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 [OsN(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^{IV} 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 was extensively examined.[1] They generally exhibit electrophilic nitride reactivity, while reactions with electrophiles were only reported in some rare cases, e.g. for organometallic nitrides.[2] 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, which are occupied in Os^n-nitrides (n < +VI). The only reported low-valent osmium nitride, i.e. the serendipitously obtained complex [Os^{IV}(N)I{O(SiMe$_2$CH$_2$PtBu$_2$)$_2$}],[3] therefore adopts a coordination geometry with threefold symmetry, in analogy to well-established iron(IV) nitrides.[4] In contrast to these, the reactivity of the osmium congener was not examined.

Osmium nitrides are involved in several model reactions relevant to N$_2$-fixation, such as the interconversion of {Os^{VI}≡N} and {Os^{II}NH$_3$} complexes by electron-proton-transfer or the coupling of {Os^V≡N} nitrides to N$_2$-bridged dimers.[5,6] In reverse, Kunkely and Vogler observed photochemical N$_2$-splitting of [(NH$_3$)$_5$Os^{II}(N$_2$)Os^{III}(NH$_3$)$_5$]$^{5+}$ (Scheme 1).[7] [Os^{VI}N(NH$_3$)$_4$]$^{3+}$ and [Os^{V}N(NH$_3$)$_4$]$^{2+}$ were proposed as initial products presumably followed by disproportionation of Os^V and hydrolysis of Os^{IV} 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).[8]

Our group studied related reactivity, such as Re mediated N$_2$-splitting and functionalization, the coupling of group 9 nitrides,

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or the hydrogenolysis of a ruthenium(IV) nitride to ammonia.[9,10,11] This precedence sparked our interest in the accessibility and the role of low-valent osmium nitrides for N$_2$ fixation strategies.

Kunkely and Vogler[6]
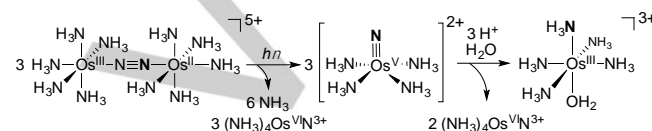
Konnick et al.[7]
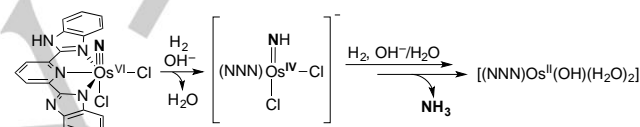
Scheme 1. Reactivity of osmium complexes relevant to N$_2$-fixation.[7,8] Proposed intermediates are shown in square brackets.

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$_2$)$_2$ (*H*PNP). Spectroscopic characterization and single crystal X-ray diffraction confirm the structural assignment.[12] The N–H oxidative addition is evidenced by the short N–Os bond length (1.894(2) Å) and planar nitrogen coordination. Salt metathesis of complex **1** with NaN$_3$ leads to immediate N$_2$ elimination and the isolation of osmium(VI) nitride [Os(N)H(PNP)]PF$_6$ (**2-PF$_6$**) in 90% yield after anion exchange (Scheme 2). NMR characterization of complex **2-PF$_6$** indicates C_s symmetry on the NMR timescale. The hydride signal is observed as a triplet at -1.34 ppm ($^2J_{HP}$ = 16 Hz).
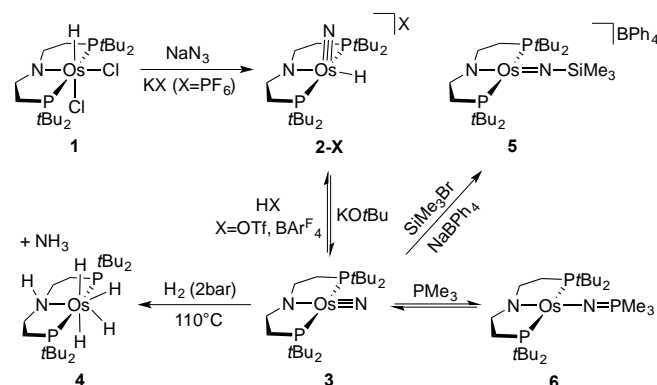
Scheme 2. Synthesis and reactivity of osmium(IV) nitride **3** (BAr$^F_4$$^-$ = B(C$_6$H$_3$-3,5-(CF$_3$)$_2$)$_4$$^-$)

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 KO*t*Bu 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 [Os^{VI}(N)Cl(H)(*H*PNP)]⁺, which was characterized spectroscopically.[12] In reverse, **3** is selectively reprotonated at the metal with acids, such as [H(OEt₂)₂][BAr^{F}₄] or HOTf (Scheme 2). This reaction reflects electrophilic attack at the HOMO of **3**, which is defined by the Os d_{z2} orbital (Figure 1). Notably, Caulton's Ru^{IV} nitride [RuN{N(SiMe₂CH₂P*t*Bu₂)₂}] is protonated by HOTf at the amido nitrogen atom.[13] The comparison qualitatively corresponds with generally enhanced metal basicity of the homologous heavier transition metals.[14]
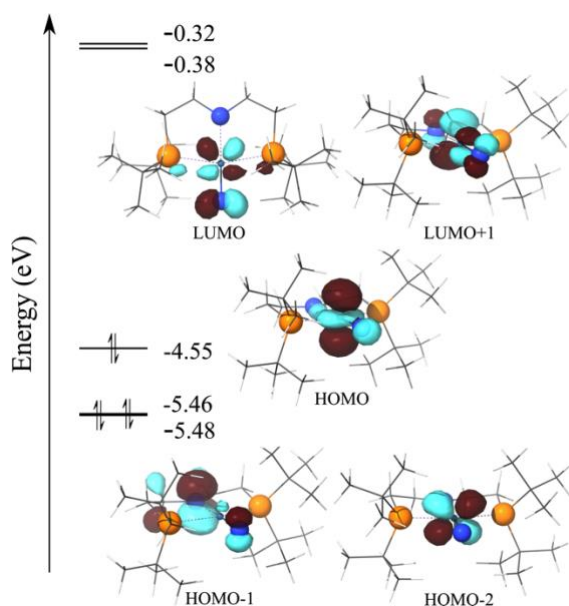

Figure 1. Frontier Kohn-Sham orbital scheme of **3**.

NMR spectroscopic characterization of diamagnetic **3** indicates C_{2v} symmetry on the NMR timescale.[12] The ¹⁵N-NMR signal of a labelled sample at 391 ppm (*vs*. O₂NCH₃) is in the typical range for metal nitrides. The Os≡¹⁴N stretching vibration was assigned to an intense IR band at 999 cm⁻¹ with a ¹⁴N/¹⁵N isotopic shift (Δv = 32 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)[9] and [IrN(PNP')] (999 cm⁻¹; PNP' = N(CHCHP*t*Bu₂)₂).[10a] However, they are at the lower end of the typical range for transition metal nitrides (950-1150 cm⁻¹).[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).[12] The Os–N2 bond length (1.6832(18) Å) is at the upper end compared with representative Os^{VI} nitrides.[5a, 15] 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-1 is dominated by the 3-center-4-electron π-interaction (Figure 1).

The nitride **3** cleanly reacts with H₂ (2 bar) at 110° in toluene to give the tetrahydride amine complex [Os(H)₄(*H*PNP)] (**4**) in about 80 % yield (Scheme 2). No reaction intermediates were observed by ³¹P NMR spectroscopy. Equimolar formation of ammonia was verified by indophenolic titration.[12] NH₃ is also assigned to a cross-peak in the ¹H-¹⁴N-HMBC NMR spectrum at -388 (¹⁴N) and 0.34 ppm (¹H), respectively (¹J_{14N-H} = 42.8 Hz). Starting from 50 % ¹⁵N labelled **3**, the two superimposed ¹H NMR signals of ¹⁴NH₃ and ¹⁵NH₃ (¹J_{15N-1H} = 61.2 Hz) are resolved at -50 °C. The ratio of the *J*-coupling constants is in agreement with the expected value (γ₁₅N/γ₁₄N = -1.41). Importantly, upon use of D₂ all N–H and Os–H ¹H NMR signals are absent affirming molecular H₂ as hydrogen source.
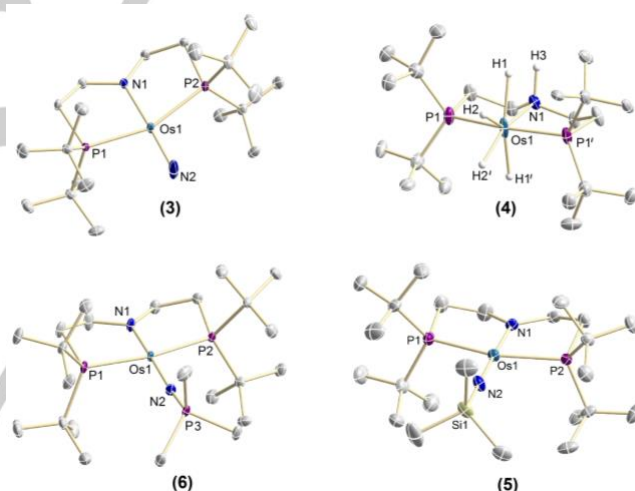

Figure 2. Molecular structures of **3**, **4**, **5-BPh₄** (only cation shown) and **6** in the crystal with thermal ellipsoids drawn at 50% probability. Hydrogen atoms except N–H and Os–H are omitted for clarity. Selected bond lengths (Å) and angles (°); **3**: Os1–N1 2.0568(13), Os1–N2 1.6832(18), 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). **6**: Os1–N1 1.920(2), Os1–N2 1.968(2), Os1–P1 2.3150(7), Os1–P2 2.3018(7), N2–P3 1.532(2); N1–Os1–N2 178.63(11), P1–Os1–P2 167.09(4), Os1–N2–P3 173.57(17).

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)$_4$(HN{CH$_2$CH$_2$PiPr$_2$)$_2$})].[16] 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.[12]

Besides ammonia formation, **3** was treated with selected electrophiles and nucleophiles to examine the unexplored reactivity of osmium(IV) nitrides. In contrast to protonation, silylation is nitride centered and imido complex [Os^{IV}(NSiMe$_3$)(PNP)]X (**5-X**, X = BPh$_4$, BAr$^F_4$) was isolated in 63% yield upon reaction with SiMe$_3$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$_3$ distance (1.733(4) Å) indicate considerable triple bonding character. The structural parameters closely resemble those of the only isolated osmium(IV) hydrocarbyl imido complex, i.e. [Os(N-2,6-C$_6$H$_3i$Pr$_2$)$_2$(PPhMe$_2$)$_2$].[17] In contrast, bent (hence nucleophilic) osmium(IV) azido- and cyanoimides result from nucleophilic attack of pseudohalides to octahedral Os^{VI}≡N as a result of Os–N π*-MO occupancy in the d^4 configuration.[18]
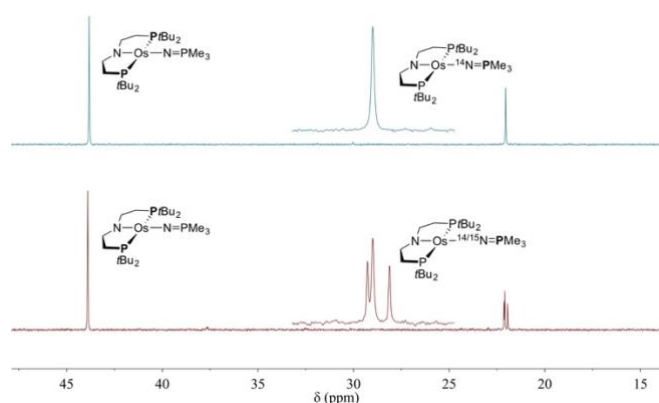

Figure 3. ^{31}P{^{1}H} NMR spectra of complex **6** (top) and **6** with 50 % ^{15}N nitride labelling (bottom), respectively.

Such nucleophilic imides are also likely products from aryl-Grignard addition and anilides were isolated after aerobic workup.[2b] Complex **3**, though, does not react with nucleophiles like MeMgBr or PPh$_3$. However, with PMe$_3$ the formation of a new compound was observed by NMR spectroscopy (Scheme 2). The high symmetry (C_{2v}) and the two ^{31}P{^{1}H}-NMR signals (43.9 and 22.1 ppm) with singlet multiplicities and 2:1 relative intensities (Figure 3) support the formation of phosphoraniminato complex [Os^{II}(N=PMe$_3$)(PNP)] (**6**). This suggestion is confirmed by use of ^{15}N-nitride labelled **3** (50 %), which results in doublet splitting ($^1J_{NP}$ = 22.7 Hz) of one ^{31}P{^{1}H} signal (22.1 ppm) and a ^{15}N{^{1}H} signal at -126.5 ppm (Figure 3). Interestingly, evaporation of the solvent leads to recovery of nitride **3** and the equilibrium constant for the nitride/phosphoraneiminato equilibrium was estimated by NMR spectroscopy (K_c = 150 M^{-1}). The reversibility of phosphine addition prevented the isolation of analytically pure **6**. However, the structural assignment from NMR spectroscopy was unequivocally confirmed by single crystal X-ray diffraction (Figure 2). In analogy to the structure of **5$^+$**, almost linear coordination of the phosporaneiminato moiety is found (Os1–N2–P3: 173.57(17)°). However, the Os–N2 bond (1.968(2) Å) is much longer compared to the parent nitride (**3**, 1.6832(18) Å) and silylimido (**5$^+$**, 1.733(4) Å) complexes confirming single-bond character. In turn, a typical double bond distance is found for the N2–P3 bond (1.532(2) Å).[19]

Phosphoraneiminato formation is generally considered archetypal reactivity of electrophilic nitrides resulting in net formal phosphine oxidation.[1e] However, this rationalization is ambiguous. For example, Hammett analysis of PAr$_3$ coupling with an iron(IV) nitride indicated electrophilic phosphine character, which was rationalized with dominating N→P–C(σ*) MO-interaction in the transition state.[19] Therefore, the formation of **6** was evaluated computationally. The DFT calculations nicely reproduce almost thermoneutral PMe$_3$ addition (ΔG_0 = -13.2 kJ/mol). A transition state (**TS**) that connects **3** with **6** on the singlet potential energy surface was found at $\Delta G^{\ddagger}$ = 60.2 kJ/mol. The Os–N–P angle (147°) in the **TS** strongly deviates from linearity as found in the product, suggesting nucleophilic attack of the phosphine lone pair at the LUMO of **3** (Figure 1). Notably, the phosphine is also strongly tilted resulting in one N–P–C angle being close to linear (165°). This **TS** geometry and elongated P–C bond to this carbon atom suggest on the other hand non-negligible N→P–C(σ*) back-bonding. The synergistic nature of these two donor-acceptor interactions in the **TS** is confirmed by natural bond orbital (NBO) analysis (Figure 4). However, natural population analysis (NPA) of the two fragments that constitute the **TS** (PMe$_3$ and **3**) indicates net charge transfer of around 0.3 e from the phosphine to the nitride. Hence, NPA suggests that P→N≡Os donation dominates and therefore overall electrophilic nitride character for this reaction.
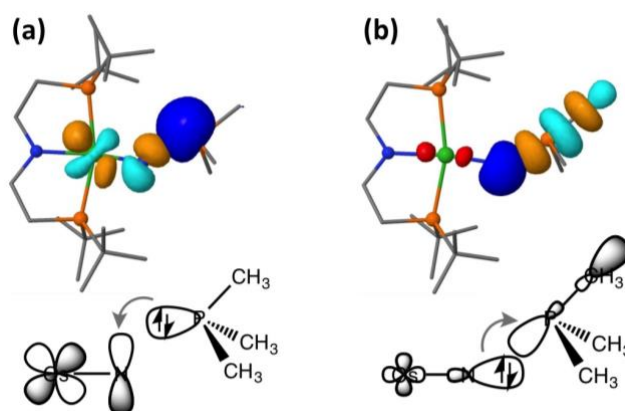

Figure 4. Computed NBOs (top) and schematic fragment orbital interactions (below) that represent the interaction of **3** and PMe$_3$ in the **TS** leading to **6**.

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 $SiMe_3Br$ 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 N_2-splitting and hydrogenation emphasizing the role of low-valent nitrides and heterolytic H_2 activation for nitrogen fixation under basic conditions.

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COMMUNICATION

The first rational synthesis for an isolable osmium(IV) nitride is reported. The title compound [Os(N){N(CH$_2$CH$_2$PtBu$_2$)$_2$}] shows ambiphilic nitride reactivity and gives ammonia upon hydrogenolysis with H$_2$ in high yield. These results emphasize the role of low-valent osmium nitrides and H$_2$ heterolysis for nitrogen fixation strategies.

H$_2$

NH$_3$ + (^{H}PNP)OsH$_4$
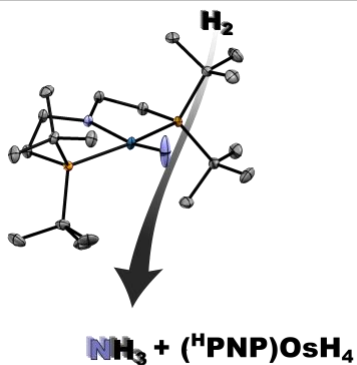
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A Terminal Osmium(IV) Nitride: Ammonia Formation and Ambiphilic Reactivity