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Formation and Reactivity of the Os(IV)−Azidoimido Complex, PPN[$Os^{IV}(bpy)(Cl)_3(N_4)$]

My Hang V. Huynh,*,[‡] R. Thomas Baker,[§] Donald L. Jameson,[||] Andrea Labouriau,[§] and
Thomas J. Meyer*,[†]

*Contribution from The Associate Laboratory Director for Strategic Research, MS A127, and the Chemistry Division,
MS J514, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

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In the chemistry of Os(VI)−nitrido complexes, a general reactivity is emerging based on formal N^- addition to a variety of nucleophiles,[1−5] examples being CN^-,[6] RSH,[7] R_2NH,[8] PR_3,[9] and SPR_3,[10] eqs 1−5.

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + CN^- \rightarrow [Os^{IV}(tpy)(Cl)_2(NCN)] \quad (1)$$

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + ArSH \rightarrow [Os^{IV}(tpy)(Cl)_2(NS(H)(Ar)]^+ \quad (2)$$

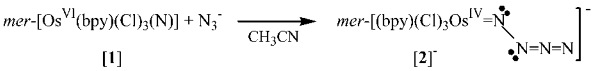
$$[Os^{VI}(tpm)(Cl)_2(N)]^+ + R_2NH \rightarrow [Os^{IV}(tpm)(Cl)_2(N(H)R_2)]^+ \quad (3)$$

$$[Os^{VI}(tpy/tpm)(Cl)_2(N)]^+ + PR_3 \rightarrow [Os^{IV}(tpy/tpm)(Cl)_2(NPR_3)] \quad (4)$$

$$[Os^{VI}(tpy/tpm)(Cl)_2(N)]^+ + SPR_3 \rightarrow {}^1/_2[Os^{IV}(tpy/tpm)(Cl)_2(NPR_3)]^+ + {}^1/_2[Os^{II}(tpy/tpm)(Cl)_2(NS)]^+ \quad (5)$$

(tpy = 2,2′:6′,2″-terpyridine,
tpm = tris(pyrazol-1-yl)methane)

We report here the novel observation that reaction between azide ion and the relatively electron-rich nitrido complex, [Os^{VI}(bpy)-$(Cl)_3$(N)] ([**1**]) (bpy = 2,2′-bipyridine), results in the stable Os^{IV}−azidoimido product, [$Os^{IV}(bpy)(Cl)_3(N_4)]^-$ ([**2**]$^-$), which contains the first example of an unbridged N_4^{2-} ligand,[11] eq 6.



$$mer\text{-}[Os^{VI}(bpy)(Cl)_3(N)] + N_3^- \xrightarrow{CH_3CN} mer\text{-}[(bpy)(Cl)_3Os^{IV}{=}N{-}N{=}N{=}N]^- \quad (6)$$

Reaction between [**1**] and $PPNN_3$ in dry CH_3CN under N_2 at 60 °C for 3 h resulted in a color change from purple to dark brown with associated changes in the visible spectrum from $\lambda_{max} = 498$ nm to 486 and 452 nm. The brown solution was evaporated to dryness by rotary evaporation, and the crude product was purified by gradient column chromatography on silica gel with CH_3CN:$C_6H_5CH_3$ mixtures (from 1:1 to 5:1 (v/v) ratio) as the eluent, followed by recrystallization from tetrahydrofuran. The product was collected (32% yield) and fully characterized by cyclic voltammetry, elemental analysis, ^1H and ^{15}N NMR, UV−vis, and infrared (Table 1) (IR) spectroscopies.[12]

Table 1. Selected Infrared Data (±2 cm^{-1}) for PPN-[$Os^{IV}(bpy)(Cl)_3(N_4)$] and Its ^{15}N-Labeled Analogues in Nujol Mulls

$[Os^{IV}(bpy)(Cl)_3(N_4)]^-$ isotopic distribution		$\nu_{asym}(N_3^-)$	$\nu(Os{-}N_\alpha)$
$[Os^{IV}{-}^{14}N^{14}N^{14}N^{14}N]^-$	[**2**]$^-$ [a]	2058	1092
$[Os^{IV}{-}^{15}N^{14}N^{14}N^{14}N]^-$	[**2***]$^-$ [b]	2056	1074
$[Os^{IV}{-}^{14}N^{15}N^{14}N^{14}N]^-$	[**2A***]$^-$ [c]	2040	1090
$[Os^{IV}{-}^{14}N^{14}N^{14}N^{15}N]^-$	[**2B***]$^-$ [c]		
$[Os^{IV}{-}^{15}N^{15}N^{14}N^{14}N]^-$	[**2A****]$^-$ [d]	2041	1073
$[Os^{IV}{-}^{15}N^{14}N^{14}N^{15}N]^-$	[**2B****]$^-$ [d]		

[a] Product from reaction between $[Os^{VI}(bpy)(Cl)_3(^{14}N)]$ and $^{14}N^{14}N^{14}N^-$.
[b] Product from reaction between $[Os^{VI}(bpy)(Cl)_3(^{15}N)]$ and $^{14}N^{14}N^{14}N^-$.
[c] Products from reaction between $[Os^{VI}(bpy)(Cl)_3(^{14}N)]$ and $^{15}N^{14}N^{14}N^-$.
[d] Products from reaction between $[Os^{VI}(bpy)(Cl)_3(^{15}N)]$ and $^{15}N^{14}N^{14}N^-$.

Direct evidence for the formation of an Os(IV)−azidoimido product comes from ^{15}N-labeling and IR measurements in Nujol mulls and ^{15}N NMR in CD_3CN. As shown in Table 1, the asymmetric stretching vibration of the azido group, $\nu_{asym}(N_3^-)$, appears at 2057 ± 2 cm^{-1} in PPN[$Os^{IV}(bpy)(Cl)_3(^{14}N^{14}N_3)$] (PPN[**2**]) and PPN[$Os^{IV}(bpy)(Cl)_3(^{15}N^{14}N_3)$] (PPN[**2***])[13] and at 2041 ± 2 cm^{-1} in mixtures of PPN[$Os^{IV}(bpy)(Cl)_3(^{14}N^{15}N^{14}N^{14}N)$] (PPN[**2A***]) and PPN[$Os^{IV}(bpy)(Cl)_3(^{14}N^{14}N^{14}N^{15}N)$] (PPN[**2B***]) or in mixtures of PPN[$Os^{IV}(bpy)(Cl)_3(^{15}N^{15}N^{14}N^{14}N)$] (PPN[**2A****]) and PPN[$Os^{IV}(bpy)(Cl)_3(^{15}N^{14}N^{14}N^{15}N)$] (PPN[**2B****]). $\nu_{asym}(N_3^-)$ appears at 2019 cm^{-1} in PPN[$^{14}N^{14}N^{14}N$] and at 2005 cm^{-1} in PPN[$^{15}N^{14}N^{14}N$]. From these data, it can be inferred that the N_3 unit is retained in [**2**]$^-$.

In the same set of IR spectra, $\nu(Os{-}^{14}N)$ appears at 1091 ± 2 cm^{-1} in PPN[**2**], PPN[**2A***], and PPN[**2B***], and $\nu(Os{-}^{15}N)$ appears at 1073 ± 2 cm^{-1} in PPN[**2***], PPN[**2A****], and PPN[**2B****]. From these data, it can be concluded that the N-atom in the $Os^{VI}{\equiv}N$ precursor is retained in the $Os^{IV}{-}N_4$ product at N_α, the N-atom bound to Os.

The proposed structure for PPN[**2**] is further confirmed by ^{15}N NMR spectrosopic data in CD_3CN for the highly labeled complexes, PPN[**2A****] and PPN[**2B****].[14] The $Os{\equiv}^{15}N$ resonance at 1187 ppm for [**1***] is shifted to 489 ppm (N_α) in PPN[**2B****]. The other resonance for PPN[**2B****] at 668 ppm can be assigned to N_δ of the $^{15}N_\alpha{}^{14}N_\beta{}^{14}N_\gamma{}^{15}N_\delta{}^{2-}$ ligand. Isotopomer PPN[**2A****] shows two doublet resonances at 489 and 730 ppm ($^1J(^{15}N{-}^{15}N) = 6.5$ Hz) due to N_α and N_β, respectively.[15] The $^{15}N{-}^{15}N$ *one-bond* coupling constant of 6.5 Hz compares well with similar values for Os dinitrogen complexes, that is, $^1J(^{15}N{-}^{15}N) = 4.5$ for *mer*-

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* Corresponding authors. E-mails: (T.J.M.) tjmeyer@lanl.gov; (M.H.V.H.) huynh@lanl.gov.
[†] Associate Laboratory Director for Strategic and Supporting Research, Los Alamos National Laboratory, MS A127, Los Alamos, NM 87545. Telephone: 505-667-8597. Fax: 505-667-5450.
[‡] Director-Funded Postdoctoral Fellow, Los Alamos National Laboratory, Chemistry Division, MS J514, Los Alamos, NM 87545. Telephone: 505-667-3968. Fax: 505-667-9905.
[§] Los Alamos National Laboratory, Chemistry Division, MS J514, Los Alamos, NM 87545.
[||] Department of Chemistry, Gettysburg College, Gettysburg, PA 17325.

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Table 2. Selected Infrared Data (±2 cm^{-1}) for $[Os^{IV}(bpy)(Cl)_3(N(OH)N_3)]$ and Their ^{15}N-Labeled Analogues in Nujol Mulls

$[Os^{IV}(bpy)(Cl)_3(N(OH)N_3)]$ isotopic distribution		$\nu_{asym}(N_3^-)$	$\nu(Os{-}N_\alpha)$	$\nu(N_\alpha{-}O)$	$\nu(O{-}H)$
$[Os^{IV}{-}^{14}N(OH)^{14}N^{14}N^{14}N]$	[**6**][a]	2058	1092	772	3404
$[Os^{IV}{-}^{15}N(OH)^{14}N^{14}N^{14}N]$	[**6***][b]	2060	1076	756	3408
$[Os^{IV}{-}^{14}N(OH)^{15}N^{14}N^{14}N]$	[**6A***][c]	2046	1091	773	3407
$[Os^{IV}{-}^{14}N(OH)^{14}N^{14}N^{15}N]$	[**6B***][c]				
$[Os^{IV}{-}^{15}N(OH)^{15}N^{14}N^{14}N]$	[**6A****][d]	2045	1074	756	3406
$[Os^{IV}{-}^{15}N(OH)^{14}N^{14}N^{15}N]$	[**6B****][d]				

[a] Product from reaction between $O{\leftarrow}NMe_3{\cdot}3H_2O$ and $PPN[Os^{IV}(bpy)(Cl)_3(^{14}N^{14}N^{14}N^{14}N)]$. [b] Product from reaction between $O{\leftarrow}NMe_3{\cdot}3H_2O$ and $PPN[Os^{IV}(bpy)(Cl)_3(^{15}N^{14}N^{14}N^{14}N)]$. [c] Products from reaction between $O{\leftarrow}NMe_3{\cdot}3H_2O$ and $PPN[Os^{IV}(bpy)(Cl)_3(^{14}N^{15}N^{14}N^{14}N)]$ and $PPN[Os^{IV}(bpy)(Cl)_3(^{14}N^{14}N^{14}N^{15}N)]$. [d] Products from reaction between $O{\leftarrow}NMe_3{\cdot}3H_2O$ and $PPN[Os^{IV}(bpy)(Cl)_3(^{15}N^{15}N^{14}N^{14}N)]$ and $PPN[Os^{IV}(bpy)(Cl)_3(^{15}N^{14}N^{14}N^{15}N)]$.

$[Os^{II}(Br)_2(^{15}N_2)(PMe_2Ph)_3]$[16] and $^1J(^{15}N{-}^{15}N) = 4.0$ for *mer*-$[Os^{II}(Cl)_2(^{15}N_2)(PMe_2Ph)_3]$.[17]

Formulation of PPN[**2**] as a diamagnetic d^4 Os(IV)−azidoimido complex containing the N_4^{2-} ligand with retention of the *mer*-geometry is consistent with its spectroscopic properties. In the ^1H NMR spectrum, the expected eight resonances of bpy appear from 8.05 to 9.22 ppm, similar to the pattern of resonances for the parent *mer*-$[Os^{VI}(bpy)(Cl)_3(N)]$. The visible spectrum in CH_3CN has a pattern of bands, $\lambda_{max} = 486$ and 452 nm, analogous to bands at 521 and 421 nm for the analogous Os(IV)−cyanoimido complex, $[Os^{IV}(bpy)(Cl)_3(NCN)]^-$.[6] Closely related reactions occur between $[Os^{VI}(Me_2bpy)(Cl)_3(N)]$ (Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine), $[Os^{VI}(phen)(Cl)_3(N)]$ (phen = 1,10-phenanthroline), or $[Os^{VI}(Ph_2phen)(Cl)_3(N)]$ (Ph_2phen = 4,7-diphenyl-1,10-phenanthroline) and $PPNN_3$ to give the corresponding Os(IV)−azidoimido products, $[Os^{IV}(L_2)(Cl)_3(N_4)]^-$ (L_2 = Me_2bpy = [**3**]$^-$, phen = [**4**]$^-$, and Ph_2phen = [**5**]$^-$). They were also isolated as PPN^+ salts and characterized by cyclic voltammetry, elemental analysis, and UV−visible and IR spectroscopies.[12]

We have begun to explore the reactivity of these novel complexes. For PPN[**2**] in 0.1 M TBAH/CH_3CN (TBAH = tetrabutylammonium hexafluorophosphate), chemically reversible waves appear in the cyclic voltammogram at $E_{1/2} = +1.40$, +0.88, and −0.82 V (versus SSCE) for the Os(VI/V), Os(V/IV), and Os(IV/III) couples, respectively. They compare with $E_{1/2} = +1.72$, +0.90, and −0.40 V for the same couples for $PPN[Os^{IV}(bpy)(Cl)_3(NCN)]$.[6] In dry CH_3CN with added $O{\leftarrow}NMe_3{\cdot}3H_2O$, a rapid color change occurs from dark to lighter brown. The product was isolated (68% yield) from the solution and characterized by elemental analysis and IR and ^1H NMR spectroscopies.[12] Its formulation as the Os(IV)−azidohydroxoamido complex, *mer*-$[Os^{IV}(bpy)(Cl)_3(^{14}N(OH)^{14}N_3)]$ ([**6**]), in eq 7 is further supported by ^{15}N-labeling. This appears to be the first example of the $N(OH)N_3^-$ ligand.

$$\begin{aligned} &mer\text{-}[Os^{IV}(bpy)(Cl)_3(NN_3)]^- + O{\leftarrow}NMe_3 + H_2O \rightarrow \\ &\qquad [\mathbf{2}]^- \\ &\qquad mer\text{-}[Os^{IV}(bpy)(Cl)_3(N(OH)N_3)] + NMe_3 + OH^- \\ &\qquad\qquad [\mathbf{6}] \end{aligned} \tag{7}$$

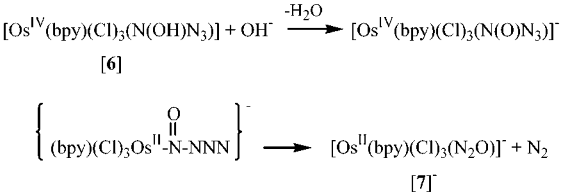
As shown in Table 2, in *mer*-$[Os^{IV}(bpy)(Cl)_3(^{14}N(OH)^{14}N_3)]$ ([**6**]) and its ^{15}N analogue, $[Os^{IV}(bpy)(Cl)_3(^{15}N(OH)^{14}N_3)]$ ([**6***]), $\nu_{asym}(N_3^-)$ appears at 2059 ± 2 cm^{-1}. In mixtures of $[Os^{IV}(bpy)(Cl)_3(^{14}N(OH)^{15}N^{14}N^{14}N)]$ ([**6A***]) and $[Os^{IV}(bpy)(Cl)_3(^{14}N(OH)^{14}N^{14}N^{15}N)]$ ([**6B***]) or of $[Os^{IV}(bpy)(Cl)_3(^{15}N(OH)^{15}N^{14}N^{14}N)]$ ([**6A****]) and $[Os^{IV}(bpy)(Cl)_3(^{15}N(OH)^{14}N^{14}N^{15}N)]$ ([**6B****]), $\nu_{asym}(N_3^-)$ appears at 2045 ± 2 cm^{-1}. As for [**2**]$^-$, these observations are consistent with the retention of the N_3 structure in the $N(OH)N_3^-$ ligand.

Reminiscent of [**2**]$^-$, it can be inferred on the basis of the IR data that the N-atom from $Os^{VI}{\equiv}N$ is retained, and that there is an N−O bond in [**6**]. $\nu(Os{-}N)$ shifts from 1091 ± 2 cm^{-1} in [**6**] and the mixture of [**6A***] and [**6B***] to 1075 ± 2 cm^{-1} in [**6***] and the mixture of [**6A****] and [**6B****]. It is not a coupled ν(NNO) stretch as shown by its insensitivity to ^{15}N substitution for ^{14}N at the N atom β to Os in [**6A***]−[**6B***] and [**6A****]−[**6B****]. Similarly, $\nu(N{-}O)$ in [**6**] and the mixture of [**6A***] and [**6B***] shifts from 772 ± 2 cm^{-1} to 756 ± 2 cm^{-1} in [**6***] and the mixture of [**6A****] and [**6B****]. A $\nu(O{-}H)$ stretch appears at 3406 ± 2 cm^{-1} in all of the Os(IV)−azidohydroxoamido complexes.

Deprotonation of the coordinated $N(OH)N_3^-$ ligand in [**6**] to the bound $N(O)N_3^{2-}$ ligand results in an instability toward N_2 evolution. When [**6**] was redissolved in 3:1 (v/v) $CH_3CN:H_2O$, pH = 9−12 containing a $NaOH/NaH_2PO_4{-}NaOH/Na_2HPO_4$ buffer, a rapid reaction occurred with the effervescence of N_2 gas evolution. The resulting brown product is the corresponding Os(II)−dinitrogen oxide complex, $[Os^{II}(bpy)(Cl)_3(N_2O)]^-$ ([**7**]$^-$), eq 8.

$$\begin{aligned} &mer\text{-}[Os^{IV}(bpy)(Cl)_3(N(OH)N_3)] + OH^- \rightarrow \\ &\qquad [\mathbf{6}] \\ &\qquad mer\text{-}[Os^{II}(bpy)(Cl)_3(N_2O)]^- + N_2 + H_2O \\ &\qquad\qquad [\mathbf{7}]^- \end{aligned} \tag{8}$$

This reaction may occur by deprotonation and internal electron transfer, eq 9.



$$\begin{aligned} &\underset{[\mathbf{6}]}{[Os^{IV}(bpy)(Cl)_3(N(OH)N_3)]} + OH^- \xrightarrow{-H_2O} [Os^{IV}(bpy)(Cl)_3(N(O)N_3)]^- \longrightarrow \\ &\left\{ (bpy)(Cl)_3Os^{II}\text{-}\overset{\overset{\displaystyle O}{\|}}{N}\text{-}NNN \right\}^- \longrightarrow \underset{[\mathbf{7}]^-}{[Os^{II}(bpy)(Cl)_3(N_2O)]^-} + N_2 \end{aligned} \tag{9}$$

The putative $Os^{II}{-}N(O)N_3$ intermediate is analogous to intermediates proposed in reactions between metal nitrosyls and azide ion, eq 10.[18]

$$\begin{aligned} &cis\text{-}[Ru^{II}(bpy)_2(NO)(Cl)]^{2+} + N_3^- \rightarrow \\ &\qquad \{Ru^{II}(bpy)_2(N(O)N_3)(Cl)\}^+ \xrightarrow{+CH_3CN} \\ &\qquad cis\text{-}[Ru^{II}(bpy)_2(NCCH_3)(Cl)]^+ + N_2O + N_2 \end{aligned} \tag{10}$$

Complex [**7**]$^-$ was isolated (42% yield) as the PPN^+ salt and characterized by elemental analysis, cyclic voltammetry, and IR (Table 3) and ^1H NMR spectroscopies.[12] It is the second example of a characterized N_2O transition-metal complex.[19]

In $PPN[Os^{II}(bpy)(Cl)_3(^{14}N^{14}NO)]$ (PPN[**7**]), the pseudosymmetric (largely N−N) N_2O stretch appears at 1245 cm^{-1} (ν_1), doubly degenerate bends appear at 536 and 533 cm^{-1} (ν_2), and a pseudo-asymmetric (largely N−O) stretch appears at 2252 cm^{-1} (ν_3), Table 3. ν_1 and ν_2 are shifted to lower energy upon coordination (gaseous N_2O: $\nu_1 = 1286$ and $\nu_2 = 589$ cm^{-1}),[20] but ν_3 is shifted to higher energy (gaseous N_2O: $\nu_3 = 2224$ cm^{-1}) as in $[Ru^{II}(NH_3)_5(N_2O)]^{2+}$ [21] and for N_2O absorbed on alkali-halide films[22] or on α-Cr_2O_3.[23]

In the product of reaction 7 followed by 8 with $[Os^{VI}(bpy)(Cl)_3(^{15}N)]$ as the starting complex and $^{14}N_3^-$, $\nu_1 = 1238$ and $\nu_3 = 2221$ cm^{-1}. The ^{15}N isotope effects on ν_1 (7 cm^{-1}) and

Table 3. Selected Infrared Data (±2 cm^{-1}) for PPN-$[Os^{II}(bpy)(Cl)_3(N_2O)]$ and Its ^{15}N-Labeled Analogues in Nujol Mulls

$[Os^{II}(bpy)(Cl)_3(N_2O)]^-$ isotopic distribution		N$_2$O bands		
		$\nu_1{}^a$ (largely N–N)	$\nu_2{}^b$	$\nu_3{}^c$ (largely N–O)
$[Os^{II}-{}^{14}N^{14}NO]^-$	$[\mathbf{7}]^{-\,d}$	1245	536, 533	2252
$[Os^{II}-{}^{14}N^{15}NO]^-$	$[\mathbf{7}*]^{-\,e}$	1238	532, 526	2221
$[Os^{II}-{}^{14}N^{14}NO]^-$	$[\mathbf{7}]^{-\,f}$	1244, 1237	535, 532	2252
$[Os^{II}-{}^{15}N^{14}NO]^-$	$[\mathbf{7A}*]^{-\,f}$			
$[Os^{II}-{}^{14}N^{15}NO]^-$	$[\mathbf{7}*]^{-\,g}$	1237, 1233	532, 525	2221, 2212
$[Os^{II}-{}^{15}N^{15}NO]^-$	$[\mathbf{7}**]^{-\,g}$			

[a] Pseudosymmetric stretch. [b] Doubly degenerate bend. [c] Pseudoasymmetric stretch. [d] Product obtained from $[Os^{IV}(bpy)(Cl)_3({}^{14}N(OH){}^{14}N^{14}N^{14}N)]$ in 3:1 (v/v) $CH_3CN:H_2O$ at pH = 10. [e] Product obtained from $[Os^{IV}(bpy)(Cl)_3({}^{15}N(OH){}^{14}N^{14}N^{14}N)]$ in 3:1 (v/v) $CH_3CN:H_2O$ at pH = 10. [f] Products obtained from $[Os^{IV}(bpy)(Cl)_3({}^{14}N(OH){}^{14}N^{14}N^{15}N)]$ and $[Os^{IV}(bpy)(Cl)_3({}^{14}N(OH){}^{15}N^{14}N^{14}N)]$ in 3:1 (v/v) $CH_3CN:H_2O$ at pH = 10. [g] Products obtained from $[Os^{IV}(bpy)(Cl)_3({}^{15}N(OH){}^{14}N^{14}N^{15}N)]$ and $[Os^{IV}(bpy)(Cl)_3({}^{15}N(OH){}^{15}N^{14}N^{14}N)]$ in 3:1 (v/v) $CH_3CN:H_2O$ at pH = 10.

ν_3 (31 cm^{-1}) are consistent with the isotopic distribution PPN-$[Os^{II}(bpy)(Cl)_3({}^{14}N^{15}NO)]$ in the product (PPN[**7***]). This conclusion is also in agreement with: (1) $\nu_1({}^{14}N^{14}NO)$ at 1244 cm^{-1}, $\nu_1({}^{15}N^{14}NO)$ at 1237 cm^{-1}, and ν_3 at 2252 cm^{-1} in the mixture of PPN[**7**] and PPN$[Os^{II}(bpy)(Cl)_3({}^{15}N^{14}NO)]$ ([**7A***]$^-$) in Table 3 and (2) $\nu_1({}^{14}N^{15}NO) = 1237$ cm^{-1}, $\nu_1({}^{15}N^{15}NO) = 1233$ cm^{-1}, $\nu_3({}^{14}N^{15}NO) = 2221$ cm^{-1}, and $\nu_3({}^{15}N^{15}NO) = 2212$ cm^{-1}. In the mixture of PPN[**7***] and PPN$[Os^{II}(bpy)(Cl)_3({}^{15}N^{15}NO)]$ (PPN[**7****]), the ^{15}N shifts of ν_2 in Table 3 are similar to those found with ^{15}N-labeling in $[Ru^{II}(NH_3)_5(N_2O)]^{2+}$ formed by Cr^{2+} reduction of $[Ru^{III}(NH_3)_5(Cl)]Cl_2$ in the presence of N_2O ($^{14}N^{14}NO$, $^{14}N^{15}NO$, and $^{15}N^{14}NO$).[19a]

The ^{15}N-labeling results in Table 3 are consistent with coordination through the terminal nitrogen of N_2O with the original N-atom from $Os^{VI}\equiv N$ appearing at the β-position in $Os^{II}-N_\alpha N_\beta O$. Given the mechanism implied in eq 9, formation of the final product must entail Os−N linkage isomerization from the α to the β position in the N_2 extrusion reaction of the $N(O)N_3{}^{2-}$ ligand. A related observation has been made in the reaction between $[Ru^{II}(NH_3)_5({}^{15}NO)]^{3+}$ and hydroxylamine ($^{14}NH_2OH$) which forms $[Ru^{II}(NH_3)_5({}^{14}N^{15}NO)]^{2+}$ and H_2O.[21]

The series of transformations starting in eq 6 with the formation of *mer*-$[Os^{IV}(bpy)(Cl)_3(NN_3)]^-$ followed by hydroxylation to form *mer*-$[Os^{IV}(bpy)(Cl)_3(N(OH)N_3)]$ and then deprotonation and extrusion of N_2 to give $[Os^{II}(bpy)(Cl)_3(N_2O)]^-$ is a remarkable sequence of reactions in the chemistry of coordinated ligands. It involves two new examples of coordinated ligands (azidoimido $N_4{}^{2-}$ and azidohydroxoamido $N(OH)N_3{}^-$) and a reaction sequence which allows for the stepwise addition of N and O atoms to a nitrido ligand.

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Supporting Information Available: Text containing characterizations is included (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) 30 MHz ^{15}N NMR measurements were conducted by using a Varian Unity series spectrometer. All ^{15}N chemical shifts are reported relative to the resonance for a saturated solution of $^{15}NH_4Cl$ in D_2O at + 353.0 ppm, referred to a neat nitromethane external standard. (b) Witanowski, M.; Stefaniak, L. In *Annual reports on NMR Spectrosopy: Nitrogen NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1983; Vol. 15, p 138.

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