Nitrogen Fixation

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Catalytic Reduction of Dinitrogen to Ammonia by Molybdenum: Theory versus Experiment

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Molybdenum complexes that contain the triamidoamine ligand $[(RNCH_2CH_2)_3N]^{3-}$ ($R=3,5\text{-}(2,4,6\text{-}iPr_3C_6H_2)_2C_6H_3$) catalyze the reduction of dinitrogen to ammonia at 22 °C and 1 atm with protons from 2,6-dimethylpyridinium and electrons from decamethylchromocene. Several theoretical studies have been published that bear on the proposed intermediates in the catalytic dinitrogen reduction reaction and their reaction characteristics, including DFT calculations on $[(HIPTNCH_2CH_2)_3N]Mo$ species (HIPT = hexaisopropylterphenyl = $3,5\text{-}(2,4,6\text{-}iPr_3C_6H_2)_2C_6H_3$), which contain the actual triamidoamine ligand that is present in catalytic intermediates. Recent theoretical findings are compared with experimental findings for each proposed step in the catalytic reaction.

1. Introduction

Dinitrogen is "fixed" to ammonia in the environment under mild conditions by nitrogenases, the most studied and best-known being the FeMo nitrogenase,[1–4] on a scale that is estimated to be about 10^8 tons of ammonia per year.[5] Nitrogenases are known that contain vanadium instead of molybdenum (which function when molybdenum is absent and vanadium is available)[6–9] or iron (which function when both molybdenum and vanadium are absent).[10–13] Hundreds of man years have been invested in studying nitrogenases, an investment that continues today. The efficiency of forming ammonia versus hydrogen decreases dramatically in the order molybdenum→vanadium→iron; that is, the FeMo nitrogenase most efficiently uses electrons, approximately producing only one H_2 per N_2 reduced, the minimum of any system, in an $8\,e^-/8\,H^+$ process. However, in spite of a huge effort by many scientists over a period of more than forty years, no proof concerning the site and mechanism of dinitrogen reduction has been forthcoming.[14]

Isolation of the first dinitrogen complex,[15] $[Ru(NH_3)_5(N_2)]^{2+}$, sparked decades of research aimed toward the reduction of dinitrogen to ammonia catalytically under mild conditions in solution with protons and electrons, or toward the combination of dinitrogen with other elements in a selective manner under mild conditions.[16–24] Catalytic reduction of dinitrogen to ammonia in solution with protons and electrons has proven to be extraordinarily challenging; one reason is that protons are typically reduced to dihydrogen readily, whereas dinitrogen is relatively resistant to reduction. The principles of reduction of dinitrogen to ammonia at a single molybdenum(0) or tungsten(0) center were established in studies that began in the late 60s, primarily by the groups directed by Chatt[16,25] and Hidai,[17,26] but no catalytic reduction of dinitrogen to ammonia in the presence of protons and electrons was ever achieved.

A series of papers and review articles by A. E. Shilov describe the catalytic reduction of dinitrogen to hydrazine.[27–29] With time, a mixture of hydrazine and ammonia is established (ca. 10:1), presumably through metal-catalyzed disproportionation of some of the hydrazine into nitrogen and ammonia. Molybdenum is required for catalytic reduction of dinitrogen to hydrazine. The reaction is run in methanol in the presence of magnesium hydroxide and a strong reducing agent, such as sodium amalgam or titanium(III). As many as 1700 equivalents of nitrogen have been reduced with at least 25 % of the electrons going toward formation of dihydrogen. Few details concerning the mechanism of this reaction have been established, although it is believed that at least two metal centers are involved in the reduction process.

We began to explore early transition metal complexes containing the triamidoamine ligand, $[(RNCH_2CH_2)_3N]^{3-}$ or $[RN_3N]^{3-}$, in the early 1990s.[30] Initial work involved ligands in which R = trimethylsilyl or C_6F_5. We found that the most convenient way to prepare $[(RNCH_2CH_2)_3N]^{3-}$ ligands, in which R is an ordinary aryl, is through Buchwald–Hartwig

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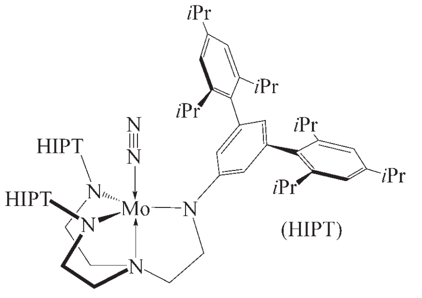
arylation[31,32] of triethylenetetramine. We were drawn to molybdenum complexes that contain the $[HIPTN_3N]^{3-}$ ligand, (HIPT = 3,5-(2,4,6-$i$$Pr_3C_6H_2)_2C_6H_3$, hexaisopropylterphenyl; see Scheme 1),[33,34] in part because it was found that $[(RNCH_2CH_2)_3N]^{3-}$ ligands in which R = 2,4,6-triisopropylphenyl, mesityl, or 2-methylphenyl would not form complexes with molybdenum.[31] The $[HIPTN_3N]^{3-}$ ligand was also designed to prevent formation of $[ArN_3N]Mo{-}N{=}N{-}Mo[ArN_3N]$ complexes that we believed to be relatively stable toward protons and electrons or that might lead to hydrazine formation instead of ammonia. The $[HIPTN_3N]^{3-}$ ligand also provides significant steric protection of a metal coordination site in a monometallic species, as well as increased solubility of complexes in nonpolar solvents.



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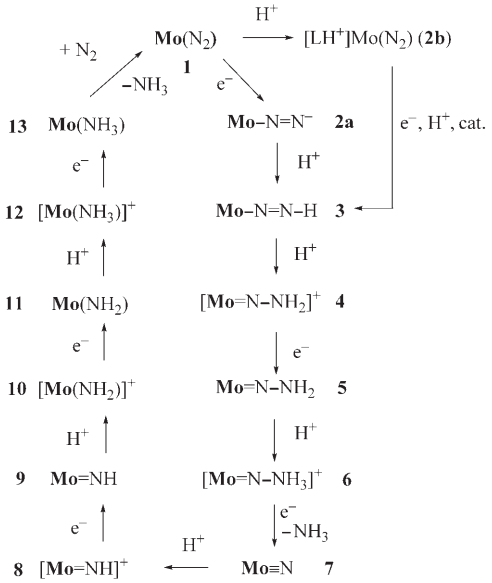
Scheme 1. The structure of $[HIPTN_3N]Mo(N_2)$, abbreviated **Mo**(N_2).

Eight of the proposed intermediates in a hypothetical "linear" reduction of dinitrogen (Scheme 2) were prepared and characterized by a variety of methods, including X-ray crystallography.[33–36] These include paramagnetic (low spin) **Mo**(N_2) (**Mo** = $[HIPTN_3N]$Mo, unless otherwise noted; **1**, Scheme 1), diamagnetic $[\mathbf{Mo}(N_2)]^-$ (**2a**), diamagnetic **Mo**–N=N–H (**3**), diamagnetic $[\mathbf{Mo}{=}N{-}NH_2][BAr'_4]$ (**4**; Ar′ = 3,5-$(CF_3)_2C_6H_3$), diamagnetic Mo≡N (**7**), diamagnetic $[\mathbf{Mo}{=}NH][BAr'_4]$ (**8**), paramagnetic $[\mathbf{Mo}(NH_3)][BAr'_4]$ (**12**), and paramagnetic (low spin) **Mo**(NH_3) (**13**). With the exception of **7**, all are extremely sensitive to oxygen and moisture. Several of these species then were employed successfully to reduce dinitrogen catalytically in heptane to ammonia with protons (in the form of [3,5-dimethylpyridinium]$[BAr'_4]$ and electrons (from decamethylchromocene).[35] About four equivalents of nitrogen (per molybdenum) are converted into ammonia (60–65 % yield versus reducing equivalents) with the balance of the reducing equivalents being used to form hydrogen. No hydrazine is formed (< 0.01 equivalent per molybdenum). We have been able to study several steps in the catalytic cycle in detail, and have shown that $[HIPTN_3N]$Cr,[37] $[HIPTN_3N]$W,[38] and $[HIPTN_3N]$V species[39] are not catalysts for the reduction of dinitrogen. We also have carried out studies of molybdenum complexes that contain some variation of the $[HIPTN_3N]^{3-}$ ligand[40,41] and have summarized recent dinitrogen reduction results in several publications.[42–44] Finally, we have shown that the success of the reduction depends dramatically upon the nature of the acid employed,[42] and that reduction is still catalytic if a weaker reducing agent, $CoCp_2$, is employed, although the yield of ammonia is approximately halved.[40] A cationic species has been detected that is believed to contain a proton bound to one of the amido nitrogens (**2b**, Scheme 2). It is proposed that an electron is added to **2b** and the resulting zwitterion is then isomerized catalytically by acid to **3**.



Scheme 2. Proposed intermediates in the reduction of dinitrogen at a $[HIPTN_3N]$Mo (**Mo**) center by the stepwise addition of protons and electrons.

Richard R. Schrock obtained his B.A. degree in 1967 from the University of California at Riverside, and his Ph.D. degree in Inorganic Chemistry in 1971 as a student of J. A. Osborn. After an NSF Postdoctoral Fellowship with Lord Jack Lewis at Cambridge University, he joined DuPont de Nemours. In 1975 he moved to the Massachusetts Institute of Technology, where he became Full Professor in 1980. The list of his awards includes the Nobel Prize in Chemistry in 2005. He is a member of the National Academy of Sciences. His interests include imido alkylidene catalysts for the metathesis of olefins, polymerizations involving alkylidenes, and the catalytic reduction of dinitrogen.

Several recent theoretical studies have been published that bear on the intermediates in the proposed catalytic dinitrogen reduction reaction and their reactions.[45–55] The first calculations (on a simplified ligand, $[(HNCH_2CH_2)_3N]^{3-}$ abbreviated to $[HN_3N]^{3-}$) were published by the Morokuma group in 2002.[50] They were concerned with a description of the "sigma *trans* promotion effect" in triamido molybdenum complexes and a comparison of binding of dinitrogen to four-coordinate versus five-coordinate triamido molybdenum(III) complexes. Calculations by Cao et al. on $[PhN_3N]$Mo species include a discussion of FeMo nitrogenase models;[45] the calculations employ ammonium as the acid and an iron–sulfur cluster as the electron source. Magistrato et al. also considered [PhN$_3$N]Mo species.[54] The Tuczek group published the results of DFT calculations for [HN$_3$N]$^{3-}$ species, such as {[HN$_3$N]Mo=N–NH$_2$}$^+$, {[HN$_3$N]Mo=N–NH$_2$}$^-$, [HN$_3$N]Mo(N$_2$), [HN$_3$N]Mo=N–NH$_2$, and {[HN$_3$N]Mo=N–NH$_3$}$^+$.[49] They carried out studies of the entire catalytic process, in which energies for the reduction and protonation steps are linked to the processes CrCp$^*_2$→[CrCp$^*_2$]$^+$ and [2,6-LutH]$^+$→2,6-Lut, the actual reagents employed in the catalytic reduction in heptane,[48,55] and have compared these studies with similar studies of hypothetical Chatt-type catalysts.[56] Reiher et al. have demonstrated to what extent the results of calculations vary with the R group in complexes that contain [RN$_3$N]$^{3-}$ ligands (e.g., R = H, Me, 3,5-Ph$_2$C$_6$H$_3$, or 3,5-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$).[46,47] Especially relevant are calculations for the full HIPT-substituted ligand system using CrCp$^*_2$ as the electron source and [2,6-LutH]$^+$ as the proton source.[46,51] Leitner and Hölscher consider the possibility of reducing dinitrogen with catalysts that contain HIPT-substituted ligands (M = Mo, Ru, Os), but with dihydrogen itself as the reducing agent.[53] The purpose of this paper is to summarize the major theoretical findings concerning [RN$_3$N]Mo species that are relevant to the proposed catalytic dinitrogen reduction scheme and to compare those data with what is known experimentally about [HIPTN$_3$N]Mo species. As results obtained for various reactions of [RN$_3$N]Mo species can vary by 20 kcal mol^{-1} or more, we will favor results for complexes that contain the [HIPTN$_3$N]$^{3-}$ ligand.[46,51]

2. The Catalytic Reduction of Dinitrogen

2.1. [HIPTN$_3$N]Mo and [HIPTN$_3$N]Mo(N$_2$) Species (Neutral, Anionic, Cationic)

The Morokuma group were the first to carry out DFT calculations on [HN$_3$N]Mo complexes.[50] They found that the $d_{x^2-y^2}$ and d_{xy} orbitals are shifted to high energy by strong antibonding interactions with the amido ligand orbitals in the trigonal plane, and the d_{z^2} orbital is shifted above the d_{xz} and d_{yz} orbitals by interaction with the apical amine donor along the z axis. The doublet state of [HN$_3$N]Mo is lowest in energy, but the quartet is only 3.1 kcal mol^{-1} higher in energy. Calculations by Reiher et al., in which the full ligand is employed, also suggest that the quartet is higher in energy than the doublet, but by 11.0 kcal mol^{-1}.[46,51] It should be noted that planar, trigonally symmetric triamido d^3 molybdenum complexes are high spin.[57–59] Tuczek and Studt calculated $\Delta G°$ for binding dinitrogen to [HN$_3$N]Mo to be −14.2 kcal mol^{-1}.[48] Only energy (enthalpy) differences were considered by Magistrato et al., who calculated the binding energy ΔE to be −29 kcal mol^{-1} for [PhN$_3$N]Mo,[54] and Reiher et al., who calculated ΔE to be −37.8 kcal mol^{-1} for binding N$_2$ to [HIPTN$_3$N]Mo [Eq (1)].[46,51]

$$[\mathrm{HIPTN_3N}]\mathrm{Mo(N_2)} \rightarrow [\mathrm{HIPTN_3N}]\mathrm{Mo} + \mathrm{N_2} \quad \Delta E = 37.8\ \mathrm{kcal\,mol^{-1}} \qquad (1)$$

Binding of dinitrogen to readily accessible low-spin [HIPTN$_3$N]Mo to give low-spin [HIPTN$_3$N]Mo(N$_2$) might be expected to take place with little or no barrier. The S = 3/2 state in [HN$_3$N]Mo(N$_2$) is 27.8 kcal mol^{-1} higher in energy than the S = 1/2 state,[48] an energy difference that should take S = 3/2 [RN$_3$N]Mo(N$_2$) species out of consideration. A recent EPR study confirms that d^3 **Mo**(N$_2$) is low spin (S = 1/2), with the z^2 orbital being substantially higher in energy than the (xz, yz) e$_g$ set.[60]

It is known that **Mo**(^{15}N$_2$) is converted into **Mo**(N$_2$) under 1 atmosphere of dinitrogen at a rate that is first order in molybdenum, with a half-life of ca. 36 h at 15 psi ($k = 5.3 \times 10^{-6}\ \mathrm{s^{-1}}$, $\Delta G^{\neq} = 24.8$ kcal mol^{-1}),[34] 32 h at 30 psi,[42] and 30 h at 55 psi.[42] These results suggest that the exchange of ^{15}N$_2$ for N$_2$ is independent of dinitrogen pressure in this range. Therefore dinitrogen exchange is dissociative, with "[HIPTN$_3$N]Mo" being the intermediate. It should be noted that [HIPTN$_3$N]Cr is high spin and binds CO surprisingly slowly to give low spin [HIPTN$_3$N]Cr(CO); [HIPTN$_3$N]Cr does not bind N$_2$, nor is dinitrogen reduced by [HIPTN$_3$N]Cr species under the standard conditions employed for molybdenum.[37] Interestingly, exchange of ^{15}N$_2$ for N$_2$ in the analogous molybdenum complex that contains the hexa-*tert*-butyl-substituted ligand [HTBTN$_3$N]Mo(N$_2$) takes place approximately 20 times more slowly ($t_{1/2} \approx 750$ h at 22 °C or $k = 2.6 \times 10^{-7}\ \mathrm{s^{-1}}$) than in [HIPTN$_3$N]Mo(N$_2$), and is also independent of pressure ($k = 3.1 \times 10^{-7}\ \mathrm{s^{-1}}$ at 5 atm).[40] As the values for the N–N stretching vibration ν_{NN} in [HTBTN$_3$N]Mo(N$_2$) and [HIPTN$_3$N]Mo(N$_2$) are identical ($\nu_{\mathrm{NN}} = 1990\ \mathrm{cm^{-1}}$), the Mo–N$_2$ bond strength must be the same in the two species. The difference in the unimolecular rate constant for loss of dinitrogen in [HTBTN$_3$N]Mo(N$_2$) and [HIPTN$_3$N]Mo(N$_2$) could be ascribed to sterics; i.e., dissociated dinitrogen in the more crowded [HTBTN$_3$N]Mo(N$_2$) system could be trapped near the metal and recoordinate to the metal more often than it escapes through the ligand canopy compared to the [HIPTN$_3$N]Mo(N$_2$) system. Another possibility is that dinitrogen is not lost directly along the z axis in a C_3 symmetric species, but only from a species that is distorted from C_3 symmetry, or from a species in which the dinitrogen is bound side-on.[61–63] The [HTBTN$_3$N]$^{3-}$ ligand might more efficiently hold dinitrogen in an end-on binding mode. Other scenarios are possible; for example, a reversible agostic C–H interaction or oxidative addition of a C–H bond to the metal may be concomitant with dinitrogen loss, and any C–H interaction with molybdenum could differ substantially in detail for complexes of the [HTBTN$_3$N]$^{3-}$ and [HIPTN$_3$N]$^{3-}$ ligands. We do not know whether N$_2$ loss in [HIPTN$_3$N]Mo(N$_2$) is also slow relative to some less crowded analogue, only that the rate of N$_2$ loss from [HTBTN$_3$N]Mo(N$_2$) is slow relatively to the rate of loss in [HIPTN$_3$N]Mo(N$_2$). Therefore, we cannot be certain that the rate constant observed for [HIPTN$_3$N]Mo(N$_2$) is an upper limit for unimolecular loss of dinitrogen. In any case, we do know the rate constant for loss of ^{15}N$_2$ from [HIPTN$_3$N]Mo(^{15}N$_2$), which is an important fact that is necessary for an argument later in Section 2.8. A calculated $\Delta E = 37.8$ kcal mol^{-1} for loss of N$_2$ from **Mo**(N$_2$)[51] should be compared with the observed $\Delta G^{\neq} = 24.8$ kcal mol^{-1} for a first-order overall exchange of dinitrogen, in which [HIPTN$_3$N]Mo is the proposed intermediate. If what is likely to be a relatively large and positive ΔS value is assumed in the process in which dinitrogen is lost, ΔG° could be about equal to $\Delta G^\ddagger$ or even smaller, as suggested by the calculated value $\Delta G^\circ = 14.2$ kcal mol^{-1} for dissociation of dinitrogen from $[HN_3N]Mo(N_2)$.[48]

The cyclic voltammogram (CV) of **Mo**(N_2) reveals a reversible oxidation to give $[\mathbf{Mo}(N_2)]^+$ and a reversible reduction to give $[\mathbf{Mo}(N_2)]^-$. A variety of $[\mathbf{Mo}(N_2)]^-$ complexes have been isolated with various cations, whereas $[\mathbf{Mo}(N_2)]^+$ has only been observed in solution IR spectra. The rate of loss of dinitrogen varies dramatically in the three species. There is essentially no exchange between $[Bu_4N]$ $[\mathbf{Mo}(^{15}N_2)]$ and N_2 (1 atm) in C_6D_6 over a period of weeks; a strong reducing agent such as $CoCp^*_2$ must be present to limit the amount of adventitious oxidation of $[\mathbf{Mo}(N_2)]^-$ to **Mo**(N_2) and a subsequent, more rapid, exchange. At the other extreme, dinitrogen exchanges in minutes in $[\mathbf{Mo}(^{15}N_2)]^+$.[42] All exchange data are consistent with calculated ΔE values for dinitrogen dissociation in the cationic, neutral, and anionic $[HIPTN_3N]^{3-}$ species of 26.5, 37.8, and 57.0 kcal mol^{-1}, respectively,[51] and $\tilde{\nu}_{NN}$ stretches at 2255 cm^{-1}, 1989 cm^{-1}, and 1855 cm^{-1} for each, respectively.

2.2. $[HIPTN_3N]Mo(N_2) \rightarrow Mo{-}N{=}NH$ (First Proton/Electron)

Addition of the first proton/electron pair converts **Mo**(N_2) into **Mo**–N=NH. It has been found that **Mo**(N_2) is readily converted into **Mo**–N=NH in benzene in the presence of [2,6-lutidinium][BAr′$_4$] and cobaltocene. Three possible mechanisms for carrying out this transformation have been proposed.[36] One mechanism involves protonation of N_β in the dinitrogen ligand to yield $[\mathbf{Mo}(N_2H)]^+$ followed by addition of an electron. The second involves reduction of **Mo**(N_2) to $[\mathbf{Mo}(N_2)]^-$ followed by protonation of N_β in the anion. The third involves a "proton-catalyzed" addition of an electron followed by a proton. We will discuss these proposals in that order. Conversion of **Mo**(N_2) into **Mo**-N=NH takes place with any combination of one of three acids ($[Et_3NH][OTf]$, $[Et_3NH][BAr'_4]$, $[2{,}6\text{-LutH}][BAr'_4]$) and of two reductants ($CoCp_2$ and $CrCp^*_2$) and is rapid in all cases. No reduction of **Mo**(N_2) takes place in the absence of acid.

Transfer of a proton to N_β in $[HIPTN_3N]Mo(N_2)$ from lutidinium is calculated to have a value of $\Delta E \approx 0$ kcal mol^{-1},[51] and $\Delta E = -14.3$ kcal mol^{-1} for the subsequent addition of an electron from $CrCp^*_2$ to $\{[HIPTN_3N]Mo(N_2H)\}^+$. These data are obtained using calculated intrinsic reaction energies, an ionization energy of 115.9 kcal mol^{-1} for $CrCp^*_2$, and the energy required for deprotonating lutidinium in vacuo of 239.1 kcal mol^{-1}.[51] Therefore, protonation of N_β in **Mo**(N_2) followed by addition of an electron would appear to be a viable pathway for converting **Mo**(N_2) into **Mo**–N=NH, at least from a thermodynamic perspective, and not accounting for entropic and solvent effects. The attempted generation of "$[\mathbf{Mo}N{=}NH]^+$" electrochemically by oxidation of **Mo**N=NH (in PhF with 0.1 M $[Bu_4N][BAr'_4]$ electrolyte, room temperature, 500 mV s^{-1}) led only to multiple irreversible oxidation waves near the ferrocene/ferrocenium couple, which is consistent with a high instability of $[\mathbf{Mo}N{=}NH]^+$.[36]

Addition of an electron from $CrCp^*_2$ to $[HIPTN_3N]Mo(N_2)$ to give $\{[HIPTN_3N]Mo(N_2)\}^-$ is calculated to be quite endothermic ($\Delta E = 71.6$ kcal mol^{-1}),[46,51] which will be typical for all neutral species shown in Scheme 2. Experimentally it is known that **Mo**(N_2) is reduced reversibly to $[\mathbf{Mo}(N_2)]^-$ at -2.01 V in C_6H_5F or -1.81 V in THF (both versus $FeCp_2/FeCp_2^+$). As the cobaltocene redox couple is found at -1.33 V in THF, Cp_2Co is too weak a reducing agent (by ca. 500 mV) to reduce **Mo**(N_2) to $[\mathbf{Mo}(N_2)]^-$ to any significant degree, even if precipitation of the resulting $[Cp_2Co]^+$ is taken into account; yet **Mo**(N_2) is converted into **Mo**-N=NH in benzene in the presence of lutidinium and Cp_2Co. In view of these facts, it seems unlikely that $[\mathbf{Mo}(N_2)]^-$ is actually formed in the catalytic reaction by reduction of **Mo**(N_2) followed by protonation of $[\mathbf{Mo}(N_2)]^-$.

Addition of one equivalent of [2,6-LutH][BAr′$_4$] to **Mo**(N_2) in fluorobenzene in the absence of a reducing agent reveals that about 20% of a new species is formed with a $\tilde{\nu}_{NN}$ absorption shifted by 67 cm^{-1} to higher energy compared to that for **Mo**(N_2), consistent with decreased backbonding into the dinitrogen ligand. No new low-energy absorption is observed, as would be expected if N_β of the dinitrogen ligand were protonated. We also have found that about 40% of $[HIPTN_3N]Mo(CO)$ ($\tilde{\nu}_{CO} = 1885$ cm^{-1}) is protonated by one equivalent of [2,6-lutidinium][BAr′$_4$] in fluorobenzene to yield "$\{[HIPTN_3N]Mo(CO)H\}^+$" in which $\tilde{\nu}_{CO} = 1932$ cm^{-1} ($\Delta = 47$ cm^{-1}).[64] This result appears to be analogous to protonation of **Mo**(N_2) and further suggests that neither N_2 nor CO is protonated directly. The smaller shift of 47 cm^{-1} upon adding a proton to **Mo**(CO) compared to 67 cm^{-1} upon adding a proton to **Mo**(N_2) is what might be expected, as the CO ligand is more strongly bound than N_2 and therefore less perturbed by any change in the backbonding ability of molybdenum. Unfortunately, although the amount of protonated **Mo**(N_2) (**2b**, Scheme 2) increases with the amount of [2,6-LutH][BAr′$_4$] added, attempts to measure the equilibrium between **1** and **2b** have failed as a consequence of slow decomposition of both compounds with time and as more acid is added. We propose that the ligand is at least partially removed at high acid concentrations to give other species, and "free" ligand is present in increasing amounts with time. Therefore the possibility of measuring any well-behaved equilibrium between **1** and **2b** seems unlikely at this stage. We also have not yet been able to obtain any useful information concerning the precise nature of **2b** from IR or NMR spectroscopic studies.

The two most Brønsted basic sites in **Mo**(N_2) are an amido nitrogen or the metal itself. In a calculation in which the full $[HIPTN_3N]^{3-}$ ligand is employed, Reiher et al. finds that protonation of an amido nitrogen atom by ludidinium takes place with $\Delta E = -9.0$ kcal mol^{-1}[46,51] and they could find no evidence for formation of $[\mathbf{Mo}(N_2)(H)]^+$ on the potential energy hypersurface; the proton always moved to a nearby amido nitrogen atom during optimization. They therefore concluded that a $[\mathbf{Mo}(N_2)(H)]^+$ species is not part of the catalytic cycle, and that protonation of an amido nitrogen is thermodynamically more favored, by ca. 9 kcal mol^{-1}, than protonation of the dinitrogen ligand. Therefore, of the three proposed pathways for conversion of **Mo**(N_2) into **Mo**–N=

NH, the "proton-catalyzed reductive protonation" of **1** (via **2b**) to give **3** [Eq. (2), where $[L]^{3-}$ is $[HIPTN_3N]^{3-}$][51] is now the favored mechanism for conversion of $\mathbf{Mo}(N_2)$ into $\mathbf{Mo}$–N=NH, largely because protonation of the ligand is more exothermic. On the basis of "one-pot" calculations, Reiher

$$\underset{\mathbf{1}}{[L]\mathbf{Mo}(N_2)} \xrightarrow[-9.0\ \text{kcal mol}^{-1}]{H^+} \underset{\mathbf{2b}}{[LH^+]\mathbf{Mo}(N_2)} \xrightarrow[+\,6.7\ \text{kcal mol}^{-1}]{e^-} [LH^+]\mathbf{Mo}(N_2^-)$$

$$\xrightarrow[-22.4\ \text{kcal mol}^{-1}]{H^+} [LH^+]\mathbf{Mo}(NNH) \xrightarrow[+\,9.8\ \text{kcal mol}^{-1}]{-H^+} \underset{\mathbf{3}}{[L]\mathbf{Mo}\text{–}N{=}NH} \qquad (2)$$

et al. believe that kinetic conclusions based solely on the thermodynamic aspects of protonation reactions are justified, i.e., protonation reactions of $\mathbf{Mo}(N_2)$ and $\mathbf{Mo}(N)$ with lutidinium have barriers of only about 5 kcal mol^{-1}. Further calculations on this subject, although difficult, should prove to be interesting. It also should be noted that base-assisted proton migrations by lutidine bound within the ligand's superstructure, e.g., $[LH^+]Mo(N_2^-)\rightarrow\mathbf{3}$, are variations that would appear to be viable.

2.3. Mo–N=NH→[Mo=N-NH$_2$]$^+$→Mo=NNH$_2$ (Second Proton/Electron)

Experimentally it has been found that protonation of **Mo**–N=NH with 1 equivalent of $[2,6\text{-LutH}][BAr'_4]$ in C_6D_6 yields a 44:56 equilibrium mixture of **Mo**–N=NH and $[\mathbf{Mo}{=}NNH_2]^+$ after 15 min at 22 °C. In ^1H NMR spectra, resonances for **Mo**–N=NH and $[\mathbf{Mo}{=}NNH_2]^+$ are broadened only slightly, which suggests that the proton exchange rate between **Mo**–N=NH and $\mathbf{Mo}{=}N\text{–}NH_2^+$ is not fast on the NMR timescale under these conditions. Proton exchange almost certainly could not take place directly in a reaction that is bimolecular in molybdenum, but would require some base, e.g., lutidine, as the proton carrier, a process that one would not necessarily expect to be fast on the NMR timescale.

Reduction of **3** by $CrCp^*_2$ is calculated to be highly disfavored ($\Delta E = 134$ kcal mol^{-1}). Protonation of **Mo**–N=NH by lutidinium at N_β of the diazenido ligand ($\Delta E = -22.5$ kcal mol^{-1}) is favored by 12.7 kcal mol^{-1} over protonation of the amido nitrogen.[51] Subsequent addition of an electron to $[\mathbf{Mo}{=}NNH_2]^+$ to give $\mathbf{Mo}{=}NNH_2$ has a calculated value of $\Delta E = 22.3$ kcal mol^{-1}, so overall addition of the second proton/electron pair [conversion of **3** into **5**, Eq. (3)] is approximately thermoneutral.[51]

$$\underset{\mathbf{3}}{\mathbf{Mo}\text{–}N{=}NH} \xrightarrow[-22.5\ \text{kcal mol}^{-1}]{H^+} \underset{\mathbf{4}}{[\mathbf{Mo}\text{–}N{=}NH_2]^+} \xrightarrow[+\,22.3\ \text{kcal mol}^{-1}]{e^-} \underset{\mathbf{5}}{\mathbf{Mo}\text{–}N{=}NH_2} \qquad (3)$$

There is evidence that decomposition of **Mo**–N=NH is accelerated by lutidinium;[34] the mechanism of which is not known. Therefore it is possible that Mo–N=NH species that contain ligands smaller than $[HIPTN_3N]^{3-}$ (see Section 2.10) fail to varying degrees as catalysts, one reason being that the diazenido species are catalytically decomposed by the acid employed to protonate them at N_β, and possibly also by the lutidine that accumulates in the reaction.[41] Therefore the stability of the **Mo**–N=NH species, and its successful protonation to give $[\mathbf{Mo}\text{–}N{=}NH_2]^+$, are both remarkable in their own right.

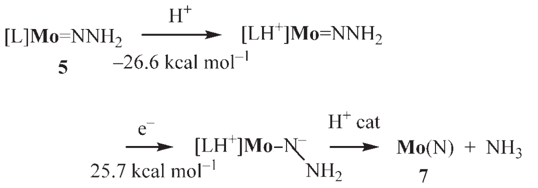
Experimentally it has been shown that treatment of $[\mathbf{Mo}{=}NNH_2]^+$ with three different metallocenes ($CoCp_2$, $CrCp^*_2$ or $CoCp^*_2$) in C_6D_6 results in complete consumption of $[\mathbf{Mo}{=}NNH_2]^+$ at room temperature over a period of ten minutes and formation of complex mixtures that contain **Mo**–N=NH, $\mathbf{Mo}{\equiv}N$, $[\mathbf{Mo}(NH_3)]^+$, $\mathbf{Mo}(NH_3)$, and ammonia;[36] no $\mathbf{Mo}{=}NNH_2$ could be observed. However, all of these molybdenum species are stable and known to yield ammonia upon further addition of protons and electrons. The NH_2 ligand in $[HN_3N]Mo{=}NNH_2$ ($S = 1/2$) is calculated to be bent at N_α, which produces a lone pair at this nitrogen atom.[49] The same bending at N_α is also calculated in $[HIPTN_3N]Mo{=}NNH_2$[51] and $[PhN_3N]Mo{=}NNH_2$.[54] The SOMO is a d_{xz} orbital that is antibonding with respect to the long pair on N_α. Bending at N_α creates the possibility that N_α could be protonated or that the NNH_2 unit could bind in an η^2 fashion. Either (or both) may be the source of the relatively dramatic disproportionations that are observed when $[\mathbf{Mo}{=}NNH_2]^+$ is reduced. Details of the disproportions are not known, but formation of nitrogen-based radicals is not out of the question. The extent to which disproportionations take place in competition with protonation of $\mathbf{Mo}{=}NNH_2$ at N_β to yield **6** under the reaction conditions is not known.

The fact that the NH_2 ligand in $\mathbf{Mo}{=}N\text{–}NH_2$ is bent at N_α raises the issue as to whether the diazenido(2−) ligand bound to molybdenum(V) should be viewed instead as isodiazene bound to molybdenum(III), and whether a *cis*- or *trans*-diazene ligand complex of molybdenum(III) is accessible through isomerization of $\mathbf{Mo}{=}N\text{–}NH_2$. Reiher et al. calculated that the *trans*-diazene complex is only 4.2 kcal mol^{-1} higher in energy than $\mathbf{Mo}{=}N\text{–}NH_2$ whereas the *cis*-diazene complex is 9.1 kcal mol^{-1} higher in energy.[51] They concluded that the *trans*-diazene isomer in particular could be accessible through isomerization of isodiazene. Such a transformation could be facilitated by a proton catalyst, which further clouds any understanding of disproportionations of $\mathbf{Mo}{=}NNH_2$.

2.4. Mo=NNH$_2$→[Mo=NNH$_3$]$^+$→Mo≡N (Third Proton/Electron)

The $\{[HN_3N]Mo{=}NNH_3\}^+$ species is calculated to have a structure in which the Mo–N–N unit is bent at N_α.[48] The SOMO has M–N_α in-plane π antibonding character and also an antibonding interaction between the lone pair on N_α and a p orbital on N_β. These antibonding interactions give rise to elongated Mo–N (1.85 Å) and N–N (1.57 Å) bonds. $\{[HN_3N]Mo{=}NNH_3\}^+$ is reduced with no barrier and with $\Delta G^\circ = -72.7$ kcal mol^{-1}, the largest of any free energy change in the proposed catalytic cycle shown in Scheme 2. Similar results were found for the $[PhN_3N]Mo$ system.[51]

In calculations dealing with the full $[HIPTN_3N]Mo$ system, Reiher et al.[51] consider protonation of an amido nitrogen in steps other than $\mathbf{1}\rightarrow\mathbf{3}$, for example for $\mathbf{5}\rightarrow\mathbf{7}$ [Eq. (4)]. It should be noted that reduction of **5** by $CrCp^*_2$ is



$$\underset{\mathbf{5}}{[\mathrm{L}]\mathbf{Mo}{=}\mathrm{NNH_2}} \xrightarrow[-26.6\ \mathrm{kcal\,mol^{-1}}]{\mathrm{H^+}} [\mathrm{LH^+}]\mathbf{Mo}{=}\mathrm{NNH_2} \xrightarrow[25.7\ \mathrm{kcal\,mol^{-1}}]{e^-} [\mathrm{LH^+}]\mathbf{Mo}{-}\mathrm{N^-}(\mathrm{NH_2}) \xrightarrow{\mathrm{H^+\ cat}} \underset{\mathbf{7}}{\mathbf{Mo}(\mathrm{N})} + \mathrm{NH_3} \qquad (4)$$

calculated to be highly disfavored ($\Delta E = 134$ kcal mol^{-1}). He finds that protonation of an amido nitrogen in **Mo**=NNH$_2$ (**5**) is actually more favored [−26.6 kcal mol^{-1}; Eq. (4)] than protonation of the β nitrogen in the NNH$_2$ ligand in **Mo**=NNH$_2$ [−9.3 kcal mol^{-1}; Eq. (5)], which is the traditional proposal in a Chatt-like scheme for dinitrogen reduction. Interestingly, attempts to locate this structure failed when HIPT was replaced by Me or H. [51] Subsequent addition of an electron followed by a proton-catalyzed rearrangement would lead to **7** plus ammonia [Eq. (4)]. However, Reiher et al. also found that [**Mo**=N-NH$_3$]$^+$ can lose NH$_3$ spontaneously to yield "[**Mo**(N)]$^+$" [Eq. (5)],[51] which is an oxidized

$$\underset{\mathbf{5}}{[\mathrm{L}]\mathbf{Mo}{=}\mathrm{NNH_2}} \xrightarrow[-9.3\ \mathrm{kcal\,mol^{-1}}]{\mathrm{H^+}} \{[\mathrm{L}]\mathbf{Mo}{-}\mathrm{NNH_3}\}^+ \xrightarrow[-14.3\ \mathrm{kcal\,mol^{-1}}]{-\mathrm{NH_3}} \{[\mathrm{L}]\mathbf{Mo}(\mathrm{N})\}^+ \xrightarrow[-24.9\ \mathrm{kcal\,mol^{-1}}]{e^-} \underset{\mathbf{7}}{[\mathrm{L}]\mathbf{Mo}(\mathrm{N})} \qquad (5)$$

form of the highly favorable nitride and which is then readily reduced to **7**. The positive charge in [**Mo**(N$_2$)]$^+$ is smeared throughout the [HIPTN$_3$N]$^{3-}$ ligand, not the **Mo**(N$_2$) system, so [**Mo**(N$_2$)]$^+$ is actually a molybdenum(VI) nitride. The exothermicity of the steps in Equation (5) suggests that this is a viable reaction pathway from a thermodynamic perspective.

2.5. Mo≡N→[Mo=NH]$^+$→Mo=NH (Fourth Proton/Electron)

It has been reported that **Mo**≡N can be protonated with [H(OEt$_2$)$_2$][BAr'$_4$] in diethyl ether to yield [**Mo**=NH][BAr'$_4$].[34] Protonation of **Mo**≡N with 1.1 equivalents of [2,6-LutH][BAr'$_4$] in C$_6$D$_6$ gave a 75:25 mixture of **Mo**≡N and [**Mo**=NH]$^+$ after 15 min at room temperature; this mixture remained unchanged after a further 20 h. [**Mo**=NH]$^+$ is a well-characterized species. Reaction of [**Mo**=NH]$^+$ with 2.2 equivalents of CrCp$_2^*$ in C$_6$D$_6$ instantly yields what is proposed to be **Mo**=NH. **Mo**=NH can be generated in solution and stored for a period of time at room temperature, as long as a small amount of CrCp$_2^*$ is present. In the absence of CrCp$_2^*$ and in the presence of [**Mo**=NH]$^+$ as a catalyst (generated through adventitious oxidation of **Mo**=NH), **Mo**=NH is slowly converted into a mixture of **Mo**≡N and **Mo**(NH$_2$). Thus, when a substoichiometric amount of CrCp$_2^*$ (ca. 0.6 equiv) was used to reduce [**Mo**=NH]$^+$ in C$_6$D$_6$, the initially formed **Mo**=NH smoothly decayed over a period of hours to form a mixture of **Mo**≡N and **Mo**(NH$_2$) and finally a mixture of **Mo**≡N and [**Mo**(NH$_3$)]$^+$.[36]

Protonation of the nitride in [HIPTN$_3$N]Mo≡N (**7**) by lutidinium to give **8** is calculated to be quite favorable [$\Delta E = -20.3$ kcal mol^{-1}, Eq. (6)],[51] whereas reduction of **8** to **9** by

$$\underset{\mathbf{7}}{\mathbf{Mo}(\mathrm{N})} \xrightarrow[-20.3\ \mathrm{kcal\,mol^{-1}}]{\mathrm{H^+}} \underset{\mathbf{8}}{[\mathbf{Mo}{=}\mathrm{NH}]^+} \xrightarrow[18.4\ \mathrm{kcal\,mol^{-1}}]{e^-} \underset{\mathbf{9}}{\mathbf{Mo}{=}\mathrm{NH}} \qquad (6)$$

CrCp$_2^*$ is calculated to have a value of $\Delta E = 18.4$ kcal mol^{-1}. Protonation of a ligand amido nitrogen in **7** is calculated to proceed with a value of $\Delta E = -7.6$ kcal mol^{-1}, i.e., it is disfavored compared to protonation of the nitride nitrogen by 12.7 kcal mol^{-1}. Reduction of **7** by CrCp$_2^*$ is calculated to be highly disfavored ($\Delta E = 92.3$ kcal mol^{-1}), as usual for neutral species.

2.6. Mo=NH→[Mo(NH$_2$)]$^+$→Mo(NH$_2$) (Fifth Proton/Electron)

Protonation of the imido ligand in **Mo**=NH by lutidinium [$\Delta E = -33.6$ kcal mol^{-1}, Eq. (7)] is favored over protonation of a ligand amido nitrogen ($\Delta E = -20.5$ kcal mol^{-1}) or reduction of **Mo**=NH ($\Delta E = 93.9$ kcal mol^{-1}).[51] Subsequent reduction of **10** with CrCp$_2^*$ is calculated to have a value of $\Delta E = 8.7$ kcal mol^{-1}.

$$\underset{\mathbf{9}}{\mathbf{Mo}{=}\mathrm{NH}} \xrightarrow[-33.6\ \mathrm{kcal\,mol^{-1}}]{\mathrm{H^+}} \underset{\mathbf{10}}{[\mathbf{Mo}{=}\mathrm{NH_2}]^+} \xrightarrow[8.7\ \mathrm{kcal\,mol^{-1}}]{e^-} \underset{\mathbf{11}}{\mathbf{Mo}(\mathrm{NH_2})} \qquad (7)$$

[HN$_3$N]Mo(NH$_2$) is calculated to have two closely spaced spin states (S = 0 and S = 1), with S = 1 being the lower in energy by 3.4 kcal mol^{-1}, whereas low-spin **Mo**(NH$_2$) is calculated to be lower in energy by 1.8 kcal mol^{-1}. Experimentally, **Mo**(NH$_2$) can be produced through deprotonation of [**Mo**(NH$_3$)]$^+$ with LiN(SiMe$_3$)$_2$ in THF; [**Mo**(NH$_3$)]$^+$ is not deprotonated by Et$_3$N. The ^{1}H NMR spectrum of **Mo**(NH$_2$) features methylene backbone resonances at −3.0 and −40.1 ppm, and a temperature dependence that is consistent with a S = 0 ground state and a dynamic high-spin/low-spin (HS/LS) equilibrium at room temperature. A HS/LS equilibrium was proposed in the related substituted imido species, [RN$_3$N]Mo(NMe$_2$) (R = Me$_3$Si, C$_6$F$_5$) on the basis of similar significantly shifted and temperature-dependent resonances in proton NMR spectra.[65] The reaction between [**Mo**(NH$_3$)]$^+$ and LiN(SiMe$_3$)$_2$ also produces small and variable amounts of **Mo**(N$_2$) and **Mo**(NH$_3$). Attempted isolation of **Mo**(NH$_2$) led to the formation of **Mo**≡N.

2.7. Mo(NH$_2$)→[Mo(NH$_3$)]$^+$→Mo(NH$_3$) (Sixth Proton/Electron)

Protonation of [HN$_3$N]Mo(NH$_2$) to yield {[HN$_3$N]Mo(NH$_3$)}$^+$ is facile; {[HN$_3$N]Mo(NH$_3$)}$^+$ has an S = 1 ground state with an S = 0 state that is 12.7 kcal mol^{-1} higher in energy.[48] Reiher et al. found the energy difference between the S = 1 and S = 0 states (9.2 to 12.2 kcal mol^{-1}) to depend upon the density functional employed.[47] The change in free energy in the protonation of [HN$_3$N]Mo(NH$_2$) (S = 1) to give {[HN$_3$N]Mo(NH$_3$)}$^+$ (S = 1) is −25.8 kcal mol^{-1}.[48] Subsequent reduction of {[HN$_3$N]Mo(NH$_3$)}$^+$ to [HN$_3$N]Mo(NH$_3$) is endergonic for CrCp$^*_2$ (2.7 kcal mol^{-1}) and CoCp$_2$ (27.9 kcal mol^{-1}). The ground state of [HN$_3$N]Mo(NH$_3$) has S = 1/2; the S = 3/2 state is 37.7 kcal mol^{-1} higher in energy.

As shown in Equation (8), **Mo**(NH$_2$) is calculated to be protonated easily. For [**Mo**(NH$_3$)]$^+$ the energy difference between the ground (S = 1) and S = 0 state is calculated to be 10.7 kcal mol^{-1}, whereas the ground (S = 1/2) state of **Mo**(NH$_3$) is calculated to be 23.7 kcal mol^{-1} below the S = 3/2 state.

$$\underset{\mathbf{11}}{\mathbf{Mo}(\mathrm{NH_2})} \xrightarrow[-21.2\ \mathrm{kcal\ mol^{-1}}]{\mathrm{H^+}} \underset{\mathbf{12}}{[\mathbf{Mo}(\mathrm{NH_3})]^+} \xrightarrow[4.5\ \mathrm{kcal\ mol^{-1}}]{\mathrm{e^-}} \underset{\mathbf{13}}{\mathbf{Mo}(\mathrm{NH_3})} \qquad (8)$$

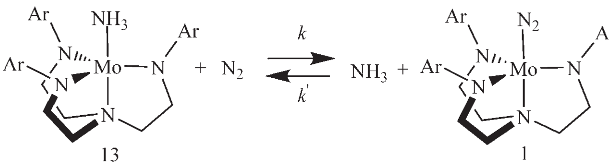
High-spin **Mo**(NH$_3$) is therefore unlikely to be relevant in the chemistry of **Mo**(NH$_3$). Reduction of [**Mo**(NH$_3$)]$^+$ requires 4.5 kcal mol^{-1}. Experimentally, [**Mo**(NH$_3$)]$^+$ can be reduced to **Mo**(NH$_3$) completely by CrCp$^*_2$ in benzene, possibly in part as a consequence of the [CrCp$^*_2$]$^+$ salt crystallizing out of solution.

Electrochemical reduction of [**Mo**(NH$_3$)]$^+$ is fully reversible in both THF and PhF.[36] Interestingly, at slow scan rates (ca. 10 mV s)$^{-1}$, waves corresponding to the reversible **Mo**(N$_2$)$^{0/-}$ couple become discernible near −1.8 V in THF. Therefore, replacement of ammonia in **Mo**(NH$_3$) with dinitrogen takes place to an observable extent (ca. 10%) after beginning the [**Mo**(NH$_3$)]$^+$ 10 mV s $^{-1}$ reduction sweep, over a period of about 30–40 seconds. We propose that conversion of **Mo**(NH$_3$) into **Mo**(N$_2$) can be observed in the electrochemical experiment because ammonia diffuses away from the electrode surface into the bulk solution relatively rapidly, thereby preventing the back reaction between ammonia and **Mo**(N$_2$) near the electrode surface. On the basis of the electrochemical results we believe that **Mo**(NH$_3$) is converted into **Mo**(N$_2$) on a time scale of minutes ($t_{1/2} \approx 35$ min; see Section 2.8).

In the latest paper on the full ligand system, Reiher et al. found that protonation of **Mo**(NH$_2$) at the NH$_2$ ligand ($\Delta E = -21.2$ kcal mol^{-1}) and at an amido nitrogen ($\Delta E = -17.3$ kcal mol^{-1}) are equally likely, but reduction of [**Mo**(NH$_3$)]$^+$ is more favorable.[51] Therefore, they conclude that protonation at a [HIPTN$_3$N]$^{3-}$ amido nitrogen is not part of the conversion of [**Mo**(NH$_3$)]$^+$ into **Mo**(NH$_3$), or in fact any part of the proposed reduction pathway in which a single nitrogen is bound to the metal (**7**–**13**). Loss of ammonia from [**Mo**(NH$_3$)]$^+$ requires an input of 35.1 kcal mol^{-1}, but only 28.2 kcal mol^{-1} is required to remove ammonia from **Mo**(NH$_3$).

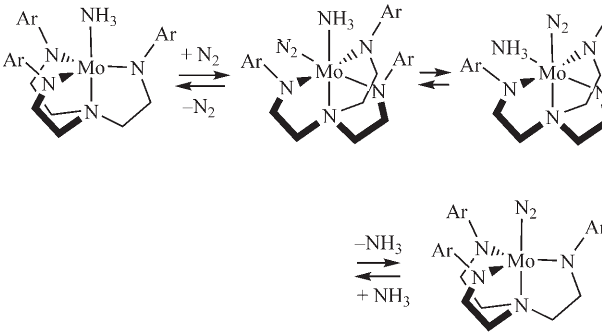
2.8. Interconversion of Mo(NH$_3$) and Mo(N$_2$)

It is known that **Mo**(NH$_3$) reacts readily with nitrogen to yield **Mo**(N$_2$), and that 1–2 h are required to establish the equilibrium between **Mo**(NH$_3$), dinitrogen, **Mo**(N$_2$), and ammonia [Eq. (9)] in a container that is closed except for sampling. The conversion of **Mo**(NH$_3$) into **Mo**(N$_2$) cannot be probed accurately, as the ammonia that is formed in solution not only back-reacts rapidly with **Mo**(N$_2$) to give **Mo**(NH$_3$), but also slowly enters the headspace above solvents such as benzene or heptane; the time required for ammonia to enter the headspace will depend on the size of the headspace and how rapidly the reaction is stirred. The equilibrium constant for this reaction [see Eq. (9)] is around 0.1 in benzene at 22 °C. By definition, ammonia that is formed will inhibit conversion of **13** into **1**.



(9)

In heptane, the conversion of **Mo**(NH$_3$) into **Mo**(N$_2$) follows what is close to first-order kinetics in molybdenum, with a half-life for the conversion at 22 °C and 1 atm of about 115 min. At 2 atm (15 psi overpressure) and under the same conditions, the half-life is ca. 45 min, which suggests that the conversion depends on the concentration of dinitrogen to the first power.[42] Conversion of **Mo**(NH$_3$) into **Mo**(N$_2$) is dramatically accelerated at 1 atm in the presence of 4 equivalents of BPh$_3$ ($t_{1/2}$ is ca. 35 min), and the ln(1−Mo/Mo$_\infty$) plot is strictly linear, because (it is proposed) BPh$_3$ removes much or all of the ammonia formed in solution relatively efficiently as Ph$_3$BNH$_3$.[42] Of course, it has to be true that the forward and reverse reactions in the conversion of **13** into **1** proceed through the same transition state. We know that ^{15}N$_2$ must first be lost from **Mo**(^{15}N$_2$) to yield [HIPTN$_3$N]Mo [Eq. 10], and that $t_{1/2}$ for dinitrogen exchange is ca. 36 h. Therefore, it cannot be true that dinitrogen must be lost from **1** before **1** can react with ammonia to yield **13**. Therefore ammonia must react with **1**, and dinitrogen must react with **13**, both to give **Mo**(N$_2$)(NH$_3$), the common intermediate in the interconversion of **Mo**(NH$_3$) and **Mo**(N$_2$). Whether **Mo**(N$_2$)(NH$_3$) is six-coordinate or five-coordinate (in which the amine donor is not bound) is not known.



(10)

Tuczek et al. found that dissociation of ammonia from [HN$_3$N]Mo(NH$_3$) is endergonic by 8.8 kcal mol^{-1}, whereas addition of dinitrogen to [HN$_3$N]Mo is exergonic ($\Delta G° =$

-14.2 kcal mol^{-1}).[48] Therefore, the overall substitution of ammonia by nitrogen in the $[HN_3N]^{3-}$ system is exergonic by 5.4 kcal mol^{-1}, strongly favoring $[HN_3N]Mo(N_2)$ ($K_{eq} = 8600$). Reiher et al. found that $\Delta E = -9.2$ to -9.9 kcal mol^{-1} for exchange of ammonia with dinitrogen in the 3,5-$Ph_2C_6H_3$ or HMT (hexamethylterphenyl) systems. In the full HIPT system, $\Delta E = -9.8$ kcal mol^{-1}. Finally, Magistrato et al. found that dissociation of ammonia from $[PhN_3N]Mo(NH_3)$ is endothermic by 21 kcal mol^{-1}, which leads to a value of $\Delta E = -8$ kcal mol^{-1} for exchange of ammonia for dinitrogen.[54] Experimentally, the equilibrium constant K between **Mo**(NH_3) and **Mo**(N_2) is observed to be about 0.1, or $\Delta G^o = 1.4$ kcal mol^{-1}. The approximate thermal neutrality of the conversion of **Mo**(NH_3) into **Mo**(N_2) along with a $t_{1/2}$ that can be as short as ca. 35 min (under 1 atm of N_2 in the presence of BPh_3) is what allows the reaction to "turn over" under the experimental conditions employed. It should be noted that attempts to form **Mo**L complexes through reduction of [**Mo**L]$^+$ species (L is THF or 2,6-lutidine) under dinitrogen yielded only **Mo**(N_2).[42] Even CV studies in fluorobenzene do not allow **Mo**(THF) to be observed before it is converted into **Mo**(N_2); the CV results suggest that conversion of **Mo**(THF) into **Mo**(N_2) is perhaps three or more orders of magnitude faster than the conversion of **Mo**(NH_3) into **Mo**(N_2). Details of the interconversion of **Mo**L complexes and **Mo**(N_2) are not known at present, nor have CV studies been carried out under argon.

Reiher et al.[47] initially argued that dinitrogen cannot attack the metal in the mesityl species from the side through one "channel" in the ligand, because the reaction cavity is not large enough to accommodate both NH_3 and N_2 at the same time. Thermal movement of phenyl substituents could open a new channel, but the old channel would close. However, if dinitrogen could attack the metal to give $[MesN_3N]Mo(NH_3)(N_2)$, a subsequent reorientation of the NH_3/N_2 pair in concert with a closing of one channel and opening of another would allow ammonia to be lost from an equatorial position to yield the dinitrogen complex [cf. Equation (10)]. The reverse would convert the $[MesN_3N]Mo(N_2)$ complex into the $[MesN_3N]Mo(NH_3)$ complex. Dissociation of apical nitrogen in the intermediate "six-coordinate" species was not considered as part of the exchange process. At this stage they suggested that the pathway involved loss of NH_3. However, arguments presented above, in particular the energy required for dissociation of N_2 from **Mo**(N_2), would appear to prevent interconversion of **Mo**(NH_3) into **Mo**(N_2) on the timescale of less than 1 hour at 22 °C. The slow exchange of N_2 in the $[HTBTN_3N]Mo(N_2)$ complex (20 times slower) reveals that something interesting is going on that strongly depends upon sterics or the precise nature of the ligand, but details are not yet known.

In preliminary studies, Reiher and his group have employed molecular dynamics calculations for the conversion of **Mo**(NH_3) into **Mo**(N_2), and they observed a six-coordinate intermediate that is formed upon attack of N_2 in the plane of the three amido nitrogens, as shown in Equation (10).[51] They therefore conclude that six-coordinate $[HIPTN_3N]Mo(NH_3)(N_2)$ can form, and that the $[HIPTN_3N]^{3-}$ ligand actually is relatively flexible, not rigid.

The result of a study[46,51] of complexes that contain the full $[HIPTN_3N]^{3-}$ ligand suggest that ammonia loss becomes more facile in the series [**Mo**(NH_3)]$^+$ < **Mo**(NH_3) < [**Mo**(NH_3)]$^-$, although the last complex has not been observed. Dinitrogen is bound more strongly in the order [**Mo**(N_2)]$^+$ < **Mo**(N_2) < [**Mo**(N_2)]$^-$, all in accord with experimental observations. For the overall conversion, ΔE for the exchange of ammonia for dinitrogen is found to be -34.9, -9.7, and $+8.7$ kcal mol^{-1} for the anionic, neutral, and cationic manifolds. If we can assume that ΔS will be small for the exchange, $\Delta E = -9.7$ kcal mol^{-1} implies that the equilibrium constant is still much larger than what is observed experimentally (0.1) at 22 °C in benzene. It is clearly difficult to calculate equilibrium constants accurately because of errors inherent in the calculations.

2.9. Net Reactions

Reiher and co-workers have been able to calculate the change in energy for several net reactions of interest in the proposed scheme for dinitrogen reduction by molybdenum species that employ lutidinium as the acid and a variety of metallocenes as reducing agents (Table 1).[46,51] All reactions in which $CrCp^*_2$ is employed are thermoneutral to exothermic, with the most exothermic being that in which ammonia is formed (-48.5 kcal mol^{-1}). It should be noted that conversion of **Mo**(NH_3) into **Mo**(N_2) is also exothermic by -9.8 kcal mol^{-1}. Two reactions in which $CoCp_2$ is employed (**Mo**(NNH)→**Mo**(NNH_2) and **Mo**(N)→**Mo**(NH)) are slightly endothermic ($+4.3$ kcal mol^{-1} and $+2.6$ kcal mol^{-1}, respectively), in keeping with the known lower efficiency for catalytic dinitrogen reduction when $CoCp_2$ is employed as the reducing agent. All the reaction steps are strongly exothermic when a stronger reducing agent ($CoCp^*_2$) is employed and two reaction steps (**Mo**(NNH)→**Mo**(NNH_2) and **Mo**(N)→**Mo**(NH)) are strongly endothermic when a weaker reducing agent ($CrCp_2$) is employed. Experimental data are not yet available for reductions that employ $CoCp^*_2$ or $CrCp_2$.

Table 1: Net energies (in kcal mol^{-1}) for reactions that employ $CrCp^*_2$ or $CoCp_2$ as the reducing agent and lutidinium as the acid.[46,51]

Starting Complex	Product(s)	$CrCp^*_2$	$CoCp_2$
Mo(N_2)	**Mo**(NNH)	−15.1	−10.5
Mo(NNH)	**Mo**(NNH_2)	ca. 0	+4.3
Mo(NNH_2)	**Mo**(N) + NH_3	−48.5	−44.0
Mo(N)	**Mo**(NH)	−1.9	+2.6
Mo(NH)	**Mo**(NH_2)	−25.1	−20.3
Mo(NH_2)	**Mo**(NH_3)	−16.5	−12.0

2.10. Alternatives to the $[HIPTN_3N]^{3-}$ Ligand

Alternatives to the $[HIPTN_3N]^{3-}$ ligand that have been explored include $[p\mathrm{BrHIPTN_3N}]^{3-}$, a ligand in which the *para* position of the central phenyl ring is brominated, $[HMTN_3N]^{3-}$ (HMT = hexamethylterphenyl), and $[HTBTN_3N]^{3-}$ (HTBT = hexa-*tert*-butylterphenyl).[40] Only the first example was found to be a catalyst for the formation of ammonia, and in yields only slightly less than those observed for $[HIPTN_3N]^{3-}$ derivatives. One measurement of the rate of conversion of $[HTBTN_3N]Mo(NH_3)$ into $[HTBTN_3N]Mo(N_2)$ under conditions analogous to those employed for **Mo**(NH_3) revealed that the half-life for conversion is approximately 30 h instead of 1–2 h for conversion of **Mo**(NH_3) into **Mo**(N_2), and proton and electron transfer is at least an order of magnitude slower than in the $[HIPTN_3N]^{3-}$ system. It remains to be seen whether proton and electron transfer in the $[HIPTN_3N]^{3-}$ system are restricted to some degree compared to rates in hypothetical, less-crowded ligand systems.

Complexes with mixed ligands were also synthesized. In these $[hybrid]^{3-}$ ligands, one of the three aryl rings is a smaller 3,5-disubstituted substituent (dimethoxy, dimethyl, or $bis(CF_3)$ groups).[41] [hybrid]Mo species will not reduce dinitrogen because a shunt in the catalytic cycle consumes protons and electrons to yield hydrogen rapidly relative to the rate of dinitrogen reduction. Evidence suggests that the shunt consists of a lutidine-catalyzed decomposition of [hybrid]-Mo−N=NH. How dihydrogen is produced when lutidine (or triethylamine) reacts with [hybrid]Mo−N=NH is not yet known, but an extremely rapid, base-dependent, bimolecular decomposition of [hybrid]Mo−N=NH through a Mo−N−$N(H)_2N$−N−Mo transition state is one possibility. It is also possible that [hybrid]Mo−N=NH species are decomposed by acid, although full experimental results are not yet available. Mo−N=NH species (as opposed to Mo−N=NR species) are extraordinarily rare in the literature, perhaps in part because of their fragile nature as a consequence of multiple possible modes of decomposition.

3. Summary

The system described herein is the only abiological catalytic reduction of dinitrogen to ammonia with protons and electrons under mild conditions. The only other catalytic dinitrogen reduction system produces hydrazine as the primary product, although molybdenum is again required.[27] There have been reports of ammonia generation in systems that contain metals from Groups 4–8, but none is catalytic in that metal. However, it is much more difficult to demonstrate catalytic turnover in the presence of protons and electrons than stoichiometric or substoichiometric ammonia formation under some set of conditions. For later metals, such as iron, one of many challenges almost certainly will be to suppress hydrogenase activity in favor of nitrogenase activity.[66]

Calculations have now been completed that support proposals concerning the mechanism of catalytic reduction of dinitrogen with $[HIPTN_3N]Mo$ catalysts in the presence of [2,6-lutidinium]$[BAr'_4]$ as the acid and decamethylchromocene as the reducing agent. The conversion of **1** into **3** is now believed to proceed via **2b** (Scheme 2), in which a proton has been added to an amido nitrogen before an electron is added to the **Mo**(N_2) system, although initial protonation of the dinitrogen ligand is still a viable option. Addition of a second proton to the negatively charged N_β atom of the dinitrogen ligand and loss of the first proton from the protonated amido nitrogen then produces **3**. Conversion of **1** into **3** is only possible because **3** is also relatively stable toward bimolecular decomposition or decomposition by the acid or its conjugate base (2,5-lutidine); conversion of **3** into **4** and reduction of **4** can then proceed. Conversion of **3** into **4** is remarkable if one considers that in some circumstances the acid could catalytically decompose **3**; when the ligand is less sterically protecting than $[HIPTN_3N]^{3-}$, this may in fact be the case. Reiher et al.[51] consider protonation of a ligand amido nitrogen in all the subsequent protonation/reduction steps (e.g., **5**→**7**, or **9**→**11**) as a means of facilitating those conversions, and that pathway is in fact energetically preferred for **5**→**7**. Protonation of the ligand amido nitrogen is especially important for the first half of the catalytic sequence in Scheme 2. Surprisingly, conversion of **13** into **1** involves formation of a six-coordinate **Mo**$(NH_3)(N_2)$ intermediate, thus avoiding formation of the "naked" **Mo** species, which is believed to be too high in energy to be formed on the timescale of the conversion of **13** into **1** in the catalytic reaction. The calculations reveal that **Mo**(NNH)→**Mo**(NNH_2) and **Mo**(N)→**Mo**(NH) are energetically the most difficult steps; in contrast, ammonia can form spontaneously from $[\mathbf{Mo}(NNH_3)]^+$, and an electron need not be added.

We can now begin to see why the nature of the acid is of great importance in the dinitrogen reduction sequence. 2,6-Lutidine has been shown to bind to molybdenum with difficulty, that is, not strictly *trans* to the amine donor, in the crystallographically characterized complex [**Mo**(2,6-lutidine)]$[BAr'_4]$.[36] Therefore, it is now believed[51] that 2,6-lutidinium can attack a $\mathbf{Mo}N_2H_y$ species through the HIPT substituents at the "top", to deliver a proton to a β nitrogen atom or even to an α nitrogen atom in a $\mathbf{Mo}NH_y$ species as the HIPT groups bend back and twist to allow that to happen. Experimentally, it is known that the success of dinitrogen reduction is sensitive to the nature of the pyridinium acid, with $[2,6\text{-}Et_2C_6H_3NH][BAr'_4]$ giving only a 23% yield of ammonia from dinitrogen, and $[2,6\text{-}Ph_2C_6H_3NH][BAr'_4]$ and $[3,5\text{-}Me_2C_6H_3NH][BAr'_4]$ giving no ammonia from dinitrogen. It might be surmised that too much steric hindrance prevents the acid from protonating the N_xH_y ligand in the $\mathbf{Mo}N_xH_y$ species, and too little steric hindrance (and/or solubility, etc.) leads to other problems, including more rapid hydrogen formation. Of course, the solubility of the acid in heptane (or lack thereof) is another potentially important variable that has not been elucidated.

There are many potentially important details of the overall mechanism that are still shrouded in mystery, among them any direct connection between reduction of dinitrogen and formation of at least one equivalent of dihydrogen, the minimum amount formed in any natural nitrogenase. It also is not known whether any C−H activation in the ligand is part of the overall reduction scheme. Finally, it is interesting to note that calculations for reduction of dinitrogen by the $[HN_3N]Mo$ system under conditions analogous to those employed experimentally for the $[HIPTN_3N]Mo$ system suggest that the amount of free energy required for preparing the reducing and acid equivalents in heptane [Eq. (11)] is 186 kcal mol^{-1}, whereas the actual reduction [Eq. (12)] is exergonic (-198.5 kcal mol^{-1}).[48] Combining equations (11) and (12) gives a standard free energy change for the reaction shown in Equation (13) of -12.5 kcal mol^{-1}, which should be compared with -3.86 kcal mol^{-1}, the free energy of formation of ammonia in the gas phase at 298 K.[67] The free-energy input calculated for the natural nitrogenase system is 197.0 kcal mol^{-1}, a value that is remarkably close to that observed for the reaction shown in Equation (11).[48,68]

$$3\,H_2 + 6\,[CrCp^*_2]^+ + 6\,Lut \rightarrow 6\,CrCp^*_2 + [6\,LutH]^+ \qquad (11)$$

$$N_2 + 6\,CrCp^*_2 + 6\,[LutH]^+ \rightarrow 2\,NH_3 + 6\,[CrCp^*_2]^+ + 6\,Lut \qquad (12)$$

$$3\,H_2 + N_2 \rightarrow 2\,NH_3 \qquad (13)$$

Now that we understand some of the principles behind catalytic dinitrogen reduction by [HIPTN$_3$N]Mo catalysts, we can begin to contemplate how to make the system more efficient. Experimental results suggest that catalytic turnover is relatively efficient initially, but cannot be pushed far beyond about 4 equivalents of dinitrogen reduced, probably as a consequence of the [HIPTN$_3$N]$^{3-}$ ligand being removed from the metal. Therefore, a good place to start is to synthesize a ligand that is more difficult to remove from the metal. However, whatever is necessary to accomplish that feat, which itself is not a trivial problem, must not disturb features of the ligand that make it successful (steric protection, flexibility, etc.). In the long run, it also is highly desirable to learn whether it is possible to carry out reduction of dinitrogen with H$^+$/H$^-$ combinations, especially those produced through heterolytic splitting of dihydrogen,[69,70] which would thereby allow dinitrogen to be reduced with dihydrogen at room temperature and pressure. Whether a heterogeneous (supported) catalyst would be inherently more efficient compared to a homogeneous catalyst solely because it is heterogeneous is also an interesting question. None of these challenges is likely to be met easily, but in the process we will learn a great deal about how to manage protons and electrons for the reduction of difficult substrates that could be useful in other circumstances.

4. Comments on Nitrogenases

The structural elucidation of the Fe/Mo nitrogenase core in 1992[71,72] generated a great deal of speculation as to where and how dinitrogen is reduced, and led to theoretical calculations and further experiments on mutant variants. However, in spite of much additional work, there is still no proof how and where dinitrogen itself is reduced in the enzyme.

Several arguments have been offered that are said to support the proposal that dinitrogen is reduced at an iron site. It is often stated that if an environment in the protein around the Fe$_7$ cluster is altered and nitrogenase activity decreases, then the site where dinitrogen is bound and reduced necessarily is nearby, i.e., an iron site. Such a conclusion is not valid, as disruption of proton and/or electron transfer that involves the Fe$_7$ cluster could still lead to lower activity for dinitrogen reduction at a molybdenum center.

Another argument as to why the molybdenum center cannot be the site of dinitrogen reduction is that sixfold coordination at molybdenum is achieved by binding of a homocitrate in a bidentate fashion and a histidine. This statement ignores the fact that the structure has been determined for the enzyme in its resting state, and that introduction of electrons and protons could labilize the homocitrate. It is not necessary to labilize the histidine, as four-coordinate molybdenum is sufficient to bind and reduce dinitrogen. Calculations now suggest that homocitrate can be labile under the right circumstances and that dinitrogen would bind strongly to molybdenum.[13,45] It seems unlikely that any of the three Mo−S bonds is likely to be cleaved, although one or more protons could be added (reversibly) to one or more sulfido ligands anywhere in the Fe$_7$S$_9$Mo core to create a more reducible cluster or metal center.

A third argument as to why the molybdenum center cannot be the site of dinitrogen reduction has been that both Fe/V and "all-iron" nitrogenases are known. However, the fact that homogeneous extracts have not been prepared for either the vanadium or all-iron enzymes, and the fact that contamination by molybdenum has been encountered in past studies of the Fe/V nitrogenase,[6] suggest that this argument is not on firm scientific ground. It could be just as likely (assuming for the moment that all nitrogenases have basically the same Fe$_7$M core[73,74]) that dinitrogen is reduced at the metal site (Mo, V, Fe) with dramatically decreasing efficiencies. Between 3.5 and 4 equivalents of dihydrogen are produced per nitrogen reduced in the Fe/V nitrogenase, whereas the "all-iron nitrogenase" produces largely dihydrogen.

The demonstration that dinitrogen can be reduced with protons and electrons in heptane to ammonia and dihydrogen by [HIPTN$_3$N]Mo catalysts at 22 °C, in which the minimum oxidation state of molybdenum is 3+, is strong evidence that a single four-coordinate molybdenum center in vivo is capable of activating and reducing dinitrogen to ammonia catalytically. Some might still argue that this finding proves nothing about the enzyme, as the [HIPTN$_3$N]$^{3-}$ ligand is not biologically relevant. Technically this statement is correct, but I contend that the fundamental characteristics of a metal, coordination number, and available oxidation states are as important, or even more important, than the precise nature of a ligand set that is based upon what is available in nature and whose structural and functional details have been highly tuned through evolution over many millions of years. It also should be noted that a homogeneous reduction is likely to be inherently more difficult than a heterogeneous one, as bimetallic reactions (electron transfer and decompositions) are possible in solution that are not possible between molybdenum sites within the enzyme. For example, the enzymatic analogue of the rare **Mo**−N=NH species could not possibly decompose in a reaction that is bimolecular in molybdenum.

Dinitrogen reduction by the FeMo nitrogenase has made it one of the most awe-inspiring catalytic reactions known in biology. I can only hope that the understanding we have achieved in the abiological system discussed herein ultimately will help further our understanding of the biological process and will lead to the development of an efficient abiological catalytic reduction of dinitrogen.

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