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Catalytic Ammonia Oxidation to Dinitrogen by a Nickel Complex

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Abstract: We report a nickel complex for catalytic oxidation of ammonia to dinitrogen under ambient conditions. Using the aryloxy radical 2,4,6-tri-*tert*-butylphenoxy ('Bu₃ArO') as H atom acceptor to cleave the N-H bond of a coordinated NH₃ ligand up to 56 equiv of N₂ per Ni center can be generated. Employing the *N*-oxyl radical 2,2,6,6-(tetramethylpiperidin-1-yl)oxyl (TEMPO) as the H-atom acceptor, ~15 equiv of N₂ per Ni center are formed. A bridging Ni-hydrazine product identified by isotopic nitrogen (¹⁵N) studies and supported by computational models indicates the N-N bond forming step occurs by bimetallic homocoupling of two paramagnetic Ni-NH₂ fragments. Ni-mediated hydrazine disproportionation to N₂ and NH₃ completes the catalytic cycle.

Ammonia (NH₃) has garnered global attention as a large-scale sustainable energy carrier due to its high energy density, ease of distribution, storage, and potential use as a transportation fuel.^[1] A drawback is the large scale NH₃ synthesis by the Haber-Bosch process imparting a significant carbon footprint.^[2] However, efficient, and potentially carbon-free methods for NH₃ synthesis using renewable energy are on the horizon.^[3] Such advancements have the potential to change the landscape for worldwide energy production and utilization from carbon-based fuels toward a nitrogen-centric energy economy.^[4]

The study of molecular catalysts for NH₃ oxidation provides a mechanistic understanding of the reaction steps required to convert the energy stored in N-H bonds into electrical or chemical energy through H₂ (and N₂) when NH₃ is utilized as a fuel.^[5] Critical to catalyst development is how to efficiently mediate the challenging cleavage of up to six N-H bonds and the formation of an N-N bond en route to N₂ formation.^[6] In 2019 Hamann, Smith, and coworkers described electrocatalytic NH₃ oxidation using a Ru polypyridyl complex.^[7] Since this seminal report, electrocatalytic NH₃ oxidation has been demonstrated by Ru,^[8] Fe,^[9] and Mn^[10] complexes. A 2021 report of an Fe complex with a polypyridyl ligand formed up to 149 equiv of N₂ per Fe center.^[9b]

Ru complexes that *chemically* catalyze the oxidation of NH₃ to N₂ were among the early systems reported in 2019. Sakata Nishibayashi, and coworkers utilized a chemical oxidant and a base to cleave N-H bonds of NH₃ using a Ru catalyst supported

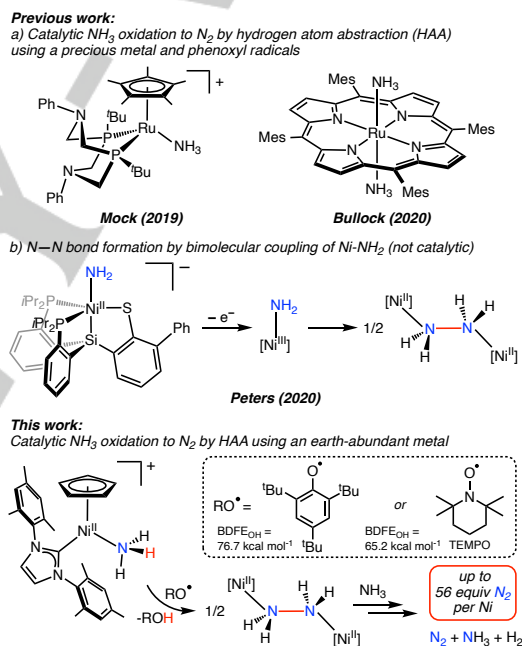


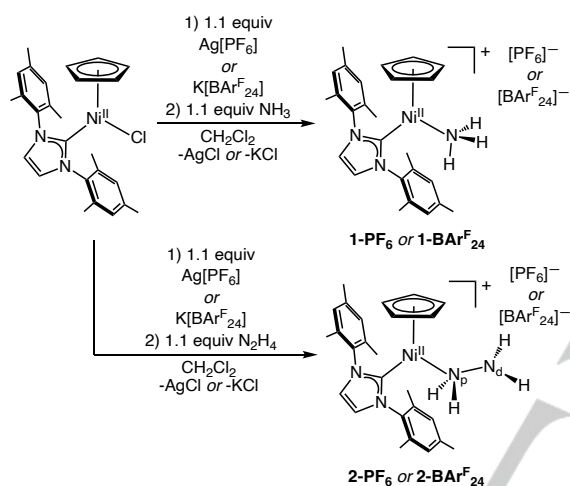
Figure 1. Top: Molecular catalysts utilizing Ru and phenoxyl radicals for catalytic NH₃ oxidation to N₂. Middle: a mechanistic study describing bimetallic coupling of Ni-NH₂ to form an N-N bond. Bottom: Catalytic NH₃ oxidation to N₂ using Ni and organic radicals as H atom acceptors described in this work. (Mes = mesityl; O-H bond dissociation free energies (BDFE_{OH}) shown above reported in benzene.^[11])

by 2,2'-bipyridyl-6,6'-dicarboxylate ligands.^[8c] In an alternative approach, we employed the 2,4,6-tri-*tert*-butylphenoxy radical ('Bu₃ArO') to catalyze NH₃ oxidation to N₂ by homolytic N-H bond cleavage,^[12] i.e. hydrogen atom abstraction (HAA) using a [Cp*Ru(diphosphine)(NH₃)]⁺ complex,^[13] Figure 1a. In 2020, Bullock and coworkers used a similar strategy with a Ru porphyrin complex for catalytic NH₃ oxidation.^[14] Using organic radicals to cleave N-H bonds of NH₃ has a practical benefit as the radical could be regenerated electrochemically from the ROH product as part of an overall catalytic cycle.^[6, 15]

While Ru has been the choice in a majority of chemical NH₃ oxidation catalysts, examples using earth-abundant metals are

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rare. Recently, Nishibayashi, Sakata, and coworkers reported chemical and electrocatalytic NH₃ oxidation to N₂ using a Mn salen complex.^[10] Brudvig and coworkers reported a copper electrocatalyst for the oxidation of NH₃ to nitrite and nitrate using aqueous conditions.^[16] In a related mechanistic study, Peters and coworkers demonstrated the N–N bond forming step by the bimolecular coupling of two Ni–NH₂ fragments to form a dinuclear Ni hydrazine complex (Figure 1b) in an overall synthetic cycle for NH₃ oxidation.^[17] Herein, we describe catalytic NH₃ oxidation to N₂ using the Ni complex [CpNi(IMes)(NH₃)]⁺[X][−] X = PF₆ or BAR^F₂₄ (**1-PF₆** or **1-BAR^F₂₄**) (Cp = C₅H₅; IMes = 1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene; Ar^F₂₄ = 3,5-(CF₃)₂C₆H₃). We show that ‘Bu₃ArO’ or TEMPO’ radical can be used as the H atom acceptor to catalytically generate N₂, Figure 1. In the proposed catalytic cycle supported by computational modeling, the N–N bond forming step occurs by the bimolecular coupling of two Ni–NH₂ fragments.



Scheme 1. Synthesis of complexes [CpNi(IMes)(NH₃)]⁺[X][−]; X = PF₆ or BAR^F₂₄ (**1-PF₆** or **1-BAR^F₂₄**) and [CpNi(IMes)(N₂H₄)]⁺[X][−]; X = PF₆ or BAR^F₂₄ (**2-PF₆** or **2-BAR^F₂₄**).

Treatment of a red dichloromethane (CH₂Cl₂) solution of CpNiCl(IMes)^[18] with 1.1 equiv of AgPF₆ or KBAR^F₂₄ followed by addition of NH₃ affords the yellow cationic Ni complexes **1-PF₆** or **1-BAR^F₂₄**, respectively (Scheme 1). Similarly, the yellow complexes [CpNi(IMes)(N₂H₄)]⁺[X][−] X = PF₆ or BAR^F₂₄ (**2-PF₆** or **2-BAR^F₂₄**) are prepared by addition of N₂H₄ to a CH₂Cl₂ solution of CpNiCl(IMes) and 1.1 equiv of AgPF₆ or KBAR^F₂₄.

The ¹H resonance corresponding to the coordinated NH₃ ligand in **1-BAR^F₂₄** exhibits solvent dependent chemical shifts. For example, a broad singlet is observed at δ 0.42 ppm in CD₂Cl₂, and in C₆D₆ the Ni–NH₃ resonance appears at δ -0.98 ppm. **1-PF₆** is insoluble in C₆D₆. A sample prepared using ¹⁵NH₃ gas, [CpNi(IMes)(¹⁵NH₃)]⁺[BAR^F₂₄][−] (**1¹⁵N-BAR^F₂₄**) affords a doublet (J_{15N-H} = 69 Hz) in the ¹H NMR spectrum for Ni–¹⁵NH₃ and ¹⁵N resonance at δ -457 ppm in C₆D₆ (δ -451 ppm in CD₂Cl₂) corroborated by the ¹H-¹⁵N HSQC spectrum. The ¹H NMR spectrum of **2-BAR^F₂₄** in CD₂Cl₂ revealed two broad resonances at δ 2.56 ppm and δ 3.11 ppm (¹⁵N cross-peaks at δ -308 ppm and δ -395 ppm, respectively, in the ¹H-¹⁵N HSQC spectrum) for the distal N_d and proximal N_p atoms, i.e. Ni–N_pH₂–N_dH₂, respectively.

The solid-state structures^[19] of **1-PF₆** and **1-BAR^F₂₄** from single crystal X-ray diffraction confirmed the presence of the NH₃

ligand coordinated to Ni with comparable Ni–N bond distances of 1.951(3) Å and 1.9476(12) Å, respectively (Figure 2). Likewise, the structure of **2-PF₆** shows the coordinated hydrazine moiety with a Ni–N_p bond length of 1.9373(11) Å and a N_p–N_d distance of 1.4636(14) Å. The crystal structures of **1-PF₆**, **1-BAR^F₂₄**, and **2-PF₆** reveal discrete interactions (ca. <3.0 Å) between the Ni–NH₃ or Ni–N₂H₄ hydrogen atoms and the CF₃ groups of [BAR^F₂₄][−] or the [PF₆][−] ion (See Supporting Information, SI).

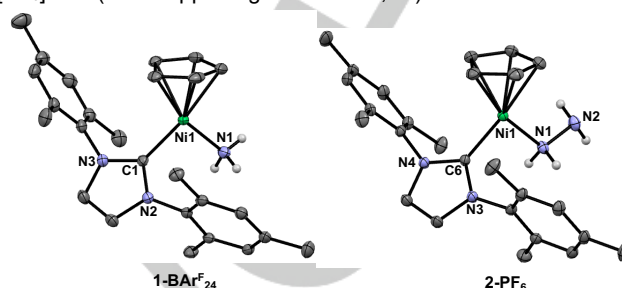


Figure 2. Molecular structures of the cation of **1-BAR^F₂₄** [CpNi(IMes)(NH₃)]⁺ and [CpNi(IMes)(N₂H₄)]⁺ **2-PF₆**. Hydrogen atoms (except for N-ligands), BAR^F₂₄ and PF₆ anions, and solvent molecules omitted for clarity. Thermal ellipsoids shown at 50% probability level. Selected bond lengths [Å] and angles [°]: **1-BAR^F₂₄** Ni1–N1: 1.9476(12), Ni1–C1: 1.8932(12); C1–Ni1–N3: 98.00(5). **2-PF₆** Ni1–N1: 1.9373(11), Ni1–C6: 1.8924(11), N1–N2: 1.4636(14); C6–Ni1–N1: 95.54(5).

In solid-state or in non-coordinating solvents **1-PF₆** and **1-BAR^F₂₄** are stable under vacuum toward NH₃ loss. Density Functional Theory (DFT) calculations^[20] (see SI for details) predict the Ni–NH₃ binding energy of ΔG° = −26.8 kcal mol^{−1} (Figure S31). Of particular importance, **2-PF₆** and **2-BAR^F₂₄** are stable in CD₂Cl₂ or fluorobenzene for days with no discernable changes to the ¹H NMR spectrum. However, [**2**]⁺ is surprisingly unstable in C₆D₆ and [D₈]THF.^[21] Dissolving crystalline **2-PF₆** or **2-BAR^F₂₄** in these solvents leads to disproportionation of the hydrazine moiety with formation of **1-BAR^F₂₄** and gaseous products NH₃, N₂, and trace amounts of H₂ (*vide infra*).^[22] **2-PF₆** exhibits similar characteristics but is insoluble in benzene.

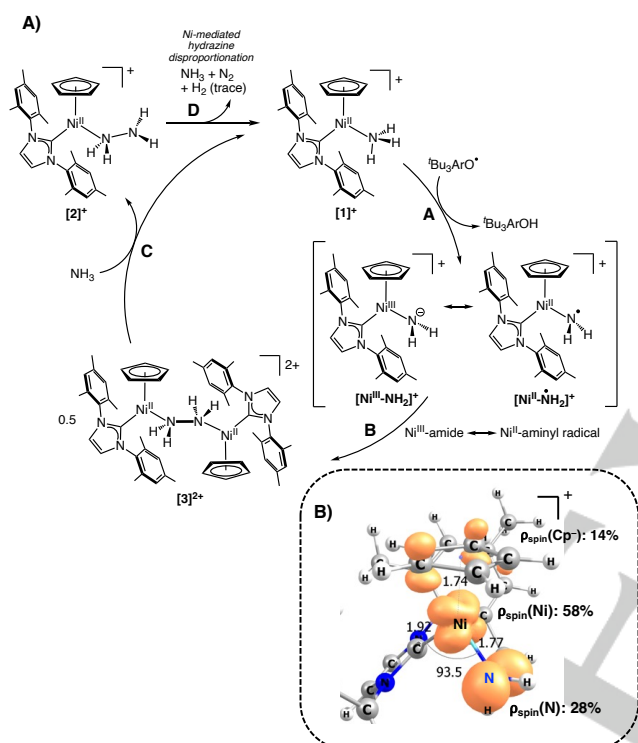
Given the noted instability of **2-BAR^F₂₄**, we probed Ni-mediated hydrazine disproportionation in independent reactions by treating a solution of **1-BAR^F₂₄** with 30 equiv of anhydrous N₂H₄. These experiments showed that disproportionation occurs to form NH₃ and N₂ as the primary products, H₂ was generated in lesser amounts (see SI).

We assessed the competency of **1-PF₆** and **1-BAR^F₂₄** to catalyze the chemical oxidation of NH₃ to N₂ under ambient conditions and a reaction time of 24 h. We noted that the counter anion identity of [**1**]⁺ has a significant impact on catalytic performance (see SI for tabulated catalytic results). Using 3.1 μmol **1-PF₆**, 800 equiv ‘Bu₃ArO’ and 200 equiv NH₃ in dimethoxyethane (DME), ~11 equiv N₂ per Ni and a trace amount of H₂ were formed. Catalytic performance improved in reactions using 1.5 μmol **1-PF₆**, 1600 equiv ‘Bu₃ArO’ and 400 equiv of NH₃ in DME, affording ~28 equiv N₂ / Ni. By employing **1-BAR^F₂₄** as the precatalyst, up to 56 equiv N₂ / Ni in DME, and ~46 equiv N₂ / Ni in acetonitrile were produced. The dramatic counterion effect on catalytic activity in polar solvents is correlated with the decreased stability of **2-BAR^F₂₄**. Moreover, the reduced solubility of postulated dicationic intermediates formed in the catalytic cycle upon homodimerization (*vide infra*) may also impact catalysis. Although **1-BAR^F₂₄** is soluble in benzene, catalytic trials produced ~12 equiv

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N_2 per Ni center. Headspace analysis by GC-MS of reactions performed in a Teflon valved NMR tube using $^{15}\text{NH}_3$ confirmed the formation of $^{15}\text{N}_2$ ($m/z = 30$) indicating the $^{15}\text{N}_2$ formed is derived from $^{15}\text{NH}_3$ (See SI).

Next, we examined the first N–H bond cleavage step and the N–N bond forming step en route to N_2 formation starting with ^{15}N -**BARF**₂₄. Scheme 2 describes the individual steps of a postulated catalytic cycle. Our mechanistic hypothesis asserted that H atom abstraction from ^{15}N -**BARF**₂₄ (Scheme 2, panel A, step A) would generate a putative intermediate that could be described by the resonance structures $[\text{CpNi}^{\text{III}}(\text{IMes})(^{15}\text{NH}_2)]^+$ ($[\text{Ni}^{\text{III}}\text{-}^{15}\text{NH}_2]^+$) or $[\text{CpNi}^{\text{II}}(\text{IMes})(^{15}\text{NH}_2)]^+$ ($[\text{Ni}^{\text{II}}\text{-}^{15}\text{NH}_2]^+$). Subsequent bimolecular homocoupling would then form $\{[\text{CpNi}^{\text{II}}(\text{IMes})]_2(\eta^1\text{-}^{15}\text{N}_2\text{H}_4)\}^{2+}$ (^{315}N -**BARF**₂₄) (Scheme 2 panel A, step B).



Scheme 2. A) Proposed catalytic cycle for NH_3 oxidation to N_2 using $[\mathbf{1}]^+$. B) Spin density contour (at $0.005 \text{ (e}^-)^2 \text{ \AA}^{-3}$) and atomic distribution (ρ_{spin}) of a single unpaired electron in $[\text{Ni}^{\text{III}}\text{-NH}_2]^+$ are from Hirshfeld analysis.^[23] Calculated bond lengths [Å] and angle [°] shown for Ni–L (L = NH_2 , C_{IMes} , ring centroid of Cp[−]) and $\text{C}_{\text{IMes}}\text{-Ni-NH}_2$.

Addition of 2 equiv of the dark blue $^t\text{Bu}_3\text{ArO}^\bullet$ to ^{15}N -**BARF**₂₄ in CD_2Cl_2 generated a golden yellow solution and the formation of $^t\text{Bu}_3\text{ArOH}$ by ^1H NMR spectroscopy. The primary products observed in the $^{15}\text{N}\{^1\text{H}\}$ NMR spectrum showed ^{15}N -**BARF**₂₄ and a new singlet resonance at δ -411 ppm assigned as ^{315}N -**BARF**₂₄. This resonance appears as a 1:2:1 triplet ($J_{\text{H-}^{15}\text{N}} = 70 \text{ Hz}$) in the ^1H coupled ^{15}N NMR spectrum as expected for the bridging ^{15}N -hydrazine ligand. The proton resonance (correlated by ^1H - ^{15}N HSQC) of the bridging ^{15}N hydrazine moiety appear as a doublet centered at δ 1.82 ppm ($J_{\text{H-}^{15}\text{N}} = 70 \text{ Hz}$) in the ^1H NMR spectrum.^{[24],[25]} Addition of excess $^{15}\text{NH}_3$ to the sample containing ^{315}N -**BARF**₂₄ afforded free $^{15}\text{N}_2\text{H}_4$. The liberated $^{15}\text{N}_2\text{H}_4$ exhibits a cross peak in the ^1H - ^{15}N HSQC spectrum at δ -341 ppm, corresponding to a ^1H resonance at δ 1.28 ppm.

The rapid consumption of $^t\text{Bu}_3\text{ArO}^\bullet$ indicates homolytic cleavage of the first N–H bond is thermodynamically favorable. From the $\text{BDFE}_{\text{O-H}}$ values in Figure 1, we estimate the first $\text{BDFE}_{\text{N-H}}$

of $[\mathbf{1}]^+$ to be less than 76 kcal mol^{-1} . Thus, NH_3 N–H bond weakening^[26] of $\sim 28 \text{ kcal mol}^{-1}$ occurs upon coordination to $[\text{CpNi}(\text{IMes})]^+$ (free NH_3 $\text{BDFE}_{\text{N-H}} = 103.3 \text{ kcal mol}^{-1}$ in gas phase; calculated to be $100.7 \text{ kcal mol}^{-1}$ in Figure S32).^[15b] Because the addition of a large excess H atom acceptors has been shown to overcome thermodynamically unfavorable reactions of $\sim 7\text{-}12 \text{ kcal mol}^{-1}$,^[13] we examined the weaker H atom acceptor, TEMPO $^\bullet$, for NH_3 oxidation. In a reaction using $1.5 \mu\text{mol}$ **1-BARF**₂₄, 1600 equiv TEMPO $^\bullet$ ($\text{BDFE}_{\text{O-H}}$ of TEMPO-H = $65.2 \text{ kcal mol}^{-1}$ in benzene)^[11] and 400 equiv of NH_3 in DME, ~ 15 equiv N_2 was formed per Ni center in 24 h.^[27] While GC-MS analysis showed the formation of $^{15}\text{N}_2$ ($m/z = 30$) using ^{15}N -**BARF**₂₄, excess TEMPO $^\bullet$, and $^{15}\text{NH}_3$, the presence of $^{14}\text{N}^{15}\text{N}$ ($m/z = 29$) and O_2 (in GC traces of large scale runs) suggest TEMPO $^\bullet$ degradation may be occurring in Ni-catalyzed formation of N_2 from NH_3 (See SI).

DFT calculations probing the electronic structure of the product generated from abstraction of the first H atom from $[\mathbf{1}]^+$ in implicit polarizable solvent continuum^[28] indicate this product is best described as a covalently coordinated amide ligand to a formally Ni^{3+} ($3d^7$) center (Scheme 2B, $[\text{Ni}^{\text{III}}\text{-NH}_2]^+$). Upon HAA, the electron hole created by the H atom abstraction relaxes into the metal d-manifold that creates a paramagnetic Ni center. The spin density contour plot in Scheme 2B, indicates three main localized contributions to the frontier orbital involved in HAT (see details in Table S6): (1) on two C atoms of the Cp[−] ring (14% *via* σ interaction), (2) at the Ni center (58%, off-axis 3d-orbital), (3) on the N atom of the amide ligand (28% *via* π -interaction). In this frontier orbital description, the IMes ligand does not exhibit a localized contribution of spin density. Furthermore, the computed ionic and covalent Ni^{III}–(NH_2)[−] bond (1.77 Å) for $[\text{Ni}^{\text{III}}\text{-NH}_2]^+$ was significantly shorter than the covalent bonding of Ni^{II}– NH_3 in **1-BARF**₂₄ and Ni^{II}– N_2H_4 in **2-PF**₆ (exp./calc.: $1.951/1.973 \text{ \AA}$ and $1.937/1.958 \text{ \AA}$; respectively; Figure S34). The computed $\sim 1/3$ of an electron spin-density on the N atom of the amide ligand of $[\text{Ni}^{\text{III}}\text{-NH}_2]^+$ indicates the presence of sufficient aminyl radical character to form the N–N bond *via* bimolecular homocoupling. The calculated free energy of 1 kcal mol^{-1} ($\Delta G^{\circ,\text{dim}}$ in Figure S33) to form $[\mathbf{3}]^{2+}$ suggests a spontaneous process for dimerization under catalytic conditions.

The presence of exogenous NH_3 facilitates the dissociation of **3-BARF**₂₄ into the precatalyst **1-BARF**₂₄ and end-on bound hydrazine complex **2-BARF**₂₄ (Scheme 2, panel A, step C). DFT calculations predict the dissociation step is highly spontaneous ($\Delta G^{\circ,\text{dis}} = \sim 28 \text{ kcal mol}^{-1}$; Figure S33).

In the final step of the catalytic cycle, the intrinsic instability of **2-BARF**₂₄ towards hydrazine disproportionation is postulated to play a critical role in N_2 formation. **2-BARF**₂₄ is unstable in most solvents other than CH_2Cl_2 , and disproportionation generates **1-BARF**₂₄ with the liberation of gaseous products N_2 , NH_3 , and H_2 (Scheme 2 panel A, step D). However, under catalytic conditions (with excess NH_3 and $^t\text{Bu}_3\text{ArO}^\bullet$ present), alternative reaction pathways were considered: (1) **3-BARF**₂₄ could react with excess $^t\text{Bu}_3\text{ArO}^\bullet$ to generate a nickel diazene ($\text{Ni-N}_2\text{H}_2$) product. Free diazene or a metal-bound diazene species can undergo disproportionation forming $\frac{1}{2} \text{ N}_2$ and $\frac{1}{2} \text{ N}_2\text{H}_4$ as Peters and coworkers recently described for another Ni complex (Figure 1b).^[17] In the present case, *in situ* diazene formation and disproportionation cannot be ruled out based on the quantified gaseous products formed in catalysis; (2) as noted above, treatment of ^{315}N -**BARF**₂₄ with excess NH_3 , liberated free hydrazine presumably by ligand exchange with **2-BARF**₂₄ generating **1-**

BAr^F₂₄. Free hydrazine could undergo disproportionation in solution with excess 'Bu₃ArO' present under catalytic conditions. However, independent experiments showed the addition of 'Bu₃ArO' to a THF solution of hydrazine led to the discrete formation of N₂ and H₂ (See SI). Since H₂ formation is very low in catalytic trials, the disproportionation of free hydrazine may be only be a nominal reaction; (3) an intramolecular N–N bond coupling mechanism (Figure S32) involving a high-spin paramagnetic, formally 20e⁻ complex [CpNi(IMes)(NH₃)₂]⁺ is energetically not competitive with the homodimerization step based on DFT calculations (Figure S33). The speciation of the Ni complex following catalysis has not been determined. Catalytic reactions performed for 48 h did not result in an increase of N₂ formation suggesting degradation of the Ni catalyst may be occurring.

In summary, we described catalytic NH₃ oxidation to N₂ by HAA mediated by Ni complexes that takes advantage of unstable hydrazine and/or diazene intermediates to generate N₂. The Ni-NH₃ N-H bond in [1]⁺, is estimated to have a BDFE_{N-H} of less than 76 kcal mol⁻¹ permitting the use of 'Bu₃ArO' or TEMPO[•] radicals in catalytic NH₃ oxidation. Importantly, the balance of N-H bond weakening in the Ni-NH₃ complex and the partial aminyl radical character of the Ni-NH₂ product are critical features for catalysis in this Ni system. Using 'Bu₃ArO', bimolecular homocoupling of two Ni-NH₂ species generates a Ni^{II}₂(N₂H₄) complex denoting the N-N bond forming step in the proposed catalytic cycle. Future efforts will focus on modifications of the ancillary ligands to improve catalyst stability and will explore this Ni system for electrocatalytic NH₃ oxidation to N₂.

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Keywords: nickel • ammonia oxidation • molecular catalyst • dinitrogen • hydrogen atom abstraction

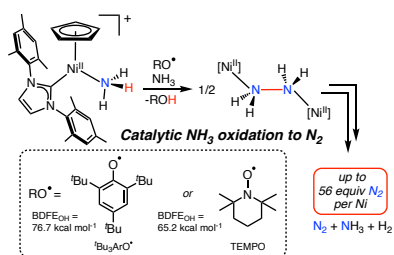
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A nickel complex for catalytic oxidation of NH_3 to N_2 is demonstrated using the radicals 2,4,6-tri-*tert*-butylphenoxy ($\text{tBu}_3\text{ArO}^\bullet$) or 2,2,6,6-tetramethylpiperidine-1-yl)oxyl (TEMPO) as the H-atom acceptor to cleave the N-H bond of a NH_3 ligand. Two Ni-NH₂ fragments form an N-N bond in a bridging Ni-hydrazine product. Ni-mediated hydrazine disproportionation affords N_2 and NH_3 in the proposed catalytic cycle. (BDFE = Bond Dissociation Free Energy)