Ammonia Oxidation by Abstraction of Three Hydrogen Atoms from a Mo−NH₃ Complex

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S *Supporting Information*

ABSTRACT: We report ammonia oxidation by homolytic cleavage of all three H atoms from a [Mo−NH₃]⁺ complex using the 2,4,6-tri-*tert*-butylphenoxyl radical to yield a Mo-alkylimido ([Mo=NR]⁺) complex (R = 2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one). Chemical reduction of [Mo=NR]⁺ generates a terminal Mo≡N nitride complex upon N—C bond cleavage, and a [Mo=NH]⁺ complex is formed by protonation of the nitride. Computational analysis describes the energetic profile for the stepwise removal of three H atoms from [Mo—NH₃]⁺ and formation of [Mo=NR]⁺.

N̲itrogen-based fuels for large-scale energy storage have the potential to dissuade the use of fossil fuels that produce environmentally harmful CO₂ emissions.[1] Ammonia is an appealing candidate because of its high energy density, ease of storage and distribution within the current infrastructure, and its ability to be used directly in a fuel cell or as a medium to store H₂.[2] Development of efficient electrocatalysts for NH₃ production from N₂ and protons and electrons, akin to biological N₂ fixation by nitrogenase enzymes,[3] could augment the energy-intensive Haber−Bosch process.[4]

Although electrocatalysts to lower the environmental impact of NH₃ synthesis are needed, catalysts for the reverse reaction, NH₃ oxidation, will also be essential to utilize energy stored in N—H bonds. NH₃ coordinates to transition metals, forming Lewis acid−base adducts.[5] Although uncommon, transition metal mediated N—H bond cleavage reactions of NH₃ have been reported,[6] including the electrochemical formation of N₂ from NH₃,[7] oxidative addition,[8] metal−ligand cooperative addition,[9] and coordination-induced bond weakening to evolve H₂, recently reported by Chirik and co-workers.[10] However, molecular transition metal catalysts for the oxidation of NH₃ to N₂ remain unknown. Understanding the reactivity and energetics of individual N—H bond formation and cleavage steps can facilitate development of N₂ reduction[11] and NH₃ oxidation by molecular catalysts.

An attractive strategy for developing a transition metal based system for electrocatalytic NH₃ oxidation involves hydrogen-atom abstraction (HAA) or proton coupled electron transfer (PCET) reactions using organic radicals with known X—H

bond strengths.[12] Several research groups[6a,13] have employed these approaches in the study of nitrogen-containing species related to N₂ reduction and metal-oxo chemistry. In particular, M-imido (M=NR, M=NH) and M-nitride species were formed from the corresponding M-amido complexes, but HAA from a M—NH₃ complex in which all three N—H bonds are cleaved is unprecedented in molecular systems. Herein we report the formation of a Mo-alkylimido (Mo=¹⁵NR) complex generated from the removal of three H atoms of an ¹⁵NH₃ ligand by the 2,4,6-tri-*tert*-butylphenoxyl radical (ᵗBu₃ArO•). In addition, we report the formation of the terminal Mo≡¹⁵N and [Mo=¹⁵NH]⁺ products derived from the [Mo=¹⁵NR]⁺ complex.

The cationic Mo—NH₃ complex *cis*-[CpMo(CO)(Pᴾʰ₂Nᵗᴮᵘ₂)(¹⁵NH₃)]⁺ (**1**) was prepared from CpMo(CO)(Pᴾʰ₂Nᵗᴮᵘ₂)Cl by halide abstraction with NaBArᶠ₄ (Arᶠ = 3,5-(CF₃)₂C₆H₃) under ¹⁵NH₃ gas (Scheme 1), and was isolated in

Scheme 1. Preparation of 1 and 2
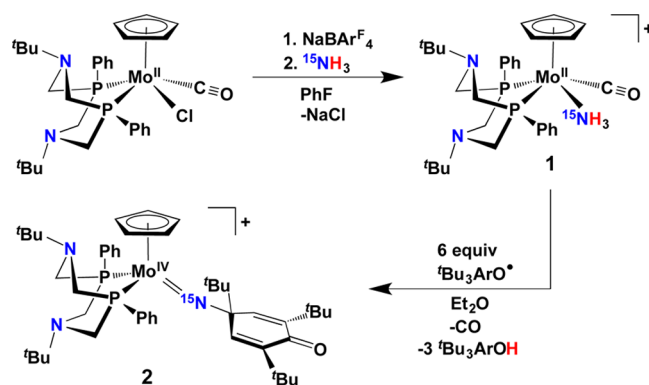
72% yield. The ³¹P{¹H} NMR spectrum of **1** displays doublets at δ 32.7 and 47.7, as expected for a complex with an asymmetrical four-legged piano-stool geometry. A singlet at δ −438.0 in the ¹⁵N{¹H} NMR spectrum (referenced to CH₃¹⁵NO₂) corresponds to the ¹⁵NH₃ ligand, while the IR spectrum exhibits a single ν_{CO} band at 1838 cm⁻¹. Complex **1** is stable in solution for weeks and under vacuum for hours
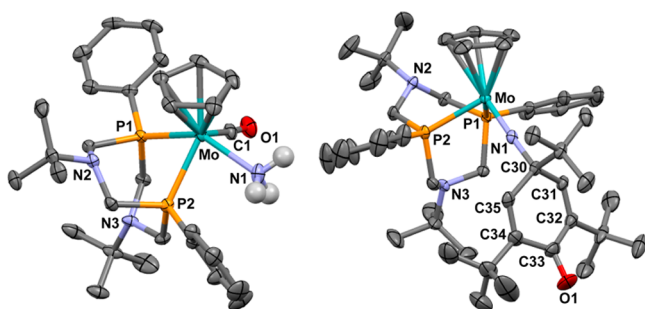
Figure 1. Molecular structures of $[CpMo(CO)(P^{Ph}_2N^{tBu}_2)(^{15}NH_3)]^+$ (**1**), (left) and $[CpMo(^{15}N^{2,4,6\text{-}tBu}C_6H_2O)(P^{Ph}_2N^{tBu}_2)]^+$ (**2**), (right). Hydrogen atoms (except for those on NH_3) and BAr^F_4 anions omitted for clarity. Thermal ellipsoids drawn at 50% probability.

without NH_3 loss. Crystallographic characterization of **1** (Figure 1) confirms the expected four-legged piano-stool geometry with cis CO and NH_3 ligands. The $P(1)—Mo—P(2)$ bond angle is 71.22(3)°, whereas the $Mo—N(1)$ bond length is 2.270(3) Å.

With the goal of preparing amido ($Mo—NH_2$) and imido ($Mo=NH$) complexes by removal of electrons and protons in the form of H atoms, we focused our attention on the reactivity of complex **1** with well-known hydrogen atom acceptors. We initially employed 1−6 equiv of TEMPO• (TEMPO• = 2,2,6,6-tetramethylpiperidine-1-oxyl), but these reactions resulted in nearly complete recovery of **1**. This suggests the homolytic N—H bond dissociation free energy (BDFE) of the NH_3 ligand is greater than that of TEMPO-H (65.2 kcal/mol in benzene).[12]

Turning to a stronger H atom acceptor, a solution of **1** in Et_2O at room temperature was added over 5 h to a Et_2O solution containing 6 equiv of 2,4,6-tri-*tert*-butylphenoxyl radical $^tBu_3ArO•$ (BDFE of $^tBu_3ArO$-H = 76.7 kcal/mol in benzene).[12] This reaction affords a diamagnetic product, isolated as orange crystals in 54% yield.[14] X-ray diffraction analysis revealed a cationic Mo-alkylimido complex, [CpMo-$(P^{Ph}_2N^{tBu}_2)(^{15}N^{2,4,6\text{-}tBu}C_6H_2O)]^+$ (**2**) (Scheme 1), in which all three H atoms were removed from the $^{15}NH_3$ ligand.

Complex **2** exhibits a symmetric three-legged piano-stool geometry, as reflected by the doublet at δ 47.1 ($^2J^{15}_{NP}$ = 6.1 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The $^{15}NH_3$-derived nitrogen atom of the $Mo=^{15}N$—R moiety is observed at δ 16.4 in the $^{15}N\{^1H\}$ NMR spectrum. The $Mo—N1—C30$ angle is nearly linear at 177.6(2)°, and the $Mo=N(1)$ bond length of 1.742(3) Å is consistent with a Mo=N double bond, as found in structurally characterized Mo-alkylimido complexes.[15] Notably, the six-membered ring of the N^tBu_3ArO unit is not planar and resembles a "dieneone" structure, indicated by the C30—C31, C30—C35 bond lengths of ca. 1.50 Å, C31—C32, C34—C35 bond lengths of ca. 1.331 Å, and short ketone-like C33—O1 bond length of 1.226(5) Å.

The N—C bond presumably results from heterocoupling of $^tBu_3ArO•$ with a $Mo—NH_x•$ (x = 0−2) species generated upon HAA from **1**. Accordingly, the major resonance contributor of $^tBu_3ArO•$, as noted by Mayer and co-workers,[16] exhibits a carbon-centered radical at the para position of the arene ring, providing an explanation for the observed N—C bond in **2** at this position. To the best of our knowledge, this is the first example of nitrogen−carbon bond formation involving $^tBu_3ArO•$. Smith and co-workers observed N—C bond formation in the reaction of a $Fe\equiv N$ complex with

triphenylmethyl radical.[17] Complexes structurally related to **2** have been reported, such as Ru-benzoquinone imines[18] formed by the reaction of a $Ru\equiv N$ complex with phenols, and a peroxy-p-quinolatocobalt(III) complex[19] from the reaction of a Co(II) complex, $^tBu_3ArOH$, and O_2.

Considering the unique electronic structure of the $Mo—^{15}N^{2,4,6\text{-}tBu}C_6H_2O$ fragment, we examined the reduction of **2**. Treatment of **2** with 2 equiv KC_8 resulted in reductive cleavage of the $^{15}N—C$ bond, furnishing the neutral, Mo(IV)-nitride, $CpMo(^{15}N)(P^{Ph}_2N^{tBu}_2)$ (**3**) (Scheme 2) in 74% NMR

Scheme 2. Preparation of 3 and 4
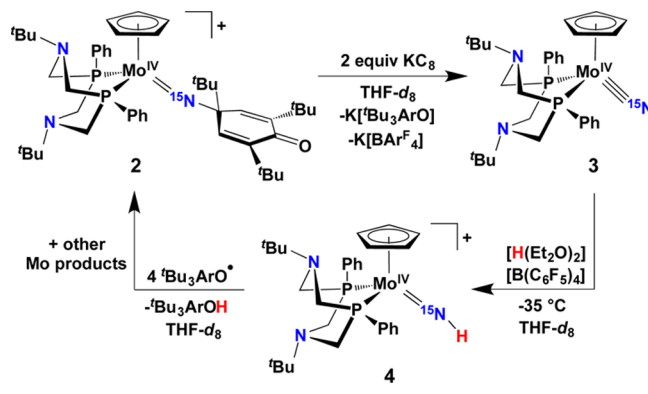
yield, with the concomitant formation of $K[BAr^F_4]$ and $K[^tBu_3ArO]$. Complex **3** displays a single resonance at δ 56.7 in the $^{31}P\{^1H\}$ NMR spectrum, and a diagnostic singlet at δ 458.4 in the ^{15}N NMR spectrum for the terminally bound $Mo\equiv^{15}N$ moiety. The IR spectrum shows a $\nu_{Mo}{}^{15}_N$ band at 1009 cm^{-1} (KBr), akin to other reported terminal Mo-nitrides,[20] especially the structurally related $(\eta^5\text{-}C_5Me_5)Mo$-$(^{14}N)(depf)$ (depf = 1,1′-bis(diethylphosphino)ferrocene) $(\nu_{Mo}{}^{14}_N = 1024$ cm$^{-1})$ prepared by Nishibayashi and co-workers.[21] Complex **3** is stable in solution at 25 °C, but degradation (noted by the liberation of free $P^{Ph}_2N^{tBu}_2$ ligand) occurs upon exposure to a vacuum, which has precluded isolation of **3** as an analytically pure solid. High-resolution electrospray mass spectrometry confirms the identity of **3**, further supporting this structural assignment (see SI). Notably, the reaction of **3** with 1 equiv of $^tBu_3ArO•$ results in unidentified phosphorus-containing Mo products as well as free $P^{Ph}_2N^{tBu}_2$ ligand, suggesting that **3** is unlikely to be an intermediate in the reaction of **1** with $^tBu_3ArO•$ to generate **2**.

Treatment of **3** (generated in situ) with 2 equiv of $[H(OEt_2)_2][B(C_6F_5)_4]$ results in formation of $[CpMo(^{15}NH)$-$(P^{Ph}_2N^{tBu}_2)]^+$ (**4**) in 88% NMR yield (Scheme 2).[22] Spectroscopically similar to **2**, complex **4** exhibits a doublet at δ 47.3 ($^2J^{15}_{NP}$ = 6.5 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The $Mo=^{15}NH$ proton appears as a doublet in the ^1H NMR spectrum at δ 6.1 (J^{15}_{NH} = 76 Hz). A cross-peak in the $^1H—^{15}N$ HSQC spectrum with a ^{15}N chemical shift of δ 24.2 corroborates this assignment.[23]

To test if HAA from **4** gives **2**, 4 equiv of $^tBu_3ArO•$ was added to a THF-d_8 solution of **4**, generating **2** in 25% NMR yield, as well as two unidentified Mo containing products by ^{31}P NMR spectroscopy (Scheme 2). This result indicates the third HAA from **1** as a viable mechanistic step, and underscores that the product selectivity is highly sensitive to the reaction conditions.[14] It is feasible that a formally $[Mo^V(^{15}N)]^+$ species exhibiting nitridyl radical character could react with $^tBu_3ArO•$

to form **2**, yield a Mo dimer by N—N homocoupling,[21] or follow undesired degradation pathways.

Electronic structure calculations based on density functional theory (DFT) were performed, using the B3LYP exchange and correlation functional[24] and D2[25] dispersion corrections, to evaluate the thermodynamic profile (at 298 K and 1 atm) for the stepwise removal of H atoms from complex **1** with ${}^tBu_3ArO^{\bullet}$ (Scheme 3).[26] We propose the sequence of HAA

Scheme 3. Stepwise Removal of H Atoms from Complex 1 with ${}^tBu_3ArO\cdot$
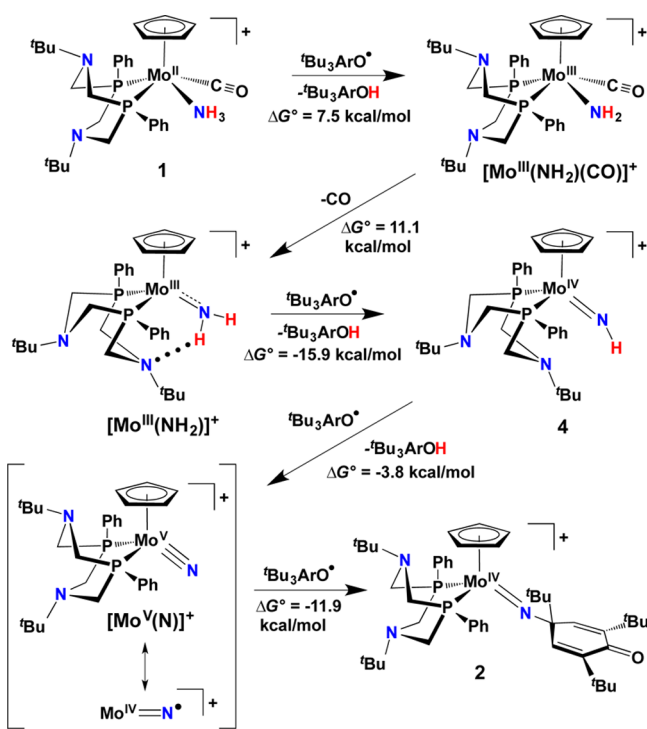
reactions in Scheme 3 as a mechanism to form **2**. The calculated N—H BDFEs in Et_2O for each Mo—NH_x species in Scheme 3 are listed in Table S3, SI. The first HAA from complex **1** is predicted to cleave the strongest N—H bond of all the Mo—NH_x ($x = 1–3$) complexes; $BDFE_{N-H}$ = 84.2 kcal/mol. Upon N—H bond cleavage, we propose rapid dissociation of CO from $[\textbf{Mo}^{\textbf{III}}(\textbf{NH}_2)(\textbf{CO})]^+$ to form $[\textbf{Mo}^{\textbf{III}}(\textbf{NH}_2)]^+$. CO loss strengthens the Mo—N bond of the Mo-amido moiety and weakens the N—H bond by ~24 kcal/mol ($BDFE_{N-H}$ = 60.8 kcal/mol), making the second HAA reaction to form **4** favorable by 15.9 kcal/mol. In agreement with this mechanism, in situ IR spectroscopy showed that treatment of **1** with 1 equiv of ${}^tBu_3ArO^{\bullet}$ led to a decrease in CO band intensity for **1**, but no new Mo—CO-containing products (Figure S28, SI). Notably, DFT suggests that $[\textbf{Mo}^{\textbf{III}}(\textbf{NH}_2)]^+$ exhibits a hydrogen bonding interaction with the pendant ${}^tBuN$ amine group, which will stabilize this intermediate en route to **2**. The third HAA reaction from complex **4** ($BDFE_{N-H}$ = 72.9 kcal/mol) is favorable by 3.8 kcal/mol, generating a formally $[\textbf{Mo}^{\textbf{V}}(\textbf{N})]^+$ species that has a resonance structure containing a nitridyl radical $[\textbf{Mo}^{\textbf{IV}}(\textbf{N}^{\bullet})]^+$ (bottom of Scheme 3). Indeed, natural bond orbital analysis[27] indicates only a small population, ~5%, of a $[Mo^{IV}(N^{\bullet})]^+$ species (see SI for a detailed description of the electronic structure), though the ${}^{15}N$—C bond forming step is proposed to occur by heterocoupling of $[Mo^{IV}(N^{\bullet})]^+$ with ${}^tBu_3ArO^{\bullet}$ to form **2**. Nishibayashi and co-workers noted

similar nominal spin-density at nitrogen in a $[(\eta^5\text{-}C_5Me_5)Mo\text{-}(N)(depf)]^+$ intermediate,[21] which contrasts with $Rh\equiv N^{\bullet}$ and $Ir\equiv N^{\bullet}$ pincer complexes from Schneider, de Bruin and co-workers.[28] Although homocoupling occurs in these examples, $[Mo^{IV}(N^{\bullet})]^+$ in the presence of excess ${}^tBu_3ArO^{\bullet}$ forms **2**, which is apparently kinetically favored over N—N coupling.

In summary, we report the oxidation of NH_3 by using ${}^tBu_3ArO^{\bullet}$ to remove three hydrogen atoms from $[Mo—{}^{15}NH_3]^+$. We postulate that heterocoupling of a nitridyl radical species $[Mo^{IV}(N^{\bullet})]^+$ with ${}^tBu_3ArO^{\bullet}$ generates **2**. Reduction of **2** liberates ${}^tBu_3ArO^-$, affording the terminal $Mo\equiv N$, **3**, which can be protonated to form $[Mo\equiv NH]^+$, **4**. In the pursuit of catalysts for NH_3 oxidation, these results demonstrate that transition metal complexes can mediate the formation of several M—NH_x ($x = 0–3$) species. By using a suitable H atom acceptor, the coupling of proton and electron transfer steps can avoid thermodynamically unfavorable intermediates that could be encountered with stepwise electron- and proton-transfer reactions, enabling the cleavage of multiple N—H bonds. Ongoing studies are aimed at studying Mo—NH_x intermediates formed electrochemically, and are focusing on the critical step of N—N bond formation toward achieving electrocatalytic oxidation of NH_3 to N_2.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b00002.

   Data for Complex **1** (CIF)

   Data for Complex **2** (CIF)

   Experimental and computational details and data (PDF)

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Notes

The authors declare no competing financial interest.

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(14) The reaction of **1** and ^{t}Bu$_3$ArO$^\bullet$ to form **2** is highly sensitive to the solvent and the rate of addition. The slow addition of **1** to 6 equiv of ^{t}Bu$_3$ArO$^\bullet$ in Et$_2$O was critical to minimize unidentified Mo products, and using THF decreases the yield of **2**. Complex **2** can be formed with as little as 2 equiv of ^{t}Bu$_3$ArO$^\bullet$, although an excess aids in forming **2** as the kinetic product.

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(22) One equivalent of ^{t}Bu$_3$ArOH is generated in this reaction as K[^{t}Bu$_3$ArO] is present as a product from generation of **3** with KC$_8$.

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