Isolation and Characterization of the Osmium(v) – Imido Complex $[Os^V(Tp)(Cl)_2(NH)]$**

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In the redox chemistry of high oxidation state osmium(vi)-nitrido ($Os^{VI}{\equiv}N$) complexes, a reversible $3e^-/3H^+$ reduction in water gives osmium(iii) – NH_3 [Eq. (1)]. Evidence has been found for osmium(iv) amido intermediates, $Os^{IV}-NH_2^+$, which are unstable with respect to disproportionation.[1]

$$[Os^{III}(tpy)(Cl)_2(NH_3)]^+ \underset{+(3e^-,\,3H^+)}{\overset{-(3e^-,\,3H^+)}{\rightleftharpoons}} [Os^{VI}(tpy)(Cl)_2(N)]^+ \qquad (1)$$

tpy = 2,2′:6′,2″-terpyridine

One-electron reduction of $Os^{VI}{\equiv}N^+$ to $Os^V{\equiv}N$ in non-aqueous solvents is followed by rapid $N\cdots N$ coupling [Eqs. (2), (3)].[2]

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ \xrightarrow{+e^-} [Os^V(tpy)(Cl)_2(N)] \qquad (2)$$

$$2[Os^V(tpy)(Cl)_2(N)] \longrightarrow [(tpy)(Cl)_2Os^{II}{-}N_2{-}Os^{II}(Cl)_2(tpy)] \qquad (3)$$

Laser flash photolysis of $[Os^{VI}(NH_3)_4(N)]^{3+}$ in the presence of electron donors such as 1,4-dimethoxybenzene gives evidence for $Os^V{\equiv}N$ as a short-lived transient that also undergoes $N\cdots N$ coupling [Eq. (4)].[3]

$$[Os^V{\equiv}N] + [Os^{VI}{\equiv}N] \rightarrow [Os^{II}{-}N{\equiv}N{-}Os^{III}] \qquad (4)$$

Thus in both cases where osmium dimers form, an $Os^V{\equiv}N$ complex has been invoked as a transient intermediate but not isolated. We report here conditions that allow $Os^V{\equiv}N$ species to be trapped either in acidic – aqueous solution as a neutral osmium(v) imido complex ($Os^V{=}NH$) or in non-aqueous solvents by N^- ion transfer before coupling can occur.

One-electron electrochemical reduction of 2.05×10^{-2} M $[Os^{VI}(Tp)(Cl)_2(N)]$ (**1**) (Tp = hydrotris(pyrazol-1-yl)borate) in CH_3CN 3.5 M in HPF_6 at $E_{app} = -1.05$ V (versus the sodium saturated calomel electrode (SSCE), E_{app} = applied potential) results in formation of $[Os^V(Tp)(Cl)_2(NH)]$ (**2**) [Eq. (5)].

$$[Os^{VI}(Tp)(Cl)_2(N)] \xrightarrow[+H^+]{+e^-} [Os^V(Tp)(Cl)_2(NH)] \qquad (5)$$

The neutral $Os^V{=}NH$ complex (**2**) has been isolated (yield = 47 %) and characterized by infrared (IR) spectroscopy ($\nu(^{14}N{-}H) = 3257\ cm^{-1}$ and $\nu(^{15}N{-}H) = 3250\ cm^{-1}$),[4a] elemental analysis,[4b] and X-ray crystallography (Figure 1).[4c] Crystals of **2** were grown by slow evaporation of CH_3CN with a stream of nitrogen from a strongly acidic CH_3CN solution containing the salts prepared by one-electron electrolytic reduction. The same synthetic method was also used to generate $[Os^V(bpy)(Cl)_3(NH)]$ (bpy = 2,2′-bipyridine) which was isolated (yield = 56 %) and characterized by IR spectroscopy ($\nu(N{-}H) = 3315\ cm^{-1}$) and elemental analysis.[5]

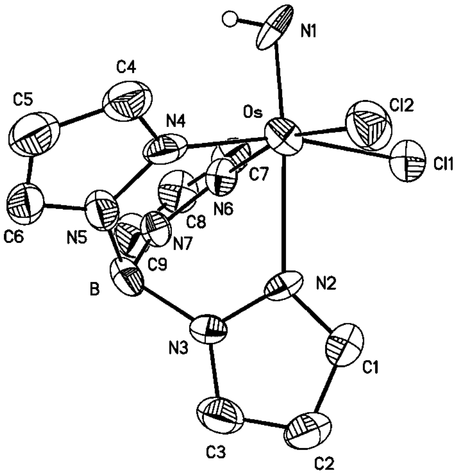

Figure 1. ORTEP diagram (thermal ellipsoids set at 30 % probability) and labeling scheme for **2**.

In the structure of **2**, the distorted octahedral arrangement of ligands around the Os center in the parent $Os^{VI}{\equiv}N$ complex is retained. The Os–Cl bond lengths of 2.320(3) and 2.329(3) Å are about the same length as the nondisordered Os–Cl length in the starting $Os^{VI}{\equiv}N$ complex, **1**.[6] There is evidence for an imido structural *trans* effect in the elongated Os–N(Tp) bond of 2.291(8) Å *trans* to the NH^{2-} ligand compared to 2.053(8) and 2.063(9) Å for the Os–N(Tp) bonds in the coordination sites *cis* to NH^{2-}. The d^3 Os–N(imido) bond of 1.749(7) Å is the longest reported for transition metal parent imido (M–NH) complexes which fall in the range of 1.638 – 1.749 Å.[7] This is the first structurally characterized example of a late transition metal parent imido complex. Others have been reported for d^0 molybdenum(vi)[8a–d] and vanadium(v);[8e] for d^2 rhenium(v),[9a] molybdenum(iv),[9b] and tungsten(iv);[9c] and d^4 rhenium(iii).[10]

The importance of protonation at the N atom in trapping osmium(v)-nitrido is evident from previous electrochemical results.[1c] One-electron reduction of $[Os^{VI}(tpm)(Cl)_2(N)]^+$ ($\mathbf{3}^+$) (tpm = tris(1-pyrazolyl)methane) in CH_3CN gives the

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

Os^{II}-N_2-Os^{II} dimer [cf. Eqs. (2), (3)]. In CH_3CN with added HPF_6, three-electron reduction leads to the osmium(III) – ammine complex as indicated by cyclic voltammetry.[1c] These observations suggest that a small amount of added HPF_6 is sufficient to change the chemistry from N ··· N coupling to reduction with the key step being protonation of the osmium(V) – nitrido unit [Eqs. (6), (7)].

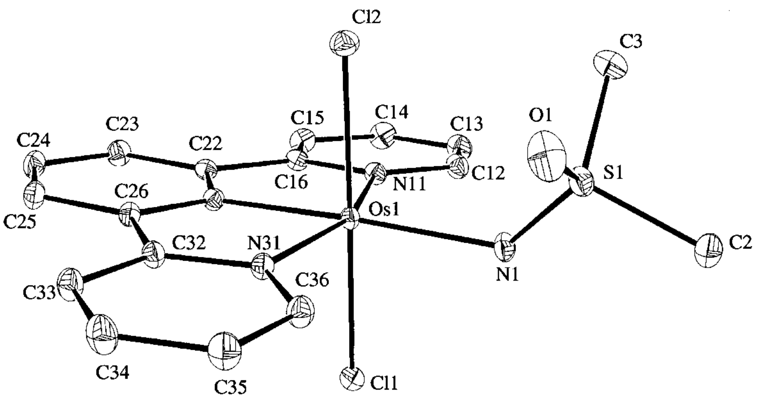

Figure 2. ORTEP diagram (thermal ellipsoids set at 30 % probability) and labeling Scheme for [**7A**]Cl.

$$[Os^{VI}(tpm)(Cl)_2(N)]^+ \xrightarrow[+H^+]{+e^-} [Os^{V}(tpm)(Cl)_2(NH)]^+ \quad (6)$$

$$[Os^{V}(tpm)(Cl)_2(NH)]^+ \xrightarrow[+2H^+]{+2e^-} [Os^{III}(tpm)(Cl)_2(NH_3)]^+ \quad (7)$$

In aqueous solution, $[Os^{V}(Tp)(Cl)_2(NH)]$ is not observed as a transient because it is unstable with regard to disproportionation.[1a] Disproportionation was confirmed in strongly acidic CH_3CN solution to which water was added. Addition of water led to the appearance of $[Os^{III}(Tp)(Cl)_2(NH_3)]$ and $[Os^{VI}(Tp)(Cl)_2(N)]$ in a 1:2 ratio as shown by the ratio of peak currents at 0.80 V (the $Os^{IV/III}$ couple of the ammine complex) to − 0.97 V (versus SSCE) (the $Os^{VI/V}$ irreversible couple of the nitrido complex). This observation is consistent with the disproportionation reaction shown in Equation (8).[11]

$$3[Os^{V}(Tp)(Cl)_2(NH)] \xrightarrow{H_2O} [Os^{III}(Tp)(Cl)_2(NH_3)] + 2[Os^{VI}(Tp)(Cl)_2(N)] \quad (8)$$

It is also possible to capture $[Os^{V}(tpy)(Cl)_2(N)]$ (**4A** = *trans* and **4B** = *cis*) in dry organic solvents before dimerization occurs by adding appropriate reductants at high concentrations as trapping agents. For example, electrochemical reduction of $[Os^{VI}(tpy)(Cl)_2(N)]^+$ ($\mathbf{5A}^+$ = *trans* and $\mathbf{5B}^+$ = *cis*) in dimethylsulfoxide (DMSO; Me_2SO) under nitrogen at a potential past that of the $Os^{VI/V}$ reduction waves, $E_{pc}(cis) = -0.31$ V and $E_{pc}(trans) = -0.45$ V (E_{pc} = cathodic peak potential versus SSCE), gives the corresponding osmium(III) – sulfoximido complexes, $[Os^{III}(tpy)(Cl)_2\{NS(O)Me_2\}]$ (**6A** = *trans* and **6B** = *cis*) [Eqs. (2) and (9)].

$$[Os^{VI}(tpy)(Cl)_2(N)] + Me_2SO \longrightarrow [Os^{III}(tpy)(Cl)_2\{NS(O)Me_2\}] \quad (9)$$

During workup, the osmium(III) products ($E_{1/2}$ $[Os^{IV/III}]$ = 0.24 V for **6A** and 0.23 V for **6B** versus SSCE) undergo air oxidation to give $[Os^{IV}(tpy)(Cl)_2\{NS(O)Me_2\}]^+$ ($\mathbf{7A}^+$ = *trans* and $\mathbf{7B}^+$ = *cis*) which were isolated as their Cl^- (77 % yield) and PF_6^- (74 % yield) salts, respectively. [**7A**]Cl was fully characterized by elemental analysis,[12] X-ray crystallography (Figure 2),[13] cyclic voltammetry, and UV/Vis spectroscopy (Supporting Information).

The reaction of the starting osmium(VI) – nitrido complex with DMSO is slow or nonexistent at room temperature. It is notable that one-electron reduction to osmium(V) – nitrido enhances oxidative reactivity much as for many free radicals compared to their precursors.[14] One-electron reduction of d^2 $Os^{VI}{\equiv}N^+$ occurs at a dπ* level that is antibonding with regard to the Os–N interaction.[15] This activates the osmium(V) – nitrido group toward N^- ion transfer. "Reductive activation" opens the possibility of exploring N^- ion transfer with reagents that have slow or no reactivity towards $Os^{VI}{\equiv}N$.

The chemistry of capturing osmium(V) – nitrido in dry organic solvents appears to be general. Depending on the reduction potentials for the $Os^{IV/III}$ couples of the products, they are formed as osmium(III) or undergo further air oxidation to osmium(IV) species. As examples, electrochemical reduction of $\mathbf{5}^+$ in the presence of high concentrations (1.0 M) of 3,5-$Me_2C_6H_3OH$ or $HNPh_2$ in CH_3CN under nitrogen gives $[Os^{III}(tpy)(Cl)_2\{N(H)OC_6H_3Me_2\}]$ (**8** = *trans*) or $[Os^{III}(tpy)(Cl)_2\{N(H)NPh_2\}]$ (**9** = *cis*). The osmium(IV) analogues, $[Os^{IV}(tpy)(Cl)_2\{N(H)OC_6H_3Me_2\}]^+$ ($\mathbf{10}^+$ = *trans*) or $[Os^{IV}(tpy)(Cl)_2\{N(H)NPh_2\}]^+$ ($\mathbf{11}^+$ = *cis*), have been isolated as PF_6^- salts ($\mathbf{10}^+$ = 53 % and $\mathbf{11}^+$ = 62 %) and characterized by IR[16] and UV/Vis spectroscopy and cyclic voltammetry (Supporting Information), and elemental analysis.[17]

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[4] Characterization data for **2**: a) IR data: ν(N–H) 3257; ν(Tp) 1495 (vs), 1459 (vs), 1407 (vs), 1394 (vs), 1307 (vs), 1211 (vs), 1050 (vs), and 982 (vs); ν(B–H) 2524 (vs); b) elemental analysis: calcd (%) for $OsBC_9H_{11}N_7Cl_2$: C 22.10, H 2.27 N 20.04; found: C 22.24, H 2.32, N 20.15; c) Crystal data: *c2/c*, monoclinic $a = 14.389(1)$, $b = 8.3716(7)$, $c = 26.443(2)$ Å, $\alpha = 90°$, $\beta = 95.382(1)°$, $\gamma = 90°$, $V = 3168.8(5)$ Å^3, $Z = 8$. Final $R_1 = 0.0476$ and $wR_2 = 0.0790$ using 6134 reflections and 200 parameters. All hydrogen atom positions, including the imido hydrogen, were located in the difference map. The H atom positions were later calculated using the HADD command (SHELXTL) with the exception of the imido H. The imido H was subsequently refined isotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163002 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] Elemental analysis calcd (%) for $[Os^{V}(bpy)(Cl)_3(NH)]$: $OsC_{10}H_9Cl_3N_3$: C 25.68, H 1.94, N 8.98; found: C 25.75, H 2.04, N 9.15.

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[11] $[\mathrm{Os^{III}(Tp)(Cl)_2(NH_3)}]$ and $[\mathrm{Os^{VI}(Tp)(Cl)_2(N)}]$ were previously isolated and characterized, reference [1c].

[12] Elemental analysis calcd (%) for **7A**Cl: $\mathrm{OsC_{17}H_{17}N_4SOCl_3 \cdot (H_2O}$ and $\mathrm{Me_2SO)}$: C 31.78, H 3.51, N 7.80; found: C 31.95, H 3.64, N 8.12. **7B**$\mathrm{PF_6}$ elemental analysis calcd (%) for $\mathrm{OsC_{17}H_{17}N_4SOCl_2PF_6}$: C 27.91, H 2.34, N 7.66; found: C 28.23, H 2.52, N 7.87.

[13] Crystal data: $P\bar{1}$, triclinic, $a = 8.9405(3)$, $b = 10.7563(3)$, $c = 13.8861(4)$ Å, $\alpha = 109.820(1)°$, $\beta = 103.443(1)°$, $\gamma = 95.231(1)°$, $V = 1217.33(6)$ Å^3, $Z = 2$. Final $R_1 = 0.033$ and $wR_2 = 0.035$ using 10537 reflections and 290 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163001 for **7A**Cl. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] IR data for **10**$\mathrm{PF_6}$ and **11**$\mathrm{PF_6}$: **10**$\mathrm{PF_6}$: ν(N–H) 3187; ν(tpy) 1458 (vs), 1449 (vs), and 1435 (vs); ν(NN) 1236 and for **11**$\mathrm{PF_6}$: ν(N–H) 3200; ν(tpy) 1481 (vs), 1449 (vs), and 1349 (vs); ν(NO) 1173.

[17] **10**$\mathrm{PF_6}$: elemental analysis calcd (%) for $\mathrm{OsC_{23}H_{20}N_4Cl_2OPF_6 \cdot CH_3CN}$: C 36.82, H 2.84, N 8.59; found: C 37.14, H 3.04, N 8.75. **11**$\mathrm{PF_6}$: elemental analysis calcd (%) for $\mathrm{OsC_{27}H_{22}N_5Cl_2PF_6}$: C 39.42, H 2.70, N 8.51; found: C 39.63, H 2.86, N 8.69.

Chiral Recognition of *O*-Phosphoserine by Mass Spectrometry[**]

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Reversible protein phosphorylation is involved in a multitude of regulatory mechanisms for the control of intracellular protein functionality.[1–4] Serine, threonine, tyrosine, and a number of other amino acid residues can be modified by the attachment of a phosphate group. The exact site of the modification has to be determined to elucidate the physiological impact of this event. This can be a very difficult task since only a small fraction of a given protein may be phosphorylated and phosphorylation may occur at multiple sites, thus giving rise to various phosphorylated forms. Although sensitive analytical methods are available for the detection and quantification of phosphorylation sites,[5–9] there is still a great need for further improvements, especially in view of the fact that both *O*-phosphoserine and -threonine cannot be unambiguously assigned by Edman sequencing.[10]

In recent years, tandem mass spectrometry (MS^n) has gained wide recognition as a powerful tool for peptide sequencing and for the identification of modified amino acids within the sequence tag.[11] This capability has encouraged the exploration of a mass spectrometric methodology for gas-phase discrimination of chiral analytes (A_R and A_S) through the measurement of the stability[12–14] and the reactivity[12, 15] of the diastereomeric complexes formed with a chiral reference molecule (ref). The kinetic method proved particularly useful for this task and was exploited by the research groups of Cooks,[13, 14, 16] Tao,[13, 14] and others.[17] The method is based on the collisionally induced dissociation (CID) of the diastereomeric cluster ions $[\mathrm{M}\cdot(\mathrm{ref})_2\cdot\mathrm{A}_R]^+$ and $[\mathrm{M}\cdot(\mathrm{ref})_2\cdot\mathrm{A}_S]^+$ (M = H or metal; Figure 1). It is convenient to define the cluster ions as "homo" when the analyte and reference have the same configuration, and "hetero" in the opposite case.

According to the foundations of the kinetic method used by Cooks and co-workers,[13, 16] CID of $[\mathrm{M}\cdot(\mathrm{ref})_2\cdot\mathrm{A}_R]^+$ and $[\mathrm{M}\cdot(\mathrm{ref})_2\cdot\mathrm{A}_S]^+$ may produce different fragmentation patterns that reflect the stability of $[\mathrm{M}\cdot\mathrm{ref}\cdot\mathrm{A}_R]^+$ (and $[\mathrm{M}\cdot\mathrm{ref}\cdot\mathrm{A}_S]^+$) relative to $[\mathrm{M}\cdot(\mathrm{ref})_2]^+$ (ΔG_R and ΔG_S, respectively).

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