THE INTERCONVERSION OF AMMONIA WITH ITS ELEMENTS BY MOLYBDENUM COMPLEXES: FUNDAMENTAL INVESTIGATIONS

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A DISSERTATION
PRESENTED TO THE FACULTY
OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE
BY THE DEPARTMENT OF CHEMISTRY

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June 2019
Abstract

Ammonia (NH$_3$) is essential for sustaining life on Earth. In addition to its role as the principal component of most modern fertilizers, ammonia is also a hydrogen-rich small molecule that is a transportable, carbon-neutral fuel alternative. The energy-efficient interconversion of ammonia with N$_2$ and H$_2$ is desirable yet presents a complex challenge owing to the movement of six electrons and six protons as well as the activation of the N≡N triple bond, one of the strongest in chemistry. At the core of energy-efficient NH$_3$ synthesis and oxidation is understanding the fundamental thermochemistry associated with the formation and cleavage of N–H bonds especially in cases where the nitrogen-containing molecule is bound to a transition metal catalyst. The research presented in this dissertation systematically establishes N–H bond dissociation free energies (BDFEs) for various classes of nitrogen ligands (ammine, amide, imide, diazenide, hydrazide) in complexes of molybdenum relevant to catalytic ammonia synthesis and oxidation cycles.

A host of molybdenum complexes supported by bis(diphosphine), terpyridine/bis(phosphine) and pyridine(diimine) ligands were synthesized, structurally characterized and the corresponding N–H BDFEs were determined experimentally and supported by density functional theory (DFT) calculations. A blueprint was established for various complexes on how coordination environment, metal oxidation state, overall charge affects N–H BDFEs and consequently, N–H bond formation/cleavage reactivity by proton-coupled electron transfer (PCET). The phenomenon of “coordination-induced bond weakening” was demonstrated in cationic terpyridine bis(phosphine) complexes of molybdenum for X–H (X = N, O) bonds in small molecules such as ammonia, hydrazine
and water, including the isolation of a nonclassical ammine complex

\[ \left[ (\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}(\text{NH}_3) \right][\text{BArF}^{24}] \{1-\text{NH}_3\}^+; (\text{PhTpy} = 4'-\text{Ph}-2,2',6',2''-\text{terpyridine}, \text{ArF}^{24} = [\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2]_4 \] that was shown to be thermodynamically unstable with respect to H\(_2\) evolution owing to an exceptionally low ammine N–H BDFE. Accordingly, the complex [1-NH\(_3\)]\(^+\) undergoes H\(_2\) loss upon mild thermolysis and can serve as a thermodynamically potent source of H-atoms in PCET reactions. A related nonclassical pyrrolidine complex of molybdenum was synthesized and applied as a mechanistic probe that provides key insight into H\(_2\) evolution from coordinated amines by deuterium labeling experiments. The applications of these fundamental studies were extended to demonstrate the interconversion of imido/amido as well as olefin/alkyl ligands by PCET in the coordination sphere of molybdenum. Additionally, a catalytic partial hydrogenation of a pyridine(diimine) chelate in a molybdenum nitrido ethylene complex was demonstrated and the thermodynamics of a plausible PCET pathway were examined by DFT.
Biographical Sketch

Máté József Bezdek was born on November 4th, 1991 in Budapest, Hungary to Károly Bezdek (professor of mathematics) and Éva Bezdek (née Balogh; high school language and literature teacher). In the fall of 2002 his family moved to Ithaca, NY, during which time he learned to speak English as a 5th grader and was introduced to the wonders of the North American lifestyle with his brothers Dániel and Márk. After an enjoyable and formative year in upstate New York, in 2003 Máté’s family permanently relocated to the foothills of the Rocky Mountains in Calgary, Alberta, Canada.

In Calgary, Máté attended St. Brigid Elementary/ Jr. High School for Grades 6–9, where he took both studying and athletics seriously and played both volleyball and basketball as a Bearcat. In Jr. High School Máté also developed a deeper interest in science and attended the Calgary Youth Science Fair annually between 2004 and 2007 with projects ranging from space exploration to pure mathematics. Mentored by his father, Máté had the chance to represent the province of Alberta at three Canada Wide Science Fairs in Vancouver (2005), Saguenay (2006) and Truro (2007) ultimately winning gold (2005) and silver (2006) medals. Máté’s science fair career peaked in his first year of high school, when he (along with his brother Dániel) qualified to represent Canada at the 2008 Intel International Science and Engineering Fair held in Atlanta, Georgia, winning second place in the mathematical science division that came with the added perk of having an asteroid named after him (Minor Planet 25038 Matebezdek).

Deciding that this experience was hard to beat, Máté retired from science fair competitions and focused his energy on various other pursuits at Notre Dame High School such as: i) trying to be a lunchtime hero at the ND intramural soccer league and ii)
serving as the founding editor-in-chief of ND’s student run newspaper, *The Current*. It was during a high school class field trip to the University of Calgary campus that Máté found himself strangely drawn to chemistry research laboratories and decided to pursue the subject in university. He graduated in 2010 from Notre Dame High School as Class Valedictorian.

While studying chemistry at the University of Calgary, Máté immediately found great satisfaction in laboratory work and involved himself in as many undergraduate research projects as possible. It was during one of these projects in Prof. Curtis Berlinguette’s lab that he was exposed to the beautiful colors and structures of coordination complexes. From this point onwards, Máté was hooked on inorganic chemistry and pursued further research projects that included a 2-month stay at the *Technische Universität Kaiserslautern* in Germany and an honors thesis conducted in the laboratory of Prof. Warren Piers where he was first introduced to the topic of small molecule activation. This experience turned out to be instrumental in his decision to attend graduate school to work on N₂ chemistry under the supervision of Prof. Paul Chirik at Princeton.

At Princeton, Máté had a vibrant scientific adventure where he had the privilege of meeting and learning from some phenomenal scientists who made working at the very frontiers of chemistry tremendously fun. These years flew by, as he met an incredible lady, made molybdenum complexes, derived square schemes, solved crystal structures and shared the thrill of discovery with an exceptional group of people. Starting in the summer of 2019 Máté will venture north and continue his chemistry career as a postdoc at MIT but will remember the Princeton years with great nostalgia.
Drága Szüleimnek
Acknowledgements

This dissertation was only possible because of the immense support I have received from my family, friends and mentors during my time in graduate school. I am eternally grateful to my parents for creating an environment at home that nurtured curiosity and creativity, for always supporting my interests and teaching me the priceless value of knowledge. My brothers Dániel and Márk have been my partners-in-crime since the very beginning, sources of laughter and perspective, for which I am very thankful.

I am deeply indebted to my advisor, Professor Paul Chirik, for his endless faith, support and mentorship over the years. Paul’s passion for science and dedication to his role as an educator have been a source of constant inspiration. Whether the discussion was science, or the philosophy thereof, I learned an immense amount from Paul as he taught me the meaning of rigorous research and the importance of asking fundamental questions that have broad implications. I am very grateful to Paul for always being enthusiastic about publishing my work, giving me intellectual freedom to pursue my ideas and helping me become a better chemist in every dimension imaginable. I am also very thankful to Prof. Robert Knowles for insight on PCET projects, Prof. John Groves for serving as a member of my thesis committee as well as Prof. Leslie Schoop for volunteering as the second reader of this thesis.

From my early years as an undergraduate researcher, I have also been very fortunate to have exceptional mentors to whom I owe tremendous thanks. At the University of Calgary, Profs. Curtis Berlinguette and Warren Piers first gave me the opportunity to work in a research laboratory, experiences that were formative in shaping my research interests. In the lab, Dr. Dmitry Pogozhev first taught me synthetic chemistry
and Dr. Adrian Houghton introduced me to Schlenk techniques and glovebox operations. When I arrived to Princeton as a first-year graduate student, Drs. Iraklis Pappas and Grant Margulieux immediately took me under their wings and taught me the skills upon which my Ph.D. was built. Grant taught me the tricks of molybdenum and ammonia chemistry including the “venerable brown color wheel” and passed down his expertise in growing single crystals and solving crystal structures. Iraklis was an incredible resource not only for synthetic chemistry and crystallography, but also for discussing concepts in PCET, thermochemical analysis, DFT computations, and discussing ideas, both chemical and philosophical. I am extremely grateful for his support and friendship.

The Chirik lab always had an energetic and welcoming ambiance and I am very thankful to Paul for assembling a group of phenomenal scientists who are an absolute pleasure to work with. The senior graduate students and postdocs in the group when I was starting out were outstanding role models whose example I tried my best to follow: Drs. Valerie Schmidt, Jamie Neely, Chris Schuster, Janelle Steves, Margaret Schauermann, Jordan Hoyt, Pony Yu, Max Friedfeld, Brian Schaefer, Jenny Obligacion and Neil Palmer are all thanked for helping me get started in lab. Later in my graduate career, I also had the privilege of meeting and working with postdocs from whom I learned a great deal: Drs. Simon Krautwald, Matthew Joannou, Florian Loose, Stephan Rummelt, Rose Kennedy, Rebeca Arévalo and Marcus Farmer. Simon is especially thanked for nightly Olives runs, quality memes, great philosophical discussions, and for being a class-act friend who was always there even after moving to Boston. Matthew is thanked for being my partner-in-reduced-metals-crime, for his outstanding taste in music and contagiously positive outlook on life, teachings on orbital symmetry and for helping me deal with any
and every maintenance issue in lab with an impressive zeal. Florian is thanked for his excitement for coordination chemistry (and chocolate) and for caring about the glovebox and departmental retreat soccer tournament (almost) as much as I did. To the next generations of graduate students, Sangmin Kim, Aaron Zhong, Tyler Pabst, Boran Lee, Peter Viereck and Paul Peterson: The group is in great hands, and I look forward to reading about the new frontiers you discover. A lab member who deserves special recognition is the one and only Dr. Jonathan Darmon. As the laboratory manager, Jon made everyday life exponentially easier for everyone in the Chirik group. He is an absolute fountain of information, is always willing to lend a helping hand and is overall a wonderful human being. To my classmate Nadia Léonard: it’s been a long road but we made it! Thank you for all your help with EPR, and always being there across the lab to share the journey of grad school. Outside of the Chirik group, I’m very thankful to Chip Le and Ben Shields for their friendship and “bro dinners” as we progressed through graduate school milestones together.

The phenomenal Princeton NMR team, Dr. István Pelczer and Ken Conover are thanked for always readily and happily helping with any specialized experiment I could think of, often on very short notice. Dr. John Eng of the Mass Spec/EPR facility has also been tremendously helpful and was always very excited to discuss new experimental methods. Dr. Phil Jeffrey is thanked for keeping the X-ray lab in top shape, for his advice on solving tricky crystals and for his flexibility when urgent crystals needed running. Chemistry support staff Meghan Krause, Sarah Mullins and Meredith LaSalle-Tarantin are also owed tremendous thanks for being amazing advocates for graduate students.
The final thanks must, of course, go to Dr. Cayetana Zárate Sáez, who I’m incredibly lucky to have met and who makes me a much happier and far stronger person. In difficult moments she was always there to put a smile on my face, and has been an amazing partner in adventures far and wide. Thank you for your unconditional love, patience and support despite being literally an ocean away at times; I am beyond excited to embark on the next chapters of our lives together!
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CHAPTER 1

Thermodynamics of N–H Bond Formation in Bis(Phosphine) Molybdenum(II)
Diazenides and the Influence of the Trans Ligand.*

Abstract

A series of bis(phosphine) molybdenum (II) diazenides [(dppe)₂Mo(NNCy)(I)], [(dppe)₂(CH₃CN)Mo(NNCy)][BArF²⁴] and [(dppe)₂(3,5-(CF₃)₂C₆H₃CN)Mo-(NNCy)][BArF²⁴] (dppe = 1,2-bis(diphenylphosphino)ethane; Cy = cyclohexyl; ArF²⁴ = (3,5-(CF₃)₂C₆H₃)₄) were synthesized and structurally characterized. Treatment of the diazenido complexes with a stoichiometric amount of [H(OEt)₂][BArF²⁴] afforded the corresponding Mo(IV) hydrazido species [(dppe)₂Mo(NNHCy)(I)][BArF²⁴], [(dppe)₂(CH₃CN)Mo(NNHCy)][BArF²⁴]₂ and [(dppe)₂(3,5-(CF₃)₂C₆H₃CN)Mo-(NNHCy)][BArF²⁴]₂, enabling the study of N–H bond dissociation free energies (BDFEs) in the classical Chatt-type bis(phosphine) diazenide platform as a function of ligand (L) trans to the nitrogenous fragment. Deprotonation and electrochemical experiments established that 3,5-(CF₃)₂C₆H₃CN afforded the least reducing Mo(IV) hydrazido complex in the series (E°₉₅ red = -1.32 V vs. Fe/Fe⁺) with the most acidic N-H bond (pKₐ < 2.6, THF), whereas CH₃CN (E°₉₅ red = -1.60 V, pKₐ < 5.5) and I⁻ (E°₉₅ red = -2.03 V, pKₐ = 9.3) gave more reducing complexes with less acidic N-H bonds. DFT computations confirm weak N-H BDFEs of 32.8 (L= I⁻), 35.4 (L = CH₃CN) and 36.2 kcal mol⁻¹ (L = 3,5-(CF₃)₂C₆H₃CN) in the hydrazido series.

* Adapted from: Bezdek, M. J.; Chirik, P. J. *Dalton Trans.* 2016, 45, 15922–15930. with permission from The Royal Society of Chemistry.
Introduction

A longstanding challenge in coordination chemistry and homogeneous catalysis is the efficient and carbon neutral synthesis of ammonia from its elements, dinitrogen (N\textsubscript{2}) and dihydrogen (H\textsubscript{2}).\textsuperscript{1} Seminal and independent studies of Chatt and Hidai demonstrated that protonation of electron-rich molybdenum(0) and tungsten(0) dinitrogen complexes with mineral acids produced stoichiometric quantities of ammonia (Figure 1.1).\textsuperscript{2,3,4} Although catalytic ammonia synthesis has remained elusive, these classical bis(phosphine) complexes were used to establish a pedagogical model, known as the “Chatt cycle”, for reduction of N\textsubscript{2} to ammonia using protons and electrons.\textsuperscript{5} In this hypothetical cycle, the group 6 transition metal dinitrogen complex undergoes stepwise protonation and reduction, cycling through metal diazenido (M\textsuperscript{I}-N=NH), hydrazido (M\textsuperscript{II}=N-NH\textsubscript{2}), nitrido (M\textsuperscript{III}=N), imido (M\textsuperscript{II}=NH), and amido (M\textsuperscript{I}-NH\textsubscript{2}) intermediates while liberating two equivalents of ammonia in the process (Figure 1.2a).\textsuperscript{6}

Considerable progress has since been made in ligand design and in the source of protons and electrons to enable the catalytic reduction of N\textsubscript{2} to NH\textsubscript{3} using well-defined molybdenum\textsuperscript{7,8,9} and iron\textsuperscript{10} precursors. Despite these efforts, including preparation of numerous intermediates, little is known about the thermodynamics of N-H bond formation with the various types of complexes relevant to an N\textsubscript{2} reduction cycle.\textsuperscript{11} Density functional theory (DFT) methods have been applied to compute the thermodynamics of each protonation and reduction event in both the Chatt\textsuperscript{12} and Schrock\textsuperscript{13} cycles with specific acid/reductant combinations. However, a fundamental understanding of N-H bond strengths of ammine, amide and imide ligands is generally absent from the literature and may ultimately prove valuable for rational design of
catalysts with improved performance. Our laboratory has initiated a program aimed at systematic evaluation of the N-H bond dissociation free energies (BDFEs) as a function of transition metal, oxidation state and supporting ligand. Studies on bis(anilido) complexes of vanadium supported by redox-active, aryl-substituted bis(imino)pyridine ligands established a significant weakening of the N-H bonds in amide ligands from 69.2 to 64.1 kcal mol\(^{-1}\) upon reduction from V(V) to V(III).\(^{14}\) Titanocene(III) chloride ammine complexes have also been generated in situ and have a calculated N-H BDFEs of 61 kcal mol\(^{-1}\).\(^{15}\) As part of these efforts, the thermodynamics of N-H bond formation in intermediates in the Chatt cycle were also of interest. Molybdenum bis(phosphine) diazenides were selected given that previous reports have established that protonation of these complexes yields isolable hydrazido products, enabling study of the second N-H bond formation step in the Chatt cycle (Figure 1.2b).\(^{16,17}\) Here we describe the synthesis and characterization of a series of molybdenum cyclohexyl diazenide compounds that feature ligands of various field strength in the coordination site \(\text{trans}\) to the nitrogen-containing ligand. Protonation of these compounds resulted in N-H bond formation and isolation of the corresponding molybdenum(IV) hydrazido complexes, thus enabling study of the thermodynamics of N-H bond formation.

\[\text{Chatt, Hidai (1975)}\]

\[
\begin{array}{c}
\text{P} \quad \text{M} \quad \text{P} \\
\text{N} \quad \text{N} \\
\text{P} \quad \text{M} \quad \text{P} \\
\text{N} \quad \text{N} \\
\end{array}
\]

\[\text{M} = \text{Mo, W} \]

\[\text{P} = \text{PPh}_2\text{Me, PPhMe}_2\]

\[\text{H}_2\text{SO}_4 \quad \text{THF or MeOH} \quad 2 \text{NH}_3 + \text{Oxidized } \text{M} \quad \text{up to 90\%}\]

\[\text{Figure 1.1. Stoichiometric ammonia synthesis by protonolysis of classical bis(phosphine) molybdenum and tungsten dinitrogen compounds.}\]
Figure 1.2. (a) Chatt cycle for ammonia synthesis. (b) N-H bond formation at molybdenum and tungsten diazenides to afford the corresponding hydrazido complexes.

Results and Discussion

Synthesis of Molybdenum Diazenido and Hydrazido Complexes. Our studies commenced with the preparation of the molybdenum(II) diazenide complex 

\[(\text{dppe})_2\text{Mo(NNCy)(I)}\] ([1]) using a procedure modified from previous literature reports.\(^{17}\) In our hands, the optimal synthetic route involved stirring a benzene solution of 

\[(\text{dppe})_2\text{Mo(N}_2\text{)}\] with cyclohexyl iodide (CyI) at room temperature for two days (Figure 1.3a). The resulting orange diamagnetic product was obtained in 87% yield following recrystallization and the NMR and IR spectroscopic data were consistent with the previous literature report.\(^{17}\)

Treatment of a THF solution of [1] with 1.1 equivalents of [H(OEt)\text{2}][\text{BArF}\text{24}] immediately furnished a yellow product identified as the molybdenum(IV) hydrazide,
[(dppe)$_2$Mo(NHCy)(I)][BArF$_{24}$] ([1-H]$^+$) in 82% yield (Figure 1.3b). In addition to a marked colour change from orange to green-yellow, this transformation was accompanied by the disappearance of the characteristic singlet in the $^{31}$P-NMR spectrum corresponding to [1] ($\delta = 53.8$ ppm, THF-$d_8$), and the concomitant appearance of a new singlet ($\delta = 38.4$ ppm, THF-$d_8$) assigned to the protonated hydrazido species [1-H]$^+$. This compound features the number of $^1$H NMR resonances consistent with $C_{2v}$ molecular symmetry, as well as a characteristic N-H band at 3300 cm$^{-1}$ in the KBr infrared spectrum.

![Chemical diagram](image)

**Figure 1.3.** (a) Preparation of [(dppe)$_2$Mo(NHCy)(I)] (ref. 17). (b) Preparation of bis(phosphine) molybdenum (II) diazenido complexes with varying trans L ligands and subsequent protonation to afford bis(phosphine) molybdenum(IV) hydrazido complexes.
With a conjugate acid-base pair of molybdenum diazenide-hydrazido complexes featuring a weak-field π-donating iodide iodide ligand in hand, variation of the trans ligand was pursued (Figure 1.3b). Halide abstraction from [1] by addition of one equiv of Na[BArF24] in the presence of 10 equivalents of CH3CN or one equivalent of (3,5-(CF3)2C6H3CN) in toluene solution afforded, after filtration and recrystallization, the corresponding cationic molybdenum (II) diazenido complexes [(dppe)2(CH3CN)Mo-(NNCy)][BArF24] ([2]+) and [(dppe)2(3,5-(CF3)2C6H3CN)Mo(NNCy)][BArF24] ([3]+) in 76% and 60% yields, respectively. Both yellow-green [2]+ and maroon [3]+ display the number of resonances in the 1H NMR and 31P NMR spectra consistent with products with C2v symmetry. Diagnostic 31P NMR resonances were observed at 63.14 ppm and 62.93 ppm, in THF-d8 for [2]+ and [3]+, respectively. In analogy to the synthesis of [1-H]+, the corresponding hydrazido dicationic complexes [2-H]2+ and [3-H]2+ were isolated in 65% and 80% yields, respectively, following straightforward addition of 1.1 eq. [H(OEt)2][BArF24] to THF solutions containing [2]+ and [3]+. In each case, diagnostic 31P NMR signals were observed at 47.23 ([2-H]2+) and 55.69 ([3-H]2+) ppm along with solid state infrared bands at 3274 cm⁻¹ ([2-H]2+) and 3251 cm⁻¹ ([3-H]2+), indicating protonation. A systematic lowering of solid-state N-H stretching frequencies is observed in the infrared spectra between [1-H]+ (vN-H = 3300 cm⁻¹), [2-H]2+ (vN-H = 3274 cm⁻¹) and [3-H]2+ (vN-H = 3251 cm⁻¹). These values should be interpreted cautiously as intermolecular effects in the solid-state such as hydrogen-bonding with the [BArF24]⁻ counterion in [2-H]2+ and [3-H]2+ may be a significant contributor to the origin of these differences.
**Solid-State Structures.** The solid-state structures of the molybdenum diazenido complexes [1], [2]⁺ and [3]⁺ were determined by X-ray diffraction and representations of the solid-state structures are presented in Figure 1.4. In all three compounds, [1], [2]⁺ and [3]⁺, idealized octahedral coordination geometries were observed, where the bidentate dppe ligands occupy the vertices of an equatorial plane with apical NNCy and trans X or L ligands (X = I ([1]); L = CH₃CN ([2]⁺), L = 3,5-(CF₃)₂C₆H₃CN ([3]⁺)) completing the coordination sphere of molybdenum. The identity of the ligand trans to the diazenido fragment has a marked influence on N=N bond distance. With [1], where a weak field, X-type, π-donor iodide is trans to the diazenido ligand, an N=N distance of 1.119(3) Å was observed, consistent with N=N double bond character. Substitution of the iodide with a neutral, principally σ-donating CH₃CN ([2]⁺) or a relatively electron poor 3,5-(CF₃)₂C₆H₃CN ([3]⁺) resulted in lengthening of the N=N bond to 1.144(4) Å and 1.216(4) Å, respectively. These observations are as expected from the trans influence as the nitrile ligands act as weak π-acceptors owing to the availability of vacant C≡N π* orbitals that are well poised to interact with the idealized t₂g set of molybdenum orbitals as described by Hoffmann and Dubois.¹⁹ Accordingly, the nitrile C≡N bond distance observed in [3]⁺ is elongated to 1.154(4) Å when compared with the C≡N contact of 1.136(4) Å in [2]⁺, further illustrating that the electron-deficient nitrile 3,5-(CF₃)₂C₆H₃CN engages in stronger π-backbonding with the d⁴ molybdenum(II) center.

**Thermodynamics of N–H Bond Formation.** The synthesis and isolation of the family of molybdenum diazenido and hydrazido compounds presents a unique opportunity to study the thermodynamics of N-H bond formation ($\Delta G_{N-H}$ or $-\text{BDFE}_{N-H}$) in the classical, bis(phosphine) molybdenum platform relevant to the Chatt cycle. As shown in Figure 1.5, the free energy change of N-H bond formation in molybdenum(II) diazenides ([1], [2]⁺, [3]⁺) can be described in terms of the reduction potential ($E^\circ_{\text{red}}$) and N-H bond acidity ($pK_a$) of the molybdenum (IV) hydrazido complexes ([1-H]⁺, [2-H]²⁺, [3-H]³⁺).

By the application of the Bordwell equation (Eq. 1.1),²⁰ the experimentally measured $E^\circ_{\text{red}}$ and $pK_a$ values can be used to determine the free energy change for the diazenido-hydrazido N–H bond-forming event.

$$\text{BDFE} = 1.37pK_a + 23.06E^\circ + C_G$$  \hspace{1cm} (1.1)
Figure 1.5. Thermochemical square scheme and relevant complexes for the determination of free energy of N–H bond formation ($\Delta G_{N-H}$) or bond dissociation (BDFE$_{N-H}$) in bis(phosphine) molybdenum complexes.

**Electrochemistry.** Electrochemical studies were conducted order to establish the reduction potentials of [1-H]$^+$, [2-H]$^{2+}$ and [3-H]$^{2+}$. The cyclic voltammogram of each complex was collected in THF solution at 295 K using 0.1 M [($n$Bu)$_4$N][PF$_6$] as the supporting electrolyte. With [1-H]$^+$ and [2-H]$^{2+}$, irreversible cathodic peaks corresponding to the Mo(IV)/Mo(III) redox couples were observed at -2.03 V and -1.60 V (vs. Fc/Fc$^+$), respectively. In contrast, the cyclic voltammogram of [3-H]$^{2+}$ featured a quasi-reversible cathodic peak assigned to the Mo(IV)/Mo(III) redox couple at -1.32 V (vs. Fc/Fc$^+$). This peak became fully reversible at a scan rate of 500 mV/sec (Figure 1.6). The observed electrochemical behavior of [3-H]$^{2+}$ suggests that the more electron
withdrawing trans ligand (3,5-(CF₃)₂C₆H₃CN) in the putative Mo(III) reduction product, [3-H]⁺ is responsible for the stability on the complex on the timescale of the electrochemical measurement at higher scan rates. No such electrochemical reversibility was observed in the cases of [1-H]⁺ and [2-H]²⁺ at scan rates of up to 1000 mV/sec. The effect of more electron-withdrawing trans ligands thus manifests not only in the significant shift of \(E°_{\text{red}}\) in the series of compounds from -2.03 V in [1-H]⁺ to -1.60 V in [2-H]²⁺ and -1.32 V in [3-H]²⁺ but also serves to stabilize the presumably unstable bis(phosphine) Mo(III) compound [3-H]⁻. Attempts to chemically access the one-electron reduced complexes [1-H], [2-H]⁺, [3-H]⁺ from [1-H]⁺, [2-H]²⁺ and [3-H]²⁺, respectively, using a range of chemical reductants were unsuccessful and resulted in unidentifiable complex mixtures (Figure 1.5). The observed chemical and electrochemical behavior of [1-H]⁺, [2-H]²⁺ and [3-H]²⁺ suggests a general instability of molybdenum(III) hydrazido compounds in the bis(phosphine)-diazenido ligand field.

![Cyclic voltammogram](image)

**Figure 1.6.** Cyclic voltammogram of [3-H]²⁺ using a glassy-carbon working electrode, a platinum wire counter electrode, a silver wire reference electrode, 0.1 M [⁺Bu₄]PF₆, and scan rates of 5, 50 and 500 mV/s in THF at 295K versus Fc/Fc⁺.
Deprotonation Experiments. To experimentally determine, or bracket the acidities of the N-H bonds in the molybdenum(IV) hydrazides [1-H]+, [2-H]2+ and [3-H]2+, deprotonation experiments were performed using bases with known pK_a values.\(^{21}\) Treating [1-H]+ with 1 eq. of 2,4,6-Me3-pyridine (pK_a(THF) = 8.1) at 295 K generated an equilibrium mixture of [1-H]+ and its conjugate base [1] in a 4:1 ratio favouring the acid form as judged by \(^{31}\)P-NMR spectroscopy, supporting a pK_a of 9.3 for [1-H]+.\(^{22}\) In stark contrast, the dicationic complexes [2-H]2+ and [3-H]2+ exhibited markedly more acidic N-H bonds and were fully deprotonated by addition of 2,4,6-Me3-pyridine as well as the weaker base pyridine, establishing the N-H pK_a in these compounds as less than 5.5 in THF at 295 K. In addition, [3-H]2+ underwent quantitative deprotonation to yield [3]+ using 2-MeO-pyridine, establishing the upper limit for the pK_a of the N-H bond as 2.6 in THF at 295 K. The significant lowering of the N-H pK_a values in [2-H]2+ and [3-H]2+ is likely driven by the increased overall charge of the dicationic complexes. In addition, the more electron poor \(trans\) ligands resulted in the more acidic N-H bonds.

Experimental and Computational Determination of N–H BDFEs. Experimentally determined values for the reduction potentials (\(E^{\circ}_{\text{red}}\)) and estimates for the N–H pK_a values in the molybdenum (IV) hydrazido complexes [1-H]+, [2-H]2+, and [3-H]2+ allowed for the determination of N–H BDFEs in the corresponding molybdenum(III) hydrazides (Eq. 1.1). In the case of [1-H], an N-H BDFE value of 32.3 kcal mol\(^{-1}\) was calculated from the Bordwell equation using a value of 66 kcal mol\(^{-1}\) for the constant \(C_G\).\(^{23}\) With [2-H]+ and [3-H]+, given that the N-H pK_a values were determined
as upper bounds, the N-H BDFEs were determined as $< 36.6 \text{ kcal mol}^{-1}$ and $< 39.0 \text{ kcal mol}^{-1}$, respectively.

To gain more accurate insight into the values of the N-H BDFEs, thermochemical DFT calculations were performed on truncated versions of $[1-\text{H}], [2-\text{H}]^+$, and $[3-\text{H}]^+$. For computational expediency, the phenyl groups of the dppe ligand were replaced with methyl groups and the $[\text{BARF}^{24-}]$ counterions were excluded entirely. The DFT computed values of 32.8, 35.4 and 36.2 kcal mol$^{-1}$ in $[1-\text{H}], [2-\text{H}]^+$ and $[3-\text{H}]^+$, respectively, are reported in Table 1.1 and are consistent with the experimentally determined N-H BDFEs.

Several trends are evident from these data. Systematically varying the identity of trans ligand from the X-type $\pi$-donating iodide to the electron poor nitriles CH$_3$CN and 3,5-(CF$_3$)$_2$C$_6$H$_3$CN resulted in anodically shifted oxidation potentials in the complexes between $[1-\text{H}]^+$ and $[3-\text{H}]^{2+}$ ($\Delta E^\circ_{\text{red}} = 0.71 \text{ V}$). However, counteracting this phenomenon is the marked lowering of the N-H $pK_a$ values in the dicationic complexes $[2-\text{H}]^{2+}$ and $[3-\text{H}]^{2+}$, such that the N-H BDFEs in the compound series strengthen marginally between $[1-\text{H}]^+$ and $[3-\text{H}]^{2+}$ ($\Delta\text{BDFE}_{\text{N-H}} = 3.4 \text{ kcal mol}^{-1}$). It is possible that these extraordinarily low N-H BDFEs are the origin of the instability of $[1-\text{H}], [2-\text{H}]^+$ and $[3-\text{H}]^+$ and preclude their isolation.$^{25}$ These results imply that a large thermodynamic driving force, in the form of a strong acid and strong reductant combination, is required to satisfy the Bordwell equation and enable the weak hydrazido N-H bond formation in a hypothetical Chatt-type $N_2$ reduction cycle. This view is consistent with previous computational studies examining the second protonation-reduction step of the Chatt cycle, wherein the protonation of the parent molybdenum(II) diazenide [(dpe)$_2$Mo(NNH)(F)] (dpe = diphosphinoethane) and subsequent reduction to form the corresponding hydrazido
complex [(dpe)₂Mo(NNH₂)(F)] were found to be exergonic ($ΔG_{H^+} = -14.5$ kcal mol⁻¹, $ΔG_e = -16.4$ kcal mol⁻¹) only under strongly acidic and strongly reducing conditions using HBF₄ in Et₂O and decamethylchromocene, respectively.¹² Similarly, previous DFT studies of the second protonation-reduction event of the Schrock catalyst predicted an exergonic ($ΔG_{H^+} = -12.6$ kcal mol⁻¹, $ΔG_e = -5.5$ kcal mol⁻¹) reaction for the stepwise protonation and reduction of [(HIPT)Mo(NNH)] (HIPT = hexaisopropylterphenyl, 3,5-(2,4,6-iPr₃C₆H₂)₂C₆H₃) to form [(HIPT)Mo(NNH₂)] using LutH⁺ (Lut = 2,6-dimethylpyridine) as the proton source and decamethylchromocene reductant, further illustrating the thermodynamic difficulty of the N-H bond forming step en route to molybdenum hydrazides.¹³

Table 1.1. Summary of Thermochemical Data for Molybdenum Hydrazide Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^{\circ}_{\text{red}}$</th>
<th>$pK_a$</th>
<th>$E_{1/2}$</th>
<th>$ΔH$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1-H]^+</td>
<td>-2.03</td>
<td>9.3</td>
<td>32.3</td>
<td>32.8</td>
</tr>
<tr>
<td>[2-H]²⁺</td>
<td>-1.60</td>
<td>&lt; 5.5</td>
<td>&lt; 36.6</td>
<td>35.4</td>
</tr>
<tr>
<td>[3-H]²⁺</td>
<td>-1.32</td>
<td>&lt; 2.6</td>
<td>&lt; 39.0</td>
<td>36.2</td>
</tr>
</tbody>
</table>

¹Peak cathodic potentials (for [1-H]^+ and [2-H]²⁺) and $E_{1/2}$ (for [3-H]²⁺) reported in V relative to Fc/Fc⁺ in THF solution with 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$ as the electrolyte. ²Acidity determined by $^{31}$P-NMR titration against standards in THF. ³Calculated value (kcal mol⁻¹) in THF from the Bordwell equation for the reaction [Mo–NNHR]$^{n+}$ → [Mo–NNR]$^{n+}$ + H⁺ assuming $C_G$(THF) = 66 kcal mol⁻¹. ⁴DFT-calculated value in kcal mol⁻¹ for the reaction [Mo–NNHR]$^{n+}$ → [Mo–NNR]$^{n+}$ + H⁺. Counterions were excluded from the computations, and the dppe ligands were truncated to dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) for computational expediency.
Conclusions

In conclusion, a series of molybdenum(II) diazenides \([(dppe)_{2}\text{Mo}(\text{NNCy})(\text{I})]\), \([(dppe)_{2}(\text{CH}_3\text{CN})\text{Mo}(\text{NNCy})]\)[BArF$_{24}$] and \([(dppe)_{2}(3,5-(\text{CF}_3)_{2}\text{C}_6\text{H}_3\text{CN})\text{Mo}(\text{NNCy})]\)[BArF$_{24}$] have been synthesized and fully characterized. Protonation of each molybdenum diazenido complex with [H(OEt)$_2$][BArF$_{24}$] afforded the corresponding molybdenum(IV) hydrazides \([(dppe)_{2}\text{Mo}(\text{NNHCy})(\text{I})]\)[BArF$_{24}$], \([(dppe)_{2}(\text{CH}_3\text{CN})\text{Mo}(\text{NNHCy})]\)[BArF$_{24}$] and \([(dppe)_{2}(3,5-(\text{CF}_3)_{2}\text{C}_6\text{H}_3\text{CN})\text{Mo}(\text{NNHCy})]\)[BArF$_{24}$]$_2$. The thermochemistry of N–H bond formation in these compounds was studied as a function of ligand (L) \textit{trans} to the diazenido ligand. Deprotonation reactions and electrochemical experiments established that the identity of the \textit{trans} ligand has a pronounced influence on the reduction potential and \(pK_a\) values of the complexes, where the complex with the most \(\pi\)-accepting, electron poor ligand 3,5-(CF$_3$)$_2$C$_6$H$_3$CN is the least reducing metal complex \((E^{\circ}_{\text{red}} = -1.32 \text{ V})\) with the most acidic N–H bond \((pK_a < 2.6)\). A marked shift to more reducing potentials and less acidic N–H bonds is observed upon utilization of CH$_3$CN \((E^{\circ}_{\text{red}} = -1.60 \text{ V}, pK_a < 5.5)\) and I \((E^{\circ}_{\text{red}} = -2.03 \text{ V}, pK_a = 9.3)\) as the \textit{trans} ligands. Computational (DFT) studies support the notion that while the identity of the \textit{trans} ligand has a clear influence on both \(E^{\circ}_{\text{red}}\) and \(pK_a\) independently, these effects work in opposition to afford low net N–H BDFEs of the putative molybdenum(III) hydrazido complex series (32.8 kcal mol$^{-1}$ \((L = \text{I})\), 35.4 kcal mol$^{-1}$ \((L = \text{CH}_3\text{CN})\) and 36.2 kcal mol$^{-1}$ \((L = 3,5-(\text{CF}_3)_{2}\text{C}_6\text{H}_3\text{CN})\)). These results demonstrate the thermochemical obstacles associated with N–H bond formation in classical bis(phosphine) molybdenum diazenides.
Experimental Section

General Considerations

All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures. Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. The compounds [(dppe)$_2$Mo(N$_2$)$_2$] and Na[BArF$_{24}$] were prepared following literature procedures. Cyclohexyl iodide (CyI) was purchased from Sigma-Aldrich, distilled under an atmosphere of argon and stored over 4 Å molecular sieves before use.

$^1$H NMR spectra were recorded on Bruker AVANCE 300 and Bruker AVANCE 500 spectrometers operating at 300.13 and 500.62 MHz respectively. $^{13}$C NMR spectra were recorded on a Bruker AVANCE 500 operating at 125.89 MHz. All $^1$H and $^{13}$C chemical shifts are reported relative to SiMe$_4$ using the $^1$H (residual) and $^{13}$C chemical shifts of the solvent as a secondary standard. $^{31}$P NMR spectra were collected on a Bruker 500 AVANCE spectrometer operating at 202.40 MHz and were referenced to 85% H$_3$PO$_4$ as an external standard. $^{19}$F NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 282.23 MHz and were referenced to CFCl$_3$ as an external standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.
Cyclic voltammograms (CVs) were collected in THF solution (1 mM in compound) with [Bu4N][PF6] (0.1 M), using a 3 mm glassy carbon working electrode, platinum wire as the counter electrode, and silver wire as the reference in a drybox equipped with electrochemical outlets. CVs were recorded using a BASi EC Epsilon electrochemical workstation and analyzed using the BASi Epsilon-EC software. All CVs were run at a scan rate of 100 mV/s at 295 K. Potentials are reported versus Fc/Fc+ and were obtained using the in situ method.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker D8 APEX3 Venture diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å) and a Cu X-ray tube (λ = 1.54178 Å). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Gouy magnetic susceptibility balance measurements were performed with a Johnson Matthey instrument that was calibrated with HgCo(SCN)4. Continuous wave EPR spectra were recorded at room temperature or at 10K on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.
**Computational Studies.** All DFT calculations were performed with the ORCA program package in the gas phase. The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT. The all-electron Gaussian basis sets were those developed by the Ahlrichs group. Triple-ζ quality basis sets def2-TZVP with one set of polarization functions on molybdenum, phosphorous and nitrogen were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used that were of double-ζ quality in the valence region and contained a polarizing set of d functions on the non-hydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX) approach were chosen to match the orbital basis. Numerical frequencies were calculated at the same level of theory to confirm the optimized geometries (no imaginary frequencies) and to derive thermochemical data. Bond dissociation free energies were computed at standard conditions of 1 atm and 25 °C including corrections for vibrational zero-point energy, as well as contributions from translational, rotational, and vibrational modes to the energy and entropy of the homolytic bond cleavage process. For molecules containing a molybdenum atom, the 0th order regular approximation (ZORA) was applied. In this case, the relevant basis sets were replaced by their relativistically recontracted versions. In the geometry optimizations and numerical frequency calculations on molybdenum complexes, counterions were excluded from the computations, and the dppe ligands were truncated to dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) for computational expediency. The electronic energy of H•, utilized in the calculation of bond dissociation free energies, at the present level of theory is 13.576 eV (313.1 kcal/mol).
Preparation of Molybdenum Complexes

Modified Preparation of [1]. A 250 mL round-bottom flask was charged with 0.500 g (0.527 mmol) of [(dppe)\textsubscript{2}Mo(N\textsubscript{2})\textsubscript{2}], 0.123 g (0.585 mmol) of cyclohexyl iodide and 100 mL of benzene. The orange solution was stirred under ambient conditions for 2 days, during which time the color of the solution changed from orange to ruby. After the concentration of the solution \textit{in vacuo} to approximately 25 mL, 100 mL of pentane was added, inducing the precipitation of yellow solids. The solids were isolated on a 20 mL medium porosity frit, washed with pentane (3 x 10 mL) and dried \textit{in vacuo} to afford the product as orange solids (0.520 g, 0.460 mmol, 87%). Crystals suitable for X-Ray diffraction studies were obtained by the vapor diffusion of pentane onto a concentrated solution of benzene at room temperature. \textit{Note:} In our hands, UV irradiation of the reaction mixture according to the previous literature report resulted in unidentified complex mixtures with no desired product formation.\textsuperscript{15}

Preparation of [1-H]+. A 20 mL scintillation vial was charged with 0.100 g (0.088 mmol) of [1] and 10 mL of THF. To the orange solution, 0.098 g (0.097 mmol) of \textsubscript{2}[H(OEt\textsubscript{2})\textsubscript{2}]\textsubscript{2}BArf\textsuperscript{24} dissolved in 5 mL THF was added, accompanied by an immediate color change from orange to green-yellow. After 15 minutes of stirring, the solution was concentrated to a minimal volume and excess pentane (10 mL) was added to induce the precipitation of solids. The solids were isolated on a 10 mL medium porosity frit, washed with pentane and dried \textit{in vacuo} to yield the product as yellow-green solids (0.146 g, 0.073 mmol, 83%). Anal Calcd for C\textsubscript{90}H\textsubscript{72}BF\textsubscript{24}IMoN\textsubscript{2}P\textsubscript{4}: C, 54.18; H, 3.64; N, 1.40.
Found: C, 54.29; H, 3.24; N, 1.204. $^1$H NMR (THF-$d_8$, 295 K): $\delta$ 9.26 (s, 1H, N-NHC$_6$H$_{11}$), 7.79 (br s, 8H, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 7.57 (s, 4H, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 7.51-7.44 (m, 8H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$ overlap with 4H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 7.36 (t, $J = 7.5$ Hz, 8H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 7.31-7.26 (m, 8H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$ overlap with 4H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 7.08 (t, $J = 7.6$ Hz, 8H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 3.39-3.33 (m, 4H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 2.89-2.81 (m, 4H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 1.33-1.28 (m, 2H, N-NHC$_6$H$_{11}$), 1.27-1.16 (m, 4H, N-NHC$_6$H$_{11}$), 0.84 (br s, 1H, N-NHC$_6$H$_{11}$), 0.68-0.60 (m, 2H, N-NHC$_6$H$_{11}$), -0.05-(-0.12) (m, 2H, N-NHC$_6$H$_{11}$). $^{13}$C NMR (THF-$d_8$, 295 K): $\delta$ 162.54 (q, $^1$J$_{C-B} = 49.8$ Hz, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 135.44 (app p, $J = 11.3$ Hz, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 135.33 (s, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 134.67 (app dt, $J = 15.6$, 7.6 Hz, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 133.97 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 133.86 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 131.53 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 130.52 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 129.75 (qq, $^2$J$_{C-F} = 32.7$, 3.7 Hz, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 129.53 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 128.60 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 125.24 (q, $^1$J$_{C-F} = 272.2$ Hz, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 117.92 (s, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 32.88 (s, N-NHC$_6$H$_{11}$), 28.93 (app p, $J = 9.4$ Hz, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 26.21 (s, N-NHC$_6$H$_{11}$), 25.65 (s, N-NHC$_6$H$_{11}$), 24.96 (s, N-NHC$_6$H$_{11}$). $^{1}$H NMR (THF-$d_8$, 295 K): $\delta$ 38.40 (s). $^1$H $^{19}$F NMR (THF-$d_8$, 295 K) $\delta$ -63.44 (s). IR (KBr, 295 K, cm$^{-1}$): 3300 (NNHC$_6$H$_{11}$).

**Preparation of [2]**. A 20 mL scintillation vial was charged with 0.213 g (0.188 mmol) of [1] dissolved in 5 mL of toluene. To the stirring orange solution, 0.184 g (0.207 mmol)
Na[BArF$^{24}$] dissolved in 1 mL of acetonitrile was added. The solution was thus stirred at ambient conditions for 18 hours, during which time the color of the solution changed to dark yellow-brown with the concomitant formation of a precipitate. The mixture was filtered through a pad of Celite and the filtrate was concentrated to approximately 3 mL. Excess pentane (10 mL) was then added to induce the precipitation of yellow solids. The solids were isolated on a 20 mL medium porosity frit, washed with pentane (3 x 3 mL) and dried *in vacuo* to yield the product as an off-yellow solid (0.273 g, 0.143 mmol, 76%). Crystals suitable for X-Ray diffraction studies were obtained by the vapor diffusion of pentane onto a concentrated solution of benzene at room temperature. Anal Calcd for C$_{92}$H$_{14}$BF$_{24}$MoN$_{3}$P$_{4}$: C, 57.91; H, 3.91; N, 2.20. Found: C, 57.75; H, 3.50; N, 1.94. $^1$H NMR (THF-$d_8$, 295 K): $\delta$ 7.79 (br s, 8H, B[(3,5-(CF$_3$)$_2$]C$_6$H$_3$)$_4$), 7.74-7.72 (m, 8H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 7.58 (s, 4H, B[(3,5-(CF$_3$)$_2$]C$_6$H$_3$)$_4$), 7.41 (t, $J = 7.4$ Hz, 4H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 7.30 (t, $J = 4.9$ Hz, 4H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 7.28 (t, $J = 7.6$ Hz, 8H, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 6.72-6.71 (m, 1.39-1.35 (m, 2H, N=NC$_6$H$_11$), 1.31-1.23 (m, 4H, N=NC$_6$H$_11$), 1.10 (s, 3H, CH$_3$CN), 1.02-0.94 (m, 1H, N=NC$_6$H$_11$), 0.91-0.85 (m, 2H, N=NC$_6$H$_11$), 0.73-0.66 (m, 2H, N=NC$_6$H$_11$). $^1$H$^{13}$C NMR (THF-$d_8$, 295 K): $\delta$ 162.63 (q, $^1J_{C,H} = 49.8$ Hz, B[(3,5-(CF$_3$)$_2$]C$_6$H$_3$)$_4$), 139.61–139.29 (m, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 135.56 (app d, $J = 7.4$ Hz, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 135.41 (s, B[(3,5-(CF$_3$)$_2$]C$_6$H$_3$)$_4$), 134.53 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 133.25 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 132.46 (s, CH$_3$CN), 130.90 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 130.14 (s, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$), 129.83
Preparation of \([2\text{-H}]^{3+}\). A 20 mL scintillation vial was charged with 0.131 g (0.069 mmol) of \([2\text{-H}]^{+}\) dissolved in 10 mL of THF. To the stirring yellow solution, 0.073 g (0.072 mmol) of [H(OEt)₂][BArF²⁴] dissolved in 1 mL THF was added and was stirred at ambient conditions for 15 minutes. The solution was then concentrated to a minimal volume in vacuo, excess pentane (15 mL) was added and the mixture stood at -30°C for 15 minutes. A brown oil was observed, and upon decantation of the faint yellow supernatant, the oil was triturated with pentane (5 x 5 mL) to afford an off-yellow solid (124 mg, 0.045 mmol, 65% yield). Anal Calcd for C₁₂₄H₈₇B₂F₄₈MoN₅₃P₄: C, 53.72; H, 3.16; N, 1.52. Found: C, 53.89; H, 3.34; N, 1.11. ¹H NMR (THF-\(d₈\), 295 K): δ 8.31 (br s, 1H, N-NHC₆H₁₁), 7.79 (br s, 16H, B[(3,5-(CF₃)₂]C₆H₃)₄], 7.61 (t, \(J = 10.0\) Hz, 4H, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂), 7.57 (s, 8H, B[(3,5-(CF₃)₂]C₆H₃)₄], 7.51 (br s, 8H, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂), 7.45 (q, \(J = 7.2\) Hz, 8H, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂), overlap with 4H, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂), 7.25 (t, \(J = 10.0\) Hz, 8H, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂), 6.85 (br s, 8H, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂), 3.26-3.20 (m, 4H, (C₆H₅)₂PCH₃CH₂P(C₆H₅)₂), 2.92-2.85 (m, 4H, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂), 1.45-1.40 (m, 2H, N-NHC₆H₁₁), 1.32 (s, 3H, CH₃CN), 1.31-1.24 (m, 4H, N-NHC₆H₁₁), 0.84-0.77
Preparation of [3]⁺. A 20 mL scintillation vial was charged with 0.165 g (0.146 mmol) of [1], 26 µL (0.153 mmol) of 3,5-(CF₃)₂C₆H₃CN and 8 mL of toluene. To the stirring solution, 0.142 g (0.160 mmol) of Na[BArF₂₄] was added, prompting an immediate color change to dark maroon. The solution was thus stirred at ambient conditions for 30 minutes. The mixture was then filtered through a pad of Celite, and the filtrate was concentrated to approximately 3 mL. Excess pentane (10 mL) was added to induce the precipitation of solids at ambient conditions over 15 minutes. The faint yellow supernatant was decanted, the solids were washed with pentane (3 x 3 mL) and dried in vacuo to yield the product as dark maroon solids (185 mg, 0.088 mmol, 60%). Crystals suitable for X-Ray diffraction studies were obtained by recrystallization from a
concentrated solution of benzene at room temperature. Anal Calcd for
C\textsubscript{90}H\textsubscript{74}BF\textsubscript{30}MoN\textsubscript{3}P\textsubscript{4}: C, 56.45; H, 3.54; N, 1.99. Found: C, 56.51; H, 3.47; N, 1.87. \textsuperscript{1}H NMR (THF-\textit{d}_8, 295 K): \textit{\delta} 8.38 (s, 1H, 3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CN), 7.80 (br s, 8H, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3}]\textsubscript{4}), 7.74 (m, 8H, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 7.58 (br s, 4H, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3}]\textsubscript{4}), 7.45 (t, \textit{J} = 7.3 Hz, 4H, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 7.32 (t, \textit{J} = 7.4 Hz, 8H, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 7.27 (t, \textit{J} = 7.3 Hz, 4H, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 7.08 (t, \textit{J} = 7.4 Hz, 8H, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 6.87 (br s, 8H, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 6.61 (s, 2H, 3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CN), 3.01-2.81 (m, 4H, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 2.73-2.60 (m, 4H, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 1.44-1.37 (m, 2H, N=NC\textsubscript{6}H\textsubscript{11}), 1.32-1.25 (m, 4H, N=NC\textsubscript{6}H\textsubscript{11}), 1.05-0.95 (m, 1H, N=NC\textsubscript{6}H\textsubscript{11}), 0.95-0.87 (m, 2H, N=NC\textsubscript{6}H\textsubscript{11}), 0.78-0.68 (m, 2H, N=NC\textsubscript{6}H\textsubscript{11}). \textsuperscript{1}H\textsuperscript{13}C NMR (THF-\textit{d}_8, 295 K): \textit{\delta} 162.63 (q, \textit{J}_{C,B} = 49.8 Hz, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3}]\textsubscript{4}), 139.30–139.05 (m, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 135.56 (app d, \textit{J} = 7.7 Hz, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 135.41 (s, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3}]\textsubscript{4}), 134.48 (s, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 133.22 (s, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 133.06 (q, \textit{J}_{C,F} = 34.4 Hz, 3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CN), 132.08 (s, 3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CN), 131.16 (s, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 130.86 (s, 3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CN), 130.46 (s, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 129.83 (qq, \textit{J}_{C,F} = 31.5, 2.9 Hz, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3}]\textsubscript{4}), 129.43 (s, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 129.12 (s, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 128.93 (br s, 3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CN), 125.32 (q, \textit{J}_{C,F} = 272.3 Hz, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3}]\textsubscript{4}), 122.96 (q, \textit{J}_{C,F} = 273.2 Hz, 3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CN), 118.0 (s, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3}]\textsubscript{4}), 111.34 (s, 3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}CN), 33.41 (s, N=NC\textsubscript{6}H\textsubscript{11}), 29.09 (app p, \textit{J} = 9.5 Hz, (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}), 25.78 (s, N=NC\textsubscript{6}H\textsubscript{11}), 25.62 (s, N=NC\textsubscript{6}H\textsubscript{11}), 24.70 (s, N=NC\textsubscript{6}H\textsubscript{11}). \textsuperscript{1}H\textsuperscript{31}P NMR (THF-\textit{d}_8, 295 K): \textit{\delta} 62.93 (s). \textsuperscript{1}H\textsuperscript{19}F NMR (THF-
\(d_8, 295 \text{ K}\) \(\delta -63.43 \text{ (s, 24F, } B[(3,5-(CF_3)_2)C_6H_3]_4), -63.82 \text{ (s, 6F, } 3,5-(CF_3)_2C_6H_3CN). \) IR (KBr, 295 \(\text{K}, \text{ cm}^{-1}) : 2223 \text{ (3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3\text{CN}), 1558 \text{ (N=CN).}

**Preparation of [3-H]^{2+}**. A 20 mL scintillation vial was charged with 0.100 g (0.047 mmol) of [3\(^+\)] dissolved in 5 mL of THF. To the stirring maroon solution, 0.049 g (0.048 mmol) of [H(OEt\(_2\)]_2[BArF\(_{24}\)] dissolved in 1 mL THF was added and was stirred at ambient conditions for 15 minutes. The solution was then concentrated to a minimal volume *in vacuo*, excess pentane (15 mL) was added and the mixture stood at -30\(^\circ\)C for 15 minutes. A brown oil was observed, and upon decantation of the faint yellow supernatant, the oil was triturated with pentane (5 x 5 mL) to afford the product as a yellow-brown solid (113 mg, 0.038 mmol, 80% yield). Anal Calcd for C\(_{131}\)H\(_{87}\)B\(_2\)F\(_{54}\)MoN\(_3\)P\(_4\): C, 52.97; H, 2.95; N, 1.41. Found: C, 52.75; H, 2.75; N, 1.38. 

\(^1\)H NMR (THF-\(d_8\), 295 K): \(\delta 8.68 \text{ (s, 1H, } 3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3\text{CN), 8.61 \text{ (br s, 1H, } N=NH\text{C}_6\text{H}_11\text{), } 7.79 \text{ (br s, 16H, } B[(3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3\text{]}_4\text{), 7.65 \text{ (t, } J = 7.4 \text{ Hz, 4H, } (C_6H_5)\text{)}_2PCH_2CH_2P(C_6H_5)\_2\text{), 7.57 \text{ (br s, 8H, } B[(3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3\text{]}_4, \text{ overlap with 8H, } (C_6H_5)\text{)}_2PCH_2CH_2P(C_6H_5)\_2\text{), 7.47 \text{ (t, } J = 7.6 \text{ Hz, 8H, } (C_6H_5)\text{)}_2PCH_2CH_2P(C_6H_5)\_2\text{), 7.44 \text{ (t, } J = 7.4 \text{ Hz, 4H, } (C_6H_5)\text{)}_2PCH_2CH_2P(C_6H_5)\_2\text{), 7.20 \text{ (t, } J = 7.6 \text{ Hz, 8H, } (C_6H_5)\text{)}_2PCH_2CH_2P(C_6H_5)\_2\text{), 7.01 \text{ (br s, 8H, } (C_6H_5)\text{)}_2PCH_2CH_2P(C_6H_5)\_2\text{), 6.62 \text{ (s, 2H, } 3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3\text{CN), 3.44-3.31 \text{ (m, 4H, } (C_6H_5)\text{)}_2PCH_2CH_2P(C_6H_5)\_2\text{), 3.01-2.90 \text{ (m, 4H, } (C_6H_5)\text{)}_2PCH_2CH_2P(C_6H_5)\_2\text{), 1.46-1.40 \text{ (m, 2H, } N-NHC_6H_11\_1\text{), 1.37-1.29 \text{ (m, 4H, } N-NHC_6H_11\_1\text{), 0.84-0.76 \text{ (m, 1H, } N-NHC_6H_11\_1\text{), 0.75-0.69 \text{ (m, 2H, } N-NHC_6H_11\_1\text{), 0.65-0.58 \text{ (m, 2H, } N-NHC_6H_11\_1\text{). }} \) \(^1\)\(H\)\(^{13}\)C NMR (THF-\(d_8\), 295 K): \(\delta 162.52 \text{ (q, } 1^J_{C=\text{B}} = 49.8 \text{ Hz, } B[(3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3\text{]}_4\text{), 135.31 \text{ (s, } B[(3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3\text{]}_4\text{), 134.38 \text{ (s,}

}
\((\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\), 134.16 (s, (\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 133.77 (s,
\((\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 133.01 (s, 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{CN}), 132.37 (s, Hz,
\((\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 130.34 (s, (\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 129.74 (qq,
\((\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 129.01 (s, (\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 128.71 (br s, 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{CN}), 125.22 (q,
\((\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 122.45 (q, 1^J\text{C:F} = 274.4 \text{ Hz}, 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{CN}), 117.91 (br s,
\((\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 108.64 (s, 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{CN}), ),
33.08 (s, N-NHC\text{C}_6\text{H}_{11}), 28.41 (app p, J = 11.3 \text{ Hz}, (\text{C}_6\text{H}_5)\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2), 25.37 (s,
N-NHC\text{C}_6\text{H}_{11}), 24.80 (s, N-NHC\text{C}_6\text{H}_{11}), 22.91 (s, N-NHC\text{C}_6\text{H}_{11}). \text{\{}^1\text{H}\text{\}}^{31}\text{P} \text{NMR (THF-}d_8, 295 \text{ K): } \delta 55.69 (s). \text{\{}^1\text{H}\text{\}}^{19}\text{F} \text{NMR (THF-}d_8, 295 \text{ K) } \delta -63.39 (s, 48F, B[(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4], -63.81 (s, 6F, 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{CN}). \text{IR (KBr, 295 K, cm}^{-1}): 3251
(\text{NNHC}_6\text{H}_{11}).\)
Additional Electrochemical Data

Figure 1.7. Cyclic voltammogram of [1-H]+ using a glassy carbon working electrode, platinum wire counter electrode, silver wire reference electrode, 0.1 M ["Bu4N][PF_6], scan rate 100 mV/sec in THF at 295 K versus Fe/Fe+. *Denotes minor impurity.

Figure 1.8. Cyclic voltammogram of [2-H]+ using a glassy carbon working electrode, platinum wire counter electrode, silver wire reference electrode, 0.1 M ["Bu4N][PF_6], scan rate 100 mV/sec in THF at 295 K versus Fe/Fe+.
DFT Input Examples

Geometry Optimizations: [{\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2}_2\text{Mo(NNC}_6\text{H}_{11})\text{I}}]

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  NewGTO 7 "def2-TZVP(-f)" end
  NewGTO 15 "def2-TZVP(-f)" end
  NewGTO 53 "def2-TZVP(-f)" end
  NewAuxGTO 42 "def2-TZVP/J" end
  NewAuxGTO 7 "def2-TZVP/J" end
  NewAuxGTO 15 "def2-TZVP/J" end
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end

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  TolErr 1e-6
end

* xyz 0 1

XYZ Coordinates

*
Numerical Frequency Calculations: [[(Me_2PCH_2CH_2PMe_2)_2Mo(NNC_6H_11)(I)]]

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NORMALPRINT NUMFREQ GRID4 NOFINALGRID PAL8 ZORA

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   NewGTO 7 "def2-TZVP(-f)" end
   NewGTO 15 "def2-TZVP(-f)" end
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   NewAuxGTO 42 "def2-TZVP/J" end
   NewAuxGTO 7 "def2-TZVP/J" end
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end

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   TolErr 1e-6
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%FREQ RESTART TRUE
CENTRALDIFF TRUE
INCREMENT 0.01
END

* xyz 0 1

XYZ Coordinates from Geometry Optimization

*
References


22 In the general case where $B_1 + HB_2^+ \rightarrow HB_1^+ + B_2$ is satisfied and $pK_a(B_1)$ is known, $pK_a(B_2)$ can be calculated according to the relation: $\Delta pK_a = \log([HB_2][B_1])/([HB_1][B_2])$.

23 The constant $C_G$ includes the free energy of H• formation ($\Delta G_f^\circ(H•) = 48.6$ kcal mol$^{-1}$) and the free energy solvation of H• in the solvent system used. For a review on related thermochemical background, see: Warren, J. J.; Tronic, T. A.; Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961–7001.


25 Such low N–H bonds strengths imply, at the very least, thermodynamic instability towards H$_2$ loss ($\Delta G_f^\circ(H•) = 48.6$ kcal mol$^{-1}$) in these complexes. We have not observed H$_2$ evolution from these systems, suggesting that the Mo(III) hydrazido complexes decompose via other (likely more rapid) pathways.
CHAPTER 2

Terpyridine Molybdenum \( \text{N}_2 \) Chemistry: Synthesis of Dinitrogen Complexes that Vary by Five Oxidation States.*

Abstract

A bimetallic molybdenum complex bridged by an activated dinitrogen ligand and supported by phosphine and terpyridine ligands, \[ \{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}\}_2(\mu_2-\text{N}_2)\][\text{BArF}^{24}]_2, (\text{PhTpy} = 4'-\text{Ph}-2,2',6',2''-\text{terpyridine}; \text{ArF}^{24} = (\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2)_4) \] was synthesized, structurally characterized and its electronic structure determined using a combination of experimental and DFT computational methods. Each molybdenum atom is best described as Mo(II) bridged by a modestly activated \([\text{N}_2]^{2-}\) ligand. The cyclic voltammogram of \[ \{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}\}_2(\mu_2-\text{N}_2)\] displays two reversible reductive and two reversible oxidative features, prompting the preparation and characterization of a series of molybdenum dinitrogen compounds spanning five oxidation states \[ \{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}\}_2(\mu_2-\text{N}_2)\][\text{BArF}^{24}]_n, n = 4, 3, 2, 1, 0. \] Vibrational Raman and \(^{15}\text{N}\) NMR spectroscopic data establish that the bridging nitrogen ligand remains intact across the redox series. EPR spectroscopy was used to probe the nature of the unpaired electron in the mixed-valent one electronic oxidized and reduced products. The SOMO is principally metal-based in \[ \{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}\}_2(\mu_2-\text{N}_2)\] and ligand localized in \[ \{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}\}_2(\mu_2-\text{N}_2)\].

Introduction

The synthesis of ammonia from its elements, $\text{N}_2$ and $\text{H}_2$ under energy efficient, carbon neutral conditions is one of the longest standing challenges in chemical synthesis. Soluble metal complexes offer the opportunity to study fundamental transformations relevant to these ambitious goals, enabling manipulation of reactivity through rational ligand design. Among transition metals, molybdenum has played a pivotal role owing to the variable oxidation states and accessibility of appropriate $d$-orbitals to accommodate coordination of $\text{N}_2$, amide, imide, diazenide and nitride ligands. Molybdenum coordination complexes were also among the first demonstrated examples of $\text{N}_2$ cleavage to metal-nitrides under mild conditions in solution.

Inspired by the structure of the nitrogenase FeMo (M) cofactor that contains both Fe and Mo atoms, considerable attention has been devoted to the development of molybdenum complexes for catalytic ammonia synthesis. Seminal studies from Chatt and Hidai demonstrated stoichiometric protonation of phosphine supported molybdenum and tungsten dinitrogen complexes to yield both ammonia and hydrazine (Figure 2.1). Synthesis and characterization of various intermediates along the $\text{N}_2$ fixation pathway resulted in the “Chatt cycle” – a blueprint for ammonia synthesis invoking a Mo(0)-Mo(III) redox cycle. Schrock and coworkers later modified this approach with tri(amido)amine molybdenum platforms and achieved the first catalytic synthesis of $\text{NH}_3$ from $\text{N}_2$ using protons and electrons. Characterization of many intermediates and catalytic entry points established a Mo(III)-Mo(VI) cycle, owing to the trianionic supporting ligand (Figure 2.1).
Figure 2.1. Notable molybdenum dinitrogen complexes relevant to ammonia synthesis or N\textsubscript{2} cleavage.

In 2010, Nishibayashi and coworkers\textsuperscript{28} reported a “PNP”-pincer supported molybdenum dinitrogen complex that was active for catalytic ammonia synthesis, again using controlled addition of sources of protons and electrons. This observation along with subsequent catalyst improvements and mechanistic studies have revived interest in Mo(0)-Mo(III) cycles for nitrogen fixation.\textsuperscript{29,30,31,32} These findings were also significant for demonstrating the utility of modular, meridionally coordinating pincer ligands in dinitrogen functionalization, a significant departure from the intense emphasis on \textit{C}\textsubscript{3} symmetric metal coordination environments (Figure 2.1).\textsuperscript{33}

Inspired by these findings, we initiated a program exploring the role of redox-active, tridentate pincers in early transition metal dinitrogen chemistry with the goal of applying cooperative metal-ligand redox events to lower barriers to M-NH\textsubscript{2} hydrogenolysis.\textsuperscript{34} As part of this effort, the aryl-substituted bis(imino)pyridine
molybdenum dinitrogen complex, [(iPrBPDI)Mo(N$_2$)$_2$(µ$_2$-N$_2$)], (iPrBPDI = 2,6-(2,6-iPr$_2$-C$_6$H$_3$N=CPh)$_2$C$_5$H$_3$N) was synthesized.$^{35}$ In contrast to the strong field PNP pincer complexes where all five dinitrogen ligands are weakly activated, the bridging N$_2$ ligand in [(iPrBPDI)Mo(N$_2$)$_2$(µ$_2$-N$_2$)] exhibits an N-N bond distance of 1.246(4) Å, consistent with an [N$_2$]$^{2-}$ ligand. Thus, the redox-active and more electron withdrawing bis(imino)pyridine chelate supports coordination of two fewer terminal N$_2$ ligands and resulted in stronger activation of the bridging dinitrogen unit.

Figure 2.2. Synthesis of a bis(imino)pyridine molybdenum dinitrogen complex and its reaction with ammonia.

Despite ground state activation of the µ$_2$-N$_2$ ligand, [(iPrBPDI)Mo(N$_2$)$_2$(µ$_2$-N$_2$)] has proven inactive for catalytic ammonia synthesis. One limitation is the incompatibility of ammonia with [(iPrBPDI)Mo(N$_2$)$_2$(µ$_2$-N$_2$)] as addition of NH$_3$ resulted in formation of a bridging imido complex arising from partial dehydrogenation and the chemical non-innocence of the bis(imino)pyridine ligand (Figure 2.2). In an attempt to prevent these pathways, the chemistry of molybdenum complexes supported by 2,2',6',2''-terpyridine
(Tpy) pincer ligands was targeted. This class of chelates is also attractive due to an ease of preparation and established redox activity\textsuperscript{36,37,38,39} which may enable unique reactivity relevant to N\textsubscript{2} fixation. Although bis(chelate), bis(terpyridine) molybdenum complexes are known and exhibit rich electrochemistry, dinitrogen complexes of this ligand class are unknown. Here we describe the synthesis and characterization of a bimetallic molybdenum system bridged by an activated dinitrogen ligand and supported by a mixed terpyridine-phosphine ligand environment, [{(PhTpy)(PPh\textsubscript{2}Me)\textsubscript{2}Mo}\textsubscript{2}(\mu\textsubscript{2}-N\textsubscript{2})][BArF\textsubscript{24}]\textsubscript{2}, (PhTpy = 4’-Ph-2,2’,6’,2’’-terpyridine). This compound undergoes two reversible oxidation and reduction events and has enabled the synthesis of family of bridging molybdenum dinitrogen complexes over five oxidation states. While three-compound redox-series of iron\textsuperscript{40,41} and cobalt\textsuperscript{42} dinitrogen complexes have been prepared, to our knowledge this is the first example of a homogeneous metal-ligand system where a bridging dinitrogen ligand remains intact across five oxidation states.

Results and Discussion

Synthesis and Characterization of [{(PhTpy)(PPh\textsubscript{2}Me)\textsubscript{2}Mo}\textsubscript{2}(\mu\textsubscript{2}-N\textsubscript{2})][BArF\textsubscript{24}]\textsubscript{2}. Our studies commenced with the synthesis of (PhTpy)MoCl\textsubscript{3}, an S = 3/2 teal solid obtained in 94% isolated yield from straightforward addition of the free chelate to (THF)\textsubscript{3}MoCl\textsubscript{3} in THF. To prevent formation of unwanted bis(chelate) molybdenum compounds, reduction of (PhTpy)MoCl\textsubscript{3} was carried out in the presence of phosphine ligands. Stirring a THF slurry of (PhTpy)MoCl\textsubscript{3} with two equivalents of 1% Na(Hg) at room temperature for 3 hours in the presence of two equivalents of PPh\textsubscript{2}Me yielded a forest green paramagnetic,
NMR silent solid identified as the octahedral molybdenum chloride derivative, 
\[ ([^{Ph}Tpy](PPh_2Me)_2Mo(Cl)] \ (1-Cl); Figure 2.3). Attempts to repeat the synthesis with 
PPh_3 in place of PPh_2Me have been unsuccessful and resulted in an intractable mixture of 
products.

Figure 2.3. Synthesis of [1-Cl] and [1-N_2]^2+.

The solid-state structure of [1-Cl] was determined by X-ray diffraction and 
established idealized octahedral coordination environment around the molybdenum with 
trans phosphine ligands (Figure 2.4). The interpyridine C_{py}-C'_{py} bond distances (C_5-C_6 
and C_{10}-C_{11} in Figure 2.4) in the terpyridine have been used as experimental reporters for 
redox activity, particularly in coordination compounds of chromium.\textsuperscript{38} While the values 
of 1.455(11) Å and 1.450(11) Å measured in [1-Cl] are consistent with one electron 
terpyridine reduction (Table 2.1), extensive experimental and computational studies by 
Wieghardt on (Tpy)_2M (M = Mo, W) compounds have established a high degree of 
covalency with second and third row metals complicating strict integer oxidation state 
assignments to both the ligand and the metal. No direct spectroscopic evidence was 
obtained for ligand radicals and broken symmetry solutions were not obtained in 
computational studies. It is likely that in [1-Cl], a similar situation arises and the
observed distortions to the terpyridine are a result of π-backbonding such that assignment of the compound in its formal Mo(I) oxidation state is appropriate.

Figure 2.4. Representation of the solid state structure of [1-Cl] at 30% probability ellipsoids. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Mo-N1: 2.138 (6), Mo-N2: 2.031 (6), Mo-N3: 2.121 (6), N1-C5: 1.386 (10), C5-C6: 1.455 (11), C6-N2: 1.394 (9), N2-C10: 1.376 (9), C10-C11: 1.450 (11), C11-N3: 1.377 (10), Mo1-Cl1: 2.494 (3), Mo1-P1: 2.473 (2), Mo1-P2: 2.480 (2), N1-Mo1-N2: 75.8 (2), N1-Mo1-N3: 151.4 (2), N2-Mo1-N3: 75.6 (2), N2-Mo1-Cl1: 177.2 (2) and P1-Mo1-P2: 172.97 (7).
Table 2.1. Selected terpyridine chelate bond metrics (Å) for [1-Cl] and analogous averaged bond distances for [(Tpy\textsuperscript{0})\textsubscript{2}Cr][PF\textsubscript{6}], [(Tpy\textsuperscript{1})\textsubscript{2}Cr][PF\textsubscript{6}] and [(Tpy\textsuperscript{2})\textsubscript{2}Mo].\textsuperscript{38}

<table>
<thead>
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<th>[1-Cl]</th>
<th>[(Tpy\textsuperscript{0})\textsubscript{2}Cr][PF\textsubscript{6}]</th>
<th>[(Tpy\textsuperscript{1})\textsubscript{2}Cr][PF\textsubscript{6}]</th>
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Magnetic and spectroscopic measurements were also carried out on [1-Cl] to gain additional insight into the electronic structure of the compound. A solid-state magnetic moment of 1.7 µB (magnetic susceptibility balance) was measured at 295 K consistent with an $S = 1/2$ ground state. Accordingly, the X-band EPR spectrum of the compound recorded in fluid benzene solution at 295 K (Figure 2.5) exhibits an isotropic signal ($g_{iso} = 1.977$) with hyperfine coupling to two 100% abundant $I = 1/2$ phosphorous atoms ($A_{iso}(^{31}P) = 49$ MHz) as well as to $^{95}$Mo and $^{97}$Mo ($A_{iso}(^{95/97}Mo) = 125$ MHz, $I = 5/2$, 15.92% $^{95}$Mo and 9.55% $^{97}$Mo). The deviation of the $g$ value from the free electron value ($g = 2.002$) as well as the hyperfine coupling pattern suggest that the singly occupied molecular orbital (SOMO) of [1-Cl] is molybdenum- rather than ligand-based. The combined structural and computational data support a low spin Mo(I) complex. An alternative possibility is a high spin Mo(II) center ($S_{Mo} = 1$) engaged in antiferromagnetic...
coupling with a terpyridine radical anion ($S_{\text{Tpy}} = 1/2$), however the inability to locate a broken symmetry (2,1) solution by DFT argues against this possibility.\textsuperscript{38}

\textbf{Figure 2.5.} X-band EPR spectrum of [1-Cl] recorded benzene solution at 295 K. Microwave frequency = 9.380 GHz, power = 0.063 mW, modulation amplitude = 4.000 G. Simulated parameters; $g_{\text{iso}} = 1.977$, $g_{\text{iso}}$ strain = 0.005, $A_{\text{iso}}$ ($^{95/97}\text{Mo}$) = 125 MHz (assuming 15.92\% naturally occurring $^{95}\text{Mo}$ and 9.55\% $^{97}\text{Mo}$), $A_{\text{iso}}$ ($^{31}\text{P}$) = 49 MHz (assuming 2 equivalent 100\% naturally occurring $^{31}\text{P}$ nuclei with $I = 1/2$), Gaussian broadening = 0.89 mT.

Attempts to reduce [1-Cl] to a formally Mo(0) terpyridine bis(phosphine) dinitrogen compound using a wide range of chemical reductants were unsuccessful resulting in unidentifiable product mixtures with release of free phosphine. Chloride ion abstraction was then pursued as a possible entry point into dinitrogen chemistry. Stirring of a toluene solution of [1-Cl] with one equivalent of Na[BArF\textsuperscript{24}] for 18 hours at ambient temperature under a dinitrogen atmosphere resulted in precipitation of a diamagnetic maroon solid. Single crystal X-ray diffraction (Figure 2.6) established the
identity of the product as the dicationic molybdenum dinitrogen compound,
\[ \{(^{\text{Ph}}\text{Tp})\text{PPhMe})_2\text{Mo}\}_2(\mu_2-\text{N}_2)[\text{BArF}^{24}]_2 \] (\text{1-N}_2^2\text{+}). The molecular geometry about each of the molybdenum centers is best described as octahedral with each monomeric subunit (defined as planes of the terpyridines) twisted by 16.6° about the Mo-N₂-Mo axis. The N(1)-N(2) bond distance of 1.203(2) Å (Table 2.2) is slightly contracted compared to the value 1.246(4) Å reported in \[(^{\text{iPr}}\text{BPDI})\text{Mo}(\text{N}_2)]_2(\mu_2-\text{N}_2)\) and is indicative of an \[\text{N}_2^2\text{-}\] bridge.\textsuperscript{35}

\textbf{Figure 2.6.} Representation of the solid-state structure of \[1-\text{N}_2\]\textsuperscript{2+} at 30% probability ellipsoids. Hydrogen atoms, the phenyl groups on the PPh₂Me ligands and the [BArF\textsuperscript{24}]\textsuperscript{-} anions omitted for clarity.
Table 2.2. Selected bond distances (Å) for \( [(\text{PhTpyp})(\text{PPh}_2\text{Me})_2\text{Mo}]_2(\mu_2-\text{N}_2)][\text{BARF}^{24}]_2 \) ([1-N₂]²⁺).

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</table>

Attempts to prepare the \(^{15}\text{N}\)-isotopologue, \([1-^{15}\text{N}_2]^{2+}\), by exposure of a THF solution of the natural abundance compound to \(^{15}\text{N}_2\) gas resulted in no exchange over the course of 14 days at room temperature, establishing the substitutional inertness of the bridging dinitrogen ligand. The \(^{15}\text{N}\)-isotopologue \([1-^{15}\text{N}_2]^{2+}\) was successfully prepared by performing the chloride abstraction from \([(\text{PhTpyp})(\text{PPh}_2\text{Me})_2\text{Mo(Cl)}]\) under a slight molar excess of \(^{15}\text{N}_2\) gas and features a singlet in the \(^{15}\text{N}\) NMR spectrum centered at \(\delta = 435\) ppm. Thus, the dimeric structure of \([1-\text{N}_2]^{2+}\) observed in the solid state is preserved in solution and is also in agreement with the THF-\(d_8\) \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectra where the
number of peaks expected for a $D_{2h}$ symmetric molecule are observed. The 2-Me-THF solution Raman spectrum also corroborates the activated nature of the bridging $N_2$ ligand. The $N_2$ band was assigned at 1563 cm$^{-1}$ based on the observed isotopic shift to 1512 cm$^{-1}$ (calculated 1510 cm$^{-1}$) for [1-$^{15}N_2$]$^{2+}$. Despite the activated dinitrogen ligand in [1-$N_2$]$^{2+}$, exposing the compound to strong acid and reducing agent, similar to the conditions described by Nishibayashi,$^{28}$ produced no detectable quantity of ammonia. In stark contrast to [(iPrBPDI)Mo($N_2$)]$_2$($\mu_2$-$N_2$), treatment of [1-$N_2$]$^{2+}$ with ammonia at ambient temperature for 18 hours produced no reaction and underscores the improved stability of the bis(phosphine) terpyridine molybdenum platform.

**Computational studies.** The diamagnetism of [1-$N_2$]$^{2+}$ limits the number of observables used to provide experimental insight into the electronic structure of the compound and as a consequence DFT studies were conducted to assign the oxidation state of both the molybdenum and the terpyridine ligands. Calculations were conducted with the B3LYP functional on a truncated version of the compound where the 4-phenyl substituents of the terpyridine ligands were replaced with hydrogens and the two BArF$^{24}$ anions and fluorobenzene solvent molecules present in the crystallographic unit cell were excluded from the computations. A qualitative molecular orbital diagram construction from the spin-restricted Kohn-Sham (RKS) output is presented in Figure 2.7.

The DFT computed HOMO, HOMO-1 and HOMO-2 are principally molybdenum based while the LUMO and LUMO+3 display significant ligand character in the form of electronically coupled terpyridine $\pi^*$ orbitals of $b_2$ and $a_2$ symmetry, respectively. The nature of the filled molecular orbitals depicted in Figure 2.7 can also be
predicted using qualitative orbital symmetry considerations for an \{M-N-N-M\} core in an approximate two-fold rotational symmetry. Using a strictly qualitative approach, the four-atom centered (Mo-N-N-Mo) molecular orbitals of \(\pi\)-symmetry can be constructed by the linear combinations of \(\text{Mo}_{dxz}, \text{Mo}_{dyz}, \text{Mo}_{dxy}, \text{N}_{px}, \text{N}_{py}\) and energetically ordered based on number of nodes.\(^{43}\) Computational results validate this classical view and demonstrate that the filled orbitals consist of molybdenum centers electronically coupled through dinitrogen \(\pi\)-orbitals of \(\pi\) symmetry arranged according to increasing number of nodes. As shown in Figure 2.7, \(\text{Mo}_{dxz}\) and \(\text{Mo}_{dyz}\) orbitals are coupled through \(\text{N}_{px}\) and \(\text{N}_{py}\) \(\pi\)-orbitals, respectively, while the \(\text{d}_{xy}\) orbitals (HOMO-1, HOMO-2) lack the appropriate symmetry required for interaction and are therefore non-bonding with respect to \(\text{N}_2\).\(^{43}\) The molybdenum atoms in the HOMO are bridged by an orbital of N-N antibonding character, while HOMO-3 and HOMO-4 feature an N-N antibonding combination, thus implying a net N-N bond order of 2. These results corroborate the activated nature of the dinitrogen bridge (\(\text{N}_2^{2-}\)) that is observed in the solid-state structure of \([\text{1-N}_2]^{2+}\). Because the computational studies accurately reproduce the diagnostic \(\text{C}_{py}-\text{C}'_{py}\) bond length in the terpyridine chelate without the population of terpyridine \(\pi^*\) orbitals, the experimentally observed bond contraction is a result of classical \(\pi\)-backbonding from the metals. Thus, from the observed metrical parameters and computational studies, both molybdenum atoms in \([\text{1-N}_2]^{2+}\) are best described as \(\text{Mo(II)}\).
Figure 2.7. Qualitative frontier molecular orbital diagram of truncated [1-N₂]²⁺ obtained from a spin-restricted B3LYP-DFT calculation. The z-axis is defined as the Mo-N₂-Mo vector.

**Electrochemical studies and redox chemistry of [1-N₂]²⁺.** The electrochemical behavior of [1-N₂]²⁺ was explored with cyclic voltammetry to probe the accessibility of oxidized and reduced compounds on this platform. The cyclic voltammogram of [1-N₂]²⁺
was collected in a 1 mM THF solution with 0.1 M [nBu₄N][PF₆] at a scan rate of 100 mV/sec and features two fully reversible oxidation waves at -0.22 V and -0.77 V, as well as two reversible reduction waves at -1.65 V and -1.86 V (measured versus the Cp₂Fe⁰/Cp₂Fe⁺ couple, Figure 2.8). Performing the electrochemical measurement in MeCN resulted in the loss of reversibility in the oxidative features, possibly due to displacement of the bridging dinitrogen ligand by the coordinating solvent.

The rich, reversible electrochemistry prompted studies into the chemical oxidation and reduction of [1-N₂]²⁺. A summary of these studies is presented in Figure 2.9. Addition of one equivalent of KC₈ to a thawing THF solution of [1-N₂]²⁺ followed by filtration and recrystallization yielded a dark violet, NMR silent product in 76% yield. Treatment of this product with one equivalent of Ag[BArF₂₄] cleanly regenerated [1-
as judged by $^1$H NMR spectroscopy, supporting formation of $[1-N_2]^\text{+}$. The solid-state magnetic moment on the monocationic complex of 1.6 µB (magnetic susceptibility balance, 295 K) is consistent with an $S = 1/2$ ground state. Accordingly, the X-band EPR spectrum recorded in fluid THF:toluene solution (1:1 by volume) at 295 K and as a THF:toluene glass (20:1 by volume) at 10 K exhibited an isotropic signal at both temperatures with $g_{\text{iso}} = 1.997$ (Figure 2.10a). The $g$-value in combination with the DFT-computed Mulliken population analysis (Figure 2.10c) suggest a principally terpyridine-based SOMO with some molybdenum character. The solution Raman spectrum of $[1-N_2]^\text{+}$ was recorded in 2-Me-THF and features an $\nu(N_2)$ band at 1530 cm$^{-1}$, which shifts to 1480 cm$^{-1}$ (Calculated 1478 cm$^{-1}$) upon isotopic labeling with $^{15}\text{N}_2$ indicating a slightly increased degree of $\text{N}=\text{N}$ bond activation upon chemical reduction.

**Figure 2.9.** Chemical one- and two-electron reduction (top) and oxidation (bottom) of $[1-N_2]^2\text{+}$. 

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Two-electron reduction of [1-N₂]²⁺ was accomplished by treatment of a thawing THF solution of the compound with two equivalents of KC₈ or with excess magnesium metal. Analogous to [1-N₂]⁺, treatment of the diamagnetic dark blue product with two equivalents of Ag[BArF₂₄] cleanly regenerated [1-N₂]²⁺ as judged by ¹H NMR.
spectroscopy. The $^{15}$N isotopologue, [1-$^{15}$N$_2$], was prepared by reduction of [1-$^{15}$N$_2$]$^{2+}$ with excess Mg metal and exhibits a sharp singlet centered at $\delta = 415$ ppm ($\delta = 435$ ppm in [1-N$_2$]$^{2+}$). The observed singlet in the $^{15}$N-NMR spectrum, together with the lack of a characteristic N$_2$ band in the solution IR spectrum demonstrate that the dimeric structure bridged by a dinitrogen ligand that is observed for [1-N$_2$]$^{2+}$ is retained in the reduced compound. The $^1$H and $^{31}$P NMR spectra of [1-N$_2$] are also consistent with $D_{2h}$ symmetry.

Stirring a THF solution of [1-N$_2$] under an atmosphere of $^{15}$N$_2$ did not result in the incorporation of $^{15}$N$_2$ into the compound indicating that the bridging dinitrogen ligand is not labilized upon chemical reduction. Attempts to obtain the Raman stretch for the bridging N$_2$ ligand were unsuccessful due to peak overlap.

One electron oxidation of [1-N$_2$]$^{2+}$ was achieved by treatment with one equivalent of Ag[BArF$_{24}$] in fluorobenzene solution and yielded [1-N$_2$]$^{3+}$ in 73% yield with the concomitant formation of Ag metal. The $S = 1/2$ ($\mu_{\text{eff}} = 1.8$ µB, magnetic susceptibility balance, 295 K) yellow-brown NMR silent compound proved stable in the solid state and in 2-Me-THF and fluorobenzene solution. Immediate decomposition was observed in MeCN consistent with the electrochemical irreversibility and over the course of hours in THF. Treatment of a 2-Me-THF solution of freshly prepared [1-N$_2$]$^{3+}$ with one equivalent of Cp$_2$Co regenerated diamagnetic [1-N$_2$]$^{2+}$ as determined by $^1$H NMR spectroscopy, confirming the chemical reversibility of the oxidation.

The X-band EPR spectrum of [1-N$_2$]$^{3+}$ was recorded in fluorobenzene:toluene (20:1) glass at 10 K and exhibits an axial signal (Figure 2.10b). The observed $g$ anisotropy ($g_{\text{max}} = g_{\text{mid}} = 2.026$, $g_{\text{min}} = 1.957$; $g_{\text{max}} - g_{\text{min}} = 0.07$) along with small hyperfine coupling to $^{95}$Mo and $^{97}$Mo ($A_{xx}^{(95/97)\text{Mo}} = A_{yy}^{(95/97)\text{Mo}} = 46$ MHz,
$A_{zz}(^{95/97}\text{Mo}) = 37$, $I = 5/2$, 15.92% $^{95}\text{Mo}$ and 9.55% $^{97}\text{Mo}$) support a molybdenum-based SOMO for $[\text{1-}-\text{N}_2]^3+$. The DFT-computed Mulliken population analysis supports this electronic structure assignment with spin density localized principally on the molybdenum atoms (Figure 2.10d). The 2-Me-THF solution Raman spectrum of $[\text{1-}-\text{N}_2]^3+$ exhibits an $\nu(\text{N}_2)$ stretching vibration at 1482 cm\(^{-1}\); shifted from 1563 cm\(^{-1}\) in $[\text{1-}-\text{N}_2]^2+$, indicative of further N=N bond activation upon oxidation.

The second oxidation event was accomplished by treatment of a 2-Me-THF solution of $[\text{1-}-\text{N}_2]^2+$ with two equivalents of Ag[BarF\(_{24}\)] (Figure 2.9). The resulting green-yellow product, $[\text{1-}-\text{N}_2]^4+$ was reduced with two equivalents of Cp\(_2\)Co to regenerate $[\text{1-}-\text{N}_2]^2+$. A solid-state magnetic moment of 2.5 $\mu$B was measured by magnetic susceptibility balance at 295 K and is consistent with an $S = 1$ ground state. An N=N stretching vibration was observed at 1477 cm\(^{-1}\) by Raman spectroscopy (2-Me-THF solution) which shifted to 1430 cm\(^{-1}\) (calculated 1427 cm\(^{-1}\)) upon isotopic labeling with $^{15}\text{N}_2$.

**Bonding Analysis of the Molybdenum Dinitrogen Complex Redox Series.** Figure 2.11 presents truncated qualitative frontier molecular orbital diagrams for all five molybdenum dinitrogen compounds across the redox series. While definitive structural information is lacking, $D_{2h}$ symmetry is assumed for all the compounds. The computational studies establish that the HOMO ($b_{3u}$) of $[\text{1-}-\text{N}_2]^2+$ exhibits both N=N bonding as well as Mo-N antibonding character. Therefore, removing electrons from this orbital results in a reduced N-N bond order and a lower frequency Raman band, in agreement with the experimental vibrations of 1563 cm\(^{-1}\) and 1482 cm\(^{-1}\) for $[\text{1-}-\text{N}_2]^2+$ and $[\text{1-}-\text{N}_2]^3+$,
respectively. The observed axial \( g_{\text{max}} = g_{\text{mid}} = 2.026 \), \( g_{\text{min}} = 1.957 \) EPR signal of \([1-N_2]^3+\) measured at 10 K as well as Mulliken spin density analysis from a spin-unrestricted B3LYP DFT calculation confirm that the unpaired electron is essentially metal based.

The molecular orbital analysis also rationalizes the trend in the vibrational data for the second oxidation product, \([1-N_2]^4+\). The observed \( S = 1 \) ground state implies that the unpaired electron populates a \( b_{3u} \) molecular orbital with significant \( \text{N-N} \) bonding character, consistent with the lack of a significant Raman \( \nu(\text{N}_2) \) shift between \([1-N_2]^3+\) and \([1-N_2]^4+\) which display \( \nu(\text{N}_2) \) bands at 1482 cm\(^{-1}\) and 1477 cm\(^{-1}\), respectively.

The qualitative molecular orbital diagram for \([1-N_2]^2+\) demonstrates that the LUMO \( (2b_{2g}) \) is principally \( \pi^* \) character with modest contribution from the Mo-\( \text{N-N-Mo} \) core with N-N antibonding character. Thus, a slight decrease of the N-N bond order is anticipated upon reduction. Both the DFT-computed Mulliken spin density and the isotropic EPR signal support a ligand-centered radical for \([1-N_2]^+\). The shift of the \( \nu(\text{N}_2) \) Raman band to higher frequency (1530 to 1563 cm\(^{-1}\)) upon one electron reduction of \([1-N_2]^2+\) is also consistent with this view. These results highlight the benefits of a redox-active terpyridine ligand in molybdenum dinitrogen chemistry. The \( \pi^* \) orbitals of the terpyridine ligands are energetically poised to store additional reducing equivalents expanding the number of members accessible in the redox series.
Figure 2.11. Qualitative frontier molecular orbital diagrams for the electron transfer events from [1-N₂]^{4+} to [1-N₂]. Only the relevant orbitals of π-symmetry in the Mo-N-N-Mo core are depicted. Only the orbitals pictured were considered for the number of D_{2h} symmetry labels with the Mo-N-N-Mo axis defined as the z direction. a Band was not assigned due to peak overlap.

<table>
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<th>Compound</th>
<th>[1-N₂]^{4+}</th>
<th>[1-N₂]^{3+}</th>
<th>[1-N₂]^{2+}</th>
<th>[1-N₂]^+</th>
<th>[1-N₂]^-</th>
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<td>S = 0</td>
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</tr>
<tr>
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<td>1482 cm⁻¹</td>
<td>1563 cm⁻¹</td>
<td>1530 cm⁻¹</td>
<td>a</td>
</tr>
</tbody>
</table>

Conclusions

A new dimolybenum dinitrogen compound, [{(Ph-Tpy)(PPh₂Me)₂Mo}₂(μ₂-N₂)][BArF^{24}]₂, was synthesized and structurally characterized following chloride abstraction from the molybdenum(I) complex {(Ph-Tpy)(PPh₂Me)₂MoCl under an atmosphere of N₂. Cyclic voltammetric studies established a rich redox chemistry and synthetic methods were used to access molybdenum dinitrogen complexes, [{(Ph-Tpy)(PPh₂Me)₂Mo}₂(μ₂-N₂)][BArF^{24}]ₙ (n = 4, 3, 2, 1, 0), across five oxidation states where the Mo-N-N-Mo core remains intact as judged by Raman and ^{15}N NMR spectroscopic studies. The nature of the unpaired electron in the mixed-valent compounds resulting from one electron oxidation and reduction of [{(Ph-Tpy)(PPh₂Me)₂Mo}₂(μ₂-N₂)][BArF^{24}]₂ was interrogated by EPR spectroscopy. In the tricationic complex, [{(Ph-Tpy)(PPh₂Me)₂Mo}₂(μ₂-N₂)]^{3+}, the SOMO is principally metal-based while in the
one electron reduced product, \[[\{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}\}_2(\mu_2-\text{N}_2)]^{1+}\) the radical in primarily chelate-based. These studies demonstrate that the orbital disposition of \([1-\text{N}_2]^{2+}\) provides access to five \text{N}_2-bridged compounds in a redox series, with the reversibility of four consecutive redox events rendering the platform highly promising for further reactivity studies of relevance to \text{N}_2 reduction.

**Experimental Section**

**General Considerations**

All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures. Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. 4’-Ph-2,2’,6’,2’’-terpyridine (\text{Ph}-\text{Tpy}), (\text{THF})_3\text{Mo(Cl)}_3, \text{Na}[\text{BARF}^{24}] \text{and Ag}[\text{BARF}^{24}] \text{were prepared following literature procedures. PPh}_2\text{Me was purchased from Sigma-Aldrich, distilled under an atmosphere of argon and stored over 4 Å molecular sieves before use.}}

\text{H NMR spectra were recorded on Bruker AVANCE 300 and Bruker AVANCE 500 spectrometers operating at 300.13 and 500.62 MHz respectively. } \text{C NMR spectra were recorded on a Bruker AVANCE 500 operating at 125.89 MHz. All } \text{H and } \text{C chemical shifts are reported relative to SiMe}_4 \text{ using the } \text{(residual) and } \text{chemical shifts of the}
solvent as a secondary standard. $^{31}$P NMR spectra were collected on a Bruker 500 AVANCE spectrometer operating at 202.40 MHz and were referenced to 85% H$_3$PO$_4$ as an external standard. $^{19}$F NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 282.23 MHz and were referenced to CFCl$_3$ as an external standard. $^{11}$B NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 96.251 MHz and were referenced to BF$_3$OEt$_2$ as an external standard. $^{15}$N NMR spectra were recorded on a Bruker 500 spectrometer operating at 50.663 MHz and $^{15}$N chemical shifts are reported relative to liquid NH$_3$ using an external standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Raman spectra were collected in 2-MeTHF solution on a Thermo-Fisher DXR Raman with a 720 nm excitation wavelength. Cyclic voltammograms (CVs) were collected in THF solution (1 mM in compound) with [nBu$_4$N][PF$_6$] (0.1 M), using a 3 mm glassy carbon working electrode, platinum wire as the counter electrode, and silver wire as the reference in a drybox equipped with electrochemical outlets. CVs were recorded using a BASi EC Epsilon electrochemical workstation and analyzed using the BASi Epsilon-EC software. All CVs were run at a scan rate of 100 mV/s at 295 K. Potentials are reported versus ferrocene/ferrocenium and were obtained using the in situ method.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker D8 APEX3 Venture diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å) and a Cu X-ray tube ($\lambda = 1.54178$ Å). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified,
and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Gouy magnetic susceptibility balance measurements were performed with a Johnson Matthey instrument that was calibrated with HgCo(SCN)$_4$. Continuous wave EPR spectra were recorded at room temperature or at 10K on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.

**Computational Studies.** All DFT calculations were performed with the ORCA program package in the gas phase. The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT. The all-electron Gaussian basis sets were those developed by the Ahlrichs group. Triple-ζ quality basis sets def2-TZVP with one set of polarization functions on molybdenum, phosphorous and nitrogen were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used that were of double-ζ quality in the valence region and contained a polarizing set of d functions on the non-hydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX) approach were chosen to match the orbital basis. The single-point calculations on (μ$_2$-N$_2$)[(PhTpy)(PPh$_2$Me)$_2$Mo]$_2$[BArF$_{24}$] ([I-N$_2$]$^+$) and (μ$_2$-N$_2$)[(PhTpy)(PPh$_2$Me)$_2$Mo]$_2$[BArF$_{24}$]$_3$ ([I-N$_2$]$^{2+}$) were carried out on the geometry-optimized structure of (μ$_2$-N$_2$)[(PhTpy)(PPh$_2$Me)$_2$Mo]$_2$[BArF$_{24}$]$_2$ ([I-N$_2$]$^{2+}$) after the appropriate charge and spin input modifications. Stuttgart–Dresden effective core
potential was used for molybdenum atoms to reduce the computational effort. The spin density was calculated at 100x100x100 resolution based on converged unrestricted DFT wave functions.

**Preparation of Molybdenum Complexes**

**Preparation of [(PhTpy)MoCl₃]**. A 250 mL round-bottom flask was charged with a stir bar, 2.239 g (7.237 mmol) of PhTpy, 3.000 g (7.166 mmol) of [(THF)₃Mo(Cl)]₃, and 150 mL THF. The reaction was stirred at room temperature for 24 hours during which time a color change from salmon to black was observed. The suspension was concentrated to 25 mL under reduced pressure and 40 mL of pentane was added to induce the precipitation of solids. The resulting precipitate was isolated on a 30 mL medium porosity frit, washed with pentane (3 x 15 mL) and dried in vacuo. The dark teal solids were used for subsequent reactions without further purification (3.465 g, 6.772 mmol, 94% yield). Anal Calcd for C₂₁H₁₅Cl₃MoN₃: C, 49.29; H, 2.95; N, 8.21. Found: C, 48.95; H, 2.80; N, 8.15. Magnetic Susceptibility: (Guoy balance, 295 K) \( \mu_{\text{eff}} = 3.6(2) \mu_B \).

**Preparation of [1-Cl]**. A 100 mL round-bottom flask was charged with a large stir bar, 0.052 g (2.262 mmol) of freshly prepared 1% sodium amalgam and 50 mL THF. With vigorous stirring, 0.395 g (1.974 mmol) of PPh₂Me were added to the slurry, followed by the addition of 0.500 g (0.977 mmol) of [(PhTpy)Mo(Cl)]₃ in one portion. The reaction was vigorously stirred at room temperature for 2 hours during which time a color change from black to dark forest-green was observed. The resulting mixture was filtered through
a pad of Celite and the solvent was removed in vacuo. The dark residue was dissolved in a minimal amount of benzene (25 mL), filtered through a pad of Celite, layered with pentane (50 mL) and stored at room temperature for 18 hours. The supernatant was decanted and the resulting dark crystalline solids were transferred onto a 30 mL medium porosity frit, washed with pentane (2 x 10 mL) and dried under reduced pressure to yield the product as lustrous black crystals (0.429 g, 0.510 mmol 52% yield). Single crystals suitable for X-ray diffraction were obtained by room temperature recrystallization from a concentrated benzene solution layered with pentane. Anal Calcd for C₄₇H₄₁ClMoN₃P₂: C, 67.11; H, 4.91; N, 5.00. Found: C, 66.94; H, 4.87; N, 4.92. Magnetic Susceptibility: (Guoy balance, 295 K) μₑff = 1.7(2) μB.

**Preparation of [1-N₂]²⁺.** A 100 mL round-bottom flask was charged with a stir bar, 0.500 g (0.594 mmol) of [1-Cl], 0.532 g (0.600 mmol) of Na[BArF₂₄] and 30 mL toluene. The reaction was stirred at room temperature for 18 hours during which time a color change from forest-green to brown was observed with concomitant formation of a precipitate. The solid was collected on a 30 mL medium porosity frit, washed with pentane (3 x 15 mL) and dried under reduced pressure to yield the crude product as maroon solids. The solids were dissolved a minimal amount of acetonitrile and the remaining salt impurities were removed by filtration through a pad of Celite. The solvent was removed under reduced pressure and the dark residue was triturated with Et₂O (1 x 10 mL) and pentane (2 x 10 mL). The resulting solids were transferred onto a 15 mL medium porosity frit, washed with pentane (3 x 10 mL) and dried under reduced pressure to yield the product as a dark maroon solid (0.710 g, 0.211 mmol 71% yield). Single
crystals suitable for X-ray diffraction were obtained by the vapor diffusion of pentane onto a concentrated fluorobenzene solution at -35 °C. Anal Calcd for C\textsubscript{158}H\textsubscript{106}B\textsubscript{2}F\textsubscript{48}Mo\textsubscript{2}N\textsubscript{8}P\textsubscript{4}: C, 56.38; H, 3.17; N, 3.33. Found: C, 55.99; H, 3.26; N, 3.20. \textsuperscript{1}H NMR (THF-\textit{d}_8, 295 K): \( \delta \) 9.78 (d, \( J = 5.8 \) Hz, 4H, Ph-Tpy), 8.30 (d, \( J = 8.2 \) Hz, 4H, Ph-Tpy), 7.67 (d, \( J = 7.6 \) Hz, 4H, Ph-Tpy), 7.56 (s, 8H, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3})\textsubscript{4}, overlap with 4H, Ph-Tpy), 7.46-7.39 (m, 6H, Ph-Tpy), 7.29 (t, \( J = 6.7 \) Hz, 4H, Ph-Tpy), 7.16 (t, \( J = 7.6 \) Hz, 8H, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})), 6.94 (t, \( J = 7.7 \) Hz, 16H, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})), 6.42 (s, 16H, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})), 1.09 (s, 12H, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})).

\textsuperscript{13}C NMR (THF-\textit{d}_8, 295 K): \( \delta \) 162.7 (q, \( 1J_{C-B} = 50.0 \) Hz, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3})\textsubscript{4}), 150.3 (s, Ph-Tpy), 148.7 (s, Ph-Tpy), 146.9 (s, Ph-Tpy), 140.6 (s, Ph-Tpy), 137.4 (s, Ph-Tpy), 135.4 (s, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3})\textsubscript{4}), 134.3 (t, \( 1J_{C-P} = 15.9 \) Hz, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})), 132.1 (s, Ph-Tpy), 131.2 (s, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})), 130.1 (s, Ph-Tpy), 129.9 (q, \( 2J_{C-F} = 31.5 \) Hz, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3})\textsubscript{4}), 129.6 (s, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})), 129.1 (s, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})), 127.8 (s, Ph-Tpy), 125.4 (q, \( 1J_{C-F} = 272 \) Hz, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3})\textsubscript{4}), 124.8 (s, Ph-Tpy), 121.0 (s, Ph-Tpy), 118.0 (s, B[(3,5-(CF\textsubscript{3})\textsubscript{2})C\textsubscript{6}H\textsubscript{3})\textsubscript{4}), 115.0 (s, Ph-Tpy), 10.6 (t, \( 1J_{C-P} = 10.1 \) Hz, P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(CH\textsubscript{3})).

\textsuperscript{31}P NMR (THF-\textit{d}_8, 295 K): \( \delta \) 16.61 (s).

\textsuperscript{19}F NMR (THF-\textit{d}_8, 295 K) \( \delta \) -63.43 (s).

\textsuperscript{11}B NMR (THF-\textit{d}_8, 295 K): \( \delta \) -6.55 (s).

\textsuperscript{15}N NMR (THF-\textit{d}_8, 295 K): \( \delta \) 435 (s). Raman (2-Me-THF, 295 K, cm\textsuperscript{-1}): 1563 (\textsuperscript{14}N=\textsuperscript{14}N), 1512 (\textsuperscript{15}N=\textsuperscript{15}N).

**Preparation of [1-\textsuperscript{15}N\textsubscript{2}]\textsuperscript{2+}**. A J-Young NMR tube with a Teflon cap was charged with 0.050 g (0.059 mmol) of [1-Cl] and 0.053 g (0.060 mmol) of Na[BArF\textsubscript{24}]. The tube was connected to the high vacuum line, evacuated and 1 mL of degassed toluene was...
condensed onto the solids. The headspace was then charged with 1 atm of $^{15}\text{N}_2$, the tube sealed and then slowly rotated on an NMR-tube rotating apparatus for 18 hours. The product was isolated as described for the natural abundance compound.

**Preparation of $[1-\text{N}_2]^{2+}$**. A 20 mL scintillation vial was charged with a magnetic stir bar, 0.245 g (0.073 mmol) of $[1-\text{N}_2]^{2+}$ dissolved in 5 mL Et₂O and was frozen in the cold well. To the thawing solution was then added 0.010 g (0.074 mmol) of potassium graphite. The solution was warmed to room temperature and stirred for 30 minutes during which time a color change from maroon to violet was observed. The solution was filtered through a pad of Celite and the solvent was removed under reduced pressure. The dark residue was suspended in a minimal amount of toluene and the remaining insoluble impurities were removed by filtration through a pad of Celite. The solvent of the filtrate was removed under reduced pressure and the residual solids were isolated on a 10 mL medium porosity frit, washed with cold pentane (2 x 3 mL) and dried to yield the product as a dark purple powder (0.139 g, 0.056 mmol, 76%). Anal Calcd for C₁₂₆H₉₄BF₂₄Mo₂N₈P₄: C, 60.47; H, 3.79; N, 4.48. Found: C, 60.27; H, 3.48; N, 4.30. Magnetic Susceptibility: (Guoy balance, 295 K) $\mu_{\text{eff}} = 1.6(2) \mu_B$. Raman (2-Me-THF, 295 K, cm⁻¹): 1530 ($^{14}\text{N}=^{14}\text{N}$), 1480 ($^{15}\text{N}=^{15}\text{N}$).

**Preparation of $[1-\text{N}_2]$ (Method A)**. A 20 mL scintillation vial was charged with a magnetic stir bar, 0.100 g (0.03 mmol) of $[1-\text{N}_2]^{2+}$, 0.108 g (4.46 mmol) of magnesium powder and 5 mL THF. The suspension was rapidly stirred at room temperature for 18 hours during which time a color change from maroon to blue was observed. The resulting
mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The dark residue was extracted with toluene (5 x 2 mL) and the insoluble impurities were removed by filtration of the combined extracts through a pad of Celite. The solvent was then removed in vacuo, and the residue was washed with cold pentane (3 x 3 mL) followed by trituration with pentane (3 x 3 mL) to yield the product as a dark blue solid (31 mg, 0.019 mmol, 64%). Anal Calcd for C_{94}H_{82}Mo_{2}N_{8}P_{4}: C, 68.86; H, 5.04; N, 6.83. Found: C, 68.72; H, 4.87; N, 6.37. 

$^1$H NMR (THF-d$_8$, 295 K): δ 9.43 (d, $J = 6.0$ Hz, 4H, Ph-Tpy), 8.05 (d, $J = 8.4$ Hz, 4H, Ph-Tpy), 8.01 (s, 4H, Ph-Tpy), 7.73 (d, $J = 7.7$ Hz, 4H, Ph-Tpy), 7.39 (t, $J = 7.6$ Hz, 4H, Ph-Tpy), 7.04 (t, $J = 7.3$ Hz, 2H, Ph-Tpy), 6.99 (t, $J = 7.3$ Hz, 8H, P(C$_6$H$_5$)$_2$(CH$_3$)), 6.78 (t, $J = 7.2$ Hz, 16H, P(C$_6$H$_5$)$_2$(CH$_3$)), 6.52 (t, $J = 7.3$ Hz, 4H, Ph-Tpy), 6.40 (br s, 16H, P(C$_6$H$_5$)$_2$(CH$_3$)), 5.91 (t, $J = 6.1$ Hz, 4H, Ph-Tpy), 1.31 (s, 12H, P(C$_6$H$_5$)$_2$(CH$_3$)). 

{$^1$H}$^{13}$C NMR (THF-d$_8$, 295 K): δ 149.1 (s, Ph-Tpy), 145.1 (s, Ph-Tpy), 142.0 (s, Ph-Tpy), 136.2 (s, P(C$_6$H$_5$)$_2$(CH$_3$)), 131.7 (s, P(C$_6$H$_5$)$_2$(CH$_3$)), 129.4 (s, Ph-Tpy), 128.9 (s, P(C$_6$H$_5$)$_2$(CH$_3$)), 128.7 (s, Ph-Tpy), 128.3 (s, P(C$_6$H$_5$)$_2$(CH$_3$)), 126.5 (s, Ph-Tpy), 124.8 (s, Ph-Tpy), 123.0 (s, Ph-Tpy), 121.6 (s, Ph-Tpy), 119.5 (s, Ph-Tpy), 114.5 (s, Ph-Tpy), 108.2 (s, Ph-Tpy), 10.6 (t, $J_{C-P} = 10.1$ Hz, P(C$_6$H$_5$)$_2$(CH$_3$)). $^{31}$P NMR (THF-d$_8$, 253 K): δ 14.9 (s). 

$^{15}$N NMR (THF-d$_8$, 298 K): δ 415 (s).

**Preparation of [1-N$_2$] (Method B).** A 20 mL scintillation vial was charged with a magnetic stir bar, 0.100 g (0.03 mmol) of [1-N$_2$]$^{2+}$, 5 mL THF and was frozen in a liquid nitrogen cooled coldwell. Potassium graphite (0.009 g, 0.067 mmol) was added and the mixture was thawed while stirring, followed by stirring at ambient temperature for 15
minutes. The workup described in Method A yielded the product as a dark blue solid (36 mg, 0.022 mmol, 74%).

**Preparation of [1-N2]^{3+}.** A 20 mL scintillation vial was charged with a magnetic stir bar and 0.100 g (0.030 mmol) of [1-N2]^{2+} dissolved in 5 mL fluorobenzene. To the stirring solution, a solution containing 0.029 g (0.030 mmol) of Ag[BArF_{24}] dissolved in 1 mL fluorobenzene was added dropwise inducing a color change from maroon to brown. After 15 minutes of stirring, the reaction mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure to yield a dark brown oily residue. The residue was triturated with pentane (5 x 5 mL), isolated on a 10 mL medium porosity frit, washed with pentane (3 x 5 mL) and dried under reduced pressure to yield the product as a dark brown powder (0.092 g, 0.022 mmol, 73%). Anal Calcd for C_{190}H_{118}B_{3}F_{72}Mo_{2}N_{8}P_{4}: C, 53.96; H, 2.81; N, 2.65. Found: C, 54.24; H, 3.12; N, 2.28.

Magnetic Susceptibility: (Guoy balance, 295 K) $\mu_{\text{eff}} = 1.8(2) \mu_B$. Raman (2-Me-THF, 295 K, cm^{-1}): 1482 (^{14}\text{N}=^{14}\text{N}).

**Preparation of [1-N2]^{4+}.** A 20 mL scintillation vial was charged with a magnetic stir bar and 0.100 g (0.030 mmol) of [1-N2]^{2+} dissolved in 5 mL 2-Me-THF. To the stirring solution, a solution containing 0.061 g (0.062 mmol) of Ag[BArF_{24}] dissolved in 2 mL 2-Me-THF was added dropwise, inducing a color change from maroon to yellow-green. After 30 minutes of stirring, the reaction mixture was filtered through a pad of Celite, and the solvent was removed under reduced pressure to yield a dark green-brown oily residue. The residue was triturated with pentane (10 x 5 mL), isolated on a 10 mL medium
porosity frit, washed with pentane (3 x 5 mL) and dried under reduced pressure to yield the product as a dark brown powder (0.120 g, 0.024 mmol, 79%). Anal Calcd for C\textsubscript{222}H\textsubscript{130}B\textsubscript{4}F\textsubscript{96}Mo\textsubscript{8}N\textsubscript{8}P\textsubscript{4}: C, 52.36; H, 2.57; N, 2.20. Found: C, 52.37; H, 2.76; N, 2.04.

Magnetic Susceptibility: (Guoy balance, 295 K) \(\mu_{\text{eff}} = 2.5(2)\ \mu_{\text{B}}\). Raman (2-Me-THF, 295 K, cm\textsuperscript{-1}): 1477 (\(^{14}\text{N} = ^{14}\text{N}\)), 1430 (\(^{15}\text{N} = ^{15}\text{N}\)).

**Preparation of the compounds** \([1-^{15}\text{N}_2]^n^+\), \(n = 0, 1, 3, 4\). The isotopically labelled dinitrogen compounds were prepared and isolated in a similar manner to \([1-\text{N}_2]^n^+\)(\(n = 0, 1, 3, 4\)) with the exception that in each case, \([1-^{15}\text{N}_2]^2^+\) was used as the starting material in place of the natural abundance compound.
Figure 2.12. Qualitative molecular orbital diagram for [1-Cl] from a spin-unrestricted B3LYP DFT calculation.
Figure 2.13. Mulliken spin density plot for [1-Cl] from a spin-unrestricted B3LYP DFT calculation.

Figure 2.14. Mulliken spin density plot for [1-N₂]⁺ from a spin-unrestricted B3LYP DFT calculation.
Figure 2.15. Mulliken spin density plot for [1-N₂]³⁺ from a spin-unrestricted B3LYP DFT calculation.
DFT Input Examples

Geometry Optimizations

[1-N₈]²⁺:

! RKS B3LYP RIJCOSX def2-SVP def2-SVP/J Normalprint SlowConv TightSCF Opt Pal8 UCO

%basis NewGTO 42 "def2-TZVP(-f)" end
   NewGTO 7 "def2-TZVP(-f)" end
   NewGTO 15 "def2-TZVP(-f)" end
   NewAuxGTO 42 "def2-TZVP/J" end
   NewAuxGTO 7 "def2-TZVP/J" end
   NewAuxGTO 15 "def2-TZVP/J" end
end

%SCF MaxIter 500
   TolE 1e-7
   TolErr 1e-6
end

* xyz 2 1

XYZ Coordinates of the dicationic fragment of the molecule from X-Ray structure

*

References


CHAPTER 3

Coordination-Induced Bond Weakening of Ammonia, Water and Hydrazine with a Molybdenum Complex.*

Abstract

Transition metal complexes containing ammonia and aquo (water) ligands have been known for over a century and have served as the foundation for modern coordination chemistry. Little is known however about the strength of the N–H or O–H bonds following coordination to the transition metal. Here we describe synthesis of a “non-classical” molybdenum ammonia complex supported by terpyridine and phosphine ligands that significantly reduces the N–H bond dissociation free energy (BDFE$_{\text{N–H}}$) from 99.5 (gas phase) to an experimentally measured value of 45.8 kcal/mol (DFT calculated = 45.1 kcal/mol). This low value enables spontaneous H$_2$ evolution upon gentle heating as well as the hydrogenation of styrene. This coordination-induced bond weakening strategy has also been applied to H$_2$ evolution from coordinated water and hydrazine. Electrochemical and theoretical methods have been used to explore the contributions of metal redox potential and acidity of the NH$_3$ ligand to account for the origin of the unusual effect.

Introduction

Ammonia and water are ubiquitous small molecules with strong bonds between hydrogen and the central atom.\(^1\) For over a century, this property has been exploited to stabilize transition metal-ammine (NH\(_3\)) and aquo (H\(_2\)O) compounds that have defined new bonding paradigms in chemistry,\(^2\) found application in cancer therapy,\(^3\) and promoted important fundamental chemical reactions such as electron transfer (Figure 3.1).\(^4\)

**Figure 3.1.** Comparison of (a) classical coordination compounds of ammonia and (b) non-classical compounds that enable bond weakening by coordination and hence hydrogen evolution.

Given its transportability and energy density, there is considerable contemporary interest in using ammonia as a hydrogen storage medium and water as a source of protons.
and electrons.\textsuperscript{5,6,7,8} In the presence of an appropriate energy source such as electricity or photons and a catalyst, H\textsubscript{2} could be generated from NH\textsubscript{3} and used as a carbon-neutral fuel. Key to realizing this challenge is activation of the strong element-hydrogen bonds and overcoming formation of transition metal complexes where ammonia or water serves as an inert spectator ligand. Strategies for homogeneous ammonia and water activation include oxidative addition to a transition metal center,\textsuperscript{9,10,11} protonolysis with transition metal hydrides and alkoxides,\textsuperscript{12,13} reaction with bimetallic compounds,\textsuperscript{14} cooperative chemistry between a transition metal and a supporting ligand,\textsuperscript{15,16,17} and through bond cleavage with reactive main group compounds.\textsuperscript{18,19,20,21} Using most of these strategies, activation of the strong X–H bond is not typically coupled to H–H bond formation. One exception is the observation of H\textsubscript{2} elimination following oxidative addition of ammonia to a tantalum(III) complex.\textsuperscript{22}

An alternative and lesser explored strategy is homolytic cleavage of the element-hydrogen bond. Because of the high gas-phase bond dissociation free energies (99.5, NH\textsubscript{3} and 111.0 kcal/mol, H\textsubscript{2}O) interaction with a transition metal or other appropriate reagent is necessary to induce bond weakening. As shown in Figure 3.1, most classical transition metal compounds with ammine (and aquo) ligands have N-H bond strengths only slightly perturbed from the gas phase value. Because experimental data are lacking, the values presented in Figure 3.1 were obtained using density functional theory.

Coordination induced bond weakening, whereby interaction of a ligand results in significant lowering of the element-hydrogen bond dissociation free energy, has recently been identified or implicated in rare instances\textsuperscript{23,24,25,26,27,28} and has been applied by Knowles\textsuperscript{29} and others\textsuperscript{30,31,32} in reactions of organic molecules involving N–H and O–H
bonds, respectively. Cuerva\textsuperscript{31,32} and our laboratory\textsuperscript{33} have demonstrated the effectiveness of bis(cyclopentadienyl) titanium(III) complexes in weakening the O-H and N-H bonds of water and ammonia, respectively. This strategy, however, has yet to be applied to the generation of dihydrogen from ammonia and water principally due to the inability to weaken the element hydrogen bond sufficiently to provide thermodynamic driving force for H\textsubscript{2} evolution (BDFE\textsubscript{E-H} < ΔGr\textsubscript{f}(H\textsuperscript{*}) = 48.6 kcal/mol, Figure 3.1)\textsuperscript{1}. In (η\textsuperscript{5-}C\textsubscript{5}Me\textsubscript{4}SiMe\textsubscript{3})\textsubscript{2}TiCl(NH\textsubscript{3}), for example, the N-H BDFE was calculated to be 61 kcal/mol, too high to spontaneously form H\textsubscript{2}\textsuperscript{33}. Here we describe a terpyridine bis(phosphine) molybdenum complex that by virtue of its coordination environment and redox properties, enables H\textsubscript{2} evolution from coordinated ammonia, water and hydrazine demonstrating a new strategy for activation of these ubiquitous small molecules.

**Results and Discussion**

![Figure 3.2. Synthesis of [1-NH\textsubscript{3}]\textsuperscript{+} and hydrogen atom abstraction using substituted phenoxy radical and chromium reagents.](image)

Chloride abstraction from [(\textsuperscript{Ph}Tpy)(PPh\textsubscript{2}Me)\textsubscript{2}MoCl] (\textsuperscript{Ph}Tpy = 4'-Ph-2,2',6',2''-terpyridine; [1-Cl])\textsuperscript{34} with Na[BArF\textsuperscript{24}] \{ArF\textsuperscript{24} = [C\textsubscript{6}H\textsubscript{3}-3,5-(CF\textsubscript{3})\textsubscript{2}]\textsubscript{4}\} in benzene solution at ambient temperature in the presence of 1 equivalent of ammonia resulted in isolation of a yellow-green crystalline solid identified as [(\textsuperscript{Ph}Tpy)(PPh\textsubscript{2}Me)\textsubscript{2}Mo(NH\textsubscript{3})][BArF\textsuperscript{24}] ([1-}
NH₃⁺) in 77% yield (Figure 3.2). The formally Mo(I) ammonia complex has an $S = 1/2$ ground state ($\mu_{\text{eff}} = 1.7(2)$ µB, 23 °C magnetic susceptibility balance) and exhibits an isotropic ($g_{\text{iso}} = 1.988$) EPR signal in fluid benzene solution (296 K) with hyperfine coupling to two 100% abundant $I = 1/2$ phosphorous atoms [$A_{\text{iso}}(^{31}\text{P}) = 33$ MHz] as well as to $^{95}$Mo and $^{97}$Mo [$A_{\text{iso}}(^{95/97}\text{Mo}) = 80$ MHz, $I = 5/2$, and 15.92% $^{95}$Mo and 9.55% $^{97}$Mo]. The solid-state structure was determined by X-ray diffraction and confirms formation of an octahedral molybdenum complex with the ammonia ligand trans to the central pyridine of the terpyridine chelate with an Mo-NH₃ bond distance of 2.236(3) Å. The solid-state infrared spectrum (KBr) of [1-NH₃]⁺ exhibits three isotopically sensitive low energy vibrations at 2919, 2899 and 2847 cm⁻¹ consistent with a coordinated ammine ligand. These vibrations are likely perturbed by hydrogen bonding, as the solid-state structure of [1-NH₃]⁺ revealed a close (2.395(3) Å) H⋯F interaction between the ammine hydrogens and the [–CF₃] group of the [BARF₂⁴]⁻ counterion (Figure 3.3). By comparison, the classical ammine complexes cis-[(Cl)₂Pt(NH₃)₂], [(NH₃)₆Co]Cl₃ and [(NH₃)₆Ru][BF₄]₂ feature higher energy solid-state N-H vibrations in the range of 3200 cm⁻¹ to 3400 cm⁻¹, close to the value of 3414 cm⁻¹ in gaseous ammonia. These values must be interpreted cautiously as the H-bonding interactions in [1-NH₃]⁺ may be the origin of the observed differences (Figure 3.3).³⁵,³⁶,³⁷,³⁸
Figure 3.3. Solid state structure of [1-NH₃]⁺ using 30% probability ellipsoids. Hydrogen atoms, except those connected to N4 have been omitted for clarity.

Experiments were conducted to establish an upper bound for the N-H bond strength in [1-NH₃]⁺. Addition of one equivalent of 2,4,6-tri-tert-butylphenoxy radical (’Bu₃C₆H₂O•; TBP) resulted in rapid H-atom abstraction from the ammonia ligand to quantitatively yield the olive-green diamagnetic molybdenum(II) amide complex, [(PhTpy)(PPh₂Me₂)Mo(NH₂)][BArF₂₄] ([1-NH₂]⁺), setting the N-H bond dissociation free energy as < 77 kcal/mol (Figure 3.2).³⁹ The benzene-d₆ ¹H NMR spectrum of [1-NH₂]⁺ exhibits the number of resonances expected for a C₂ᵥ symmetric compound with a diagnostic downfield triplet centered at 10.02 ppm (¹J_P-H = 16.7 Hz) assigned to the terminal amide hydrogens. The benzene-d₆ ¹⁵N NMR spectrum of [1-¹⁵NH₂]⁺, prepared
from $^{15}$NH$_3$, features a triplet centered at 235.5 ppm ($^1$$J_{N,H}$ = 68.5 Hz), as well as a doublet in $^{31}$P-NMR spectrum at 15.58 ppm ($^2$$J_{P,N}$ = 4.1 Hz). The infrared spectrum (KBr) of [1-NH$_3$]$^+$ contains two peaks assignable to a -NH$_2$ fragment at 3354 cm$^{-1}$ and 3287 cm$^{-1}$, shifting to 2512 cm$^{-1}$ and 2426 cm$^{-1}$, respectively in the deuterated isotopologue [1-ND$_2$]$^+$. The solid-state structure was determined by X-ray diffraction (Figure 3.11) establishing an octahedral molybdenum complex in analogy with [1-NH$_3$]$^+$. The Mo-NH$_2$ bond distance of 1.994(3) Å is considerably contracted compared with the Mo-NH$_3$ distance of 2.236(3) Å in [Mo-NH$_3$]$^+$, consistent with formation of an anionic ligand.

To further bracket the N-H bond strength in [1-NH$_3$]$^+$, the ammonia complex was treated with [($\eta^5$-C$_5$Me$_5$)Cr(CO)$_3$)$_2$ (Figure 3.2). Immediate and quantitative formation of [1-NH$_2$]$^+$ and [($\eta^5$-C$_5$Me$_5$)Cr(CO)$_3$(H)] established an N-H BDFE of <62 kcal/mol$^{40}$ suggesting that H$_2$ formation may be possible. Density functional theory calculations on the ammonia complex [1-NH$_3$]$^+$ revealed a computed N-H bond strength of 45.1 kcal/mol consistent with H-atoms abstraction experiment.

The remarkably low N-H bond strength of coordinated ammonia in [1-NH$_3$]$^+$ suggested that spontaneous H$_2$ formation should be possible. Gently heating a benzene-$d_6$ solution of [1-NH$_3$]$^+$ to 60 °C for 6 hours resulted in clean and quantitative formation of [1-NH$_2$]$^+$ with concomitant H$_2$ evolution as confirmed by Toepler pump experiments (92% yield of H$_2$, Figure 3.4a). Carrying out the reaction in the presence of 1.5 equivalents of styrene furnished ethylbenzene in 25% yield, providing additional evidence for bond weakening by coordination and application of ammonia as a hydrogen storage medium for the reduction of organic molecules. In this case, the reduction of the
olefin likely occurs via successive hydrogen atom transfer steps, as experiments in the presence of excess phosphine produced no inhibition. Performing the same procedure with \([1\text{-ND}_{3}]^+\) yielded 1’,2’-d2-ethylbenzene (27%) with 1’-d1-ethylbenzene (27%), 2’-d1-ethylbenzene (24%) and ethylbenzene (22%) also detected by quantitative \(^{13}\text{C}\)-NMR spectroscopy (see Experimental Section). Overall, a 1:1 ratio of deuterium incorporation into the methylene and methyl positions of styrene was observed by \(^2\text{H}\) NMR spectroscopy. These results are consistent with reversible H-atom transfer between \([1\text{-ND}_{3}]^+\) and styrene and provide direct chemical evidence for the DFT computed N-H BDFE of 45.1 kcal/mol as the C-H BDFE adjacent to a benzylic radical is known to be 45 kcal/mol\(^{11,42}\).

**Figure 3.4.** Molybdenum (a) ammonia, (b) hydrazine and (c) aquo complexes that exhibit bond weakening by coordination and spontaneous hydrogen evolution.
Studies were also conducted to explore the molecularity of H\textsubscript{2} evolution from [1-NH\textsubscript{3}]\textsuperscript{+}. A crossover experiment was performed whereby a 1:1 mixture of [1-NH\textsubscript{3}]\textsuperscript{+} and [1-ND\textsubscript{3}]\textsuperscript{+} was heated to 60°C for 6 hours and the evolved gas collected and analyzed. Both H\textsubscript{2} and D\textsubscript{2} were detected by \textsuperscript{1}H and \textsuperscript{2}H NMR spectroscopy, respectively, together with substatistical amount of HD gas (H\textsubscript{2}:HD, 5:1; \textsuperscript{1}H NMR). The observation of HD gas is likely a result of isotopic exchange between coordinated ammine ligands. To support such pathways are operative, a 1:1 mixture of [1-NH\textsubscript{2}]\textsuperscript{+} and [1-ND\textsubscript{2}]\textsuperscript{+} was prepared and monitored by \textsuperscript{31}P NMR spectroscopy. A statistical mixture of isotopomers, [1-NH\textsubscript{2}]\textsuperscript{+}, [1-NHD\textsuperscript{+}] and [1-ND\textsubscript{2}]\textsuperscript{+} was observed immediately following mixing (see Experimental Section). Based on these results, a pathway involving bimetallic H\textsubscript{2} evolution is disfavored; intermolecular chemistry with a large N–H or N–D kinetic isotope effect, however, cannot be rigorously eliminated.

The spontaneous liberation of H\textsubscript{2} from coordinated ammonia prompted investigation of other ubiquitous small molecules to determine the generality of hydrogen evolution from bond weakening by coordination. DFT calculations on the putative molybdenum aquo ([1-OH\textsubscript{2}]\textsuperscript{+}) and hydrazine ([1-(κ\textsuperscript{2}-N\textsubscript{2}H\textsubscript{4})]\textsuperscript{+}) complexes established exceedingly weak O-H and N-H bonds of 33.7 and 34.6 kcal/mol, respectively. Accordingly, treatment of a benzene solution containing [1-(Cl)] with one equivalent of Na[BArF\textsubscript{24}] in the presence of hydrazine or water furnished the diamagnetic yellow-brown solids [(P\textsuperscript{\textsuperscript{Pr}}Tpy)(PPh\textsubscript{2}Me\textsubscript{2})\textsubscript{2}Mo(κ\textsuperscript{2}-NHNH\textsubscript{2})][BArF\textsubscript{24}] ([1-(κ\textsuperscript{2}-NHNH\textsubscript{2})]\textsuperscript{+}) and [(P\textsuperscript{\textsuperscript{Pr}}Tpy)(PPh\textsubscript{2}Me\textsubscript{2})\textsubscript{2}Mo(OH)][BArF\textsubscript{24}] [1-OH]\textsuperscript{+}, in 68% and 61% yields, respectively. In each case, H\textsubscript{2} gas evolution was confirmed by Toepler pump experiments (73% and 58%
yield of H$_2$, respectively, Figure 3.4b, 3.4c). While the benzene-$d_6$ $^1$H, $^{13}$C, and $^{31}$P NMR spectra of [1-OH]$^+$ are consistent with a $C_{2v}$ symmetric compound, the side-on bound hydrazido ligand in [1-(κ$^2$-NHNH$_2$)]$^+$ lowers the overall symmetry of the molecule to $C_s$.

The synthesis of the deuterated isotopologues [1-(κ$^2$-NDND$_2$)]$^+$ and [1-OD]$^+$ were carried out using N$_2$D$_4$ and D$_2$O, respectively, and enabled assignment of the N-H/D and O-H/D peaks in the solid-state (KBr) infrared spectrum. The N-H peaks in the IR spectrum (KBr) of [1-(κ$^2$-NHNH$_2$)]$^+$ appear at 3315 cm$^{-1}$, 3240 cm$^{-1}$ and 3186 cm$^{-1}$ (2547 cm$^{-1}$, 2503 cm$^{-1}$, 2434 cm$^{-1}$ in [1-(κ$^2$-NDND$_2$)]$^+$, while the spectrum of [1-OH]$^+$ features a sharp -OH peak at 3558 cm$^{-1}$ (2627 cm$^{-1}$ in [1-OD]$^+$). These results, in combination with the spectroscopic data, support the assignment of the hydrazido and hydroxo ligands in [1-(κ$^2$-NHNH$_2$)]$^+$ and [1-OH]$^+$, respectively. The formation of the putative hydrazine and water adduct complexes [1-κ$^2$-N$_2$H$_4$]$^+$ and [1-OH$_2$]$^+$ en route to H$_2$ evolution was probed by performing the syntheses of [1-(κ$^2$-N$_2$H$_4$)]$^+$ and [1-OH$_2$]$^+$ in the presence of 1 equiv. of $t$Bu$_3$C$_6$H$_2$O•. In both cases, immediate and quantitative formation of [1-OH]$^+$ and [1-(κ$^2$-NHNH$_2$)]$^+$ was observed by $^1$H-NMR spectroscopy along with the stoichiometric generation of $t$Bu$_3$C$_6$H$_2$OH. Importantly, no H$_2$ was evolved in these reactions, implying the intermediacy of “non-classical” metal-bound hydrazine and aquo complexes preceding H$_2$ evolution in the absence of a radical abstracting reagent.

The solid-state structures of [1-(κ$^2$-NHNH$_2$)]$^+$ (Figure 3.12) and [1-OH]$^+$ (Figure 3.13) were determined by X-ray diffraction. With [1-OH]$^+$, an octahedral coordination geometry around molybdenum was observed with trans phosphine ligands similar to [1-NH$_3$]$^+$ and [1-NH$_2$]$^+$. The coordination environment of [1-(κ$^2$-NHNH$_2$)]$^+$ is best described as pentagonal bipyramidal, where the tridentate terpyridine chelate and the
bidentate hydrazido ligand occupy the vertices of an equatorial pentagon with apical phosphine ligands completing the coordination sphere of molybdenum. The solid-state structure of \([\text{1-(κ}^2-\text{NHNH}_2)]^+\) revealed a rare example of a side-on bound κ²-hydrazido fragment, consistent with the \(C_s\) molecular symmetry observed by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy.

Having demonstrated the generality of the method, elucidation of the properties of the transition metal that enable bond weakening by coordination were of interest. Equation 1.1 presents the Bordwell equation\(^{43,44}\) which expresses the bond dissociation free energy of a given N-H bond in terms of the redox potential of the metal complex and acidity of the N-H bond upon oxidation. As such, the electrochemical behavior of \([\text{1-NH}_3]^+\) was examined, and the one-electron oxidized compound \([\text{1-NH}_3]^{2+}\) was synthesized with the goal of experimentally determining the \(pK_a\) and thereby obtaining an experimental value for the N-H BDFE in \([\text{1-NH}_3]^+\) (Figure 3.5a).

\[
\text{BDFE} = 1.37pK_a + 23.06E^\circ + C_G \tag{1.1}
\]

The cyclic voltammogram of the formally Mo(I) complex \([\text{1-NH}_3]^+\) exhibits two reversible anodic waves, one at -1.09 V (relative to Fc/Fc⁺) assigned to one electron oxidation to the dicationic complex, \([\text{1-NH}_3]^{2+}\). The second wave, centered at -0.57 V, is assigned as the second oxidation event to furnish the two-electron oxidized compound, \([\text{1-NH}_3]^{3+}\). The cyclic voltammogram also contains a quasi-reversible cathodic wave at -2.56 V likely corresponding to the reduction event to yield \([\text{1-NH}_3]^0\).
Figure 3.5. (a) Thermochemical expression for N-H bond dissociation free energies. Oxidation potentials and pKₐ measurements for a series of molybdenum complexes of varying oxidation states. Bolded values are experimentally measured, while italics are DFT computed. aValues obtained from gas-phase DFT calculations. bOxidation potentials reported relative to Fc/Fc⁺ in THF solution with 0.1 M [nBu₄N][PF₆] as the electrolyte. cCalculated value in THF from the Bordwell equation for the reaction [Moⁿ⁻¹-NH₃]ᵐ⁺₁ → [Moⁿ⁻¹-NH₂]ᵐ⁺, assuming the corresponding DFT-calculated N-H BDFE value and Cₛₒ㎜(THF) = 66 kcal mol⁻¹.

With experimental oxidation potentials in hand for [1-NH₃]²⁺, [1-NH₃]⁺, and [1-NH₃]⁰, the isolation of the one-electron oxidized product [1-NH₃]²⁺ was targeted in order to carry out N-H pKₐ determinations and hence BDFE measurement for [1-NH₃]⁺.

Addition of [H(OEt)₂][BARF²⁴] to [1-NH₂]⁺ yielded the NMR and EPR silent S = 1 product (μₑffective = 2.7 μB, 23 °C magnetic susceptibility balance), [(Ph₂Tpy)(PPh₂Me)₂Mo(NH₃)][BARF²⁴]₂ (1-NH₃)²⁺ in 78% yield. The N-H pKₐ of [1-NH₃]²⁺ was determined by measurement of the equilibrium concentration ratio with
concentrations its conjugate base \([\text{1-NH}_2]^+\) in the presence of 2-methoxy pyridine (\(pK_a = 2.6, \text{THF}\)).\(^{46}\) Using this method, the average of multiple equilibration experiments established the \(pK_a\) of \([\text{1-NH}_3]^{2+}\) as 3.6 in THF solution (Table 3.1 and Figure 3.10). This value, coupled with the experimentally determined \(E^{\circ}_{\text{ox}}\) of \([\text{1-NH}_3]^+\) (-1.09 V) allowed for the determination of an experimental THF solution N-H BDFE of 45.8 kcal/mol using the Bordwell equation for \([\text{1-NH}_3]^+\), which is in excellent agreement with the DFT-computed gas-phase value of 45.1 kcal/mol. Thus both the acidity, likely arising from the overall cationic charge on the complex, and the reducing nature of the metal, a result of the formal Mo(I) oxidation state, contribute to the observed N-H bond weakening in \([\text{1-NH}_3]^+\).

To elucidate the individual contributions of metal reduction potential and N-H \(pK_a\) on the phenomenon of bond weakening, computational (DFT) studies were carried out to determine the N-H bond dissociation free energies in the series of complexes \([\text{1-NH}_3]^{2+}\), \([\text{1-NH}_3]^+\), and \([\text{1-NH}_3]^0\). The successive one electron reduction from \([\text{1-NH}_3]^{2+}\) to \([\text{1-NH}_3]^+\) to \([\text{1-NH}_3]^0\) results in a concomitant lowering of the N-H bond dissociation free energy (Figure 3.5b). Using the DFT-computed N-H BDFEs and experimentally determined oxidation potentials, application of the Bordwell equation allows evaluation of the respective \(pK_a\) values for the members of the redox series where an experimental determination is not possible. It should be noted that the \(pK_a\) values determined in Figure 3.5b correspond to the oxidized form of the compound presented, as shown in the square scheme in Figure 3.5a.

While calculated differences of \(\sim 11\) kcal/mol of N-H bond dissociation free energy accompany each one electron redox step, the dominant term in the Bordwell
equation varies depending on the charge of the molybdenum complex. The most reduced member of the series, \([\text{1-NH}_3]^{0}\), has the least acidic N-H bond (\(pK_a = 20.1\)) and demonstrates that the large negative potential (\(E^\circ_{\text{ox}} = -2.56\)) is the dominant component of the bond weakening phenomenon. Attempts to synthesize this compound by chemical reduction of \([\text{1-NH}_3]^+\) have been unsuccessful yielding a complex mixture of products upon treatment with potassium graphite (\(\text{KC}_8\)). While the origin of the decomposition is not definitive, isolation of a compound with an N-H bond dissociation free energy of 34.5 kcal/mol is likely challenging.

Notably, the corresponding molybdenum cation, \([\text{1-NH}_3]^+\) has a \(pK_a\) 17 units lower than the value calculated for \([\text{1-NH}_3]^0\), consistent with known trends in metal aquo complexes, where increased charge density and electropositivity increases O-H acidity.\(^{47}\) The observed hydrogen bonding in the solid-state structure between the N-H supports the calculated \(pK_a\). Notably, further increase in acidity is minimal upon the second oxidation to \([\text{1-NH}_3]^{2+}\) as only a slight decrease in \(pK_a\) to 2.2 was observed. The leveling in acidity suggests that while both \([\text{1-NH}_3]^{2+}\) and \([\text{1-NH}_3]^+\) have weak N-H bonds, the spontaneous \(\text{H}_2\) evolution with the latter is largely driven by the reduction potential of the formally Mo(I) complex.

**Conclusion**

Elucidation and delineation of the origin of coordination induced bond weakening provide design principles for applications ranging from catalysis to bioinorganic chemistry to alternative energy. In cases where the function of ligands containing N-H
and O-H is to stabilize metal complexes, often with various oxidation states throughout a catalytic cycle, combinations of redox potentials and \( pK_a \) s that promote this effect should be suppressed. Alternatively, in cases such as small molecule activation or hydrogen storage application, these properties can be rationally tuned to favor weakening of element-hydrogen bonds. The kinetic stabilization of \([1-\text{NH}_3]^+\), a molecule with an unusually weak N-H bond should inspire synthetic efforts to prepare additional examples of “non-classical” coordination compounds.

**Experimental Section**

**General Considerations**

All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.\(^{48}\) Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Small amounts (2 mL) of hydrazine were dried over BaO before careful distillation from behind a blast shield. **DANGER: anhydrous hydrazine can be explosive in large amounts at high temperatures and should be distilled with extreme caution.** Anhydrous ammonia was prepared via ammonia condensation onto sodium metal, forming an amber electrolyte and was subjected to three freeze-pump-thaw cycles before use. **DANGER: When using the**
sodium electrolyte method to dry ammonia, use small quantities with extreme caution to avoid violent H\textsubscript{2}\textsubscript{g\textsubscript{s}} evolution from the reaction of sodium metal with residual water in ammonia. When storing the ammonia electrolyte in a closed vessel, regularly expose the mixture to freeze pump thaw cycles to avoid pressure buildup over time. 2-methoxy-pyridine (2-OMe-Py) was purchased from Sigma-Aldrich, dried over CaH\textsubscript{2} before vacuum distillation and stored over 4 Å molecular sieves before use.

\[(\text{PhTpy})(\text{PPhMe})_2\text{Mo(Cl)}\] \{[1-Cl]\}\textsuperscript{34} \[\{\eta^5-\text{C}_5\text{Me}_5\text{Cr(CO)}_3\}_2\textsuperscript{49} 2,4,6\text{-}terr-butylphenoxyl radical (tBu\textsubscript{3}ArO)\textsuperscript{50} and Na[BArF\textsubscript{24}]\textsuperscript{51} were prepared following literature procedures.

\textsuperscript{1}H NMR spectra were recorded on Bruker AVANCE 300 and Bruker AVANCE 500 spectrometers operating at 300.13 and 500.62 MHz respectively. \textsuperscript{13}C NMR spectra were recorded on a Bruker AVANCE 500 operating at 125.89 MHz. All \textsuperscript{1}H and \textsuperscript{13}C chemical shifts are reported relative to SiMe\textsubscript{4} using the \textsuperscript{1}H (residual) and \textsuperscript{13}C chemical shifts of the solvent as a secondary standard. \textsuperscript{31}P NMR spectra were collected on a Bruker 500 AVANCE spectrometer operating at 202.40 MHz and were referenced to 85% H\textsubscript{3}PO\textsubscript{4} as an external standard. \textsuperscript{19}F NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 282.23 MHz and were referenced to CFCl\textsubscript{3} as an external standard. \textsuperscript{11}B NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 96.251 MHz and were referenced to BF\textsubscript{3}OEt\textsubscript{2} as an external standard. \textsuperscript{15}N NMR spectra were recorded on a Bruker 500 spectrometer operating at 50.663 MHz and \textsuperscript{15}N chemical shifts are reported relative to liquid NH\textsubscript{3} using an external standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Gouy magnetic susceptibility balance measurements were performed.
with a Johnson Matthey instrument that was calibrated with HgCo(SCN)$_4$. Continuous wave EPR spectra were recorded at room temperature on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.$^{52}$

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker D8 APEX3 Venture diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å) and a Cu X-ray tube ($\lambda = 1.54178$ Å). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

Computational N-H Bond Dissociation Free Energy (BDFE$_{\text{N-H}}$) Determinations. All DFT calculations were performed with the ORCA program package in the gas phase.$^{53}$ The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.$^{54,55,56}$ The all-electron Gaussian basis sets were those developed by the Ahlrichs group.$^{57,58,59}$ Triple-ζ quality basis sets def2-TZVP with one set of polarization functions on molybdenum, phosphorous and nitrogen were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used that were of double-ζ quality in the valence region and contained a polarizing set of d functions on
the non-hydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX)\textsuperscript{60,61,62} approach were chosen to match the orbital basis.\textsuperscript{63,64,65} Numerical frequencies were calculated at the same level of theory to confirm the optimized geometries (no imaginary frequencies) and to derive thermochemical data. Bond dissociation free energies were computed at standard conditions of 1 atm and 25 °C including corrections for vibrational zero-point energy, as well as contributions from translational, rotational, and vibrational modes to the energy and entropy of the homolytic bond cleavage process. For molecules containing a molybdenum and ruthenium atoms, the 0th order regular approximation (ZORA) was applied.\textsuperscript{66} In this case, the relevant basis sets were replaced by their relativistically recontracted versions. In the geometry optimizations and numerical frequency calculations on molybdenum complexes, the 4’-Ph-2,2’,6’,2’’-terpyridine ligand was truncated to 2,2’,6’,2’’-terpyridine in order to reduce the requisite computational effort. The electronic energy of H•, utilized in the calculation of bond dissociation free energies, at the present level of theory is 13.576 eV (313.1 kcal/mol).

**Experimental N-H Bond Dissociation Free Energy (BDFE\textsubscript{N-H})**

**Determinations.** An experimental measure for the N–H bond dissociation free energy (BDFE\textsubscript{N-H}) of [\textbf{1-NH}_3]^+ was obtained using the Bordwell Equation (Equation 1.1). The value $E^\circ_{\text{ox}}$ of [\textbf{1-NH}_3]^+ was determined using cyclic voltammetry (CV). CVs were collected in THF solution (1 mM in compound) with [\textsuperscript{6}Bu_4N][PF_6] (0.1 M), using a 3 mm glassy carbon working electrode, platinum wire as the counter electrode, and silver wire as the reference in a drybox equipped with electrochemical outlets. CVs were recorded
using a BASi EC Epsilon electrochemical workstation and analyzed using the BASi Epsilon-EC software. All CVs were run at a scan rate of 100 mV/s at 23 °C. Potentials are reported versus Fc/Fc\(^+\) and were obtained using the \textit{in situ} method. A \(pK_a\) of [1-NH\(_3\)]\(^{2+}\) was determined by using the 2-methoxy-pyridine/2-methoxy-pyridinium (2-OMe-Py/2-OMe-PyH\(^+\); \(pK_a\)(THF) = 2.6)\(^{16}\) acid/base pair reference wherein relative concentrations the components were determined by \(^1\)H-NMR spectroscopy. The \(pK_a\) of [1-NH\(_3\)]\(^{2+}\) relative to the reference acid/base pair was calculated according to literature procedures.\(^{67}\)

**Preparation of Molybdenum Complexes**

**Preparation of [1-NH\(_3\)]\(^+\).** In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.200 g (0.238 mmol) of [1-Cl] and 0.213 g (0.240 mmol) of Na[BArF\(_{24}\)]. The vessel was sealed and connected to a high vacuum line, where 20 mL of degassed (via 3x freeze pump thaw cycles) benzene was condensed onto the solids, followed by the addition of 0.250 mmol of ammonia in a 13.1 mL gas bulb (202 mmHg, 296 K). The vessel was then sealed and the mixture stirred at room temperature for 18 hours. The reaction vessel was then brought back into the glovebox and the mixture was filtered through a pad of Celite, followed by the concentration of the solution to a volume of approximately 5 mL. Excess pentane (20 mL) was layered onto the concentrated solution to induce the precipitation of a dark oil over the course of 1 hour at room temperature. The mother liquor was decanted, and the oil was washed with cold pentane (3 x 5 mL) followed by trituration with pentane (5 x 5 mL) to yield the
product as foamy black solids (0.310 g, 0.184 mmol, 77%). Crystals suitable for X-ray diffraction studies were obtained by recrystallization at -35°C from a concentrated solution of fluorobenzene and pentane. Magnetic Susceptibility: (Guoy balance, 295 K) μ\text{eff} = 1.7(2) \muB. Two sets of samples, prepared on two different occasions, were sent for elemental analysis to check the reproducibility of the method. Anal Calcd for C_{79}H_{56}BF_{24}MoN_{4}P_{2}: C, 56.28; H, 3.35; N, 3.32. Found Sample 1: C, 55.93; H, 3.04; N, 2.92. Found Sample 2: C, 56.31; H, 3.16; N, 3.17. IR (KBr, 295 K, cm\(^{-1}\)): 2919, 2899, 2847 (-NH\(_3\)). *For comparison to N-H vibrations of classical ammine complexes cis-[(Cl)\(_2\)Pt(NH\(_3\))\(_2\)], [(NH\(_3\))\(_6\)Co]Cl\(_3\) and [(NH\(_3\))\(_6\)Ru][BF\(_4\)]\(_2\) and gaseous ammonia see references 35,36,37,38.

**Preparation of [1-ND\(_3\)]\(^+\).** The d\(_3\)-isotopologue was prepared and isolated in a similar manner to [1-NH\(_3\)]\(^+\) with the exception that ND\(_3\) was used in place of NH\(_3\). IR (KBr, 295 K, cm\(^{-1}\)): 2497, 2408, 2386 (-ND\(_3\)).

**Preparation of [1-NH\(_2\)]\(^+\).** In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.300 g (0.357 mmol) of [1-Cl] and 0.319 g (0.360 mmol) of Na[BArF\(_{24}\)]. The vessel was sealed and connected to a high vacuum line, where 20 mL of degassed (by 3x freeze pump thaw cycles) benzene was condensed onto the solids, followed by addition of 0.428 mmol of ammonia in a 13.1 mL gas bulb (603 mmHg, 296K). The reaction vessel was then sealed and the mixture stirred at 60°C under vacuum for 18 hours. Using a Toepler pump, 0.163 mmol (58 mmHg, 52.0 mL, 296 K; 0.457 equivalents per Mo) of gas was collected after 18 hours. The gas was passed over a
bed of CuO pre-heated to 200 °C. After this procedure, no gas was collected, confirming the identity of the evolved gas as H₂. The reaction vessel was then brought back into the glovebox and the mixture was filtered through a pad of Celite, followed by the removal of the solvent in vacuo. The dark residue was washed with pentane (3 x 3 mL) followed by trituration with pentane (5 x 5 mL) to yield the product as foamy black solids (0.456 g, 0.271 mmol, 76%). Crystals suitable for X-ray diffraction studies were obtained by recrystallization at -35 °C from a concentrated solution of fluorobenzene and pentane.

Anal Calcd for C₇₀H₅₅BF₂₄MoN₄P₂: C, 56.31; H, 3.29; N, 3.33. Found: C, 56.44; H, 3.40; N, 3.16. ¹H NMR (benzene-d₆, 295 K): δ 10.02 (t, ³JPH = 16.7 Hz, 2H, Mo-NH₂), 8.78 (d, J = 6.1 Hz, 2H, PhTpy), 8.50 (s, 8H, B[(3,5-(CF₃)₂)C₆H₃]₄), 7.69 (s, 4H, B[(3,5-(CF₃)₂)C₆H₃]₄), 7.63 (s, 2H, PhTpy), 7.46 (t, J = 7.2 Hz, 2H, PhTpy), 7.34 (d, J = 8.3 Hz, 2H, PhTpy), 7.30 (t, J = 7.4 Hz, 1H, PhTpy), 6.86 (t, J = 7.4 Hz, 4H, P(C₆H₅)₂(CH₃)), 6.73 (t, J = 7.6 Hz, 8H, P(C₆H₅)₂(CH₃)), 6.49 (t, J = 7.4 Hz, 2H, PhTpy), 6.27 – 6.18 (m, 8H, P(C₆H₅)₂(CH₃)), 6.17 – 6.11 (m, 2H, PhTpy), 0.31 (s, 6H, P(C₆H₅)₂(CH₃)). ¹³C NMR (benzene-d₆, 295 K): δ 163.22 (q, ¹JCB = 49.7 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 146.56 (s, PhTpy), 145.63 (s, PhTpy), 140.28 (s, PhTpy), 138.29 (s, PhTpy), 130.54 (q, ²JC-F = 16.5 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 130.35 (app t, J = 5.7 Hz, P(C₆H₅)₂(CH₃)), 129.95 (s, P(C₆H₅)₂(CH₃), 129.88 (s, P(C₆H₅)₂(CH₃)), 129.62 (s, PhTpy), 129.44 (s, PhTpy), 128.99 (app t, J = 4.3 Hz, P(C₆H₅)₂(CH₃)), 128.68 (s, PhTpy), 127.53 (s, PhTpy), 125.50 (q, ¹JC-F = 272 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 122.96 (s, PhTpy), 122.41 (s, PhTpy), 118.92 (s, PhTpy), 118.50 (s, B[(3,5-(CF₃)₂)C₆H₃]₄), 112.71 (s, PhTpy)) 8.76 (app t, J = 10.2 Hz,
P(C₆H₅)₂(CH₃)). \{¹H\}³¹P NMR (benzene-d₆, 295 K): δ 15.58 (s). \{¹H\}¹⁹F NMR (benzene-d₆, 295 K) δ -63.62 (s). IR (KBr, 295 K, cm⁻¹): 3354, 3287 (-NH₂).

Preparation of [1⁻¹⁵NH₂]⁺. The ¹⁵N isotopologue was prepared using an identical procedure to [1-NH₂]⁺ with the exception that ¹⁵NH₃ was used in place of NH₃. \(^{1}H\) NMR (benzene-d₆, 295 K): δ 10.02 (10.02 (dt, \(^{1}J_{N-H} = 68.4, {^{3}J_{P-H} = 16.8}\) Hz, 2H, Mo⁻¹⁵NH₂), 8.78 (d, \(J = 6.2\) Hz, 2H, PhTpy), 8.48 (s, 8H, B[(3,5-(CF₃)₂]C₆H₃]₄, overlap with 2H, PhTpy), 7.68 (s, 4H, PhTpy), 7.60 (d, \(J = 8.3\) Hz, 2H, PhTpy), 7.46 (t, \(J = 7.8\) Hz, 2H, PhTpy), 7.34 (d, \(J = 8.3\) Hz, 2H, PhTpy), 7.32 – 7.26 (m, 1H, PhTpy), 6.86 (t, \(J = 7.4\) Hz, 4H, P(C₆H₅)₂(CH₃)), 6.73 (t, \(J = 7.7\) Hz, 8H, P(C₆H₅)₂(CH₃)), 6.52 – 6.44 (m, 2H, PhTpy), 6.24 – 6.20 (m, 8H, P(C₆H₅)₂(CH₃)), 6.17 – 6.11 (m, 2H, PhTpy), 0.31 (app t, \(J = 2.5\) Hz, 6H, P(C₆H₅)₂(CH₃)). \{¹H\}³¹P NMR (benzene-d₆, 295 K): δ 15.58 (d, \(^{2}J_{P,N} = 4.1\) Hz). \(^{15}N\) NMR (benzene-d₆, 295 K): δ 235.5 (t, \(^{1}J_{N-H} = 68.5\) Hz).

Preparation of [1-ND₂]⁺. The d₂-isotopologue was prepared and isolated in a similar manner to [1-NH₂]⁺ with the exception that ND₃ was used in place of NH₃. \(^{2}H\) NMR (500 MHz, benzene-d₆, 295 K): δ 10.09 (br s, Mo-ND₂). \{¹H\}³¹P NMR (benzene-d₆, 295 K): δ 15.64 (s). IR (KBr, 295 K, cm⁻¹): 2512, 2426 (-ND₂).

Preparation of [1-(κ²-NHNH₂)]⁺. In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.300 g (0.357 mmol) of [1-Cl], 0.319 g (0.360 mmol) of Na[BArF²₄] and 14 uL (0.446 mmol) of hydrazine and was immediately frozen in a liquid-nitrogen cooled coldwell. The vessel was sealed and connected to a high
vacuum line and the headspace was removed *in vacuo*. Degassed (via 3x freeze pump thaw cycles) benzene was then condensed onto the solids and the mixture was stirred at room temperature under vacuum for 30 minutes during which time a color change from forest green to brown was observed. Using a Toepler pump, 0.130 mmol (46 mmHg, 52.0 mL, 296 K; 0.365 equivalents per Mo) of gas was collected after 30 minutes. The gas was passed over a bed of CuO pre-heated to 200 °C. After this procedure, no gas was collected, confirming the identity of the evolved gas as H₂. The reaction vessel was then brought back into the glove box and the mixture was filtered through a pad of Celite, followed by the removal of the solvent *in vacuo*. The dark residue was washed with pentane (3 x 3 mL) followed by trituration with pentane (5 x 5 mL) to yield the product as foamy brown solids (0.410 g, 0.241 mmol, 68%). Crystals suitable for X-ray diffraction studies were obtained by recrystallization at -35°C from a concentrated solution of fluorobenzene and hexane. Anal Calcd for C₇₀H₅₆BF₂₄MoN₅P₂: C, 55.81; H, 3.32; N, 4.12. Found: C, 55.66; H, 3.03; N, 4.13. ¹H NMR (benzene-d₆, 295 K): δ 9.34 (d, J = 5.5 Hz, 1H, PhTpy), 8.49 (s, 8H, B[(3,5-(CF₃)₂)C₆H₅]₄, overlap with 2H, PhTpy), 7.95 (s, 1H, PhTpy), 7.87 (d, J = 6.0 Hz, 1H, PhTpy), 7.75 (d, J = 6.4 Hz, 1H, PhTpy), 7.70 (s, 4H, B[(3,5-(CF₃)₂)C₆H₅]₄), 7.68-7.63 (m, 2H, PhTpy), 7.45 (t, J = 7.7 Hz, 2H, PhTpy), 7.38 (d, J = 8.1 Hz, 1H, PhTpy), 7.29 (t, J = 7.3 Hz, 1H, PhTpy), 7.09 – 7.00 (m, 1H, PhTpy), 6.92 – 6.82 (m, 4H, P(C₆H₅)₂(CH₃)), 6.81 – 6.66 (m, 8H, P(C₆H₅)₂(CH₃)), 6.53 – 6.48 (m, 1H, PhTpy), 6.45 – 6.40 (m, 1H, PhTpy), 6.27-6.21 (m, 4H, P(C₆H₅)₂(CH₃)), 6.17-6.11 (m, 4H, P(C₆H₅)₂(CH₃)), 4.21 (d, J = 7.2 Hz, 2H, Mo-NHNH₂), 3.78-3.70 (m, 1H, Mo-NHNH₂), 0.05 (s, 6H, P(C₆H₅)₂(CH₃)). ¹³C NMR (benzene-d₆, 295 K): δ 162.89 (q, J_C-B = 49.7 Hz, B[(3,5-(CF₃)₂)C₆H₅]₄), 149.89 (s, PhTpy), 148.96 (s, PhTpy),
146.86 (s, PhTpy), 144.14 (s, PhTpy), 142.64 (s, PhTpy), 139.98 (s, PhTpy), 138.30 (s, PhTpy), 136.06 (s, PhTpy), 135.51 (s, B[(3,5-(CF$_3$)$_2$]C$_6$H$_3$]$_4$), 134.91 (s, PhTpy), 134.14 (s, B[(3,5-(CF$_3$)$_2$]C$_6$H$_3$]$_4$), 132.64 (s, PhTpy), 129.72 (s, P(C$_6$H$_5$)$_2$(CH$_3$)), 129.62 (s, P(C$_6$H$_5$)$_2$(CH$_3$)), 129.57 (s, P(C$_6$H$_5$)$_2$(CH$_3$)), 128.81 (s, P(C$_6$H$_5$)$_2$(CH$_3$)), 127.20 (s, PhTpy), 126.93 (s, PhTpy), 125.34 (q, $^1$J$_{CF}$ = 273 Hz, B[(3,5-(CF$_3$)$_2$]C$_6$H$_3$]$_4$), 122.63 (s, PhTpy), 121.19 (s, PhTpy), 121.08 (s, PhTpy), 118.16 (s, B[(3,5-(CF$_3$)$_2$]C$_6$H$_3$]$_4$), 113.37 (s, PhTpy), 112.39 (s, PhTpy), 112.24 (s, PhTpy), 6.52 (s, P(C$_6$H$_5$)$_2$(CH$_3$)). $^3^1$P NMR (benzene-$d_6$, 295 K): δ 8.94 (s). $^1$H$^{19}$F NMR (benzene-$d_6$, 295 K) δ -61.99 (s). IR (KBr, 295 K, cm$^{-1}$): 3315, 3240, 3186 (N$_2$H$_3$).

Preparation of [1-(κ$^2$-NDND$_2$)]$^+$. The $d_5$ isotopologue was prepared and isolated in a similar manner to [1-κ$^2$-NHNH$_2$]$^+$ with the exception that N$_2$D$_4$ was used in place of N$_2$H$_4$. $^2$H NMR (500 MHz, benzene-$d_6$, 295 K): δ 4.06 (br s, overlapping Mo-NDND$_2$). $^1$H$^{31}$P NMR (benzene-$d_6$, 295 K): δ 9.02 (s). IR (KBr, 295 K, cm$^{-1}$): 2547, 2503, 2434 (-NDND$_2$).

Preparation of [1-OH]$^+$. In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.150 g (0.178 mmol) of [1-Cl] and 0.160 g (0.180 mmol) of Na[BArF$_{24}$]. The vessel was sealed and connected to a high vacuum line where degassed benzene was condensed onto the solids. While maintaining a temperature of -78°C, degassed (by Ar purge) water (4 µL, 0.223 mmol) was added to the mixture via micro-syringe under a positive flow of argon. The vessel was sealed, the headspace was
evacuated and the reaction mixture was heated at 60°C for 6 hours, during which time a color change from forest green to brown was observed. Using a Toepler pump, 0.052 mmol (18 mmHg, 52.0 mL, 296 K; 0.29 equivalents per Mo) of gas was collected after 6 hours. The gas was passed over a bed of CuO pre-heated to 200 °C. After this procedure, no gas was collected, confirming the identity of the evolved gas as H₂. The solvent of the reaction was removed in vacuo, and the residue was dried under vacuum for 18 hours to remove residual water. The vessel was then brought back into the glovebox and the residue was extracted with toluene, and the combined extracts were filtered through a pad of Celite, followed by the removal of the solvent in vacuo. The dark residue was washed with pentane (3 x 3 mL) followed by trituration with pentane (5 x 5 mL) to yield the product as foamy brown solids (0.182 g, 0.108 mmol, 61%). Crystals suitable for X-ray diffraction studies were obtained by recrystallization at -35°C from a concentrated solution of fluorobenzene and pentane. Anal Calcd for C₇₉H₅₄BF₂₄MoN₃OP₂: C, 56.28; H, 3.23; N, 2.49. Found: C, 55.94; H, 2.93; N, 2.35. 

¹H NMR (benzene-d₆, 295 K): δ 13.44 (t, JₚH = 14.2 Hz, 1H, Mo-OH), 8.84 (d, J = 6.2 Hz, 2H, PhTpy), 8.44 (s, 8H, B[(3,5-(CF₃)₂C₆H₃]₄, overlap with 2H, PhTpy), 7.79 (s, 2H, PhTpy), 7.66 (s, 4H, B[(3,5-(CF₃)₂C₆H₃]₄), 7.62 (d, J = 7.3 Hz, 2H, PhTpy), 7.53 (d, J = 8.3 Hz, 2H, PhTpy), 7.48 (t, J = 7.5 Hz, 2H, PhTpy), 7.29 (t, J = 7.4 Hz, 1H, PhTpy), 6.84 (t, J = 7.4 Hz, 4H, P(C₆H₅)₂(CH₃)), 6.70 (t, J = 7.6 Hz, 8H, P(C₆H₅)₂(CH₃)), 6.44 (t, J = 7.6 Hz, 2H, PhTpy), 6.21–6.08 (m, 8H, P(C₆H₅)₂(CH₃)), 6.09 (t, J = 6.6 Hz, 2H, PhTpy), 0.18 (s, 3H, P(C₆H₅)₂(CH₃)). 

¹³C NMR (benzene-d₆, 295 K): δ 162.87 (q, JₜC-B = 49.7 Hz, B[(3,5-(CF₃)₂C₆H₃]₄), 144.98 (s, PhTpy), 143.92 (s, PhTpy), 140.32 (s, PhTpy), 137.32 (s, PhTpy), 135.50 (s, B[(3,5-(CF₃)₂C₆H₃]₄), 131.45 (s, PhTpy), 130.23 (q, JₜC-F = 16.9 Hz,
Preparation of [1-OD]$^+$: The deuterated isotopologue was prepared and isolated in a similar manner to [1-OH]$^+$ with the exception that D$_2$O was used in place of H$_2$O. $^2$H NMR (500 MHz, benzene-$d_6$, 295 K): $\delta$ 13.55 (br s, Mo-O-D). $^1$H$^{31}$P NMR (benzene-$d_6$, 295 K): $\delta$ 12.06 (s). IR (KBr, 295 K, cm$^{-1}$): 2627 (-OD).

Preparation of [1-NH$_3$]$^{2+}$: In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, 0.052 g (0.031 mmol) of [1-NH$_3$]$^{2+}$ and 3 mL of fluorobenzene. To the stirring solution, a solution containing 0.033 g (0.032 mmol) of [(HOEt$_2$)$_2$][BArF$_{24}$] and 1 mL of fluorobenzene was added dropwise, inducing an immediate color change from olive green to red-brown. After stirring at room temperature for 15 minutes, the volume of the solution was reduced to ca. 1 mL in vacuo and excess pentane (5 mL) was added to induce the immediate precipitation of dark brown solids. The supernatant was decanted, and the solids were successively washed with cold toluene (1 mL) and pentane (3 x 3 mL) followed by trituration with pentane (5 x 3 mL). The dark residue was then dried in vacuo to give the product as a dark red solid (0.061 g, 0.024 mmol, 78%). Anal Calcd for
C111H68B2F48MoN4P2: C, 52.30; H, 2.69; N, 2.20. Found: C, 52.06; H, 2.40; N, 1.89.

Magnetic susceptibility (Guoy balance, 295 K): $\mu_{\text{eff}} = 2.7 \mu_B$. IR (KBr, 295 K, cm⁻¹): 3282, 3202, 3180 (⁻NH₃).

**Additional Reactions and Associated NMR Data**

**PCET reaction between [1-NH₃]⁺ and 'Bu3ArO•.** A J-Young NMR tube equipped with a Teflon cap was charged with 0.051 g (0.030 mmol) of [1-NH₃]⁺, 0.008 g (0.031 mmol) of 'Bu3ArO•, 0.006 g (0.032 mmol) of Cp₂Fe internal standard and 0.6 mL benzene-d₆ and shaken for 1 minute. An immediate color change to olive green was observed and subsequent ¹H and ³¹P-NMR analysis established formation of [1-NH₂]⁺ and 'Bu₃C₆H₂OH (>97% NMR yield vs Cp₂Fe internal standard).

**PCET reaction between [1-NH₃]⁺ and [(η⁵-C₅Me₅)Cr(CO)₃]₂.** A J-Young NMR tube equipped with a teflon cap was charged with 0.023 g (0.014 mmol) of [1-NH₃]⁺, 0.004 g (7.37 µmol) of [(η⁵-C₅Me₅)Cr(CO)₃]₂, 0.003 g (0.016 mmol) of Cp₂Fe internal standard and 0.6 mL benzene-d₆ and shaken for 1 minute. An immediate color change to olive green was observed and subsequent ¹H and ³¹P NMR analysis indicated formation of [1-NH₂]⁺ and [(η⁵-C₅Me₅)Cr(CO)₃(H)] (>97% NMR yield vs Cp₂Fe internal standard).

**Thermal H₂ liberation from [1-NH₃]⁺.** A J-Young NMR tube equipped with a Teflon cap was charged with 0.051 g (0.030 mmol) of [1-NH₃]⁺, 0.006 g (0.032 mmol) of Cp₂Fe internal standard and 0.6 mL benzene-d₆. The NMR tube was sealed, connected to a high
vacuum line and exposed to freeze pump thaw cycles (3x). The tube was then sealed and
heated at 60°C under vacuum for 6 hours. During the course of the reaction, a color
change to olive green was observed and subsequent $^1$H and $^{31}$P-NMR analysis established
formation of $[1\text{-NH}_2]^+$ (>97% NMR yield vs Cp$_2$Fe internal standard) as well as H$_2$.

**Reaction of putative $[1-(\kappa^2\text{-NH}_2\text{NH}_2)]^+$ with $\text{Bu}_3\text{ArO}^•$.** A J-Young NMR tube
equipped with a Teflon cap was charged with 0.048 g (0.057 mmol) of $[1\text{-Cl}]$, 0.051 g
(0.058 mmol) of Na[BarF$_{24}$], 0.015 g (0.058 mmol) of $\text{Bu}_3\text{ArO}^•$, 2.0 µL (0.063 mmol) of
N$_2$H$_4$, 0.011 g (0.059 mmol) of Cp$_2$Fe internal standard and 0.6 mL benzene-$d_6$ and was
shaken for 1 minute. An immediate color change to brown was observed and subsequent
$^1$H and $^{31}$P-NMR analysis established formation of $[1-(\kappa^2\text{-NHNH}_2)]^+$ and $\text{Bu}_3\text{ArOH}$
(>97% NMR yield vs Cp$_2$Fe internal standard).

**Reaction of Putative $[1\text{-OH}_2]^+$ with $\text{Bu}_3\text{ArO}^•$.** A J-Young NMR tube equipped with a
Teflon cap was charged with 0.085 g (0.101 mmol) of $[1\text{-Cl}]$, 0.090 g (0.102 mmol) of
Na[BarF$_{24}$], 0.027 g (0.103 mmol) of $\text{Bu}_3\text{ArO}^•$, 0.019 g (0.102 mmol) of Cp$_2$Fe internal
standard. The tube was evacuated on a high vacuum line, where a de-gassed mixture (3x
freeze pump thaw cycles) containing 0.6 mL benzene-$d_6$ and 2.0 µL (0.111 mmol) of
water was vacuum condensed onto the solids. The mixture was thawed and shaken for 5
minutes. A color change to brown was observed and subsequent $^1$H and $^{31}$P-NMR
analysis established formation of $[1\text{-OH}]^+$ and $\text{Bu}_3\text{C}_6\text{H}_2\text{OH}$ (>97% NMR yield vs Cp$_2$Fe
internal standard).
**Reaction of [1-ND₃]⁺ with styrene.** A J-Young NMR tube equipped with a Teflon cap was charged with 0.095 g (0.056 mmol) of [1-ND₃]⁺, 8.0 µL (0.070 mmol) of styrene, 0.008 g (0.043 mmol) of Cp₂Fe internal standard and 0.6 mL benzene-d₆ and heated at 60°C for 6 hours. A color change to olive green was observed and subsequent ¹H and ³¹P NMR analysis indicated statistical formation of [1-NH₂]⁺, [1-NHD]⁺ and [1-ND₂]⁺ as well as a mixture of 1’,2’-d₂-ethylbenzene, 1’-d₁-ethylbenzene, 2’-d₁-ethylbenzene and ethylbenzene (in an approximate relative ratio of 1:1:1:1) in a combined NMR yield of 25% vs Cp₂Fe internal standard.

**Figure 3.6.** Benzene-d₆ quantitative ¹³C{¹H}-NMR spectrum of the reaction between [1-ND₃]⁺ and styrene at 23 °C.
Crossover experiment with [1-NH$_3$]$^+$ and [1-ND$_3$]$^+$. A J-Young NMR tube equipped with a teflon cap was charged with 0.020 g (0.012 mmol) of [1-NH$_3$]$^+$, 0.020 g (0.012 mmol) of [1-ND$_3$]$^+$, dissolved in 0.6 mL of benzene-d$_6$. The NMR tube was sealed, connected to a high vacuum line and exposed to freeze pump thaw cycles (3x). The tube was then sealed and heated at 60°C under vacuum for 6 hours. During the course of the reaction, a color change to olive green was observed and subsequent $^1$H and $^{31}$P-NMR analysis established statistical and quantitative formation of [1-NH$_2$]$^+$, [1-ND$_2$]$^+$, and [1-NHD]$^+$. 

**Figure 3.7.** Benzene-d$_6$ $^{31}$P $^1$H-NMR spectrum of the reaction between [1-NH$_3$]$^+$ and [1-ND$_3$]$^+$ at 23 °C. Inset: Region of the Benzene-d$_6$ $^1$H-NMR spectrum of the reaction between [1-NH$_3$]$^+$ and [1-ND$_3$]$^+$ showing H$_2$ and HD evolution.
Mixing experiment with $[1{-}\text{NH}_2]^+$ and $[1{-}\text{ND}_2]^+$. A J-Young NMR tube equipped with a Teflon cap was charged with 0.020 g (0.012 mmol) of $[1{-}\text{NH}_2]^+$, 0.020 g (0.012 mmol) of $[1{-}\text{ND}_2]^+$, dissolved in 0.6 mL of benzene-$d_6$. The NMR tube was sealed and shaken for 15 minutes. Subsequent $^1\text{H}$ and $^{31}\text{P}$-NMR analysis established statistical and quantitative formation of $[1{-}\text{NH}_2]^+$, $[1{-}\text{ND}_2]^+$, and $[1{-}\text{NHD}]^+$.

Mixing experiment with $[1{-}\text{NH}_2]^+$ and $[1{-}\text{ND}_3]^+$. A J-Young NMR tube equipped with a teflon cap was charged with 0.015 g (0.009 mmol) of $[1{-}\text{NH}_2]^+$, 0.015 g (0.009 mmol) of $[1{-}\text{ND}_3]^+$, dissolved in 0.6 mL of benzene-$d_6$. The NMR tube was sealed and shaken for 15 minutes. Subsequent $^1\text{H}$ and $^{31}\text{P}$-NMR analysis established statistical and quantitative formation of $[1{-}\text{NH}_2]^+$, $[1{-}\text{ND}_2]^+$, and $[1{-}\text{NHD}]^+$ with respect to the diamagnetic $[1{-}\text{NH}_2]^+$ starting material.
EPR Spectroscopic Data

**Figure 3.8.** X-band EPR spectrum of [1-NH$_3$]$^+$ recorded in benzene solution at 23 °C. Microwave frequency = 9.380 GHz, power = 2.000 mW, modulation amplitude = 2.000 G. Simulated parameters; $g_{\text{iso}} = 1.988$, $g_{\text{iso str}} = 0.007$, $A_{\text{iso}}^{(95/97\text{Mo})} = 80$ MHz (assuming 15.92% naturally occurring $^{95}\text{Mo}$ with $I = 5/2$ and 9.55% naturally occurring $^{97}\text{Mo}$ with $I = 5/2$), $A_{\text{iso}}^{(31\text{P})} = 33$ MHz (assuming 2 equivalent 100% naturally occurring $^{31}\text{P}$ nuclei with $I = 1/2$), Gaussian broadening = 0.15 mT.
**Electrochemical Data**

![Cyclic voltammogram](image)

**Figure 3.9.** Cyclic voltammogram of $[1\text{-NH}_3]^+$ using a glassy carbon working electrode, platinum wire counter electrode, silver wire reference electrode, 0.1 M $[^\text{a}]{\text{Bu}}_4\text{N}[\text{PF}_6]$, scan rate 100 mV/sec in THF at 23 °C versus Cp$_2$Fe/Cp$_2$Fe$^+$.  

**pK$_a$ Determinations**

**Representative pK$_a$ determination procedure.** In a typical experiment, a J-Young NMR tube equipped with a teflon cap was charged with 0.048 g (0.019 mmol) of $[1\text{-NH}_3]^{2+}$, 2.0 µL (0.019 mmol) of 2-OMe-Py, 0.004 g (0.022 mmol) of Cp$_2$Fe internal standard and 0.6 mL THF-$d_8$. The NMR tube was sealed, shaken for 5 minutes, and its $^1$H-NMR spectrum recorded.

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<th>3</th>
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<td>4.1</td>
<td>2.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Table 3.1: Results of equilibration experiments with \([1-\text{NH}_3]^{2+}\) and 2-OMe-Py.

Figure 3.10. Representative THF-d$_8$ $^1$H-NMR spectrum of the reaction between \([1-\text{NH}_3]^{2+}\) and 2-OMe-Py at 23 °C. Peaks integrated to determine relative concentration determinations of the diamagnetic species in equilibrium are marked.
Figure 3.11. Representation of the solid-state structure of [1-NH2]+ using 30% probability ellipsoids. Hydrogen atoms, except those attached to N3 have been omitted for clarity.
Figure 3.12. Representation of the solid-state structure of $[1\cdot\kappa^2\cdot\text{NHNH}_2]^+$ using 30% probability ellipsoids. Hydrogen atoms, except those attached to N4 and N5 have been omitted for clarity.
Figure 3.13. Representation of the solid-state structure of [1-OH]$^+$ using 30% probability ellipsoids. Hydrogen atoms, except those attached to O1 have been omitted for clarity.
DFT Input Examples

Geometry Optimizations

! RKS B3LYP RIJCOSX def2-SVP def2-SVP/J Normalprint SlowConv TightSCF Opt Pal8 UCO ZORA

%basis NewGTO 42 "def2-TZVP(-f)" end
   NewGTO 7 "def2-TZVP(-f)" end
   NewGTO 15 "def2-TZVP(-f)" end
   NewAuxGTO 42 "def2-TZVP/J" end
   NewAuxGTO 7 "def2-TZVP/J" end
   NewAuxGTO 15 "def2-TZVP/J" end
end

%SCF MaxIter 500
   TolE 1e-7
   TolErr 1e-6
end

* xyz 1 1

XYZ Coordinates from X-Ray Structure Excluding [BArF$^{24}$]$^-$ Counterion and $^{Ph}$Tpy truncated to Tpy.

*
Numerical Frequency Calculations

! RKS B3LYP RIJCOSX SLOWCONV TIGHTSCF DEF2-SVP DEF2-SVP/J
NORMALPRINT NUMFREQ GRID4 NOFINALGRID PAL8 ZORA

%basis NewGTO 42 "def2-TZVP(-f)" end
  NewGTO 7 "def2-TZVP(-f)" end
  NewGTO 15 "def2-TZVP(-f)" end
  NewAuxGTO 42 "def2-TZVP/J" end
  NewAuxGTO 7 "def2-TZVP/J" end
  NewAuxGTO 15 "def2-TZVP/J" end
end

%SCF MaxIter 500
  TolE 1e-7
  TolErr 1e-6
end

%FREQ RESTART TRUE
CENTRALDIFF TRUE
INCREMENT 0.01
END

* xyz 1 1

XYZ Coordinates from Geometry Optimization

*

References


CHAPTER 4

Interconversion of Molybdenum Imido and Amido Complexes by Proton-Coupled Electron Transfer.∗

Abstract

Interconversion of the molybdenum amido [(PPhTpy)(PPh2Me)2Mo(NHtBuAr)][BArF24] (PPhTpy = 4′-Ph-2,2′,6,2″-terpyridine; tBuAr = 4-tert-butyl-C6H4; ArF24 = [C6H3-3,5-(CF3)2]4) and imido [(PPhTpy)(PPh2Me)2Mo(NtBuAr)][BArF24] complexes has been accomplished by proton coupled electron transfer (PCET). Tert-butylphenoxyl radical was used as an oxidant and the non-classical ammine complex [(PPhTpy)(PPh2Me)2Mo(NH3)][BArF24] as the reductant. The amido N-H BDFE formed and cleaved in the sequence was experimentally bracketed between 45.8 and 52.3 kcal/mol, in agreement with a DFT-computed value of 48 kcal/mol. The N–H BDFE in combination with electrochemical data eliminate proton transfer as the first step in the N–H bond forming sequence and favor initial electron transfer or concerted pathways.

Introduction

Proton coupled electron transfer (PCET)1 or its concerted variant, hydrogen atom transfer (HAT),1c are key to energy management in biological processes2a,b including the natural nitrogen cycle2c and are attractive strategies for forming or cleaving X–H (X = C, N, O) bonds in synthetic chemistry. The reversible formation and cleavage of N–H bonds

by PCET in soluble transition metal complexes, for example, are fundamental steps applicable to the interconversion of ammonia (NH₃) with its elements dinitrogen (N₂) and dihydrogen (H₂)³⁴ as well as in catalysis involving metal-ligand cooperativity.⁵ For NH₃/N₂ interconversion by PCET, understanding the thermochemistry of discrete N-H bond forming/cleaving steps⁶⁷ is needed to develop processes compatible with renewable H₂ as well as fixing N₂ with minimal chemical overpotential.⁸

![Figure 4.1](image)

**Figure 4.1.** (a) The potential relevance of imido/amido complexes of molybdenum in the interconversion of NH₃/N₂ by PCET. (b), (c) Comparison of selected molybdenum imido structural motifs highlighting the strategy reported in this work.

Coordination complexes of molybdenum are useful probes to study N-H bond formation/cleavage by PCET (Figure 4.1) due to a demonstrated role in NH₃ synthesis⁹ and oxidation chemistry including N₂ cleavage,¹⁰ stoichiometric and catalytic NH₃ synthesis¹¹¹²¹³ and most recently the N-H bond activation of ammine ligands¹⁴ as well as H₂ generation by coordination induced bond weakening.¹⁵ Our laboratory has been engaged in obtaining a systematic understanding of the thermochemistry associated with
N-H bond formation and cleavage in complexes potentially relevant to N₂ fixation and NH₃ oxidation cycles.⁸,¹⁵a,¹⁶ The fundamental insights gained from these studies will likely extend beyond ammonia chemistry and may be applied to catalysts that contain N-H bonds and operate by metal-ligand cooperativity.⁵

With molybdenum, a particularly challenging PCET reaction to study is the interconversion of imido (Mo=NR) and amido (Mo-NHR) compounds (Figure 4.1a). Most isolable molybdenum imidos are high oxidation state compounds with the Mo=NR ligand serving as a spectator particularly when hydrides¹⁷ or alkylidenes¹⁸ are present (Figure 4.1b). As a consequence, reports of well-defined N-H bond forming chemistry with Mo=NR compounds by PCET are rare. Electrochemical experiments by Pickett¹⁹ and Tuczek²⁰ have demonstrated that Chatt-type bis(diphosphine) Mo(IV) alkylimido complexes undergo in situ protonation upon reduction to Mo(III), implicating higher reactivity for the lower oxidation state compound. Extraction of the thermodynamic parameters from these processes is complicated by further electron transfer chemistry and ligand exchange reactions. Inspired by these observations, investigation of N-H bond formation to molybdenum imido complexes and the microscopic reverse, N-H bond homolysis from molybdenum amide complexes by PCET was pursued (Figure 4.1c). Here we describe the synthesis of a terpyridine bis(phosphine) molybdenum anilido complex and determine the thermodynamics of reversible N-H bond formation by PCET.
Results and Discussion

Stirring a benzene solution of \((\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{MoCl}\) \((\text{PhTpy} = 4’-\text{Ph}-2,2’,6,2’’-\text{terpyridine})\)\(^{21}\) in the presence of one equiv. of each NaBArF\(^{24}\) \({\text{ArF}}^{24} = [\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2]_4\) and 4-tert-butylaniline at 60 °C for 3 hours afforded the dark green diamagnetic molybdenum amido complex \([\{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}(\text{NHtBuAr})\}]\text{[BArF}^{24}\text{]}\) \((1-\text{NH(tBuAr)}^+)\) in 92% yield (Figure 4.2). The H\(_2\) byproduct was confirmed by \(^1\text{H}\) NMR spectroscopy and Toepler pump experiments (70% yield). The reaction likely proceeds through a non-classical 4-tert-butylaniline complex, \([\{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}(\text{NH}_2\text{tBuAr})\}]\text{[BArF}^{24}\text{]}\) with N-H bonds that are thermodynamically unstable to H\(_2\) loss \([\Delta G_f^\circ(\text{H•}) < 48.6 \text{ kcal/mol}]\).\(^1\text{d}\)

![Figure 4.2](image.png)

**Figure 4.2.** Synthesis of \([1-\text{NH(tBuAr)}]^+\) by dehydrogenation of 4-tert-butylaniline.

The solid-state structure of \([1-\text{NH(tBuAr)}]^+\) established an idealized octahedral geometry with a planar aryl-substituted amido ligand \((\text{Mo-Namido} = 1.982(2) \text{ Å}; \text{Namido-Caryl} = 1.419(3) \text{ Å})\) \textit{trans} to the central pyridine ring of the terpyridine chelate (Figure 4.3a). The \(^{31}\text{P}\{^1\text{H}\}\)-NMR spectrum of \([1-\text{NH(tBuAr)}]^+\) in benzene-\(d_6\) exhibits two mutually coupled doublets centered at 16.67 and 10.02 ppm \((^2J_{p-P,\text{trans}} = 191.4 \text{ Hz})\) indicative of overall \(C_s\) molecular symmetry. This assignment is also supported by the \(^1\text{H}\)
NMR data collected in benzene-$d_6$, where two distinct sets of resonances corresponding to inequivalent PPh$_2$Me ligands were observed together with a diagnostic downfield doublet of doublets centered at 12.53 ppm ($^{3}J_{H-P} = 15.9, 10.1$ Hz) assigned to the amido hydrogen. The observed molecular symmetry of $[\text{1-NH(tBuAr)}]^+$ in solution is a consequence of a restricted rotation about the Mo-N$_{\text{amido}}$ bond that renders the hemispheres of the molecule above and below the plane of the terpyridine chelate chemically inequivalent on the NMR timescale. No coalescence of signals was observed up to 110$^\circ$C in toluene-$d_8$, highlighting the high barrier to molybdenum-amido bond rotation. While steric effects cannot be excluded,$^{22}$ the density functional theory (DFT) computed molecular orbitals show a $\pi$-interaction between the N-lone pair of the amido ligand and the molybdenum $d_{yz}$ orbital (HOMO-2) that likely increases the barrier to rotation (Figure 4.3b).

![Figure 4.3](image)

**Figure 4.3.** (a) Solid-state structure of $[\text{1-NH(tBuAr)}]^+$ at 30% probability ellipsoids. Hydrogen atoms (except amido H4A) and the [BARF$^{24}$] counterion have been omitted for clarity. (b) Illustration of the DFT-computed HOMO-2 in $[\text{1-NH(tBuAr)}]^+$. 
A very low amido N-H bond dissociation free energy (BDFE) of 48 kcal/mol was computed by DFT for [1-NH(tBuAr)]⁺. While spontaneous H₂ evolution was not observed upon mild heating, addition of one equiv. of 2,4,6-tri-tert-butylphenoxy radical (tBu₃ArO•) to [1-NH(tBuAr)]⁺ yielded [[(PhTPy)(PPh₂Me₂)₂Mo(NAr)][BARF₂₄]]⁻ ([1=N(tBuAr)]⁺) as a purple- brown dark solid in 93% yield as well as tBu₃ArOH (O-H BDFE = 77 kcal/mol) (Figure 4.4).²³

![Figure 4.4. Synthesis of [1=N(tBuAr)]⁺ by oxidative PCET.](image)

The solid-state structure of [1=N(tBuAr)]⁺ was determined by X-ray diffraction and confirmed the formation of an idealized octahedral complex similar to [1-NH(tBuAr)]⁺, with an Mo-Nimido distance of 1.777(3) Å. This value is consistent with an imido ligand but is slightly elongated as Mo=NR bond lengths typically range from 1.69 to 1.75 Å.²⁴ The Mo-N-CtBuAr bond angle changed from 135.5(2)° in [1-NH(tBuAr)]⁺ to 179.4(3)° in [1=N(tBuAr)]⁺, consistent with the generation of a linear “X₂”-type imido ligand (Figure 4.5).
Figure 4.5. Solid-state structure of $[1=N(tBuAr)]^+$ at 30% probability ellipsoids. Hydrogen atoms and the $[BArF_{24}]^+$ counterion have been omitted for clarity.

Magnetic and spectroscopic measurements were conducted on $[1=N(tBuAr)]^+$ to probe its electronic structure. A solid-state magnetic moment of 1.7 $\mu_B$ (23 $^\circ$C, magnetic susceptibility balance) consistent with an $S = 1/2$ ground state was measured and the X-band EPR spectrum exhibits an isotropic signal ($g_{iso} = 2.020$) in toluene glass (7K) with significant coupling to two inequivalent nitrogen atoms [$A_{iso}(^{14}N) = 46$ MHz, 61 MHz; Figure 4.6a]. By contrast, the isotropic signal shows coupling to two equivalent phosphorous atoms but not to the $^{14}N$ nuclei in fluid toluene solution [$g_{iso} = 2.013$, $A_{iso}(^{31}P) = 110$ MHz, 296K; Figure 4.12]. Both the observed $g$-value and the lack of significant hyperfine coupling to the metal center suggest that the SOMO of $[1=N(tBuAr)]^+$ has significant ligand character. The DFT-computed Mulliken spin density plot supports spin density on the terpyridine chelate and the aryl-substituted imido ligand (Figure 4.6b). The electronic structure of $[1=N(tBuAr)]^+$ is therefore best described as Mo(IV) with one-electron delocalized over the terpyridine and the aryl
imido π* orbitals. This electronic structure is likely important for stabilizing \([1=N(tBuAr)]^+\) by avoiding a reactive Mo(III) radical species with a populated Mo=NR π* orbital, rendering the one electron redox processes and the overall thermodynamics favorable for N-H bond formation by PCET.

**Figure 4.6.** (a) X-band EPR spectrum of \([1=N(tBuAr)]^+\) recorded at 7K in toluene glass (microwave frequency = 9.379 GHz, power = 2.00 mW, power attenuation = 20.0 dB, modulation amplitude = 4.000 G). Simulation of \([1=N(tBuAr)]^+: g_{iso} = 2.020, A_{iso}(^{14}N) = 46\) MHz, \(A_{iso}(^{14}N) = 61\) MHz \((^{14}N, I = 1, 99.6\%)\). (b) Spin density plot for \([1=N(tBuAr)]^+\) obtained from a gas-phase DFT calculation at the B3LYP level of theory.

Having demonstrated oxidative PCET to generate \([1=N(tBuAr)]^+\) from \([1-NH(tBuAr)]^+\), the reverse reaction, namely, homolytic N-H bond formation from the molybdenum imido complex was of interest. Addition of reagents with known E–H BDFE values was conducted to establish the thermodynamic requirements for the interconversion of the imido and amido complexes by PCET. The rhodium hydride, \((\eta^5-C_5Me_5)(py-Ph)RhH ([Rh-H]; py-Ph = 2-pyridylphenyl)\) was initially selected because of
the well-established chemistry as an H-atom donor as well as the availability of thermochemical data on the Rh-H bond strength (BDFE_{Rh-H} = 52.3 kcal/mol). Upon addition of one equivalent of [Rh-H] to [1-N(tBuAr)]^+ in THF, no N-H bond formation chemistry was observed. In the absence of a large kinetic barrier to PCET, the transfer of a hydrogen atom between the two complexes is likely thermodynamically unfavorable and established an upper limit for the N-H BDFE of [1-NH(tBuAr)]^+ as 52.3 kcal/mol in THF (Figure 4.7, top). This result also suggested that an H-atom donor with an X-H BDFE weaker than this value was necessary to affect the desired N-H bond formation reaction, an aim that is limited by the availability of reagents with weak bonds near the thermodynamic threshold for H\textsubscript{2} evolution [ΔG\textsubscript{f}(H\bullet) = 48.6 kcal/mol].

Figure 4.7. PCET pathways for the interconversion of [1-NH(tBuAr)]^+ and [1=N(tBuAr)]^+.
One notable exception is the isolable non-classical molybdenum ammine complex \[\{(\text{Ph}Tpy)(\text{PPh}_2\text{Me})_2\text{Mo}((\text{NH}_3))\}[\text{BARF}^{24}]\ (\text{[1-NH}_3])^+\] that contains a remarkably weak N-H BDFE of 45.8 kcal/mol (THF),\textsuperscript{15a} that could, in principle, serve as an effective hydrogen atom donor for such thermodynamically challenging bond formations. Indeed, treatment of \([1=N(t\text{BuAr})]^+\) with one equivalent of \([1-\text{NH}_3]^+\) quantitatively generated the products of PCET, diamagnetic \([1-\text{NH}(t\text{BuAr})]^+\) and \([(\text{Ph}Tpy)(\text{PPh}_2\text{Me})_2\text{Mo}((\text{NH}_2))]\[\text{BARF}^{24}\] \(\text{[1-NH}_2]^+)\) over the course of 18 hours at room temperature, as judged by \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectroscopies. Importantly, PCET between \([1-\text{NH}_3]^+\) and \([1=N(t\text{BuAr})]^+\) is thermodynamically favored and defines the lower limit for the N-H BDFE in \([1-\text{NH}(t\text{BuAr})]^+\) as 45.8 kcal/mol (Figure 4.7, bottom). This set of experiments establishes the N-H BDFE range of \([1-\text{NH}(t\text{BuAr})]^+\) as 45.8-52.3 kcal/mol (THF), in good agreement with the computationally determined N-H BDFE of 48 kcal/mol. Notably, this N-H BDFE is significantly lower than those of previously reported amido complexes of both late and early metals, which typically fall in the range of 64-91 kcal/mol.\textsuperscript{4a,8a,16a,28}

To examine the origin of the unusually weak amido N-H bond strength in \([1-\text{NH}(t\text{BuAr})]^+\), the N-H BDFE in the corresponding “parent” amido complex \([1-\text{NH}_2]^+\) was of interest and computed by DFT as 64 kcal/mol. The Bordwell equation (Equation 1.1) describes a BDFE in terms of the oxidation potential of the metal complex and N-H \(p\text{K}_a\) upon oxidation. Electrochemical studies by cyclic voltammetry (CV) established that the oxidation potentials of \([1-\text{NH}(t\text{BuAr})]^+\) and \([1-\text{NH}_2]^+\) are closely matched at -0.56 V and -0.55 V, respectively (THF, vs. Fc/Fc\textsuperscript{+}). According to (Equation 1.1), the N-H bond in \([1-\text{NH}(t\text{BuAr})]^+\) is therefore weaker than in \([1-\text{NH}_2]^+\) due to a lower N-H \(p\text{K}_a\) term where the aryl \(\pi\)-system has minimal impact on the oxidation potential of the complex.
This effect is unusual in that relative X–H acidity in metal complexes is typically related to the overall charge.  

\[ \text{BDFE} = 1.37pK_a + 23.06E^\circ + C_G \]  

(1.1)

As shown in Figure 4.8, the conversion of \([1\text{=N(tBuAr)}]^+\) to \([1\text{-NH(tBuAr)}]^+\) with \([1\text{-NH}_3]^+\) may proceed via 3 possible pathways: (1) electron transfer followed by proton transfer (ET/PT); (2) proton transfer followed by electron transfer (PT/ET); or (3) concerted hydrogen atom transfer (HAT). The ET component of the PCET reaction was investigated by cyclic voltammetry (CV). The CV of \([1\text{-NH(tBuAr)}]^+\) in THF exhibits an oxidation wave at -0.56 V (vs. Fc/Fc\(^+\)) to generate \([1\text{-NH(tBuAr)}]^2+\). Under the same conditions, a reduction potential of -1.17 V was measured for the formally Mo(III) compound \([1\text{=N(tBuAr)}]^+\) to yield \([1\text{=N(tBuAr)}]\). Isolation of both \([1\text{-NH(tBuAr)}]^2+\) and \([1\text{=N(tBuAr)}]\) was attempted and would be valuable for probing the thermodynamics of the PT steps in Figure 4.8 but were unfortunately hampered by the instability of the complexes in solution. The pK\(_a\) bounds in THF solution for the PT steps were instead indirectly evaluated using the Bordwell equation (Equation 1.1) by applying the experimentally determined N–H BDFE range for \([1\text{-NH(tBuAr)}]^+\) and \(E^\circ\) values. The pK\(_a\) of \([1\text{-NH(tBuAr)}]^2+\) was estimated to be between -6 and -1 in THF, while the upper- and lower pK\(_a\) bounds for \([1\text{-NH(tBuAr)}]^+\) were similarly calculated as 6 and 11, respectively.
Based on these results, a PT/ET pathway involving initial proton transfer from \([1-\text{NH}_3]^+\) \((pK_a = 20.1, \text{THF})^{15a}\) to \([1=\text{N(tBuAr)}]^+\) \((pK_a = -6 \text{ to } -1)\) is eliminated, as this step is highly endoergic \((\Delta G^\circ_{\text{PT}} = +29 \text{ to } +36 \text{ kcal/mol})\). While the subsequent electron transfer from \([1-\text{NH}_2]\) \((E^\circ_{\text{ox}} = -2.58 \text{ V})^{30}\) to \([1=\text{NH}(\text{tBuAr})]^2+\) \((E^\circ_{\text{red}} = -0.54 \text{ V})^{30}\) to yield the products \([1-\text{NH}_2]^+\) and \([1=\text{NH}(\text{tBuAr})]^+\) is predicted to be favorable, a ground state \(\Delta G^\circ_{\text{PT}}\) of +29 to 36 kcal/mol would likely prevent the reaction from taking place at room temperature by a PT/ET pathway. By contrast, initial electron transfer from \([1-\text{NH}_3]^+\) \((E^\circ_{\text{ox}} = -1.09 \text{ V})^{15a}\) to \([1=\text{N(tBuAr)}]^+\) \((E^\circ_{\text{red}} = -1.26 \text{ V})^{30}\) followed by proton transfer from \([1-\text{NH}_3]^2+\) \((pK_a = 3.6, \text{THF})^{15a}\) to \([1=\text{N(tBuAr)}]\) \((pK_a = 6 \text{ to } 11)\) is more thermodynamically viable at room temperature \((\Delta G^\circ_{\text{ET}} = +4 \text{ kcal/mol}; \Delta G^\circ_{\text{PT}} = -3 \text{ to } -10 \text{ kcal/mol})\). Therefore, a stepwise ET/PT pathway or a concerted HAT mechanism is likely operative in the conversion of \([1=\text{N(tBuAr)}]^+\) to \([1=\text{NH}(\text{tBuAr})]^+\) with \([1-\text{NH}_3]^+.\) Upon
treatment of \([1=N(tBuAr)]^+\) with a 1:1 mixture of \([1-NH_3]^+\) and \([1-ND_3]^+\) the relative ratios of the product isotopologues \([1-NH(tBuAr)]^+\) and \([1-ND(tBuAr)]^+\) were quantified by \(^{31}\text{P}\) NMR spectroscopy and a kinetic isotope effect (KIE, \(k_H/k_D\)) of 3.3(1) (23°C) was determined for the transformation. While consistent with both stepwise and concerted pathways, this moderate KIE establishes that electron transfer is not rate limiting during PCET. Importantly, the reaction of \([1=N(tBuAr)]^+\) with \([1-NH_3]^+\) to yield \([1-NH(tBuAr)]^+\) and \([1-NH_2]^+\) models the comproportionation of imide and ammine intermediates in a functioning system interconverting \(\text{NH}_3\) with its elements.\(^{31}\)

**Conclusion**

In summary, the synthesis and interconversion of molybdenum imido and amido complexes by PCET has been demonstrated. Experimental and computational investigations have revealed a remarkably low N-H BDFE in the molybdenum amido complex and thermochemical investigations eliminate an N-H bond-forming pathway involving PT-ET. Such thermochemical insights may prove valuable for understanding N-H bond formation in molybdenum imido complexes by PCET, of potential relevance to \(\text{NH}_3/\text{N}_2\) interconversion as well as catalysts with N-H bonds operating by metal-ligand cooperativity.
Experimental Section

General Considerations

All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures. Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. The compounds $[{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo(Cl)}}]$33, $[{(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo(NH}_3)}][\text{BArF}_2]$34, 2,4,6-tri-tert-butylphenoxyl radical ($\text{Bu}_3\text{ArO}^\bullet$)$^{35}$, $(\eta^5\text{-C}_5\text{Me}_5)(\text{py-Ph})\text{RhH}$,$^{36}$ $(\eta^5\text{-C}_5\text{Me}_5)(\text{py-Ph})\text{Rh}$,$^{37}$ and $\text{Na[BRaF}_2$]$^{38}$ were prepared according to literature procedures. 4-tert-butylaniline was purchased from Sigma-Aldrich, distilled under vacuum, and stored over 4 Å molecular sieves before use. Quantification and volume of hydrogen was measured with a Toepler pump equipped with copper oxide burn tube.

NMR spectra were recorded on a Bruker AVANCE 300 spectrometer operating at 300.13 MHz for $^1$H NMR or Bruker 500 spectrometer operating at 125.71 MHz for $^{13}$C NMR at 23 °C. All chemical shifts are reported relative to SiMe$_4$ using $^1$H (residual) chemical shifts of the solvent as a secondary standard. All $^1$H NMR coupling constants are reported in Hz. $^{13}$C NMR chemical shifts are reported relative to SiMe$_4$ using chemical shifts of the solvent as a secondary standard where applicable. $^{31}$P NMR spectra were collected on a Bruker 500 AVANCE spectrometer operating at 202.40 MHz and
were referenced to 85% H₃PO₄ as an external standard. ¹⁹F NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 282.23 MHz and were referenced to CFCl₃ as an external standard.

Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Solid-state magnetic moments were determined using a Johnson Matthey magnetic susceptibility balance that was calibrated with HgCo(SCN)₄, collected at 23 °C, unless otherwise noted. Continuous wave EPR spectra were recorded at room temperature on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.³⁹

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker D8 VENTURE DUO diffractometer system equipped with molybdenum and copper X-ray tubes (λ = 0.71073 and 1.54184 Å respectively). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. All data were collected at -173 °C.

CVs were collected in THF solution (10 mM in compound) with [nBu₄N][PF₆] (0.1 M), using a 3 mm glassy carbon working electrode, platinum wire as the counter electrode, and silver wire as the reference in a drybox equipped with electrochemical
outlets. CVs were recorded using a BASi EC Epsilon electrochemical workstation and analyzed using the BASi Epsilon-EC software. All CVs were run at 23 °C. Potentials are reported versus Fc/Fc\(^+\) and were obtained using the \textit{in situ} method.

UV-visible absorption spectra were recorded on an Agilent 8453 diode array UV/Vis spectrophotometer. Samples were charged into a quartz cuvette fitted with a J-Young Teflon cap in a glovebox and transferred to the spectrometer to record absorption spectra.

All DFT calculations were performed with the ORCA program package in the gas phase.\(^{40}\) The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.\(^{41}\) The all-electron Gaussian basis sets were those developed by the Ahlrichs group.\(^{42}\) Triple-\(\zeta\) quality basis sets def2-TZVP with one set of polarization functions on molybdenum, phosphorous and nitrogen were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used that were of double-\(\zeta\) quality in the valence region and contained a polarizing set of d functions on the non-hydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX)\(^{43}\) approach were chosen to match the orbital basis.\(^{44}\) Numerical frequencies were calculated at the same level of theory to confirm the optimized geometries (no imaginary frequencies) and to derive thermochemical data. Bond dissociation free energies were computed at standard conditions of 1 atm and 25 °C including corrections for vibrational zero-point energy, as well as contributions from translational, rotational, and vibrational modes to the energy and entropy of the homolytic bond cleavage process. For molecules containing a molybdenum atom, the 0th order regular approximation
(ZORA) was applied.\textsuperscript{45} In this case, the relevant basis sets were replaced by their relativistically recontracted versions. In the geometry optimizations and numerical frequency calculations of molybdenum complexes, the 4’-Ph-2,2’,6’,2”-terpyridine ligand was truncated to 2,2’,6’,2”-terpyridine in order to reduce the requisite computational effort. The electronic energy of H\textsuperscript{•}, utilized in the calculation of bond dissociation free energies, at the present level of theory is 13.576 eV (313 kcal/mol).

**Experimental pK\textsubscript{a} Range Determinations**

An experimental indirect measure for the pK\textsubscript{a} range in THF solution for the unstable complexes \([1\text{-NH(tBuAr)}]^2+\) and \([1=\text{N(tBuAr)}]\) was obtained using the rearranged Bordwell Equation:

$$pK_a = \frac{\text{BDFE}\text{N-H} - 23.06 \ E^\circ - C_G}{1.37}$$  \hspace{1cm} (4.1)

E\textsuperscript{\circ} values for the appropriate redox couple half-wave potentials were determined using cyclic voltammetry (CV) in THF. Where quasi-reversible or irreversible waves were observed, scan rates were increased (up to 1000 mV/sec) to obtain more accurate half-wave potentials. BDFE\text{N-H} was assumed as the experimentally determined N-H BDFE range (THF solution) for \([(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo(NHtBuAr)}][\text{BArF}_24]\) (45.8-52.3 kcal/mol) with C\textsubscript{G} value of 66 kcal/mol in THF.\textsuperscript{46}
Preparation of Molybdenum Complexes

Preparation of $[1\text{-NH}(\text{tBuAr})]^+$. In the glovebox, a 25 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.155 g (0.184 mmol) of $[1\text{-Cl}]$ and 0.171 g (0.193 mmol) of Na[BArF$_{24}$]. A solution containing 30 µL (0.186 mmol) of 4-tert-butylaniline dissolved in 10 mL of benzene was then added. The vessel was sealed and connected to the high vacuum line where it was degassed by 3 freeze pump thaw cycles.† The reaction mixture was then stirred at 60 °C under vacuum for 3 hours. Using a Toepler pump, 0.064 mmol (60 mmHg, 19.8 mL, 23 °C) of gas was collected, and was passed over a bed of CuO pre-heated to 200 °C. After this procedure, no gas was collected, confirming the identity of the evolved gas as H$_2$. The reaction vessel was brought back into the glovebox and the mixture was filtered through a pad of Celite, followed by the removal of the solvent in vacuo. The dark residue was washed with pentane (3 x 3 mL) followed by trituration with pentane (5 x 3 mL) to yield the product as a foamy dark green solid (0.309 g, 0.170 mmol, 92%). Crystals suitable for single crystal X-ray diffraction studies were obtained from the vapor diffusion of pentane into a concentrated fluorobenzene solution of the product at -34 °C. Anal Calcd for C$_{89}$H$_{67}$BF$_{24}$MoN$_4$P$_2$: C, 58.82; H, 3.72; N, 3.08. Found: C, 58.50; H, 3.58; N, 3.06. $^1$H NMR (benzene-$d_6$, 23 °C): δ 12.53 (dd, $^3J_{\text{H-P}} = 15.9$, 10.1 Hz, 1H, NH$_{\text{tBuAr}}$), 8.96 (d, $^3J_{\text{H-H}} = 5.9$ Hz, 2H, Ph$_{\text{Tpy}}$), 8.49 (s, 8H, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 7.69 (s, 4H, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$), 7.58 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, Ph$_{\text{Tpy}}$), 7.53-7.47 (m, 4H, Ph$_{\text{Tpy}}$ (2H), overlap with Ph$_{\text{Tpy}}$ (2H)), 7.38 (d, $^3J_{\text{H-H}} = 8.3$ Hz, 2H, Ph$_{\text{Tpy}}$), 7.36-7.30, (m, 1H, Ph$_{\text{Tpy}}$), 7.08 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 2H, NH$_{\text{tBuAr}}$), 6.96-6.90

† It is important to degas the reaction mixture immediately after the addition of reactants, as [(Ph$_{\text{Tpy}}$)(PPh$_3$Me)$_2$Mo(Cl)] and Na[BArF$_{24}$] will react in the presence of N$_2$ to form the dimeric N$_2$ complex [(Ph$_{\text{Tpy}}$)(PPh$_3$Me)$_2$Mo$_2$(μ₂-N$_2$)][BArF$_{24}$].
(m, 4H, NHtBuAr (2H), overlap with PhTpy (2H)), 6.79-6.71 (m, 6H, PPh₂Me), 6.58-6.49 (m, 6H, PPh₂Me), 6.34-6.27 (m, 6H, PPh₂Me (4H), overlap with PhTpy (2H)), 5.84 (t, 3\(J_{H-H} = 8.7\) Hz, 4H, PPh₂Me), 1.22 (s, 9H, NHtBuAr), 0.52 (app d, 3\(J_{P-P} = 5.7\) Hz, 3H, PPh₂Me), 0.14 (app d, 3\(J_{P-P} = 6.2\) Hz, 3H, PPh₂Me). ¹³C{¹H} NMR (benzene-d₆, 23 °C): \(\delta\)

162.90 (q, ¹JC-B = 49.8 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 155.56 (app t, J = 7.8 Hz, NHtBuAr), 147.61 (s, PhTpy), 145.66 (s, PhTpy), 140.86 (s, PhTpy), 137.76 (s, PhTpy), 136.03 (s, NHtBuAr), 135.52 (s, B[(3,5-(CF₃)₂)C₆H₃]₄), 133.37 (br s, PPh₂Me), 133.12 (br s, PPh₂Me), 130.17 (s, PPh₂Me), 130.09 (s, PPh₂Me), 129.98 (q, ²JC-F = 36.2 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 129.88 (s, PhTpy), 129.60 (s, PPh₂Me), 129.50 (s, PPh₂Me), 129.35 (s, NHtBuAr), 129.19 (s, NHtBuAr), 128.98 (s, PPh₂Me), 128.91 (s, PPh₂Me), 128.86 (s, NHtBuAr), 128.35 (s, PhTpy), 128.13 (s, PhTpy), 125.33 (q, ¹JC-F = 272 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 123.05 (s, PhTpy), 121.24 (s, PhTpy), 119.04 (s, PhTpy), 118.17 (s, B[(3,5-(CF₃)₂)C₆H₃]₄), 112.62 (s, PhTpy), 34.41 (s, NHtBuAr), 31.32 (s, NHtBuAr), 7.58 (app d, \(J = 19.4\) Hz, PPh₂Me), 6.93 (app d, \(J = 21.4\) Hz, PPh₂Me). ³¹P{¹H} NMR (benzene-d₆, 23 °C): \(\delta\)

16.67 (d, ²Jₚ-P, trans = 191.4 Hz), 10.02 (d, ²Jₚ-P, trans = 191.4 Hz). ¹⁹F{¹H} NMR (benzene-d₆, 23 °C): \(\delta\) -62.00 (s, B[(3,5-(CF₃)₂)C₆H₃]₄).

**Preparation of [1=N(tBuAr)]⁺.** In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar and 0.113 g (0.062 mmol) of [1-NH(tBuAr)]⁺ dissolved in 8 mL of toluene. To the rapidly stirring solution, 0.017 g (0.065 mmol) of Bu₃ArO dissolved in 1 mL of toluene was added dropwise over the course of 1 minute. An immediate color change from green to brown-purple was observed together with the formation of an oily precipitate. The stirring was stopped after 15 minutes and the reaction mixture was
concentrated to ~ 3 mL *in vacuo*. Excess pentane (10 mL) was layered on top of the concentrate, and the mixture was allowed to stand at -35 °C for 1 hour. The supernatant was then decanted away from the dark brown-purple residue, and was discarded. The residue was washed with pentane (3 x 5 mL) followed by trituration with pentane (3 x 3 mL) to yield the product as a dark brown solid (0.105 g, 0.058 mmol, 93%). Crystals suitable for single crystal X-ray diffraction studies were obtained from the slow diffusion of pentane into a toluene solution of the product at room temperature. Anal Calcd for C_{89}H_{66}BF_{24}MoN_4P_2: C, 58.86; H, 3.66; N, 3.08. Found: C, 58.79; H, 3.90; N, 2.89.

Magnetic susceptibility (Guoy balance, 23 °C): $\mu_{\text{eff}} = 1.7 \mu_B$.

**Additional Reactions and Associated Spectroscopic Data**

**N–H bond formation by PCET in [1=N(tBuAr)]^+.** In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, 0.016 g (8.8 μmol) of [1=N(tBuAr)]^+ and 0.015 g (8.8 μmol) of [1-NH_3]^+ dissolved in 3 mL of Et_2O. The reaction mixture was rapidly stirred at room temperature for 18 hours. After this time the reaction solvent was removed *in vacuo* and replaced with benzene-d_6. $^1$H and $^{31}$P NMR analysis indicated the formation of [1-NH(tBuAr)]^+ and [1-NH_2]^+ as the products of the reaction.

**Determination of a kinetic isotope effect for the PCET reaction.** In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, 0.019 g (10 μmol) of [1=N(tBuAr)]^+, 0.009 g (5.2 μmol) of [1-NH_3]^+ and 0.009 g (5.2 μmol) of [1-ND_3]^+.
dissolved in 3 mL of Et₂O. The reaction mixture was rapidly stirred at room temperature for 18 hours. After this time the reaction solvent was removed in vacuo and replaced with benzene-<i>d</i><sub>6</sub>. A mixture of the isotopologues [1-NH(tBuAr)]<sup>+</sup> and [1-ND(tBuAr)]<sup>+</sup> was observed, together with the formation of [1-NH₂]<sup>+</sup>, [1-NHD]<sup>+</sup> and [1-ND₂]<sup>+</sup>. The ratio of [1-NH(tBuAr)]<sup>+</sup> to [1-ND(tBuAr)]<sup>+</sup> was obtained by integrating the corresponding <sup>31</sup>P-NMR signals for these complexes. The experiment was repeated 3 times. The value for the kinetic isotope effect was found using this method to be 3.3(1) at 23°C.‡

Figure 4.9. Representative <sup>31</sup>P{¹H} NMR spectrum of the PCET reaction between [1=N(tBuAr)]<sup>+</sup> and a 1:1 mixture of [1-NH₃]<sup>+</sup> and [1-ND₃]<sup>+</sup> in benzene-<i>d</i><sub>6</sub> at 23°C. Black: [1-NH(tBuAr)]<sup>+</sup>, Red: [1-ND(tBuAr)]<sup>+</sup>, Blue: [1-NH₂]<sup>+</sup>, Magenta: [1-NHD]<sup>+</sup>, Green: [1-ND₂]<sup>+</sup>.

Control experiment to probe N–H/D exchange in [1-NH(tBuAr)]<sup>+</sup>. In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, 0.019 g (10 µmol) of [1-NH(tBuAr)]<sup>+</sup>, 0.009 g (5.2 µmol) of [1-ND₃]<sup>+</sup>, 0.004 g (2.3 µmol) of [1-NH₂]<sup>+</sup> and 0.004

‡ One equivalent (total) of the complexes [1-NH₃]<sup>+</sup> and [1-ND₃]<sup>+</sup> was added to [1=N(tBuAr)]<sup>+</sup>, as excess paramagnetic material results in broadened <sup>31</sup>P-NMR signals that precludes a quantification of the diamagnetic isotopologues [1-NH(tBuAr)]<sup>+</sup> and [1-ND(tBuAr)]<sup>+</sup> by <sup>31</sup>P-NMR integration.
g (2.3 µmol) of [1-ND₂]⁺ dissolved in 3 mL of Et₂O. The reaction mixture was rapidly stirred at room temperature for 18 hours. After this time the reaction solvent was removed in vacuo and replaced with benzene-d₆. A statistical mixture of the isotopologues [1-NH₂]⁺, [1-NHD]⁺ and [1-ND₂]⁺ was observed, consistent with N-H/D exchange between the “parent” amido starting materials [1-NH₂]⁺, and [1-ND₂]⁺. However, only trace N-H/D exchange was observed for [1-NH(tBuAr)]⁺ to yield [1-ND(tBuAr)]⁺, indicating N-H/D exchange for this complex is slow on the timescale of the PCET reaction (18 hours).

Figure 4.10. ³¹P{¹H} NMR spectrum of the N-H/D exchange control reaction between [1-NH(tBuAr)]⁺ and a 2:1:1 mixture of [1-ND₃]⁺, [1-NH₂]⁺ and [1-ND₂]⁺ in benzene-d₆ at 23°C. Black: [1-NH(tBuAr)]⁺, Blue: [1-NH₂]⁺, Magenta: [1-NHD]⁺, Green: [1-ND₂]⁺.

Attempted dehydrogenation of [1-NH(tBuAr)]⁺. In the glovebox, a Teflon capped J-Young NMR tube was charged with 0.020 g (0.011 mmol) of [1-NH(tBuAr)]⁺ dissolved in 0.6 mL of benzene-d₆. The tube was sealed and connected to the high vacuum line where the solution was degassed (via three freeze-pump-thaw cycles). The tube was then
sealed and heated at 60°C for 5 days. No formation of [1=N(tBuAr)]⁺ or H₂ were detected by EPR and ¹H-NMR spectroscopy, respectively, indicating that the thermodynamically weak N-H bond in [1-NH(tBuAr)]⁺ [45.8 kcal/mol – 52.3 kcal/mol (exp), 48 kcal/mol (DFT)] does not lead to H₂ evolution upon mild heating.

**Attempted hydrogenation of [1=N(tBuAr)]⁺.** In the glovebox, a Teflon capped J-Young NMR tube was charged with 0.020 g (0.011 mmol) of [1=N(tBuAr)]⁺ dissolved in 0.6 mL of benzene-d₆. The tube was sealed and connected to the high vacuum line where the solution was degassed (via three freeze-pump-thaw cycles) prior to the addition of 1 atm of H₂ at -196°C (ca. 4 atm H₂ at 23 °C). The tube was sealed, heated at 60°C for 5 days and monitored. No formation of [1-NH(tBuAr)]⁺ was observed by ¹H and ³¹P NMR spectroscopy, indicating that direct hydrogenation is not a viable pathway for the synthesis of this complex from [1=N(tBuAr)]⁺.

**PCET reaction of [1-NH(tBuAr)]⁺ with [Rh].** In the glovebox, a 20 mL scintillation vial was charged with 0.020 g (0.011 mmol) of [1-NH(tBuAr)]⁺ and 0.005 g (0.013 mmol) of [Rh] dissolved in 3 mL of THF. The solution was stirred at room temperature overnight. After this time, an aliquot was taken from the reaction mixture and the solvent of the aliquot was removed in vacuo to yield a dark brown residue. The residue was then dissolved in 0.2 mL of toluene and analyzed by EPR spectroscopy. The complete conversion of [Rh] was observed, together with the formation of a mixture containing [1=N(tBuAr)]⁺ and an unidentified EPR-active [Mo] complex (Figure 4.11).
Additional EPR Spectroscopic Data

**Figure 4.11.** X-band EPR spectrum of the crude reaction product of [1-NH(tBuAr)]^+ and [Rh] recorded at 296 K in toluene solution (microwave frequency = 9.378 GHz, power = 2.00 mW, power attenuation = 20.0 dB, modulation amplitude = 4.00 G). Fit 1 ([1-N(tBuAr)]^+): g\textsubscript{iso} = 2.013, A\textsubscript{iso}(^{31}\text{P}) = 110 MHz (^{31}\text{P}, I = 1/2, 100%). Fit 2 (Unidentified [Mo] complex): g\textsubscript{iso} = 1.978, A\textsubscript{iso} (^{95/97}\text{Mo}) = 127 MHz (^{95}\text{Mo}, I = 5/2, 15.92%; ^{97}\text{Mo}, I = 5/2, 9.55%), A\textsubscript{iso} (^{31}\text{P}) = 47 MHz (^{31}\text{P}, I = 1/2, 100%).

**Figure 4.12.** X-band EPR spectrum of [1-N(tBuAr)]^+ recorded at 296 K in toluene solution (microwave frequency = 9.378 GHz, power = 2.00 mW, power attenuation = 20.0 dB, modulation amplitude = 4.000 G). Simulation of [1-N(tBuAr)]^+: g\textsubscript{iso} = 2.013, A\textsubscript{iso}(^{31}\text{P}) = 110 MHz (^{31}\text{P}, I = 1/2, 100%).
Electrochemical Data

**Figure 4.13.** Cyclic voltammogram of the complex \([1\text{-NH(tBuAr)}]^{+}\) (10 mM in THF) at 100 mV/sec scan rate. The oxidation potential \((E_{O1})\) and reduction potential \((E_{R1})\) are given as half-wave potentials.

**Figure 4.14.** Cyclic voltammogram of the oxidation wave \((E_{O1})\) of the complex \([1\text{-NH(tBuAr)}]^{+}\) (10 mM in THF) at scan rates ranging from 100 mV/sec to 500 mV/sec. Oxidation potentials \((E_{O1})\) given as half-wave potentials.
Figure 4.15. Cyclic voltammogram of the complex \([1=N(tBuAr)]^+\) (10 mM in THF) at 100 mV/sec scan rate. The oxidation potential (\(E_{O1}\)) and reduction potentials (\(E_{R1}\) and \(E_{R2}\)) are given as half-wave potentials.

Figure 4.16. Cyclic voltammograms of the reduction waves (\(E_{R1}\) and \(E_{R2}\)) of the complex \([1=N(tBuAr)]^+\) (10 mM in THF) at scan rates ranging from 100 mV/sec to 1000 mV/sec. Reduction potentials (\(E_{R1}\) and \(E_{R2}\)) given as half-wave potentials.
Figure 4.17. Cyclic voltammogram of the complex [1-NH$_2$]$^+$ (10 mM in THF) at 100 mV/sec scan rate. The oxidation potential ($E_{O1}$) is given as a half-wave potential. Reduction potentials ($E_{R1}^*$ and $E_{R2}^*$) are given as cathodic peak potentials.

Figure 4.18. Cyclic voltammograms of the reduction waves ($E_{R1}$ and $E_{R2}^*$) of the complex [1-NH$_2$]$^+$ (10 mM in THF) at scan rates ranging from 100 mV/sec to 1000 mV/sec. Reduction potential ($E_{R1}$) given as a peak cathodic potential at 100 mV/sec scan rate, and as half-wave potentials at higher scan rates (200 mV/sec to 1000 mV/sec).
X-Ray Structural Data

Figure 4.19. Solid-state structure of [1-NH(tBuAr)]\textsuperscript{+} at 30% probability ellipsoids. Hydrogen atoms except for amido H4A have been omitted for clarity.

Table 4.1. Selected bond lengths (\textgreek{\AA}) and angles (\textdegree) for [1-NH(tBuAr)]\textsuperscript{+}.

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<th>Bond</th>
<th>Length (\textgreek{\AA})</th>
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<td>Mo1—N4</td>
<td>1.982 (2)</td>
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<tr>
<td>Mo1—N1</td>
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<td>2.111 (2)</td>
</tr>
<tr>
<td>Mo1—P1</td>
<td>2.4852 (6)</td>
</tr>
<tr>
<td>Mo1—P2</td>
<td>2.5324 (7)</td>
</tr>
<tr>
<td>N1—C5</td>
<td>1.369 (3)</td>
</tr>
<tr>
<td>C5—C6</td>
<td>1.448 (3)</td>
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<tr>
<td>C6—N2</td>
<td>1.371 (3)</td>
</tr>
<tr>
<td>N2—C10</td>
<td>1.372 (3)</td>
</tr>
<tr>
<td>C10—C11</td>
<td>1.450 (4)</td>
</tr>
<tr>
<td>C11—N3</td>
<td>1.373 (3)</td>
</tr>
<tr>
<td>N4—C48</td>
<td>1.419 (3)</td>
</tr>
<tr>
<td>Mo1—N4—C48</td>
<td>135.51 (17)</td>
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</tbody>
</table>
Figure 4.20. Solid-state structure of [1=N(tBuAr)]$^+$ at 30% probability ellipsoids. Hydrogen atoms and a pentane solvent molecule have been omitted for clarity.

Table 4.2. Selected bond lengths (Å) and angles (°) for [1=N(tBuAr)]$^+$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
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<tbody>
<tr>
<td>Mo1—N4</td>
<td>1.777 (3)</td>
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</tr>
<tr>
<td>Mo1—N1</td>
<td>2.142 (3)</td>
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<tr>
<td>Mo1—N2</td>
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<td>Mo1—N3</td>
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<td>Mo1—P1</td>
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</tr>
<tr>
<td>Mo1—P2</td>
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<tr>
<td>N1—C5</td>
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</tr>
<tr>
<td>C5—C6</td>
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<tr>
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<tr>
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<tr>
<td>Mo1—N4—C48</td>
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DFT Computational Results

Molecular Orbitals and Spin Density Plots

Figure 4.21. Representations of (a) LUMO; (b) HOMO; (c) HOMO-1; d) and (e) HOMO-2 for [1-NH(tBuAr)]^+ obtained from a spin-restricted Kohn-Sham gas phase DFT calculation at the B3LYP level of theory.
Figure 4.22. Representations of (a) Mulliken spin density plot and population analysis (b) LUMO; (c) SOMO; (d) SOMO-1; (e) SOMO-2 for \([\text{1=N(tBuAr)}]^{+}\) obtained from a spin-unrestricted Kohn-Sham gas phase DFT calculation at the B3LYP level of theory.
DFT Input Examples

Geometry Optimizations

! RKS B3LYP RIJCOSX def2-SVP def2-SVP/J Normalprint SlowConv TightSCF Opt Pal8 UCO ZORA

%basis NewGTO 42 "def2-TZVP(-f)" end
    NewGTO 7 "def2-TZVP(-f)" end
    NewGTO 15 "def2-TZVP(-f)" end
    NewAuxGTO 42 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
    NewAuxGTO 15 "def2-TZVP/J" end
end

%SCF MaxIter 500
    TolE 1e-7
    TolErr 1e-6
end

* xyz 1 1

XYZ Coordinates from crystal structure.

*
Numerical Frequency Calculations

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NORMALPRINT NUMFREQ GRID4 NOFINALGRID PAL8 ZORA

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    NewGTO 7 "def2-TZVP(-f)" end
    NewGTO 15 "def2-TZVP(-f)" end
    NewAuxGTO 42 "def2-TZVP/J" end
    NewAuxGTO 7 "def2-TZVP/J" end
    NewAuxGTO 15 "def2-TZVP/J" end
end

%SCF MaxIter 500
    TolE 1e-7
    TolErr 1e-6
end

%FREQ RESTART TRUE
CENTRALDIFF TRUE
INCREMENT 0.01
END

* xyz 1 1

XYZ Coordinates from Geometry Optimization

*
Calculated Gibbs Free Energies

Table 4.3. Calculated Gibbs free energies of molybdenum complexes for amido N–H BDFE determinations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Spin State</th>
<th>Calculated Gibbs Free Energy (Eh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1-NH(tBuAr)]⁺</td>
<td>S = 0</td>
<td>-6952.67034732</td>
</tr>
<tr>
<td>[1=N(tBuAr)]⁺</td>
<td>S = 1/2</td>
<td>-6952.09498794</td>
</tr>
<tr>
<td>[1-NH₂]⁺</td>
<td>S = 0</td>
<td>-6564.82883137</td>
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<tr>
<td>[1=NH]⁺</td>
<td>S = 1/2</td>
<td>-6564.22813000</td>
</tr>
</tbody>
</table>

References


6 For selected DFT studies on the thermodynamics of N-H bond formation in the Schrock and Chatt cycles with specific acid-reductant combinations, see: (a) Stephan, G. C.; Sivasankar, C.; Studt, F.; Tuczek, F. Chem. – Eur. J., 2008, 14, 644; b) Thimm, W.;


[1-NH(tBuAr)]+ was treated with (η5-C5Me5)(py-Ph)Rh and furnished [1=N(tBuAr)]+ as observed by EPR spectroscopy. While this suggests PCET with the reagent pair is kinetically feasible, the formation of an unidentified [Mo] side product precludes thermochemical conclusions. See Experimental Section for complete experimental details.

Reported Rh-H BDFE in MeCN solution (52.3 kcal/mol) is a satisfactory estimate of THF value according to re-determined [Rh-H] $E^\circ$ and pKa values in THF solution (ref. 8a).


$E^\circ$ value from CV recorded at increased scan rate to enhance wave reversibility. See Experimental Section for electrochemical details.

The comproportionation is expected to be more exoergic with a “parent” imido [1=NH]⁺ owing to the weaker N-H BDFE in [1-NH(tBuAr)]+ compared to [1-NH2]⁺.


CHAPTER 5

Proton-Coupled Electron Transfer to a Molybdenum Ethylene Complex Yields a β-Agostic Ethyl: Structure, Dynamics and Mechanism.

Abstract

The interconversion of molybdenum ethylene and ethyl complexes by proton-coupled electron transfer (PCET) is described, an unusual transformation in organometallic chemistry. The cationic molybdenum ethylene complex

\[
[({}^{\text{Ph}}\text{Tpypy})(\text{PPh}_2\text{Me})_2\text{Mo}(\text{C}_2\text{H}_4)][\text{BARF}^{24}] \quad (\text{1-CH}_2\text{H}_3)^+; {}^{\text{Ph}}\text{Tpypy} = 4'-\text{Ph}-2,2',6,6''-\text{terpyridine},
\]

ArF\(^{24}\) = [C\(_6\)H\(_3\)-3,5-(CF\(_3\))\(_2\)]\(_4\)) was synthesized, structurally characterized, and its electronic structure established by a combination of spectroscopic and computational methods. The overall electronic structure is best described as a molybdenum(III) complex with a metallacyclop propane and a redox neutral terpyridine ligand. Addition of the non-classical ammine complex \([({}^{\text{Ph}}\text{Tpypy})(\text{PPh}_2\text{Me})_2\text{Mo}(\text{NH}_3)][\text{BARF}^{24}] \quad (\text{1-NH}_3)^+\) to \([\text{1-CH}_2\text{H}_3]^+\) resulted in a net C–H bond-forming PCET reaction to yield the molybdenum ethyl

\[
[({}^{\text{Ph}}\text{Tpypy})(\text{PPh}_2\text{Me})_2\text{Mo}(\text{CH}_2\text{CH}_3)][\text{BARF}^{24}] \quad (\text{1-CH}_2\text{CH}_3)^+ \quad \text{and amido}
\]

\[
[({}^{\text{Ph}}\text{Tpypy})(\text{PPh}_2\text{Me})_2\text{Mo}(\text{NH}_2)][\text{BARF}^{24}] \quad (\text{1-NH}_2)^+\) compounds. The reaction was reversed by addition of 2,4,6-tri-tert-butylphenoxy radical to \([\text{1-CH}_2\text{CH}_3]^+\). The solid-state structure of \([\text{1-CH}_2\text{CH}_3]^+\) established a β-agostic ethyl ligand that is maintained in solution as judged by variable temperature \(^1\text{H}\) and \(^{13}\text{C}\) NMR experiments. A combination of variable-temperature NMR experiments and isotopic labeling studies were used to

probe the dynamics of [1-CH$_2$CH$_3$]$^+$ and established restricted $\beta$-agostic -CH$_3$ rotation at low temperature ($\Delta G^\ddagger = 9.8$ kcal mol$^{-1}$ at -86 °C) as well as ethyl isomerization by $\beta$-hydride elimination-olefin rotation-reinsertion ($\Delta H^\ddagger = 19.3 \pm 0.6$ kcal mol$^{-1}$; $\Delta S^\ddagger = 3.4 \pm$ cal mol$^{-1}$ K$^{-1}$). The $\beta$-(C–H) bond-dissociation free energy (BDFE) in [1-CH$_2$CH$_3$]$^+$ was determined experimentally as 57 kcal mol$^{-1}$ (THF) supported by a DFT-computed value of 52 kcal mol$^{-1}$ (gas phase). Comparison of pK$_a$ and electrochemical data for the complexes [1-C$_2$H$_4$]$^+$ and [1-NH$_3$]$^+$ in combination with a deuterium kinetic isotope effect ($k_H/k_D$) of 3.5(2) at 23 °C support a PCET process involving initial electron transfer followed by protonation leading to the formation of [1-CH$_2$CH$_3$]$^+$ and [1-NH$_2$]$^+$ or a concerted pathway. The data presented herein provides a structural, thermochemical and mechanistic foundation for understanding the PCET reactivity of organometallic complexes with alkene and alkyl ligands.

**Introduction**

Redox reactions coupled to the transfer of protons are ubiquitous in biology$^1$ and have been widely applied in synthesis and energy science. These proton-coupled electron transfer (PCET)$^2$ processes are commonly mediated by transition metals and include the industrial oxidation of hydrocarbons$^3$ as well as the 4H$^+/4e^-$ oxidation of water (H$_2$O) in solar fuel conversion schemes.$^4$ Following the recognition that PCET reactivity between an H-atom donor (X–H) and acceptor (Y) is dictated by differences in X–H and Y–H bond strengths, the determination of bond dissociation free energies (BDFEs) have proven key for understanding PCET reactivity in transition metal complexes.$^2d$ A host of BDFEs are now known for metal complexes across the transition series with PCET
typically involving X–H bonds (X = N, O) of aquo, hydroxo or amine ligands bound to the metal center, remote positions in chelating ligands, or transition metal hydrides (Figure 5.1).

![Diagram of PCET reactions involving X–H bonds (X = M, N, O)](image)

**Well-Established: PCET Involving X–H Bonds (X = M, N, O)**

![Examples of transition metal PCET reactions involving X–H bonds (X = M, N, O).](image)

**Rare: Thermochemical Studies on Ligand C–H Bond Strengths**

![Selected thermochemical studies on ligand C–H bond strengths.](image)

**This Work: Interconversion of Olefin/Alkyl Complexes by PCET**

![The strategy reported in this work.](image)

**Figure 5.1.** (a) Examples of transition metal PCET reactions involving X–H bonds (X = M, N, O). (b) Selected thermochemical studies on ligand C–H bond strengths. (c) The strategy reported in this work.

Organometallic complexes with alkene and alkyl ligands are used as precatalysts or implicated as intermediates in important catalytic reactions including alkene polymerization, metathesis and the functionalization of olefins. Despite the ubiquity of
PCET, application of this process to the $1H^+/1e^-$ interconversion of alkyl and alkene ligands has not been generally recognized or applied as a fundamental transformation in organometallic chemistry. Part of the limitation arises from the lack of information regarding $C–H$ BDFEs in coordinated olefins and transition metal alkyls, with previous research focusing on the thermochemistry of hydride ($H^+/2e^-$) transfer from ligands in organometallic complexes. In rare instances, ligand $C–H$ bond strengths have been estimated for alkoxides, benzylic $C–H$ bonds in coordinated arenes, a protonated metallocene as well as in a pincer chelate (Figure 5.1b). For metal alkene and alkyl complexes, Fryzuk and coworkers proposed intramolecular transfer of hydrogen atoms between ethyl and ethylene ligands in a tantalum complex to account for the experimentally observed scrambling of protons between these sites. Overall, well-defined and fully characterized examples of intermolecular $1H^+/1e^-$ PCET reactions with transition metal alkyls to yield olefin complexes have not been described nor have essential thermochemical parameters such as the associated BDFEs been measured.

Our laboratory has recently reported the non-classical ammine complex, $[(\text{Ph}Tpy)(\text{PPh}_2\text{Me})_2\text{Mo}(\text{NH}_3)]\text{[BArF}_{24}]$ (1-$\text{NH}_3^+$; $\text{Ph}Tpy = 4′-\text{Ph}-2,2′,6′,2″$-terpyridine, $\text{ArF}_{24} = [\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2]_4$) where the ammine $N–H$ bond (BDFE$_{N–H}$ = 46 kcal mol$^{-1}$) is weaker than the thermodynamic threshold for spontaneous hydrogen evolution ($\Delta G^0(\text{H}^\bullet) = 48.6$ kcal mol$^{-1}$). Indeed, warming the compound to 60 ºC resulted in loss of H$_2$ gas and formation of the corresponding molybdenum amido product. Subsequent studies have demonstrated that the ammine complex also serves as an effective H-atom donor and can be used to promote formation of a relatively weak N-H bond in a related molybdenum amido complex $[(\text{Ph}Tpy)(\text{PPh}_2\text{Me})_2\text{Mo}(\text{NtBuAr})]\text{[BArF}_{24}]$ (tBuAr = 4-
The hydrogenation of styrene to ethylbenzene has also been observed using [1-NH₃]⁺ as the hydrogen atom source, suggesting PCET reactivity was plausible with this compound.

The combination of facile 1H⁺/1e⁻ chemistry from the formally Mo(I) ammine complex [1-NH₃]⁺ together with the observation of olefin reduction prompted exploration of the interconversion of olefin and alkyl complexes separated by a single hydrogen atom (Figure 5.1c). Observation of such a process requires a kinetically and thermodynamically accessible one-electron redox couple but ultimately uncovers an underrecognized fundamental transformation in organometallic chemistry that may be operative or leveraged in catalysis. Here we describe realization of this goal with demonstration that the cationic molybdenum ethylene complex

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[(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo(C}_2\text{H}_4)][\text{BArF}_{24}] (\text{1-C}_2\text{H}_4^+)\text{ undergoes PCET and overall accepts an H-atom to yield the } \beta\text{-agostic ethyl } [(\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo(CH}_2\text{CH}_3)][\text{BArF}_{24}] (\text{1-CH}_2\text{CH}_3^+)\text{ with [1-NH}_3^+]\text{ serving as the H-atom donor. The structure and dynamics of [1-CH}_2\text{CH}_3^+]\text{ are described, and a thermochemical study of the } \beta-(\text{C–H})\text{ BDFE is presented. Finally, the mechanism of C–H bond forming PCET reaction between [1-C}_2\text{H}_4^+\text{ and [1-NH}_3^+]\text{ is examined.}
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Results and Discussion

Synthesis, Characterization and PCET Reactivity of the Molybdenum Ethylene Complex [1-C₂H₄]⁺. Our studies commenced with the synthesis of the cationic molybdenum ethylene complex [1-C₂H₄]⁺. Stirring a benzene solution of
(PhTpy)(PPh₂Me₂)MoCl ([1-Cl])¹⁸ in the presence of one equiv each of Na[BArF₂₄] and ethylene at room temperature for 18 hours afforded [1-C₂H₄]⁺ as a green-brown solid in 88% yield (Figure 5.2). The solid-state structure of [1-C₂H₄]⁺ was determined by single-crystal X-ray diffraction and established an idealized octahedral geometry with an η²-ethylene ligand coordinated trans to the central pyridine ring of the terpyridine chelate with apical PPh₂Me ligands completing the coordination sphere of molybdenum (Figure 5.3). The formally Mo(I) complex has an S = ½ ground state with a measured solid-state magnetic moment of 1.7 µₜ at 23 °C (magnetic susceptibility balance). Accordingly, [1-C₂H₄]⁺ exhibits a rhombic EPR signal in toluene glass at 7 K that was simulated using the g-values gₓ = 2.122, gᵧ = 2.031, and gₜ = 1.998 (Figure 5.4a). The deviation of the observed g-values from gₑ (gₑ = 2.002) indicates a principally molybdenum-centered singly-occupied molecular orbital (SOMO), supported by the DFT-computed Mulliken spin density plot of the complex (Figure 5.4b). The observed g-anisotropy in the EPR spectrum of [1-C₂H₄]⁺ is characteristic of a low-spin Mo(III) complex¹⁹ and indicates the molybdenum-ethylene bonding interaction is likely best described as a metallacyclop propane.²⁰ This electronic structure assignment is supported by the elongated ethylene C–C bond distance observed in the solid-state structure of [1-C₂H₄]⁺ (1.425(6) Å).

![Figure 5.2. Synthesis of [1-C₂H₄]⁺ by chloride abstraction.](image-url)
**Figure 5.3.** Solid-state structure of [1-C$_2$H$_4$]$^+$ with 30% probability ellipsoids. The hydrogen atoms and the [BArF$_{24}$]$^-$ counterion have been omitted for clarity.

**Figure 5.4.** (a) X-band EPR spectrum of [1-C$_2$H$_4$]$^+$ recorded in toluene glass at 7 K. Collection and simulation parameters: microwave frequency = 9.378 GHz, power = 2.0 mW, modulation amplitude = 4.0 G; $g_x = 2.122$, $g_y = 2.031$, and $g_z = 1.998$. (b) DFT computed spin-density plot for [1-C$_2$H$_4$]$^+$ obtained from Mulliken population analysis in the gas-phase at the B3LYP level of theory.
With [1-C₂H₄]+ in hand, the PCET reactivity as an H-atom acceptor was explored. Treatment of [1-C₂H₄]+ with organic H-atom donors such as cyclohexadiene (CHD) and 2,4,6-tri-tert-butylphenol (tBu₃ArOH) produced no reaction even at elevated temperature (60 °C) and extended reaction times (7 days), suggesting C–H bond formation by PCET is thermodynamically unfavorable using these reagents (BDFE₇C₆H(CHD) = 68 kcal mol⁻¹, BDFE₇O-H(tBu₃ArOH) = 77 kcal mol⁻¹). Accordingly, the cationic molybdenum ammine complex [1-NH₃]+ was selected as the H-atom donor due to an exceedingly weak homolytic N-H bond strength, (BDFE₇N-H = 46 kcal mol⁻¹) and precedent for forming relatively weak N-H bonds when conventional H-atom donors were unsuccessful. Because both [1-NH₃]+ and [1-C₂H₄]+ have identical terpyridine/bis(phosphine) coordination environments, the reaction chemistry is simplified as non-productive ancillary ligand exchange is thermoneutral. Accordingly, treatment of a THF-d₈ solution of [1-C₂H₄]+ with 1 equiv of [1-NH₃]+ quantitatively furnished the diamagnetic products of PCET, [1-CH₂CH₃]+ and [1-NH₂]+ over the course of 5 hours at room temperature (Figure 5.5; see below for characterization of [1-CH₂CH₃]+). The reaction was not inhibited by the addition of excess PPh₂Me (10 equiv), an observation supporting a PCET pathway involving terpyridine bis(phosphine) molybdenum complexes. The observed reactivity represents an unusual net H-atom addition to the molybdenum olefin complex where the alkyl product was cleanly generated. The C–H bond forming PCET reaction was readily reversed by addition of 1 equiv of tBu₃ArO• to [1-CH₂CH₃]+ in benzene-d₆, quantitatively yielding [1-C₂H₄]+ and tBu₃ArOH within minutes at room temperature. While this result defines the range for the strength of the C–H bond formed in [1-CH₂CH₃]+ as 46–77 kcal mol⁻¹, closer and more detailed examination of the ethyl C–H
BDFE formed in [1-CH₂CH₃]⁺ as well as the mechanism of PCET with [1-NH₃]⁺ are described in subsequent sections.

![Diagram](image-url)

**Figure 5.5.** Interconversion of [1-C₂H₄]⁺ and [1-CH₂CH₃]⁺ by PCET.

**Independent Synthesis, Structural Characterization and Dynamics of the β-Agostic Molybdenum Ethyl Complex** [1-CH₂CH₃]⁺. Attempts to separate [1-CH₂CH₃]⁺ from [1-NH₂]⁺ following the PCET reaction were unsuccessful and motivated discovery of an alternate synthetic route. The independent synthesis of [1-CH₂CH₃]⁺ was accomplished by a stepwise oxidation-alkylation sequence (Figure 5.6). Addition of [Cp₂Fe][BArF²⁴] to a toluene solution of [1-Cl] following by stirring for 18 hours at room temperature furnished [((Ph)Tpy)(PPh₂Me)_2Mo(Cl)][BArF²⁴] ([1-Cl]⁺) as a yellow-green solid in quantitative yield. Subsequent alkylation was accomplished by mildly heating an Et₂O/benzene solution (1:1, v/v) of [1-Cl]⁺ at 45 °C with Et₂Zn for 24 hours, yielding [1-CH₂CH₃]⁺ as a brown solid in 86% yield (Figure 5.6). Both the ³¹P{¹H} and ¹H NMR spectra of [1-CH₂CH₃]⁺ in benzene-d₆ at 23 °C are consistent with C₂ᵥ molecular...
symmetry in solution. A single $^{31}$P{¹H} NMR signal was observed at 13.09 ppm and diagnostic $^1$H resonances were observed at 3.33-3.17 and -0.51 ppm for the –CH$_2$– and –CH$_3$ protons of the ethyl ligand, respectively. The solid-state structure of [1-CH$_2$CH$_3$]$^+$ was determined by single-crystal X-ray diffraction and revealed a β-agostic interaction between the molybdenum center and a β-ethyl hydrogen (Figure 5.7). The agostic hydrogen atom (H49A) was located on the difference map and was refined to a close Mo1–H49A distance of 1.99(6) Å. A Mo1–H49A–C49 angle (106.4 deg) was observed as well as a shortened ethyl C–C contact (1.452(4) Å) consistent with increased sp$^2$ character at the ethyl carbons. While ethyl complexes of molybdenum have been structurally characterized, to our knowledge β-agostic ethyl ligands have not been observed with this metal.

Figure 5.6. Independent synthesis of [1-CH$_2$CH$_3$]$^+$ by one-electron oxidation-alkylation.
The β-agostic interaction observed in the solid-state structure of \([1-\text{CH}_2\text{CH}_3]^+\) was confirmed in solution by low-temperature \(^1\text{H}\) and \(^{13}\text{C}\) NMR experiments. The \(^1\text{H}\) NMR spectrum of \([1-\text{CH}_2\text{CH}_3]^+\) in THF-\(d_8\) at \(-107\) °C exhibits the number of resonances consistent with overall \(C_3\) molecular symmetry, in agreement with the geometry observed in the solid state. Notably, the \(^1\text{H}\) NMR spectrum collected at \(-107\) °C revealed inequivalent non-agostic and agostic methyl protons with resonances at 2.21 and -3.90 ppm, respectively (Figure 5.17). The \(^1J_{C-H}\) coupling constant of the agostic H was determined from low-temperature \(^{13}\text{C}\) NMR experiments. The isotopomers \([1-^{13}\text{CH}_2\text{CH}_3]^+\) and \([1-\text{CH}_2^{13}\text{CH}_3]^+\) were prepared by the alkylation of \([1-\text{Cl}]^+\) with a mixture of \(^{13}\text{C}\)-labelled diethylzinc isotopomers \((^{13}\text{CH}_3\text{CH}_2)_2\text{Zn}, (^{13}\text{CH}_3\text{CH}_2)(\text{CH}_3^{13}\text{CH}_2)\text{Zn}\) and \((\text{CH}_3^{13}\text{CH}_2)_2\text{Zn}\). At 23 °C, the \(^{13}\text{C}\) NMR spectrum of the
isotopomeric mixture containing [1-\textsuperscript{13}CH\textsubscript{2}CH\textsubscript{3}]\textsuperscript{+} and [1-CH\textsubscript{2}\textsuperscript{13}CH\textsubscript{3}]\textsuperscript{+} exhibits two prominent signals: a triplet and a quartet assigned to the \(\alpha\)- and \(\beta\)-carbons of the ethyl ligand at 54.01 and 6.67 ppm with \(J_{CH}\) of 147.3 Hz and 122.3 Hz, respectively. Collecting the \(^{13}\text{C}\) NMR spectrum at -107 °C revealed that the \(\beta\)-carbon signal approaches higher-order coupling with a significantly reduced \(J_{C-H}\) of 97.2 Hz while the C–H coupling constant for the \(\alpha\)-carbon is unchanged (Figure 5.20). These \(J_{C-H}\) values confirm reduced C–H orbital overlap at the \(\beta\)-carbon as a result of a 3-centered, 2-electron agostic interaction with molybdenum.\textsuperscript{25}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Alternate view of the solid-state structure of [1-CH\textsubscript{2}CH\textsubscript{3}]\textsuperscript{+} along the P1–Mo1–P2 axis with ellipsoids at 30% probability. Hydrogen atoms (except those connected to C48 and C49), the terpyridine 4'-Ph, PPh\textsubscript{2}Me ligands and the [BARF\textsuperscript{24}]\textsuperscript{-} counterion have been omitted for clarity. Selected bond distances (Å) and angles (deg): Mo1—C48 2.194(2), C48—C49 1.452(4), Mo1—H49A 1.99(6), Mo1—N1 2.2022(18), Mo1—N2 2.0811(18), Mo1—N3 2.1461(19), N1—C5 1.366(3), C5—C6 1.449(3), C6—N2 1.375(3), N2—C10 1.381(3), C10—C11 1.442(3), C11—N3 1.369(3), Mo1—H49A—C49 106.4.}
\end{figure}

Variable temperature solution NMR studies demonstrated that dynamic processes are operative in [1-CH\textsubscript{2}CH\textsubscript{3}]\textsuperscript{+}. The two distinct resonances observed in the low-
temperature $^1$H NMR spectrum of $[1-\text{CH}_2\text{CH}_3]^+$ for the agostic and non-agostic $\beta$-methyl protons coalesce at -86 °C, indicative of a $\beta$-methyl rotation dynamic (Figure 5.9a). The barrier for this process was estimated by the fast-exchange approximation$^{26}$ and was determined to be 9.8 kcal mol$^{-1}$ at -86 °C. This value is comparable to $\beta$-agostic rotational barriers reported in the range 8.0-8.8 kcal mol$^{-1}$ for cationic $\alpha$-diimine complexes of Ni and Pd relevant to olefin polymerization.$^{27}$ Because $\beta$-agostic interactions are commonly invoked as precursors to $\beta$-hydride elimination processes,$^8$ ethyl isomerization dynamics were also investigated for $[1-\text{CH}_2\text{CH}_3]^+$ (Figure 5.9b). If such a pathway is operative, coalescence of the $\alpha$- and $\beta$-ethyl $^{13}$C NMR signals would be expected at elevated temperatures. Accordingly, rates of ethyl isomerization were measured by $^{13}$C NMR line broadening techniques$^{28}$ in toluene-$d_8$ solution containing the isotopomers $[1-^{13}\text{CH}_2\text{CH}_3]^+$ and $[1-\text{CH}_2^{13}\text{CH}_3]^+$ between 60 and 102 °C. Eyring analysis in this temperature range produced activation parameters of $\Delta H^\ddagger = 19.3 \pm 0.6$ kcal mol$^{-1}$ and $\Delta S^\ddagger = 3.4 \pm 1.7$ cal K$^{-1}$ mol$^{-1}$ for the isomerization (Figure 5.10). Comparing these values to the activation parameters reported for analogous $\beta$-hydride elimination processes in the cationic $\beta$-agostic ethyl complexes of Pd ($\Delta H^\ddagger = 6.1 \pm 0.2$ kcal mol$^{-1}$; $\Delta S^\ddagger = -5.2 \pm 0.9$ cal K$^{-1}$ mol$^{-1}$)$^{27b}$ and Ni ($\Delta H^\ddagger = 13.2$ kcal mol$^{-1}$; $\Delta S^\ddagger = -4.2$ cal K$^{-1}$ mol$^{-1}$)$^{27c}$ reveals a comparably modest $\Delta S^\ddagger$ but higher enthalpy of activation in $[1-\text{CH}_2\text{CH}_3]^+$. 

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Deuterium labeling experiments were conducted to chemically confirm β-hydride elimination processes in [1-CH$_2$CH$_3$]$^+$. Monitoring a benzene-$d_6$ containing [1-Cl]$^+$ and 1,1-$d_2$-EtLi revealed scrambling of the deuterium label within minutes at room
temperature with statistical formation of the corresponding $d_2$-ethyl isotopomers $[1-CD_2CH_3]^+$, $[1-CHDCH_2D]^+$ and $[1-CH_2CHD_2]^+$ that were identified by isotopic perturbation of resonance (IPR). This technique relies on the zero-point energy differences between terminal/agostic C–H bonds compared to terminal/agostic C–D bonds resulting in an accumulation of the lighter isotope in the agostic position and a noticeable $\beta$-CH chemical shift separation for the partially deuterated isotopomers.

Accordingly, IPR was observed for $[1-CD_2CH_3]^+$, $[1-CHDCH_2D]^+$ and $[1-CH_2CHD_2]^+$ that exhibit $\beta$-CH resonances at -0.53, -0.70 and -0.90 ppm, respectively (Figure 5.11). This observation further supports the presence of an agostic interaction while also providing evidence for rapid deuterium scrambling (Figure 5.12a).

![Figure 5.11](image)

**Figure 5.11.** The $\beta$-CH$_3$ region of the $^1$H NMR spectrum (500 MHz, benzene-$d_6$, 23 °C) of the isotopomeric mixture containing $[1-CD_2CH_3]^+$, $[1-CHDCH_2D]^+$ and $[1-CH_2CHD_2]^+$.
CD of the labeling experiments, three separate experiments were conducted wherein 1,1-{	extit{d}2}-EtLi to molybdenum, an additional isotopic labeling experiment was conducted that instead involved a PCET pathway (Figure 5.12b). Monitoring a benzene-{	extit{d}6} solution containing [1-C2D4]\textsuperscript{+} and [1-NH3]\textsuperscript{+} yielded a statistical isotopomeric mixture containing [1-CHDCD3]\textsuperscript{+} and [1-CD2CHD2]\textsuperscript{+} within 5 minutes at room temperature. Immediate H incorporation at both the \( \alpha \)- and \( \beta \)-carbons was thus established, consistent with rapid deuterium scrambling pathways. In the absence of rapid scrambling pathways, exclusive proton incorporation at \( \beta \)-carbon is expected.

Importantly, upon performing each labeling experiment in the presence of excess PPh2Me (10 equiv), product formation was not suppressed and the isotopomeric ratio of products was not perturbed. Taken together, these results are consistent with \( \beta \)-hydride elimination/olefin rotation/reinsertion processes in [1-CH2CH3]\textsuperscript{+} that proceed through a 7-coordinate, terpyridine bis(phosphine) molybdenum olefin hydride intermediate (Figure 5.9b). To probe \textit{inter}molecular C–H/D exchange that may complicate the interpretation of the labeling experiments, three separate experiments were conducted wherein [1-CD2CD3]\textsuperscript{+} was treated with [1-C2H4]\textsuperscript{+} (1 equiv) or [1-CH2CH3]\textsuperscript{+} (1 equiv) or free

![Figure 5.12](https://example.com/figure512.png)

**Figure 5.12.** Deuterium labeling experiments to probe \( \beta \)-hydride elimination in [1-CH2CH3]\textsuperscript{+}.
ethylene (5 equiv). In all cases, partially deuterated isotopomers were not observed after 48 hours of stirring at 23 °C, ruling out intermolecular C–H/D exchange on the timescale of intramolecular β-hydride elimination (See Experimental Section).

**Determination of the β-(C–H) Bond Dissociation Free Energy in [1-CH2CH3]+.**

Having established the structure and dynamics of [1-CH2CH3]⁺, thermochemical studies were conducted to probe the β-(C–H) BDFE. Because [1-C2H4]⁺ and [1-CH2CH3]⁺ differ only by a hydrogen atom, a thermochemical square scheme can be constructed that defines the BDFE of the β-(C–H) (Figure 5.13). It is important to note that the reorganization energy component of this bond strength definition is expected to be significant, as a new Mo–C interaction stabilizes the alkene product. This interaction will drive C–H bond cleavage processes in [1-CH2CH3]⁺ and must be overcome in order to achieve C–H bond formation in [1-C2H4]⁺. Therefore its inclusion in the C–H BDFE definition is essential for understanding the PCET reactivity of [1-CH2CH3]⁺. The Bordwell equation (Equation 1.1)^3⁰ can then be used to quantify the C–H BDFE in terms of a 1-electron redox couple (E°; estimated from E₁/₂ of a reversible electrochemical wave), the β-(C–H) pKₐ and the solvent-specific H⁺/H• standard reduction potential (C_G). The electrochemical behavior of [1-C2H4]⁺ was therefore of interest and the isolation of the neutral ethylene complex [1-C2H4] was targeted to evaluate the E° and pKₐ terms in Figure 5.13 and to experimentally determine the C–H BDFE in [1-CH2CH3]⁺ using the Bordwell equation.

\[
\text{BDFE} = 1.37pK_a + 23.06E^\circ + C_G 
\]  

(1.1)
While thermochemical data for agostic alkyl C–H bonds are principally absent from literature, reports by Milstein, Kirchner and van der Vlugt are notable in demonstrating the deprotonation of agostic aryl C–H bonds in pincer complexes of Rh,31 Mn,32 Fe,33 Ni34 and Co35 using NEt3 as a base, thereby defining upper bounds for the C–H pKas in these complexes. More recently, Hulley and coworkers have estimated that η2-arene coordination results in acidic arene C–H bonds with pKas of 3–6 (MeCN) upon coordination to Pd(II).36 These results, along with those established for related metal-dihydrogen complexes,37 suggest that a similar C–H acidification and consequent homolytic bond weakening may arise in β-agostic alkyl complexes, further motivating a quantitative thermochemical study on the β-(C–H) BDFE in [1-CH₂CH₃]⁺.

![Thermochemical expression for the β-(C–H) BDFE in [1-CH₂CH₃]⁺.](image)

**Figure 5.13.** Thermochemical expression for the β-(C–H) BDFE in [1-CH₂CH₃]⁺.

The cyclic voltammogram (CV) of [1-C₂H₄]⁺ was collected in THF solution and exhibits reversible anodic and cathodic waves with half-wave potentials ($E_{1/2}$) of -0.75 V and -1.35 V (vs Cp₂Fe/Cp₂Fe⁺), respectively (Figure 5.14). While the wave at -0.75 V
can be assigned to a one-electron oxidation to $[\text{1-C}_2\text{H}_4]^2^+$, the second wave at -1.35 V is relevant to Figure 5.13 and corresponds to a reduction event furnishing the neutral ethylene complex $[\text{1-C}_2\text{H}_4]$. With this reduction potential in hand, the isolation of $[\text{1-C}_2\text{H}_4]$ was targeted to determine the $pK_a$ of its conjugate acid $[\text{1-CH}_2\text{CH}_3]^+$ and thereby the $\beta$-(C–H) BDFE. Accordingly, one-electron reduction of $[\text{1-C}_2\text{H}_4]^+$ with one equiv of Cp$_2$Co in thawing toluene solution yielded $[\text{1-C}_2\text{H}_4]$ in 53% yield after recrystallization (Figure 5.15a). The solid-state structure of $[\text{1-C}_2\text{H}_4]$ was determined by single-crystal X-ray diffraction and the coordination geometry is analogous to $[\text{1-C}_2\text{H}_4]^+$. In contrast to the paramagnetic cation however, $[\text{1-C}_2\text{H}_4]$ is diamagnetic and exhibits the number of resonances expected for a $C_{2v}$ symmetric complex with a diagnostic triplet at 2.97 ppm ($\delta$, $3^\text{J}P\text{H} = 10.4$ Hz) assignable to the ethylene hydrogens.

Figure 5.14. Cyclic voltammogram of $[\text{1-C}_2\text{H}_4]^+$ using a glassy-carbon working electrode, a platinum wire counter electrode, a silver wire reference electrode, 0.2 M [nBu$_4$N][PF$_6$], and a scan rate of 100 mV/s in THF at 23 °C versus Cp$_2$Fe/Cp$_2$Fe$^+$. The reduction potential (R1) and the oxidation potential (O1) are reported as half-wave potentials ($E_{1/2}$). For a scan starting at $i=0$, see the Experimental Section.
The C–H pKa of [1-CH₂CH₃]⁺ was determined using ¹H NMR spectroscopy by addition of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) as the pKa reference and measurement of the equilibrium concentration ratio with the conjugate base [1-C₂H₄]⁺ (Figure 5.15b). An average of three equilibration experiments yielded a pKa of 16.3 in THF for [1-CH₂CH₃]⁺. Using the relevant redox couple \( E^\circ = -1.35 \text{ V, THF} \) this pKa value enabled calculation of the \( \beta-(\text{C–H}) \) BDFE in [1-CH₂CH₃]⁺ as 57 kcal mol⁻¹ in THF, in good agreement with a DFT-computed value of 52 kcal mol⁻¹.³⁸ These results define both the \( \beta \)-agostic and terminal \( \beta-(\text{C–H}) \) BDFEs according to the definition in Figure 5.13 because a new Mo–C interaction stabilizes the product of H-atom loss from all \( \beta-(\text{C–H}) \) positions and leads to the formation [1-C₂H₄]⁺. Therefore, while the experimentally determined \( \beta-(\text{C–H}) \) BDFE of 57 kcal mol⁻¹ (THF) likely contains different free energies of reorganization for the agostic and terminal \( \beta-(\text{C–H}) \) bonds, this value is expected to govern the overall thermodynamics of 1H⁺/1e PCET reactivity for the [1-CH₂CH₃]⁺/[1-C₂H₄]⁺ pair at ambient conditions independent of which \( \beta-(\text{C–H}) \) bond is involved (see Figure 5.26). It is important to note that the \( \beta-(\text{C–H}) \) BDFE was measured at ambient conditions where a rapid \( \beta-(\text{CH₃}) \) rotation dynamic interconverts agostic and terminal C–H bonds and may kinetically attenuate the influence of the \( \beta \)-agostic interaction on the \( \beta-(\text{C–H}) \) BDFE. The magnitude of this effect may be estimated from the barrier for \( \beta-(\text{CH₃}) \) rotation \( (\Delta G^\ddagger) \), measured as 9.8 kcal mol⁻¹ at -86°C (see above). Importantly, the \( \beta-(\text{C–H}) \) pKa in [1-CH₂CH₃]⁺ is several tens of units lower than that of uncoordinated alkanes, (16.3 vs. >48)²d contributing to the exceedingly low \( \beta-(\text{C–H}) \) BDFE in [1-CH₂CH₃]⁺ that can be compared to a value of 92.9 kcal mol⁻¹ in free ethane.²d
Figure 5.15. (a) Synthesis of [1-C₂H₄] by single-electron reduction. (b) pKₐ equilibration studies involving [1-CH₂CH₃]⁺ and [1-C₂H₄].

As implied by Figure 5.13, the loss of an H-atom equivalent from [1-CH₂CH₃]⁺ is driven by the stability of the olefin complex [1-C₂H₄]⁺, thereby resulting in a net weak C–H bond in the parent metal alkyl. It is therefore instructive to compare the C–H BDFE in [1-CH₂CH₃]⁺ to that of the analogous α-agostic methyl complex [1-CH₃]⁺ to assess whether an agostic interaction gives rise a bond weakening of similarly large magnitude in the absence of an incipient metal-olefin complex. While the preparation of this complex has not yet been realized, the C–H BDFE in [1-CH₃]⁺ was examined by DFT computations yielding a value of 69 kcal mol⁻¹ (gas phase, see Experimental Section). Importantly, while both [1-CH₂CH₃]⁺ and [1-CH₃]⁺ exhibit agostic interactions, the degree of bond weakening in the latter complex is mitigated by the formation of a potentially unstable, formally Mo(III) methyldiene product. Therefore, observation of an agostic interaction does not necessarily imply a significantly weakened bond, wherein the stability of the complex upon H-atom loss must also be considered when estimating the degree of bond weakening.
Mechanism of PCET Reaction between [1-C₂H₄]⁺ and [1-NH₃]⁺. Having determined fundamental thermochemical parameters $E^\circ$ and $pK_a$ for [1-CH₂CH₃]⁺, the pathway of the PCET reaction forming the $\beta$-(C–H) bond was examined. Shown in Figure 5.16, three mechanistic possibilities for the PCET reaction between [1-C₂H₄]⁺ and [1-NH₃]⁺ were considered: 1) concerted hydrogen atom transfer (HAT; diagonal); 2) electron transfer followed by proton transfer (ET/PT; right-down); or 3) proton transfer followed by electron transfer (PT/ET; down-right). Examining whether there is an appropriate match between the relevant one-electron redox couples ($E^\circ$) or $pK_a$s of the reactants at individual ET or PT step of the cycle is an effective approach for probing the thermodynamic accessibility of each PCET pathway. Accordingly, the ET/PT mechanism was first considered. Previously we reported the [1-NH₃]⁺/[1-NH₃]²⁺ couple as -1.09 V (THF, 23 °C, vs Cp₂Fe/Cp₂Fe⁺)¹⁶ which is in thermodynamic proximity to the [1-C₂H₄]/[1-C₂H₄]⁺ couple of -1.35 V (vide supra). Therefore, ET from [1-NH₃]⁺ to [1-C₂H₄]⁺ is expected to be slightly endoergic with $\Delta G^\circ_{ET} = +6.0$ kcal mol⁻¹. Subsequent PT from [1-NH₃]²⁺ ($pK_a = 3.6$)¹⁶ to [1-C₂H₄] (pKₐ = 16.3) is favorable, with $\Delta G^\circ_{PT} = -17$ kcal mol⁻¹. Therefore, an ET/PT pathway leading to the formation of [1-CH₂CH₃]⁺ and [1-NH₂]⁺ is thermodynamically accessible. To provide support for the PT component of this pathway, the complex [1-NH₃]²⁺ was prepared by our previously reported procedures¹⁶ and was treated with one equiv of [1-C₂H₄]. The reaction cleanly and quantitatively furnished the diamagnetic products [1-CH₂CH₃]⁺ and [1-NH₂]⁺ over the course of 1 hour in fluorobenzene solution supporting the thermodynamic and kinetic feasibility of a PT step following initial ET.
Figure 5.16. Square scheme showing PCET mechanisms for the conversion of [1-C₂H₄]⁺ to [1-CH₂CH₃]⁺ (solid arrows), overlaid with thermodynamic parameters contributing to the C–H BDFE (THF) in [1-CH₂CH₃]⁺ (gray, dashed arrows). All experimental pKₐ determinations were conducted in THF solution. \( E^\circ \) values reported as half-wave potentials (0.2 M \([nBu₄N][PF₆]\), 100 mV/s scan rate in THF at 23 °C versus \( \text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+ \)) unless otherwise noted. \(^a\) Thermochemical data from Ref. 16. \(^b\) Peak cathodic potential of a quasi-reversible wave. \(^c\) Thermochemical data from Ref. 17. \(^d\) Indirectly calculated from Bordwell equation using experimentally determined BDFE C–H and \( E^\circ \) values.

To probe the thermodynamics of the PT/ET pathway in Figure 5.16, the CV of [1-CH₂CH₃]⁺ was collected and exhibits a reversible anodic wave with \( E_{1/2} = -0.76 \) V (THF, 23 °C, vs \( \text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+ \)) that corresponds to the [1-CH₂CH₃]⁺/[1-CH₂CH₃]²⁺ redox couple (Figure 5.23). While the isolation of [1-CH₂CH₃]²⁺ was attempted by treatment of [1-CH₂CH₃]⁺ with [\( \text{Cp}_2\text{Fe}\)][\( \text{BArF}^{24} \)], this complex proved too unstable in THF solution for further study. As a result, the pKₐ of [1-CH₂CH₃]²⁺ was indirectly evaluated with the Bordwell equation using the experimentally determined C–H BDFE for [1-CH₂CH₃]⁺ (57 kcal mol⁻¹) and the \( E^\circ \) value for the [1-CH₂CH₃]⁺/[1-CH₂CH₃]²⁺ redox couple (-0.76 V). A pKₐ of 6 (THF) was thus estimated for [1-CH₂CH₃]²⁺. Therefore, there is a pKₐ mismatch between [1-NH₃]⁺ (pKₐ = 20)\(^6\) and [1-C₂H₄]⁺ that renders initial PT between
these complexes thermodynamically unfavorable with $\Delta G^{\circ}_{PT} \approx +19$ kcal mol$^{-1}$. Based on these results, a stepwise ET/PT or a concerted hydrogen atom transfer (HAT) mechanism are likely favored in the C–H bond forming PCET reaction between [1-C$_2$H$_4$]$^+$ and [1-NH$_3$]$^+$ over the PT/ET pathway.

In an attempt to distinguish the stepwise ET/PT and concerted HAT mechanisms for the PCET reaction between [1-C$_2$H$_4$]$^+$ and [1-NH$_3$]$^+$, a deuterium kinetic isotope effect (KIE; $k_H/k_D$) was measured. Upon treatment of [1-C$_2$H$_4$]$^+$ with a 1:1 mixture of [1-NH$_3$]$^+$ and [1-ND$_3$]$^+$, the relative ratio of the product isotopologs [1-CH$_2$CH$_3$]$^+$ and [1-CH$_2$CH$_2$D]$^+$ was determined by $^1$H NMR spectroscopy (see Experimental Section). Using this approach, a normal, primary KIE of 3.5(2) (23 °C) was measured. While this result does not allow us to rigorously rule out HAT, such pathways are typically favored in the absence of a thermodynamically accessible stepwise mechanism and often exhibit large H/D isotope effects as a consequence.$^{2d}$ Given the reasonable thermodynamic coupling between the 1e$^-$ redox potentials of [1-C$_2$H$_4$]$^+$ and [1-NH$_3$]$^+$, we currently favor a mechanistic picture involving stepwise ET/PT for the conversion of the molybdenum olefin complex to the corresponding alkyl.

**Conclusion**

In summary, a cationic molybdenum ethylene complex [1-C$_2$H$_4$]$^+$ supported by terpyridine and bis(phosphine) ligands has been synthesized and its PCET reactivity as an H-atom acceptor has been established. Addition of the non-classical ammine complex [1-NH$_3$]$^+$ to [1-C$_2$H$_4$]$^+$ resulted in a C–H bond forming PCET reaction and furnished the ethyl complex [1-CH$_2$CH$_3$]$^+$ together with the corresponding amido [1-NH$_2$]$^+$. Structural and spectroscopic studies revealed a $\beta$-agostic interaction in [1-CH$_2$CH$_3$]$^+$, which
undergoes ethyl isomerization via rapid $\beta$-hydride elimination, olefin rotation, reinsertion processes. Electrochemical and $pK_a$ measurements were conducted as part of a thermochemical square scheme and established an unusually weak $\beta$-(C–H) BDFE of 57 kcal mol$^{-1}$ in [1-CH$_2$CH$_3$]$^+$. Comparison of the relevant 1e$^-$ redox couples and $pK_a$ values in [1-C$_2$H$_4$]$^+$ and [1-NH$_3$]$^+$ in combination with a measured deuterium kinetic isotope effect rule out a proton-transfer/electron transfer mechanism in the PCET reaction, and instead support a pathway involving electron transfer/proton transfer or a concerted process. The data presented in this study provide rare insight into the structure, dynamics and PCET reactivity of organometallic complexes with alkene and alkyl ligands and offers a new pathway for their interconversion.

**Experimental Section**

**General Considerations**

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (nitrogen) dry box unless otherwise noted. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures. Celite was dried at 180 °C under vacuum for 3 days prior to use. Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Ethylene was purchased from Matheson Tri-Gas Inc., passed through a column of 4 Å molecular sieves and Drierite, and stored in a thick-walled glass vessel over 4 Å molecular sieves. Diethylzinc was purchased from Sigma-Aldrich and used as received.
Cp₂Co was purchased from Sigma-Aldrich and purified by vacuum sublimation. DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) was purchased from Sigma-Aldrich, purified by vacuum distillation and stored over 4 Å molecular sieves. The following compounds were prepared according to literature procedures: [1-Cl]₄₀, [1-NH₃]⁺₄¹, [1-NH₃]²⁺₄¹ Na[BArF²⁴]₄², [Cp₂Fe][BArF²⁴]₄₃, 2,4,6-tri-tert-butylphenoxyl radical (tBu₃ArO•)₄₄, 1,1-
-d₂-EtLi, 1-¹³C-EtLi, EtLi-d₁₀.₄₅

¹H NMR spectra were recorded on either Bruker AVANCE 400 or 500 spectrometers operating at 399.80 MHz or 500.46 MHz, respectively. ¹³C NMR spectra were recorded on either Bruker AVANCE 400 or 500 spectrometer operating at 100.54 MHz or 125.85 MHz, respectively. ³¹P NMR spectra were collected on a Bruker 400 or 500 AVANCE spectrometers operating at 161.84 MHz or 202.40 MHz, respectively, and were referenced to 85% H₃PO₄ as an external standard. ¹⁹F NMR spectra were collected on a Bruker 400 AVANCE spectrometer operating at 376.15 MHz and were referenced to CFCl₃ as an external standard. All ¹H and ¹³C NMR chemical shifts are reported in ppm relative to SiMe₄ using the ¹H (benzene-d₆: 7.16 ppm) and ¹³C (benzene-d₆: 128.06 ppm) chemical shifts of the solvent as a standard. ¹H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent, obsc = obscured), coupling constants (Hz), integration, assignment. For variable temperature NMR experiments, the temperature of the sample solution was calibrated using Glycol (80 wt%) in DMSO-d₆ for high temperature experiments (23°C to 107°C) and using methanol for low temperature experiments (23°C to -107°C).
Continuous wave EPR spectra were recorded on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.\textsuperscript{46}

Elemental analyses were performed at Robinson Microlit Laboratories, Inc., in Ledgewood, NJ. Solid-state magnetic moments were determined using a Johnson Matthey Magnetic Susceptibility Balance that was calibrated with HgCo(SCN)\textsubscript{4}.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker VENTURE D8 PHOTON 100 diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å) and a Cu X-ray tube ($\lambda = 1.54178$ Å). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

CVs were collected in THF solution (2 mM in compound) with [$n$Bu\textsubscript{4}N][PF\textsubscript{6}] (0.2 M), using a 3 mm glassy carbon working electrode, platinum wire as the counter electrode, and silver wire as the reference in a drybox equipped with electrochemical outlets. CVs were recorded using a BASi EC Epsilon electrochemical workstation and analyzed using the BASi Epsilon-EC software. All CVs were run at 23 °C. Potentials are reported versus Cp\textsubscript{2}Fe/Cp\textsubscript{2}Fe\textsuperscript{+} and were obtained using the \textit{in situ} method.
All DFT calculations were performed with the ORCA program package in the gas phase. The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT. The all-electron Gaussian basis sets were those developed by the Ahlrichs group. Triple-ζ quality basis sets def2-TZVP with one set of polarization functions on molybdenum, phosphorous and nitrogen were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used that were of double-ζ quality in the valence region and contained a polarizing set of d functions on the non-hydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX) approach were chosen to match the orbital basis. Numerical frequencies were calculated at the same level of theory to confirm the optimized geometries (no imaginary frequencies) and to derive thermochemical data. Bond dissociation free energies were computed at standard conditions of 1 atm and 25 °C including corrections for vibrational zero-point energy, as well as contributions from translational, rotational, and vibrational modes to the energy and entropy of the homolytic bond cleavage process. For molecules containing a molybdenum atom, the 0th order regular approximation (ZORA) was applied. In this case, the relevant basis sets were replaced by their relativistically recontracted versions. The electronic energy of H•, utilized in the calculation of bond dissociation free energies, at the present level of theory is 312 kcal/mol.
Preparation of Molybdenum Complexes

Preparation of [1-C₂H₄]⁺. In the glovebox, a 20 mL thick-walled glass vessel was charged with a magnetic stir bar, [1-Cl] (0.100 g, 0.119 mmol) and Na[BArF₂⁴] (0.106 g, 0.120 mmol). The vessel was sealed and connected to the high vacuum line where the headspace was evacuated. Benzene (3 mL, previously de-gassed by 3x freeze-pump-thaw cycles) was vacuum transferred to the solids and ethylene (0.125 mmol) was admitted. The vessel was sealed and the mixture was stirred at room temperature for 18 hours. The vessel was brought back into the glovebox, where the mixture was filtered through a pad of Celite, and the solvent was removed in vacuo. The dark residue was washed with pentane (10 mL) and dried in vacuo to yield [1-C₂H₄]⁺ as a dark green solid (0.177 g, 0.104 mmol, 88%). Single crystals suitable for X-Ray diffraction studies were obtained by vapor diffusion of pentane to a concentrated fluorobenzene solution of [1-C₂H₄]⁺ at -35°C. Anal Calcd for C₈₁H₅₇BF₂₄MoN₃P₂: C, 57.33; H, 3.39; N, 2.48. Found: C, 57.30; H, 2.99; N, 2.36. Magnetic Susceptibility (Guoy balance, 23 °C): \( \mu_{\text{eff}} = 1.7 \mu_B \).

The isotopologue [1-C₂D₄]⁺ was prepared in a manner similar to [1-C₂H₄]⁺ with the exception that ethylene-\( d_4 \) was used in place of ethylene.

Preparation of [1-Cl]⁺. In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar and [Cp₂Fe][BArF₂⁴] (0.126 g, 0.120 mmol). A solution of [1-Cl] (0.100 g, 0.119 mmol) dissolved in 10 mL of toluene was added in one portion. The suspension was stirred at room temperature for 18 hours, during which time a color change to green-yellow was observed. The solution was filtered through a pad of Celite and was concentrated to a minimal volume (3 mL) in vacuo. The mixture was layered
with pentane (10 mL) and stood at -35°C for 3 hours. During this time, dark solids crystallized. The yellow-brown supernatant was decanted, and pentane (10 mL) was added to the residue. The mixture was stirred for 15 minutes to extract remaining ferrocene, the supernatant was decanted, and the dark solids were dried in vacuo to yield [1-Cl]+ as a dark yellow-green solid (0.200 g, 0.117 mmol, 99%). Single crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of pentane into a concentrated toluene solution of [1-Cl]+ at -35°C. Anal Calcd for C_79H_53BClF_24MoN_3P_2: C, 55.67; H, 3.13; N, 2.47. Found: C, 55.66; H, 3.02; N, 2.55.

1H NMR (500 MHz, benzene-d_6, 23 ºC): δ 20.32 (br s, 2H, PhTpy), 9.63 (d, J_HH = 8.5 Hz, 2H, PhTpy), 9.55 (t, J_HH = 7.6 Hz, 1H, PhTpy), 9.14 (d, J = 8.5 Hz, 2H, PhTpy), 8.39 (br s, 16H, B[(3,5-(CF_3)_2)C_6H_3]_4, overlap with PPh_2Me), 7.62 (br s, 8H, PPh_2Me), 7.21 (t, J_HH = 7.7 Hz, 4H, PPh_2Me), 7.27 (t, J_HH = 8.0 Hz, 2H, PhTpy), 3.01 (br s, 2H, PhTpy), 2.25 (br s, 2H, PhTpy), 0.33 (br s, 6H, PPh_2Me), -7.07 (br s, 2H, PhTpy).

13C{1H} NMR (400 MHz, benzene-d_6, 23 ºC): δ 234.22 (s, PhTpy), 219.42 (s, PhTpy), 218.41 (s, PhTpy), 214.37 (s, PhTpy), 182.45 (s, PhTpy), 162.79 (q, J_CB = 49.8 Hz, B[(3,5-(CF_3)_2)C_6H_3]_4), 139.87 (s, PhTpy), 135.43 (s, B[(3,5-(CF_3)_2)C_6H_3]_4), 132.53 (s, PPh_2Me), 129.95 (q, J_CF = 31.35 Hz, B[(3,5-(CF_3)_2)C_6H_3]_4), 129.69 (s, PPh_2Me), 129.31 (s, PhTpy), 129.07 (s, PPh_2Me), 125.94 (br s, PPh_2Me), 125.64 (s, PhTpy), 125.24 (q, J_CF = 272.6 Hz, B[(3,5-(CF_3)_2)C_6H_3]_4), 118.17 (s, B[(3,5-(CF_3)_2)C_6H_3]_4), 116.12 (s, PhTpy), 94.90 (s, PhTpy), 80.08 (br s, PPh_2Me), 24.05 (s, PhTpy), 20.56 (br s, PhTpy).

19F{1H} NMR (400 MHz, benzene-d_6, 23 ºC): δ -61.98 (s, B[(3,5-(CF_3)_2)C_6H_3]_4).
**Preparation of [1-CH₂CH₃]⁺.** In the glovebox, a 20 mL scintillation vial was charged with [1-Cl]⁺ (0.100 g, 0.059 mmol). In a separate 20 mL scintillation vial, Et₂Zn (0.013 mL, 0.126 mmol) was dissolved in Et₂O/benzene (4 mL; 1:1 v/v). The Et₂Zn solution was then added to the vial containing [1-Cl]⁺ and the mixture was transferred to a 25 mL thick-walled glass vessel equipped with a Teflon cap and a magnetic stir bar. The vessel was sealed, and the mixture was heated at 45 °C while stirring for 24 hours. During this time, a color change from dark green to dark brown-green was observed. The vessel was brought back into the glovebox, the mixture was transferred to a 20 mL scintillation vial and the solvent was removed *in vacuo*. The dark solids were extracted with toluene (5 mL) and the combined extracts were filtered through a pad of Celite. The solvent was removed *in vacuo*, and the dark residue was washed with pentane (3 x 10 mL) followed by drying *in vacuo* to yield [1-CH₂CH₃]⁺ as a dark brown solid (0.086 g, 0.051 mmol, 86%). Single crystals suitable for X-Ray diffraction studies were obtained by vapor diffusion of pentane to a concentrated fluorobenzene solution of [1-CH₂CH₃]⁺ at -35°C.

Anal Calcd for C₈₁H₅₈BF₂₄MoN₃P₂: C, 57.29; H, 3.44; N, 2.47. Found: C, 56.94; H, 3.27; N, 2.40. ¹H NMR (400 MHz, benzene-δ₆, 23 °C): δ 8.91 (br s, 2H, Ph₄Tpy), 8.49 (br s, 8H, B[(3,5-(CF₃)₂)C₆H₃]₄), 7.70 (s, 4H, B[(3,5-(CF₃)₂)C₆H₃]₄), 7.53 (br s, 2H, Ph₄Tpy), 7.51 (br s, 2H, Ph₄Tpy), 7.42 (t, 3J₃JHH = 7.8 Hz, 2H, Ph₄Tpy), 7.37 – 7.25 (m, 3H, Ph₄Tpy), 6.81 (t, 3J₃JHH = 7.4 Hz, 4H, PPh₂Me), 6.74 (d, 3J₃JHH = 7.4 Hz, 2H, Ph₄Tpy), 6.66 (br s, 8H, PPh₂Me), 6.43 (t, 3J₃JHH = 6.1 Hz, 2H, Ph₄Tpy), 6.05 (br s, 8H, PPh₂Me), 3.33 – 3.17 (m, 2H, CH₂CH₃), 0.38 (app t, J = 2.6 Hz, 6H, PPh₂Me), -0.51 (t, 3J₃JHH = 7.6 Hz, 3H, CH₂CH₃). ¹³C {¹H} NMR (400 MHz, benzene-δ₆, 23 °C): δ 162.89 (q, 1J₁CB = 49.8 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 139.90 (s, Ph₄Tpy), 137.82 (s, Ph₄Tpy), 137.40 (s, Ph₄Tpy), 135.53 (s, B[(3,5-(CF₃)₂)C₆H₃]₄).
31P\{^1H\} NMR (400 MHz, benzene-d$_6$, 23 ºC): δ 13.09 (s, PPh$_2$Me).

19F\{^1H\} NMR (400 MHz, benzene-d$_6$, 23 ºC): δ -62.00 (s, B[(3,5-(CF$_3$)$_2$)C$_6$H$_3$]$_4$). The isotopologue [1-CD$_2$CD$_3$]$^+$ was prepared in a manner similar to [1-CH$_2$CH$_3$]$^+$ with the exception that Et$_2$Zn-$d_{10}$ was used in place of Et$_2$Zn. The isotopomeric mixture containing [1-1$^{13}$CH$_2$CH$_3$]$^+$ and [1-CH$_2$$^{13}$CH$_3$]$^+$ was prepared in a manner similar to [1-CH$_2$CH$_3$]$^+$ with the exception that in situ generated $^{13}$C-Et$_2$Zn$^{24}$ was used in place of Et$_2$Zn.

Preparation of [1-C$_2$H$_4$]. In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar and [1-C$_2$H$_4$]$^+$ (0.122 g, 0.072 mmol) dissolved in 4 mL of toluene. A separate 20 mL scintillation vial was charged with Cp$_2$Co (0.014 g, 0.074 mmol) dissolved in 1 mL of toluene. Both vials were frozen in a liquid-nitrogen-cooled coldwell. While thawing, the Cp$_2$Co solution was added to the thawing solution of [1-C$_2$H$_4$]$^+$. The mixture was warmed to room temperature and stirred for 15 minutes. The mixture was then filtered through a pad of Celite and the solvent was removed in vacuo. The dark residue was then suspended in Et$_2$O (3 mL) and stood at -35 ºC for 1 hour. The resulting precipitates were isolated on a glass frit (15 mL, fine-porosity), washed with cold Et$_2$O (-35 ºC, 3 x 2 mL) and dried in vacuo to yield the product as a dark green solid (0.032 g,
0.038 mmol, 53%). Single crystals suitable for X-ray diffraction studies were obtained from a concentrated Et₂O solution of [1-C₂H₄] at -35°C. Anal Calcd for C₄₉H₄₅MoN₃P₂: C, 70.58; H, 5.44; N, 5.04. Found: C, 70.44; H, 4.94; N, 4.82. ¹H NMR (400 MHz, benzene-d₆, 23 ºC): δ 9.85 (d, 3JHH = 6.2 Hz, 2H, PhTpy), 8.18 (s, 2H, PhTpy), 7.90-7.87 (m, 4H, PhTpy), 7.47 (t, 3JHH = 7.7 Hz, 2H, PhTpy), 7.25 (t, 3JHH = 7.4 Hz, 1H, PhTpy), 6.82 (t, 3JHH = 7.4 Hz, 2H, PhTpy), 6.79 (t, 3JHH = 7.3 Hz, 4H, PPh₂CH₃), 6.69 (t, 3JHH = 7.5 Hz, 8H, PPh₂CH₃), 6.58 (t, 3JHH = 6.5, 2H, PhTpy), 6.32-6.28 (m, 8H, PPh₂CH₃), 2.97 (t, 3JPH = 10.4 Hz, 4H, C₂H₄), 0.68 (app t, J = 2.5 Hz, 6H, PPh₂CH₃). ¹³C{¹H} NMR (400 MHz, benzene-d₆, 23 ºC): δ 152.65 (s, PhTpy), 148.05 (s, PhTpy), 143.59 (s, PhTpy), 141.92 (s, PhTpy), 134.50 (app t, J = 13.7 Hz, PPh₂CH₃), 130.58 (app t, J = 5.5 Hz PPh₂CH₃), 129.27 (s, PhTpy), 127.69 (app t, J = 3.9 Hz, PPh₂CH₃), 126.91 (s, PhTpy), 126.09 (s, PhTpy), 126.05 (br s, PPh₂CH₃), 121.37 (s, PhTpy), 121.32 (s, PhTpy), 118.60 (s, PhTpy), 108.81 (s, PhTpy), 50.70 (t, 2JPC = 5.5 Hz, C₂H₄), 8.23 (app t, J = 9.1 Hz, PPh₂CH₃). ³¹P{¹H} NMR (benzene-d₆, 23 ºC): δ 7.63 (s, PPh₂Me).
Variable Temperature NMR Data

Figure 5.17. Variable temperature $^1$H NMR (500 MHz) spectra of [1-CH$_2$CH$_3$]$^+$ in THF-$d_8$. The resonances corresponding to the ethyl CH$_3$ protons are labeled.
Figure 5.18. Variable temperature $^1$H NMR (500 MHz) spectra of [I-CH$_2$CH$_3$]$^+$ in THF-$d_8$. The peaks corresponding to the ethyl CH$_3$ protons are marked with an asterisk (*) and the coalescence temperature is highlighted.
Figure 5.19. Variable temperature $^{13}$C-{$^1$H} NMR (500 MHz) spectra of the isotopomeric mixture containing [1-$^{13}$CH$_2$CH$_3$]$^+$ and [1-CH$_2$$^{13}$CH$_3$]$^+$ in toluene-$d_8$. 
Figure 5.20. Variable temperature $^{13}$C NMR (500 MHz) spectra of the isotopomeric mixture containing $[\text{1-}^{13}\text{CH}_2\text{CH}_3]^+$ and $[\text{1-CH}_2^{15}\text{CH}_3]^+$ in THF-$d_8$.

Additional Reactions and Associated NMR Data

PCET reaction between $[\text{1-NH}_3]^+$ and $[\text{1-C}_2\text{H}_4]^+$. In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.035 g (0.021 mmol) of $[\text{1-NH}_3]^+$, 0.035 g (0.021 mmol) of $[\text{1-C}_2\text{H}_4]^+$, and 0.001 g (0.005 mmol) of a Cp$_2$Fe internal standard dissolved in 0.6 mL THF-$d_8$. The tube was sealed and after 5 hours of stirring at room temperature, quantitative formation of $[\text{1-CH}_2\text{CH}_3]^+$ and $[\text{1-NH}_2]^+$ was observed by $^1\text{H}$ and $^{13}\text{P}$ NMR spectroscopy in a 1:1 ratio. Repeating the reaction in the presence of 10
equiv. (0.21 mmol) of PPh$_2$Me or using benzene-$d_6$ in place of THF-$d_8$ resulted in no change to reaction outcome.

**PCET reaction between [1-CH$_2$CH$_3$]$^+$ and tBu$_3$ArO•.** In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, 0.035 g (0.021 mmol) of [1-CH$_2$CH$_3$]$^+$ and 0.001 g (0.005 mmol) of a Cp$_2$Fe internal standard dissolved in 0.4 mL benzene-$d_6$. To the stirring solution, 0.006 g (0.023 mmol) of tBu$_3$ArO• dissolved in 0.2 mL of benzene-$d_6$ was added dropwise. Stirring was continued for 5 minutes at room temperature. The quantitative formation of tBu$_3$ArOH was observed by $^1$H NMR spectroscopy, and the formation of [1-C$_2$H$_4$]$^+$ was observed by EPR spectroscopy.

**Protonation Reaction of [1-C$_2$H$_4$] with [1-NH$_3$]$^{2+}$.** In the glovebox, a 20 mL scintillation vial was charged with 0.026 g (0.010 mmol) of [1-NH$_3$]$^{2+}$, 0.009 g (0.011 mmol) of [1-C$_2$H$_4$], and 0.001 g (0.005 mmol) of a Cp$_2$Fe internal standard dissolved in 2 mL of fluorobenzene. The solution was stirred at room temperature for 1 hour, after which time the solvent was removed in vacuo and the residue was dissolved in 0.6 mL benzene-$d_6$. Quantitative formation of [1-CH$_2$CH$_3$]$^+$ and [1-NH$_2$]$^+$ was observed by $^1$H and $^{13}$P NMR spectroscopy in a 1:1 ratio.

**Deuterium labeling experiment with 1,1-$d_2$-EtLi.** In the glovebox, a 20 mL scintillation vial was charged with 0.030 g (0.018 mmol) of [1-Cl]$^+$ dissolved in 5 mL of toluene and was frozen in a liquid-nitrogen-cooled coldwell. A solution containing 1,1-$d_2$-EtLi (0.030 mL, 0.018 mmol, 0.584 M in toluene) was added to the thawing solution of [1-Cl]$^+$. The
mixture was warmed to room temperature and stirred for 5 minutes. The mixture was then filtered through a pad of Celite and the solvent was removed in vacuo. The residue was dissolved in 0.6 mL of benzene-$d_6$, and statistical formation of $[\text{1-CD}_2\text{CH}_3]^+$, $[\text{1-CHDCH}_2\text{D}]^+$ and $[\text{1-CH}_2\text{CHD}_2]^+$ was observed by $^1$H NMR spectroscopy. The reaction was repeated in the presence of 10 equiv. (0.18 mmol) of PPh$_2$Me with identical results.

Deuterium labeling PCET experiment. In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.020 g (0.012 mmol) of $[\text{1-C}_2\text{D}_4]^+$ and 0.020 g (0.012 mmol) of $[\text{1-NH}_3]^+$ dissolved in 0.6 mL benzene-$d_6$. The tube was sealed, stirred at room temperature and monitored. After minutes of stirring, the isotopomers $[\text{1-CD}_2\text{CHD}_2]^+$ and $[\text{1-CHDCD}_3]^+$ were observed in a 1:1 ratio by $^1$H NMR spectroscopy. The reaction was repeated in the presence of 10 equiv. (0.12 mmol) of PPh$_2$Me with identical results.
Figure 5.21. $^1$H NMR (500 MHz) spectra of the reaction between [1-C$_2$D$_4$]$^+$ and [1-NH$_3$]$^+$ in benzene-$d_6$ at 23°C at various time intervals. Diagnostic resonances corresponding to the products [1-NH$_2$]$^+$, [1-CHDCD$_3$]$^+$ and [1-CD$_2$CHD$_2$]$^+$ have been highlighted.
Figure 5.22. Expanded view of the $^1$H NMR (500 MHz) spectra of the reaction between [1-$\text{C}_2\text{D}_4$]$^+$ and [1-$\text{NH}_3$]$^+$ in benzene-$d_6$ at 23°C at various time intervals showing the formation of products. Diagnostic resonances corresponding to the products [1-$\text{CHDCD}_3$]$^+$ and [1-$\text{CD}_2\text{CHD}_2$]$^+$ have been highlighted.

**Intermolecular C-H/D exchange control experiment.** In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.020 g (0.012 mmol) of [1-$\text{CD}_2\text{CD}_3$]$^+$ and 0.020 g (0.012 mmol) of [1-$\text{C}_2\text{H}_4$]$^+$ dissolved in 0.6 mL benzene-$d_6$. The tube was sealed, stirred at room temperature and monitored. After 48 hours of stirring, no partially deuterated isotopologues were observed by $^1$H NMR spectroscopy. The experiment was repeated at 60°C (48 h) to probe self-exchange PCET at elevated temperatures and yielded identical results (no exchange).
**Intermolecular C-H/D exchange control experiment.** In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.020 g (0.012 mmol) of [1-CD$_2$CD$_3$]$^+$ and 0.020 g (0.012 mmol) of [1-CH$_2$CH$_3$]$^+$ dissolved in 0.6 mL benzene-$d_6$. The tube was sealed, stirred at room temperature and monitored. After 48 hours of stirring, no partially deuterated isotopologues were observed by $^1$H NMR spectroscopy.

**Intermolecular C-H/D exchange control experiment.** In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.017 g (0.010 mmol) of [1-CD$_2$CD$_3$]$^+$ dissolved in 0.6 mL benzene-$d_6$. The tube was sealed, and connected to the high vacuum line. The solvent was frozen and the headspace of the NMR tube was evacuated and ethylene (0.050 mmol) was admitted. The vessel was sealed, stirred at room temperature and monitored. After 48 hours of stirring, no partially deuterated isotopologues were observed by $^1$H NMR spectroscopy.
Electrochemical Data

Figure 5.23. Cyclic voltammogram of \([1-\text{CH}_2\text{CH}_3]^+\) at 100 mV/sec scan rate. The oxidation potential (O1) is given as a half-wave potential.

Figure 5.24. Cyclic voltammogram of \([1-\text{C}_2\text{H}_4]^+\) at 100 mV/sec scan rate starting from \(i = 0\). The oxidation potential (O1) and reduction potential (R1) are given as a half-wave potentials.
**pKₐ Determinations**

**Representative pKₐ determination procedure.** In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.032 g (0.019 mmol) of [1-CH₂CH₃]⁺ and 0.003 mL (0.022 mmol) of a mesitylene internal standard dissolved in 0.6 mL THF-d₈. DBU (0.0028 mL, 0.019 mmol) was added to the tube via microsyringe. The tube was sealed, stirred at room temperature for 30 minutes and the ¹H NMR spectrum was recorded. The [DBU-H]⁺/[DBU] acid/base pair was used as the pKₐ reference anchor (pKₐ(THF) = 16.6). The pKₐ of [1-CH₂CH₃]⁺ relative to the reference was calculated according to literature procedures.

**Figure 5.25.** Representative ¹H NMR (500 MHz) spectrum of the equilibrium between [1-CH₂CH₃]⁺, [1-C₂H₄]⁺, DBU and [DBU-H]⁺ (top) stacked with a spectrum of [1-CH₂CH₃]⁺ (bottom) in THF-d₈ at 23°C.
Note: The pKₐ determination for [1-CH₂CH₃]⁺ was carried out at ambient conditions, where a rapid β-(CH₃) rotation dynamic interconverts β-agostic and terminal β-(C–H) bonds and may kinetically attenuate the influence of the β-agostic interaction on the β-(C–H) pKₐ, and by extension, the β-(C–H) BDFE. However, as shown in Figure 5.26, the values obtained from equilibration experiments define the C–H BDFE values of both β-agostic and terminal C–H bonds in [1-CH₂CH₃]⁺, where differences arise in reorganization energies, and not in the overall thermodynamics of PCET.

Figure 5.26. Qualitative free energy diagram depicting differences in reorganization energies implicit in the C–H BDFE definitions of β-agostic and terminal β-(C–H) bonds in [1-CH₂CH₃]⁺. Note that the overall free energy changes of H-atom loss from both β-agostic (red) and terminal C–H bonds (blue) in [1-CH₂CH₃]⁺ leading to the formation of [1-C₂H₄]⁺ are equal as defined.
KIE Determination

The KIE for the PCET reaction between \([1-\text{C}_2\text{H}_4]^+\) and \([1-\text{NH}_3]^+\) was determined using the following method. The complex \([1-\text{C}_2\text{H}_4]^+\) was treated with a 1:1 mixture of \([1-\text{NH}_3]^+\) and \([1-\text{ND}_3]^+\) in THF. The relative concentrations of the products of PCET, \([1-\text{CH}_2\text{CH}_3]^+\) and the \(d_1\)-isotopomers \([1-\text{CHDCH}_3]^+\) and \([1-\text{CH}_2\text{CH}_2\text{D}]^+\), were determined by \(^1\text{H}\)-NMR spectroscopy. Isotopic perturbation of resonance (IPR) at the \(\beta-\text{CH}_3\) signal of \([1-\text{CH}_2\text{CH}_2\text{D}]^+\) enabled observation of this complex by \(^1\text{H}\)-NMR spectroscopy.

\[ \text{Figure 5.27. KIE determination for the PCET reaction between } [1-\text{C}_2\text{H}_4]^+ \text{ and } [1-\text{NH}_3]^+. \]

The KIE of the overall reaction is then given by the relation:

\[
\text{KIE} = \frac{k_H}{k_D} = \frac{[1-\text{CH}_2\text{CH}_3]^+}{[1-\text{CHDCH}_3]^+ + 1.5[1-\text{CH}_2\text{CH}_2\text{D}]^+}
\]

(5.1)

where \([1-\text{CH}_2\text{CH}_3]^+\), \([1-\text{CHDCH}_3]^+\) and \([1-\text{CH}_2\text{CH}_2\text{D}]^+\) refer to the \(\beta-\text{CH}_3\) signal integral values corresponding to each complex in the \(^1\text{H}\)-NMR spectrum of the reaction mixture.

Assuming rapid \(\beta-\text{H}\) elimination processes equilibrate \([1-\text{CHDCH}_3]^+\) and \([1-\text{CH}_2\text{CH}_2\text{D}]^+\) to a 1:1 mixture (\textit{vide supra}) then the expression can be simplified:

\[
\text{KIE} = \frac{k_H}{k_D} = \frac{[1-\text{CH}_2\text{CH}_3]^+}{3[1-\text{CH}_2\text{CH}_2\text{D}]^+}
\]

(5.2)
The $\beta$-CH$_3$ signals of [1-CH$_2$CH$_3$]$^+$ and [1-CHDCH$_3$]$^+$ overlap since no significant IPR is operative that can distinguish these complexes. The above relation can then be expressed in terms of the ratio of two measurable $^1$H NMR integrals: $A$ (the sum of $\beta$-CH$_3$ integrals in [1-CH$_2$CH$_3$]$^+$/[1-CHDCH$_3$]$^+$) and $B$ (the $\beta$-CH$_3$ integral in [1-CH$_2$CH$_2$D]$^+$):

$$\text{KIE} = \frac{k_H}{k_D} = \frac{A - 1.5B}{3B} = \frac{1}{3} \left( \frac{A}{B} \right) - 0.5$$  (5.3)

**Representative KIE determination procedure.** In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.035 g (0.021 mmol) of [1-C$_2$H$_4$]$^+$, 0.017 g (0.010 mmol) of [1-NH$_3$]$^+$ and 0.017 g (0.010 mmol) of [1-ND$_3$]$^+$ dissolved in 0.6 mL THF-$d_8$. The tube was sealed, stirred at room temperature and the $^1$H-NMR spectrum was recorded. The experiment was repeated 3 times. The value for the KIE was determined using this method as 3.5(2) at 23 °C.

**Figure 5.28.** Representative $^1$H NMR (400 MHz) spectrum of the reaction between [1-C$_2$H$_4$]$^+$ and [1-NH$_3$]$^+$/[1-ND$_3$]$^+$ (1:1) in THF-$d_8$ at 23°C. Inset shows $\beta$-CH$_3$ region.
demonstrating the isotopologues that exhibit IPR. **A:** $[1-\text{CH}_2\text{CH}_3]^+$ and $[1-\text{CHDC}\text{H}_3]^+$ (overlap). **B:** $[1-\text{CH}_2\text{CH}_2\text{D}]^+$.

**Intermolecular product H/D exchange control experiment.** In the glovebox, a J-Y Young NMR tube fitted with a Teflon cap was charged with 0.050 g (0.030 mmol) of $[1-\text{CH}_2\text{CH}_3]^+$, 0.050 g (0.030 mmol) of $[1-\text{ND}_2]^+$ dissolved in 0.6 mL THF-$d_8$. The tube was sealed and stirred at room temperature for 5 hours. The $^1\text{H}$ NMR spectrum of the product mixture was recorded, and no partially deuterated molybdenum ethyl isotopologues were observed by $^1\text{H}$ NMR spectroscopy.

![NMR spectrum](image)

**Figure 5.29.** $^1\text{H}$ NMR (400 MHz) spectrum of the reaction mixture containing $[1-\text{CH}_2\text{CH}_3]^+$ and $[1-\text{ND}_2]^+$ in THF-$d_8$ at $23^\circ\text{C}$ after 5 hours of stirring. Inset shows $\beta$-CH$_3$ region demonstrating no partially deuterated isotopologues.
X-Ray Structural Data

Figure 5.30. Solid-state structure of $[1$-$\text{C}_2\text{H}_4][\text{BArF}^{24}]$ at 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.
Figure 5.31. Solid-state structure of [1-Cl][BArF$_{24}$] at 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.
Figure 5.32. Solid-state structure of [1-CH₂CH₃][BARF₂₄] at 30% probability ellipsoids. Hydrogen atoms except those connected to C48 and C49 have been omitted for clarity.
Figure 5.33. Solid-state structure of [1-C$_2$H$_4$] at 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.
DFT Input Examples

Geometry Optimizations

#Filename
! RKS B3LYP RIJCOSX ZORA ZORA-def2-SVP SARC/J Normalprint SlowConv
TightSCF Opt Pal8 UCO

%basis NewGTO 42 "old-ZORA-TZVP" end
NewGTO 15 "ZORA-DEF2-TZVP(-f)" end
  NewGTO 7 "ZORA-DEF2-TZVP(-f)" end
NewAuxGTO 42 "SARC/J" end
NewAuxGTO 15 "SARC/J" end
NewAuxGTO 7 "SARC/J" end
end

%SCF MaxIter 500
  TolE 1e-7
  TolErr 1e-6
end

* xyz 1 1

XYZ Coordinates from crystal structure.

*
Numerical Frequency Calculations

#Filename

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Normalprint Numfreq Grid4 Nofinalgrid Pal8

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  NewGTO 7 "ZORA-DEF2-TZVP(-f)" end
  NewGTO 15 "ZORA-DEF2-TZVP(-f)" end
  NewAuxGTO 42 "SARC/J" end
  NewAuxGTO 7 "SARC/J" end
  NewAuxGTO 15 "SARC/J" end
end

%SCF MaxIter 500
  TolE 1e-7
  TolErr 1e-6
end

%FREQ RESTART TRUE
CENTRALDIFF TRUE
INCREMENT 0.01
END

* xyz 1 1

XYZ Coordinates from geometry optimization.

*
Calculated Gibbs Free Energies

Table 5.1. Calculated Gibbs free energies of molybdenum complexes for alkyl C–H BDFE determinations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Spin State</th>
<th>Calculated Gibbs Free Energy (Eh)</th>
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</thead>
<tbody>
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<td>[1-CH₂CH₃]⁺</td>
<td>S = 0</td>
<td>-6830.47810830</td>
</tr>
<tr>
<td>[1-C₂H₄]⁺</td>
<td>S = 1/2</td>
<td>-6829.89851504</td>
</tr>
<tr>
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<td>-6791.18362246</td>
</tr>
<tr>
<td>[1-CH₂]⁺</td>
<td>S = 1/2</td>
<td>-6790.57712653</td>
</tr>
</tbody>
</table>

References


15 For examples of related studies invoking intramolecular H-abstraction in transition metal alkyl/alkylidene/alkylidyne complexes, see: (a) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevski, D. A. Synthesis 1991, 234. (b) Fellmann, J. D.; Schrock, R.


22 The lower bound (46 kcal mol–1) is defined by the N–H BDFE in [1-NH3]+, while the upper bound (77 kcal mol–1) is defined by the O–H BDFE in tBu3ArOH.


24 The 13C-labeled organozinc reagent was prepared by treatment of 1-13C-EtLi with ZnCl2 in analogy to the reported preparation of Et2Zn-d10: Diccianni, J. B.; Heitmann, T.; Diao, T. *J. Org. Chem.* 2017, 82, 6895–6903. We have found that during the transmetalation from Li to Zn, the 13C-label scrambles between 1- and 2-positions, such that the zinc reagent is likely better described as an isotopomeric mixture containing (13CH3CH2)2Zn, (13CH3CH2)(CH313CH2)Zn and (CH313CH2)2Zn. We note that the exact ratio of this isotopomeric mixture is without consequence for our purposes, as rapid intramolecular isomerization pathways in the molybdenum product equilibrate the 13C-label between α- and β-ethyl positions to a mixture (described in later sections).


CHAPTER 6

Coordination-Induced N–H Bond Weakening in a Molybdenum Pyrrolidine Complex: Isotopic Labeling Provides Insight into H₂ Evolution.

Abstract

We report the synthesis and characterization of a cationic molybdenum pyrrolidine complex supported by terpyridine and bis(phosphine) ligands that exhibits significant N–H bond weakening by coordination. The bond dissociation free energy (BDFE) of the pyrrolidine N–H bond was determined to be in the range 44–51 kcal mol⁻¹, supported by a density functional theory-computed value of 48 kcal mol⁻¹. The remarkably weak NH bond enabled H₂ evolution upon gentle heating and furnished the corresponding molybdenum pyrrolidide complex. Isotopic labeling experiments support a proposed mechanism involving unimolecular H₂ evolution followed by a bimolecular proton-coupled electron transfer step leading to product formation. These results offer key insight into the H₂ formation pathway in a nonclassical amine complex of molybdenum with a N–H BDFE below the thermodynamic threshold for H₂ evolution.

Introduction

Metal coordination can alter the bonding properties of ligands, including the lowering of homolytic X–H (X = C, N, O) bond dissociation free energies (BDFEs).¹ Termed coordination-induced bond weakening, this phenomenon is key to understanding the thermochemistry of proton-coupled electron transfer (PCET) processes²,³,⁴ in transition metal complexes with implications for biology,⁵,⁶,⁷ organic synthesis⁸,⁹ as well
as energy science.\textsuperscript{10,11,12} In contrast to the extensive thermochemical data available for organic molecules however, systematic reports of ligand X–H BDFEs have only recently emerged for metal complexes across the periodic table and generally remain scarce.\textsuperscript{1} In rare instances, coordination-induced bond weakening has been demonstrated or proposed to have a dramatic impact on the X–H BDFEs of ligands where the degree of bond weakening is quantified in terms of a 1e\textsuperscript{−} redox couple (\(E^\circ\)), X–H \(pK_a\), and the solvent-specific H\textsuperscript{+} standard reduction potential (\(C_G\)).\textsuperscript{13}

\[
\text{BDFE}_{X-H} = 1.37 \ (pK_a) + 23.06(E^\circ) + C_G
\]  

(1.1)

Metal-ligand combinations that have low X–H BDFEs are desirable in synthetic chemistry as potent H-atom sources that undergo reductive PCET with substrates such as epoxides, olefins, and enamines.\textsuperscript{8,9} For instance, Cuerva\textsuperscript{14,15} and later Gansäuer\textsuperscript{16} have demonstrated that Cp\textsubscript{2}TiCl (Cp = C\textsubscript{5}H\textsubscript{5}) in combination with THF/water mixtures effected the reductive ring opening of epoxides that is enabled by the OH bond weakening in water of over 60 kcal mol\textsuperscript{−}1 (Figure 6.1a, left). Flowers\textsuperscript{17} and Mayer\textsuperscript{18} reported that SmI\textsubscript{2}(H\textsubscript{2}O)\textsubscript{n} mixtures are effective for achieving thermodynamically challenging reductions of anthracene and enamines, respectively, with an estimated O–H BDFE of 26 kcal mol\textsuperscript{−}1 engendered by the coordination of H\textsubscript{2}O to Sm(II) (Figure 6.1a, right). Intriguingly, while such reagents have the weakest known effective X–H BDFEs that render them thermodynamically unstable with respect to H\textsubscript{2} evolution, (\(\Delta G^\circ(H\textsubscript{•}) = 48.6\) kcal mol\textsuperscript{−}1)\textsuperscript{1} no such reactivity has been reported.
Figure 6.1. (a) Examples of coordination-induced O–H bond weakening and associated reactivity. (b) Reported molybdenum ammine complex that undergoes both PCET and H\textsubscript{2} evolution ([Mo]\textsuperscript{+} = [(Ph\textsubscript{Tpy})(PPh\textsubscript{2}Me)\textsubscript{2}Mo]\textsuperscript{+}; Ar = 4-tert-butyl-C\textsubscript{6}H\textsubscript{4}). (c) The strategy reported in this work.

As part of a research program exploring molybdenum complexes supported by potentially redox-active ligands relevant to the interconversion of ammonia (NH\textsubscript{3}) with its elements,\textsuperscript{19,20} our laboratory recently reported the synthesis of a well-defined nonclassical ammine complex, [(Ph\textsubscript{Tpy})(PPh\textsubscript{2}Me)\textsubscript{2}Mo(NH\textsubscript{3})][BaF\textsubscript{24}] ([1-NH\textsubscript{3}]\textsuperscript{+}; Ph\textsubscript{Tpy} = 4′-Ph-2,2′,6′,2″-terpyridine, ArF\textsubscript{24} = [C\textsubscript{6}H\textsubscript{3}-3,5-(CF\textsubscript{3})\textsubscript{2}]\textsubscript{4}) that was shown to exhibit substantial ammine NH bond weakening with an experimentally measured N–H BDFE of 46 kcalmol\textsuperscript{−1}, weaker than the thermodynamic threshold for spontaneous hydrogen...
evolution. Kinetically stable at room temperature, [**1-NH₃**]⁺ is a competent PCET reagent that has been shown to deliver H-atom equivalents to acceptors such as styrene as well as related molybdenum imido and ethylene complexes

\[
[(PhTpy)(PPh₂Me)₂Mo(NtBuAr)][BArF²⁴] \text{ ([1-(NtBuAr)]}⁺; tBuAr=4-tert-butyl-C₆H₄) \text{ and}
\]

\[
[(PhTpy)(PPh₂Me)₂Mo(C₂H₄)][BArF²⁴] \text{ ([1-(C₂H₄)]}⁺), \text{ to furnish ethylbenzene or the corresponding molybdenum amido and ethyl complexes, [1-(NHzBuAr)]}⁺ \text{ and [1-(CH₂CH₃)]}⁺\text{ (Figure 6.1b, Path A).}
\]

In stark contrast to SmI₂(H₂O)ₙ however, mild thermolysis of [**1-NH₃**]⁺ at 60 °C led to H₂ evolution with the concomitant generation of the corresponding molybdenum amido [**1-NH₂**]⁺ (Figure 6.1b, Path B). While thermochemical studies suggest that PCET from [**1-NH₃**]⁺ occurs by electron transfer followed by proton transfer or a concerted pathway, to date no experimental mechanistic information has been reported for the H₂ evolution reactivity. Insight into the dehydrogenation mechanism of [**1-NH₃**]⁺ is therefore of interest to guide the development of kinetically stable, yet thermodynamically potent PCET reagents as well as to provide design principles for bond activation in the context of NH₃ oxidation and catalysis involving metal-ligand cooperation.

Following the discovery of [**1-NH₃**]⁺, important questions immediately arose concerning the molecularity of the H₂ evolution step. While attempts were made to address this question in our original report by deuterium labeling experiments, we found that exchangeable N–H bonds present in both the molybdenum ammine starting material and amido product complicated interpretation of our results. As a consequence, we envisioned the application the secondary amine pyrrolidine as a mechanistic probe to provide more insight into the transformation. We hypothesized that coordination of
pyrrolidine to the cationic terpyridine bis(phosphine) molybdenum(I) structural motif will result in N–H bond weakening on the order of that observed for ammonia and give rise to analogous H₂ evolution to yield to corresponding secondary alkyl amido product (Figure 6.1c). Because NH/D exchange between the pyrrolidine starting materials is degenerate and the expected molybdenum pyrrolidide product does not contain exchangeable N–H bonds, crossover experiments can be conducted between N–H/D pyrrolidine isotopologs to support, or refute, a bimolecular H₂ evolution pathway (Figure 6.1c). In addition, pyrrolidide α-(C–H) bonds are well-poised to undergo β-H elimination, thereby reporting on potential Mo–D intermediates generated during dehydrogenation.

Herein, we report the synthesis and characterization of the targeted cationic molybdenum pyrrolidine complex [(PhTpy)(PPh₂Me₂)₂Mo(NH(pyrr))][BArF₂₄] ([1-NH(pyrr)]⁺; NH(pyrr) = pyrrolidine). The electronic structure of [1-NH(pyrr)]⁺ is examined, and thermochemical studies are presented that establish significant N–H bond weakening in coordinated pyrrolidine that indeed enables spontaneous H₂ evolution. Isotopic labeling studies with the N–D isotopolog are described that provide insight into the H₂ evolution pathway in [1-NH(pyrr)]⁺ and are generalized to the originally reported nonclassical ammine complex [1-NH₃]⁺.
Results and Discussion

Our studies commenced with the synthesis of the terpyridine bis(phosphine) molybdenum pyrrolidine complex \([1\text{-NH(pyrr)}]^+\). Stirring a benzene solution containing \([\text{[P^Tpy}(\text{PPh}_2\text{Me})_2\text{MoCl}] \ ([1\text{-Cl}])\) and 1 equivalent of each Na[BArF\(^{24}\)] and pyrrolidine at room temperature for 18 hours furnished \([1\text{-NH(pyrr)}]^+\) as a dark green solid in 85 % yield (Figure 6.2a). The solid-state infrared spectrum (KBr) of \([1\text{-NH(pyrr)}]^+\) shows an isotopically sensitive NH vibration at 3246 cm\(^{-1}\) that shifts to 2400 cm\(^{-1}\) in the isotopolog \([1\text{-ND(pyrr)}]^+\), consistent with the coordination of pyrrolidine upon chloride abstraction. The formally Mo(I) complex \([1\text{-NH(pyrr)}]^+\) has an \(S = \frac{1}{2}\) ground state as evidenced by a solid-state magnetic moment of 1.7(2) (Guoy balance, 23 °C). The EPR spectrum of \([1\text{-NH(pyrr)}]^+\) was collected in toluene glass at 8 K and exhibits a rhombic signal that was readily simulated with the \(g\)-values \(g_x = 2.020, g_y = 2.005, g_z = 1.968\) (Figure 6.2b). This EPR spectrum closely resembles the rhombic signal observed for \([1\text{-NH}_3]^+\) at 7 K (see Experimental Section), suggesting that the electronic structures of the “parent” ammine and pyrrolidine complexes are analogous. Accordingly, the DFT-computed Mulliken spin density plot for \([1\text{-NH(pyrr)}]^+\) supports a molybdenum-centered singly-occupied molecular orbital (SOMO, Figure 6.2c) in agreement with the electronic structure previously determined for \([1\text{-NH}_3]^+\).\(^{21}\)
Figure 6.2. (a) Synthesis of [1-NH(pyrr)]\(^+\) by chloride abstraction. (b) X-band EPR spectrum of [1-NH(pyrr)]\(^+\) recorded in toluene glass at 8 K. Collection and simulation parameters: microwave frequency = 9.381 GHz, power = 2.0 mW, modulation amplitude = 4.0 G; \(g_x = 2.020, g_y = 2.005, g_z = 1.968\). (c) DFT-computed spin density plot for [1-NH(pyrr)]\(^+\) obtained from Mulliken population analysis in the gas-phase at the B3LYP level of theory.

Efforts were next directed at experimentally establishing bounds for the NH-BDFE in [1-NH(pyrr)]\(^+\). Homolytic cleavage of the pyrrolidine N–H bond in [1-NH(pyrr)]\(^-\) was accomplished by addition of 1 equivalent of 2,4,6-tri-\textit{tert}-butylphenoxy radical (tBu\(_3\)C\(_6\)H\(_2\)O•) to quantitatively yield the diamagnetic molybdenum(II) pyrrolidide complex, \([([\text{PhTpy})(\text{PPh}_2\text{Me})_2\text{Mo}(\text{NC}_4\text{H}_8)][\text{BArF}_{24}]\{\text{1-N(pyrr)}\}^+)\) within 30 minutes at room temperature (Figure 6.3a, top). The benzene-\(d_6\) \(^1\)H NMR spectrum of [1-N(pyrr)]\(^+\) exhibits the number of resonances consistent with \(C_{2v}\) molecular symmetry in solution, with diagnostic pyrrolidide \(\alpha\)- and \(\beta\)-(C–H) signals at 4.04 and 1.75 ppm, respectively, and a single \({\text{1H}}\{^{31}\text{P}\) peak at 11.95 ppm that is consistent with \textit{trans}-PPh\(_2\)Me ligands.
coordinated to cationic molybdenum(II) amido.\textsuperscript{21,22} While the H-atom abstraction reactivity establishes the N–H BDFE in \([1{-}\text{NH(pyrr)}]^{+}\) as < 77 kcal mol\(^{-1}\), the pyrrolidine product \([1{-}\text{N(pyrr)}]^{+}\) was also accessed by thermal dehydrogenation of the pyrrolidine complex (Figure 6.3a, bottom). Mildly heating \([1{-}\text{NH(pyrr)}]^{+}\) at 60 °C for 48 hours yielded \([(1{-}\text{N(pyrr)})]^{+}\) in 98 % yield with the concomitant formation of \(\text{H}_2\) as confirmed by Toepler pump experiments (81% yield of \(\text{H}_2\)). The spontaneous dehydrogenation reactivity observed establishes the upper bound of the N–H BDFE in \([1{-}\text{NH(pyrr)}]^{+}\) as the free energy of \(\text{H}^{\bullet}\) formation from \(\text{H}_2\) in benzene solution (≈51 kcal mol\(^{-1}\)).\textsuperscript{1}

![Figure 6.3](image)

**Figure 6.3.** (a) Synthesis of \([1{-}\text{N(pyrr)}]^{+}\) by dehydrogenation or hydrogen atom abstraction. (b) Thermodynamic square scheme showing \(pK_a\) and \(E^\circ\) components contributing to the N–H BDFE in \([1{-}\text{NH(pyrr)}]^{+}\).

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The low upper bound for the N–H BDFE in [1-NH(pyrr)]⁺ complicates estimation of its absolute value given the dearth of reference reagents near the thermodynamic threshold for H₂ evolution. Therefore, the NH BDFE was instead estimated using a thermochemical square scheme (Figure 6.3b). In particular, the electrochemical behavior of [1-N(pyrr)]⁺ was of interest to probe the thermodynamics of accessing the 1-electron reduced pyrrolidide complex [1-N(pyrr)] that in turn enables estimation of the \( E^\circ \) and \( pK_a \) terms in Figure 6.3b. The cyclic voltammogram (CV) of [1-N(pyrr)]⁺ was collected in THF solution and exhibits two reversible anodic waves with \( E_{1/2} = -0.63 \text{ V} \) and 0.08 V vs Fc/Fe⁺ \( \{ \text{Fc} = [\text{Cp}_2\text{Fe}] \} \) assignable to oxidations to yield [1-N(pyrr)]²⁺ and [1-N(pyrr)]³⁺, respectively. In addition, a quasi-reversible cathodic wave is observed in the CV of [1-N(pyrr)]⁺ at \( E_{1/2} = -2.10 \text{ V} \) that corresponds to a reduction to yield the neutral pyrrolidide complex [1-N(pyrr)] and was of interest for estimating the N–H BDFE in [1-NH(pyrr)]⁺.

**Figure 6.4.** Cyclic voltammogram of [1-N(pyrr)]⁺ (2 mM in THF, black trace) and [1-N(pyrr)]⁺ in the presence of 1.0 equiv. [TBD–H][BArF²⁺] (red trace) using a glassy carbon working electrode, a platinum wire counter electrode, a silver wire reference electrode, 0.2 M \([nBu_4N][PF_6] \) and a scan rate of 100 mV sec⁻¹ in THF at 23 °C versus Fc/Fe⁺.
Attempts to synthesize \([\text{1-N(pyrr)}]\) by one-electron reduction of \([\text{1-NH(pyrr)}]^+\) afforded intractable product mixtures and as a result, the lower bound for the pK\(_a\) of \([\text{1-NH(pyrr)}]^+\) was estimated by \textit{in situ} protonation experiments in the electrochemical cell. Shown in Figure 6.4, upon collecting the CV of \([\text{1-N(pyrr)}]^+\) in the presence of 1 equivalent of \([\text{TBDH}][\text{BArF}^{24}]\) (TBD = triazabicyclodecene), the cathodic wave became irreversible with a concomitant positive shift of the peak cathodic potential from \(E_{\text{pc}} = -2.17 \text{ V}\) (no \([\text{TBDH}][\text{BArF}^{24}]\)) to -2.13 \text{ V} (1.0 equiv. \([\text{TBDH}][\text{BArF}^{24}]\)). These observations are consistent with an EC mechanism involving fast electron transfer (E) followed by rate limiting proton transfer (C) from \([\text{TBDH}][\text{BArF}^{24}]\) to \textit{in situ} generated \([\text{1-N(pyrr)}]\).\textsuperscript{32,33} Evaluation of the peak potential as a function added acid allowed the determination of the bimolecular proton transfer rate constant as \(k_{\text{PT}} = 1.3 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}\), a rare quantification of amido ligand protonation kinetics (see Experimental Section for experimental details). While the quasi-reversibility of the cathodic wave in \([\text{1-N(pyrr)}]^+\) precludes the extraction of equilibrium parameters for the EC reaction, the observation of the rapid protonation of \textit{in situ} generated \([\text{1-N(pyrr)}]\) by the weak acid \([\text{TBDH}][\text{BArF}^{24}]\) implies that the pK\(_a\) of this acid (19.4)\textsuperscript{34} is likely a satisfactory lower bound for the pK\(_a\) of \([\text{1-NH(pyrr)}]^+\).\textsuperscript{35} These data, in combination with the \(E^\circ\) value for the \([\text{1-N(pyrr)}]^+/[\text{1-N(pyrr)}]\) couple \(E_{1/2} = -2.10 \text{ V}\), define the lower bound for the N–H BDFE in \([\text{1-NH(pyrr)}]^+\) as \(\approx 44 \text{ kcal mol}^{-1}\) in THF. Together with the observation of spontaneous H\(_2\) evolution from the complex, an experimental bound for the N–H BDFE of 44–51 kcal mol\(^{-1}\) is thus obtained for \([\text{1-NH(pyrr)}]^+\), in close agreement with a DFT-computed value of 48 kcal mol\(^{-1}\) (gas phase). These data establish \([\text{1-NH(pyrr)}]^+\) as a rare example of a
nonclassical amine complex that is thermodynamically unstable with respect to H\textsubscript{2} evolution.

We next turned our attention to deuterium labeling experiments to gain insight into the pathway of H\textsubscript{2} evolution in [1-NH(pyrr)]\textsuperscript{+}. Mildly heating the ND isotopolog [1-ND(pyrr)]\textsuperscript{+} at 60 °C for 48 hours and analyzing the evolved gases by \textsuperscript{1}H NMR spectroscopy revealed the generation of H\textsubscript{2} and HD gases in a 9:1 ratio. To probe the amount of D\textsubscript{2} formed, the evolved gases were passed over CuO at 200 °C for 30 minutes, collected and analyzed as the isotopologs of H\textsubscript{2}O. Unlike the non-exchangeable isotopologs of H\textsubscript{2}, rapid H/D exchange equilibrates protons and deuterons in the water product and the resulting H\textsubscript{2}O:HDO ratio is expected to reflect overall deuterium content, including D\textsubscript{2}. Accordingly, the \textsuperscript{1}H NMR spectrum of the combustion product established a H\textsubscript{2}O:HDO ratio of 6:1, and therefore an overall H\textsubscript{2}:(HD+D\textsubscript{2}) ratio of 6:1 prior to combustion. Importantly, these results demonstrate that < 5% of D\textsubscript{2} is evolved during the dehydrogenation of [1-ND(pyrr)]\textsuperscript{+} and imply substantial deuterium incorporation in the molybdenum pyrrolidide product denoted as [(1-N(pyrr-d\textsubscript{n}))\textsuperscript{+}] in Figure 6.5a.

In order to determine the fate of deuterium label following dehydrogenation of [1-ND(pyrr)]\textsuperscript{+}, the quantification and location of the deuterium content in the molybdenum pyrrolidide product [(1-N(pyrr-d\textsubscript{n}))\textsuperscript{+}] was pursued. Notably, the \textsuperscript{2}H NMR spectrum of [(1-N(pyrr-d\textsubscript{n}))\textsuperscript{+}] showed significant deuterium incorporation in the \(\alpha\)-pyrrolidide position (4.04 ppm), corroborated by \{\textsuperscript{1}H\}\textsuperscript{13}C NMR spectroscopy that revealed an isotopic perturbation of both \(\alpha\)- and \(\beta\)-pyrrolidide carbon resonances. In addition to the expected triplet for the \(\alpha\)-pyrrolidine carbon in [(1-N(pyrr)]\textsuperscript{+} at 71.44 ppm (\(\text{^3}J_{C-P} = 11.6\) Hz), a broad peak was observed at 71.05 ppm that corresponds to a deuterated \(\alpha\)-pyrrolidide.
carbon in [(1-N(pyrr-d_n)]^+ that is broadened due to coupling to deuterium as well as two equivalent phosphorus atoms in the trans-PPh_2Me ligands (Figure 6.5b). Additionally, three distinct singlets were observed at 26.75, 26.63 and 26.51 ppm that correspond to the pyrrolidide β-carbon signals of [(1-N(pyrr)]^+, [(1-N(pyrr-d_n)]^+ and [(1-N(pyrr-d_2)]^+, respectively, with isotopic shifts arising due to remote deuteration at the α-pyrrolidide carbon (Figure 6.5b). Because coupling to the two equivalent phosphorous atoms in PPh_2Me ligands complicated assignment and quantification of the pyrrolidide isotopomers and isotopologs present in [(1-N(pyrr-d_n)]^+, the pyrrolidide ligand was liberated from the coordination sphere of molybdenum by protonolyis and analyzed as free pyrrolidine. Accordingly, treatment of [(1-N(pyrr-d_n)]^+ with excess HCl generated [1-Cl]^+ and pyrrolidinium-d_n chloride (n = 0–2) as judged by ^1H NMR spectroscopy. Further treatment of the reaction mixture with the base TBD and vacuum transfer of the volatiles enabled exclusive isolation of pyrrolidine-d_n (n = 0–2). By this method, quantitative ^13C NMR and mass spectrometric analysis established the presence of pyrrolidine (50 %), pyrrolidine-2-d_1 (40 %), pyrrolidine-2,5-d_1,d_1 (8 %) and pyrrolidine-2,2-d_2 (2 %) by comparison of the acquired spectrum to those of independently synthesized materials (Figure 6.5c). These results establish that [(1-N(pyrr-d_n)]^+ contains α-(d_0-d_2) isotopologs at the pyrrolidide ligand including two distinct d_2-isotopomers. The mechanistic significance of these isotopologs is discussed below.
Figure 6.5. (a) Isotope labeling experiment and pyrrolide ligand liberation in [{1-N(pyrr-\(d_n\))}]+. *For reaction conditions, see Supporting Information. (b) Pyrrolide \(\alpha\)- and \(\beta\)-carbon region of the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum (benzene-\(d_6\), 23 °C) of [{1-N(pyrr-\(d_n\))}]+ exhibiting isotopic perturbation of resonance. (c) Quantitative \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum (benzene-\(d_6\), 23 °C) of a mixture containing pyrrolidine (50 %), pyrrolidine-2,4-\(d_2\) (8 %) and pyrrolidine-2,2-\(d_2\) (2 %) liberated from [{1-N(pyrr-\(d_n\))}]+ by protonolysis. The red line represents a fit of the data, and the blue lines shows the deconvolution of the individual peaks.
The observation of isotopic perturbation of resonance in the pyrrolidide $\beta$-carbon signals in \([(1-N(\text{pyrr-d}_{n}))^+]\) (Figure 6.5b) provides a convenient spectroscopic handle for probing the degree of pyrrolidide deuteration over the course of the dehydrogenation reaction. Accordingly, monitoring the relative areas of isotopically shifted $\beta$-pyrrolidine carbon signals in \([(1-N(\text{pyrr-d}_{n}))^+]\) (26.75–26.51 ppm) by quantitative $^{13}$C NMR revealed that the ratio of $d_0$:$d_1$+$d_2$ pyrrolidide isotopologs remained constant over the course of the dehydrogenation of \([1-\text{ND(pyrr})]^+]\) (48 h, 60 °C). These results support rapid deuterium incorporation into the pyrrolidide ligand relative to molybdenum pyrrolidide product formation and are consistent with the observation of low deuterium content in the evolved gases. In order to probe whether the $\text{H}_2$ evolution reaction is bimolecular or unimolecular in nature, a key crossover experiment was conducted wherein \([1-\text{NH(pyrr})]^+\) and \([1-\text{ND(pyrr})]^+\) were mixed in a 1:1 ratio and heated in benzene solution at 60 °C for 48 h (Figure 6.6). The evolved gases were collected, analyzed and found to contain $\text{H}_2$, $(\text{HD}+\text{D}_2)$ in a 14:1 ratio. The pyrrolidide ligand was liberated at the conclusion of the reaction by the protonolysis procedure described previously and found to contain pyrrolidine (74 %), pyrrolidine-2-$d_1$ (23 %), pyrrolidine-2,5-$d_1$,$d_1$ (3 %) and pyrrolidine-2,2-$d_2$ (< 1 %). Because the relative percentages of $\text{H}_2$ and pyrrolidine isotopologs are approximately half of the values observed in the dehydrogenation of \([1-\text{ND(pyrr})]^+]\) where no \([1-\text{NH(pyrr})]^+\) was added, these results indicate no deuterium crossover and support unimolecular deuterium scrambling and $\text{H}_2$ evolution pathways.
Figure 6.6. Crossover experiment between [1-NH(pyrr)]^\text{+} 1-ND(pyrr)]^\text{+} and subsequent pyrrolidide ligand liberation by protonolysis. *For reaction conditions, see Supporting Information.

Further experiments were conducted to examine the effect of added phosphine as well as the reversibility of the deuterium scrambling and H\textsubscript{2} evolution. Interestingly, addition of 10 equiv. of PPh\textsubscript{2}Me to [1-NH(pyrr)]^\text{+} inhibited the dehydrogenation reaction, with \textasciitilde 10 % diamagnetic [(1-N(pyrr))]^\text{+} observed after heating at 60 °C for 1 day and \textasciitilde 30 % after 4 days. Furthermore, addition of 4 atm of D\textsubscript{2} to the [(1-N(pyrr))]^\text{+} product produced no detectable quantities of [(1-N(pyrr-d\textsubscript{2})]^\text{+} after 60 °C of heating at 5 days. These data suggest that phosphine dissociation is likely necessary for H\textsubscript{2} evolution reactivity and that the overall H\textsubscript{2} evolution reaction is irreversible.

A proposed H\textsubscript{2} evolution pathway that is consistent with the experimental results is presented in Figure 6.7. N–H(D) oxidative addition takes place upon phosphine dissociation, and is followed by pyrrolidide β-H elimination\textsuperscript{36} and reinsertion processes that account for scrambling of the deuterium label principally into the α-pyrrolidine position. Unimolecular H\textsubscript{2} evolution proceeds by reductive elimination of H\textsubscript{2} from a proposed molybdenum dihydride imine intermediate. The resulting molybdenum azametallocyclopropane complex is then proposed to undergo a bimolecular, irreversible PCET reaction with the molybdenum(I) pyrrolidine starting material to generate the molybdenum(II) pyrrolidide product and accounts for the generation of pyrrolidide-d\textsubscript{2} isotopomers when the reaction involves remaining [1-ND(pyrr)]^\text{+}. This step is proposed...
to proceed in analogy to the reported reactivity of $[1\text{-NH}_3]^+$ undergoing reductive PCET to related molybdenum imido and ethylene complexes $[1\text{-}(\text{NtBuAr})]^+$ and $[1\text{-}(\text{C}_2\text{H}_4)]^+$ to furnish $[1\text{-NH}_2]^+$ as well as the ethyl and aryl amido complexes $[1\text{-}(\text{C}_2\text{H}_4)]^+$ and $[1\text{-}(\text{NHtBuAr})]^+$, respectively. In contrast to H$_2$ evolution, the PCET reactivity of $[1\text{-NH}_3]^+$, has been previously found to proceed independent of added phosphine and is therefore proposed to take place between bis(phosphine) molybdenum complexes in Figure 6.7. It is important to note that an intermolecular PCET event must occur to account for the net $1\text{H}^+/1\text{e}^-$ change between the $S = 1/2\ [1\text{-NH(pyr)}]^+$ starting material and $S = 0\ [1\text{-N(pyr)}]^+$ product. However, deuterium scrambling and H$_2$ evolution likely precedes bimolecular product forming PCET to account for the observation of constant pyrrolidide isotopolog ratios in $[(1\text{-N(pyr-d})_n)]^+$ as a function of reaction progress as well as the low deuterium content in the evolved gases.

![Proposed H$_2$ evolution pathway and pyrrolidide ligand deuterium incorporation leading to the formation of $[(1\text{-N(pyr-d})_n)]^+$](image)

**Figure 6.7.** Proposed H$_2$ evolution pathway and pyrrolidide ligand deuterium incorporation leading to the formation of $[(1\text{-N(pyr-d})_n)]^+$.
The insights gained from the isotopic labeling experiments can be generalized to
the \( \text{H}_2 \) evolution reaction in the nonclassical ammine complex \([\text{1-NH}_3]^+\). In analogy to \([\text{1-NH(pyrr)}]^+\), Figure 6.8 shows a proposed pathway for \([\text{1-NH}_3]^+\) that involves
unimolecular \( \text{H}_2 \) evolution step and intermolecular product forming PCET.

Computational analysis of the BDFEs of the intermediates reveals that phosphine
dissociation does not have a significant impact on the ammine N–H BDFE, wherein
thermoneutral N–H oxidative addition event (\( \Delta G^\circ = 1 \text{ kcal mol}^{-1} \)) generates a proposed
molybdenum amido hydride intermediate with weak N–H and Mo–H BDFEs of 54 kcal
mol\(^{-1}\) and 44 kcal mol\(^{-1}\), respectively, with an average BDFE near the thermodynamic
threshold for \( \text{H}_2 \) evolution (BDFE\(_{\text{avg}}\) = 49 kcal mol\(^{-1}\)). This is proposed to be a key feature
of the molybdenum system, as exergonic ammonia N–H oxidative addition would
generate a strong MH bonds from which H\(_2\) elimination is expected to be endergonic.\(^{37}\)

Key literature precedent for the subsequent 1,2-H\(_2\) elimination step is Wolczanski’s
observation of \( \text{H}_2 \) evolution from (silox)\(_3\)Ta(NH\(_2\))(H) (silox = tBu\(_3\)SiO), a complex that
was prepared by oxidative addition of ammonia.\(^{38}\) The final step of the pathway is
intermolecular PCET between the starting ammine complex \([\text{1-NH}_3]^+\) and the proposed
“parent” imido intermediate \([\text{1=NH}]^+\) to generate two equivalents of the amido product
\([\text{1-NH}_2]^+\). This PCET step is predicted to be exergonic by 21 kcal mol\(^{-1}\) due to
coordination-induced bond weakening in \([\text{1-NH}_3]^+\) (BDFE\(_{\text{N-H}}\) = 47 kcal mol\(^{-1}\)) relative to
the amido N–H bond formed (BDFE\(_{\text{N-H}}\) = 68 kcal mol\(^{-1}\)). As mentioned previously, this
step has direct precedent in that our group demonstrated that the aryl imido complex \([\text{1-(N\(_t\)BuAr)}]^+\) reacts with \([\text{1-NH}_3]^+\) to generate the corresponding amido complexes \([\text{1-(NH/tBuAr)}]^+\) and \([\text{1-NH}_2]^+\), a reaction that was shown to have a lower overall driving
force than the reaction involving a “parent” amido. Overall, the proposed mechanism presented is consistent with our originally reported crossover experiment whereby a 1:1 mixture of [1-NH3]+ and [1-ND3]+ were heated, and nonstatistical amount of HD gas was observed, likely owing to a unimolecular H₂ evolution step as proposed in Figure 6.8. Therefore, when both phosphine ligands are coordinated, [1-NH₃]+ and [1-NH(pyrr)]⁺ behave as potent PCET reagents similar to Cp₂TiCl(THFₓ/H₂Oᵧ) and SmI₂(H₂O)ₙ wherein phosphine dissociation is the likely gateway to the observed dehydrogenation reactivity. While the phenomenon of coordination-induced bond weakening provides the overall thermodynamic driving force for H–H bond formation, it is likely the access to molybdenum hydride intermediates upon phosphine dissociation that provides a kinetic pathway to H₂ evolution.

![Figure 6.8. Proposed H₂ evolution pathway and pyrrolidide ligand deuterium incorporation leading to the formation of [(1-N(pyrr-d₁)]⁺.](image-url)
Conclusions

In conclusion, the synthesis and characterization of a cationic molybdenum pyrrolidine complex \([\text{1-NH(pyrr)}]^+\) supported by terpyridine and bis(phosphine) ligands was described. Significant weakening of the pyrrolidine N–H bond was demonstrated upon coordination to the molybdenum center that enables spontaneous H\(_2\) evolution reactivity, with the N–H BDFE in \([\text{1-NH(pyrr)}]^+\) determined experimentally to be in the range 44–51 kcal mol\(^{-1}\) supported by a DFT-computed value of 48 kcal mol\(^{-1}\). Deuterium labeling experiments were conducted and the results support a dehydrogenation mechanism involving a unimolecular H\(_2\) evolution followed by a product-forming intermolecular PCET. The insights provided herein are envisioned to aid the application of coordination-induced bond weakening for the synthesis of complexes with exceptionally weak bonds, both in settings where H\(_2\) evolution reactivity may be desirable as well as for cases where it is to be avoided.

Experimental Section

General Considerations

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (nitrogen) dry box unless otherwise noted. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.\(^3\)\(^9\) Celite was dried at 180 °C under vacuum for 3 days prior to use. Deuterium gas was purchased from Cambridge Isotope Labs (>99.8% purity), and passed through a column of \(\text{MnO}_2\) supported on
vermiculite and 3 Å molecular sieves prior to use on a Schlenk manifold. Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. Pyrrolidine was purchased from Sigma-Aldrich, vacuum distilled from CaH₂ and stored over 4 Å molecular sieves. TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene) was purchased from Sigma-Aldrich, dried under high vacuum and used without further purification. HCl (2.0 M in Et₂O) was purchased from Sigma-Aldrich and used as received. The following compounds were prepared according to literature procedures: [1-Cl]₂⁻ Na[BArF₂⁴]₄, 2,4,6-tri-tert-butylphenoxyl radical (tBu₃ArO•), pyrrolidine-1-d, and [TBD–H][BArF₂⁴].

¹H NMR spectra were recorded on a Bruker AVANCE 500 spectrometer operating at 500.46 MHz. ¹³C NMR spectra were recorded on a 500 spectrometer operating at 125.85 MHz. ³¹P NMR spectra were collected on a 500 AVANCE spectrometers operating at 202.40 MHz, and were referenced to 85% H₃PO₄ as an external standard. ¹⁹F NMR spectra were collected on a Bruker 400 AVANCE spectrometer operating at 376.15 MHz and were referenced to CFCl₃ as an external standard. All ¹H and ¹³C NMR chemical shifts are reported in ppm relative to SiMe₄ using the ¹H (benzene-đ₆: 7.16 ppm) and ¹³C (benzene-đ₆: 128.06 ppm) chemical shifts of the solvent as a standard. ¹H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent, obs = obscured), coupling constants (Hz), integration, assignment.
High-resolution mass spectra were obtained on an Agilent 7200 gas chromatography/mass spectrometry system using electron impact time-of-flight (EI-TOF).

Continuous wave EPR spectra were recorded on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.\textsuperscript{44}

Elemental analyses were performed at Robinson Microlit Laboratories, Inc., in Ledgewood, NJ. Solid-state magnetic moments were determined using a Johnson Matthey Magnetic Susceptibility Balance that was calibrated with HgCo(SCN)\textsubscript{4}.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker VENTURE D8 PHOTON 100 diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å) and a Cu X-ray tube ($\lambda = 1.54178$ Å). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

CVs were collected in THF solution (2 mM in compound) with [nBu\textsubscript{4}N][PF\textsubscript{6}] (0.2 M), using a 3 mm glassy carbon working electrode, platinum wire as the counter electrode, and silver wire as the reference in a drybox equipped with electrochemical outlets. CVs were recorded using a BASi EC Epsilon electrochemical workstation and
analyzed using the BASi Epsilon-EC software. All CVs were run at 23 °C. Potentials are reported versus Cp₂Fe/Cp₂Fe⁺ and were obtained using the in situ method.

All DFT calculations were performed with the ORCA program package in the gas phase. The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT. The all-electron Gaussian basis sets were those developed by the Ahlrichs group. Triple-ζ quality basis sets def2-TZVP with one set of polarization functions on molybdenum, phosphorous and nitrogen were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used that were of double-ζ quality in the valence region and contained a polarizing set of d functions on the non-hydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX) approach were chosen to match the orbital basis. Numerical frequencies were calculated at the same level of theory to confirm the optimized geometries (no imaginary frequencies) and to derive thermochemical data. Bond dissociation free energies were computed at standard conditions of 1 atm and 25 °C including corrections for vibrational zero-point energy, as well as contributions from translational, rotational, and vibrational modes to the energy and entropy of the homolytic bond cleavage process. For molecules containing a molybdenum atom, the 0th order regular approximation (ZORA) was applied. In this case, the relevant basis sets were replaced by their relativistically recontracted versions. The electronic energy of H•, utilized in the calculation of bond dissociation free energies, at the present level of theory is 312 kcal/mol.
Preparation of Molybdenum Complexes

**Preparation of [1-NH(pyrr)]⁺.** In the glovebox, a J-Young NMR tube was charged with [1-Cl] (0.048 g, 0.057 mmol) and Na[BArF\textsuperscript{24}] (0.053 g, 0.060 mmol), pyrrolidine (0.005 mL, 0.060 mmol) and benzene (0.6 mL). The vessel was quickly sealed with a Teflon cap and connected to the high vacuum line where the mixture was de-gassed by 3x freeze-pump-thaw cycles. The tube was sealed and rotated end-over-end at room temperature for 18 hours. The tube was then brought back into the glovebox, where the mixture was filtered through a pad of Celite, and the solvent was removed *in vacuo*. The dark residue was washed with pentane (3 x 3 mL) and dried *in vacuo* to yield [1-NH(pyrr)]⁺ as a dark green solid (0.084 g, 0.048 mmol, 85%). Anal Calcd for C\textsubscript{83}H\textsubscript{62}BF\textsubscript{24}MoN\textsubscript{4}P\textsubscript{2}: C, 57.29; H, 3.59; N, 3.22. Found: C, 56.95; H, 3.58; N, 3.27. Magnetic Susceptibility (Guoy balance, 296 K): \(\mu_{\text{eff}} = 1.7(2) \mu_{\text{B}}\). IR (KBr, 296 K, cm\textsuperscript{-1}): 3246 (NHpyrr), 2400 (NDpyrr).

The isotopologue [1-ND(pyrr)]⁺ was prepared in a manner similar to [1-NH(pyrr)]⁺ with the exception that pyrrolidine-1-d was used in place of pyrrolidine.

**Preparation of [1-N(pyrr)]⁺ (Method A).** In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.194 g (0.231 mmol) of [1-Cl], 0.215 g (0.242 mmol) of Na[BArF\textsuperscript{24}], 0.020 mL (0.240 mmol) of pyrrolidine and 3 mL of benzene. The vessel was quickly sealed with a Teflon valve and connected to the high vacuum line where the mixture was de-gassed by 3x freeze-pump-thaw cycles. The reaction vessel was then sealed and the mixture stirred at 60 °C under vacuum for 48 hours. Using a Toepler pump, 0.094 mmol (0.407 equivalents per Mo) of gas was
collected. The gas was passed over a bed of CuO pre-heated to 200 °C. After this procedure, no gas was collected, confirming the identity of the evolved gas as H₂. The reaction vessel was then brought back into the glovebox and the mixture was filtered through a pad of Celite, followed by the removal of the solvent in vacuo. The dark residue was washed with pentane (3 x 3 mL) followed by trituration with pentane (5 x 5 mL) to yield the product as a dark brown solid (0.394 g, 0.227 mmol, 98%). Anal Calcd for C₈₅H₆₁BF₂₄MoN₄P₂: C, 57.32; H, 3.54; N, 3.22. Found: C, 57.06; H, 3.42; N, 3.15. ¹H NMR (benzene-d₆, 295 K): δ 8.92 (d, 3J_C-H = 6.1 Hz, 2H, PhTpy aryl-CH), 8.48 (s, 8H, B[(3,5-(CF₃)₂)C₆H₃]₄), overlap with 2H, PhTpy aryl-CH), 7.71 (s, 4H, B[(3,5-(CF₃)₂)C₆H₃]₄), 7.49 (br s, 2H, PhTpy aryl-CH), 7.48 (br s, 2H, PhTpy aryl-CH), 7.30 (br s, 1H, PhTpy aryl-CH), 7.25 (br s, 2H, PhTpy aryl-CH), 6.78 (t, 3J_C-H = 7.5 Hz, 2H, PhTpy aryl-CH), 6.51 (t, 3J_C-H = 6.6 Hz, 2H, PhTpy aryl-CH), 6.09 – 6.04 (m, 8H, PhTpy aryl-CH), 4.04 (br s, 4H, N(pyrr) α-CH₂), 1.75 (br s, 4H, N(pyrr) β-CH₂), 0.55 (s, 6H, P(C₆H₅)₂(CH₃)). ¹³C {¹H} NMR (benzene-d₆, 295 K): δ 162.88 (q, 1J_C-B = 49.8 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 145.12 (s, PhTpy aryl-C), 145.77 (s, PhTpy aryl-C), 139.62 (s, PhTpy aryl-C), 138.24 (s, PhTpy aryl-C), 136.41 (s, PhTpy aryl-C), 135.54 (s, B[(3,5-(CF₃)₂)C₆H₃]₄), 132.56 (app t, J = 16.0 Hz, P(C₆H₅)₂(CH₃)), 130.28 (app t, J = 5.5 Hz, P(C₆H₅)₂(CH₃)), 129.99 (q, 2J_C-F = 31.8 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 129.45 (s, P(C₆H₅)₂(CH₃), 129.35 (s, P(C₆H₅)₂(CH₃)), 129.03 (s, PhTpy aryl-C), 128.60 (s, PhTpy aryl-C), 128.54 (s, PhTpy aryl-C), 127.26 (s, PhTpy aryl-C), 125.35 (q, 1J_C-F = 272 Hz, B[(3,5-(CF₃)₂)C₆H₃]₄), 119.02 (s, PhTpy aryl-C), 118.18 (br s, B[(3,5-(CF₃)₂)C₆H₃]₄), 112.41 (s, PhTpy aryl-C), 71.44 (t, 3J_C-P = 11.6 Hz, N(pyrr) α-C), 57.32 δ
26.75 (s, N(pyrr) β-C), 8.66 (app t, J = 9.2 Hz, P(CH₃)₂(CH₃)). ³¹P{¹H} NMR (benzene-
-d₆, 295 K): δ 11.95 (s).

**Preparation of [1-N(pyrr)]⁺ (Method B).** In the glovebox, a J-Young NMR tube fitted
with a Teflon cap was charged with 0.050 g (0.029 mmol) of [1-NH(pyrr)]⁺, and 0.6 mL
of benzene. The tube was sealed and connected to the high vacuum line where the solvent
was de-gassed by 3x freeze-pump-thaw cycles.¹ The tube was sealed and placed in a
temperature-controlled oil bath (60 °C) for 48 hours. The tube was then brought back into
the glovebox and product isolation was carried out as described in Method A to yield
analytically pure [1-N(pyrr)]⁺ as a dark brown solid (0.048 g, 0.028 mmol, 96 %).

**Preparation of Pyrrolidine Isotopologs**

**Synthesis of pyrrolidine-2-d₁.** A literature report⁵² was modified. In the glovebox, a 100
mL 3-neck flask fitted with a Schlenk adapter was charged with a magnetic stir bar, and
N-Boc-pyrrolidine (0.9 mL, 5.13 mmol) dissolved in 50 mL of Et₂O. The vessel was
sealed and connected to the Schlenk line, where it was cooled to -78 °C. To the stirring
solution, sec-BuLi (5 mL, 6.68 mmol, 1.35 M in cyclohexane) was added dropwise. The
reaction was stirred at -78 °C for 5 hours, during which time the formation of a white
precipitate was observed. After stirring for 5 hours, methanol-d₄ (0.417 mL, 10.27 mmol)
was added dropwise and stirred for 10 minutes while warming to room temperature. The

¹ It is important to degas the reaction mixture as pyrrolidine appears to be labile at elevated temperatures in the presence of N₂ to
form the dimeric N₂ complex [[][(⁵⁷Tpy][PPh₃Me]₂Mo)₂(N₂)]²⁺. The poor solubility of the dicatonic complex in benzene
causes precipitation of this side product and likely drives the reaction. In order to prevent the formation of this side product, the
dehydrogenation can alternatively be carried out under an Ar atmosphere. However, in order to prevent pressure buildup in the
closed vessel for larger scales, performing the reaction under vacuum was preferred.
resulting suspension was then filtered through a pad of Celite, and solvent was removed
*in vacuo* to yield N-Boc-pyrrolidine-*dₙ* as a colorless oil (0.768 g, ~4.46 mmol, ~87 %).

Under open-air conditions, a 250 mL round-bottom flask was charged with N-Boc-
pyrrolidine-*dₙ* (0.8 mL, ~4.5 mmol) dissolved in 5 mL of Et₂O. To the stirring solution,
HCl (3.4 mL, 13.6 mmol, 4.0 M in dioxane) was added dropwise. The mixture was
stirred at room temperature for 2 hours. After this time, the solvent of the reaction was
removed *in vacuo*. The residue was slightly oily and was washed with additional Et₂O (3
x 50 mL), dried *in vacuo*. The residue was additionally dried under high vacuum
overnight and transferred to the glovebox. In the glovebox, the solids were isolated on a
fine-porosity sintered glass frit, washed with pentane (3 x 10 mL) and dried *in vacuo* to
yield pyrrolidine-*dₙ*•HCl as a white solid. (0.300 g, ~2.76 mmol, ~61 %).

In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar,
pyrrolidine-*dₙ*•HCl (0.006 g, ~0.058 mmol). To the stirring vial, a solution of TBD (0.024
g, 0.174 mmol) dissolved in 0.6 mL benzene-*d₆* was added. The suspension was stirred
for 15 minutes, the vial was tipped to wash the precipitates on the vial walls, and stirred
again for 15 minutes. The mixture was then transferred to a 50 mL thick-walled glass
vessel, sealed, connected to the high vacuum line where it was de-gassed via 3x freeze-
pump-thaw cycles. The volatiles of the reaction mixture were then vacuum transferred to
a J-Young NMR tube the isotopic composition of the liberated pyrrolidine was
established by quantitative ¹³C{¹H} NMR spectroscopy to be pyrrolidine (82 %) and
pyrrolidine-2-*d₁* (18 %).
**Figure 6.9.** Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (benzene-$d_6$, 23 °C) of a mixture containing pyrrolidine (82 %) and pyrrolidine-2-$d_1$ (18 %) prepared by an independent route.

**Synthesis of pyrrolidine-2,5-$d_1,d_1$, and pyrrolidine-2-$d_2$.** A literature report was modified. In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar and (−)-sparteine (0.875 g, 3.73 mmol) dissolved in 10 mL of Et$_2$O. A second 50 mL thick-walled glass vessel was charged with sec-BuLi (2.7 mL, 3.73 mmol, 1.39 M in cyclohexane). A third 200 mL thick-walled glass vessel was charged with a magnetic stir bar and N-Boc-pyrrolidine (0.5 mL, 2.87 mmol) dissolved in 25 mL of Et$_2$O. The three vessels were sealed with Teflon valves and connected to the Schlenk line, where the Teflon valves were replaced with rubber septa under a positive flow of Ar. Using a cannula, the sec-BuLi solution was added to the pre-cooled (-78 °C) sparteine solution and stirred at -78 °C for 15 minutes. After this time, the sec-BuLi/(−)-sparteine
mixture was added to the pre-cooled (-78 °C) solution containing the N-Boc pyrrolidine via cannula. The resulting mixture was stirred at -78 °C for 5 hours. At the completion of the reaction, methanol-d₄ (0.24 mL) was added dropwise at -78 °C and the reaction mixture was warmed to room temperature over the course of 15 minutes. DI water (10 mL) was added to the mixture, and extracted with Et₂O (2 x 10 mL). The combined Et₂O fractions were then washed with 5% aqueous H₃PO₄ (20 mL), dried with MgSO₄ and filtered over Celite. Rotary evaporation of the solvent yielded N-Boc-pyrrolidine-d₄ as a clear oil (0.442 g, ~2.57 mmol, 89 %). The product was de-gassed by 3x freeze-pump-thaw cycles, brought back into the glovebox where it was lyophilized from benzene (3 x 3 mL) and dried under vacuum for 1 hour. The labeling procedure was then repeated with the N-Boc-pyrrolidine-d₄ thus obtained in order to generate d²-isotopologs. Deprotection of the Boc group and subsequent deprotonation were carried out in analogy to the independent synthesis of pyrrolidine-2-d₁ described above. The isotopic composition of pyrrolidine was established by quantitative ¹³C{¹H} NMR spectroscopy to be pyrrolidine (8 %) and pyrrolidine-2-d₁ (42 %), pyrrolidine-2,5-d₁,d₁ (41 %) and pyrrolidine-2-d₂ (9 %).
Figure 6.10. Quantitative $^{13}$C-$^1$H NMR spectrum (benzene-$d_6$, 23 °C) of a mixture containing pyrrolidine (8 %) and pyrrolidine-$2-d_I$ (42 %), pyrrolidine-$2,5-d_I,d_I$ (41 %) and pyrrolidine-$2-d_2$ (9 %) prepared by an independent route.
Figure 6.11. Quantitative $^{13}$C-$^1$H NMR spectrum (benzene-$d_6$, 23 °C) of a mixture containing pyrrolidine (8 %) and pyrrolidine-$2-d_1$ (42 %), pyrrolidine-$2,5-d_1,d_1$ (41 %) and pyrrolidine-$2-d_2$ (9 %) prepared by an independent route. Data was processed with low exponential apodization (0.2 Hz).

Deuterium Labeling Experiments and Associated Data

Preparation of [1-N(pyrr-$d_n$)]$^+$ (n = 0–2) (Method A). In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.200 g (0.238 mmol) of [1-Cl], 0.221 g (0.250 mmol) of Na[BArF$^{24}$], 0.021 mL (0.250 mmol) of pyrrolidine-N-$d_i$ and 3 mL of benzene. The vessel was quickly sealed with a Teflon valve and connected to the high vacuum line where the mixture was de-gassed by 3x freeze-pump-thaw cycles. The reaction vessel was then sealed and the mixture stirred at 60 °C under vacuum for 48
hours. The reaction vessel was then brought back into the glovebox and product isolation was carried out as described for [1-N(pyrr)]$^+$ (Method A) to yield analytically pure [1-N(pyrr-$d_n$)]$^+$ (n = 0–2) as a dark brown solid (0.404 g, 0.232 mmol, 98 %). $^2$H NMR (benzene, 295 K): $\delta$ 4.04 (br s, N(pyrr) $\alpha$-CD).

**Preparation of [1-N(pyrr-$d_n$)]$^+$ (n = 0–2) (Method B).** In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.050 g (0.029 mmol) of [1-ND(pyrr)]$^+$, and 0.6 mL of benzene. The tube was sealed and connected to the high vacuum line where the solvent was de-gassed by 3x freeze-pump-thaw cycles. The tube was sealed and placed in a temperature-controlled oil bath (60 °C) for 48 hours. The tube was then brought back into the glovebox and product isolation was carried out as described for [1-N(pyrr)]$^+$ (Method A) to yield analytically pure [1-N(pyrr-$d_n$)]$^+$ (n = 0–2) as a dark brown solid (0.048 g, 0.028 mmol, 96 %). The isotopic composition of [1-N(pyrr-$d_n$)]$^+$ (n = 0–2) was found to be independent of the method used for its preparation (A or B) as determined by $^{13}$C{$^1$H} NMR spectroscopic analysis of the liberated pyrrolidide ligand upon protonolysis (see below).
Figure 6.12. $^1$H NMR (500 MHz) spectrum of [1-N(pyr-dₙ)]⁺ (n = 0, 1, 2) in benzene-d₆ at 23 °C. Note the low integration at the N(pyr) α-CH₂ resonance compared to β-CH₂ (3.43 vs 4) that indicates deuteration at the α position, confirmed by $^{13}$C{$^1$H} NMR spectroscopy.

Liberation of pyrrolidide ligand in [1-N(pyr-dₙ)]⁺ (n = 0–2). In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.078 g (~0.045 mmol) of [1-N(pyr-dₙ)]⁺ (prepared via Method A or B) and dissolved in 1 mL of Et₂O. The vessel was sealed with a Teflon valve and connected to the high vacuum line where HCl (0.11 mL, 0.224 mmol, 2.0 M in Et₂O) was added via syringe under a positive flow of N₂. The mixture was stirred at room temperature for 15 minutes, during which time a color change from brown to green-brown was observed with the concomitant formation of precipitates. The mixture was de-gassed by 3x freeze-pump-thaw cycles and the solvent of the reaction was distilled away from the residue and $^1$H NMR analysis of the
residue indicated quantitative consumption of \([1\text{-N(pyrr-}d_n)]^+\) and formation of \([1\text{-Cl}]^+\).

The residue was dried under high vacuum for 2 hours. After this time, the reaction vessel was brought back into the glovebox where 0.041 g (0.293 mmol) of TBD dissolved in 0.6 mL of benzene-\(d_6\) was added. The vessel was sealed and mixture was stirred at room temperature for 15 minutes, followed by manual agitation of the reaction vessel to dissolve residue on side walls, followed by stirring at room temperature for an additional 15 minutes. The vessel was then connected to the high vacuum line and the volatiles were vacuum transferred to a J-Young NMR tube. The isotopic composition of the liberated pyrrolidine was established by quantitative \(^{13}\text{C}\{^1\text{H}\} \text{NMR spectroscopy.}

Figure 6.13. Fitted quantitative \(^{13}\text{C}\{^1\text{H}\} \text{NMR spectrum (benzene-}d_6, 23 \degree\text{C}) of a mixture containing pyrrolidine (50 %), pyrrolidine-2-\(d_1\) (40 %), pyrrolidine-2,5-\(d_1,d_1\) (8 %) and pyrrolidine-2,2-\(d_2\) (2 %) liberated from \([(1\text{-N(pyrr-}d_n)]^+\) by protonolysis. The violet line represents a fit of the data, and the blue lines shows the deconvolution of the individual peaks.
Table 6.1. Assignments and relative integrations of the peaks observed in Figure 6.13.

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<sup>a</sup> Values used to determine product percentages due to favorable peak deconvolution.
Figure 6.14. Quantitative $^{13}\text{C}{^1\text{H}}$ NMR spectrum (benzene-$d_6$, 23 °C) of a mixture containing pyrrolidine (50 %), pyrrolidine-2-$d_1$ (40 %), pyrrolidine-2,4-$d_2$ (8 %) and pyrrolidine-2,2-$d_2$ (2 %) liberated from [(1-N(pyrr-$d_5$)]$^+$ by protonolysis (bottom, magenta), overlaid with an independently prepared mixture containing pyrrolidine (78 %) and pyrrolidine-2-$d_1$ (18 %) (top, blue). This spectrum supports the chemical shift assignment for pyrrolidine-2-$d_1$ as the major isotopolog present upon the liberation of the pyrrolidide ligand in [(1-N(pyrr-$d_5$)]$^+$. 
Figure 6.15. Quantitative $^{13}\text{C}_{\text{1H}}$ NMR spectrum (benzene-$d_6$, 23 °C) of a mixture containing pyrrolidine (50 %), pyrrolidine-$2-d_1$ (40 %), pyrrolidine-$2,5-d_1,d_1$ (8 %) and pyrrolidine-$2,2-d_2$ (2 %) liberated from [(1-N(pyrr-d_n))$^+$ by protonolysis (bottom, magenta), overlaid with an independently prepared mixture containing pyrrolidine (8 %), pyrrolidine-$2-d_1$ (42 %), pyrrolidine-$2,5-d_1,d_1$ (41 %) and pyrrolidine-$2,2-d_2$ (9 %) (top, blue). This spectrum supports the chemical shift assignment for pyrrolidine isotopomers and isotopologs present upon the liberation of the pyrrolidide ligand in [(1-N(pyrr-d_n))$^+$. 
Figure 6.16. Quantitative $^{13}$C{$^1$H} NMR spectrum (benzene-$d_6$, 23 °C) of a mixture containing pyrrolidine (50 %), pyrrolidine-2-$d_1$ (40 %), pyrrolidine-2,5-$d_1,d_1$ (8 %) and pyrrolidine-2,2-$d_2$ (2 %) liberated from [(1-N(pyrr-$d_n$))$^+$ by protonolysis (bottom, magenta), overlaid with an independently prepared mixture containing pyrrolidine (8 %), pyrrolidine-2-$d_1$ (42 %), pyrrolidine-2,5-$d_1,d_1$ (41 %) and pyrrolidine-2,2-$d_2$ (9 %) (top, blue). This spectrum supports the chemical shift assignment for pyrrolidine isotopomers and isotopologs present upon the liberation of the pyrrolidide ligand in [(1-N(pyrr-$d_n$))$^+$. Data was processed with low exponential apodization (0.2 Hz) to better resolve isotopolog/isotopomer peaks.
**Figure 6.17.** Mass spectrum of pyrrolidine (bottom), overlaid with a mixture containing pyrrolidine (50 %), pyrrolidine-2-\textit{d} (40 %), pyrrolidine-2,5-\textit{d}\textsubscript{1} (8 %) and pyrrolidine-2,2-\textit{d}\textsubscript{2} (2 %) liberated from [(1-N(pyrr-\textit{d})\textsubscript{n})\textsuperscript{+}] by protonolysis (top).

**Quantification of H\textsubscript{2} isotopologs formed during dehydrogenation of pyrrolidine-N-\textit{d}.** In the glovebox, a 50 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.200 g (0.238 mmol) of [1-Cl], 0.221 g (0.250 mmol) of Na[BArF\textsubscript{24}], 0.021 mL (0.250 mmol) of pyrrolidine-N-\textit{d} and 3 mL of benzene. The vessel was quickly sealed with a Teflon valve and connected to the high vacuum line where the mixture was degassed by 3x freeze-pump-thaw cycles. The reaction vessel was then sealed and the mixture stirred at 60 °C under vacuum for 48 hours. After this time, using a Toepler pump, 0.094 mmol (0.407 equivalents per Mo) of gas was collected. The gas was passed over a bed of CuO pre-heated to 200 °C, and the combustion product was collected in a
liquid nitrogen-cooled trap. The contents of the trap were then vacuum transferred to a J-Young NMR tube containing benzene-$d_6$ (0.6 mL) and analyzed by $^1$H NMR spectroscopy. The relative amounts of $\text{H}_2\text{O}$, HDO and $\text{D}_2\text{O}$ thus formed were calculated from the ratio of [H$_2$O]:[HDO] observed by $^1$H NMR and the relation:

\[
\text{H}_2\text{O} + \text{D}_2\text{O} \rightleftharpoons 2 \text{HDO} \quad K = 3.8 \ (23 \ ^\circ\text{C})
\]

\[K \approx 3.8 (23 ^\circ\text{C})\]

\[0.26 \ 0.28 \ 0.30 \ 0.32 \ 0.34 \ 0.36 \ 0.38 \ 0.40 \ 0.42 \ 0.44 \ 0.46\]

\[ 1.2 \ 1.4 \ 1.6 \ 1.8 \ 2.0 \ 2.2 \ 2.4 \ 2.6 \ 2.8 \ 3.0 \ 3.2 \]

\[\text{H}_2\text{O} \quad \text{HDO} \quad \text{D}_2\text{O}\]

**Figure 6.18.** $^1$H NMR spectrum (benzene-$d_6$, 23 °C) of the captured combustion product following the dehydrogenation of pyrrolidine-N-$d_1$.

**Crossover Experiment between [1-NH(pyrr)]$^+$ and [1-ND(pyrr)]$^+$.** In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.040 g (0.023 mmol) of [1-ND(pyrr)]$^+$, 0.040 g (0.023 mmol) of [1-NH(pyrr)]$^+$ and 0.6 mL of benzene-$d_6$. The tube was sealed and connected to the high vacuum line where the solvent was de-gassed.
by 3x freeze-pump-thaw cycles. The tube was sealed and placed in a temperature-controlled oil bath (60 °C) for 48 hours. A quantitative $^{13}$C{$^{1}$H} NMR spectrum was recorded after 3 hours (Figure 6.19) and after 48 hours (Figure 6.20) of stirring to monitor the isotopic composition of the pyrrolidide ligand in the molybdenum product. The tube was then brought back into the glovebox and product isolation was carried out as described for [1-N(pyrr)]$^{+}$ (Method A). The isotopic composition of the evolved gases and the pyrrolidide ligand were determined as described above.

**Figure 6.19.** Fitted quantitative $^{13}$C{$^{1}$H} NMR spectrum (benzene-$d_6$, 23 °C) of the $\beta$-pyrrolidide region of the crossover experiment between [1-NH(pyrr)]$^{+}$ and [1-ND(pyrr)]$^{+}$ after heating at 60 °C for 3 hours. The violet line represents a fit of the data, and the blue lines shows the deconvolution of the individual peaks.
Table 6.2. Relative integrations of the peaks observed in Figure 6.19.

<table>
<thead>
<tr>
<th>δ (multiplicity)</th>
<th>Assignment</th>
<th>Integration (MestReNova Curve Fit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.75 (s)</td>
<td>[1-N(pyrr)]⁺</td>
<td>116468.521</td>
</tr>
<tr>
<td>26.63 (s)</td>
<td>[1-N(pyrr-d₁)]⁺</td>
<td>16919.566</td>
</tr>
</tbody>
</table>

Figure 6.20. Fitted quantitative $^{13}$C{$^{1}$H} NMR spectrum (benzene-$d_s$, 23 °C) of the β-pyrrolidide region of the crossover experiment between [1-NH(pyrr)]⁺ and [1-ND(pyrr)]⁺ after heating at 60 °C for 3 hours. The violet line represents a fit of the data, and the blue lines shows the deconvolution of the individual peaks.

Table 6.3. Assignments and relative integrations of the peaks observed in Figure 6.20.

<table>
<thead>
<tr>
<th>δ (multiplicity)</th>
<th>Assignment</th>
<th>Integration (MestReNova Curve Fit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.75 (s)</td>
<td>[1-N(pyrr)]⁺</td>
<td>164161.551</td>
</tr>
<tr>
<td>26.63 (s)</td>
<td>[1-N(pyrr-d₁)]⁺</td>
<td>24513.016</td>
</tr>
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</table>
Figure 6.21. Quantitative $^{13}\text{C} \{^{1}\text{H}\} \text{ NMR spectrum (benzene-}d_6, 23 \, ^\circ\text{C) of a mixture containing pyrrolidine (74 %), pyrrolidine-2-}d_1 (23 \, \%), \text{pyrrolidine-2,5-}d_1, d_1 (3 \, \%) \text{ and pyrrolidine-2,2-}d_2 (< 1 \, \%) \text{ liberated from the product of the crossover experiment between } [1-\text{NH(pyr)}]^+ \text{ and } [1-\text{ND(pyr)}]^-.$
Figure 6.22. Fitted quantitative $^{13}$C-$^1$H NMR spectrum (benzene-$d_6$, 23 °C) of a mixture containing pyrrolidine (74 %), pyrrolidine-2-$d_1$ (23 %), pyrrolidine-2,5-$d_1,d_1$ (3 %) and pyrrolidine-2,2-$d_2$ (< 1 %) liberated from the product of the crossover experiment between [1-NH(pyrr)]$^+$ and [1-ND(pyrr)]$^-$. Data was processed with low exponential apodization (0.2 Hz) to better resolve isotopolog/isotopomer peaks. The violet line represents a fit of the data, and the blue lines shows the deconvolution of the individual peaks. For individual peak assignments see Table 6.1.

Additional Reactions and Associated NMR Data

PCET reaction between [1-NH(pyrr)]$^+$ and tBu$_3$ArO•. In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, 0.038 g (0.022 mmol) of [1-NH(pyrr)]$^+$ and 2 mL of toluene. To the stirring solution, 0.006 g (0.023 mmol) of tBu$_3$ArO• dissolved in 0.5 mL of toluene was added dropwise. During the addition, a color change from dark green to brown was observed, and the solution was stirred at.
room temperature for an additional 30 minutes. The solvent was then removed in vacuo, and the quantitative formation of [1-N(pyrr)]\(^+\) and tBu\(_3\)ArOH was observed by \(^1\)H NMR spectroscopy (vs mesitylene internal standard).

**Thermolysis of [1-NH(pyrr)]\(^+\) in the presence of excess PPh\(_2\)Me.** In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.028 g (0.016 mmol) of [1-NH(pyrr)]\(^+\), 0.030 mL (0.161 mmmol) of PPh\(_2\)Me and 0.6 mL of benzene-\(d_6\). The tube was sealed and placed in a temperature-controlled oil bath (60 °C) and monitored by \(^1\)H and \(^{31}\)P\(_{\{1\}H}\) spectroscopies.

![Figure 6.23. \(^{31}\)P\(_{\{1\}H}\) spectra taken at various intervals during the thermolysis [1-NH(pyrr)]\(^+\) in the presence of 10 equiv. of PPh\(_2\)Me. The 4 day mark represents ~ 30 % yield.](image)
Reaction of [1-N(pyrr)]⁺ with D₂. In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.026 g (0.015 mmol) of [1-N(pyrr)]⁺, and 0.6 mL of benzene-d₆. The tube was sealed and connected to the high vacuum line where the headspace was evacuated and D₂ (4 atm) was admitted. The tube was sealed and placed in a temperature-controlled oil bath (60 °C) for 5 days. After this time, a quantitative $^{13}$C{¹H} NMR spectrum was recorded and showed no deuterium incorporation in the pyrroldide ligand.

Additional EPR Spectroscopic Data

![Figure 6.24. Overlaid X-band EPR spectra of [1-NH(pyrr)]⁺ (black), [1-NH₃]⁺ (blue) recorded at 7 K in toluene glass and a fit of the data (red). Collection and simulation parameters: microwave frequency = 9.381 GHz, power = 2.0 mW, modulation amplitude = 4.0 G; $g_x = 2.020, g_y = 2.005, g_z = 1.968.$]
Determination of $k_{PT}$ between [1-N(pyrr)] and [TBD–H][BArF$_{24}$]

We assume that an electron transfer (ET) event is followed by a rapid, irreversible proton transfer (PT) between [1-N(pyrr)] and [TBD–H][BArF$_{24}$] in the electrochemical cell:

$$\text{In this case, the observed rate constant for the chemical step (proton transfer) can be expressed as:}$$

$$k_{\text{obs}} = k_{PT}[\text{TBD–H}] \quad 6.1$$

Where $k_{PT}$ is the second-order rate constant for proton transfer and [TBD–H] is the concentration of the acid. It has been shown$^{54}$ that the peak cathodic potential of the ET event varies as a function of acid concentration according to:

$$E_p = E_{1/2} - 0.78 \frac{RT}{F} + \frac{RT}{2F} \ln \left( \frac{k_{obs}RT}{Fv} \right) \quad 6.2$$

Where $E_p =$ Peak cathodic potential; $E_{1/2} =$ Potential of cathodic wave in the absence of acid; $R =$ gas constant; $T =$ temperature; $F =$ Faraday’s constant; $v =$ scan rate.

Therefore, plotting the peak potential ($E_p$) as a function of ln([TBD–H]$^+$) allows the determination of $k_{obs}$ and by extension, $k_{PT}$.
Figure 6.25. Cyclic voltammograms of complex [1-N(pyrr)]⁺ (2 mM in THF) in the presence of 0 M (black trace) to $1.2 \times 10^{-3}$ M (red trace) of [TBD–H][BArF$_{24}$] using a glassy carbon working electrode, a platinum wire counter electrode, a silver wire reference electrode, 0.2 M [nBu$_4$N][PF$_6$] and a scan rate of 100 mV sec$^{-1}$ in THF at 23 °C versus Fc/Fc$^+$. 

Figure 6.26. Plot of peak cathodic potential ($E_{pc}$) for the [1-N(pyrr)]⁺/[1-N(pyrr)] wave as a function of ln([TBD–H]+). The slope is equal to 0.0132 with $R^2 = 0.999$. 
Figure 6.27. Plot of $k_{obs}$ obtained as a function of [TBD–H]$^+$ concentration. The slope yields $k_{PT} = 1.3 \times 10^3$ M$^{-1}$ sec$^{-1}$ with $R^2 = 0.996$.

DFT Input Examples

Geometry Optimizations

#Filename
! RKS B3LYP RIJCOSX ZORA ZORA-def2-SVP SARC/J Normalprint SlowConv TightSCF Opt Pal8 UCO

%basis NewGTO 42 "old-ZORA-TZVP" end
NewGTO 15 "ZORA-DEF2-TZVP(-f)" end
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NewAuxGTO 42 "SARC/J" end
NewAuxGTO 15 "SARC/J" end
NewAuxGTO 7 "SARC/J" end
end

%SCF MaxIter 500
    ToLE 1e-7
    ToLErr 1e-6
end

* xyz 1 1

XYZ Coordinates.

*
Numerical Frequency Calculations

#Filename

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Normalprint Numfreq Grid4 Nofinalgrid Pal8

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  NewGTO 7 "ZORA-DEF2-TZVP(-f)" end
  NewGTO 15 "ZORA-DEF2-TZVP(-f)" end
  NewAuxGTO 42 "SARC/J" end
  NewAuxGTO 7 "SARC/J" end
  NewAuxGTO 15 "SARC/J" end
end

%SCF MaxIter 500
  TolE 1e-7
  TolErr 1e-6
end

%FREQ RESTART TRUE
CENTRALDIFF TRUE
INCREMENT 0.01
END

* xyz 1 1

XYZ Coordinates from geometry optimization.

*
DFT-Computed Energies

![Chemical structures and reactions]

Table 6.4. Calculated Gibbs free energies of molybdenum complexes for N–H BDFE determinations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Spin State</th>
<th>Calculated Gibbs Free Energy (Eh)</th>
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</thead>
<tbody>
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<td>[1-NH(pyrr)]⁺</td>
<td>S = 1/2</td>
<td>-6963.71188352</td>
</tr>
<tr>
<td>[1-N(pyrr)]⁺</td>
<td>S = 0</td>
<td>-6963.1363953</td>
</tr>
<tr>
<td>[1-NH₃]⁺</td>
<td>S = 1/2</td>
<td>-6807.89698148</td>
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<tr>
<td>[1-NH₂]⁺</td>
<td>S = 0</td>
<td>-6807.32504940</td>
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<tr>
<td>[2-NH₃]⁺</td>
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<tr>
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<td>[1-NH]⁺</td>
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</tbody>
</table>
References

34 A more accurate definition for this lower bound is complicated by the dearth of reagents with higher known $pK_a$ values in THF that do not decompose $[1-N(pyr)]^+$. 


CHAPTER 7

Homolytic Ammonia N–H Bond Activation, Nitride Formation and Pyridine(diimine) Chelate Hydrogenation in Molybdenum Complexes.*

Abstract

The homolytically weakened N-H bonds in \([iPrPDI]Mo(NH_3)_2(\eta^2-C_2H_4)\) \((iPrPDI = 2,6-(2,6-iPr_2C_6H_3N=CMe)_2C_5H_5N)\) enabled hydrogen atom abstraction and synthesis of a terminal nitride \([iPrPDI]Mo(N)(C_2H_4)\) \((1-(N)(\eta^2-C_2H_4))\) from coordinated ammonia, a key step in NH_3 oxidation. Interestingly, addition of H_2 gas to \(1-(N)(\eta^2-C_2H_4)\) in the presence of the rhodium hydride catalyst \([\eta^5-C_5Me_5(py-Ph)Rh(H)]\) \(([Rh–H]; py-Ph = 2-phenylpyridine)\) resulted in partial hydrogenation of the central pyridine of the \(iPrPDI\) chelate to yield \([iPrTHPDI]Mo(N)(C_2H_4)\) \((2-(N)(\eta^2-C_2H_4)); iPrTHPDI = 2,6-(2,6-iPr_2C_6H_3N=CMe)_2C_5H_5N)\). The nitrido products \(1-(N)(\eta^2-C_2H_4)\) and \(2-(N)(\eta^2-C_2H_4)\) were structurally and spectroscopically characterized, and their electronic structures examined by density functional theory (DFT). The stepwise addition of H-atoms from \([Rh–H]\) to \(1-(N)(\eta^2-C_2H_4)\) was computed to be thermodynamically viable by DFT.

Introduction

Initially prepared as modular terpyridine mimics, pyridine(diimines) (PDIs) have emerged as a privileged ligand class in homogeneous catalysis, particularly with Earth

abundant transition metals. Following independent reports from Brookhart, Bennett and Gibson describing high activity PDI iron(II) and cobalt(II) dihalide catalyst/methylaluminoxane (MAO) activator combinations for ethylene polymerization, PDI ligands have since been applied in the cycloaddition and hydrofunctionalization of olefins, carbonyl hydrosilylation, C–H functionalization as well as small molecule activation including N₂, NH₃, O₂, and CO₂. The rich reaction chemistry observed with transition metals, main group and f-block elements bearing PDI ligands can often be traced to their chemical and electronic versatility, owing to their relative ease of synthesis and the accessibility of low-lying π* orbitals of a₂ and b₂ symmetry. As a consequence, PDI ligands can exhibit both redox activity and noninnocence by either engaging in reversible 1e⁻ redox chemistry with a metal center or serving as traditional π-acids with a high degree of covalency, respectively. PDI ligands are also chemically non-innocent and can undergo alkylation, H-atom migration, oxidation, deprotonation and consequently, dimerization chemistry upon treatment with nucleophiles and bases (Figure 7.1a–g). While ligand modification chemistry arising from electrophilic sites and acidic C–H bonds can be detrimental to the catalytic performance of PDI complexes, these features can also be leveraged to achieve productive reactivity such as the activation of inert small molecules by metal-ligand cooperation (Figure 7.1h).

Molybdenum complexes supported by PDI ligands exhibit ligand modification chemistry as well as unusual electronic structures. For example, addition of NH₃ to the aryl-substituted PDI dinitrogen complex, [{(iPrBPDI)Mo(N₂)}₂(μ₂, η¹, η¹-N₂)] (iPrBPDI = 2,6-(2,6-iPr₂-C₆H₃N=CPH)₂C₅H₅N) resulted in imine N'imine=C'imine bond cleavage and
conversion to a terminal aryl imide, where ammonia served as the irreversible source of hydrogen (Figure 7.1h). In contrast, use of a more chemically inert terpyridine ligand, a non-classical molybdenum(I) ammine complex, [(PhTpy)(PPh₂Me₂)Mo(NH₃)][BARF²⁴] (PhTpy, 4’-Ph-2,2',6',2”-terpyridine; BARF²⁴ = [C₆H₃-3,5-(CF₃)₂]₄) was isolated and a remarkably low N-H bond dissociation free energy of 45.8 kcal/mol was measured. This significant bond weakening (NH₃(g) = 99.5 kcal/mol) enables spontaneous H₂ evolution upon mild heating (BDFE_N-H < ΔG°(H•) = 48.6 kcal/mol). 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 pyridine(diimine) molybdenum ammonia complex that exhibits significant N–H bond weakening by coordination. This strategy enabled synthesis of a terminal molybdenum nitride from NH₃ by a series of hydrogen atom abstraction events, key steps in ammonia oxidation. We also describe an extension of these studies and report a distinct PDI modification pathway involving partial hydrogenation of the pyridine ring. The molecular and electronic structures of the molybdenum nitride complexes bearing the parent and hydrogenated pyridine(diimine) chelate were determined.
Figure 7.1. Selected PDI ligand modifications. (a) Imine C-alkylation; (b) pyridine N-alkylation; (c) double imine C-alkylation; (d) H-atom migration; (e) deprotonation-dimerization; (f) alkylation-dimerization; (g) oxidation; (h) metal-ligand cooperation.

Results and Discussion

The computationally predicted weak ammine N-H bonds in

\[ ([\text{iPrPDIMo(NH}_3]_2(\eta^2-C_2H_4))] \quad (1-(\text{NH}_3)_2(\eta^2-C_2H_4))] \quad \text{iPrPDI} = 2,6-(2,6-iPr}_2C_6H_3N=CMet)_2C_5H_3N \) (BDFEN-H(DFT) = 51 kcal/mol) 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 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-butylphenoxy radical (tBu3ArO•). 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 KC8. Direct synthesis of a terminal metal-nitride from coordinated ammonia remains elusive by HAA and was targeted with \[ (1-(\text{NH}_3)_2(\eta^2-C_2H_4))] \quad \text{[27]}
Addition of three equiv of \( tBu_3ArO^- \) to a benzene solution of \([1-(NH_3)_2(\eta^2-C_2H_4)]\) resulted in rapid formation of \( tBu_3ArOH \) (\( BDFE_{O-H} = 77 \text{ kcal/mol} \))\(^2\) as well as a red-orange, paramagnetic product identified as the terminal molybdenum nitride, \([\text{[iPrPDI]}\text{Mo(N)(}\eta^2-C_2H_4\text{)]})\) isolated in 61% yield after recrystallization (Figure 7.2a). 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.

![Chemical structure and reaction scheme](image)

**Figure 7.2.** (a) Nitride formation from coordinated ammonia and solid-state structure of \([1-(N)(\eta^2-C_2H_4)]\) at 30% probability ellipsoids. Hydrogen atoms were omitted for clarity. (b) X-band EPR spectrum of \([1-(N)(\eta^2-C_2H_4)]\) recorded at 23 °C in toluene solution (see SI for fitting parameters). (c) Spin density plot for \([1-(N)(\eta^2-C_2H_4)]\) 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 \([1-(N)(\eta^2-C_2H_4)]\) was determined by X-ray diffraction and confirms ethylene coordination (\(d(C=C) = 1.410(4) \text{ Å}\)) as well as formation of the
terminal nitride ligand (Figure 7.2a; 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(tBu)Ar]\(_3\) (Ar = 3,5-C\(_6\)H\(_3\)Me\(_2\)) (\(\nu\)(Mo≡N = 1042 cm\(^{-1}\); Mo≡\(^{15}\)N = 1014 cm\(^{-1}\)).\(^{29}\) The distortions to the bond distances of the bis(imino)pyridine support one electron reduction to the radical anionic form of the ligand.\(^{30}\) Both magnetic measurements and the X-band EPR spectrum recorded at 296 K established an \(S = \frac{1}{2}\) ground state. The observed \(g_{iso}\) of 2.00 with a relatively small \(A^{(\text{95,97}Mo)}\) value of 21 MHz supports a ligand- rather than metal-based SOMO (Figure 7.2b). The DFT computed spin density (Figure 7.2c) 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)(\(\eta^2\)-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.\(^{31}\)

The reactivity of [1-(N)(\(\eta^2\)-C\(_2\)H\(_4\))] under reductive proton-coupled electron transfer (PCET)\(^{32}\) conditions was next examined. Addition of three equivalents of the rhodium hydride [Rh–H] to [1-(N)(\(\eta^2\)-C\(_2\)H\(_4\))] in THF solution resulted in a color change from orange-red to green over the course of 15 minutes at room temperature. Monitoring the reaction by \(^1\)H NMR spectroscopy revealed formation of a diamagnetic product identified as (\(i\)PrTHPDI)Mo(N)(C\(_2\)H\(_4\)) ([2-(N)(\(\eta^2\)-C\(_2\)H\(_4\))]; \(i\)PrTHPDI = 2,6-(2,6-\(i\)Pr\(_2\)-
C₆H₅N=CMe)₂C₅H₆N), the product of three H-atom additions from [Rh–H] to the {iPrPDI} chelate in [1-(N)(η²-C₂H₄)] (Figure 7.3). The benzene-d₆ ¹H NMR spectrum of blue (λₓₘₐₓ = 625 nm) [2-(N)(η²-C₂H₄)] exhibits the number of resonances consistent with C₅ molecular symmetry as indicated by four distinct iPr methyl resonances at 1.43, 1.19, 1.01 and 0.98 ppm. The partial hydrogenation of the {iPrPDI} chelate was identified by the lack of diagnostic downfield C–H resonances assignable to the 3-, 4- and 5- pyridine positions along with the concomitant appearance of signals in the aliphatic region (2.01–1.21 ppm). Also consistent with C₅ molecular symmetry was the observation of a doublet of doublets in the ¹³C NMR spectrum of [2-(N)(η²-C₂H₄)] assigned to the ethylene carbons (¹JC–H =156.7, 149.2 Hz). Analysis of [2-(¹⁵N)(η²-C₂H₄)], prepared from hydrogenation of [1-(¹⁵N)(η²-C₂H₄)], by ¹⁵N{¹H} NMR spectroscopy revealed a singlet at + 1040 ppm, consistent with the presence of a terminal molybdenum nitride.

The solid-state structure of [2-(N)(η²-C₂H₄)] was determined by single-crystal X-ray diffraction and confirmed coordination of ethylene and nitride ligands (d(C=C) = 1.420(3) Å; d(Mo≡N) = 1.644(2) Å) as well as the partial hydrogenation of the central pyridine of the {iPrPDI} chelate. Ligand reduction was also evidenced by structural distortion with the lowering of the 4-pyridine carbon below the chelate plane by 0.654 Å (Figure 7.4), a geometry expected from the generation of three sp³ carbon centers in [2-(N)(η²-C₂H₄)]. Remarkably, reduction of the ethylene and imine ligands was not observed despite ample precedent for these functionalities to undergo Rh-catalyzed hydrogenation.
Figure 7.3. Partial hydrogenation of the pyridine(diimine) chelate in $[1-(N)(\eta^2-C_2H_4)]$ by stoichiometric or catalytic reaction with [$\text{Rh–H}$].

![Chemical structure](image)

Figure 7.4. Solid-state structure of $[2-(N)(\eta^2-C_2H_4)]$ with ellipsoids at 30 % probability. Hydrogen atoms (except those connected to C4, C5 and C6) have been omitted for clarity. Selected bond distances (Å): Mo1–N1 2.215(2), Mo1–N2 2.171(2), Mo1–N3 2.214(2), Mo1–N4 1.644(2), C34–C35 1.420(3), N1–C2 1.326(2), C2–C3 1.423(2), C3–C4 1.501(3), C4–C5 1.524(3), C5–C6 1.526(3), C6–C7 1.497(3), C7–C8 1.419(3), N3–C8 1.323(2).

The unusual chelate modification in $[2-(N)(\eta^2-C_2H_4)]$ prompted determination of the electronic structure of the complex and assignment of the redox state of the new ligand. While the diamagnetism of $[2-(N)(\eta^2-C_2H_4)]$ limits the number of experimental observables for an electronic structure determination, DFT computations were nevertheless carried out to investigate the oxidation state of the molybdenum and the corresponding redox state of the $^{iPr}$THPDI ligand. Calculations were conducted at the B3LYP level of theory and used to construct a qualitative molecular orbital diagram for $[2-(N)(\eta^2-C_2H_4)]$. As shown in Figure 7.5, the highest occupied molecular orbital...
(HOMO) and the lowest unoccupied molecular orbital (LUMO) of \([2-(\text{N})(\eta^2-\text{C}_2\text{H}_4)]\) are \(^{\text{tPr}}\text{THPDI}\) ligand based π* orbitals of a" and a’ symmetry, respectively, supporting a closed shell, anionic description for \(^{\text{tPr}}\text{THPDI}\).\(^{35}\) HOMO-7 and HOMO-8 exhibit molybdenum d\(_{yz}\) and d\(_{xz}\) character engaged in π-bonding with nitrogen p\(_y\) and p\(_x\) orbitals, respectively, consistent with a nitrido Mo≡N triple bond. Finally, HOMO-1 exhibits significant ethylene π* character, consistent with the elongated ethylene(C=C) bond length of 1.420(3) Å observed in the solid-state structure of \([2-(\text{N})(\eta^2-\text{C}_2\text{H}_4)]\). This value is statistically indistinguishable from the ethylene(C=C) bond length of 1.425(6) Å reported for the cationic molybdenum ethylene complex \([\text{(PhTpy)}\text{(PPh}_2\text{Me})_2\text{Mo(C}_2\text{H}_4)]\text{[BARF}^{24}\text{]}\) (PhTpy = 4'-Ph-2,2',6',2''-terpyridine, BARF\(^{24}\) = \([\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2]_4\)) that exhibits EPR spectroscopic features consistent with a Mo(III) metallacyclopropane.\(^{36}\) Furthermore, the C-H coupling constants (\(^1J_{\text{C-H}} = 156.7, 149.2\) Hz) observed for coordinated ethylene in the \(^{13}\text{C}\) NMR spectrum of \([2-(\text{N})(\eta^2-\text{C}_2\text{H}_4)]\) are in the range reported for methylene carbons of ethyl (147.3 Hz)\(^{36}\) and “alkylidene-like” \(\eta^2\)-vinyl (160 Hz)\(^{37}\) ligands of molybdenum. Therefore, the electronic structure of the complex is likely best described as a Mo(VI) metallacyclopropane nitride supported by a singly reduced \(^{\text{tPr}}\text{THPDI}\) ligand. In this electronic structure description, \((^{\text{tPr}}\text{THPDI})^-\) is isoeletronic with anionic dipyridylazaallyl ligands which exhibit a rich coordination chemistry with a host of transition metals.\(^{38}\) Localized orbital bonding analysis (LOBA)\(^{39}\) was performed by DFT and also supports a 6+ oxidation state assignment at molybdenum in \([2-(\text{N})(\eta^2-\text{C}_2\text{H}_4)]\).
Figure 7.5. Molecular orbital illustrations and populations for [2-(N)(η^2-C_2H_4)] obtained from a spin-restricted DFT calculation at the B3LYP level of theory. The z-axis is defined as the Mo≡N vector. HOMO: iPrTHPDI (a') 6 % Mo, 94 % L
LUMO: iPrTHPDI (a') 4 % Mo, 96 % L
HOMO-1: Mo(d_z2)–C=C(σ^*) 48 % Mo, 52 % L
HOMO-7: Mo(d_xd_zd_yd_z)–N(π^*) 30 % Mo, 70 % L
HOMO-8: Mo(d_xd_yd_zd_y)–N(π^*) 30 % Mo, 70 % L

Because the complex [2-(N)(η^2-C_2H_4)] was the only product observed by ^1H NMR spectroscopy form the reaction of [2-(N)(η^2-C_2H_4)] with [Rh–H], the fate of the Rh complex was investigated by EPR spectroscopy. A single isotropic signal at g = 2.070 was observed at the completion of the reaction in toluene solution at room temperature, consistent with the formation of the paramagnetic Rh(II) complex [(η^5-C_5Me_5)(py-Ph)Rh] ([Rh]), the product of H-atom loss from [Rh–H]. Because [Rh] is known to react with H_2 gas to regenerate the rhodium hydride starting material, [Rh–H] was next employed in catalytic amounts using H_2 gas as the terminal reductant. Indeed, conducting the reaction using 5 mol % [Rh–H] under 4 atm of H_2 in THF generated [2-(N)(η^2-C_2H_4)] in quantitative NMR yield after 72 hours at room temperature. To investigate whether related molybdenum iPrPDI complexes exhibit similar reactivity, (iPrPDI)MoCl_3, (iPrPDI)Mo(η^6-C_6H_6) and (iPrPDI)Mo(CO)_4 were treated with 25 mol % [Rh–H] and stirred under 4 atm of H_2. However, in each case, no reaction was observed for up to 6 days at room temperature, and intractable product mixtures were obtained upon heating to 60 °C for 18 h. These results suggest that [1-(N)(η^2-C_2H_4)] is uniquely suited for well-defined hydrogenation chemistry with [Rh–H] and is likely due to the stability of the
molybден-нитрид-этиленовый ядро. В результате, реактивность происходит на лиганде $^\text{ipr}$PDI, приводя к окислению Mo(VI) в конечном продукте.

Given that the coordinately saturated, 18e– complex [Rh–H] is an effective H–atom donor that is known to react by PCET,$^{40,42}$ DFT computations were conducted in order to probe the thermodynamics of a plausible C–H bond forming PCET pathway leading to the formation of [2-(N)(η$^2$-C$_2$H$_4$)]. As presented in Figure 7.6 and Table 7.1, sequential addition of H-atoms from [Rh–H] was computed at both the B3LYP and PW6B95 levels of theory to be approximately thermoneutral or exergonic for plausible PCET pathways forming the intermediates [3-H$_1$], [4-H$_1$] or [3,4-H$_2$] with C–H bond dissociation free energies (BDFEs) in the range 48-60 kcal mol$^{-1}$ (BDFE$_{\text{Rh–H}}$ = 52 kcal mol$^{-1}$). By contrast, consecutive formation of C–H bonds at the 3- and 5-pyridine positions was computed to be endergonic by ~20 kcal mol$^{-1}$ leading to intermediate [3,5-H$_2$] (BDFE$_{\text{C–H}}$ = 32 kcal mol$^{-1}$) and is likely disfavored (Figure 7.6, dashed arrow). These computational results suggest that PCET from [Rh–H] to the pyridine(diimine) chelate in [1-(N)(η$^2$-C$_2$H$_4$)] is thermodynamically feasible for each H-atom addition step. However, it is important to note that the initial site of H-atom addition to [1-(N)(η$^2$-C$_2$H$_4$)] is unknown, as reaction intermediates were not observed during the course of the hydrogenation. Therefore, the structures depicted in Figure 7.6 can, in principle, be accessed by intramolecular hydrogen atom transfer in analogy to intramolecular alkyl group migrations observed in PDI ligands.$^{44}$ In addition, the possibility that a PCET pathway is circumvented altogether by pyridine(C–C) insertion into the rhodium-hydrogen bond cannot be rigorously excluded.
Figure 7.6. Plausible H-atom addition pathways in [1-(N)(η²-C₂H₄)].

Table 7.1: DFT-computed C–H BDFEs for sequential H-atom addition in [1-(N)(η²-C₂H₄)]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Pyridine Position</th>
<th>Level of Theory</th>
<th>C–H BDFE(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[3-H₁]</td>
<td>3</td>
<td>B3LYP</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PW6B95</td>
<td>52</td>
</tr>
<tr>
<td>[4-H₁]</td>
<td>4</td>
<td>B3LYP</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PW6B95</td>
<td>50</td>
</tr>
<tr>
<td>[3,4-H₂]</td>
<td>3</td>
<td>B3LYP</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PW6B95</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>B3LYP</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PW6B95</td>
<td>57</td>
</tr>
<tr>
<td>[3,5-H₂]</td>
<td>3/5</td>
<td>B3LYP</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PW6B95</td>
<td>32</td>
</tr>
<tr>
<td>[2-(N)(η²-C₂H₄)]</td>
<td>3/5</td>
<td>B3LYP</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PW6B95</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>B3LYP</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PW6B95</td>
<td>96</td>
</tr>
</tbody>
</table>

\(^a\)Values computed in kcal mol\(^{-1}\) in the gas-phase.

Conclusions

In summary, coordination-induced bond weakening was observed in a molybdenum bis(ammine) complex supported by a redox active ligand that enabled hydrogen atom abstraction and synthesis of a terminal molybdenum nitride. Partial hydrogenation of a pyridine(diimine) chelate was demonstrated in the molybdenum...
nitride product with a rhodium hydride catalyst and the thermodynamics of a plausible 
C–H bond forming PCET pathway were examined. The transformations described herein
provide unique insight into the ammonia oxidation and chelate hydrogenation chemistry
of molybdenum complexes bearing a potentially redox active ligand.

Experimental Section

General Considerations

All air- and moisture-sensitive manipulations were carried out using vacuum line,
Schlenk and cannula techniques or in an MBraun inert atmosphere (nitrogen) dry box
unless otherwise noted. The solvents used for air- and moisture-sensitive manipulations
were dried and deoxygenated using literature procedures.\textsuperscript{45} Celite was dried at 200 °C
under vacuum for 3 days prior to use. Deuterated solvents for NMR spectroscopy were
distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular
sieves. Hydrogen gas was purchased from Airgas National Welders and passed through a
column of MnO\textsubscript{2} supported on vermiculite and 3 Å molecular sieves prior to use on a
Schlenk manifold. Rigorously anhydrous ammonia was prepared via the condensation of
anhydrous ammonia gas (Sigma-Aldrich) onto thinly cut sodium metal strips (typically
not more than 0.010 g Na) in a sealable thick-walled sealable vessel, forming an amber
electrolyte and was subjected to three freeze-pump-thaw cycles before use. \textbf{DANGER:}
\textit{When using the sodium electrolyte method to dry ammonia, use small quantities with
extreme caution to avoid violent H\textsubscript{2}(g) evolution from the reaction of sodium metal with
residual water in ammonia. When storing the ammonia electrolyte in a closed vessel,
regularly expose the mixture to freeze pump thaw cycles to avoid pressure buildup over

time. Ethylene was purchased from Matheson Tri-Gas Inc., passed through a column of
4 Å molecular sieves, Drierite, and manganese oxalate and stored in a thick-walled
sealable glass vessel over 4 Å molecular sieves. The following compounds were prepared
according to literature procedures: [(iPrPDI)Mo(η⁶-C₆H₆)],¹⁰ (η⁵-C₅Me₅)(py-Ph)Rh(H)
([Rh–H]; py-Ph = 2-phenylpyridine),⁴⁶ 2,4,6-tri-tert-butylphenoxy radical (tBu₃ArO•).⁴⁷

¹H NMR spectra were recorded on a Bruker AVANCE 500 spectrometer
operating at 500.46 MHz. ¹³C NMR spectra were recorded on a Bruker AVANCE 500
spectrometer operating at 125.85 MHz. ¹⁵N NMR spectra were recorded on a Bruker 500
spectrometer operating at 50.663 MHz, and ¹⁵N chemical shifts are reported relative to
liquid NH₃ using an external standard. All ¹H and ¹³C NMR chemical shifts are reported
in ppm relative to SiMe₄ using the ¹H (benzene-d₆: 7.16 ppm) and ¹³C (benzene-d₆:
128.06 ppm) chemical shifts of the solvent as a standard. ¹H NMR data for diamagnetic
compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t
= triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent, obsc =
obscurred), coupling constants (Hz), integration, assignment.

Continuous wave EPR spectra were recorded on an X-band Bruker EMXPlus
spectrometer equipped with an EMX standard resonator and a Bruker PremiumX
microwave bridge. The spectra were simulated using EasySpin for MATLAB.⁴⁸

Elemental analyses were performed at Robinson Microlit Laboratories, Inc., in
Ledgewood, NJ.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil
in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer
head of a Bruker VENTURE D8 PHOTON 100 diffractometer equipped with a molybdenum X-ray tube \((\lambda = 0.71073 \text{ Å})\) and a Cu X-ray tube \((\lambda = 1.54178 \text{ Å})\). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

UV-visible absorption spectra were recorded on an Agilent 8453 diode array UV/Vis spectrophotometer. Samples were charged into a quartz cuvette fitted with a J-Young Teflon cap in a glovebox and transferred to the spectrometer to record absorption spectra.

All DFT calculations were performed with the ORCA program package in the gas phase. The geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP or PW6B95 level of DFT. The all-electron Gaussian basis sets were those developed by the Ahlrichs group. Triple-\(\zeta\) quality basis sets def2-TZVP with one set of polarization functions on molybdenum, phosphorous and nitrogen were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used that were of double-\(\zeta\) quality in the valence region and contained a polarizing set of d functions on the non-hydrogen atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX) approach were chosen to match the orbital basis. Numerical frequencies were calculated at the same level of theory to confirm the
optimized geometries (no imaginary frequencies) and to derive thermochemical data. Bond dissociation free energies were computed at standard conditions of 1 atm and 25 °C including corrections for vibrational zero-point energy, as well as contributions from translational, rotational, and vibrational modes to the energy and entropy of the homolytic bond cleavage process. For molecules containing a molybdenum atom, the 0th order regular approximation (ZORA) was applied. In this case, the relevant basis sets were replaced by their relativistically recontracted versions. The electronic energy of H•, utilized in the calculation of bond dissociation free energies, at the present level of theory is 312 kcal/mol. Localized orbital bonding analysis (LOBA) was performed on Molden output files using the Multiwfn program package.

**Preparation of Molybdenum Complexes**

**Preparation of [1-(N)(η²-C₂H₄)].** In the glovebox, a 50 mL thick walled sealable glass vessel was charged with a magnetic stir bar, 0.200 g (0.305 mmol) of [(iPrPDI)Mo(η⁶-C₆H₆)] and 10 mL of benzene. The vessel was sealed and connected to a high-vacuum line where the solution was degassed (via three freeze-pump-thaw cycles) prior to the addition of 2.1 equivalents (0.640 mmol) of NH₃ by calibrated gas bulb (902 Torr from a 13.1 mL size gas bulb) at -173 °C. An additional 1.0 equivalent (0.305 mmol) of ethylene was then added by calibrated gas bulb (430 Torr from a 13.1 mL size gas bulb) at -173 °C. The solution was thawed and stirred at room temperature for 30 minutes during which time a color change from brown to yellow-brown was observed. The reaction vessel was then brought back into the glovebox where a solution containing 0.241 g (0.924 mmol) of ³Bu₃ArO• dissolved in 3 mL of toluene was added dropwise under rapid
stirring. The solution was thus stirred at room temperature for 30 minutes, during which time a series of color changes were observed from yellow-brown to orange-brown, and finally to pink-red. The solvent of the reaction mixture was removed in vacuo and the orange-brown residue was re-crystallized from 5 mL of pentane at -35°C. The resulting crystalline solids were isolated on a 15 mL fine-porosity frit and washed with cold pentane (3 x 5 mL, -35°C) to afford 0.115 g (0.186 mmol, 61% yield) of product as a dark maroon powder. The ¹⁵N isotopologue [1-(¹⁵N)(η²-C₂H₄)] was prepared using an identical procedure with the exception that ¹⁵NH₃ was used in place of NH₃. Anal Calcd for C₃₅H₄₇MoN₄: C, 67.83; H, 7.64; N, 9.04. Found: C, 67.48; H, 7.41; N, 8.76. Magnetic Susceptibility: (magnetic susceptibility balance 23 °C ) μₑffective = 1.99(2) µB. IR(KBr pellet): νMo≡N = 1036 cm⁻¹; νMo≡¹⁵N = 1004 cm⁻¹.

Preparation of [2-(N)(η²-C₂H₄)] (Method A): In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar and 0.021 g (0.034 mmol) of [1-(N)(η²-C₂H₄)] dissolved in 1 mL of THF. To the stirring solution, 0.040 g (0.103 mmol) of [Rh–H] was added. The reaction was stirred at room temperature for 15 minutes during which time a color change from dark orange to dark green was observed. The solvent was removed in vacuo, the dark green residue was suspended in 3 mL of toluene and filtered through a pad of Celite. The dark green filtrate was layered with pentane (5 mL) and stood at -35 °C for 3 days. After this time, the molybdenum product-containing green-blue supernatant was decanted away from the orange-yellow crystals, and the solvent of the supernatant was removed in vacuo. The resulting dark blue residue was extracted with 3 mL of pentane, filtered through a pad of Celite and stood at -35 °C for 18 h. The
supernatant was decanted, and the blue crystalline material obtained was dried in vacuo to afford \([2-(N)(\eta^2-C_2H_4)]\) (0.005 g, 0.008 mmol, 24% crystalline yield). Single crystals suitable for X-Ray diffraction studies were obtained from a concentrated pentane solution of \([2-(N)(\eta^2-C_2H_4)]\) at -35°C. The \(^{15}\text{N}\) isotopologue \([2-\{(^{15}\text{N})(\eta^2-C_2H_4)\}]\) was prepared using an identical procedure with the exception that \([1-\{(^{15}\text{N})(\eta^2-C_2H_4)\}]\) was used in place of \([1-(N)(\eta^2-C_2H_4)]\). Anal Calcd for C\(_{35}\)H\(_{50}\)MoN\(_4\): C, 67.50; H, 8.09; N, 9.00. Found: C, 67.10; H, 7.82; N, 8.71. \(^1\text{H}\) NMR (benzene-\(d_6\), 23 °C): δ 7.21 (d, \(^3\)J\(_{H-H}\) = 7.6 Hz, 2H, aryl-CH), 7.13 (t, \(^3\)J\(_{H-H}\) = 6.6 Hz, 2H, aryl-CH), 7.05 (d, \(J = 7.4\) Hz, 2H, aryl-CH), 4.07–3.97 (m, 2H, iPr CH), 2.64–2.55 (m, 2H, iPr CH), 2.39 (dd, \(^3\)J\(_{H-H,\text{trans}}\) = 12.4 Hz, \(^2\)J\(_{H-H,\text{gem}}\) = 4.9 Hz, 2H, C\(_2\)H\(_4\)), 2.26–2.19 (m, 2H, backbone CH\(_2\)), 2.01-1.91 (m, 2H, backbone CH\(_2\)), 1.66 (s, 6H, backbone CH\(_3\)), 1.43 (d, \(^3\)J\(_{H-H}\) = 6.7 Hz, 6H, iPr CH\(_3\)), 1.28–1.21 (m, 2H, backbone CH\(_2\)), 1.19 (d, \(^3\)J\(_{H-H}\) = 6.9 Hz, 6H, iPr CH\(_3\)), 1.06 (dd, \(^3\)J\(_{H-H,\text{trans}}\) = 12.4 Hz, \(^2\)J\(_{H-H,\text{gem}}\) = 4.9 Hz, 2H, C\(_2\)H\(_4\)), 1.01 (d, \(^3\)J\(_{H-H}\) = 6.9 Hz, 6H, iPr CH\(_3\)), 0.98 (d, \(^3\)J\(_{H-H}\) = 6.9 Hz, 6H, iPr CH\(_3\)), 1.19 (d, \(^3\)J\(_{H-H}\) = 6.9 Hz, 6H, iPr CH\(_3\)). \(^{13}\text{C}\{^1\text{H}\} \text{NMR (benzene-}d_6, 23 \degree \text{C):} \delta 174.51 \text{ (ipso N–C), 147.26 (ipso-aryl N–C), 143.37 (iPr ipso aryl-C), 138.97 (iPr ipso aryl-C), 126.06 (aryl-CH), 124.92 (aryl-CH), 123.01 (aryl-CH), 51.71 (C\(_2\)H\(_4\)), 28.80 (iPr CH), 27.74 (iPr CH), 25.16 (iPr CH\(_3\)), 25.13 (backbone CH\(_2\)), 24.48 (iPr CH\(_3\)), 24.31 (iPr CH\(_3\)), 23.58 (iPr CH\(_3\)), 22.74 (backbone CH\(_2\)), 19.01 (backbone CH\(_3\)). \(^{15}\text{N}\{^1\text{H}\} \text{NMR (benzene-}d_6, 23 \degree \text{C):} \delta 1040 \text{ (s, nitrido N). UV-Vis (}\lambda_{\text{max}}, \text{toluene, }23\degree\text{):} \text{624 nm (}\varepsilon \approx 4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}\)).

**Preparation of \([2-(N)(\eta^2-C_2H_4)]\) (Method B):** A 200 mL thick-walled glass vessel was charged with a magnetic stir bar, 0.022 g (0.035 mmol) of \([1-(N)(\eta^2-C_2H_4)]\), 0.70 mg (1.78 µmol, added as 0.5 M stock solution in THF) of \([\text{Rh–H}]\) and 2 mL of THF. The
vessel was sealed and connected to the high vacuum line where the headspace was evacuated and H₂ (1 atm at –196 °C; ~ 4 atm at 23 °C) was admitted. The vessel was sealed and stirred at room temperature for 72 h. A series of color changes were noted over the course of the reaction starting from dark pink-red to orange, maroon, black, blue-green and finally dark blue, indicating reaction completeness. The vessel was then brought back into the glovebox where the reaction mixture was transferred to a 20 mL scintillation vial and the solvent was removed in vacuo. The dark blue residue was extracted with pentane (3 x 2 mL) and the combined extracts were filtered through a pad of Celite. The filtrate was concentrated to 3 mL and stood at -35 °C for 48 h. The crystalline solids were isolated, washed with cold (~35 °C) pentane and dried in vacuo to afford [2-(N)(η²-C₂H₄)] as a dark blue solid (0.014 g, 0.022 mmol, 63 %).

Attempted iPrPDI pyridine reduction in [(iPrPDI)Mo(CO)₄], [(iPrPDI)Mo(η⁶-C₆H₆)] and [(iPrPDI)MoCl₃]. In the glovebox, a J-Young NMR tube fitted with a Teflon cap was charged with 0.061 mmol of either [(iPrPDI)Mo(CO)₄], [(iPrPDI)Mo(η⁶-C₆H₆)] or [(iPrPDI)MoCl₃], 0.006 g (0.015 mmol) of [Rh–H] and (0.001 g (0.005 mmol) of a Cp₂Fe internal standard dissolved in 0.3 mL THF-d₈. The tube was sealed and connected to the high vacuum line and frozen. The tube headspace was evacuated and H₂ (1 atm at –196 °C; ~ 4 atm at 23 °C) was admitted. The tube was sealed, rotated end-over-end at room temperature and monitored by ¹H NMR spectroscopy. In each case, no evidence for iPrPDI hydrogenation was obtained after 72 h and heating the reaction mixtures to 60°C for 18 h yielded intractable product mixtures.
**Electronic Structure Discussion**

Figure 7.7. (a) Addition of three hydrogen atom equivalents to $\text{iPrPDI}$. (b) Potentially redox-active forms of $\text{iPrTHPDI}$. Symmetry labels from $C_s$ point group. Only closed-shell variants of ($\text{iPrTHPDI}$) and ($\text{iPrTHPDI}$)$_3^-$ are depicted.

As shown in Figure 7.7a, addition of three H-atom equivalents to a neutral $\text{iPrPDI}$ ligand generates an $\text{iPrTHPDI}$ chelate with an unpaired electron in its neutral form. Therefore, one- or three-electron ligand reductions are necessary to generate a closed-shell forms of $\text{iPrTHPDI}$. In analogy to $\text{iPrPDI}$, two $\pi^*$ orbitals of $a''$ and $a'$ symmetry are available to accommodate redox events at the ligand. Computation of occupied and unoccupied $a''$ and $a'$ orbitals, respectively, together with the overall diamagnetism of $[2-(\text{N})(\eta^2-\text{C}_2\text{H}_4)]$ support a closed shell, anionic $\text{iPrTHPDI}$ chelate (Figure 7.7b). Broken-symmetry solutions were not located for $[2-(\text{N})(\eta^2-\text{C}_2\text{H}_4)]$ and therefore a diradical, anionic description for $\text{iPrTHPDI}$ is disfavored.


DFT-Computed Energies

**Table 7.2.** Calculated Gibbs free energies of molybdenum complexes for C–H BDFE determinations. Bolded compounds refer to those with experimentally known spin states. For intermediates, both low-spin ($S = 0$ or 1/2) and high spin ($S = 1$ or 3/2) configurations were examined, and the results for lowest energy spin-states are reported.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Spin State</th>
<th>Calculated Gibbs Free Energy (Eh; B3LYP)</th>
<th>Calculated Gibbs Free Energy (Eh; PW6B95)</th>
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</thead>
<tbody>
<tr>
<td>[1-(N)(η^2-C_2H_4)]</td>
<td>$S = 1/2$</td>
<td>-5667.68508342</td>
<td>-5672.47825649</td>
</tr>
<tr>
<td>[3-H_1]</td>
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<tr>
<td>[4-H_1]</td>
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<td>-5668.25896789</td>
<td>-5673.05545464</td>
</tr>
<tr>
<td>[3,4-H_2]</td>
<td>$S = 1/2$</td>
<td>-5668.85108690</td>
<td>-5673.64711609</td>
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<td>[3,5-H_2]</td>
<td>$S = 1/2$</td>
<td>-5668.81056393</td>
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<tr>
<td>[2-(N)(η^2-C_2H_4)]</td>
<td>$S = 0$</td>
<td>-5669.45821065</td>
<td>-5674.25654368</td>
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For examples of terminal transition metal nitride synthesis from coordinated ammine ligands employing other oxidants see (a) Eikey, R. A.; Abu-Omar, M. M.  


Disregarding potential redox activity, addition of three hydrogen atom equivalents to the iprPDI ligand in [1-(N)(η2-C2H4)] would generate a chelate bearing an unpaired electron in its neutral form in [2-(N)(η2-C2H4)]. See Experimental Section for details.


Control experiments established no reaction between $[1-(N)(\eta^2-C_2H_4)]$ and H$_2$ in the absence of [Rh–H] under these reaction conditions.


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