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Os(II)−Nitrosyl and Os(II)−Dinitrogen Complexes from Reactions between Os(VI)−Nitrido and Hydroxylamines and Methoxylamines

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Abstract: Reactions between the Os(VI)−nitrido salts (e.g., *trans*-[Os^{VI}(tpy)$(Cl)_2$(N)]PF_6 (tpy = 2,2′:6′,2″-terpyridine), *cis*-[Os^{VI}(tpy)$(Cl)_2$(N)]PF_6, and *fac*-[Os^{VI}(tpm)$(Cl)_2$(N)]PF_6 (tpm = tris(pyrazol-1-yl)methane)) and the hydroxylamines (e.g., H_2NOH and MeHNOH) and the methoxylamines (e.g., H_2NOMe and MeHNOMe) in dry MeOH at room temperature give three different types of products. They are Os(II)−dinitrogen (e.g., *trans*-, *cis*-, or *fac*-[Os^{II}−N_2]), Os(II)−nitrosyl [Os^{II}−NO]$^+$ (e.g., *trans*- or *cis*-[Os^{II}−NO]$^+$), Os(IV)−hydroxyhydrazido (e.g., *cis*-[Os^{IV}−N(H)N(Me)(OH)]$^+$), and Os(IV)−methoxyhydrazido (e.g., *trans*-/*cis*-[Os^{IV}−N(H)N(H)(OMe)]$^+$, and *trans*-/*cis*-[Os^{IV}−N(H)N(Me)(OMe)]$^+$) adducts. The products depend in a subtle way on the electron content of the starting nitrido complexes, the nature of the hydroxylamines, the nature of the methoxylamines, and the reaction conditions. Their appearance can be rationalized by invoking the formation of a series of related Os(IV) adducts which are stable or decompose to give the final products by two different pathways. The first involves internal 2-electron transfer and extrusion of H_2O, MeOH, or MeOMe to give [Os^{II}−N_2]. The second which gives [Os^{II}−NO]$^+$ appears to involve seven-coordinate Os(IV) intermediates based on the results of an ^{15}N-labeling study.

Introduction

Many reactions have been reported between nitrogen hydrides (H_2NNH_2, H_2NOH, NH_3, and N_3^-) and metal nitrosyls (M−NO),[1] between hydroxylamine (H_2NOH) and metal oxo compounds (M═O),[2] and of the oxidation of metal hydroxylamino (M−N(H)(OH)) to metal nitroxyl (M−N(H)O) complexes.[3] In the chemistry of high oxidation state metal nitrido (e.g., [Os^{VI}≡N]) complexes, a general reactivity is emerging based on formal N^- addition to a variety of nucleophiles,[4−8] examples being R_2NH,[9] PR_3,[10] SPR_3,[11] RSH,[12] ROH,[13] S(O)Me_2,[13] HPR_2,[14] and CN.[15] The characteristic feature of these

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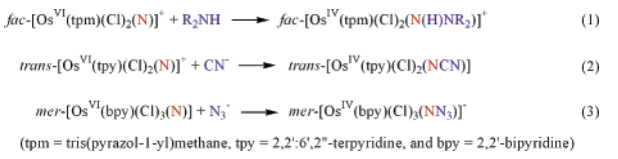
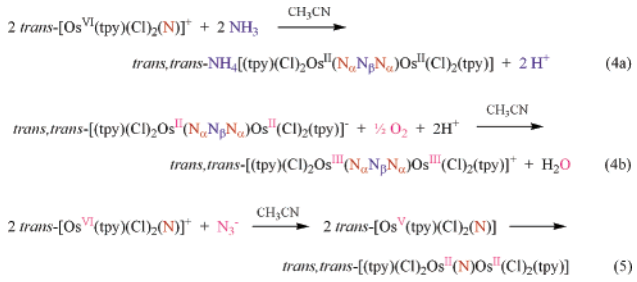
reactionsis the formal transfer of N^-, analogous to oxygen atom transfer from metal oxo complexes, i.e.,



(tpm = tris(pyrazol-1-yl)methane, tpy = 2,2':6',2"-terpyridine, and bpy = 2,2'-bipyridine)

Besides these N^--transfer reactions, a coupling chemistry between [Os^{VI}≡N] and nitrogen hydrides was also reported,[16−18,19c] e.g., reaction with NH_3 to give an azido-bridged dimer (M−N_3−M), eqs 4a,b,[17] and with N_3^- to give a nitrogen-bridged dimer (M−N−M), eq 5.[19c]



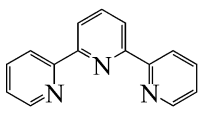
We report here a remarkably diverse reactivity between the series of nitrido complexes (*trans*-[Os^{VI}(tpy)$(Cl)_2$(N)]$^+$ (*trans*-[Os^{VI}≡N]$^+$), *cis*-[Os^{VI}(tpy)$(Cl)_2$(N)]$^+$ (*cis*-[Os^{VI}≡N]$^+$), and *fac*-[Os^{VI}(tpm)$(Cl)_2$(N)]$^+$ (*fac*-[Os^{VI}≡N]$^+$)) and the hydroxylamines (H_2NOH and MeHNOH) and methoxylamines (H_2NOMe and MeHNOMe) in MeOH at room temperature.

Experimental Section

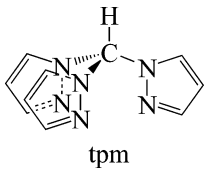
The following complexes and salts appear in this study:

trans-[Os^{VI}(tpy)$(Cl)_2$(N)]PF_6	*trans*-[Os^{VI}≡N]PF_6
cis-[Os^{VI}(tpy)$(Cl)_2$(N)]PF_6	*cis*-[Os^{VI}≡N]PF_6
fac-[Os^{VI}(tpm)$(Cl)_2$(N)]PF_6	*fac*-[Os^{VI}≡N]PF_6
trans-[Os^{II}(tpy)$(Cl)_2(N_2)$]	*trans*-[Os^{II}−N_2]
cis-[Os^{II}(tpy)$(Cl)_2(N_2)$]	*cis*-[Os^{II}−N_2]
fac-[Os^{II}(tpm)$(Cl)_2(N_2)$]	*fac*-[Os^{II}−N_2]
trans-[Os^{II}(tpy)$(Cl)_2$(NO)]PF_6	*trans*-[Os^{II}−NO]PF_6
cis-[Os^{II}(tpy)$(Cl)_2$(NO)]PF_6	*cis*-[Os^{II}−NO]PF_6
trans-[Os^{IV}(tpy)$(Cl)_2$(N(H)N(H)(OMe))]PF_6	*trans*-[Os^{IV}−N(H)N(H)(OMe)]PF_6
cis-[Os^{IV}(tpy)$(Cl)_2$(N(H)N(H)(OMe))]PF_6	*cis*-[Os^{IV}−N(H)N(H)(OMe)]PF_6
cis-[Os^{IV}(tpy)$(Cl)_2$(N(H)N(Me)(OH))]PF_6	*cis*-[Os^{IV}−N(H)N(Me)(OH)]PF_6
trans-[Os^{IV}(tpy)$(Cl)_2$(N(H)N(Me)(OMe))]PF_6	*trans*-[Os^{IV}−N(H)N(Me)(OMe)]PF_6
cis-[Os^{IV}(tpy)$(Cl)_2$(N(H)N(Me)(OMe))]PF_6	*cis*-[Os^{IV}−N(H)N(Me)(OMe)]PF_6

Abbreviations and Formulas used in the text include the following: tpy = 2,2′:6′,2″-terpyridine; tpm = tris(pyrazol-1-yl)methane; TBAH = $[Bu_4N]PF_6$ = tetrabutylammonium hexafluorophosphate; Me = methyl; and PPN^+ = bis(triphenylphophoranylidene)ammonium cation. The ligands are illustrated below:



tpy



tpm

Materials. House-distilled water was purified with a Barnstead E-Pure deionization system. High-purity acetonitrile was used as received from Aldrich. Osmium tetraoxide (>99%) was purchased from Pressure Chemical Company. Hydroxylamine (H_2NOH·HCl), *N*-methyl-hydroxylamine (MeHNOH·HCl), methoxylamine (H_2NOMe·HCl), and *N*,*O*-dimethyl-hydroxylamine (MeHNOMe·HCl) were purchased from Aldrich and used without further purification. Deuterated 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° for 2 days. Other chemicals employed in the preparation of compounds were reagent grade and used without further purification.

Instrumentation and Measurement. Electronic absorption spectra were acquired by using a Hewlett-Packard model 8453 diode array UV−visible spectrophotometer in quartz cuvettes. Spectra in the near-IR region were recorded on a Perkin-Elmer Lambda 19 spectrophotometer by using a matched pair of 10-mm path length quartz cell. Elemental analyses were performed at Los Alamos National Laboratory and by Atlantic Microlabs (Norcross, GA). FT-IR spectra were recorded on a Nexus 670 FT-IR spectrophotometer at 4 cm^{-1} resolution interfaced with an IBM-compatible PC. IR measurements were made in Nujol Mulls. ^{1}H NMR spectra were obtained in d_6-DMSO recorded on a JEOL-300 Fourier transform spectrometer.

Cyclic voltammetric experiments were measured at scan rates 100, 200, 400, and 800 mV/s with the use of a PAR model 263 potentiostat, and bulk electrolyses were performed with a PAR model 173 potentiostat/galvanostat. All measurements were conducted in a three-compartment cell in DMF with 0.2 M TBAH as the supporting electrolyte. A 1.0-mm platinum-working electrode was used for these measurements. All potentials (±2 mV) are referenced to the saturated sodium chloride calomel electrode (SSCE, 0.236 V versus NHE) at room temperature and are uncorrected for junction potentials. In all cases, the auxiliary electrode was a platinum wire. The solution in the working compartment was deoxygenated by N_2 bubbling.

Synthesis and Characterization. The following complexes and salts were prepared by literature procedures: *trans*-[Os^{VI}(tpy)$(Cl)_2$(N)]PF_6,[19a] *cis*-[Os^{VI}(tpy)$(Cl)_2$(N)]PF_6,[19b] *fac*-[Os^{VI}(tpm)$(Cl)_2$(N)]PF_6,[19c] *trans*-[Os^{II}(tpy)$(Cl)_2$(NO)]PF_6,[20] and *cis*-[Os^{II}(tpy)$(Cl)_2$(NO)]PF_6.[20]

***trans*-[Os^{II}(tpy)$(Cl)_2(N_2)$] (*trans*-[Os^{II}−N_2]).** In a 100-mL Erlenmeyer flask, *trans*-[Os^{VI}≡N]PF_6 (300 mg, 0.46 mmol) was stirred in 30 mL of MeOH. One equivalent of MeHNOH·HCl (38.4 mg) and NaOMe (82.7 mg of 30% methanolic solution) in 5 mL of MeOH was added while stirring over a period of 3 min. After 15 min, a dark-brown precipitate formed during stirring was filtered, washed with fresh MeOH, and air-dried. Yield: 0.190 g (79.2%). Anal. Calcd for $OsC_{15}H_{11}Cl_2N_5$:C 34.49; H 2.12; N 13.41. Found: C 34.59; H 2.23; N 13.68.

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Infrared (cm^{-1}, Nujol Mulls): ν(tpy) 1464, 1458, and 1378; $\nu(^{14}N\equiv{}^{14}N)$ 2110 (vs) and $\nu(^{15}N\equiv{}^{14}N)$ 2074 (vs); and $\nu(Os-{}^{14}N)$ 498 (vs) and $\nu(Os-{}^{15}N)$ 485 (vs).

***cis*-[Os^{II}(tpy)(Cl)$_2$(N$_2$)] (*cis*-[Os^{II}−N$_2$]).** In a 100-mL Erlenmeyer flask, *cis*-[Os$^{VI}\equiv$N]PF$_6$ (300 mg, 0.46 mmol) was stirred in 30 mL of MeOH. One equivalent of $H_2NOMe\cdot HCl$ (38.4 mg) and NaOMe (82.7 mg of 30% methanolic solution) in 5 mL of MeOH was added while stirring. After 30 min, the minor product, *cis*-[Os^{IV}(tpy)(Cl)$_2$(N(H)N(H)(OMe))]PF$_6$ (*cis*-[Os^{IV}−N(H)N(H)(OMe)]PF$_6$) that precipitated during stirring was filtered off through a fine frit, and the brown filtrate was reduced to dryness. Upon addition of 5 mL of CH_3CN, NaCl was filtered off, and the product was obtained by recrystallization from CH_3CN/Et_2O. Yield: 0.163 g (67.9%). Anal. Calcd for $OsC_{15}H_{11}Cl_2N_5$: C 34.49; H 2.12; N 13.41. Found: C 34.64; H 2.31; N 13.52. Infrared (cm^{-1}, Nujol Mulls): ν(tpy) 1465, 1455, and 1377; $\nu(^{14}N\equiv{}^{14}N)$ 2052 (vs) and $\nu(^{15}N\equiv{}^{14}N)$ 2018 (vs); and $\nu(Os-{}^{14}N)$ 467 (vs) and $\nu(Os-{}^{15}N)$ 455 (vs). ^{1}H NMR for (δ, DMSO) for *cis*-[Os^{IV}(tpy)(Cl)$_2$(N(H)N(H)(OMe))]PF$_6$: 11 aromatic protons from tpy = 9.0−7.8 ppm and methyl protons = 4.1 ppm.

***fac*-[Os^{II}(tpm)(Cl)$_2$(N$_2$)] (*fac*-[Os^{II}−N$_2$]).** In a 100-mL Erlenmeyer flask, *fac*-[Os$^{VI}\equiv$N]PF$_6$ (300 mg, 0.47 mmol) was stirred in 30 mL of MeOH. One equivalent of hydroxylamine ($H_2NOH\cdot HCl$ and $MeHNOH\cdot HCl$) or methoxylamine ($H_2NOMe\cdot HCl$ and $MeHNOMe\cdot HCl$) and NaOMe (82.7 mg of 30% methanolic solution) in 5 mL of MeOH were added to the above solution while stirring. After 30 min (hydroxylamine = MeHNOH), a greenish yellow precipitate formed during stirring was filtered, washed with fresh MeOH, and air-dried. Yield: 0.230 g (96.6%). Anal. Calcd for $OsC_{10}H_{10}Cl_2N_8$: C 23.86; H 2.00; N 22.26. Found: C 23.96; H 2.12; N 22.41. Infrared (cm^{-1}, Nujol Mulls): ν(tpm) 1464, 1458, 1437, and 1405; $\nu(^{14}N\equiv{}^{14}N)$ 2062 (vs) and $\nu(^{15}N\equiv{}^{14}N)$ 2028 (vs); and $\nu(Os^{II}-{}^{14}N)$ 461 (vs) and $\nu(Os^{II}-{}^{15}N)$ 451 (vs).

***trans*-[Os^{II}(tpy)(Cl)$_2$(NO)]PF$_6$ (*trans*-[Os^{II}−NO]PF$_6$).**[20] In a 100-mL Erlenmeyer flask, *trans*-[Os$^{VI}\equiv$N]PF$_6$ (300 mg, 0.46 mmol) was stirred in 30 mL of MeOH. One equivalent of $H_2NOH\cdot HCl$ (31.9 mg) and NaOMe (82.7 mg of 30% methanolic solution) in 5 mL of MeOH was slowly added while stirring. After an hour, the brown filtrate solution was reduced to dryness using rotary evaporation. The product was recrystallized from CH_3CN/Et_2O. Yield: 0.292 g (95.1%). Anal. Calcd for $OsC_{15}H_{11}Cl_2N_4OPF_6$: C 26.92; H 1.66; N 8.37. Found: C 27.12; H 1.82; N 8.46. Infrared (cm^{-1}, Nujol Mulls): ν(tpy) 1484, 1466, and 1377; $\nu(^{14}N\equiv O)$ 1853 (vs) and $\nu(^{15}N\equiv O)$ 1818 (vs); and $\nu(Os-{}^{14}N)$ 618 (vs) and $\nu(Os-{}^{15}N)$ 605 (vs). ^{1}H NMR (δ, DMSO): 11 aromatic protons from tpy = 9.0−8.0 ppm.

***cis*-[Os^{II}(tpy)(Cl)$_2$(NO)]PF$_6$ (*cis*-[Os^{II}−NO]PF$_6$).**[20] *cis*-[Os^{II}−NO]PF$_6$ was prepared by a method similar to that used for *trans*-[Os^{II}−NO]PF$_6$ except that *cis*-[Os$^{VI}\equiv$N]PF$_6$ was used as the starting material. Infrared (cm^{-1}, Nujol Mulls): ν(tpy) 1479, 1465, and 1377; $\nu(^{14}N\equiv O)$ 1881 (vs) and $\nu(^{15}N\equiv O)$ 1844 (vs); and $\nu(Os-{}^{14}N)$ 593 (vs) and $\nu(Os-{}^{15}N)$ 580 (vs). ^{1}H NMR (δ, DMSO): 11 aromatic protons from tpy = 9.5−8.1 ppm.

***trans*-[Os^{II}(tpy)(Cl)$_2$(^{15}NO)]PF$_6$ (*trans*-[Os^{II}−^{15}NO]PF$_6$).**[20] In a 100-mL Erlenmeyer flask, *trans*-[Os$^{VI}\equiv{}^{15}$N]PF$_6$ (300 mg, 0.46 mmol) was stirred in 30 mL of MeOH. One equivalent of $O\leftarrow NMe_3\cdot H_2O$ (51.1 mg) was added while stirring. After 30 min, the product was filtered and washed with fresh MeOH. *cis*-[Os^{II}(tpy)(Cl)$_2$(^{15}NO)]PF$_6$ was prepared by a method similar to that used for *trans*-[Os$^{II}-{}^{15}$NO]PF$_6$ except that *cis*-[Os$^{VI}\equiv{}^{15}$N]PF$_6$ was used as the starting material. Yield was quantitative in both cases.

***trans*-[Os^{IV}(tpy)(Cl)$_2$(N(H)N(H)(OMe))]PF$_6$ (*trans*-[Os^{IV}−N(H)N(H)(OMe)]PF$_6$).** This salt was prepared by a method similar to that used for *cis*-[Os^{II}−N$_2$] and *cis*-[Os^{IV}−N(H)N(H)−(OMe)]PF$_6$ except that *trans*-[Os$^{VI}\equiv$N]PF$_6$ was used as the starting material. *trans*-[Os^{II}−N$_2$] is the minor product, and *trans*-[Os^{IV}−N(H)N(H)(OMe)]PF$_6$ is the major product. Yield: 0.216 g (67.1%). Anal. Calcd for $OsC_{16}H_{16}Cl_2N_5OPF_6$: C 27.44; H 2.30; N 10.00. Found: C 27.75; H 2.59; N 10.37. Infrared (cm^{-1}, Nujol Mulls): ν(tpy) 1460, 1452, and 1377; $\nu(^{14}N-H)$ 3186; $\nu(^{15}N-H)$ 3180; ν(N−H) 3060; $\nu(Os-{}^{14}N)$ 1079 (vs); $\nu(Os-{}^{15}N)$ 1061 (vs); and $\nu(PF_6)$ 848 (vs). ^{1}H NMR (δ, DMSO): 11 aromatic protons from tpy = 9.1−7.9 ppm and methyl protons = 4.1 ppm.

***cis*-[Os^{IV}(tpy)(Cl)$_2$(N(H)N(Me)(OH))]PF$_6$ (*cis*-[Os^{IV}−N(H)N(Me)(OH)]PF$_6$).** This salt was prepared by a method similar to that used for *trans*-[Os^{II}−N$_2$] except that *cis*-[Os$^{VI}\equiv$N]PF$_6$ was used as the starting material. Yield: 0.223 g (69.3%). Anal. Calcd for $OsC_{16}H_{16}Cl_2N_5O-PF_6$: C 27.44; H 2.30; N 10.00. Found: C 27.65; H 2.48; N 10.31. Infrared (cm^{-1}, Nujol Mulls): ν(tpy) 1481, 1457, and 1377; $\nu(^{14}N-H)$ 3082; $\nu(^{15}N-H)$ 3075; $\nu(Os-{}^{14}N)$ 1078 (vs); $\nu(Os-{}^{15}N)$ 1065 (vs); and $\nu(PF_6)$ 842 (vs). ^{1}H NMR (δ, DMSO): 11 aromatic protons from tpy = 9.1−7.2 ppm and methyl protons = 4.2 ppm.

***trans*-[Os^{IV}(tpy)(Cl)$_2$(N(H)N(Me)(OMe))]PF$_6$ (*trans*-[Os^{IV}−N(H)N(Me)(OMe)]PF$_6$).** In a 100-mL Erlenmeyer flask, *trans*-[Os$^{VI}\equiv$N]PF$_6$ (300 mg, 0.46 mmol) was stirred in 30 mL of MeOH. One equivalent of $HMeNOMe\cdot HCl$ (44.8 mg) and NaOMe (82.7 mg of 30% methanolic solution) in 5 mL of MeOH was added while stirring. After 2 h, the brown filtrate solution was reduced to dryness by using rotary evaporation. The product was crystallized from the mixture of CH_3CN/Et_2O. Yield: 0.302 g (92.1%). Anal. Calcd for $OsC_{17}H_{18}Cl_2N_5OPF_6$: C 28.58; H 2.54; N 9.80. Found: C 28.64; H 2.64; N 9.92. Infrared (cm^{-1}, Nujol Mulls): ν(tpy) 1464, 1456, and 1368; $\nu(^{14}N-H)$ 3345; $\nu(^{15}N-H)$ 3337; $\nu(Os-{}^{14}N)$ 1080 (vs); $\nu(Os-{}^{15}N)$ 1066 (vs); and $\nu(PF_6)$ 845 (vs). ^{1}H NMR (δ, DMSO): 11 aromatic protons from tpy = 8.8−7.4 ppm and methyl protons = 4.4 and 4.5 ppm.

***cis*-[Os^{IV}(tpy)(Cl)$_2$(N(H)N(Me)(OMe))]PF$_6$ (*cis*-[Os^{IV}−N(H)N(Me)(OMe)]PF$_6$).** This salt was prepared by a method similar to that used for *trans*-[Os^{IV}−N(H)N(Me)(OMe)]PF$_6$ except that *cis*-[Os$^{VI}\equiv$N]PF$_6$ was used as the starting material. Anal. Calcd for $OsC_{17}H_{18}Cl_2N_5OPF_6$: C 28.58; H 2.54; N 9.80. Found: C 28.79; H 2.82; N 10.04. Infrared (cm^{-1}, Nujol Mulls): ν(tpy) 1462, 1453, and 1378; $\nu(^{14}N-H)$ 3480; $\nu(^{15}N-H)$ 3472; $\nu(Os-{}^{14}N)$ 1090 (vs); $\nu(Os-{}^{15}N)$ 1067 (vs); and $\nu(PF_6)$ 844 (vs). ^{1}H NMR data (δ, DMSO): 11 aromatic protons from tpy = 8.72−7.49 ppm and 6 methyl protons = 3.41−3.28 ppm. ^{1}H NMR (δ, DMSO): 11 aromatic protons from tpy = 8.9−7.3 ppm and methyl protons = 4.5 and 4.6 ppm.

Results

UV−Visible Spectra, ^{1}H NMR, and Redox Chemistry. For the tpm Os(II)−N$_2$ complex ([Os^{II}(tpm)(Cl)$_2$(N$_2$)]), characteristic $\pi \rightarrow \pi^*$ (tpm) bands appear in the UV at 207, 217, and 245 nm. Metal-to-ligand charge transfer (MLCT) bands of high

Table 1. UV−Visible and Electrochemical Data for Salts **4**−**6** in DMF

salt	λ_{max}, nm ($\epsilon \times 10^3$ M^{-1} cm^{-1})	$E_{1/2}$ vs SSCE[a] Os(VI/V)[b]	Os(V/IV)[c]	Os(IV/III)[c]	Os(III/II)[c]
$[Os^{IV}(tpy)(Cl)_2(N(H)N(H)(OMe))]^+$ (*trans*-[**4A**]PF_6)	415 (6.69 × 10^3); 322 (2.92 × 10^4); and 278 (2.93 × 10^4)	+1.13	+0.70	−0.13	−0.94
$[Os^{IV}(tpy)(Cl)_2(N(H)N(Me)(OH))]^+$ (*cis*-[**5**]PF_6)	417 (6.66 × 10^3); 324 (2.61 × 10^4); and 275 (2.81 × 10^4)	+1.15	+0.86	+0.23	−0.95
$[Os^{IV}(tpy)(Cl)_2(N(H)N(Me)(OMe))]^+$ (*trans*-[**6A**]PF_6)	472 (5.62 × 10^3); 327 (2.31 × 10^4); and 272 (2.78 × 10^4)	+0.88	+0.32	−0.39	−0.96
$[Os^{IV}(tpy)(Cl)_2(N(H)N(Me)(OMe))]^+$ (*cis*-[**6B**]PF_6)	427 (5.96 × 10^3); 382 (7.26 × 10^3); 323 (2.56 × 10^4); and 278 (2.53 × 10^4)	+0.88	+0.29	−0.12	−0.95

[a] Volts vs SSCE in 0.2 M TBAH/DMF. [b] The potentials for these couples refer to the deprotonated couples $[Os^{VI}-NNRR']^{2+}/[Os^{V}-NNRR']^{+}$. $E_{1/2}$ values are unaffected by the addition of HPF_6. [c] Oxidation to Os(V) results in deprotonation. The $E_{1/2}$ values cited are for the couples $[Os^{V}-NNRR']^{+}/[Os^{IV}-N(H)NRR']^{+}$, $[Os^{IV}-N(H)NRR']^{+}/[Os^{III}-N(H)NRR']$, and $[Os^{III}-N(H)NRR']/[Os^{II}-N(H)NRR']^{-}$, respectively.

Table 2. Visible and Near-Infrared Band Assignments for the Os(IV) N_β-Hydroxyhydrazido and N_β-Methoxyhydrazido Adducts in DMF

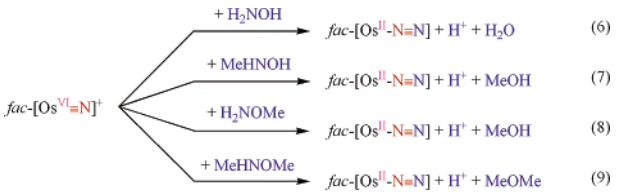
complex	band energy, nm (cm^{-1}) ($\epsilon \times 10^3$ in M^{-1} cm^{-1})	assignment
$[Os^{IV}(tpy)(Cl)_2(N(H)N(H)(OMe))]^+$ (*trans*-[**4A**]PF_6)	883 (1.02)	$d\pi_2 \rightarrow d\pi^*$
	666 (2.54)	$d\pi_1 \rightarrow d\pi^*$
	495 (5.93)	MLCT
	424 (6.54)	MLCT
$[Os^{IV}(tpy)(Cl)_2(N(H)N(Me)(OH))]^+$ (*cis*-[**5**]PF_6)	862 (1.05)	$d\pi_2 \rightarrow d\pi^*$
	732 (1.86)	$d\pi_1 \rightarrow d\pi^*$
	575 (4.24)	MLCT
	474 (5.75)	MLCT
$[Os^{IV}(tpy)(Cl)_2(N(H)N(Me)(OMe))]^+$ (*trans*-[**6A**]PF_6)	876 (2.05)	$d\pi_2 \rightarrow d\pi^*$
	793 (2.27)	$d\pi_1 \rightarrow d\pi^*$
	671 (3.55)	MLCT
	577 (4.88)	MLCT
$[Os^{IV}(tpy)(Cl)_2(N(H)N(Me)(OMe))]^+$ (*cis*-[**6B**]PF_6)	881 (1.44)	$d\pi_2 \rightarrow d\pi^*$
	755 (1.80)	$d\pi_1 \rightarrow d\pi^*$
	581 (4.14)	MLCT
	496 (5.21)	MLCT

intensity appear at $\lambda_{max} = 314$ nm with $\epsilon = 7.15 \times 10^3$ M^{-1} cm^{-1} and $\lambda_{max} = 459$ nm with $\epsilon = 1.73 \times 10^3$ M^{-1} cm^{-1}. The detailed origin of UV−visible bands for the tpy complexes will be discussed in a later section. UV−visible spectroscopic data for the Os(IV)−N_β-hydroxyhydrazido and N_β-methoxyhydrazido complexes prepared in this work are summarized in Table 1. Band assignments are given in Table 2. ^{1}H NMR spectra are dominated by the aromatic protons from tpy, ~9.5−7.2 ppm, and by the methyl proton, ~4.6−4.1 ppm.

All of the N_β-hydroxyhydrazido and N_β-methoxyhydrazido complexes have extensive one-electron redox chemistries. The cyclic voltammograms of *trans*-$[Os^{IV}-N(H)N(H)(OMe)]PF_6$, *cis*-$[Os^{IV}-N(H)N(Me)(OH)]PF_6$, *trans*-$[Os^{IV}-N(H)N(Me)(OMe)]PF_6$, and *cis*-$[Os^{IV}-N(H)N(Me)(OMe)]PF_6$ in 0.2 M TBAH/DMF provide evidence for chemically reversible Os(VI/V), Os(V/IV), Os(IV/III), and Os(III/II) couples on the cyclic voltammetric time scale at a scan rate of 200 mV/s. Reduction potentials listed in Table 1 occur in potential ranges comparable to those for reversible redox couples based on $PPN[Os^{IV}(bpy)(Cl)_3(NCN)]$[15] and *trans*-$[Os^{IV}(tpy)(Cl)_2(NN-(CH_2)_4O)]$.[21] The $E_{1/2}$ values for the Os(VI/V) couples in Table 1 were unaffected by the addition of HPF_6 and refer to the deprotonated couples $[Os^{VI}-NNRR']^{2+}/[Os^{V}-NNRR']^{+}$. The Os(IV) complexes are protonated in DMF, and the Os(V/IV) couples are $[Os^{V}-NNRR']^{+}/[Os^{IV}-N(H)NRR']^{+}$.

Synthesis and Mechanism of Formation. When *fac*-$[(tpm)(Cl)_2Os^{VI}\equiv N]PF_6$ is allowed to react with the series of two hydroxylamines (H_2NOH and MeHNOH) and 2 methoxylamines (H_2NOMe and MeHNOMe) in MeOH at room temperature, net reactions occur on time scales varying from 20 to 60 min as shown by color changes from orange to greenish yellow. There is no evidence for an intermediate or intermediates. The product in all four cases, eqs 6−9, is the previously reported dinitrogen complex *fac*-$[Os^{II}(tpm)(Cl)_2(N_2)]$, *fac*-$[Os^{II}-N_2]$.[19c] It and its ^{15}N-labeled form, *fac*-$[Os^{II}-{}^{15}N\equiv{}^{14}N]$ prepared by reaction with the *fac*-$[Os^{VI}\equiv{}^{15}N]^+$ nitrido complex, were isolated quantitatively and characterized by IR ($\nu(^{14}N^{14}N)$ = 2073; $\nu(Os^{II}-{}^{14}N)$ 461 (vs); $\nu(^{15}N^{14}N) = 2036$ cm^{-1}; and $\nu(Os^{II}-{}^{15}N)$ 451 (vs) in Nujol Mulls) and elemental analysis. Based on the IR data, the ^{15}N atom of the initial nitrido group remains bound to Os in *fac*-$[Os^{II}-N_2]$ as shown by the ^{15}N-labeling study.

As can be seen in the reactions in eqs 6−9, a common feature in all of these reactions in a formal sense is the use of both hydroxylamine and methoxylamine as a source of NH with concomitant loss of H_2O, MeOH, or MeOMe. The latter was identified by GC−MS ($m/z = 46$). In all cases, there is a net change in oxidation state at the metal from VI to II, eqs 6−9.



Under the same conditions, the reactions between *trans*-$[Os^{VI}\equiv N]PF_6$ and MeHNOH and between *cis*-$[Os^{VI}\equiv N]PF_6$ and H_2NOMe give *trans*-$[Os^{II}(tpy)(Cl)_2(N_2)]$ and *cis*-$[Os^{II}(tpy)(Cl)_2(N_2)]$, respectively, analogous to the reactions in eqs 7 and 8.

There is a contrasting reactivity under the same conditions between *trans*- or *cis*-$[Os^{VI}\equiv N]PF_6$ and H_2NOH. The products of these reactions are the corresponding Os(II)−nitrosyl complexes, *trans*- and *cis*-$[Os^{II}(tpy)(Cl)_2(NO)]PF_6$ (*trans*- and *cis*-

(21) Huynh, M. H. V.; El-Samanody, E.-S.; Demadis, K. D.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 3075−3085.

Table 3. Products Isolated from the Reactions between *trans*-, *cis*-, and *fac*-$[Os^{VI}{\equiv}N]PF_6$ and Various Hydroxylamines in CH_3OH at Room Temperature[a]

Hydroxylamines	*Trans*-$[Os^{VI}{\equiv}N]PF_6$	*Cis*-$[Os^{VI}{\equiv}N]PF_6$	*Fac*-$[Os^{VI}{\equiv}N]PF_6$
H_2NOH	$[Os^{II}\text{-}NO]^+$	$[Os^{II}\text{-}NO]^+$	$[Os^{II}\text{-}N_2]$
MeHNOH	~ 80 % $[Os^{II}\text{-}N_2]$ + ~ 20 % $[Os^{II}\text{-}NO]^+$	$[Os^{IV}{=}N(H)N(Me)(OH)]^{+\,b}$ (~ 80 %) + ~ 10 % $[Os^{II}\text{-}N_2]$ + ~ 10 % $[Os^{II}\text{-}NO]^+$	$[Os^{II}\text{-}N_2]$
H_2NOMe	$[Os^{IV}{=}N(H)N(H)(OMe)]^+$ (~ 70 %) + ~ 30 % $[Os^{II}\text{-}N_2]$	~ 70 % $[Os^{II}\text{-}N_2]$ + $[Os^{IV}{=}N(H)N(H)(OMe)]^+$ (~ 30 %)	$[Os^{II}\text{-}N_2]$
MeHNOMe	$[Os^{IV}{=}N(H)N(Me)(OMe)]^+$	$[Os^{IV}{=}N(H)N(Me)(OMe)]^+$	$[Os^{II}\text{-}N_2]$

[a] Percentages of isolated products are indicated. [b] Unstable toward decomposition into *cis*-$[Os^{II}{-}N_2]$ and *cis*-$[Os^{II}{-}NO]^+$ over a period of days.

$[Os^{II}{-}NO]PF_6$),[20] and NH_3, eq 10, as shown by infrared spectroscopy and X-ray crystallography.

In this reaction, there is a change in oxidation state at the metal from Os(VI) to Os(II) with formal O-atom transfer from H_2NOH to the nitrido ligand. It is analogous to the reaction between *trans*- or *cis*-$[Os^{VI}{\equiv}N]PF_6$ and $O{\leftarrow}NMe_3$ which gives *trans*- or *cis*-$[Os^{II}{-}NO]PF_6$ with an oxidation state change from Os(VI) to Os(II).[20]

We have investigated the underlying mechanisms that lead to such dramatically different products by taking advantage of the family of complexes, *trans*-$[Os^{VI}{\equiv}N]PF_6$, *cis*-$[Os^{VI}{\equiv}N]PF_6$, and *fac*-$[Os^{VI}{\equiv}N]PF_6$. The results are summarized in Table 3. Electrochemical measurements on the irreversible $Os^{VI}{\equiv}N^+/Os^{V}{\equiv}N$ couples suggest that the electron content at the metal increases in the order *cis* ($E_{pc} = -0.28$ V) < *trans* ($E_{pc} = -0.41$ V) < *fac* ($E_{pc} = -0.47$ V).[11,22]

An ^{15}N-labeling study was conducted on the reactions between *trans*- and *cis*-$[Os^{VI}{\equiv}^{15}N]PF_6$ and H_2NOH. The products were *trans*- and *cis*-$[Os^{II}{-}^{14}NO]PF_6$ as shown by infrared and UV−visible spectroscopies. This remarkable result shows that the N-atom of the nitrosyl ligand is derived from the hydroxylamine rather than from the nitrido ligand and that the mechanism does not involve simple oxygen atom transfer.

Careful inspection of these reactions by spectroscopic monitoring in MeOH at room temperature reveals that they proceed through discrete intermediates with $\lambda_{max} = 339$ nm for the *trans*- and 346 nm for the *cis*- complex. Attempts to isolate the intermediates have thus far been unsuccessful because they are unstable with regard to further reaction to give *trans*- and *cis*-$[Os^{II}{-}NO]PF_6$.

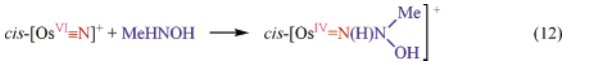
(22) (a) Meyer, T. J.; Huynh, M. H. V. *Inorg. Chem.* **2003**, *42*, 8140−8160 (Invited Inorganic Award Paper). (b) Demadis, K. D.; El-Samanody, E.-S.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 838−839.

In the reactions between *trans*- and *cis*-$[Os^{VI}{\equiv}N]PF_6$ and MeHNOMe, still a third type of product was obtained, eq 11. The products in this case were the Os(IV)−N_β-methoxyhydrazido complexes, *trans*- and *cis*-$[Os^{IV}(tpy)(Cl)_2(N_\alpha(H)N_\beta(Me)(OMe))]PF_6$ (*trans*- and *cis*-$[Os^{IV}{=}N_\alpha(H)N_\beta(Me)(OMe)]PF_6$, which can be viewed as arising from formal N^--transfer from the nitrido complex to *N,O*-dimethylhydroxylamine, a reactivity analogous to that found for the reactions in eqs 1−3.

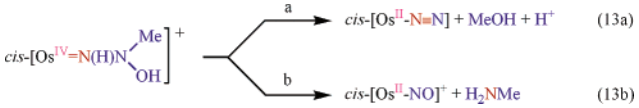
The Os(IV)−N_β-methoxyhydrazido products and their ^{15}N-labeled analogues were isolated and characterized by elemental analysis, cyclic voltammetry, and UV−visible and infrared spectroscopies.

In all cases, ^{15}N labeling and IR revealed that the N atom of the initial nitrido group remained bound to Os in the Os(IV) adducts. For example, $\nu(Os^{IV}{-}N)$ for *trans*-$[Os^{IV}{=}N_\alpha(H)N_\beta(Me)(OMe)]^+$ shifts from 1080 cm^{-1} in $\nu(Os^{IV}{-}^{14}N)$ to 1066 cm^{-1} in $\nu(Os^{IV}{-}^{15}N)$.

The analogous Os(IV)−N_β-hydroxyhydrazido product, *cis*-$[Os^{IV}(tpy)(Cl)_2(N_\alpha(H)N_\beta(Me)(OH))]PF_6$ (*cis*-$[Os^{IV}{=}N_\alpha(H)N_\beta(Me)(OH)]PF_6$), was obtained as the major product in the reaction between *cis*-$[Os^{VI}{\equiv}N]PF_6$ and MeHNOH under the same conditions, eq 12. It was also isolated and characterized by elemental analysis, cyclic voltammetry, and UV−visible and infrared spectroscopies.

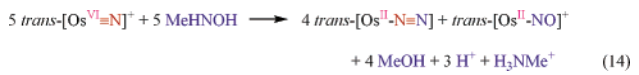


However, when *cis*-$[Os^{IV}{=}N(H)N(Me)(OH)]PF_6$ is allowed to remain in solution for ~24 h at 35 °C, it decomposes to give a 1:1 mixture of *cis*-$[Os^{II}{-}NO]PF_6$ and *cis*-$[Os^{II}{-}N_2]$ as products as shown by infrared and UV−visible spectroscopies, eqs 13a,b.



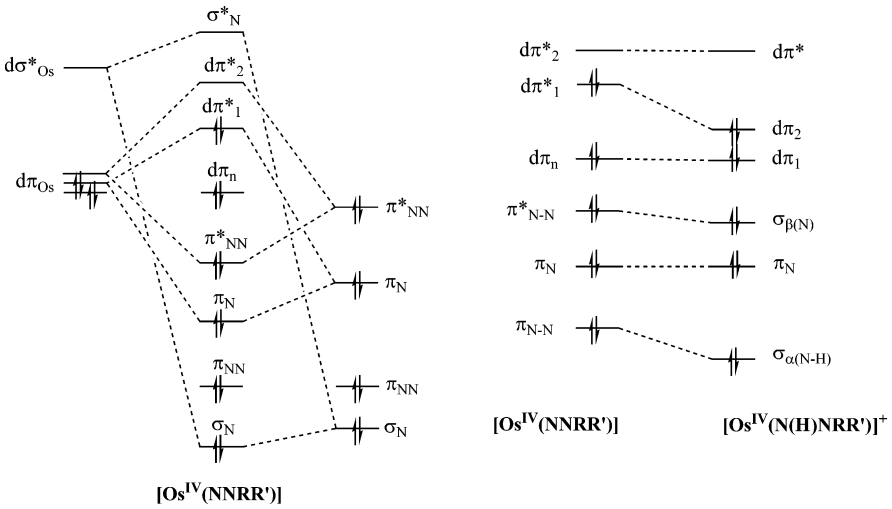
The simultaneous appearance of both products points to *cis*-$[Os^{IV}{=}N_\alpha(H)N_\beta(Me)(OH)]^+$ as a common intermediate. The results of ^{15}N-labeling in the starting *cis*-$[Os^{VI}{\equiv}^{15}N]^+$ nitrido complex reveal that the nitrido nitrogen is retained in *cis*-$[Os^{II}{-}^{15}N^{14}N]$ and lost in *cis*-$[Os^{II}{-}^{14}NO]^+$

In the reaction between *trans*-$[Os^{VI}{\equiv}N]PF_6$ and MeHNOH, eq 14, an intermediate was observed spectrophotometrically, $\lambda_{max} = 350$ and 336 cm^{-1}, presumably, *trans*-$[Os^{IV}(tpy)(Cl)_2(N_\alpha(H)N_\beta(Me)(OH))]PF_6$ (*trans*-$[Os^{IV}{=}N_\alpha(H)N_\beta(Me)(OH)]PF_6$). This intermediate decomposed on a time scale of minutes to give *trans*-$[Os^{II}{-}N_2]$ as the major product (~80%) and *trans*-$[Os^{II}{-}NO]^+$ as the minor product (~20%) as shown in eq 14.

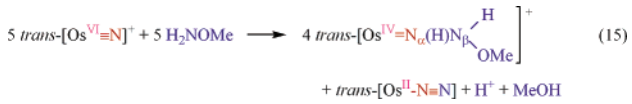


The reaction between *trans*-$[Os^{VI}{\equiv}N]PF_6$ and H_2NOMe, eq 15, over a period of 30 min gave *trans*-$[Os^{IV}(tpy)(Cl)_2(N_\alpha(H)N_\beta(H)(OMe))]PF_6$ (*trans*-$[Os^{IV}{=}N_\alpha(H)N_\beta(H)(OMe)]PF_6$) as the

Scheme 1

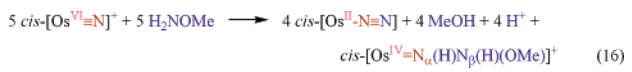


major product (70%) and *trans*-[Os^{II}−N_2] as a minor product (30%), Table 3. The Os(IV) adduct decomposes on longer time scales to give [Os^{II}−N_2].



(15)

The reaction between *cis*-[Os^{VI}≡N]PF_6 and H_2NOMe, eq 16, gave *cis*-[Os^{II}(tpy)$(Cl)_2(N_2)$] (*cis*-[Os^{II}−N_2]) as the major product (70%) with *cis*-[Os^{IV}=N_α(H)N_β(H)(OMe)]PF_6 as a minor product (~30%), Table 3. Again, the [Os^{II}−N_2] complex would presumably be the sole product at longer reaction times.



(16)

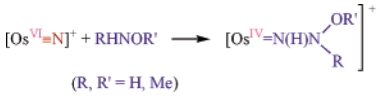
Discussion

Electronic Spectra. The energy level diagram in Scheme 1, derived earlier for a series of Os(IV)−hydrazido complexes, *trans*-[Os^{IV}(tpy)$(Cl)_2(NN(CH_2)_4O)$],[21] provides a basis for assigning the visible and near-IR spectra for the protonated Os(IV) adduct, *trans*-[Os^{IV}(tpy)$(Cl)_2(N(H)N(CH_2)_4O)$]PF_6. Band assignments are tabulated in Table 2. In the Scheme, the orbitals $d\pi^*_1$ and $d\pi^*_2$ are antibonding and largely $d\pi$(Os) in character. $d\pi^*_2$ results from $d\pi$(Os) mixing with π^*_{NN}, the antibonding complement of π_{NN}. $d\pi^*_1$ derives from $d\pi$(Os) mixing with π_N which is largely $2p_{\pi,N}$ in character. The $d\pi$(Os) orbital has δ symmetry with regard to the Os−NNRR′ interaction and is nonbonding in the π framework.

Protonation at N_α in Os−$N_\alpha N_\beta$RR′ changes the hybridization at N_α to sp^2. There is a single $d\pi$(Os)−π interaction, with π^*_{NN}, to give $d\pi^*$ which is antibonding and largely Os in character.

In the spectrum of the protonated Os(IV) complex *trans*-[Os^{IV}(tpy)$(Cl)_2$(N_α(H)N_β(H)(OMe))]$^+$ (in DMF), interconfigurational (IC), $d\pi \rightarrow d\pi$ bands appear at 666 nm ($d\pi_1 \rightarrow d\pi^*$) and 883 nm ($d\pi_2 \rightarrow d\pi^*$) where the assignments are based on Scheme 1. On the basis of these band energies and by assuming common pairing and reorganizational energies, the energy separation between $d\pi_2$ and $d\pi_1$ is found to be 3.7×10^3 cm^{-1}. Metal-to-ligand charge transfer (MLCT) bands, $d\pi \rightarrow \pi^*$(tpy), appear at 424 and 495 nm. Analogous bands are observed for *cis*-[Os^{IV}(tpy)$(Cl)_2$(N_α(H)N_β(Me)(OH))]$^+$ with $d\pi_1 \rightarrow d\pi^*$ appearing at 732 nm, $d\pi_2 \rightarrow d\pi^*$ at 862 nm ($[E(d\pi_2) - E(d\pi_1)] = 2.1 \times 10^3$ cm^{-1}), and MLCT bands at 474 and 575 nm. Similar band patterns are observed for *trans*-[Os^{IV}(tpy)$(Cl)_2$(N_α(H)N_β(Me)-(OMe))]$^+$ and *cis*-[Os^{IV}(tpy)$(Cl)_2$(N_α(H)N_β(Me)(OMe))]$^+$. The observation of IC bands for these complexes supports the Os(IV) oxidation state assignment and the ordering in Scheme 1. Similar bands have been reported in related hydrazido complexes such as *trans*-[Os^{IV}(tpy)$(Cl)_2$(N_α(H)$N_\beta(CH_2)_4O$)]$^+$ [22] and [Os^{IV}-(tpy)(bpy)(N_α(H)$N_\beta(CH_2)_4O$)]$^{3+}$.[21]

Mechanism of Formation of the Os(IV) Adducts. The products obtained in the reactions between the series of nitrido complexes and the hydroxylamines or methoxylamines, in MeOH at room temperature, are summarized in Table 3. The multiplicity of products can be explained by invoking a common type of intermediate produced by formal N^--transfer from the nitrido to the hydroxylamine or methoxylamine. N^--transfer is accompanied by reduction of Os(VI) to Os(IV). For the reactions between *trans*- or *cis*-[Os^{VI}≡N]PF_6 and MeHNOMe, the resulting adducts are the final products, eq 17.



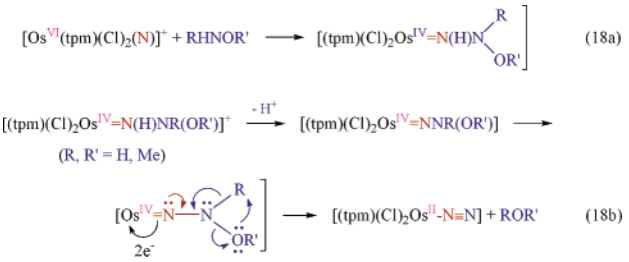
(17)

For the reactions between *cis*- or *trans*-[Os^{VI}≡N]PF_6 and MeHNOH or H_2NOMe, the adducts can be isolated or observed spectrophotometrically but are unstable on longer time scales toward decomposition into mixtures of [Os^{II}−N_2] and [Os^{II}−NO]$^+$. The ^{15}N-labeling results show that the original nitrido N atom remains bound to Os in the Os(IV) adducts.

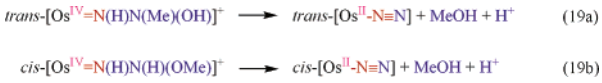
Decomposition to Give [Os^{II}−N_2]. The fate of the initial Os(IV) intermediates in MeOH at room temperature depends critically on both the hydroxylamine or methoxylamine and the Os(VI)−nitrido complex. For the tpm complex, which is the most electron rich, there is a single decomposition pathway. In all cases, the product is *fac*-[Os^{II}(tpm)$(Cl)_2(N_2)$].

Given the clear evidence for Os(IV) adducts as intermediates in the reactions involving *cis*-[Os^{IV}(tpy)$(Cl)_2$(N(H)N(H)-(OMe))]$^+$ and *trans*-[Os^{IV}(tpy)$(Cl)_2$(N(H)N(Me)(OH))]$^+$, these reactions presumably involve initial adduct formation, eq 18a, followed by decomposition, eq 18b. Decomposition can be

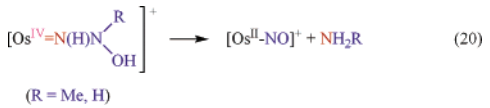
viewed as arising from internal electron transfer from the coordinated N_β-hydroxyhydrazido or N_β-methoxyhydrazido ligand to Os(IV) with concomitant loss of H_2O, MeOH, or MeOMe, eq 18b. The decomposition reactions are accelerated by excess hydroxylamine or methoxylamine and, by inference, involve initial deprotonation followed by electron transfer. The initial nitrido nitrogen atoms remains bound to Os(II) in the final product as shown by ^{15}N-labeling.



For the more electron deficient *trans*- and *cis*-complexes, the $[Os^{IV}-N_\alpha(H)N_\beta(Me)(OMe)]PF_6$ adducts are stable, presumably because of the absence of a dissociable O−H proton, MeOMe is kinetically not a good leaving group. By contrast, MeOH is a good leaving group as shown by the appearance of $[Os^{II}-N_2]$ as a product in Table 3. This is true whether the methyl group is bound to N as in *trans*-$[Os^{IV}{=}N_\alpha(H)N_\beta(Me)(OH)]^+$ or to O as in *cis*-$[Os^{IV}{=}N_\alpha(H)N_\beta(H)(OMe)]^+$, eqs 19a,b.

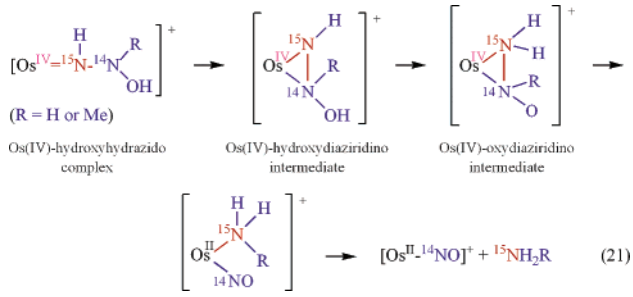


Decomposition to Give $[Os^{II}-NO]^+$. The Os(IV) adducts have a competitive decomposition pathway that results in formation of nitrosyl products. On the basis of the product summary in Table 3, nitrosyl formation is found only to occur for those cases where there is a dissociable O−H proton in the original hydroxylamine, MeHNOH and NH_2OH, eq 20. Also, on the basis of the results of the ^{15}N-labeling experiments, the N-atom of the nitrosyl comes from the hydroxylamine and not from the nitrido N-atom.

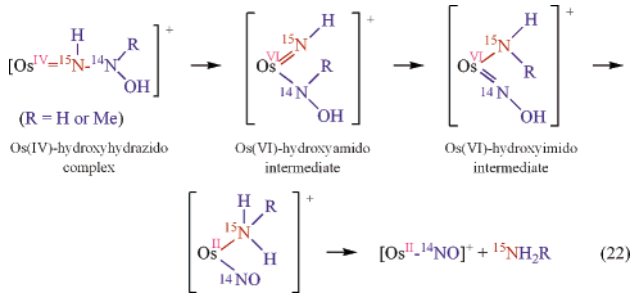


The formation of $[Os^{II}-NO]^+$ products from the reactions between *trans*-/*cis*-$[Os^{VI}{\equiv}N]^+$ and H_2NOH is reminiscent of known reactions between transition metal oxo complexes and hydroxylamines.[2] For example, the reaction between $[Mo^{VI}(dedtc)_2(O)_2]$ (dedtc = *N*,*N*-diethyl dithiocarbamate) and H_2NOH gives the Mo−nitrosyl complex, $[Mo^{II}(dedtc)_3(NO)]$. The net reaction can be viewed as involving a reductive nitrosylation with NO being derived by a combination of oxidation of hydroxylamine and reductive deoxygenation of Mo.[2b] Reductive nitrosylation has also been observed in reactions between H_2NOH and a series of Mn/Fe porphyrins,[2c,d] and dioxoruthenium(VI) prophyrins.[2a] A nitrosyl complex of myoglobin forms from H_2NOH in the presence of hydrogen peroxide.[2e] Mechanisms related to those suggested in eqs 21 and 22 below may be operative in these reactions as well.

The experimental observations made for the appearance of nitrosyl products can be rationalized by invoking a mechanism or mechanisms involving coordination expansion at Os. A possible mechanism is illustrated in eq 21. In this mechanism, the first step involves internal chelation of the hydroxyhydrazido ligand to give an Os(IV)−hydroxydiaziridino intermediate which undergoes H-transfer to form an Os(IV)−oxydiaziridino intermediate. The latter intermediate undergoes a sequence of internal atom/electron transfers, e.g., R → ^{15}N followed by internal electron transfer from the oxydiaziridino ligand to Os(IV). This mechanism would explain the ^{15}N-labeling result and the requirement for a dissociable proton on oxygen.



The same result would obtain by invoking initial internal electron transfer from Os(IV) to the hydroxyhydrazido ligand to form Os(VI)−hydroxyamido which is followed by H and R transfer to give Os(VI)−hydroxyimido. The nitrosyl complex would appear, following internal electron transfer.



Invoking seven-coordinate Os(IV) as in eq 21 is reasonable because there are precedents.[23] For instance, protonation of certain six-coordinate Os(II) complexes is known to give seven-coordinate Os(IV) hydrides, eq 23.[23b]

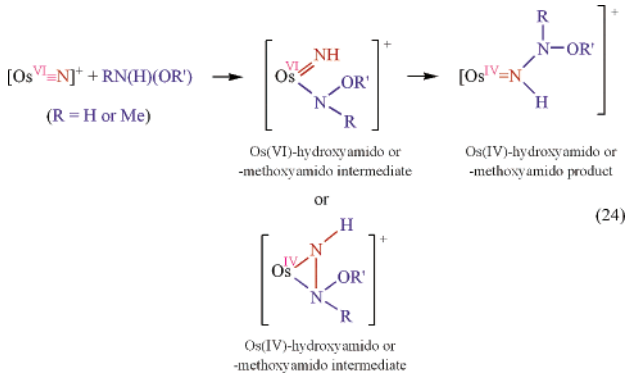
$$\textit{trans}\text{-}[Os^{II}(L_2)(PPh_3)_2(CO)(H)]^+ + CF_3OOH \rightleftharpoons \textit{trans}\text{-}[Os^{II}(L_2)(PPh_3)_2(CO)(H)_2]^{2+} + CF_3COO^- \quad (23)$$

L_2 = 2,2′-bipyridine; 4,4′-Me_2-2,2′-bypyridine; and 5,5′-Me_2-2,2′-bipyridine

The mechanisms in eqs 21 and 22 suggest that a viable pathway for formal N^--transfer in the reactions between the

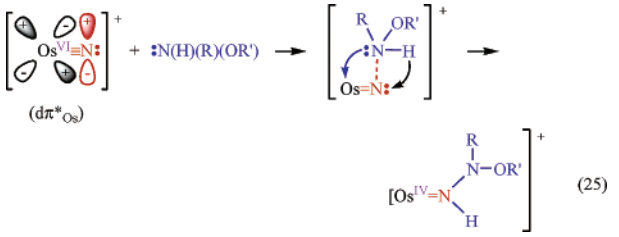
(23) (a) Li, Z.-W.; Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1993**, *115*, 10384. (b) Sullivan, B. P.; Lumpkin, R. S.; Meyer, T. J. *J. Inorg. Chem.* **1987**, *26*, 1247−1252. (c) Esteruelas, M. A.; Garcia-Yebra, C.; Olivan, M.; Onate, E. *Organometallics* **2000**, *19*, 3260−3262. (d) Crochet, P.; Esteruelas, M. A.; Lopez, A. M.; Martinez, M. P.; Olivan, M.; Onate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 4500−4509. (e) Gusev, D. G.; Hubener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716−3731. (f) Helberg, L. E.; Orth, S. D.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1996**, *35*, 5584−5594. (g) Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1996**, *510*, 267−279. (h) Williams, D. S.; Coia, G. M.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 586−592.

hydroxylamines and the nitrido complexes may be coordination expansion with formation of the Os(VI)−hydroxyamido or Os(VI)−hydroxyimido intermediates as shown in eq 22.



(24)

The mechanism may also involve N^--transfer as shown in eq 25 analogous to oxygen atom transfer. In this reaction, initial electron pair donation to a dπ* orbital is followed by an electron transfer to Os, N···N bond formation, and change in hybridization at the nitrido N atom. As written, the reaction is synchronous without the intervention of an intermediate.



(25)

Oxygen atom transfer is an available pathway for the nitrido complexes. Reactions between *cis*- or *trans*-$[Os^{VI}{\equiv}^{15}N]^+$ and O←NMe_3 in CH_3CN at room-temperature result in nitrosyl formation with the ^{15}N label coordinated to Os, eq 26, Experimental Section.

cis-/*trans*-$[Os^{VI}(tpy)(Cl)_2(^{15}N)]^+ + O{\leftarrow}NMe_3 \longrightarrow$ *cis*-/*trans*-$[Os^{II}(tpy)(Cl)_2(^{15}NO)]^+ + NMe_3$ (26)

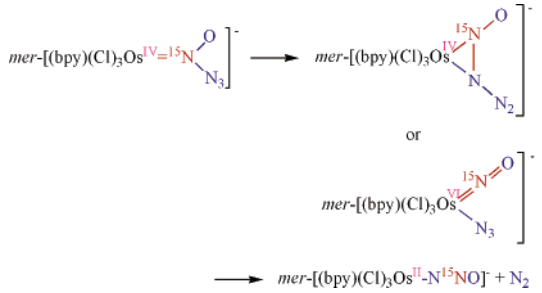
Related Reactions. The reactivity of the Os(IV) adducts observed here may help explain earlier observations made on related reactions. A reaction occurs between *mer*-$[Os^{VI}(bpy)(Cl)_3(N)]$ and N_3^- to give the Os(IV)−azidoimido adduct in eq 27.[17]

mer-$[Os^{VI}(bpy)(Cl)_3(N)] + PPNN_3 \longrightarrow$ *mer*-$PPN[Os^{IV}(bpy)(Cl)_3(NN_3)]$ (27)

The analogous reaction between *fac*-$[Os^{VI}(tpm)(Cl)_2(N)]^+$ and N_3^- gives *fac*-$[Os^{II}(tpm)(Cl)_2(N_2)]$.[19c] It seems reasonable to propose that the latter reaction also occurs through an azidoimido intermediate, in this case, *fac*-$[Os^{IV}(tpm)(Cl)_2(N_4)]$, but that it is unstable toward internal $N_4^{2-} \rightarrow$ Os(IV) 2-electron transfer and loss of N_2 as shown in eq 28.

fac-$[Os^{VI}{\equiv}N]^+ + N_3^- \longrightarrow$ *fac*-$[Os^{IV}{=}N(N_3)] \longrightarrow$ *fac*-$[Os^{II}{-}N{\equiv}N] + N_2$ (28)

Reaction between the azidoimido complex and O←$NMe_3{\cdot}H_2O$ gives the azidohydroxoimido complex, *mer*-$[Os^{IV}(bpy)(Cl)_3(N(OH)N_3)]$. It is also an Os(IV) adduct with p$K_a \approx 9$ for the dissociable O−H proton in 1:1 (v/v) CH_3CN:H_2O at room temperature. Loss of the proton at high pH results in decomposition to give the N_2O complex, *mer*-$[Os^{II}(bpy)(Cl)_3(N_2O)]^-$. An ^{15}N-labeling experiment showed that the nitrido N-atom ends up in the β-position of the coordinated N_2O. This points to an internal rearrangement, perhaps related to the reactions in eqs 21 and 22, followed by loss of N_2, eq 29.



$\longrightarrow$ *mer*-$[(bpy)(Cl)_3Os^{II}{-}N^{15}NO]^- + N_2$ (29)

As a final observation, it is interesting to note that the Os(IV) adduct *trans*-$[Os^{IV}(tpy)(Cl)_2(N_\alpha(H)N_\beta(H)(OMe))]^+$ appears as a pseudostable intermediate. This points to the possibility of finding reverse pathways for the activation of coordinated N_2 in relatively electron-deficient N_2 complexes, eq 30.

$[Os^{II}{-}N{\equiv}N] + MeOH + H^+ \longrightarrow [Os^{IV}{=}N(H)N(OH)Me]^+$ (30)

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