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Hydrazine Formation via Coupling of a $\text{Ni}^{\text{III}}\text{-NH}_2$ RadicalNina X. Gu,^[a] Paul H. Oyala,^[a] and Jonas C. Peters ^{*,[a]}

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Abstract: $\text{M}(\text{NH}_x)$ intermediates involved in N–N bond formation are central to ammonia oxidation (AO) catalysis, an enabling technology to ultimately exploit ammonia (NH_3) as an alternative fuel source. While homocoupling of a terminal amide species (M-NH_2) to form hydrazine (N_2H_4) has been proposed, well-defined examples are without precedent. Herein, we discuss the generation and electronic structure of a $\text{Ni}^{\text{III}}\text{-NH}_2$ species that undergoes bimolecular coupling to generate a $\text{Ni}^{\text{II}}_2(\text{N}_2\text{H}_4)$ complex. This hydrazine adduct can be further oxidized to a structurally unusual $\text{Ni}_2(\text{N}_2\text{H}_2)$ species; the latter releases N_2 in the presence of NH_3 , thus establishing a synthetic cycle for Ni-mediated AO. Distribution of the redox load for $\text{H}_2\text{N-NH}_2$ formation via NH_2 coupling between two metal centers presents an attractive strategy for AO catalysis using Earth-abundant, late first-row metals.

Ammonia offers attractive opportunities for energy storage and use, for example as a hydrogen fuel carrier or as an energy-dense fuel.¹ For such applications, catalysts that mediate the $6\text{e}^-/6\text{H}^+$ conversion of ammonia to N_2 are key and have been the subject of many studies.² Well-defined molecular model systems are amenable to detailed mechanistic interrogation of this multi-electron process.

Stoichiometric AO to N_2 has been demonstrated for complexes featuring Group 8 and earlier transition metals,³ and more recently, homogeneous AO catalysis mediated by Ru^4 and Fe^5 complexes has been achieved. Notably, several of these molecular catalyst systems (or closely-related derivatives) can also mediate water oxidation catalysis (WOC),⁶ raising the question as to whether ammonia and water oxidation proceed through conceptually related pathways.

For WOC, the intermediacy of metal oxo species has been broadly implicated, and OO bond formation is often posited to occur via oxo coupling or nucleophilic attack of a metal oxo intermediate by H_2O (Fig. 1).⁷ In analogy to WOC, intermediates featuring metal-nitrogen multiple bonds (specifically, metal nitride ($\text{M}\equiv\text{N}$) and imide ($\text{M}=\text{NR}$) intermediates) have been proposed for several systems that mediate ammonia oxidation.³ Furthermore, bimolecular nitride^{3,8} and imide⁹ coupling, and the nucleophilic attack of amines on terminal imides^{3,10} and nitrides,¹¹ have been implicated in relevant NN bond forming reactions.

In contrast, well-defined examples of NN bond formation through coupling of parent amide intermediates (M-NH_2) are lacking, despite having been previously posited in catalytic AO mediated by (tetramesitylporphyrin) $\text{Ru}(\text{NH}_3)_2$.^{4d} The coupling of two unobserved Ru-NH_2 fragments has also been implicated in the stoichiometric AO cycle mediated by a cofacial $\{(\text{porphyrin})\text{Ru}(\text{NH}_3)_2\}$ system,¹² and examples of reductive elimination of an N–N single bond from conceptually related

M-NR_2 ¹³ and $\text{M-N}=\text{R}$ ¹⁴ species have been reported, but are highly uncommon.

Water Oxidation: Common Pathways for OO Bond Formation

Ammonia Oxidation: Common Pathways for NN Bond Formation

Alternative Pathway (This Work): Bimolecular Coupling of M-NH_2

Figure 1. (top) Proposed pathways for OO bond formation (middle) Proposed pathways for NN bond formation (bottom) Proposed N–N coupling pathway from a Ni-NH_2 species

A significant factor that limits access to these metal-mediated reductive eliminations is the thermodynamically weak N–N bond that is formed (e.g. bond dissociation enthalpy of $\text{H}_2\text{N-NH}_2$ is ca. 66 kcal/mol).¹⁵ Mechanistic interrogation of well-defined M-NH_2 and M-NR_2 complexes competent for N–N single bond reductive elimination is thus of general interest.^{13a,14}

Herein, we report the first example of a molecular Ni system that mediates stepwise NH_3 oxidation. A reactive, formal $\text{Ni}^{\text{III}}\text{-NH}_2$ species is proposed as the key intermediate en route to hydrazine formation via bimolecular reductive elimination; further N_xH_y oxidation can be accessed from the resulting $\text{Ni}^{\text{II}}_2(\text{N}_2\text{H}_4)$ complex to ultimately yield NH_3 -derived N_2 .

Our group recently reported the tetradentate ligand, $\text{HSiP}_2\text{S}^{\text{Pr}}$,¹⁶ and Ni-bound species, $[(\text{SiP}_2\text{S})\text{Ni}]_2(\text{N}_2)$ (**1**).¹⁷ Treatment of **1** with ammonia provides $(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{NH}_3)$ (**2**), and deprotonation of the NH_3 ligand with $n\text{BuLi}$ affords $[(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{NH}_2)]\text{Li}$ (**3**), which can also be prepared by treatment of **1** with LiNH_2 (Scheme 1). Ni complexes featuring a terminal NH_2 ligand are relatively uncommon, and to our knowledge, reported examples are limited to four-coordinate, pincer-ligated Ni^{II} species.¹⁸

Cyclic voltammetry data of **3** with 0.4 M $[\text{NBu}_4][\text{PF}_6]$ in THF reveals an oxidation event at -0.72 V vs. $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$, corresponding to its formal $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ couple. The reaction of **3** with one equivalent of $[\text{Cp}_2\text{Fe}][\text{BAR}^{\text{F}}_4]$ at -78 °C in 1,2-dimethoxyethane (DME) regenerates the ammonia adduct **2** in ca. 60% yield. Most interesting is the concomitant generation of an N–N coupled hydrazine product, $[(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}]_2(\text{N}_2\text{H}_4)$ (**4**, ca. 40% yield). Of note, neither H_2 nor free NH_3 are detected. Complex **4** can be

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independently generated via treatment of **1** with N_2H_4 . Its solid-state structure bears an NN bond of 1.488(4) Å (Fig. 2A, see SI for additional XRD data), slightly elongated compared to free hydrazine (1.449 Å).¹⁹

Scheme 1. Synthesis of compounds **2-5**. ArO = 2,4,6-tri-*tert*-butylphenoxyl radical

Figure 2. Crystal structures of compounds (A) **4** and (B) **6**. Solvent molecules, disordered components, and C-H hydrogens omitted for clarity. Ellipsoids shown at 50% probability.

NMR data reveal that oxidation of the ^{15}N - and ^2H -labeled derivatives of **3**, $[(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(^{15}\text{NH}_2)]\text{Li}$ and $[(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{ND}_2)]\text{Li}$, respectively, affords the corresponding $[(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(^{15}\text{N}_2\text{H}_4)]$ and $[(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(^{15}\text{N}_2\text{D}_4)]$ complexes as the N–N coupled products, which confirm that the coordinated hydrazine is exclusively

amide-derived. The observation of hydrazine via the oxidation of **3** suggests a direct role for a $\text{Ni}^{\text{III}}(\text{NH}_2)$ species in the N–N coupling step. One possibility is that N–N bond formation occurs between two molecules of $(\text{SiP}_2\text{S})\text{Ni}^{\text{III}}(\text{NH}_2)$ (**3^{ox}**). Alternatively, a reaction between **3^{ox}** and **3** to form a monoanion, $\{[(\text{SiP}_2\text{S})\text{Ni}]_2(\text{N}_2\text{H}_4)\}^-$, followed one-electron oxidation, leads to the same product. We disfavor the latter scenario as we observe that treatment of **3** with 0.5 equivalents of $[\text{Cp}_2\text{Fe}][\text{BAR}^{\text{F}}_4]$ in DME at -78°C fails to generate an EPR-active species (as would be expected for $\{[(\text{SiP}_2\text{S})\text{Ni}]_2(\text{N}_2\text{H}_4)\}^-$). Furthermore, the one-electron reduced congener of **4** is a mixed-valent $\text{Ni}^{\text{I}}/\text{Ni}^{\text{II}}$ species with the Ni^{I} center bearing 19 e^- , and thus likely an unstable, high-energy species. This argument is consistent with the CV data on **4** collected in 0.4 M $[\text{NBu}_4][\text{PF}_6]$ in THF at 25°C , which reveals an irreversible reduction event with an onset at ca. -3 V vs. $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$.

We thus favor a mechanism for N–N coupling where two $\text{Ni}^{\text{III}}\text{--NH}_2$ fragments directly to generate **4**; the competing generation of **2** following the oxidation of **3** is presumed to arise from H-atom abstraction of DME solvent by $\text{Ni}^{\text{III}}\text{--NH}_2$. Consistent with this proposal, carrying out the oxidation of **3-2H** with twenty-fold dilution results in near quantitative formation of the amine product, $(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{ND}_2\text{H})$, and NMR spectroscopy confirms the presence of the N–H proton. Only trace amounts of the hydrazine adduct are generated under these conditions.

It is useful to compare this mechanistic picture with a previous study from our lab, where we demonstrated that the same SiP_2S ligand could support a related $\text{Ni}^{\text{III}}\text{--H}$ species that undergoes release of H_2 .¹⁷ This step was posited to occur via a transition state featuring direct H–H coupling between two $\text{Ni}^{\text{III}}\text{--H}$ fragments, in analogy to the proposed N–N coupling pathway proposed here (Fig. 3).

Figure 3. Comparison of proposed H–H and N–N bond formation by $(\text{SiP}_2\text{S})\text{Ni}^{\text{III}}\text{X}$ species

Attempts to observe **3^{ox}** by oxidation of **3** with $[\text{Cp}_2\text{Fe}][\text{BAR}^{\text{F}}_4]$ were unsuccessful (see SI). However, we find that small quantities of an $S = \frac{1}{2}$ $\text{Ni}^{\text{III}}\text{--NH}_2$ can be generated by H-atom abstraction from $(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{NH}_3)$ **2** with 2,4,6-tri-*tert*-butylphenoxyl radical in 2-MeTHF. Based on UV-vis data, the H-atom abstraction of **2** by the phenoxyl radical is more favorable at lower temperatures; new features at 670 nm and 870 nm grow in upon cooling the solution from -78°C to -130°C , and this is reversible upon warming the solution, demonstrating that this process is in equilibrium. Given the significantly increased stability of the observed Ni^{III} amide compared to in situ-generated **3^{ox}**, we propose that treatment of the phenoxyl radical with **2** results in a Ni^{III} amide stabilized by H-bonding to 2,4,6-tri-*tert*-butylphenol $((\text{SiP}_2\text{S})\text{Ni}^{\text{III}}\text{--NH}_2\cdots\text{H--OAr}$, **3^{ox}**, Eq. 1). Such a scenario rationalizes the observation that **3^{ox}** formation is favorable at lower temperatures, due to the entropic penalties associated the H-bond stabilized amide species.

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Due to this observed equilibrium, unreacted phenoxyl radical was invariably observed in the EPR spectrum, in addition to a rhombic signal attributed to 3^{ox} ($g = [2.223, 2.084, 2.027]$, see SI). Pulse EPR data on 3^{ox} and analogous ^{15}N - and ^2H -labeled species ($3^{\text{ox-}^{15}\text{N}}$ and $3^{\text{ox-}^2\text{H}}$, prepared from $(\text{SiP}_2\text{S})\text{Ni}^{\text{III}}(^{15}\text{NH}_3)$ and $(\text{SiP}_2\text{S})\text{Ni}^{\text{III}}(\text{ND}_3)$ respectively) resolve hyperfine couplings to one isotopically sensitive nitrogen and two isotopically sensitive hydrogen nuclei. The hyperfine couplings to two distinct hydrogen nuclei were detected through Q-band ^1H - ^2H Davies ENDOR, with $A(^1\text{H}_\alpha) = \pm[10.3, -5.0, -4.3]$ MHz and $A(^1\text{H}_\beta) = \pm[7.0, -4.2, -4.0]$ MHz, (see SI for additional discussion and spectra). Additionally, hyperfine coupling to two ^{31}P nuclei are observed and simulated as $A(^{31}\text{P}_\alpha) = \pm[285, 270, 110]$ MHz, $A(^{31}\text{P}_\beta) = \pm[120, 125, 375]$ MHz. The hyperfine coupling to ^{14}N was determined as $A(^{14}\text{N}) = \pm[-2.57, -0.86, -1.35]$ MHz through a combination of X- and Q-band hyperfine sublevel correlation spectroscopy (HYSCORE) of 3^{ox} and $3^{\text{ox-}^{15}\text{N}}$. Based on the experimental hyperfine values, spin density on the amide N is estimated at $|\rho_{\text{N}2s}| \approx 0.001 e^-$ in the $2s$ orbital and a sum of $|\rho_{\text{N}2p}| < 0.01 e^-$ within the three $2p$ orbitals. Additionally, spin density at the amide protons of $|\rho_{\text{H}\alpha}| \approx 0.0007 e^-$ and $|\rho_{\text{H}\beta}| \approx 0.0008 e^-$ are estimated. Given these small estimated spin density values on the NH_2 fragment, species 3^{ox} is best described as a Ni-centered metalloradical, rather than a Ni-bound aminyl radical (Fig. 4). Additional support for this electronic structure description is provided by the extremely high electric field gradient asymmetry ($\eta = 1$) at ^{14}N , as determined from the nuclear quadrupole coupling measured via HYSCORE, which is consistent with a lone pair at a trisubstituted, pyramidalized N (see SI for additional discussion).

Figure 4. Resonance structures of 3^{ox} and $3^{\text{ox-}}$, formulated as a Ni metalloradical or aminyl radical.

We subsequently prepared the corresponding Ni^{III} anilide, $(\text{SiP}_2\text{S})\text{Ni}^{\text{III}}(\text{NHPh})$ (6^{ox}) to obtain spectroscopic data on an amide derivative free of H-bonding. Complex 6^{ox} could be accessed by oxidation of the Ni^{II} anilide $[(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{NHPh})]\text{Li}$ (**6**), as well as H-atom abstraction from its Ni^{II} aniline precursor, $(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{NH}_2\text{Ph})$ (**7**), with 2,4,6-tri-*tert*-butylphenoxyl radical (see SI for full synthetic details). Both synthetic routes afforded identical CW EPR spectra, which support the structural assignment of 6^{ox} and indicate that there is not an H-bonding interaction between the resulting $\text{Ni}(\text{III})$ anilide and phenol when 6^{ox} is generated via H-atom abstraction.

The EPR spectrum of 6^{ox} is well-simulated as a rhombic signal ($g = [2.175, 2.070, 2.0125]$) with coupling to two ^{31}P nuclei ($A(^{31}\text{P}_\alpha) = \pm[255, 220, 160]$ MHz, $A(^{31}\text{P}_\beta) = \pm[175, 280, 290]$ MHz). Preparation of the ^{15}N - and ^2H -labeled analogues ($6^{\text{ox-}^{15}\text{N}}$, $6^{\text{ox-}^2\text{H}}$) by H-atom abstraction from $(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(^{15}\text{NH}_2\text{Ph})$ and $(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{ND}_2\text{Ph})$, respectively, results in similar CW EPR spectra as the natural abundance sample. Again, a combination of pulse EPR spectroscopies on 6^{ox} , $6^{\text{ox-}^{15}\text{N}}$, and $6^{\text{ox-}^2\text{H}}$ were utilized to determine hyperfine coupling to an isotopically sensitive nitrogen ($A(^{14}\text{N}) = \pm[-4.28, -31.37, -4.28]$ MHz and an isotopically sensitive hydrogen nucleus ($A(^1\text{H}) = \pm[21.5, 17, 6]$ MHz). Based on these values, spin density of $|\rho_{\text{H}}| \approx 0.01 e^-$ is estimated on the

N-H hydrogen, and $|\rho_{\text{N}2s}| \approx 0.007 e^-$ and $|\rho_{\text{N}2p}| \approx 0.16 e^-$ are estimated on the anilide N.

The gas-phase DFT-optimized structure of 6^{ox} (M06-L, def2tzvp [Ni] and def2svp [all other atoms]) bears a planar NPh fragment, and the spin density map exhibits significant spin delocalization into the phenyl π -system. These calculated results suggest that the spin-bearing N $2p$ orbital is in conjugation with the phenyl π -system, which likely contributes to the increased stability of 6^{ox} compared to 3^{ox} . Compared to the H-bonded $3^{\text{ox'}}$, 6^{ox} bears greater spin density on N, indicative of greater aminyl character. Relatedly, we posit that the absence of the H-bonding interaction in 3^{ox} yields enhanced aminyl character compared to $3^{\text{ox'}}$. This notion is consistent with 3^{ox} engaging in N-centered radical reactivity to form **2** and **4**, reacting as a “Ni- NH_2 ” aminyl species.²⁰ Gas-phase DFT calculations of 3^{ox} are consistent with such a depiction; a Mulliken spin density of $0.4 e^-$ is estimated on N, and $0.5 e^-$ on Ni (see SI).

Given that phenoxyl radicals have been used in AO reactions,^{3,21} we were pleased to find that treatment of the hydrazine adduct **4** with two equivalents of 2,4,6-tri-*tert*-butylphenoxyl radical generates two equivalents of the phenol and corresponding diazene complex, $[(\text{SiP}_2\text{S})\text{Ni}^{\text{II}}(\text{trans-N}_2\text{H}_2)]$ (**5**, $d_{\text{NN}} = 1.277(2) \text{ \AA}$, Fig. 2B). This diazene adduct is structurally unusual for a late first-row metal. To the best of our knowledge, there is only one example of a Ni complex featuring a coordinated N_2H_2 unit, bound side-on to a single Ni center.²² A related $\text{Cu}_2(\text{trans-N}_2\text{H}_2)$ species has also been described.²³ In the absence of an H-atom abstractor, the hydrazine complex **4** slowly undergoes disproportionation in THF at 25°C to yield **2** and **5**. Intermediate species have not been observed in this disproportionation reaction.

With the aim of regenerating the dinitrogen complex **1** with 2,4,6-tri-*tert*-butylphenoxyl radical, attempts to further oxidize **5** did not prove fruitful. However, treatment of **5** with excess NH_3 results in quantitative displacement of N_2H_2 by NH_3 at Ni, yielding **2**. Free N_2H_2 is unstable toward disproportionation to $\frac{1}{2} \text{N}_2$ and $\frac{1}{2} \text{N}_2\text{H}_4$,²⁴ and hence liberates NH_3 -derived N_2 in this system upon displacement from Ni (Scheme 2).

Scheme 2. Stepwise oxidation of NH_3 mediated by $(\text{SiP}_2\text{S})\text{Ni}$ species.

N_2H_2 displacement from **5** thus closes an overall Ni-mediated AO cycle and regenerates the ammonia adduct **2**. In this stoichiometric cycle, the conversion of 2 NH_3 to $\frac{1}{2} \text{N}_2$ and $\frac{1}{2} \text{N}_2\text{H}_4$ constitutes a net $4e^-/4\text{H}^+$ process; under potential turnover conditions, the N_2H_4 generated upon N_2H_2 disproportionation can in principle undergo further iterative oxidation via hydrazine-bridged **4** and diazene-bridged **5** to achieve the $6e^-/6\text{H}^+$ conversion of 2 NH_3 to N_2 . Ongoing studies are directed towards exploring this goal.

We have described the first Ni-mediated, homogeneous AO sequence, where the key N-N bond forming step is consistent

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with homocoupling between two $\text{Ni}^{\text{III}}\text{-NH}_2$ species featuring significant aminyl character to generate a hydrazine-bridged complex. Metal complexes that mediate ammonia oxidation reactions may traverse a broad oxidation state range during turnover (e.g. $\text{M}^n + \text{NH}_3 \rightarrow \text{M}^{n+3}\text{N} + 3 \text{H}^+$). It is thus notable that the AO cycle described herein is carried out between the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ oxidation states. This narrow redox range is attributable to the fact that the NN bond forming step can occur from an M-NH_2 species (as opposed to a higher valent intermediate featuring a metal-nitrogen multiple bond), and that the redox load for $\text{H}_2\text{N-NH}_2$ reductive elimination is distributed between two metal centers, an attractive strategy for facilitating such catalysis using Earth-abundant, late first-row metals.

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- (1) (a) R. Lan, S. Tao, *Front. Energy Res.* **2014**, *2*, 1-4. (b) R. F. Service, *Science*, **2018**, DOI: 10.1126/science.aau7489.
- (2) (a) L. Chmielarz, M. Jabłońska, *RSC Adv.* **2015**, *5*, 43408-43431. (b) K. Siddharth, Y. Chan, L. Wang, M. Shao, *Curr. Opin. Electrochem.* **2018**, *9*, 151-157.
- (3) Dunn, P. L.; Cook, B. J.; Johnson, S. I.; Appel, A. M.; Bullock, R. M. *J. Am. Chem. Soc.* **2020**, DOI: 10.1021/jacs.0c08269.
- (4) (a) F. Habibzadeh, S. L. Miller, T. W. Hamann, M. R. Smith III, *Proc. Natl. Acad. Sci.* **2019**, *116*, 2849-2853. (b) P. Bhattacharya, Z. M. Heiden, G. M. Chambers, S. I. Johnson, R. M. Bullock, M. T. Mock, *Angew. Chem. Int. Ed.* **2019**, *58*, 11618-11624. (c) K. Nakajima, H. Toda, K. Sakata, Y. Nishibayashi, *Nat. Chem.* **2019**, *11*, 702-709. (d) P. Dunn, S. I. Johnson, W. Kaminsky, R. M. Bullock, *J. Am. Chem. Soc.* **2020**, *142*, 3361-3365.
- (5) M. D. Zott, P. Garrido-Barros, J. C. Peters, *ACS Catal.* **2019**, *9*, 10101-10108.
- (6) (a) L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privavlov, A. Llobet, L. A. Sun, *Nat. Chem.* **2012**, *4*, 418-423. (b) J. L. Fillol, Z. Codolà, I. Garcia-Bosch, L. Gómez, J. J. Pla, M. Costas, *Nat. Chem.* **2011**, *3*, 807-813. (c) J. J. Concepcion, J. W. Jurss, J. L. Templeton, T. J. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 16462-16463.
- (7) (a) M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark, *Chem. Rev.* **2014**, *114*, 11863-12001. (b) J. D. Blakemore, R. H. Crabtree, G. W. Brudvig, *Chem. Rev.* **2015**, *23*, 12974-13005. (c) R. Matheu, P. Garrido-Barros, M. Gil-Sepulcre, M. Z. Ertem, X. Sala, C. Gimbert-Surinach, A. Llobet, *Nat. Rev. Chem.* **2019**, *3*, 331-341.
- (8) T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2004**, *126*, 6252-6254.
- (9) (a) N. P. Mankad, P. Müller, J. C. Peters, *J. Am. Chem. Soc.* **2010**, *132*, 4083-4085. (b) I. G. Powers, J. M. Andjaba, X. Luo, J. Mei, C. Uyeda, *J. Am. Chem. Soc.* **2018**, *140*, 4110-4118. (c) S.-M. Yiu, W. W. Y. Lam, C.-M. Ho, T.-C. Lau, *J. Am. Chem. Soc.* **2007**, *129*, 803-809.
- (10) G. M. Coia, P. S. White, T. J. Meyer, D. A. Wink, L. K. Keefer, W. M. Davis, *J. Am. Chem. Soc.* **1994**, *116*, 3649-3650.
- (11) Q.-Q. Su, K. Fan, X.-D. Huang, J. Xiang, S.-C. Cheng, C.-C. Ko, L.-M. Zheng, M. Kurmoo, T.-C. Lau, *Dalton Trans.* **2020**, *49*, 4084-4092.
- (12) J. P. Collman, J. E. Hutchison, M. S. Ennis, M. A. Lopez, R. Guillard, *J. Am. Chem. Soc.* **1992**, *114*, 8074-8080.
- (13) (a) J. B. Diccianni, C. Hu, T. Diao, *Angew. Chem. Int. Ed.* **2016**, *55*, 7534-7538. (b) M. D. Kosobokov, A. Sandleben, N. Vogt, A. Klein, D. A. Vicić, *Organometallics* **2018**, *37*, 521-525.
- (14) (a) M. C. Ryan, Y. J. Kim, J. B. Gerken, F. Wang, M. M. Aristov, J. R. Martinelli, S. S. Stahl, *Chem. Sci.* **2020**, *11*, 1170-1175. (b) A. J. Pearce, R. P. Harkins, B. R. Reiner, A. C. Wotal, R. J. Dunscomb, I. A. Tonks, J. Am. Chem. Soc. **2020**, *142*, 4390-4399. (c) F. Wang, J. B. Gerken, D. M. Bates, Y. J. Kim, S. S. Stahl, *J. Am. Chem. Soc.* **2020**, *142*, 12349-12356.
- (15) J. J. Warren, T. A. Tronic, J. M. Mayer, *Chem. Rev.* **2010**, *110*, 6961-7001.
- (16) N. X. Gu, P. H. Oyala, J. C. Peters, *J. Am. Chem. Soc.* **2018**, *140*, 6374-6382.
- (17) N. X. Gu, P. H. Oyala, J. C. Peters, *J. Am. Chem. Soc.* **2020**, *142*, 7827-7835.
- (18) For examples of terminal Ni-NH₂ species, see: (a) J. Cámpora, P. Palma, D. del Río, M. M. Conejo, E. Álvarez, *Organometallics* **2004**, *23*, 5653-5655. (b) D. Adhikari, S. Mossin, F. Basuli, B. R. Dible, M. Chipara, H. Fan, J. C. Huffman, K. Meyer, D. J. Mindiola, *Inorg. Chem.* **2008**, *47*, 10479-10490. (c) A. H. Mousa, J. Bendix, O. F. Wendt, *Organometallics* **2018**, *37*, 2581-2593.
- (19) K. Kohata, T. Fukuyama, K. Kuchitsu, *J. Phys. Chem.* **1982**, *86*, 602-606.
- (20) For examples of metal-bound, substituted aminyl radicals, see: (a) T. Büttner, J. Geier, G. Frison, J. Harmer, C. Calle, A. Schweiger, H. Schönberg, H. Grützmacher, *Science* **2005**, *307*, 235-238. (b) N. P. Mankad, W. E. Antholine, R. K. Szilagyi, J. C. Peters, *J. Am. Chem. Soc.* **2009**, *131*, 3878-3880. (c) D. Adhikari, S. Mossin, F. Basuli, J. C. Huffman, R. K. Szilagyi, K. Meyer, D. J. Mindiola, *J. Am. Chem. Soc.* **2008**, *130*, 3676-3682.
- (21) (a) P. Bhattacharya, Z. M. Heiden, E. S. Wiedner, S. Raugei, N. A. Piro, W. S. Kassel, R. M. Bullock, M. T. Mock, *J. Am. Chem. Soc.* **2017**, *139*, 2916-2919. (b) B. J. Cook, S. I. Johnson, G. M. Chambers, W. Kaminsky, R. M. Bullock, *Chem. Commun.* **2019**, *55*, 14058-14061.
- (22) C. Köthe, B. Braun, C. Herwig, C. Limberg, *Eur. J. Inorg. Chem.* **2014**, 5296-5303.
- (23) K. Fujisawa, H. Lehnert, Y. Ishikawa, K. Okamoto, *Angew. Chem. Int. Ed.* **2004**, *43*, 4944-4947.
- (24) D. M. Stanbury, *Inorg. Chem.* **1991**, *30*, 1293-1296.

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Entry for the Table of Contents

Ni_x(N_yH_z) complexes are synthesized and characterized as intermediates in the homogenous Ni-mediated ammonia oxidation cycle described herein. Data on the key N–N bond formation step are consistent with the homocoupling of a Ni^{III}–NH₂ species to yield a Ni^{II}–bound hydrazine adduct.