A Terminal Osmium(IV) Nitride: Ammonia Formation and Ambiphilic Reactivity

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Abstract: Low-valent osmium nitrides are discussed as intermediates in nitrogen fixation schemes. However, rational synthetic routes that lead to isolable examples are currently unknown. Here, the synthesis of the square-planar osmium(IV) nitride [Os(N(PNP))] (PNP = N(CH$_2$CH$_2$PtBu$_2$)$_2$) is reported upon reversible deprotonation of osmium(VI) hydride [Os(N)(H)(PNP)]. The Os$^+$ complex shows ambiphilic nitride reactivity with SiMe$_3$Br and PMe$_3$, respectively. Importantly, the hydrogenolysis with H$_2$ gives ammonia and the polyhydride complex [OsH$_4$(HPNP)] in 80% yield. Hence, our results directly demonstrate the role of low-valent osmium nitrides and of heterolytic H$_2$ activation for ammonia synthesis with H$_2$ under basic conditions.

The chemistry of osmium(VI) nitrides were extensively examined.$^1$ They generally exhibit electrophilic nitrides but nucleophilic nitride reactivity was also reported and can be fine-tuned by subtle variations of the ligand field in some cases. The dominance of the d$^2$ electronic configuration in tetragonal ligand field results from the strong destabilization of the two d-orbitals with Os–N π*-character. Accordingly, the only reported low-valent osmium nitride, i.e. the serendipitously obtained complex [Os$^{IV}$(N)(SiMe$_3$CH$_2$CH$_2$PtBu$_2$)$_2$], adopts a distorted tetrahedral coordination geometry.$^2$ However, the reactivity of this compound was not examined.

Osmium nitrides are involved in several model reactions relevant to N$_2$-fixation, such as the interconversion of {Os$^{IV}$(N)} and {Os$^{IV}$(NH$_3$)} complexes by electron-proton-transfer or the coupling of {Os$^{IV}$(N)} nitrides to N$_2$-bridged dimers.$^{3,4}$ In reverse, Kunkely and Vogler observed photochemical N$_2$-splitting of [(NH$_3$)$_5$Os$^{II}$(N)$_2$Os$^{IV}$ (NH$_3$)$_3$]$^{5+}$ (Scheme 1).$^5$ [Os$^{IV}$N(NH$_3$)$_3$]$^{3+}$ and [Os$^{IV}$N(NH$_3$)$_3$]$^{2+}$ were proposed as initial products presumably followed by disproportionation of Os$^{IV}$ and hydrolysis of Os$^{II}$ to give NH$_3$ with a theoretical yield of 16%. Along these lines, Konnick et al. reported the formation of NH$_3$ (32%) upon hydrogenolysis (35 bar H$_2$) of an osmium(VI) nitride in basic aqueous solution (Scheme 1).$^6$

Our group studied related reactivity, such as Re mediated N$_2$-splitting and functionalization, the coupling of group 9 nitrides, or the hydrogenolysis of a ruthenium(IV) nitride to ammonia.$^{7,8,9}$ This precedence sparked our interest in the accessibility and the role of low-valent osmium nitrides for N$_2$ fixation strategies.

![Scheme 1. Reactivity of osmium complexes relevant to N$_2$-fixation.$^{6,9}$ Proposed intermediates are shown in square brackets.](image)

The osmium(IV) complex [OsHCl$_2$(PNP)] (1) is obtained in around 60% yield upon reaction of [OsCl$_2$(PPh$_3$)$_3$] with amine ligand HN(CH$_2$CH$_2$PtBu$_2$)$_2$(HPNP). Spectroscopic characterization and single crystal X-ray diffraction confirm the structural assignment.$^6$ The N–H oxidative addition is evidenced by the short N–Os bond length.

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(1.894(2) Å) and planar nitrogen coordination. Salt metathesis of complex 1 with NaN₃ leads to immediate N₂ elimination and the isolation of osmium(VI) nitride [Os(N)H(PNP)]PF₆ (2-PF₆) in 90% yield after anion exchange (Scheme 2). NMR characterization of complex 2-PF₆ indicates Cᵥ symmetry on the NMR timescale. The hydride signal is observed as a triplet at -1.34 ppm (J_HH = 16 Hz).

Scheme 2. Synthesis and reactivity of osmium(IV) nitride 3 (BAR₄ = B(C₆H₅)(3,5-(CF₃)₂)₄).

Despite the extensive body of work on osmium(VI) nitrides, 2-PF₆ surprisingly is the first example that also carries a hydride ligand. Such a compound is a plausible intermediate in basic nitride hydrogenolysis. In fact, reductive deprotonation of 2-PF₆ with KOtBu gives rise to the immediate formation of osmium(IV) nitride [OsN(PNP)] (3) in 90 % isolated yield (Scheme 2). 2-Cl deprotonation is even observed without additional base: Dissolving 2-Cl in THF results in disproportionation into 3 and [Os²⁺(N)Cl(H)(HPNP)]⁺, which was characterized spectroscopically. In reverse, 3 is selectively reprotonated at the metal with acids, such as [H(OEt₂)₂][BAR₄] or HOTf (Scheme 2). This reaction reflects electrophilic attack at the HOMO of 3, which is defined by the Os dₓ₂ orbital (Figure 1). Notably, Caulton’s Ru nitride [RuN[N(SiMe₂CH₂PBU₂)₂]] is protonated by HOTf at the amido nitrogen atom. The comparison qualitatively corresponds with generally enhanced metal basicity of the homologous heavier transition metals.

Figure 1. Frontier Kohn-Sham orbital scheme of 3.

NMR spectroscopic characterization of diamagnetic 3 indicates Cᵥ symmetry on the NMR timescale. The 

\[ ^{15}N \] NMR signal of a labelled sample at 391 ppm (vs. \( \text{O}_2\text{NCH}_3 \)) is in the typical range for metal nitrides. The Os=\(^{15}N\) stretching vibration was assigned to an intense IR band at 999 cm\(^{-1}\) with a \(^{15}N\)\(^{15}N\) isotopic shift (\( \Delta \nu = 32 \text{ cm}^{-1} \)) that is in perfect agreement with the harmonic oscillator approximation. This value compares well with our previously reported nitrides [RuN(PNP)] (976 cm\(^{-1}\)) and [IrN(PNP)] (999 cm\(^{-1}\); PNP = N(CH₃CH₂PFBU₂). However, they are at the lower end of the typical range for transition metal nitrides (950-1150 cm\(^{-1}\)).

Single-crystal X-ray diffraction confirms the monomeric structure of 3 and for the first time square-planar coordination for an osmium nitride (Figure 2). Small distortion arises from the pincer bite angle (P₁-Os₁-P₂: 159.600(14)°) and slight bending of the N₁-Os-N₂ angle (168.02(11)°). However, computational evaluation of this
bending mode reveals a minute barrier over the range 180±15° and corresponds with the ellipsoidal N2 thermal displacement parameters (Figure 2). The Os–N2 bond length (1.6832(18) Å) is at the upper end compared with representative Os\textsuperscript{VI} nitriles. This observation and the relatively low stretching vibration (vide supra) can be attributed to competitive trans bonding of the amide and nitride ligands. In fact, the HOMO\textsuperscript{IV} is also assigned to a superimposed \( ^{1}H \) NMR signals of \(^{14}NH_{2}\) and \(^{15}NH_{3}\) (\( \gamma_{15N} = 61.2 \) Hz) are resolved at -50 °C. The ratio of the J-coupling constants is in agreement with the expected value (\( \gamma_{14N} = 1.41 \)). Importantly, upon use of \( D_{2} \) all N–H and Os–H \(^{1}H \) NMR signals are absent affirming molecular \( H_{2} \) as hydrogen source.

The nitride 3 cleanly reacts with \( H_{2} \) (2 bar) at 110 °C in toluene to give the tetrahydride amine complex [Os(H)\textsubscript{3}(HPNP)] (4) in about 80 % yield (Scheme 2). No reaction intermediates were observed by \(^{31}P \) NMR spectroscopy. Equimolar formation of ammonia was verified by indophenolic titration. \(^{1}H \) NH\textsubscript{3} is also assigned to a cross-peak in the \(^{1}H,^{14}N\)-HMBC NMR spectrum at -388 (\(^{14}N \)) and 0.34 ppm (\(^{1}H \)), respectively (\( \gamma_{14N} = 42.8 \) Hz). Starting from 50 % \(^{15}N \) labelled 3, the two superimposed \(^{1}H \) NMR signals of \(^{14}NH_{2}\) and \(^{15}NH_{3}\) (\( \gamma_{15N} = 61.2 \) Hz) are resolved at -50 °C. The ratio of the J-coupling constants is in agreement with the expected value (\( \gamma_{15N} = 1.41 \)). Importantly, upon use of \( D_{2} \) all N–H and Os–H \(^{1}H \) NMR signals are absent affirming molecular \( H_{2} \) as hydrogen source.

**Figure 2.** Molecular structures of 3 (top left), 4 (top right), and 5-BPh\textsubscript{4} (bottom, only cation) in the crystal with thermal ellipsoids drawn at 50 % probability. Hydrogen atoms except N–H and Os–H are omitted for clarity. Selected bond lengths (Å) and angles (°); 3: Os1–N1 2.0568(13), Os1–N2 1.6832(18), Os1–P1 2.3460(4), Os1–P2 2.3523(4); N1–Os1–N2 168.02(11), P1–Os1–P2 159.600(14). 4: Os1–N1 2.210(5), Os1–P1 2.3112(8), Os1–H1 1.78(5), Os1–H2 1.77(5); P1–Os1–P1‘ 166.57(4), N1–Os1–H1 71.0(15), N1–Os1–H2 143.6(16). 5: Os1–N1 1.988(3), Os1–N2 1.733(4), Os1–P1 2.3846(12), Os1–P2 2.3825(12); N1–Os1–N2 177.78(17), P1–Os1–P2 160.80(4), Os1–N2–Si1 176.0(3).

At room temperature, complex 4 exhibits a broad signal for the backbone NH proton and three broadened signals in the hydride region. The latter split to four distinct signals (1:1:1:1) upon cooling to -50°C. This observation supports a tetrahydride structure, as was proposed by Gusev and co-workers for the analogous complex [Os(H)\textsubscript{3}([CH\textsubscript{2}CH\textsubscript{3}P\textsubscript{2}])\textsubscript{2}]. Further evidence is provided by the molecular structure of 4 (Figure 2): Two long (H1–H2: 2.11(7) Å) and one shorter (H2–H2*: 1.70(9) Å) H–H distance were found which suggests classification as tetrahydride with one compressed dihydride moiety. A computational model of 4 supports this structural assignment.

Besides ammonia formation, 3 was treated with selected electrophiles and nucleophiles to examine the unexplored reactivity of osmium(IV) nitriles. In contrast to protonation, silylation is nitride centered and imido complex [Os\textsuperscript{IV}(NSiMe\textsubscript{3})(PNP)]X (5–X, X = BPh\textsubscript{4}, BAr\textsuperscript{F}) was isolated in 63 % yield upon reaction with SiMe\textsubscript{3}Br after halide exchange (Scheme 2). The differing selectivity is mainly attributed to steric effects as smaller electrophiles like MeOTf gave mixtures of several non-separable compounds. Nitride silylation is supported by \(^{1}H\)-NOESY spectroscopy and single-crystal X-ray diffraction (Figure 2). The almost linear imido ligand (Os1–N2–Si1: 176.0(3)°) and short Os–NSiMe\textsubscript{3} distance (1.733(4) Å) indicate considerable triple bonding character. The structural parameters closely resemble those of the only isolated osmium(IV) hydrocarbonyl imido complex, i.e. [Os(N\textsubscript{2}C\textsubscript{6}H\textsubscript{3}Pr\textsubscript{2}2(PPhMe\textsubscript{2})\textsubscript{2}]. In contrast, bent (hence nucleophilic) osmium(IV) azido- and cyanoimides result from nucleophilic attack of pseudohalides to octahedral Os\textsuperscript{VI}N as a result of Os–N π*-MO occupancy in the d\textsuperscript{0} configuration.
The role of low-nitride reversible reductive deprotonation of an osmium(VI) hydride. The use of nitride and its versatile reactivity was observed by NMR spectroscopy (Scheme 2). The high symmetry of nitride and the two \(^{31}\text{P}[^{1}\text{H}]\)-NMR signals (43.9 and 22.1 ppm) with singlet multiplicities and 2:1 relative intensities (Figure 3) support the formation of phosphoraninamato complex \([\text{Os}^{III}\{\text{N=PMe}_3\}(\text{PNP})]\) (6). This suggestion is confirmed by use of \(^{15}\text{N}\)-nitride labelled 3 (50 %), which results in double splitting (\(\delta_{J_HP} = 22.7\) Hz) of one \(^{31}\text{P}[^{1}\text{H}]\) signal (22.1 ppm) and a \(^{15}\text{N}\) signal at \(-126.5\) ppm (Figure 3). However, evaporation of the solvent leads to recovery of nitride 3 indicating reversibility of PMe\(_3\) addition. The equilibrium constant was estimated by NMR spectroscopy (K\(_e\) = 150 M\(^{-1}\)).

In summary, the first straightforward synthesis of an osmium(IV) nitride is reported upon unprecedented, reversible reductive deprotonation of an osmium(VI) hydride. The ambiphilic reactivity is demonstrated with SiMe\(_3\)Br and PMe\(_3\), respectively, and provides versatile entries into nitride transfer. Importantly, full hydrogenolysis of the nitride to ammonia is observed in high yield. Hence, the formation of 3 by deprotonation of an osmium(VI) nitride and its versatile hydrogenation provides a strategy to link \(\text{N}_2\)-splitting and hydrogenation emphasizing the role of low-valent nitrides and heterolytic \(\text{H}_2\) activation for nitrogen fixation under basic conditions.

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