, M. H. V.; White, P. S.; Meyer, T. J. Synthesis and Redox Reactivity of Os(IV)−hydrazido Complexes. Manuscript in preparation.

(8) Johnson, C. K. *ORTEP: A Fortran Thermal Ellipsoid Plot Program*; Technical Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(9) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Table 2. Bond Lengths (Å) for *cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)]^{2+}$

Os(l)−N(l)	1.971(7)	C(12)−C(13)	1.451(11)	C(33)−C(34)	1.374(21)
Os(l)−N(11)	2.062(7)	N(14)−C(15)	1.133(12)	C(34)−C(35)	1.382(22)
Os(l)−N(l4)	2.062(7)	C(15)−C(16)	1.465(13)	C(35)−C(36)	1.386(14)
Os(l)−N(21)	2.093(7)	N(21)−C(22)	1.336(12)	C(36)−C(42)	1.460(15)
Os(l)−N(31)	1.982(6)	N(21)−C(26)	1.382(11)	N(41)−C(42)	1.375(12)
Os(l)−N(41)	2.072(7)	C(22)−C(23)	1.396(15)	N(41)−C(46)	1.354(12)
N(1)−N(2)	1.243(9)	C(23)−C(24)	1.374(22)	C(42)−C(43)	1.400(13)
N(2)−C(3)	1.476(11)	C(24)−C(25)	1.374(22)	C(43)−C(44)	1.374(20)
N(2)−C(7)	1.489(10)	C(25)−C(26)	1.373(14)	C(44)−C(45)	1.368(20)
C(3)−C(4)	1.503(13)	C(26)−C(32)	1.451(14)	C(45)−C(46)	1.368(14)
C(4)−O(5)	1.446(12)	N(31)−C(32)	1.345(12)	C(51)−C(52)	1.414(18)
O(5)−C(6)	1.425(12)	N(31)−C(36)	1.348(12)	C(52)−N(53)	1.125(18)
C(6)−C(7)	1.514(12)	C(32)−C(33)	1.402(13)	N(11)−C(12)	1.125(11)

Table 3. Angles (deg) for *cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)]^{2+}$

N(1)−Os(1)−N(11)	93.4(3)	C(34)−C(35)−C(36)	117.6(11)	Os(1)−N(11)−C(12)	176.2(7)
N(2)−C(7)−C(6)	108.1(7)	C(35)−C(36)−C(42)	127.2(10)	C(33)−C(34)−C(35)	123.1(9)
N(l)−Os(1)−N(14)	175.2(3)	N(31)−C(36)−C(35)	119.3(10)	N(31)−C(36)−C(42)	113.5(7)
N(l)−Os(1)−N(21)	94.9(3)	N(41)−C(42)−C(43)	119.9(10)	N(11)−C(12)−C(13)	179.1(9)
N(l)−Os(1)−N(31)	85.9(3)	C(42)−C(43)−(44)	120.1(10)	Os(1)−N(14)−C(15)	177.1(6)
C(43)−C(44)−C(45)	119.5(10)	N(1)−Os(l)−N(41)	88.2(3)	N(14)−C(15)−C(16)	178.8(8)
N(11)−Os(1)−N(14)	89.83(25)	Os(1)−N(21)−(22)	128.6(6)	Os(1)−N(41)−(46)	128.7(6)
N(11)−Os(1)−N(21)	102.7(3)	Os(1)−N(21)−C(26)	112.0(6)	C(42)−N(41)−C(46)	118.4(8)
N(11)−Os(1)−N(31)	178.0(3)	C(22)−N(21)−C(26)	119.3(8)	C(36)−C(42)−N(41)	115.8(7)
N(11)−Os(1)−N(41)	98.4(3)	N(21)−C(22)−C(23)	121.7(10)	C(36)−C(42)−C(43)	124.2(9)
N(14)−Os(1)−N(31)	90.8(3)	C(22)−C(23)−C(24)	119.1(11)	Os(1)−N(41)−C(42)	112.6(6)
N(14)−Os(1)−N(41)	87.8(3)	C(23)−C(24)−C(25)	119.0(10)	N(21)−Os(l)−N(31)	79.3(3)
C(44)−C(45)−C(46)	119.5(10)	C(24)−C(25)−C(26)	120.9(11)	N(21)−C(26)−C(32)	116.0(8)
N(21)−Os(1)−N(41)	158.5(3)	N(21)−C(26)−C(25)	119.9(10)	C(25)−C(26)−C(32)	124.1(9)
N(31)−Os(1)−N(41)	79.8(3)	N(41)−C(46)−C(45)	122.7(10)	O(5)−C(6)−C(7)	112.6(7)
Os(1)−N(1)−N(2)	130.9(5)	C(51)−C(52)−N(53)	177.4(15)	C(4)−O(5)−C(6)	109.7(7)
N(1)−N(2)−C(3)	121.3(6)	Os(1)−N(31)−C(32)	118.4(6)	N(1)−N(2)−C(7)	127.1(7)
Os(1)−N(31)−C(36)	118.0(6)	C(32)−C(33)−C(34)	117.1(11)	N(2)−C(3)−C(4)	109.5(7)
C(32)−N(31)−C(36)	123.4(7)	N(31)−C(32)−C(33)	119.4(10)	C(3)−C(4)−O(5)	111.2(7)
C(26)−C(32)−N(31)	113.8(7)	C(26)−C(32)−C(33)	126.7(9)	C(3)−N(2)−C(7)	111.5(6)

oxidation was conducted similarly. The yields of the sulfoxides from SEt_2 and SPh_2 were 91 and 93%, respectively.

Reactions of the Os(VI)−Hydrazido Complexes. A series of reactions including alcohol oxidation, comproportionation, and electron transfer were investigated. The results are described below.

Benzyl Alcohol Oxidation. In 0.1 M TBAH/CH_3CN, electrogenerated **1**, **2**, and **3** displayed oxo-like reactivity[1] in their oxidation of benzyl alcohol to give the corresponding Os(V)−hydrazido complexes as shown by UV−vis spectrophotometry[1] and benzaldehyde (GC-MS). The stoichiometry of the reaction of **1** with benzyl alcohol is shown in eq 1

$$2trans\text{-}[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+} + PhCH_2OH \rightarrow 2trans\text{-}[Os^{V}(tpy)(Cl)_2(NN(CH_2)_4O)]^{+} + PhCHO + 2H^{+} \quad (1)$$

The kinetics of this reaction were studied in CH_3CN at 25.0 ± 0.1 °C by conventional UV−vis monitoring at $\lambda_{max} = 421$ nm (Figure 2). Under pseudo-first-order conditions, with a large excess of benzyl alcohol (3.95×10^{-2} to 2.77×10^{-1} M), the results are consistent with the rate law in eq 2

$$\frac{-d[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+}}{dt} = k_{benzyl}\,[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)^{2+}]\,[PhCH_2OH] = k_{obs}\,[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)^{2+}] \quad (2)$$

with $k_{obs} = k_{benzyl}[PhCH_2OH]$ (Supporting Information Figure 3) and k_{benzyl} (25 °C, CH_3CN) = $(1.80 \pm 0.07) \times 10^{-4}$ M^{-1} s^{-1} as the average of three independent determinations. The order of oxidation of benzyl alcohol by **1**, **2**, and **3** is qualitatively consistent with their oxidizing ability, **1** < **2** < **3**.

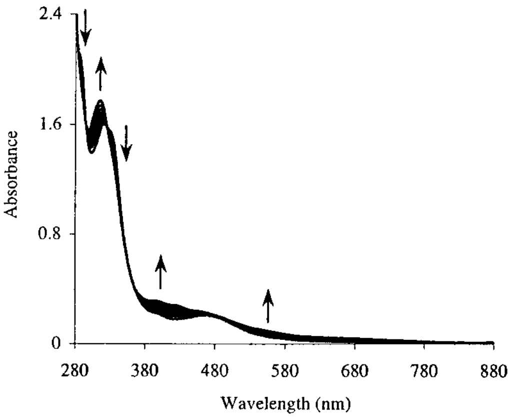

Figure 2. Spectral changes upon addition of 0.85 M $PhCH_2OH$ to 1.0 × 10^{-4} M of **1** in CH_3CN, 720 s/scan.

Under comparable conditions, complete conversion of Os(VI) to Os(V), as monitored by UV−vis spectroscopy, occurred after 10 h for **1**, 8 h for **2**, and 5.5 h for **3**.

Comproportionation. The comproportionation reaction between **1** and **7** (eq 3)

$$Os^{IV}{=}N(H)N(CH_2)_4O^{+} + Os^{VI}{\equiv}NN(CH_2)_4O^{2+} \rightarrow 2Os^{V}{\equiv}NN(CH_2)_4O^{+} + H^{+} \quad (3)$$

was studied by stopped-flow mixing with UV−vis monitoring. The comproportionation rate constant, k_{comp}, for the reaction between electrochemically generated **1** and **7** in 1:60 (v/v) H_2O/CH_3CN (pH = 1, μ = 0.1 M, and in KNO_3) was $(5.7 \pm 0.1) \times 10^{6}$ M^{-1} s^{-1} as the average of three independent determinations. The concentrations of electrochemically generated **1** and **7** were 5.3×10^{-5} to 5.2×10^{-4} M and 1.1×10^{-5} to 1.2×10^{-4} M, respectively, in this study.

Electron Transfer. Electrogenerated **1** is reduced by one electron to **5** ($n = 1$) and then either electrochemically or chemically in the presence of acid to **7**. In the absence of acid, reduction is followed by isomerization and solvolysis to form **8**. This complex undergoes further slow solvolysis on a time scale of 3−4 days to form **9**. Further details of the deprotonated Os(IV)−hydrazido chemistry will be presented in a future paper.[7]

Electrogenerated **1** undergoes a rapid reaction with PPh_3 in CH_3CN to give **9** ($\lambda_{max} = 421$ nm, $\epsilon = (1.09 \pm 0.04) \times 10^4$ M^{-1} cm^{-1}) and $OPPh_3$, eq 4, with H_2O coming from the solvent. The metal complex was characterized by cyclic voltammetry, crystallography (Figure 1), and UV−vis, ^1H NMR, and IR spectroscopies and $OPPh_3$ by ^{31}P NMR (30.5 ppm, $CDCl_3$) and IR (cm^{-1}, KBr disk: $\nu_{P=O}$ 1189) spectroscopies.

$$\textit{trans}\text{-}[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+} + PPh_3 + H_2O + 2CH_3CN \rightarrow \textit{cis}\text{-}[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)]^{2+} + OPPh_3 + 2H^+ + 2Cl^- \quad (4)$$

Rapid reactions occur between electrochemically generated **1** and the sulfides, $SR_2 = SEt_2$ or SPh_2, to give **5** and the corresponding sulfoxides, eq 5, with H_2O coming from the solvent.

$$2\textit{trans}\text{-}[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+} + SR_2 + H_2O \rightarrow 2\textit{trans}\text{-}[Os^{V}(tpy)(Cl)_2(NN(CH_2)_4O)]^{+} + S(O)R_2 + 2H^+ \quad (5)$$

From kinetic studies in CH_3CN at 25.0 ± 0.1 °C, these reactions are found to be first order in both Os(VI) and the sulfide with $k(SEt_2) = (1.33 \pm 0.02) \times 10^{-1}$ M^{-1} s^{-1} and $k(SPh_2) = (1.12 \pm 0.05) \times 10^{-1}$ M^{-1} s^{-1}. The stoichiometry in eq 5 was confirmed by UV−vis spectroscopy for the Os(V)−hydrazido complex and by GC-MS for the sulfoxides.

Structure and Bonding. An ORTEP diagram of **9**, prepared by reduction of **1** by PPh_3, is shown in Figure 1. The crystal contains discrete **9** cations and PF_6^- anions. Isomerization and solvolysis of the Cl^- ligands accompany the reduction in this case. In the product, there is no evidence for the structural trans effect noted in **4**.[5] The Os(1)−N(11) and Os(1)−N(14) bond lengths are identical (2.062(7) Å). The $N_\alpha{-}N_\beta$ bond length of 1.243(9) Å lies within the normal range for hydrazido ligands (1.21(2)−1.296(11) Å).[11] The $N(NCCH_3){-}Os{-}N$(hydrazido) angle is essentially linear at 175.2(3)°. The $Os{-}N_\alpha{-}N_\beta$ angle of 130.9(5)° and the Os(1)−N(1) bond length of 1.971(7) Å are consistent with double bonding between Os(IV) and N_α.[11]

Discussion

This paper provides an elucidation of the redox chemistry of the Os(VI)−hydrazido complex, **1**. The reactions studied include one-electron transfer, comproportionation, and net hydride transfer in the oxidation of benzyl alcohol.

Electron Transfer. There is an extensive multiple electron transfer chemistry for the hydrazido complexes based on sequential electron transfer and the couples Os(VI/V), Os(V/IV), and Os(IV/III).[2−4] The orbital basis for the multiple electron transfer chemistry has been described.[3] Electron transfer is typically rapid, and the redox couples are electrochemically reversible or nearly so.[3] Crystallographic studies have revealed that electron transfer is accompanied by significant structural changes at the Os−hydrazido unit, induced by changes in electron content.[2,11]

Electron transfer is facile for the Os(VI) complexes and appears to account for the reaction products observed in the reactions with SEt_2 and SPh_2. These reactions are first order in Os(VI) and sulfide with $k(SEt_2) = (1.33 \pm 0.02) \times 10^{-1}$ M^{-1} s^{-1} and $k(SPh_2) = (1.12 \pm 0.05) \times 10^{-1}$ M^{-1} s^{-1} in CH_3CN at 25.0 ± 0.1 °C. In these cases, rapid reduction of Os(VI) to Os(V) occurs in an initial step with slower reduction to Os(IV) with the sulfide in excess. The Os(V) → Os(IV) step was not studied in quantitative detail, but Os(IV)−hydrazido as **8** was the product in both cases, as shown by UV−vis spectrophotometry.

The mechanisms of these reactions presumably involve an initial one-electron transfer (eq 6)

$$\textit{trans}\text{-}[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+} + SR_2 \xrightarrow{k_{SR_2}} \textit{trans}\text{-}[Os^{V}(tpy)(Cl)_2(NN(CH_2)_4O)]^{+} + \dot{S}R_2^{\,+} \quad (6)$$

followed by a second, rapid oxidation of the intermediate sulfur cation-radical (eq 7)

$$\textit{trans}\text{-}[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+} + \dot{S}R_2^{\,+} + H_2O \xrightarrow{\text{rapid}} \textit{trans}\text{-}[Os^{V}(tpy)(Cl)_2(N(H)N(CH_2)_4O)]^{2+} + OSR_2 + H^+ \quad (7)$$

The comproportionation reaction between **1** and **7** also involves net electron transfer. It occurs with $k = (5.7 \pm 0.1) \times 10^6$ M^{-1} s^{-1} in 1:60 (v/v) H_2O/CH_3CN (pH = 1, $\mu = 0.1$ M in KNO_3) and at 25.0 ± 0.1 °C. The reaction is highly favored. From electrochemical measurements under these conditions, $\Delta G° = -0.48$ eV.[3]

$$Os^{VI}{\equiv}NN(CH_2)_4O^{2+} + Os^{IV}{=}N(H)N(CH_2)_4O^{+} \xrightarrow{k_{comprop}} 2Os^{V}{\equiv}NN(CH_2)_4O^{+} + H^+ \quad (8)$$

There is a change in proton content at the site that is initially Os(IV) in the net reaction. Under the conditions of the experiment, Os(IV) exists in the protonated form, **4**, since $pK_a = 3.20 \pm 0.05$. Os(V) is unprotonated under these conditions.[3] Given the change in proton content, the mechanism presumably involves proton loss from Os(IV) followed by electron transfer or initial electron transfer followed by proton transfer.

The reaction between **1** and PPh_3 is rapid and gives **9**, eq 4. Reduction of **5** to Os(IV)−hydrazido by PPh_3 is far slower and is followed by isomerization and solvolysis of one of the Cl^- ligands to give **8**, which occurs on a time scale of minutes.[7] Solvolysis of the second Cl^- ligand from **8** is much slower (3−4 days).

On the basis of these observations: (1) the reaction between PPh_3 and **1** does not occur through Os(V) as an intermediate and (2) the reaction induces loss of both Cl^- ligands and net solvolysis. A mechanism can be written consistent with these observations and eq 9, involving Cl-atom transfer followed by hydrolysis with trace H_2O to give $OPPh_3$.[12]

$$\textit{trans}\text{-}[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+} + PPh_3 + 2CH_3CN + H_2O \rightarrow \textit{cis}\text{-}[Os^{IV}(tpy)(NCCH_3)_2(NN(CH_2)_4O)]^{2+} + 2H^+ + 2Cl^- + OPPh_3 \quad (9)$$

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(11) Kahlal, S.; Saillard, J.-Y.; Hamom, J.-R. Manzur, C.; Carrillo, D. *J. Chem. Soc., Dalton Trans.* **1998**, 1229.

In the oxidation of benzyl alcohol, benzaldehyde was the product for all three Os(VI)−hydrazido oxidants. The kinetic study with **1** showed that the rate law is first order in both Os(VI) and the alcohol.

The reaction may occur by initial one-electron transfer. However, as suggested for the oxidation of 2-propanol by *cis*-$[\mathrm{Ru^{IV}(bpy)_2(py)(O)}]^{2+}$,[13] this reaction may also occur by a two-electron step and initial hydride transfer (eqs 10−12)

$$\mathrm{Os^{VI}NN(CH_2)_4O^{2+} + PhCH_2OH \xrightarrow{k_{benzyl}} Os^{IV}N(H)N(CH_2)_4O^{+} + PhCHOH^{+}} \quad (10)$$

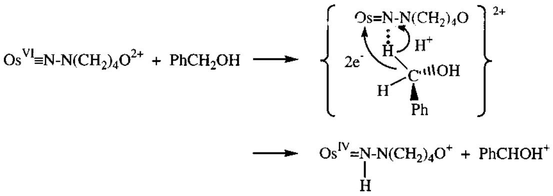
$$\mathrm{PhCHOH^{+} \rightleftharpoons PhCHO + H^{+}} \quad (11)$$

$$\mathrm{Os^{VI}NN(CH_2)_4O^{2+} + Os^{IV}N(H)N(CH_2)_4O^{+} \xrightarrow{k_{comp}} 2Os^{V}NN(CH_2)_4O^{+} + H^{+}} \quad (12)$$

with $k_{\mathrm{benzyl}} = (1.80 \pm 0.07) \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{\mathrm{comp}} = (5.7 \pm 0.1) \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}}$.

Qualitatively, the order of increasing reactivity toward oxidation of the alcohol follows the Os(VI/IV) (or Os(VI/V)) redox potentials with the two-electron potentials, **3** (0.94 V) > **2** (0.91 V) > **1** (0.89 V) in $\mathrm{CH_3CN}$ vs SSCE.[3,7] The potentials of the Os(VI/V) couple are 1.52, 1.30, and 0.98 V.[3]

An appealing feature of the hydride transfer mechanism is the implied utilization by the complex of a combination of the two-electron acceptor capability of Os(VI) and the proton acceptor abilities of N_α or N_β to achieve a synchronous two-electron, one-proton transfer, eq 13.



(13)

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Supporting Information Available: Figures 1−3, tables containing crystal data, atomic coordinates, isotropic thermal parameters, bond distances and angles, and packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) (a) Patois, C.; Berteverrando, S.; Savignac, P. *Bull. Soc. Chim. France* **1993**, *130*, 485. (b) Fridland, S. V.; Dmitrieva, N. V.; Salakhov, I. S. *Zh. Obshch. Khim.* **1980**, *50*, 784. (c) Horstmann, S.; Schnick, W. *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 127. (d) Weller, F.; Nusshär, D.; Dehnicke, K.; Gingl, F.; Strähle, J. *Z. Anorg. Allg. Chem.* **1991**, *602*, 7.

(13) (a) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106. (b) Thompson, M. S.; DeGiovani, W. F.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.* **1984**, *25*, 4972.