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Ammonia Activation, H_2 Evolution and Nitride Formation from a Molybdenum Complex with a Chemically and Redox Non-Innocent Ligand.

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Supporting Information Placeholder

ABSTRACT: Treatment of the bis(imino)pyridine molybdenum η^6-benzene complex $(^{iPr}PDI)Mo(\eta^6\text{-}C_6H_6)$ (^{iPr}PDI, 2,6-(2,6-$i$$Pr_2C_6H_3N{=}CMe)_2C_5H_3N$) with NH_3 resulted in coordination induced haptotropic rearrangement of the arene to form $(^{iPr}PDI)Mo(NH_3)_2(\eta^2\text{-}C_6H_6)$. Analogous η^2-ethylene and η^2-cyclohexene complexes were also synthesized and the latter crystallographically characterized. All three compounds undergo loss of the η^2-coordinated ligand followed by N-H bond activation, bis(imino)pyridine modification and H_2 loss. A dual ammonia activation approach has been discovered whereby reversible M-L cooperativity and coordination induced bond weakening likely contribute to dihydrogen formation. Significantly, the weakened N-H bonds in $(^{iPr}PDI)Mo(NH_3)_2(\eta^2\text{-}C_2H_4)$ enabled hydrogen atom abstraction and synthesis of a terminal nitride from coordinated ammonia, a key step in NH_3 oxidation.

The synthesis of ammonia from its elements, H_2 and N_2 and the reverse process, liberation of dihydrogen from NH_3, are key steps for developing NH_3 as a potential carbon-free fuel and hydrogen carrier.[1,2,3] While considerable effort has been devoted to the understanding and discovery of molecular catalysts for ammonia synthesis,[4] by comparison much less is known about H_2 formation following NH_3 activation. One challenge is overcoming the σ-donating ability of ammonia and its propensity to act as a supporting ligand in coordination chemistry. Organometallic and coordination compounds are known to promote N-H bond cleavage by oxidative addition,[5,6] deprotonation,[7] cooperative chemistry between the ligand and the metal[8] or reactions with multiple transition metals.[9] Main group compounds, specifically nucleophilic carbenes,[10a] frustrated Lewis pairs,[10b] diarylstannylenes,[10c] germylenes[10d] as well as constrained phosphorous(III)[10e,10f] and silicon(II) sites[10g] are also known to promote ammonia activation. In most of these cases, formation of H_2 is not observed following N-H bond cleavage. One notable exception is a report from Wolczanski and coworkers describing H_2 formation following oxidative addition of NH_3 and α-hydrogen abstraction from the resultant tantalum amidohydride.[6]

Molybdenum complexes bearing redox-active bis(imino)pyridine and terpyridine ligands have recently been shown to exhibit a rich ammonia activation chemistry, including H_2 formation. Addition of NH_3 to the bis(imino)pyridine molybdenum dinitrogen complex, $[\{(^{iPr}BPDI)Mo(N_2)\}_2(\mu_2,\eta^1,\eta^1\text{-}N_2)]$ ($^{iPr}BPDI$, 2,6-(2,6-$i$$Pr_2C_6H_3N{=}CPh)_2C_5H_3N$) resulted in sequential N-H bond activations ultimately forming bridging parent imido ligands (μ-NH) along with conversion of the one imines on the chelate to a terminal aryl imido.[11] Ammonia serves as a source of hydrogen during the modification of the bis(imino)pyridine ligand and is irreversible. In contrast, use of a more chemically inert terpyridine ligand, a non-classical molybdenum(I) ammine complex, $[(^{Ph}Tpy)(PPh_2Me)_2Mo(NH_3)][BArF^{24}]$ (^{Ph}Tpy, 4'-Ph-2,2',6',2"-terpyridine; $ArF^{24} = [C_6H_3\text{-}3,5\text{-}(CF_3)_2]_4$) was isolated and a remarkably low N-H bond dissociation free energy of 45.8 kcal/mol was measured.[12] This significant bond weakening ($NH_{3(g)}$ = 99.5 kcal/mol)[13] enables spontaneous H_2 evolution upon mild heating ($BDFE_{N\text{-}H} < \Delta G°(H\bullet) = 48.6$ kcal/mol).[13] Discovery of transition metal complexes that promote multiple potentially reversible N-H bond activation events remains a significant challenge in ammonia oxidation. Here we describe a family of bis(imino) pyridine molybdenum bis(ammine) η^2-benzene and alkene complexes that promote H_2 evolution from ammonia as well as reversible N-H bond activation that combines metal-ligand cooperativity and bond weakening by coordination. This strategy enabled synthesis of a terminal molybdenum nitride from NH_3 by a series of hydrogen atom abstraction events, key steps in ammonia oxidation.

The diamagnetic bis(imino)pyridine molybdenum benzene complex, $(^{iPr}PDI)Mo(\eta^6\text{-}C_6H_6)$ (**1-(η^6-C_6H_6)**; ^{iPr}PDI, 2,6-(2,6-$i$$Pr_2C_6H_3N{=}CMe)_2C_5H_3N$) was isolated in 88% yield by straightforward reduction of $(^{iPr}PDI)MoCl_3$ with 1% Na(Hg) in benzene solution. Benzene coordination was confirmed by observation of a singlet at 3.56 ppm in the benzene-d_6 ^1H NMR spectrum. There was no evidence for arene exchange even upon heating to 80 °C for days. The solid-state structure of **1-(η^6-C_6H_6)** was determined by X-ray diffraction and the bond distances of the bis(imino)pyridine chelate ($C_{imine}\text{-}N_{imine}$ = 1.332(1) and 1.344(1); $C_{ipso}\text{-}C_{imine}$ = 1.418(1) and 1.410(1) Å) are consistent with a closed shell dianionic chelate arising from strong π-backbonding, suggesting the Mo(II) oxidation state is most appropriate.[14]

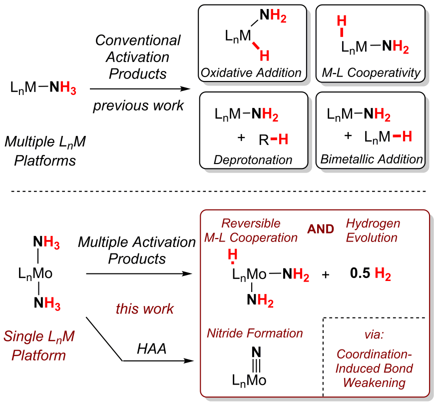

Figure 1. Comparison of selected ammonia activation methods highlighting the strategy reported in this work.

Addition of two equivalents of NH_3 gas to a thawing benzene solution of **1-(η⁶-C_6H_6)** resulted in formation of a C_s symmetric compound identified as $(^{iPr}PDI)Mo(NH_3)_2(\eta^2\text{-}C_6H_6)$ (**1-(NH_3)$_2$(η²-C_6H_6)**; Figure 2). Observation of three distinct resonances at 3.45, 5.22 and 5.53 ppm together with 2-D ^1H NMR experiments confirmed the unusual η^2 hapticity of the arene ring (see SI for details). Distinct NH_3 environments were observed at -1.31 and -1.91 ppm, consistent with a static η^2 benzene ligand, although exchange with free benzene was observed over the course of 90 minutes at 23 °C. While Harman and coworkers have reported examples of η^2-coordinated molybdenum complexes of naphthalene and other heterocycles,[15a] to our knowledge **1-(NH_3)$_2$what(η²-C_6H_6)** is the only monometallic example with benzene.[15b-f]

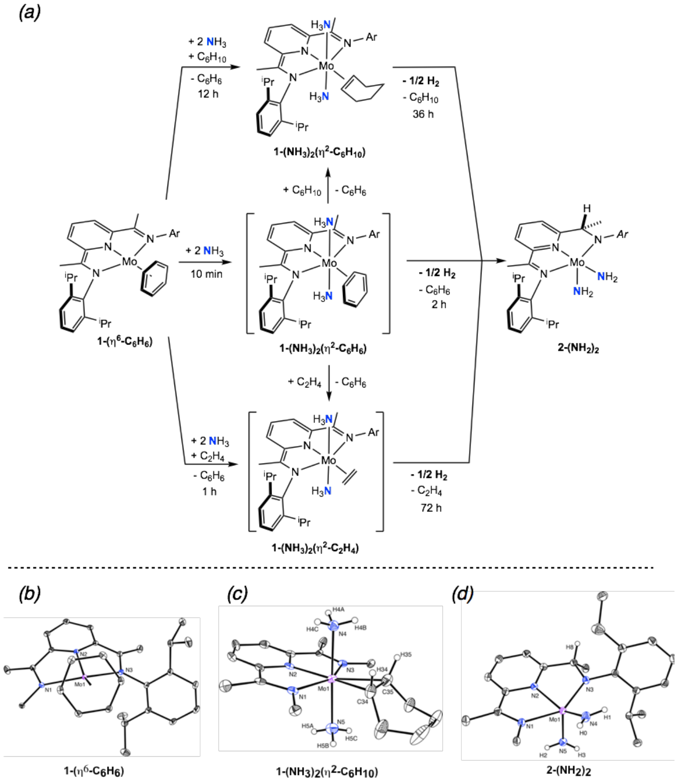

Figure 2. (a) Coordination, activation and hydrogen release from bis(imino)pyridine molybdenum compounds with η^2-benzene, cyclohexene, and ethylene ligands. Solid-state structures of (b) **1-(η⁶-C_6H_6)**, (c) **1-(NH_3)$_2$(η²-C_6H_{10})** and (d) **2-(NH_2)$_2$** at 30% probability ellipsoids. Most hydrogen atoms were omitted for clarity.

Because **1-(NH_3)$_2$(η²-C_6H_6)** proved too reactive for isolation in the solid state, related alkene complexes were synthesized. Addition of ethylene or cyclohexene to **1-(NH_3)$_2$(η²-C_6H_6)** resulted in the formation of C_{2v} and C_s symmetric products, respectively, corresponding to complexes of the type $(^{iPr}PDI)Mo(NH_3)_2(\eta^2$-alkene) (alkene = C_2H_4, **1-(NH_3)$_2$(η²-C_2H_4)**; C_6H_{10}, **1-(NH_3)$_2$(η²-C_6H_{10})**). These compounds were also synthesized in a single step from sequential addition of ammonia and the appropriate alkene to **1-(η⁶-C_6H_6)**. The single-crystal X-ray structure of the cyclohexene derivative confirms formation of a six-coordinate molybdenum complex with *trans*-ammine ligands. The bond distances of the bis(imino)pyridine are similar to those in **1-(η⁶-C_6H_6)** and support a Mo(II) oxidation state assignment.

Each $(^{iPr}PDI)Mo(NH_3)_2(\eta^2$- alkene) complex was kinetically unstable and underwent conversion to the same paramagnetic, NMR-silent violet product at 23 °C (Figure 2a). The time for conversion was dependent on the identity and amount of alkene; complete conversion was observed with the benzene compound in benzene-d_6 over the course of 2 hours at 23 °C. With the corresponding ethylene compound, consumption of the diamagnetic starting material required 72 hours; for cyclohexene derivative, 36 hours was needed. Addition of 10 equiv of ethylene to **1-(NH_3)$_2$(η²-C_2H_4)** extended the half life of the complex to 240 hours, supporting a pathway where alkene dissociation is necessary to facilitate ammonia activation. X-ray diffraction established the identity of the product of each reaction as $(^{iPr}PIA)Mo(NH_2)_2$ (**2-(NH_2)$_2$**; ^{iPr}PIA = 2-(2,6-$iPr_2C_6H_3N$=CMe), 6-(2,6-$iPr_2C_6H_3N$-CHMe)C_5H_3N), arising from NH_3 activation and hydrogen transfer to the imine carbon of the ^{iPr}PDI chelate. Formation of two amide ligands leaves one hydrogen atom unaccounted in the final molybdenum product. Collecting the volatiles of the reaction by Toepler pump and combustion in a CuO burn tube confirmed formation of 0.5 equiv of hydrogen gas (93%), demonstrating H_2 evolution accompanies ammonia activation en route to **2-(NH_2)$_2$**.

Chelate modification in **2-(NH_2)$_2$** was confirmed by X-ray diffraction (Figure 2d), where the newly introduced hydrogen atom on the modified ^{iPr}PIA backbone as well as those residing on the amide ligands were located and freely refined. A solid-state magnetic moment of 1.89(2) μ_B was measured at 23 °C, consistent with an S = ½ ground state. Accordingly, the X-band EPR spectrum of **2-(NH_2)$_2$** exhibits an isotropic signal (g_{iso} = 1.97) with hyperfine coupling to both ^{95}Mo (I =5/2, 15.9%) and ^{97}Mo (I = 5/2, 9.6%) spin active nuceli ($A_{iso}(^{95/97}Mo)$ = 139 MHz, Figure 3b), suggesting that the singly-occupied molecular orbital of **2-(NH_2)$_2$** is principally molybdenum based.

Protonation studies were conducted with **2-(NH_2)$_2$** to establish the fidelity of the new formed C-H bond in the ^{iPr}PIA ligand. Addition of one equivalent of lutidinium triflate ([LutH]OTf) resulted in isolation of a red paramagnetic powder identified as $(^{iPr}PDI)Mo(NH_3)_2OTf$ (**1-(NH_3)$_2$(OTf)**). Apart from lutidine, no other organic or gaseous byproducts were detected during the course of the reaction. One-electron oxidation of in situ prepared **1-(NH_3)$_2$(η²-C_6H_6)** with $[(\eta^5\text{-}C_5H_5)_2Fe][OTf]$ provided an alternative route to **1-(NH_3)$_2$(OTf)**. The metrical parameters obtained from X-ray diffraction, magnetic and EPR spectroscopic data support the description of **1-(NH_3)$_2$(OTf)** as a low-spin Mo(III) complex. Remarkably, this protonation reaction resulted in reconstitution of both ammonia ligands in addition to regenerating of the bis(imino) pyridine chelate, where [LutH]OTf and the ^{iPr}PIA backbone C-H bond served as the hydrogen sources. While the initial site of protonation and the sequence of N-H bond forming and C-H bond cleavage steps remain unknown, the observed reactivity is a rare reversal of the previously demonstrated chelate modification arising from M-L ligand cooperativity in ammonia N-H bond activation.[11]

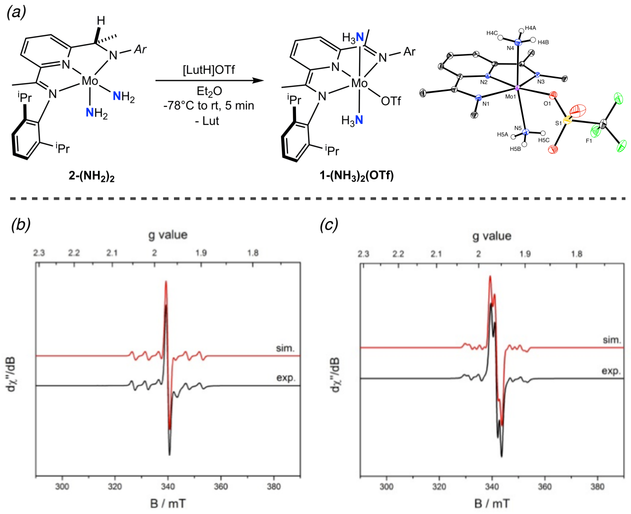

Figure 3. (a) Reconstitution of the bis(imino)pyridine and ammonia ligands by protonation and solid-state structure of **1-(NH$_3$)$_2$OTf** at 30% probability ellipsoids. Most hydrogen atoms were omitted for clarity. X-band EPR spectra of (b) **2-(NH$_2$)$_2$** and (c) **1-(NH$_3$)$_2$OTf** recorded at 23 ^{o}C in toluene solution (see SI for fitting parameters).

The observed reversible chelate modification chemistry and hydrogen evolution from the bis(imino) pyridine molybdenum ammine complexes prompted computation of the thermodynamics of N-H bond activation during the conversion of **1-(NH$_3$)$_2$(η^2-C$_2$H$_4$)** to **2-(NH$_2$)$_2$**. With **1-(NH$_3$)$_2$(η^2-C$_2$H$_4$)**, an ammine N-H BDFE of 51.0 (58.8) kcal/mol was computed using density functional theory (DFT), where the two values presented were obtained from generation of low- and high-spin products following H-atom abstraction. Notably, these values weaken substantially to a range between 22.5 and 49.4 kcal/mol upon dissociation of the olefin (Figure S14), suggesting that the putative 5-coordinate intermediate, **1-(NH$_3$)$_2$** is a non-classical ammine complex,[12] being thermodynamically unstable towards H$_2$ loss, in this case also subject to PDI ligand backbone modification. This is corroborated by the finding that the product complex **2-(NH$_2$)$_2$** features considerably stronger DFT-computed amide N-H bonds (58.3 (66.4) kcal/mol (basal); 66.4 (60.3) kcal/mol (apical)) as well as a PIA ligand backbone C-H bond with a BDFE of 67.4 (60.2) kcal/mol (Figure S14). These computational results suggest that the phenomenon of bond weakening by coordination precedes N-H bond activation, setting the thermodynamics in place to favor of the unique reactivity observed and is consistent with the experimentally observed inhibition of ammonia activation by excess arene or alkene.

The computationally predicted weak N-H bonds in **1-(NH$_3$)$_2$(η^2-C$_2$H$_4$)** suggested that the synthesis of molybdenum nitrides from coordinated ammonia by hydrogen atom abstraction (HAA) may be plausible. Such a sequence is key for oxidation of ammonia but by and large has remained elusive experimentally. Recently Mock and coworkers reported abstraction of all three H-atoms in coordinated ammonia in a cyclopentadienyl molybdenum compound by treatment with 2,4,6-tri-*tert*-butylphenoxyl radical (*t*Bu$_3$ArO•).[16] A molybdenum alkylimido product was isolated from this sequence rather than the terminal nitride. Nitrogen-carbon bond formation occurs with the phenoxy radical reagent at some point during the HAA sequence; the terminal nitride was ultimately synthesized by subsequent reduction with KC$_8$. Direct synthesis of a terminal metal-nitride from coordinated ammonia remains elusive by HAA and was targeted with **1-(NH$_3$)$_2$(η^2-C$_2$H$_4$)**.[8e,17] The dimeric chromium complex, [(η^5-C$_5$Me$_5$)Cr(CO)$_3$]$_2$, was chosen initially for HAA because the bond strength of the resulting metal-hydride product (BDFE$_{\text{Cr-H}}$ = 62 kcal/mol) should provide sufficient thermodynamic driving force for HAA.[18] However, upon treatment of in situ prepared **1-(NH$_3$)$_2$(η^2-C$_2$H$_4$)** with one equiv of [(η^5-C$_5$H$_5$)Cr(CO)$_3$], a complex mixture of products was obtained, likely arising from undesired participation of the carbonyl ligands of the chromium dimer or hydride product.[19] By contrast, addition of three equiv of *t*Bu$_3$ArO• to a benzene solution of **1-(NH$_3$)$_2$(η^2-C$_2$H$_4$)** resulted in rapid formation of *t*Bu$_3$ArOH (BDFE$_{\text{O-H}}$ = 77 kcal/mol)[20] as well as a red-orange, paramagnetic product identified as the terminal molybdenum nitride, ($^{i\text{Pr}}$PDI)Mo(N)(η^2-C$_2$H$_4$) (**1-(N)(η^2-C$_2$H$_4$)**) isolated in 61% yield after recrystallization (Figure 4a). This result demonstrates that each N-H BDFE in the sequence of HAA events during the course of the reaction is sufficiently weak (<77 kcal/mol) for abstraction to take place using 2,4,6-tri-*tert*-butylphenoxyl radical.

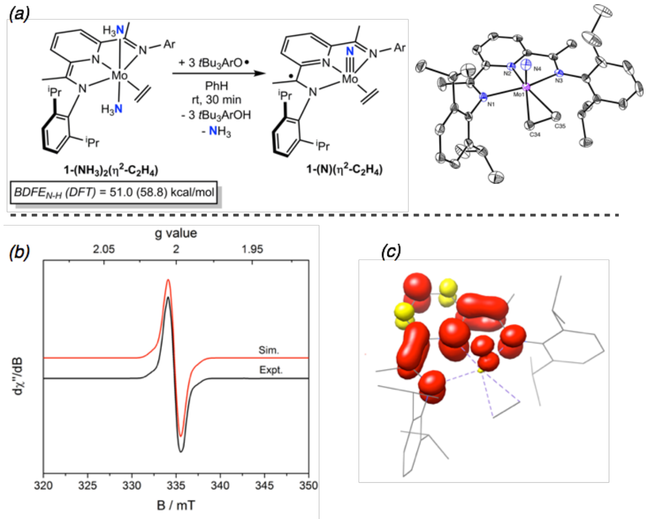

Figure 4. (a) Nitride formation from coordinated ammonia and solid-state structure of **1-(N)(η^2-C$_2$H$_4$)** at 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. (b) X-band EPR spectrum of **1-(N)(η^2-C$_2$H$_4$)** recorded at 23 ^{o}C in toluene solution (see *SI* for fitting parameters). (c) Spin density plot for **1-(N)(η^2-C$_2$H$_4$)** obtained from a Mulliken population analysis in a full-molecule gas phase DFT calculation at the B3LYP level of theory.

The solid-state structure of **1-(N)(η^2-C$_2$H$_4$)** was determined by X-ray diffraction and confirms ethylene coordination (d(C=C) = 1.410(4) Å) as well as formation of the terminal nitride ligand (d(Mo≡N) = 1.653(2) Å). The Mo≡N stretch was located at 1036 cm^{-1} in the solid-state infrared spectrum (KBr pellet) and shifts to 1004 cm^{-1} upon isotopic labeling with ^{15}N. These values are comparable to those reported by Cummins for Mo[N(*t*Bu)*Ar*]$_3$ (*Ar* = 3,5-C$_6$H$_3$Me$_2$) (ν(Mo≡N = 1042 cm^{-1}; Mo≡^{15}N = 1014 cm^{-1}).[21] The distortions to the bond distances of the bis(imino)pyridine support one electron reduction to the radical anionic form of the ligand.[22] Both magnetic measurements and the X-band EPR spectrum recorded at 296 K established an S = ½ ground state. The observed g_{iso} of 2.00 with a relatively small A($^{95/97}$Mo) value of 21 MHz supports a ligand- rather than metal-based SOMO (Figure 4b). The DFT computed spin density (Figure 4c) also supports this electronic structure depiction of low-spin Mo(IV) with a principally bis(imino)pyridine-based SOMO arising from one electron reduction. These results highlight the versatility of the bis(imino)pyridine molybdenum platform to accommodate both neutral NH$_3$ and terminal nitride coordination along with electronic adjustments of the redox-active chelate. Observation of the ligand-centered radical in **1-(N)(η^2-C$_2$H$_4$)** is also unusual as most second and third row transition metal complexes of bis(imino)pyridine ligands adopted a closed-shell two-electron reduced form.[23]

In summary, molybdenum ammine complexes have been synthesized with both a chemically- and redox-active bis(imino)pyridine ligand that promotes the reversible N-H activation of NH_3 upon alkene dissociation Coordination induced bond weakening of the ammine ligands was observed, that in combination with ligand cooperativity, enables H_2 loss and provides a coordination environment that supports both ammonia and nitride ligands. Efforts are now directed at nitride coupling and N_2 evolution[24] to complete the ammonia oxidation sequence.

ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization data, NMR spectra, and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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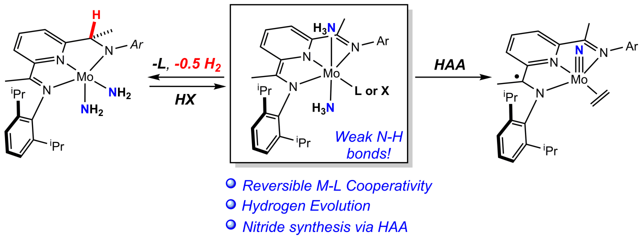
TOC Graphic


H
N
Ar
Mo
N
N
^{i}Pr
^{i}Pr
NH$_2$
NH$_2$
-L, -0.5 H$_2$
HX
H$_3$N
Ar
N
Mo
N
N
L or X
H$_3$N
^{i}Pr
^{i}Pr
Weak N-H bonds!
HAA
N
N
Ar
Mo
N
N
^{i}Pr
^{i}Pr
Reversible M-L Cooperativity
Hydrogen Evolution
Nitride synthesis via HAA