



AFRL-OSR-VA-TR-2014-0354

Synthesis of Fuels and Value-Added Nitrogen-Containing

**PAUL Chirik
TRUSTEES OF PRINCETON UNIVERSITY**

**11/24/2014
Final Report**

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTE
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE	3. DATES COVERED (From - To)		
4. TITLE AND SUBTITLE			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION / AVAILABILITY STATEMENT					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)

Synthesis of Fuels and Value-Added Nitrogen-Containing Compounds from N₂

Paul J. Chirik, Princeton University

Final Performance Report

Award Number: FA9550-11-1-0252

Personnel: Paul J. Chirik (Principal Investigator)
Dr. Carsten Milsmann (Postdoctoral Fellow)
Dr. Zöe Turner (Postdoctoral Fellow)
Grant Margulieux (Graduate Student)

Executive Summary. Our first support from the AFOSR enabled investigations for our research group to explore new paradigms for the interconversion of ammonia and hydrazine with its elements, N₂ and H₂. If successful, such research would be transformative as these important fuels and energy storage media could be synthesized under batch type conditions compatible with sources of renewable hydrogen. Thus, our efforts would be significant in reducing the carbon footprint associated with the synthesis of many nitrogen-based propellants and fuels. Key to our program has been the recognition of the role of hydrogen atom transfer (HAT) as a new method for making and breaking N-H bonds and its influence on the reversible cleavage of strong N-N bonds. Our AFOSR funded program has also definitely established that redox-active ligands – those that can undergo reversible one electron transfer events with a transition metal – have a transformative impact on the thermochemistry associated with N-H bonds in important nitrogen-containing intermediates relevant to catalytic cycles for N₂ fixation. Earth abundant transition metals such as vanadium, titanium and molybdenum are at the core of our studies to be compatible with the economic and sustainability requirements of potential applications. Notably our findings have provided *new catalysis concepts* to be explored in developing and understanding the molecular dynamics of catalysis involving N₂, hydrazine and ammonia.

Summary of Major Findings from Air Force Research Office Support

- Exploration of hydrogen atom transfer (HAT) as a new concept for catalytic ammonia and hydrazine synthesis compatible with renewable (CO₂-free) hydrogen.
- Demonstration of the unique role of redox-active ligands for increasing the thermodynamic favorability of N-H bond formation from renewable H₂.
- Development of theoretical methods for accurate computation of N-H bond dissociation free energies.
- Observation of unprecedented NH₃ oxidation in a redox- and chemically-active molybdenum complex providing molecular insight into H₂ storage and fuel cell applications.
- Development of new transition metal platforms, prepared from earth abundant transition metals that promote both N-N bond cleavage and reversible N-H assembly.

I. Introduction and Project Goals. The Haber-Bosch ammonia synthesis is one of the great technological achievements of the 20th century, having revolutionized agriculture and hence the world food economy. Because this chemistry only operates efficiently as a continuous process with a constant stream of ultrapure hydrogen, it is inherently incompatible with the conditions used to generate hydrogen from renewable sources. Hydrogen storage is one possible method to circumvent this limitation, although the scale required would demand major technological advances. A more attractive proposition is to discover metal catalysts that promote the hydrogenation of N₂ to ammonia at low hydrogen pressure under intermittent, batch-type conditions. Unfortunately, no practical catalysts are known for such a transformation.

Ammonia is also an attractive fuel and energy storage medium. Energy density is an important criterion in the evaluation of any potential fuel. When combined with ease of distribution, liquid fuels are obvious candidates. While the energy density by mass of H₂ is unrivaled, it has poor energy density by volume and as a result practical applications require high pressures. Current hydrogen transport technology requires steel tanks at 200 bar pressure with an energy density of 2.2 MJ/L. For an equivalent energy content H₂ at 200 bar requires 16 times the volume of gasoline or 6 times the volume of liquid ammonia. For the large volumes required in an infrastructure relying on carbon neutral, renewable energy, hydrogen liquefaction would be required. This process currently consumes ~35% of hydrogen's energy content and transporting H₂ via pipeline requires thicker pipe made of higher-grade steel to minimize embrittlement.¹ These problems have been the primary drivers for seeking alternative means of storing H₂. Ammonia has received consideration because its energy density is comparable to methanol, and in contrast to CO₂, N₂ is the most abundant gas in the Earth's atmosphere making it an ideal feedstock for energy storage.² Ammonia's history as a fuel has included powering buses in Belgium during World War II and propelling the X-15 aircraft to set speed and altitude records. NH₃ is also distributed by pipeline throughout the U.S. and has an energy carrying capacity approximately twice that of H₂ and 1.5 times that of natural gas, making it an attractive fuel.³

Compared to ammonia synthesis, NH₃ oxidation has received much less attention, and inspiration from Nature is limited as NH₃ oxidations, including those carried out under anaerobic conditions, either generate or require nitrogen oxides in their reactions.⁴ Ammonia oxidation is analogous to H₂O oxidation with the exception that the reaction occurs at a much lower potential. The conversion of NH₃ to N₂ and H₂ has a minimum barrier of 8.2 kcal/mol. With no overpotential, ~ 10% of the energy content of the H₂ produced would be required to surmount this barrier, rendering generation of H₂ and N₂ from NH₃ an attractive process. However, NH₃ has a much lower autoionization constant than H₂O (10⁻³³ vs. 10⁻¹⁴), which creates a significant overpotential for its electrolysis under neutral conditions. Consequently, electrolysis has typically been carried out in alkaline media, where reasonable catalytic currents have been obtained at modest overpotentials.⁵ Unfortunately, precious metal catalysts are required, and costs associated with implementation on the scale required to meet energy needs may be prohibitive. It is desirable to use earth abundant catalysts to facilitate N-N bond formation but most earth abundant metals form metal oxides in alkaline media. Thus, new approaches are required for carrying out NH₃ oxidations with earth abundant metal catalysts. This fundamental scientific challenge, along with carbon neutral ammonia synthesis, has been the core of our AFOSR funded program. Specifically, we aim to develop *new catalyst concepts* relevant to ammonia synthesis and oxidation.

II. Results from Prior Funding Period. Our primary effort during the past funding period was on developing fundamental transformations relevant to ammonia synthesis and oxidation using earth abundant metals. Vanadium and molybdenum were of particular interest due to their terrestrial abundance and well-established role in both biological and transition metal catalyzed nitrogen fixation. The independent reports by Schrock⁶ and Nishibayashi⁷ of catalytic ammonia synthesis with well-defined molybdenum coordination complexes as pre-catalysts inspired our hypothesis (Figure 1). We note that catalytic N₂ reduction was only achieved when lutidinium salts were combined with outer

sphere reductants such as $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$. In the Schrock system, successive proton and electron transfers have been proposed. Both the high proton affinity of 5.12 eV (comparable to methane) of N_2 and its negative electron affinity make addition of a single proton or electron highly unfavorable and reduction through a free one electron reduced species unlikely. A more kinetically and thermodynamically more feasible pathway involves initial reduction of the acid by the outer sphere electron source forming lutinyl radicals with an N-H bond dissociation free energy of 37 kcal/mol. Generation of a compound with such a weak N-H bond is well poised to undergo hydrogen atom transfer to coordinated dinitrogen to initiate the catalytic reduction sequence. *One primary goal of our AFOSR funded program was to demonstrate hydrogen atom transfer as a new pathway for N-H bond formation.*

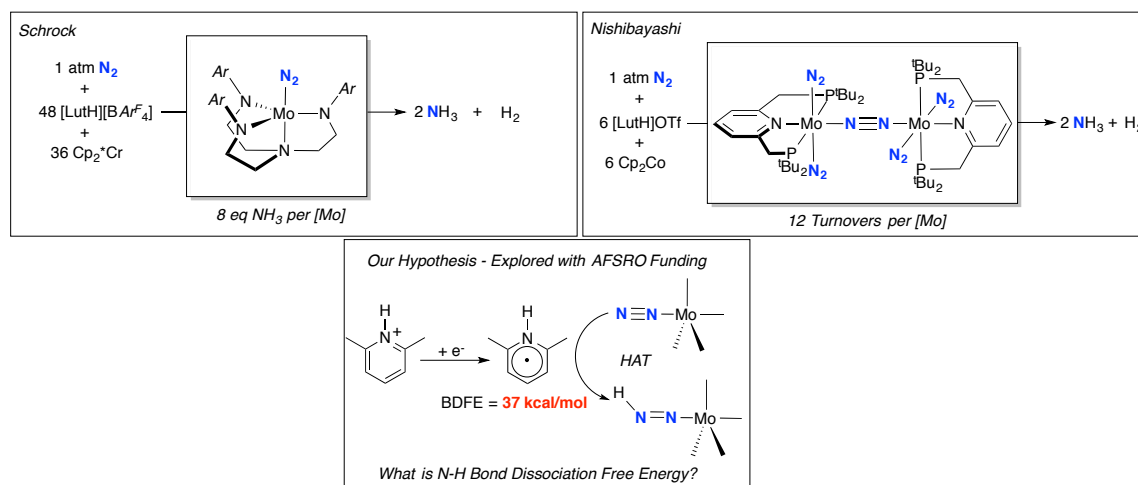


Figure 1. Molecular molybdenum catalysts for ammonia synthesis and the possibility of hydrogen atom transfer as the mechanism for N-H bond formation.

The recognition that HAT pathways are potentially operative in N-H bond formation involving coordinated N_2 is transformative in developing new catalytic methods for N_2 reduction and a myriad of applications are possible. Concerted pathways where protons and electrons are exchanged in a single elementary step have the advantage of a shared transition state that allows a favorable energetic driving force associated with one N-H bond-forming step to compensate for unfavorable energetics in others without requiring an intermediate. This potentially minimizes deleterious side reactions such as unproductive N_2 dissociation. An idealized catalytic cycle for applying this new approach to the synthesis of ammonia or more uniquely, hydrazine is illustrated in Figure 2. We envision using an appropriate metal reagent as co-catalyst to promote HAT to coordinated N_2 (and related intermediates) on a different metal center and that dihydrogen could be used to regenerate the co-catalyst and ultimately serve as the stoichiometric source of both protons and electrons. We are also encouraged by the precedent provided by Halpern for the catalytic reduction of anthracene to dihydroanthracene by hydrogen atom transfer using cobalt hydrides⁸ and Norton's well-documented reduction of both olefins and alkynes using metal hydride reagents operating by a similar mechanistic pathway.^{9,10}

Coupling N-N bond cleavage to N-H bond formation and ultimately ammonia and hydrazine synthesis via HAT is attractive but poses a fundamental challenge in coordination chemistry. A fundamental knowledge of the bond dissociation free energies (BDFEs) of various nitrogen ligands (M-N=NH, M-N-NH₂, M=NH, M-NH₂, etc) en route to N_2H_4 or NH_3 is necessary to determine the thermodynamic feasibility of such a cycle as a function metal, oxidation state and identity of the

supporting ligands. In addition, the bonding properties associated with metal-nitrogen bonds seem to be at odds with the thermodynamics for catalysis. Specifically, late metal imides are known to form strong N-H bonds via HAT,¹¹ a concept applied to important catalytic reactions such as the amination of unactivated C-H bonds,¹² but often lack the reduction potential to induce cleavage of strong N-N multiple bonds. On the other hand, early transition metal complexes are sufficiently reducing to promote N₂ cleavage¹³ yet form strong metal-nitrogen bonds that are often inert to further functionalization chemistry.^{14, 15} Gaining a thorough understanding of the thermodynamic parameters associated with N-H bond formation via HAT, particularly in early transition metal complexes known to promote N-N cleavage, is therefore essential for rational design of soluble metal complexes for the synthesis of value added nitrogen-containing compounds from N₂.

One strategy to overcome this limitation is to engage the supporting ligand in redox chemistry. Our group has pioneered the application of “redox-active ligands” – those that engage in reversible one electron chemistry with the metal – to the activation of strong bonds by earth abundant transition metals.¹⁶ The electronic flexibility imparted by the supporting ligand enables, similar to cofactors in enzymatic catalysis, lower barriers for key bond cleavage and may perturb N-H bond strengths to facilitate N-N bond cleavage and N-H bond formation from the same metal platform.

A. Vanadium Chemistry. Early in our AFOSR funded program we demonstrated the feasibility of this approach with respect to N-N bond cleavage. The bis(imino)pyridine vanadium dinitrogen complex, [(ⁱPrBPDl)V(THF)]₂(μ₂-N₂) was synthesized and determination of its electronic structure by spectroscopy, computational and magnetic studies established a vanadium(III) compound with a bis(imino)pyridine dianion and a bridging [N₂]²⁻ fragment. Notably, addition of organic diazenes, such as azobenzene or ^tBuN=N^tBu to [(ⁱPrBPDl)V(THF)]₂(μ₂-N₂) resulted in rapid *four electron* N=N bond cleavage to furnish the corresponding vanadium bis(imido) complexes (Figure 3). It is important to note that the cleavage of this strong bond occurs at ambient temperature and almost immediately upon mixing. Analysis of the resulting (ⁱPrBPDl)V(NR)₂ compounds by solid state magnetometry, DFT calculations and EPR spectroscopy revealed principally ligand centered radicals, demonstrating a vanadium(V) product with a bis(imino)pyridine radical anion as the SOMO. Thus the overall four electron reductive cleavage of the N=N bond proceeds via cooperative redox events between the supporting ligands and the vanadium centers thereby providing the first experimental support for our hypothesis. An initial account of this work was communicated to *Angew. Chem. Int. Ed.*

The bis(imino)pyridine vanadium bis(imido) compounds have proven an effective platform for subsequent studies to establish the feasibility of HAT methods for N-H bond formation and to determine the associated BDFEs. As shown in Figure 4, protonation

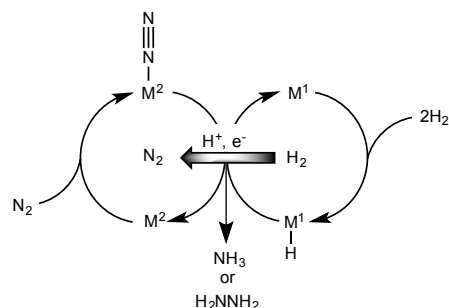
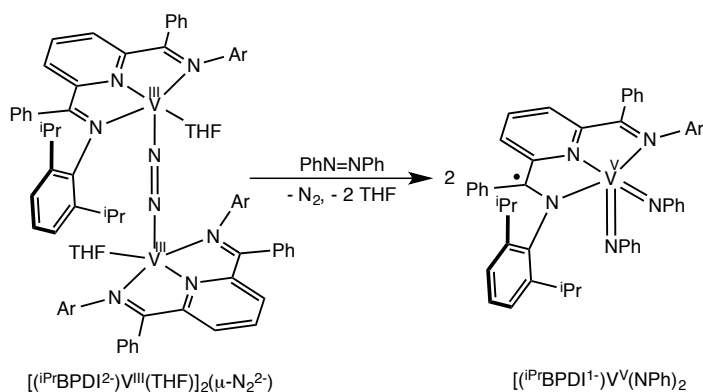


Figure 2. Application of hydrogen atom transfer (HAT) to the catalytic synthesis of ammonia or hydrazine compatible with renewable (CO₂-free) hydrogen.



Redox occurs cooperatively between the metal and the ligand.

Figure 3. Four-electron cleavage of RN=NR compounds highlighting metal-ligand cooperativity.

experiments coupled with electrochemical measurements established both the requisite pK_a and potentials to determine the BDFE. The experimental value of 65 kcal/mol is in excellent agreement with the DFT computed assessment of 69 kcal/mol. These results are transformative in establishing the role of redox-active ligands in assembling N-H bonds and demonstrate formation from H_2 and metal co-catalysis is thermodynamically feasible. Vanadium imide complexes have been known for decades are often used as spectator ligands due to their resistance to participate in reaction chemistry. The ability to reversibly assemble N-H bonds from protons and electrons or hydrogen atoms via weak H-atom donors such as TEMPO, provides definitive experimental proof of the enabling role of metal-ligand cooperativity. Aspects of this work were recently published as an article in the *Journal of the American Chemical Society*.

More detailed investigations into constituent steps in the proton-coupled electron transfer sequence highlight the role of the redox-active bis(imino)pyridine ligand. As shown in Figure 5, protonation of the vanadium bis(imido) generated the expected cationic imido-amido compound. Notably the ligand-based SOMO is the starting vanadium compound transforms into a metal-based radical upon formation of the N-H bond. This is critical in the H-atom transfer sequence as the neutral ligand is reduced at a lower thermodynamic potential than if the redox events were purely metal based.

The vanadium dinitrogen complex, $[(iPr)BPDI)V(THF)]_2(\mu_2-N_2)$ also promotes the two electron oxidative cleave of N-N bonds in various hydrazines to form the corresponding vanadium bis(amido) complexes. Spectroscopic, structural and computational studies support an assignment as a vanadium(III) complexes with chelate radical anions. As shown in Figure 6, mechanistic studies established the importance of hydrogen atom transfer chemistry in this process as interconversion of vanadium bis(amido), bis(imido) and mixed amido-imido complexes was accomplished via these pathways. Crossover experiments established exchange of vanadium amido ligands occurs only upon the interaction of the metal complexes with free hydrazines and that no exchange of imido ligands was possible. These results support initial hydrogen atom transfer from the amido ligand to hydrazine with N-N bond cleavage – demonstrating how HAT process can enable the cleavage of N-N bonds. DFT calculations were used to estimate the free energy for the addition of a single hydrogen atom to 1,2-diphenylhydrazine with concomitant N-N bond cleavage. A value of -67.2 kcal/mol was obtained and if an N-H bond strength of 69 kcal/mol is assumed in $(iPr)BPDI)V(NPh)(HNPh)$, HAT should be accessible under thermal conditions. This is

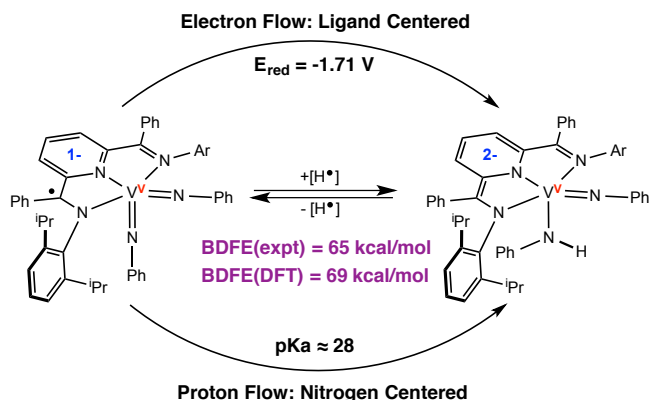


Figure 4. N-H bond formation via HAT with van bis(imido) chemistry highlighting the enabling role redox-active ligands.

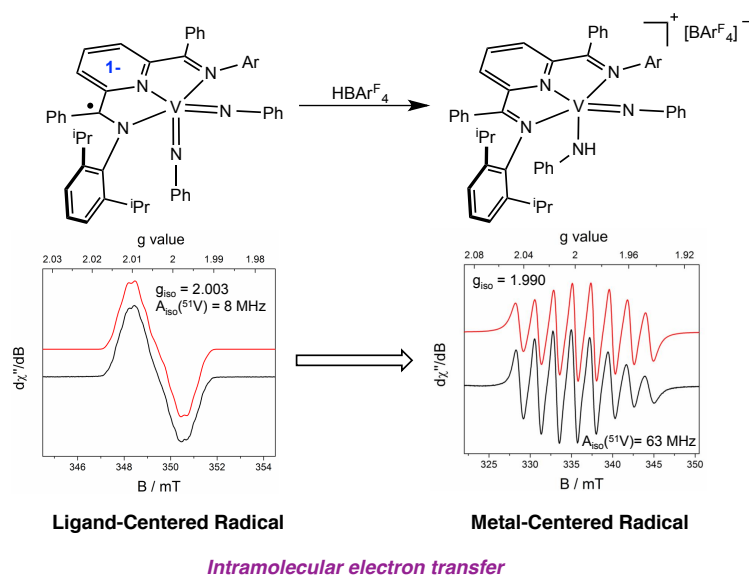


Figure 5. Imide protonation highlighting cooperative metal-electron transfer.

consistent with the observation that dihydroanthracene with a C-H BDFE of 76 kcal/mol is competent for the reduction of azobenzene at high ($T > 250\text{ }^{\circ}\text{C}$) temperatures.¹⁷ Following initial HAT, the anilide radical can abstract a hydrogen atom from free hydrazine for generate a second equivalent of aniline. Alternatively, the anilide radical is capable of abstracting a hydrogen atom from a second equivalent of the vanadium complex to complete the catalytic cycle. Notably, free aniline could be liberated from the metal coordination sphere, a key demonstration of an essential step in a catalytic cycle for either nitrogen fixation or ammonia oxidation.

Our studies with vanadium highlight the electronic flexibility of the bis(imino)pyridine framework and how its readily accessible redox states enable the metal to finely adjust to the changing environment and alter homolytic N-H BDFEs. Importantly, trends opposite those expected in classical Werner-type compounds were observed, where lower oxidation states and hence higher d -counts result in strong N-H bonds due to diminished N-H π -bonding in the product. The redox active ligand allows the vanadium to maintain a high oxidation state and hence V-N π -bonding upon hydrogen atom abstraction, inverting the expected N-H BDFEs. Notably, AFOSR support enabled the development of a new paradigm for developing synthetic and ideally catalytic schemes for the conversion of ammonia and hydrazine with its constituent elements.

A. Molybdenum. To provide calibration with classical complexes containing dinitrogen ligands, molybdenum complexes with traditional phosphine ligands were prepared and studies conducted to determine the N-H bond dissociation free energies. As shown in Figure 7, the protonation of the previously reported¹⁸ cyclohexyl-substituted, N_2 -derived diazenide was studied and the pK_a determined as 10.5 by titration with various acids. This measurement, coupled with determination of the redox potential of the diazenide cation, resulted in the first experimentally determined BDFE in a metal diazenide of this type. The value of 32 kcal/mol was corroborated with DFT (computed value = 33 kcal/mol). Clearly this value is too weak to accomplish N-H bond formation via HAT and provides an important benchmark and rationale for the exploration of redox-active ligands in a system of this type.

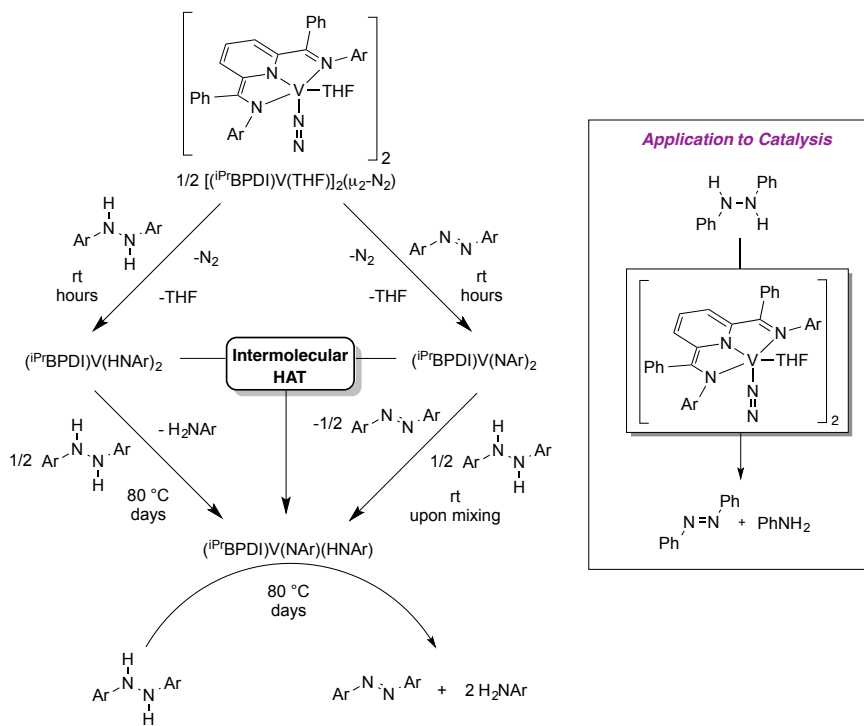
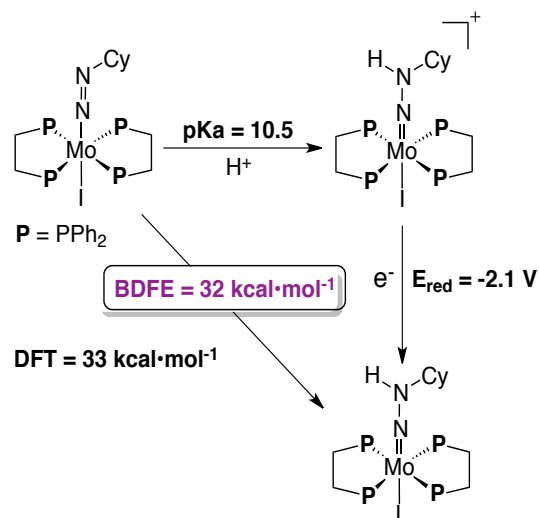


Figure 6. Mechanism and role of hydrogen atom transfer in hydrazine oxidative addition promoted by $[(i\text{PrBPDI})\text{V}(\text{THF})]_2(\mu_2\text{-N}_2)$ and application to catalysis.

The impact of redox-active ligands on the thermochemistry of N-H bond formation has been clearly established by DFT calculations on the molybdenum compounds shown in Figure 8. Replacement of one of the chelating bis(phosphines) with an electronically responsive α -diimine ligand has a dramatic impact on the resulting N-H BDFE in the molybdenum diazenide. A value of 53 kcal/mol was computed by DFT and is significant because it is within the range (52 kcal/mol) required for H₂ splitting with a metal co-catalyst. Also significant is that the computations indicate that the introduction of a second α -diimine offers little additional improvement to the N-H thermochemistry as the BDFE increases only to 54 kcal/mol. These observations are transformative for complex design and demonstrate that at least in the molybdenum chemistry, introduction of one redox-active ligand has a significant effect on N-H bond forming thermochemistry. Current studies are focused on preparing the compounds shown in Figure 8 and experimentally verifying the computational findings.

The demonstrated impact of redox active ligands in vanadium and phosphine molybdenum chemistry inspired preparation of bis(imino)pyridine molybdenum dinitrogen compounds. We are also interested in these compounds as related bis(phosphino)pyridine-ligated molybdenum derivatives are the most active molecular catalysts for the reduction of N₂ to ammonia. However, little is known about the identity of catalytic intermediates or the mechanism of turnover.¹⁹ The target bis(imino)pyridine molybdenum dinitrogen complex, [(ⁱPrBPDl)MoN₂]₂(μ_2 -N₂) was synthesized from sodium amalgam reduction of the corresponding molybdenum trichloride, (ⁱPrBPDl)MoCl₃. Examination of the metrical parameters of the pyridine diimine chelate established two-electron reduction of the ligand. The N-N distance of 1.246(4) Å indicates an [N₂]²⁻ ligand therefore establishing each metal center as Mo(III). Thus, the reduction of (ⁱPrBPDl⁰)Mo^{III}Cl₃ occurs over two ligands – the pyridine diimine and the dinitrogen while the oxidation state of the metal is maintained. This contrasts the [PNP]Mo-based dinitrogen complex of Nishibayashi as this involves an



Metal-centered redox imposes a large energetic barrier to HAT

Figure 7. Determination of N-H bond dissociation energies in molybdenum complexes bearing traditional redox innocent supporting ligands.

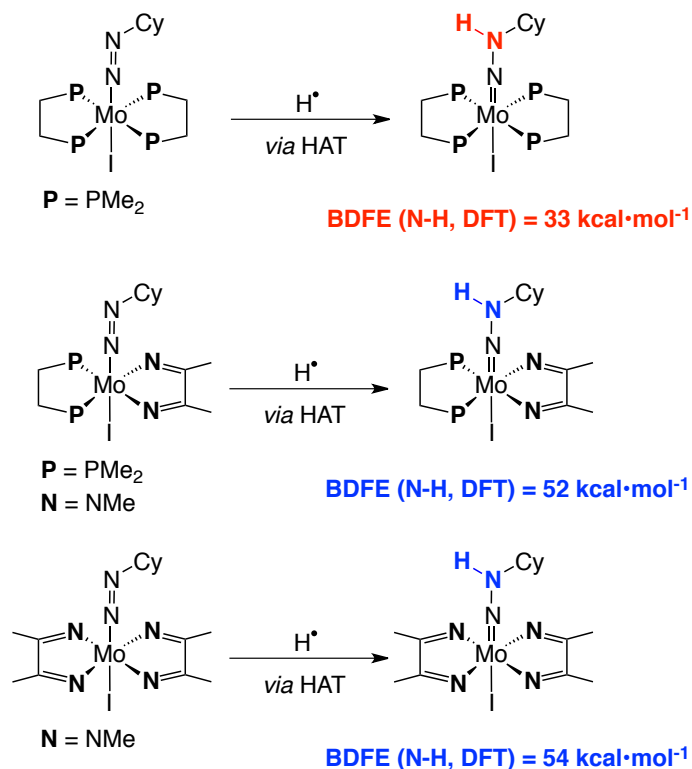


Figure 8. Demonstration of the effect of redox-active ligands on enabling N-H bond formation from renewable H₂.

exclusively metal-based reduction process. Details of this effort have recently been published in *Angew. Chem. Int. Ed.*

The reaction of $[(^{iPr}BPDI)MoN_2]_2(\mu_2-N_2)$ with ammonia has produced unexpected results and opened a new pathway of investigation in our AFOSR funded program. Addition of four equivalents of NH_3 gas to a thawing diethyl ether solution of $[(^{iPr}BPDI)MoN_2]_2(\mu_2-N_2)$ yielded a diamagnetic, red-brown molybdenum product identified as $[(^{iPr}BPIBn)Mo(=NAr^{Dipp})]_2(\mu_2, \eta^1, \eta^1-NH)_2$ ($^{iPr}BPIBn = 2,6-(2,6-^{iPr}_2-C_6H_3N=CPh)(CH_2Ph)-C_5H_3N$) (Figure 9). The bond distances in the κ^2 -imino(pyridine) ligand are consistent with a one electron reduced bidentate chelate, thereby supporting Mo(V) oxidation states. This product was also obtained from addition of 1.5 equivalents of hydrazine with loss of N_2 and is likely a result of initial disproportionation of hydrazine to form ammonia, which engages in similar chemistry with $[(^{iPr}BPDI)MoN_2]_2(\mu_2-N_2)$.

As mentioned in the Introduction, the reverse of the ammonia synthesis reaction, the oxidation of NH_3 to N_2 and H_2 , is also of considerable interest due to potential applications in hydrogen storage and fuel cell chemistry. Compared to ammonia synthesis, much less is known about NH_3 oxidation and few molecular catalysts are known to promote the reaction. The first step in such a cycle likely involves N-H oxidative addition of ammonia, a relatively challenging transformation as the preference for M- NH_3 dative interactions must be overcome. Mechanistic studies using primary and secondary amines resulted in isolation of metal-hydride intermediates, establishing their intermediacy in the NH_3 (and N_2H_4) oxidation process. This along with concomitant metal-imide formation likely drives the conversion of ammonia to a parent imido ligand. Such insights, particularly those involving metal-ligand cooperativity may ultimately prove valuable in the synthetic schemes for the interconversion of ammonia with its elements.

One such possible cycle is shown in Figure 10 using the redox-active bis(imino)pyridine molybdenum complex as the catalyst platform. During our AFOSR funded program, we have prepared many examples of potential intermediates along such as cycle. These compounds are highlighted in the boxes in Figure 10 and isolation of these compounds allow full characterization and determination of the electronic structure which in turn provides insight into the electron flow between the ligand and the metal during essential bond cleavage and assembly steps. In the cases examined, the bis(imino)pyridine chelate transforms between its dianionic and monanionic forms and as a consequence the metal can support dinitrogen (N_2), amide (NH_2) and imide (NH) ligands. While isolated examples of each are known in molybdenum chemistry, single systems that support all three are indeed rare and to our knowledge no examples exist where a redox active chelate mediates electron transfer steps throughout the cycle.

The elucidation of synthetic routes to important intermediates in both nitrogen reduction and ammonia oxidation enables determination of the thermodynamics of N-H BDFEs. Systematic protonation of the bis(imino)molybdenum complex, $(^{iPr}PDI)Mo(NAr)_2$ ($Ar = tolyl$) established a pKa value between 16.6 and 19.4 in THF. One electron reduction of the protonated product forms $(^{iPr}BPDI)Mo(NAr)NHA_r$ with a redox potential of -0.61 V (relative to Fc/Fc^+ in THF). Taken together, an N-H BDFE between 75-78 kcal/mol has been experimentally measured (Figure 11). DFT verifies this value at 76 kcal/mol. This value is also stronger than the value of 65 kcal/mol for the related vanadium example. This is the first time that N-H BDFEs have been systematically measured as a function of

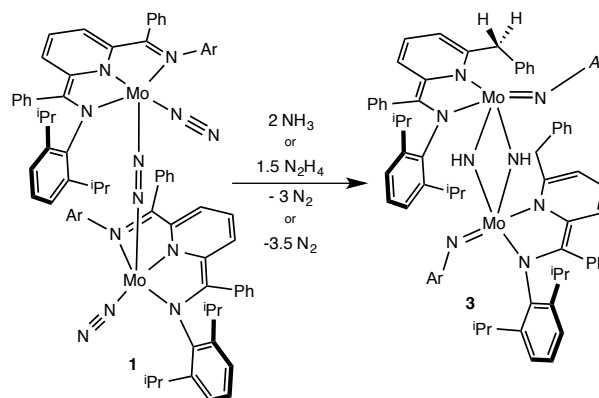


Figure 9. Rare example of ammonia (and hydrazine) oxidation by a bis(imino)pyridine molybdenum complex.

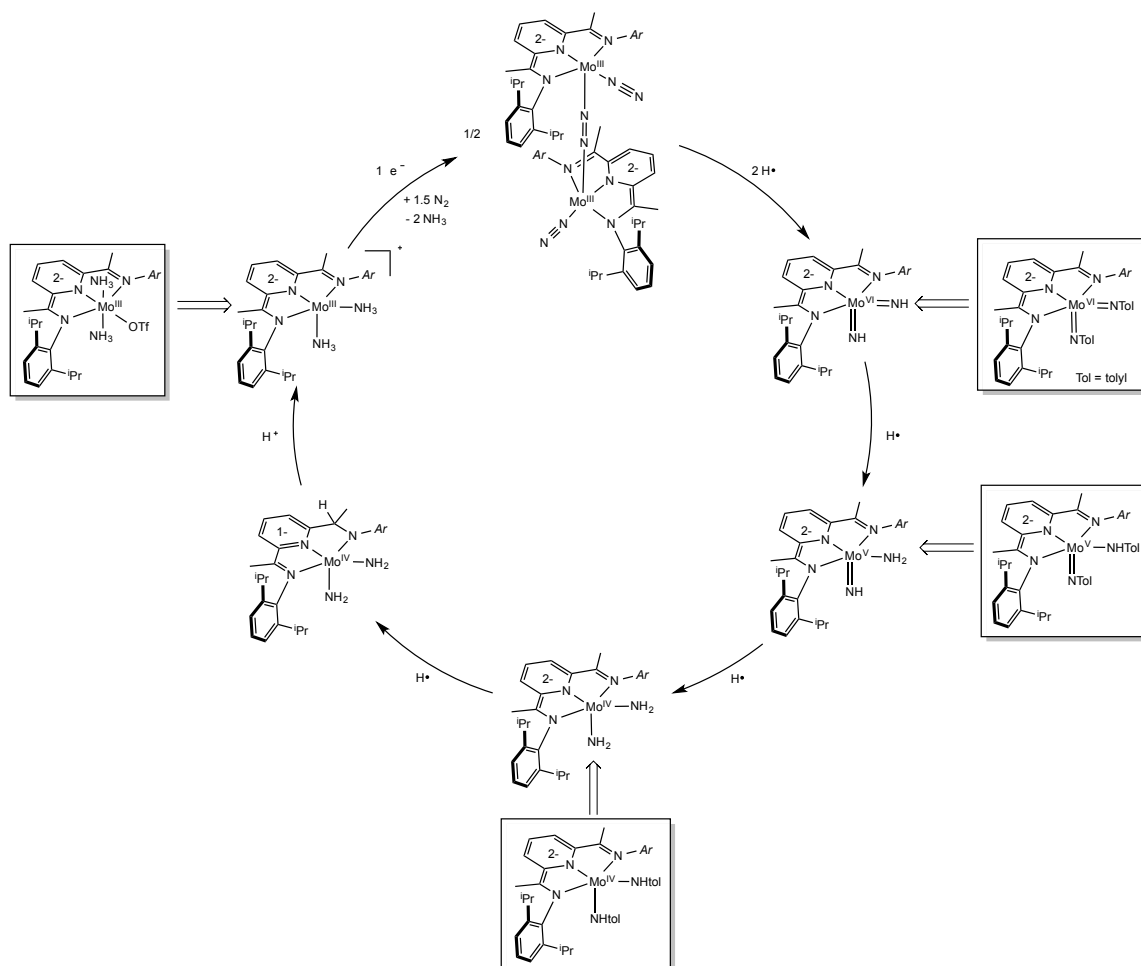


Figure 10. Demonstration of the effect of redox-active ligands on enabling N-H bond formation from renewable H₂.

transition metal with similar supporting ligands. What is notable in both cases is that the redox activity of the bis(imino)pyridine *strengthens* the resulting N-H bonds from early transition metal imido complexes. These studies provide definitive experimental support demonstrating the thermodynamic feasibility for ammonia synthesis via hydrogen atom transfer from renewable H₂.

Concurrent with these efforts, we have also been exploring related molybdenum platforms for ammonia oxidation. The bis(imino)pyridine core has been preserved as the redox activity of the chelate is likely responsible for the unique NH₃ and N₂H₄ oxidation chemistry observed with [(ⁱPrBPDl)MoN₂]₂(μ₂-N₂). We recently discovered that the bis(imino)pyridine molybdenum benzene compound (note the benzyl groups on the supporting ligand have been replaced by methyl substituents thereby altering the redox potential for reversible electron transfer) is a useful entry point for this chemistry. As shown in Figure 12, notable transformations include the addition of NH₃ or N₂H₄ to form the corresponding bis(amide) compound where a hydrogen has been added to the chelate. Observation of intermediates in the ammonia chemistry revealed formation of an unusual η²-benzene compound upon ammonia coordination. The ligand protonation is notable because it demonstrates that the bis(imino)pyridine *is not only a reservoir for electrons but also for protons*, thereby mimicking a cofactor in enzymatic catalysis. The hydrogen addition has proven reversible as protonation of the molybdenum bis(amide) with lutidinium triflate (the common acid in molecular N₂ reduction catalysis), furnishes a molybdenum bis(ammonia) compound where one proton originated from the ligand. Thus, both the

redox and chemical participation of the chelate are critical in key steps in ammonia synthesis. To our knowledge, such reactivity is unprecedented.

Treatment of $(iPrPDA)Mo(NH_2)_2$ with $[Ph_3C][BAR^F_4]$ resulted in net ammonia oxidation to form a bridging imido compound. Again, this is a rare example of metal imido formation from oxidation of ammonia. Our results are remarkable in that net oxidation of the compound triggers N-H bond scission, usually a transformation observed under reductive conditions, and results in rupture of multiple N-H bonds. This concept may prove more broadly useful and is currently under investigation in our laboratory. Other notable reactivity with $(iPrPDI)Mo(\eta^6-C_6H_6)$ includes N-N bond cleavage of 1,2-diphenylhydrazine to yield the molybdenum(VI) bis(imido) complex. Hydrogen atom transfer accompanies the N-N bond scission as free aniline was observed as a byproduct of the reaction. A manuscript describing this unique chemistry is in preparation.

Additional synthetic efforts have produced other molybdenum compounds that contain various nitrogeneous ligands that differ by oxidation and protonation state. A summary of these extensive efforts is presented in Figure 13. The sheer volume of compounds presented in the Figure highlights the flexibility of the bis(imino)pyridine molybdenum platform in supporting every type of nitrogen ligand ranging from nitride to ammonia. We are therefore confident that we will be able to determine the various N-H BDFEs along the conversion from coordinated dinitrogen through metal-nitride and ultimately to ammonia. Special attention will be devoted to understanding how the electronic structure of the molybdenum compounds is modulated by the redox-active bis(imino)pyridine. The chemistry presented in Figure 13 also highlights the ability of the bis(imino)pyridine to engage in HAT chemistry as the imine methyl positions have also proven chemically active.

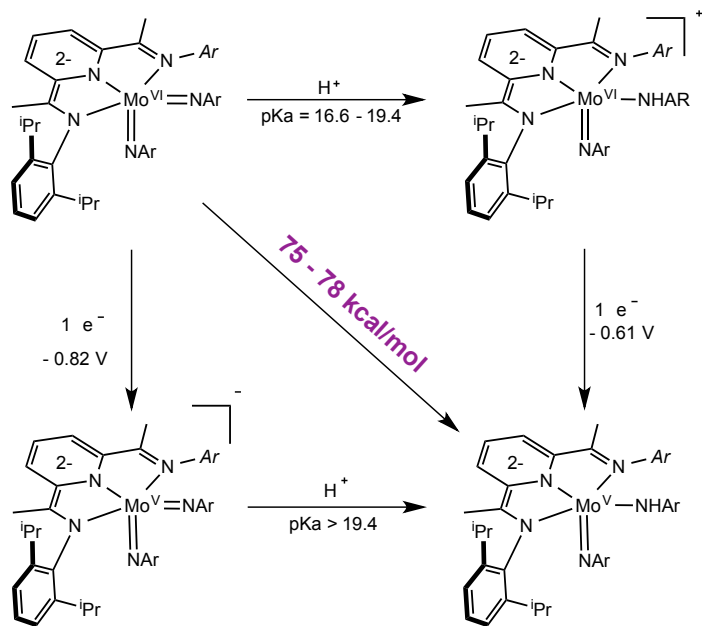


Figure 11. Square scheme for determination of N-H BDFE.

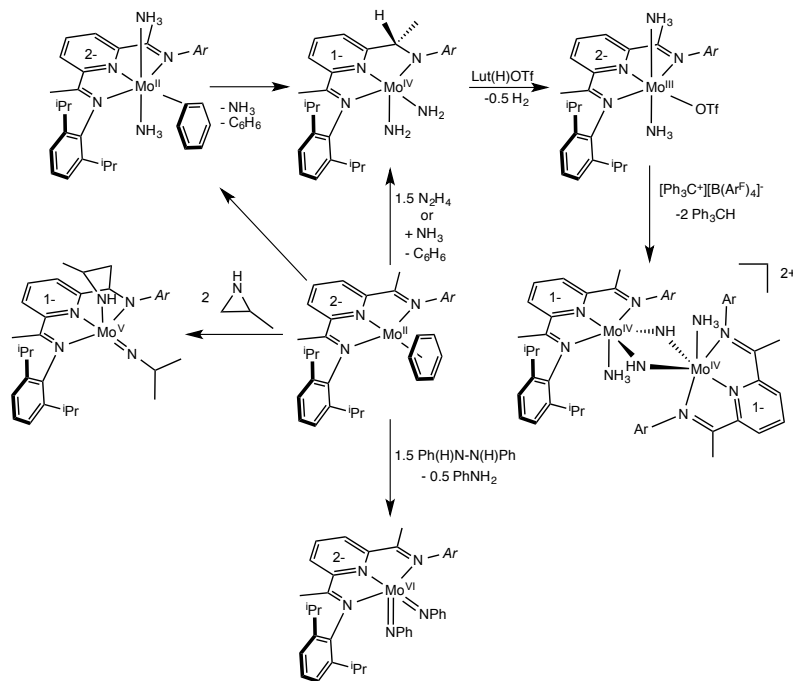


Figure 12. Transformations relevant to ammonia oxidation promoted by $(iPrPDI)Mo(\eta^6-C_6H_6)$.

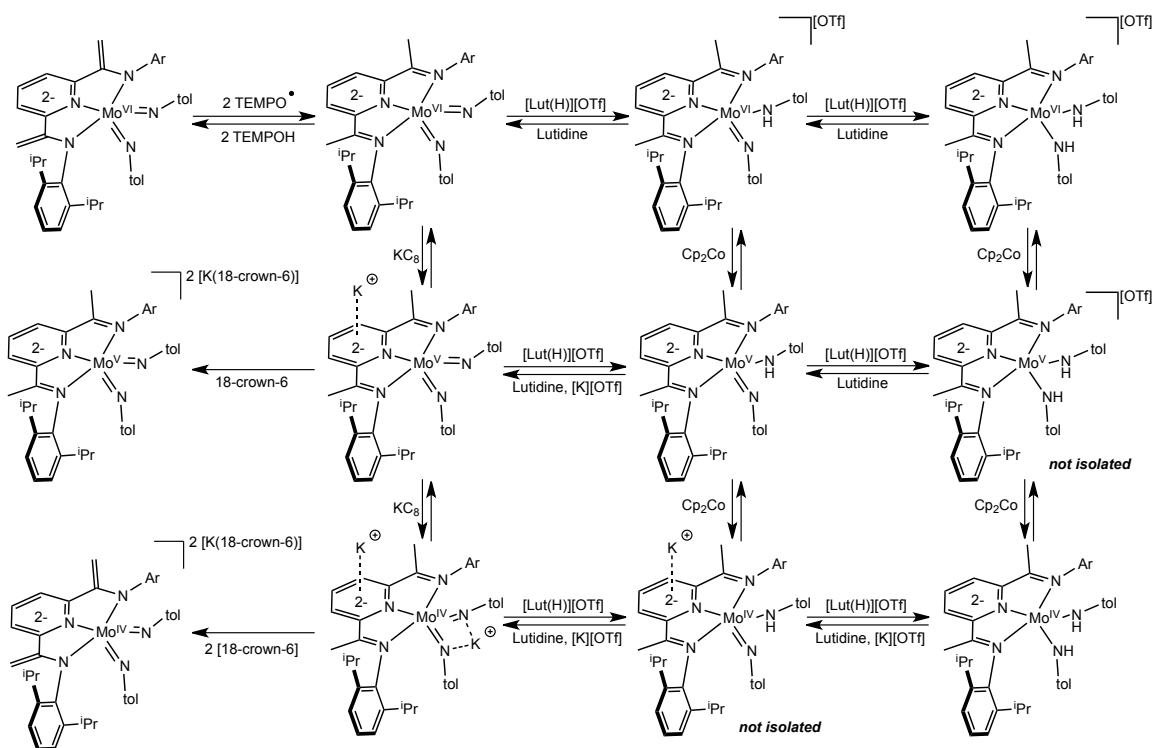


Figure 13. Square schemes synthetically available in bis(imino)pyridine molybdenum chemistry for determination of N-H BDFEs.

III. Summary and Outlook. The integration of new synthetic platforms, physical and spectroscopic measurements and state-of-the-art computational methods have allowed our research group to provide unprecedented insights into new approaches for nitrogen fixation to ammonia and hydrazine as well as the reverse process, the oxidation of NH_3 and N_2H_4 to the elements. Enabled by AFOSR support, we have demonstrated the unique role of redox-active ligands in imparting the thermochemistry required to assemble N-H bonds from potentially renewable hydrogen sources. The early transition metals employed furnish sufficiently high reduction potentials to also promote N-N bond cleavage. This new and likely transformative approach to nitrogen fixation and ammonia interconversion relies on the application of hydrogen atom transfer whereby protons and electrons move in a single elementary step to impart new reactivity. If successful, these methods will allow essential fuels and hydrogen storage media, NH_3 and N_2H_4 , to be prepared for a carbon neutral future

The work from the prior funding cycle is merely the beginning. Our prior support has allowed our research group to establish the kinetic and thermodynamic feasibility of our approach. We have produced four high profile and high impact publications in the most competitive and selective journals in chemistry and more manuscripts are currently in preparation. Importantly, we outlined the blueprint in both ligand and metal complex design to rationally synthesize molecules from early abundant transition metals that reliably and predictably construct and deconstruct of N-H bonds – the requisite fundamental chemistry for the interconversion of NH_3 and N_2H_4 with their constituent elements. The future is now set to evolve this chemistry into more useful catalytic cycles and develop the co-catalysts required for the key hydrogen activation step. If enabled, broadly useful chemistry for the synthesis and controlled decomposition of important nitrogen-containing molecules will be realized.

IV. Publications Citing AFOSR Support.

Margulieux, G. W.; Turner, Z. R.; Chirik, P. J. "Synthesis and ligand modification chemistry of a molybdenum dinitrogen complex: Redox and chemical activity of a bis(imino)pyridine ligand." *Angew. Chem. Int. Ed.* **2014**, *53*, Early View. (DOI: 10.1002/anie.210408725).

Milsmann, C.; Semproni, S. P.; Chirik, P. J. "N-N bond cleavage of 1,2-diarylhydrazines and N-H bond formation via H-atom transfer in vanadium complexes supported by a redox-active ligand." *J. Am. Chem. Soc.* **2014**, *136*, 12099-12107.

Russell, S. K.; Hoyt, J. M.; Bart, S. C.; Milsmann, C.; Stieber, S. C. E.; Semproni, S. P.; DeBeer, S.; Chirik, P. J. "Synthesis, electronic structure and reactivity of bis(imino)pyridine iron carbene complexes: Evidence for a carbene radical." *Chem. Sci.* **2014**, *5*, 1168-1174.

Milsmann, C.; Turner, Z. R.; Semproni, S. P.; Chirik, P. J. "Azo N=N bond cleavage with a redox-active vanadium compound involving metal-ligand cooperativity." *Angew. Chem. Int. Ed.* **2012**, *51*, 5386-5390.

V. References Cited.

¹ Sherif, S. A.; Barbir, F.; Veziroglu, T. N. *J. Sci. Ind. Res.* **2003**, *62*, 46.

² (a) Zamfirescu, C.; Dincer, I. *J. Power Sources* **2008**, *185*, 459. (b) C. H.; Johannessen, T.; Sorensen, R. Z.; Norskov, J. K. *Catal. Today* **2006**, *111*, 140.

³ "A feasibility study of implementing an Ammonia Economy," Bartels, J. R., Iowa State University, 2008, <http://lib.dr.iastate.edu/cgi/viewcontent.cgi?article=2119&context=etd>.

⁴ Kartal, B.; Maalcke, W. J.; de Almeida, N. M.; Cirpus, I.; Gloerich, J.; Geerts, W.; Op den Camp, H. J. M.; Harhangi, H. R.; Janssen-Megens, E. M.; Francoijs, K.-J.; Stunnenberg, H. G.; Keltjens, J. T.; Jetten, M. S. M.; Strous, M. *Nature* **2011**, *479*, 127.

⁵ Boggs, B. K.; Botte, G. G. *Electrochim. Acta* **2010**, *55*, 5287.

⁶ Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955.

⁷ Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120.

⁸ Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, 7186.

⁹ Tang, L.; Papish, E. T.; Abramo, G. P.; Norton, J. R.; Baik, M.-H.; Friesner, R. A.; Rappé, A. *J. Am. Chem. Soc.* **2003**, *125*, 10093-10102.

¹⁰ Estes, D. P.; Norton, J. R.; Jockusch, S.; Sattler, W. *J. Am. Chem. Soc.* **2012**, *134*, 15512–15518.

¹¹ Berry, J. F. *Comm. Inorg. Chem.* **2009**, *30*, 28.

- ¹² (a) Kornecki, K. P.; Berry, J. F. *Chem. Eur. J.* **2011**, *17*, 5827. (b) Lyaskovskyy, V.; Olivos Suarez, A. I.; Lu, H.; Jiang, H. Zhang, X. P.; de Bruin, B. J. *Am. Chem. Soc.* **2011**, *133*, 12264. (c) Wiese, S.; McAfee, J. L.; Pahls, D. R.; McMullin, C. L.; Cundari, T. R.; Warren, T. H. *J. Am. Chem. Soc.* **2012**, *134*, 10114. (d) King, E. R.; Hennessy, E. T.; Betley, T. A. *J. Am. Chem. Soc.* **2011**, *133*, 4917. (e) Hennessy, E. T.; Betley, T. A. *Science*, **2013**, *340*, 591.
- ¹³ (a) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200-202*, 379. (b) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. (c) Shaver, M. P.; Fryzuk, M. D. *Adv. Synth. Cat.* **2003**, *345*, 1061.
- ¹⁴ (a) Nugent, W. A., Mayer J. M. *Metal-Ligand Multiple Bonds*, John Wiley & Sons: New York, **1988**. (b) Eikey, R. A.; Abu-Omar, M. M. *Coord. Chem. Rev.* **2003**, *243*, 83.
- ¹⁵ Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T.; *J. Am. Chem. Soc.* **1996**, *118*, 591.
- ¹⁶ Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794.
- ¹⁷ Coellen, M.; Rüchardt, C. *Chem. – Eur. J.* **1995**, *1*, 564.
- ¹⁸ Busby, D. C.; George, T. A.; Iske, S. D. A.; Wagner, S. D. *Inorg. Chem.* **1981**, *20*, 22.
- ¹⁹ Kuriyama, S.; Arashiba, K.; Nakajima, K.; Tanaka, H.; Kamaru, N.; Yoshizawa, K.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2014**, *136*, 9717.