Nitrogen Fixation

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

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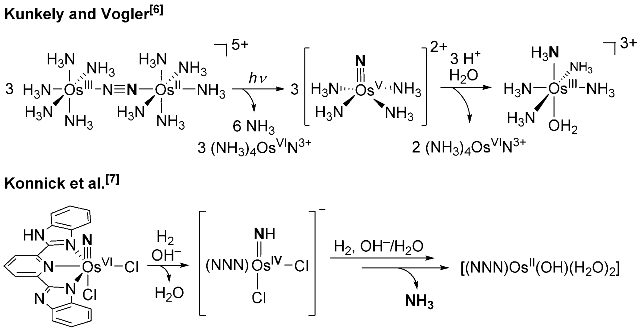
Abstract: *Low-valent osmium nitrides are discussed as intermediates in nitrogen fixation schemes. However, rational synthetic routes that lead to isolable examples are currently unknown. Here, the synthesis of the square-planar osmium(IV) nitride [OsN(PNP)] (PNP = $N(CH_2CH_2P(tBu)_2)_2$) is reported upon reversible deprotonation of osmium(VI) hydride $[Os(N)H(PNP)]^+$. The Os^{IV} complex shows ambiphilic nitride reactivity with $SiMe_3Br$ 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 nucleophilic reactivity was only reported in some rare cases, for example, 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 OsN π^*-character, which are occupied in Os^n-nitrides ($n < +$VI). The only reported low-valent osmium nitride, that is, the serendipitously obtained complex $[Os^{IV}(N)I\{O(SiMe_2CH_2PtBu_2)_2\}]$,[3] therefore adopts a four-coordinate osmium with distorted tetrahedral coordination, in analogy to well-established iron(IV) nitrides.[4] In contrast to these, the reactivity of the osmium congener was not examined.

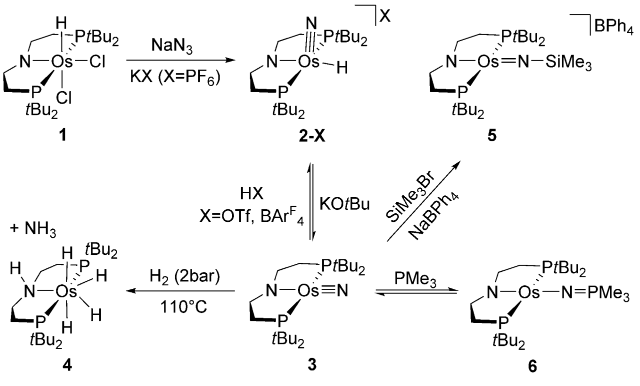
Osmium nitrides are involved in several model reactions relevant to N_2-fixation, such as the interconversion of $\{Os^{VI}{\equiv}N\}$ and $\{Os^{II}NH_3\}$ complexes by electron-proton transfer or the coupling of $\{Os^{V}{\equiv}N\}$ nitrides to N_2-bridged dimers.[5,6] In reverse, Kunkely and Vogler observed photochemical N_2-splitting of $[(NH_3)_5Os^{II}(N_2)Os^{III}(NH_3)_5]^{5+}$ (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 and hydrolysis of Os^V 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]



Scheme 1. Reactivity of osmium complexes relevant to N_2-fixation.[7,8] Proposed intermediates are shown in square brackets.

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.[9–11] This precedence sparked our interest in the accessibility and the role of low-valent osmium nitrides for N_2 fixation strategies.

The osmium(IV) complex $[OsHCl_2(PNP)]$ (**1**) is obtained in 60% yield upon reaction of $[OsCl_2(PPh_3)_3]$ with amine ligand $HN(CH_2CH_2PtBu_2)_2$ (*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



Scheme 2. Synthesis and reactivity of osmium(IV) nitride **3** ($BAr^F{}_4{}^- = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4{}^-$).

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the NMR timescale. The hydride signal is observed as a triplet at −1.34 ppm ($^2J_{HP} = 16$ Hz).

Despite the extensive body of work on osmium(VI) nitrides, **2-PF$_6$** 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-PF$_6$** 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 $[H(OEt_2)_2][BAr^F{}_4]$ or HOTf (Scheme 2). This reaction reflects electrophilic attack at the HOMO of **3**, which is defined by the Os d$_{z^2}$ orbital (Figure 1). Notably, Caulton's Ru^{IV} nitride [RuN{N(SiMe$_2$CH$_2$P*t*Bu$_2$)$_2$}] 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]

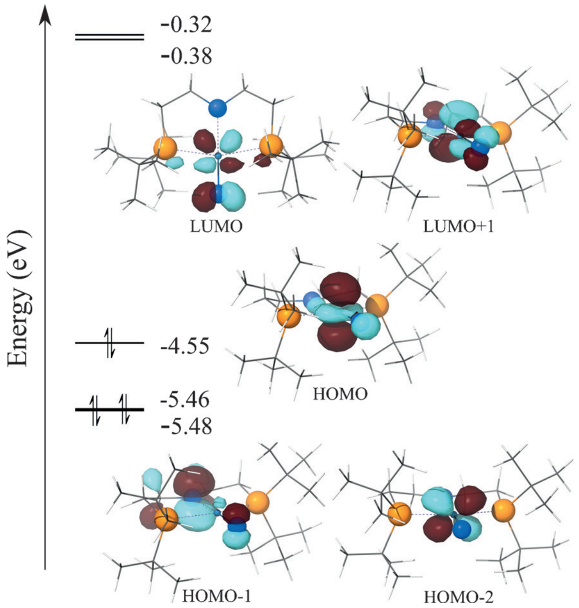

Figure 1. Frontier Kohn–Sham orbital scheme of **3**.

NMR spectroscopic characterization of diamagnetic **3** indicates C_{2v} symmetry on the NMR timescale.[12] The ^{15}N-NMR signal of a labeled sample at 391 ppm (vs. O$_2$NCH$_3$) is in the typical range for metal nitrides. The Os≡^{14}N stretching vibration was assigned to an intense IR band at 999 cm^{-1} with a ^{14}N/^{15}N isotopic shift ($\Delta\nu = 32$ 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})[11] and [IrN(PNP′)] (999 cm^{-1}; PNP′ = N(CHCHP*t*Bu)$_2$).[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-Os1-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 Os1−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 (see above) 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).

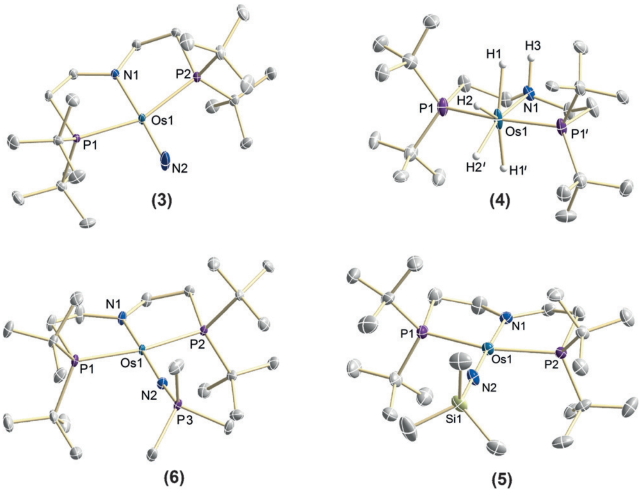

Figure 2. Molecular structures of **3**, **4**, **5-BPh$_4$** (only cation shown) and **6** in the crystal with thermal ellipsoids drawn at 50% probability. Hydrogen atoms except N−H and Os−H are omitted for clarity. Selected bond lengths [Å] and angles [°]; **3**: Os1-N1 2.0568(13), Os1-N2 1.6832(18), 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).

The nitride **3** cleanly reacts with H$_2$ (2 bar) at 110°C 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 ^{31}P NMR spectroscopy. Equimolar formation of ammonia was verified by indophenolic titration.[12] NH$_3$ is also assigned to a cross-peak in the ^{1}H-^{14}N HMQC NMR spectrum at −388 (^{14}N) and 0.34 ppm (^{1}H), respectively ($^1J_{^{14}N\text{-}^1H} = 42.8$ Hz). Starting from 50% ^{15}N-labeled **3**, the two superimposed ^{1}H NMR signals of ^{14}NH$_3$ and ^{15}NH$_3$ ($^1J_{^{15}N\text{-}^1H} = 61.2$ Hz) are resolved at −50°C. The ratio of the *J*-coupling constants is in agreement with the expected value ($\gamma_{^{15}N}/\gamma_{^{14}N} = -1.41$). 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.

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 coworkers for the analogous complex $[Os(H)_4\{HN(CH_2CH_2P\textit{i}Pr_2)_2\})]$.[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 $SiMe_3Br$ 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 ^1H-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, that is, $[Os(N\text{-}2,6\text{-}C_6H_3\textit{i}Pr_2)_2(PPhMe_2)_2]$.[17] In contrast, bent (hence nucleophilic) osmium(IV) azido- and cyanoimides result from nucleophilic attack of pseudohalides to octahedral $Os^{VI}{\equiv}N$ as a result of Os−N π*-MO occupancy in the d^4 configuration.[18]

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 $^{31}P\{^1H\}$-NMR signals (43.9 and 22.1 ppm) with singlet multiplicities and 2:1 relative intensities (Figure 3) support the formation of phosphoraneiminato complex $[Os^{II}(N{=}PMe_3)(PNP)]$ (**6**). This suggestion is confirmed by use of ^{15}N-nitride labeled **3** (50 %), which results in doublet splitting ($^1J_{NP} = 22.7$ Hz) of one $^{31}P\{^1H\}$ signal (22.1 ppm) and a $^{15}N\{^1H\}$ 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 ($K_c = 150\,\text{M}^{-1}$). 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 $\mathbf{5}^+$, 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 ($\mathbf{5}^+$, 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 ($\Delta G_0 = -13.2\ \text{kJ mol}^{-1}$). A transition state (**TS**) that connects **3** with **6** on the singlet potential energy surface was found at $\Delta G^{\neq} = 60.2\ \text{kJ mol}^{-1}$. 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

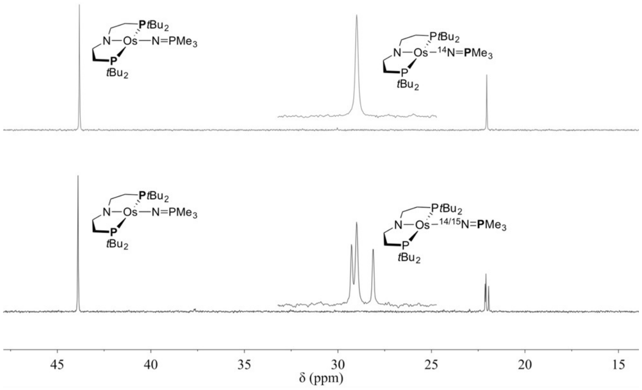

Figure 3. $^{31}P\{^1H\}$ NMR spectra of complex **6** (top) and **6** with 50 % ^{15}N nitride labeling (bottom), respectively.

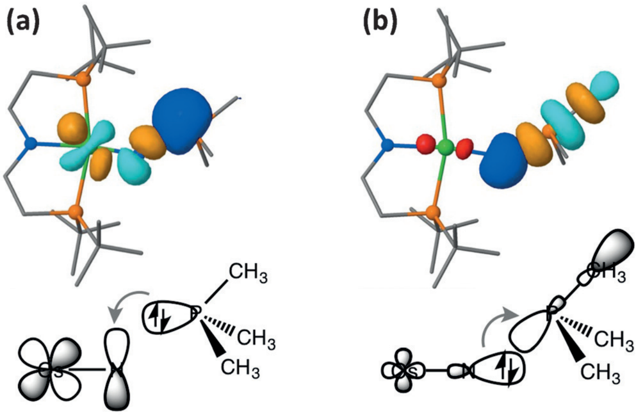

Figure 4. Computed NBOs (top) and schematic fragment orbital interactions (below) that represent the interaction of **3** and PMe_3 in the **TS** leading to **6**.

phosphine to the nitride. Hence, NPA suggests that $P\rightarrow N\equiv Os$ donation dominates and therefore overall electrophilic nitride character for this reaction.

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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