Molybdenum Triamidoamine Systems. Reactions Involving Dihydrogen Relevant to Catalytic Reduction of Dinitrogen

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Abstract

[HIPTN$_3$N]Mo(N$_2$) (**Mo**N$_2$) ([HIPTN$_3$N]$^{3-}$ = [(HIPTNCH$_2$CH$_2$)$_3$N]$^{3-}$ where HIPT = 3,5-(2,4,6-i-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) reacts with dihydrogen slowly (days) at 22 °C to yield [HIPTN$_3$N]MoH$_2$ (**Mo**H$_2$), a compound whose properties are most consistent with it being a dihydrogen complex of Mo(III). The intermediate in the slow reaction between **Mo**N$_2$ and H$_2$ is proposed to be [HIPTN$_3$N]Mo (**Mo**). In contrast, **Mo**N$_2$, **Mo**NH$_3$, and **Mo**H$_2$ are interconverted rapidly in the presence of H$_2$, N$_2$, and NH$_3$, and **Mo**H$_2$ is the lowest energy of the three Mo compounds. Catalytic runs with **Mo**H$_2$ as a catalyst suggest that it is competent for reduction of N$_2$ with protons and electrons under standard conditions. [HIPTN$_3$N]MoH$_2$ reacts rapidly with HD to yield a mixture of [HIPTN$_3$N]MoH$_2$, [HIPTN$_3$N]MoD$_2$, and [HIPTN$_3$N]MoHD, and rapidly catalyzes H/D exchange between H$_2$ and D$_2$. **Mo**H$_2$ reacts readily with ethylene, PMe$_3$, and CO to yield monoadducts. Reduction of dinitrogen to ammonia in the presence of 32 equivalents of added hydrogen (vs. Mo) is not catalytic, consistent with dihydrogen being an inhibitor of dinitrogen reduction.

Introduction

Dinitrogen is reduced to ammonia under mild conditions by nitrogenases, the most studied and best known being the FeMo nitrogenase.[1] In all cases dihydrogen is also formed. The minimum amount of dihydrogen, approximately one equivalent per dinitrogen reduced, is formed in the FeMo nitrogenase system at high pressures (e.g. 50 atm N$_2$).[2] Formation of one equivalent of dihydrogen per two equivalents of ammonia amounts to a 75% yield of ammonia in terms of reducing equivalents employed. At 1 atm the yields of ammonia vary between 40 and 60%.[3] How dihydrogen is formed and the extent to which its formation is coupled to the reduction of dinitrogen are still unknown. One possibility is that dihydrogen is formed through one or more metal-catalyzed reactions at sites that are different from where dinitrogen is reduced. Another view is that one equivalent of dihydrogen is formed at the same site where dinitrogen is reduced and one equivalent of dihydrogen *must* be formed for every dinitrogen reduced. What is known with certainty is that dihydrogen inhibits dinitrogen reduction.[3] Furthermore, under a D$_2$ atmosphere two equivalents of HD are formed during turnover of dinitrogen to ammonia, but no deuterium is incorporated into the solvent (H$_2$O) or into the ammonia formed.[1a]

In 2003 it was shown that dinitrogen can be reduced catalytically to ammonia with protons and electrons by molybdenum complexes that contain the [HIPTN$_3$N]$^{3-}$ ligand ([HIPTN$_3$N]$^{3-}$ = [(HIPTNCH$_2$CH$_2$)$_3$N]$^{3-}$ where HIPT is 3,5-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$), examples being [HIPTN$_3$N]Mo(N$_2$), [HIPTN$_3$N]Mo-N=NH, and [HIPTN$_3$N]Mo(NH$_3$).[4] The only other abiological catalytic reduction of dinitrogen by protons and electrons requires molybdenum but produces hydrazine as a primary product, with ammonia being formed through a relatively common metal-catalyzed disproportionation of hydrazine to ammonia and dinitrogen.[5] In the [HIPTN$_3$N]Mo system dinitrogen binds end-on to a single Mo and is reduced by repeated alternate addition of a proton and an electron in the manner first proposed by Chatt.[6] The

experimental results in various triamidoamine molybdenum systems are now strongly supported by numerous theoretical studies, the most relevant being studies that employ the full $[HIPTN_3N]^{3-}$ ligand.[7] These and other theoretical results are consistent with the experimental findings and proposed mechanism.[8] Ammonia is formed selectively (no hydrazine is detected) with an efficiency of 55–65% in electrons. The remaining reducing equivalents are used to form dihydrogen. The amount of ammonia increases from 63 % at 1 atm (15 psi) to 71 % at 30 psi when $[HIPTN_3N]Mo(N_2)$ is employed.[9] Experiments have not yet been conducted at pressures above 30 psi. The amount of dinitrogen that can be reduced is limited to ~4 equivalents under the conditions employed, in large part because the $[HIPTN_3N]^{3-}$ ligand is removed from the metal in the presence of protons and reducing agent. It is clear that ammonia is an inhibitor as a consequence of the necessary conversion of $[HIPTN_3N]Mo(NH_3)$ (**Mo**NH_3) to **Mo**N_2 via intermediate **Mo**$(NH_3)(N_2)$ and because the equilibrium constant for this equilibrium ($[\mathbf{Mo}N_2][NH_3]/[\mathbf{Mo}NH_3][N_2]$) is 0.1 in benzene at 22°C.

Since dihydrogen is formed along with ammonia in the $[HIPTN_3N]Mo$ system we became interested in the dihydrogen chemistry of **Mo**N_2 and of other $[HIPTN_3N]Mo$ derivatives that have been isolated and characterized. We also wanted to understand why **Mo**H is as efficient a catalyst precursor as $[HIPTN_3N]Mo$ complexes that are proposed to lie on the catalytic pathway, e.g., **Mo**N_2 or **Mo**-N=NH.[10] Selected reactions that involve dihydrogen and various $[HIPTN_3N]Mo$ complexes are reported here.

Results

Synthesis of [HIPTN$_3$N]Mo(H$_2$)

$[HIPTN_3N]Mo(N_2)$ (**Mo**N_2) reacts with dihydrogen slowly (2–3 days at 22 °C in C_6D_6) in solution to yield $[HIPTN_3N]Mo(H_2)$ (**Mo**H_2). By ^1H NMR after 48 hours the resonances corresponding to **Mo**N_2 are no longer visible if the atmosphere is removed and replaced with hydrogen after 24 hours. Addition of dinitrogen to **Mo**H_2 leads to slow reformation of **Mo**N_2. A magnetic susceptibility measurement on **Mo**H_2 in solution (Evans method; μ_{eff} = 1.4–1.5 BM) is consistent with S = ½ and therefore with **Mo**H_2 being either a d^1 or a low spin d^3 species. **Mo**N_2 reacts with D_2 to yield **Mo**D_2 at the same rate as **Mo**N_2 reacts with H_2. (A convenient method of distinguishing **Mo**D_2, **Mo**H_2, and **Mo**HD is described later.) The ability to prepare **Mo**D_2 rules out any H/D scrambling that might result from reversible CH activation in the ligand and subsequent exchange of D for H. Attempts to prepare **Mo**HD from **Mo**N_2 and HD resulted in formation of a 1:2:1 mixture of **Mo**H_2, **Mo**HD and **Mo**D_2. No IR absorption assignable to some IR active MoH or MoD mode could be found for either **Mo**H_2 or **Mo**D_2 in pentane at 22°C. The absence of any readily observed MoH IR modes is more consistent with **Mo**H_2 being a Mo(III) dihydrogen complex than a Mo(V) dihydride.[11]

A persistent impurity present in early syntheses of **Mo**H_2 turned out to be **Mo**Cl, traces of which are formed upon oxidation of $[\mathbf{Mo}N_2]^-$ with $ZnCl_2$.[12] We found that oxidation of $[\mathbf{Mo}N_2]^-$ with zinc acetate instead of zinc chloride led to samples of **Mo**N_2 that were free of **Mo**Cl, and therefore samples of **Mo**H_2 that were free of **Mo**Cl. Unfortunately, we were not able to obtain crystals of **Mo**H_2 suitable for a complete X-ray structural study. Crystals obtained from a dilute pentane solution diffracted poorly, although it was clear from the preliminary structural solution that the $[HIPTN_3N]^{3-}$ ligand was coordinated to the metal in the usual manner to give essentially a trigonal monopyramidal species, and nothing could be observed in the coordination pocket.

MoH_2 also can be prepared by heating solid samples of **Mo**N_2 under an atmosphere of dihydrogen at 60 °C for one week. Traces of an unidentified yellow species appear at temperatures above 70 °C. It is difficult to push the reaction to completion at 60 °C in the solid state unless the sample of **Mo**N_2 is ground to a fine powder and the atmosphere is refreshed

periodically with dihydrogen. Even then, a trace (~1 %) of **Mo**N_2 (according to NMR spectra) always seems to be present in the final product. At 60 °C the risk of some irreversible decomposition is significant, so synthesis in solution at 22 °C is the preferred method.

MoH_2 is extremely sensitive towards traces of oxygen and water and toward dinitrogen, both in solution and in the solid phase. Even in the solid state samples of **Mo**H_2 under dinitrogen at −30 °C slowly form some **Mo**N_2. **Mo**H_2 also decomposes slowly *in vacuo* at approximately the same rate as it reacts with dinitrogen to yield **Mo**N_2. For example, after three days *in vacuo* virtually all of the original **Mo**H_2 has decomposed. Attempts to crystallize and identify the decomposition product or products of **Mo**H_2 have been unsuccessful. The final decomposition product does not react with dihydrogen to reform **Mo**H_2 and no free ligand is found in NMR spectra of partially decomposed samples. Multiple attempts to obtain a satisfactory elemental analysis of **Mo**H_2 failed. We conclude that **Mo**H_2 is not stable over the long term in the absence of hydrogen. Therefore, samples are best prepared as needed, although they can be stored in solution or in the solid state under 1 atm of dihydrogen. The amount of **Mo**H_2 in solution can be followed conveniently through observation of a resonance for the three equivalent para protons on the central phenyl rings in the HIPT substituents (hereafter referred to as the H_p resonance) at 5.12 ppm at 22 °C. (See below for other NMR details.) Although various studies (see later section) suggest that **Mo** is the intermediate in the conversion of **Mo**H_2 into **Mo**N_2, and vice versa, no evidence for formation of a stable "naked" species, **Mo**, has yet been obtained. It should be noted that **Mo**N_2 does *not* decompose to any significant degree *in vacuo* under conditions where **Mo**H_2 does.

MoH_2 reacts readily with ethylene, CO, and PMe$_3$. Addition of ethylene to **Mo**H_2 results in formation of **Mo**(C_2H_4),[13] with only a trace of H_2 (~ 1% in solution) and ethane (~33% in solution versus an internal standard) being observed, according the NMR spectra of **Mo**H_2 under an ethylene atmosphere (C_6D_6, 22 °C, 12h). (The amounts of H_2 and ethane in the gas phase were not determined.) The reaction is complete in a much shorter time than is required if the reaction were to proceed via formation of **Mo**. According to these results ethylene is hydrogenated to a significant extent. Since a solution of **Mo**(C_2H_4) in C_6D_6 at 22 °C under a hydrogen atmosphere is unchanged for weeks, ethane must be formed when ethylene attacks **Mo**H_2. Formation of ethane is most readily explained in classic terms, i.e., reaction of ethylene with a Mo(V) dihydride to give an ethyl hydride intermediate followed by reductive elimination. The Mo(V) dihydride need not be the ground state as long as it is readily accessible, i.e., from a Mo(III) dihydrogen complex.

MoCO[13] is formed immediately upon exposure of a solution of **Mo**H_2 (or a solid sample more slowly) to an atmosphere of CO. However, the amount of dihydrogen formed as a product of this reaction when it was carried out in solution or in the solid state on samples that had been exposed to vacuum for some time was found to be less than one equivalent, typically between 0.30 and 0.70 equivalents, depending on the sample's history. However, when freshly prepared samples of **Mo**H_2 in toluene were degassed and treated with CO, 0.95±0.05, 0.86±0.08, and 0.93±0.02 equivalents of H_2 were found in the atmosphere above the solution in three different experiments. Therefore **Mo**H_2 clearly contains one equivalent of hydrogen.

A solution of **Mo**H_2 turned red after one hour upon addition of trimethylphosphine and red **Mo**(PMe$_3$) was isolated in good yield (55% recrystallized) after 24 hours. The NMR spectrum of **Mo**(PMe$_3$) is very similar to that of **Mo**N_2 and **Mo**CO. Again less than one equivalent of dihydrogen was found in the gas phase when typically prepared **Mo**H_2 samples in toluene were treated with several equivalents of PMe$_3$.

The results of the reactions between **Mo**H_2 and ethylene, CO, and PMe$_3$ suggest that only one equivalent of dihydrogen is present in **Mo**H_2. However, the speed of these reactions also

suggests that these reactions do not proceed through loss of dihydrogen to give intermediate **Mo**, but through attack by ethylene, CO, and PMe$_3$ on **MoH$_2$**. None of these results settles the question concerning whether **MoH$_2$** is a dihydrogen complex or a classic dihydride, something in between, or something else entirely. (See later.)

The variable temperature NMR spectrum of **MoH$_2$** is shown in Figure 1. At −60 °C four backbone methylene protons can be observed at 9 (barely visible), −4, −40, and −62 ppm as a consequence of a "locking" of the ligand backbone in one C$_3$ conformation at low temperature, a known property of triamidoamine complexes.[14] As shown in Figure 2 at −60 °C the H$_p$ resonance is found at 4.4 ppm (#) and six isopropyl methine resonances (*) are present, consistent with only one type of HIPT substituent being present and each HIPT being in some locked, "twisted" configuration in which all methine protons are inequivalent in a given HIPT substituent. The H$_p$ resonance remains sharp down to −90 °C. As the temperature is raised the methylene proton resonances shift as a consequence of Curie-Weiss behavior and broaden and merge as a result of an interconversion of the two possible C$_3$ configurations of the ligand backbone to yield two backbone methylene resonances in a molecule with C$_{3v}$ symmetry on the NMR time scale.[15] The methylene protons whose average resonance is found near −35 ppm equilibrate at approximately room temperature (see Figure 1). Above room temperature two methylene resonances emerge near −35 ppm and 3 ppm and two methine resonances are found in a ratio of 2:1, consistent with C$_{3v}$ symmetry on the NMR time scale and rapid rotation about the nitrogen-aryl bonds. This behavior is similar to that of other Mo(III) complexes of this type such as **MoN$_2$**,[12] **MoCO**,[13] and **MoNH$_3$**,[16] and Mo(IV) species such as **MoCl**,[12] [**MoNH$_3$**]$^+$,[12] **MoH**,[12] and **MoMe**.[13] This behavior is also found for Mo(III) and Mo(IV) complexes that contain a [TMSN$_3$N]$^{3-}$ or [C$_6$F$_5$N$_3$N]$^{3-}$ ligand such as [TMSN$_3$N]MoMe or [TMSN$_3$N]MoCl.[17,18]

The value of ΔG‡ for equilibration of the methylene protons can be obtained by plotting the methylene chemical shifts versus 1/T and thereby obtaining the distance between two methylene resonances (Δν$_c$) at T$_c$, the temperature of coalescence. From k$_c$ = πΔν$_c$/√2 at T$_c$ and k$_c$ = k$_B$T/h exp(−ΔG‡/RT), a ΔG‡ value of 11.7 kcal/mol was obtained. Values of ΔG‡ for the C$_3$ to C$_{3v}$ conversion in [TMSN$_3$N]MoMe and [TMSN$_3$N]MoCl were found to be 8.2 ± 0.2 kcal/mol and 9.2 ± 0.2 kcal/mol.[19] For **MoN$_2$** a value of ΔG‡ = 8.5 ± 0.4 kcal/mol was found; the error is larger since the methylene resonances become relatively broad below T$_c$. For **MoCl** and **MoCO** no ΔG‡ could be obtained because the backbone signals were too broad or disappear into the baseline below T$_c$.[20] The value of ΔG‡ for the C$_3$ to C$_{3v}$ conversion in **MoH$_2$** is higher by ~2 kcal/mol than any other observed in a triamidoamine complex of this general type.

In the process of exploring **MoH$_2$**, **MoHD**, and **MoD$_2$** species we noticed that the H$_p$ protons could be observed (at 500 MHz) at 5.158 ppm for **MoD$_2$**, 5.138 ppm for **MoHD**, and 5.125 ppm for **MoH$_2$** at 22 °C (Figure 3). Observation of only one **MoHD** resonance is consistent with a species that has C$_{3v}$ symmetry on the NMR time scale.

Cyclic voltammetry studies on **MoH$_2$** in PhF revealed no oxidation or reduction wave for **MoH$_2$** between + 1 and −2.8 V.

Details of reactions involving MoN$_2$ or MoH$_2$

The reaction between **MoN$_2$** and H$_2$ in C$_6$D$_6$ was followed in proton NMR studies with mesitylene as an internal standard at pressures between 1/3 and 3 atm. The rate of the reaction does not depend upon H$_2$ pressure in this range. The rate constant (k$_{-3}$, Scheme 1) was found to be 3.4 × 10^{-6} s^{-1} (t$_{1/2}$ = 57 h). Therefore, we propose that the exchange of N$_2$ for H$_2$ consists of rate-limiting loss of dinitrogen to yield unobservable trigonal monopyramidal **Mo** (equation

1). Formation of **MoH$_2$** from **MoN$_2$** appears to be slower than exchange of ^{15}N$_2$ for N$_2$ in **Mo** (^{15}N$_2$)
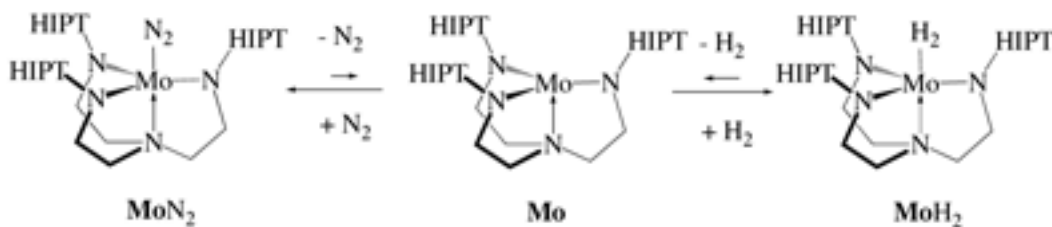
$$\text{(1)}$$

(t$_{1/2}$ = 35 h) in the presence of a large excess of normal N$_2$, a reaction that also is not pressure dependent and is proposed to take place via formation of intermediate **Mo**.[9] One would not expect such a discrepancy (t$_{1/2}$ = 57 h vs. 35 h) to be ascribable to an ^{15}N isotope effect, although the reaction of **MoN$_2$** with ^{15}N$_2$ has not been done. It should be noted that exchange of ^{15}N$_2$ in [HTBTN$_3$N]Mo(^{15}N$_2$) (HTBT = hexa-t-butylterphenyl) is slower by a factor of 20 than what it is in **Mo**^{15}N$_2$,[10] even though the ν_{N2} values are identical in the two species. Details concerning dinitrogen exchange in various circumstances remain to be resolved. For the moment we will assume that the reaction of **MoN$_2$** with H$_2$ proceeds via the **Mo** intermediate. The rate of reaction of **MoN$_2$** with H$_2$ is the same in the presence of [Collidinium][BAr$_{F4}$] (Ar$_F$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) and collidine = 2,4,6-NC$_5$H$_2$Me$_3$) or CrCp*$_2$.

The reaction between **MoH$_2$** and N$_2$ in C$_6$D$_6$ was followed by means of proton NMR with mesitylene as an internal standard at pressures less than or greater than one atmosphere. The reaction between **MoH$_2$** and N$_2$ does not depend on N$_2$ pressure, and the rate limiting step therefore is loss of H$_2$ from **MoH$_2$**. The reaction between **MoH$_2$** and N$_2$ is relatively slow (t$_{1/2}$ = 8 days). From a plot of ln[**MoH$_2$**] versus time over a period of six days (five points) a value of k$_3$ = 1.0 × 10^{-6} s^{-1} was obtained (cf. k$_{-3}$ = 3.4 × 10^{-6} s^{-1} for the reaction between **MoN$_2$** and H$_2$). The equilibrium constant for the reaction of **MoN$_2$** with hydrogen, K$_{eq}$ = K$_3$ = [**MoH$_2$**][N$_2$]/[**MoN$_2$**][H$_2$], was found to be ~150 in C$_6$D$_6$ at 22 °C, i.e., dihydrogen exchanges with dinitrogen in **MoN$_2$** about ~3x faster than dinitrogen exchanges with dihydrogen in **MoH$_2$**. Since the equilibrium between **MoN$_2$**, **MoH$_2$**, N$_2$, and H$_2$ is reached relatively slowly (days) at one atmosphere, *direct* interconversion of **MoN$_2$** and **MoH$_2$** almost certainly can be neglected during the time of a typical catalytic reduction of N$_2$ (6 h).[4a] These results suggest also that protonation of **MoH** to give [**MoH$_2$**]$^+$, reduction of [**MoH$_2$**]$^+$ to **MoH$_2$**, and conversion of **MoH$_2$** to **MoN$_2$** cannot be the mechanism by which **MoH** is drawn into a successful catalytic for dinitrogen reduction.[10]

In contrast to the slow reaction between **MoN$_2$** and H$_2$ (and *vice versa*), **MoNH$_3$** reacts with H$_2$ within minutes to yield **MoH$_2$**. After 10 minutes, conversion of **MoNH$_3$** to **MoH$_2$** under one atmosphere of H$_2$ in C$_6$D$_6$ was more than 80% complete according to NMR spectra. The reverse reaction is also fast. Roughly 4 equivalents of NH$_3$ (dried over a freshly prepared sodium mirror) were added to a C$_6$D$_6$ solution of **MoH$_2$** from which all N$_2$ had been removed. Since the concentrations of NH$_3$, H$_2$, **MoNH$_3$**, and **MoH$_2$** can all be determined in solution, K$_{eq}$ (= K$_2$ = [**MoH$_2$**][NH$_3$]/[**MoNH$_3$**][H$_2$]) for the reaction between **MoNH$_3$**, and **MoH$_2$** could be determined; K$_2$ was found to be ~12 in C$_6$D$_6$ at 22 °C. Since K$_1$ = [**MoNH$_3$**][N$_2$]/[**MoN$_2$**][NH$_3$] = 10,[16] K$_3$ (which equals K$_1$K$_2$) therefore should be ~120, consistent with the measured value for K$_3$ (150; see above).

A 1:5 mixture of **Mo**NH$_3$ and **Mo**H$_2$ in C$_6$D$_6$ under 1 atm of dinitrogen was examined by proton NMR. Almost all **Mo**NH$_3$ had disappeared after five minutes and a 2:1 mixture of **Mo**H$_2$ and **Mo**N$_2$ was formed. This result is to be expected since a large excess of dinitrogen is present and **Mo**H$_2$ is the most stable of the three adducts. The relationships between **Mo**N$_2$, **Mo**NH$_3$, and **Mo**H$_2$ are shown in Scheme 1. The two reactions that involve ammonia are second order overall, while the exchange of hydrogen and nitrogen (in the absence of ammonia) is first order overall.

Catalytic runs with **Mo**H$_2$ as a catalyst suggest that it is competent for reduction of N$_2$ with protons and electrons under standard conditions.[4] Ammonia is formed in 52% yield (from N$_2$) relative to reducing equivalents added (cf. 60–65% yield from N$_2$ with other catalysts such as **Mo**N$_2$.) The lower yield of ammonia, along with the data shown in Scheme 1 and discussed above could be taken as evidence that dihydrogen inhibits reduction of dinitrogen, i.e., ~1 equivalent of dihydrogen is present from the beginning of the experiment. Both ammonia and dihydrogen remove **Mo**N$_2$ from the system to yield **Mo**NH$_3$ and **Mo**H$_2$. Therefore turnover to give ammonia (relative to dihydrogen) should slow as ammonia and dihydrogen are formed. Since the rate constants for **Mo**H$_2$→**Mo**NH$_3$ and **Mo**NH$_3$ →**Mo**N$_2$ are of the order or faster than the time frame of the catalytic reduction (6 hours), a catalytic reaction in which **Mo**H$_2$ is present in the system is viable.

Catalytic runs employing **Mo**≡N were carried out in a modified reactor designed to allow a small amount of gas to be injected before a standard reduction. After demonstrating that the reactor can be used successfully outside the inert atmosphere box in a standard run, including one in which additional dinitrogen was injected, two runs were carried out after injection of 5% and 10% of dihydrogen. These runs produced approximately *one equivalent of ammonia from **Mo**≡N, but no ammonia from dinitrogen*. Therefore we conclude that a *large* amount of dihydrogen (5% is approximately 32x the amount of Mo) prevents formation of any ammonia from dinitrogen. It remains to be seen whether relatively small amounts of dihydrogen also lead to observable inhibition, as proposed in the experiment noted immediately above.

Reactions that involve HD or D$_2$

When a solution that contains 0.1% of **Mo**H$_2$ is placed under a 1:1 mixture of H$_2$ and D$_2$, an equilibrium 1:2:1 ratio of H$_2$, HD, and D$_2$ is formed in 2 h (equation 2). When a solution of **Mo**H$_2$ is exposed to a large excess of HD a 1:2:1 ratio of H$_2$, HD, and D$_2$ also forms rapidly. This fast H/D exchange process is the reason why it is not possible to obtain the **Mo**HD complex; only a mixture of **Mo**H$_2$, **Mo**HD, and **Mo**D$_2$ is formed, as noted earlier. An attempt to prepare **Mo**HD from **Mo**N$_2$ and HD in the solid phase also yielded a 1:2:1 mixture of **Mo**H$_2$, **Mo**HD, and **Mo**D$_2$, but relatively inefficiently; one week at 60 °C was required when starting from **Mo**N$_2$.

$$H_2 + D_2 \xrightarrow{\textbf{Mo}H_2 \text{ cat}} 0.5\,H_2 + HD + 0.5\,D_2$$
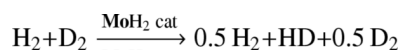
Exactly how H-H, D-D, and H-D scission (equation 2) is accomplished is not known. It seems doubtful that hydrogen could attack the metal in a Mo(III) dihydrogen complex or a Mo(V) dihydride to give some sort of "**Mo**H$_4$" species, since the last remaining orbital of the three available to bind H$_2$ in the coordination pocket of **Mo**, or to form a dihydride, would contain a single electron. One interesting possibility is that scission is accomplished through a heterolytic cleavage to give an intermediate in which H or D is bound to one amido nitrogen, as shown for **Mo**H$_2$ in equation 3; reversible oxidation of MoHN$_H$ to a Mo(V) trihydride, MoH$_3$N$_H$, would then
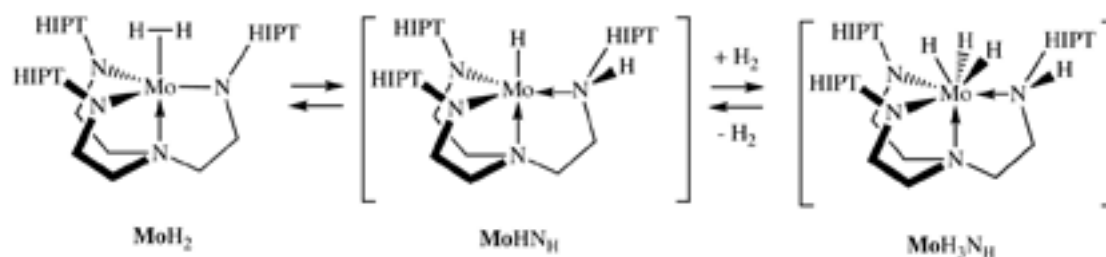
(3)
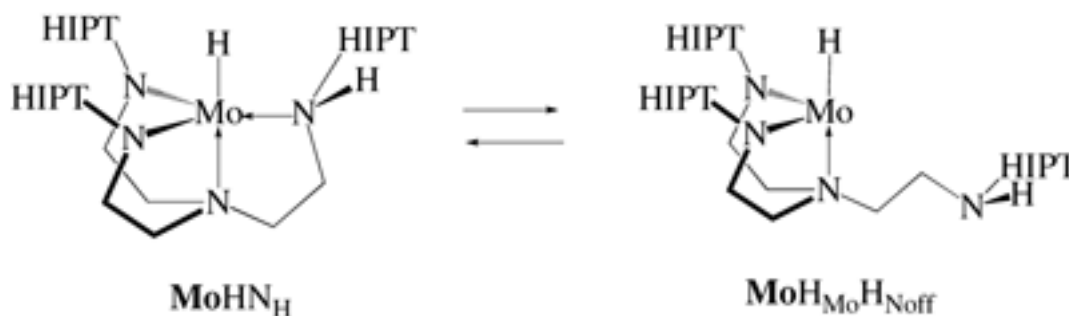
(4)

result in H/D scrambling. This mechanism is sufficient to account for rapid exchange if MoHN$_H$ is formed rapidly and reversibly from **MoH$_2$** and if MoHN$_H$ reacts rapidly and reversibly with H$_x$D$_{2-x}$. Dissociation of one arm in **MoHN$_H$** to give **MoH$_{Mo}$H$_{Noff}$** (equation 4) would also open positions at the metal for coordination and exchange of H and D, as well as H/D exchange reactions that are bimolecular in Mo. Whether formation of **MoH$_{Mo}$H$_{Noff}$** would be fast enough to account for the observed rapid HD exchange between H$_2$, D$_2$, and HD is not known. In any case, we can at least have some confidence that heterolytic splitting of dihydrogen is a requirement for rapid H/D exchange, either via **MoHN$_H$** or **MoH$_{Mo}$H$_{Noff}$**. Heterolytic splitting of dihydrogen or especially formation of **MoH$_{Mo}$H$_{Noff}$** (equation 4) could plausibly be involved in processes that lead to decomposition of **MoH$_2$** in the absence of hydrogen. It does not seem likely that **MoHN$_H$** is the ground state, however, since we have not been able to find a Mo-H or N-H stretch in the solution IR spectrum.

As noted earlier, treatment of **MoH$_2$** in solution with a large excess of D$_2$ results in formation of **MoD$_2$**. The reaction does not depend upon the pressure of D$_2$ at the pressures explored (up to 4 atm) and has a half-life of ~24 hours at one atmosphere of D$_2$ ($k = 8.0 \times 10^{-6}$ s^{-1}). The reverse reaction has the same k within one significant figure, so the isotope effect, if any, is too small to measure with any accuracy under the conditions employed. Since the reaction between **MoH$_2$** and N$_2$ proceeds with a first order $k_{-3} = 1.0 \times 10^{-6}$ s^{-1}, while the reaction between **MoH$_2$** and D$_2$ to form **MoD$_2$** proceeds with a first order $k = 8.0 \times 10^{-6}$ s^{-1}, **Mo** cannot be a common intermediate in the two reactions. In the presence of a large excess of D$_2$ only **MoD$_2$** is formed from **MoH$_2$** through mass action. We propose that formation of **MoD$_2$** in a reaction between **MoH$_2$** and a large amount of D$_2$ proceeds via a mechanism that is the same as that shown in equation 3.

A solution that contains **Mo**H$_2$ and **Mo**D$_2$ under argon yields **Mo**HD after several days. Equilibrium is reached with a half reaction time of ~28 hours for a 24 mM solution of total molybdenum species. The rate of **Mo**HD formation from **Mo**H$_2$ and **Mo**D$_2$ was found to increase as the molybdenum concentration increased. If we *assume* that the exchange reaction is bimolecular in Mo, then an apparent rate constant of k$_{-1}$ = 6.8 × 10^{-4} M^{-1} s^{-1} can be derived for the disappearance of **Mo**HD.[21] One could propose that a reaction that is actually bimolecular in Mo is required, e.g., **Mo**H$_{Mo}$H$_{Noff}$ (equation 4) could form a {Mo(μ$_2$-H)}$_2$ dimer, {**Mo**H$_{Mo}$H$_{Noff}$}$_2$, which would result in H/D exchange. The steric feasibility of forming {**Mo**H$_{Mo}$H$_{Noff}$}$_2$ is supported through molecular mechanics simulations (Spartan). It remains to be seen whether this "slow" H/D exchange reaction actually could take place via loss of some H$_2$ from **Mo**H$_2$ (or D$_2$ from **Mo**D$_2$) followed by HD exchange as shown in equation 3 under circumstances where the rate depends upon Mo concentration but does not involve a reaction that is actually bimolecular in Mo. A more worrisome possibility, especially since the long term stability of **Mo**H$_2$ is not secure, is that this relatively slow "background" H/D exchange reaction could involve products of decomposition of **Mo**H$_2$. Therefore the precise nature of the slow background H/D reaction remains in doubt.

Discussion and Conclusions

One of the important findings from this work is that **Mo**N$_2$, **Mo**NH$_3$, and **Mo**H$_2$ are in ready equilibrium in the presence of H$_2$, N$_2$, and NH$_3$, with **Mo**H$_2$ being the lowest energy of the three species (Scheme 1). Therefore, both ammonia and dihydrogen should inhibit turnover, with dihydrogen being the most effective inhibitor since it converts **Mo**NH$_3$ into **Mo**H$_2$, which results in conversion of more **Mo**N$_2$ into **Mo**NH$_3$. Dihydrogen does not *directly* compete with dinitrogen for the Mo(III) center since interconversion of **Mo**N$_2$ and **Mo**H$_2$ is slow in the presence of only dinitrogen and dihydrogen. In a typical catalytic reaction the amount of ammonia and dihydrogen relative to dinitrogen is miniscule, so there is some question as to how much the **Mo**N$_2$ concentration decreases under catalytic conditions as NH$_3$ and H$_2$ are formed and therefore the degree to which turnover actually is inhibited by NH$_3$ and H$_2$. Loss of ligand from the metal under catalytic conditions is likely to be the more serious and ultimately disasterous problem.

The second important finding is that H/D exchange at **Mo**H$_2$ is facile. Therefore if a catalytic dinitrogen reduction were to be carried out in the presence of a large amount of D$_2$ relative to Mo, dinitrogen reduction should be inhibited and twice as much HD should be formed as H$_2$ is formed in the absence of D$_2$. Both inhibition (by H$_2$ or D$_2$) and formation of HD (in the presence of D$_2$) are observed in the natural FeMo system during turnover.[1] Further experiments are planned that are aimed at investigating inhibition of dinitrogen reduction and possible formation of HD in the presence of D$_2$ in the system that we have described here.

The mechanism by which **Mo**H functions as a catalyst precursor has not been settled as a consequence of the studies reported here. Since **Mo**H is known to react with lutidinium to yield [**Mo**(Lut)]$^+$,[16] protonation of **Mo**H to give [**Mo**H$_2$]$^+$, followed by reduction of [**Mo**H$_2$]$^+$ to **Mo**H$_2$ is an insufficient explanation, since the direct reaction between **Mo**H$_2$ and dinitrogen to give **Mo**N$_2$ we now know is slow. Exchange of dihydrogen in [**Mo**H$_2$]$^+$ for dinitrogen to yield [**Mo**N$_2$]$^+$, followed by reduction of [**Mo**N$_2$]$^+$ to **Mo**N$_2$ is still a viable option.

Reactions that involve H$_2$ or D$_2$ have been studied to some degree in triamido amine systems other than the one described here. For example, **Mo**H was found to react slowly with D$_2$ to yield **Mo**D and HD,[16] while [(TMSNCH$_2$CH$_2$)$_3$N]WH was found to react slowly with H$_2$ to give isolable [(TMSNCH$_2$CH$_2$)$_3$N]WH$_3$.[22] Finally, relatively slow H/D exchange in [(C$_6$F$_5$NCH$_2$CH$_2$)$_3$N]ReH$_2$ was observed upon heating samples in solution under mixtures of H$_2$ and D$_2$.[15] Exchange in the Re system was proposed to involve formation of intermediate

18 electron [(CH$_2$CH$_2$NC$_6$F$_5$)$_2$NCH$_2$CH$_2$NHC$_6$F$_5$]ReH, followed by dissociation of the amine donor in the CH$_2$CH$_2$NHC$_6$F$_5$ arm, thereby exposing the 16e metal center to oxidative addition to Re(III) to give a Re(V) trihydride. "Arm-off" species also have been observed in triamidoamine systems. For example, addition of MeMgCl to {[N (CH$_2$CH$_2$NTMS)$_2$(CH$_2$CH$_2$NMe$_2$)]Mo(NNTMS)}OTf produced structurally characterized [N(CH$_2$CH$_2$NTMS)$_2$(CH$_2$CH$_2$NMe$_2$)]Mo(CH$_3$)(NNTMS) in which the amine donor in the CH$_2$CH$_2$NMe$_2$ arm was not coordinated to the metal.[23] Experimental evidence suggests that an amido nitrogen in **Mo**N$_2$ is protonated to give cationic {[(HIPTNHCH$_2$CH$_2$)N (CH$_2$CH$_2$NHIPT)$_2$]MoN$_2$}$^+$, which is much more susceptible to reduction to [(HIPTNHCH$_2$CH$_2$)N(CH$_2$CH$_2$NHIPT)$_2$]MoN$_2$, and that the ligand eventually is removed from the metal, thereby limiting catalytic turnover to approximately four under the conditions employed. Therefore, there is some precedent for formation of **Mo**N$_{Mo}$H$_{Noff}$ at some stage (equation 2).

Splitting of dihydrogen heterolytically across a metal-ligand bond (often a Ru-N bond[24]) has been proposed or observed in many circumstances. For example, in Noyori-type Ru-based ketone hydrogenation catalysts the dihydrogen(amido) complexes in the catalytic cycle are calculated to be too high in energy to be observed; only the hydride(amine) forms are observed. [25] External bases can act as a catalyst proton shuttle of a proton between the metal and the ligand.[26] Heterolytic splitting has also been proposed for complexes that contain metals other than ruthenium.[27] These findings provide support for the proposed heterolytic splitting of dihydrogen across a Mo-N$_{amido}$ bond to form **Mo**HN$_H$ (equation 4). Evidence suggests that this heterolytic splitting is relatively rapid on the chemical time scale (allowing rapid H/D exchange at Mo), and may even be rapid on the NMR time scale at room temperature. However, as mentioned earlier, (negative) IR data do not support the ground state being **Mo**HN$_H$. Therefore, we still favor the proposal that **Mo**H$_2$ is a Mo(III) dihydrogen complex, a Mo(V) dihydride, or something in between, and that **Mo**HN$_H$ can be formed in a rapid equilibrium. Formation of **Mo**HN$_H$ seems to be a likely contributor to the instability of **Mo**H$_2$ under some conditions.

There is circumstantial evidence that other types of "arm-off" species might be formed under catalytic conditions since an amido nitrogen in **Mo**N$_2$ is known to be protonated and the ligand ultimately stripped from the metal. Among the puzzling results that might be explained through addition of H to an amido nitrogen and formation of "arm-off" species are the following: (i) **Mo**-N=NH is known to decompose slowly to **Mo**H;[12a] (ii) **Mo**=NH is known to decompose to yield a mixture of **Mo**≡N and **Mo**NH$_2$;[16] (iii) [Hybrid]Mo-N=NH species, in which the "hybrid" ligand is significantly smaller than [HIPTN$_3$N]$^{3-}$, are relatively unstable toward 3,5-lutidine, the conjugate base of the acid employed in a typical catalytic reduction of dinitrogen; hydrogen is evolved and [hybrid]MoN$_2$ species are formed; (iv) [Hybrid]Mo-^{15}N=^{15}NH species have been observed to exchange with N$_2$ to yield [Hybrid]Mo-N=NH species at a rate slightly faster than the rate at which they decompose to yield [hybrid]MoN$_2$.[28] Species in which an H is present on an amido nitrogen, whether the resulting amine donor is still coordinated to the metal or not, are still possible intermediates during catalytic turnover, although formation of "arm-off" species is a logical first step that ultimately leads to catalyst decomposition.

Experimental section

General

All manipulations of air- and moisture-sensitive compounds were carried out by standard Schlenk and glovebox techniques under an atmosphere of nitrogen or argon using flame- and oven dried glassware, including NMR tubes. Ether, pentane, methylene chloride and toluene were purged with nitrogen, passed through activated alumina columns, and freeze-pumpthaw degassed three times if necessary; THF, heptane and C$_6$D$_6$ were distilled from a dark purple

Na/benzophenone ketyl solutions; PhF was distilled from P_2O_5 under N_2 and THF-d_8 was used as received; all dried and deoxygenated solvents were stored over molecular sieves in a nitrogen or argon-filled glovebox. LiN(TMS)$_2$ (sublimed) and [CoCp*$_2$]PF$_6$ were used as received, unless indicated otherwise. CrCp*$_2$ was prepared via literature procedures using LiCp* instead of NaCp*.[29] CoCp*$_2$ was prepared from [CoCp*$_2$]PF$_6$ by reduction with crushed sodium and purified by sublimation.[29] [2,4,6-collidinium]BAr$_F$ was prepared in a procedure similar to [2,6-lutidinium]BAr$_F$. Syntheses of **Mo**N$_2$, **Mo**H, **Mo**CO, **Mo**(C$_2$H$_4$) and [**Mo**NH$_3$]$^+$ have been published.[12,13,16] All metal complexes were stored in the dark, under N_2 or Ar at −35 °C. All NMR spectra were recorded on a Varian Mercury 300 or 500 MHz spectrometer and referenced to the residual protio solvent peaks.

Synthesis of [HIPTN$_3$N]MoH$_2$

MoN$_2$ (379 mg) was dissolved in 15 mL toluene in the inert atmosphere box and the solution was freeze-pump-thawed 4 times in a Schlenk flask. H$_2$ was introduced into the flask and the solution was heated for two days at 70 °C. The atmosphere in the flask was refreshed repeatedly by freeze-pump-thawing the solution several times and refilling the flask with H$_2$. The solvent was evaporated from the mixture. The residue was extracted with pentane under an argon atmosphere and the mixture was quickly passed through a frit. A brown powder precipitated from the filtrate. The product was filtered off; yield 225 mg of **Mo**H$_2$ (60%): ^{1}H NMR (C$_6$D$_6$, 20°C) δ 7.28 (s, 12H, 3,5,3″,5″-*H*), 5.15 (s, 3H, 2′-*H*), 2.98 (septet, J_{HH} = 6.9 Hz, 6H, 4,4″-C*H*Me$_2$), 2.88 (br septet, 12H, 2,6,2″,6″-C*H*Me$_2$), 1.39 (d, J_{HH} = 6.9 Hz, 36H, 4,4″-CH(C*H$_3$*)$_2$), 1.3 (very br s, 36H, 2,6,2″,6″-CH(C*H$_3$*)$_2$), 1.17 (br s, 36H,,6,2″,6″-CH(C*H$_3$*)$_2$). The 4′,6′-*H* resonance has not been observed, and the NC*H$_2$* signals are not observed at room temperature due to coalescence. In spite of many attempts at elemental analysis of **Mo**H$_2$ no satisfactory and repeatable results were obtained.

Alternative synthesis of [HIPTN$_3$N]MoH$_2$

A sample of very finely crushed **Mo**N$_2$ was evacuated and placed under an H$_2$ atmosphere. The solid sample was heated at 60 °C for a week, during which time the atmosphere was refreshed several times with H$_2$, leading to formation of **Mo**H$_2$. The NMR spectrum of the material from this reaction is identical to that above. **Mo**D$_2$ was prepared using the same procedure using D$_2$ instead of H$_2$.

Quantitation of hydrogen in [HIPTN$_3$N]MoH$_2$

A Schlenk flask of known volume is loaded with 31 mg of [HIPTN$_3$N]MoN$_2$ in 1.0 mL of toluene. The flask is then sealed with a rubber septum. A separate 500 mL Schlenk flask is then filled with H$_2$ and frozen in liquid N$_2$ for 20 minutes. The Schlenk flask containing the [HIPTN$_3$N]MoN$_2$ solution is freeze/pump/thaw degassed and connected to the Schlenk bomb containing H$_2$ still immersed in liquid N$_2$. The two are allowed to equilibrate for 10 minutes and isolated from one another. The is repeated after 24 and 48 hours. By ^{1}H NMR the resonances corresponding to MoN$_2$ are no longer visible within 48 hours. After 72 hours the sample of [HIPTN$_3$N]MoH$_2$ is frozen in liquid N$_2$ and purged with a flow of N$_2$ gas for 10 minutes. The solution was then removed from liquid N$_2$ and allowed to warm under a flow of N$_2$ gas for an additional 10 minutes. The sample was then sealed and 2.0 mL of CO was injected to form [HIPTN$_3$N]MoCO and hydrogen was measured in the atmosphere after five minutes. Four GC measurements employing 20 μL samples yielded an average of 0.95 ± 0.05 equivalents of H$_2$ per metal center. A run employing 36 mg of [HIPTN$_3$N]MoH$_2$ gave an average (four measurements) of 0.86 ± 0.08 equivalents of H$_2$, while a third employing 61 mg of [HIPTN$_3$N]MoH$_2$ gave an average of 0.93 ± 0.02 equivalents of H$_2$ (five measurements).

Gas chromatographic quantitation of hydrogen

An HP 6890 Series GC equipped with a 50 m × 0.530 mm, 25 μm, HP MoleSieve column and a TCD (Thermal Conductivity Detector) is used for the detection and quantification of H_2. An injection temperature of 150° C, an oven temperature of 200° C, and a detector temperature of 250° C are used with a flow rate of carrier gas (N_2) at 8 psi or 5 mL/min. Under these conditions with sample volumes of 20 μL, H_2 is detectable at 1.12 minutes. The sample volumes were corrected for the partial pressure of toluene and the volume of CO added.

Synthesis of [HIPTN$_3$N]Mo(PMe$_3$)

MoH$_2$ (220 mg) was dissolved in toluene and treated with a slight excess (30 μL) of PMe$_3$. The reaction mixture turned red within an hour. After 24 h the toluene was removed *in vacuo* and the red product was recrystallized from pentane to give 125 mg of **Mo**(PMe$_3$) (55 % yield): ^{1}H NMR (C$_6$D$_6$, 20 °C) *δ* 19.2 (br s, 9H, P*Me*$_3$), 15.8 (br s, 6H, NC*H*$_2$), 6.55 (s, 12H, 3,5,3″,5″-*H*), 2.43 (br septet, 6H, 4,4″-C*H*Me$_2$), 1.8 (br s, 36H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 0.94 (d, 36H, 4,4″-CH(C*H*$_3$)$_2$), 0.88 (br s, 15H, 2,6,2″,6″-C*H*Me$_2$ and 2′-*H*), 0.55 (br s, 36H, 2,6,2″, 6″-CH(C*H*$_3$)$_2$), −7.3 (br s, 6H, 4′,6′-*H*), −25.9 (br s, 6H, NC*H*$_2$). Anal. Calcd for C$_{117}$H$_{168}$MoN$_4$P: C, 79.91; H, 9.69; N, 5.46. Found: C, 79.50; H, 9.87; N, 5.06.

General procedures for reductions of dinitrogen in the presence of dihydrogen

A catalytic apparatus is set up in the glove box according to previously published methods[4a] using a receiving flask fitted with a side arm containing a 0–4 K Teflon plug, and a rubber septum for gas sampling or addition. The apparatus is then taken from the glove box and connected to a Schlenk line where the internal pressure is equilibrated to atmosphere under an N_2 flow. The apparatus is then removed from the line and attached to the syringe drive. A pressure-Lok$^®$ syringe is flushed three times and filled with H_2 drawn from a flask under a constant H_2 purge. The syringe is locked and brought to the catalytic apparatus where it is opened and H_2 slowly driven out until the desired volume is reached. In a continuous motion the syringe is injected into the septum being careful not to over-pressurize the side arm. The plug is then opened and the desired volume of H_2 is injected into the system and mixed by pumping the syringe three times. The system is then allowed to equilibrate for 10 minutes, and the Teflon stopper is then closed. After 10 minutes the syringe is started and the run completed as previously described.[4a] Analysis of ammonia is also done by the previously reported indophenol method.[4a]

Catalytic reduction of dinitrogen employing the modified reactor

The catalytic apparatus described above had a total volume of 82.0 mL. To a receiving flask containing 9.0 mg (5.31 μmol) of [HIPTN$_3$N]MoN and 321 mg (0.325 mmol) of Collidinium {BAr′$_4$}1.0 mL of heptane is added. The syringe barrel is then loaded with 81 mg (0.249 mmol) of Cp$_2$*Cr in 9.1 mL of heptane. With the apparatus having a remaining headspace of 72.9 mL, 4.5 mL (0.200 mmol) of N_2 was added to the system as described above. Addition of 4.5 mL of N_2 increases the internal pressure of the apparatus by 6.3%. Upon completion of the catalytic run and indophenol analysis 6.4 equivalents of ammonia were obtained relative to molybdenum.

Catalytic reduction of dinitrogen in the presence of dihydrogen

To a catalytic reaction as described above 4.5 mL (0.200 mmol) of H_2 were added. Addition of 4.5 mL (0.200 mmol) of H_2 increased the internal pressure of the apparatus by 6.3 %, and H_2 accounted for 6.3 % of the N_2/H_2 mixture, or 32 equivalents of H_2 versus Mo. Upon completion of the catalytic run and indophenol analysis an average of 0.87 equivalents of ammonia were obtained relative to molybdenum, or 0 from dinitrogen.

In a second run 9.0 mL (0.400 mmol) of H_2 were added. The internal pressure increased by 12.3% and H_2 to give a N_2/H_2 mixture in which 11.6 % consisted of dihydrogen, or 65 equivalents of H_2 versus Mo. Upon completion and analysis of the catalytic run 0.89 equivalents of ammonia were obtained relative to molybdenum, or 0 from dinitrogen.

Acknowledgments

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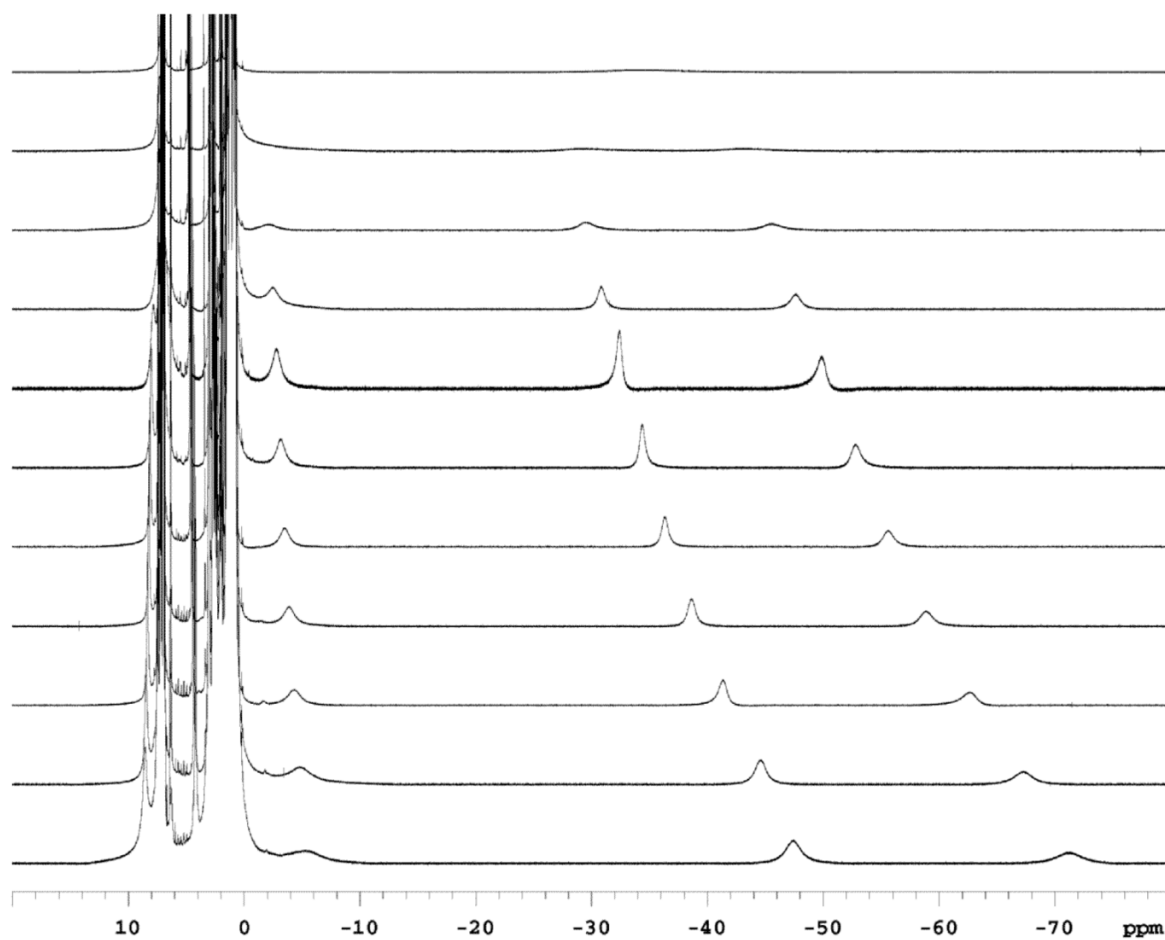29. Robbins JL, Edelstein N, Spencer B, Smart JC. J Am Chem Soc 1982;104:1882.

Figure 1.
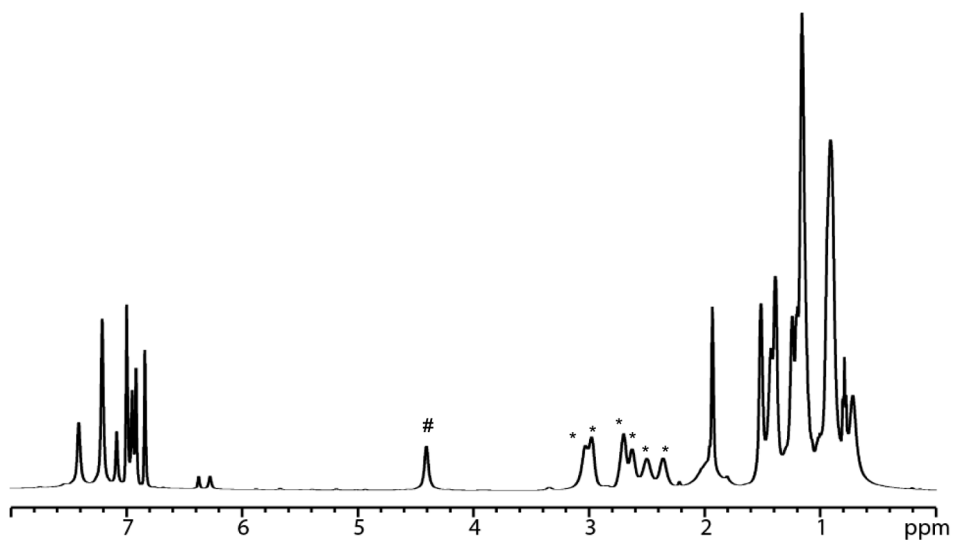VT NMR stack plot of **MoH**$_2$ from −80 °C (bottom) to 20 °C (top) in steps of 10 °C.

Figure 2.
Proton NMR spectrum of **Mo**H$_2$ at −60 °C in toluene-d$_8$ between 0 and 8 ppm. Only one resonance is observed for the HIPT H$_p$ protons (#), which shifts with temperature. The presence of six isopropyl methine resonances (*) suggest that the six isopropyl groups in each HIPT group are inequivalent.
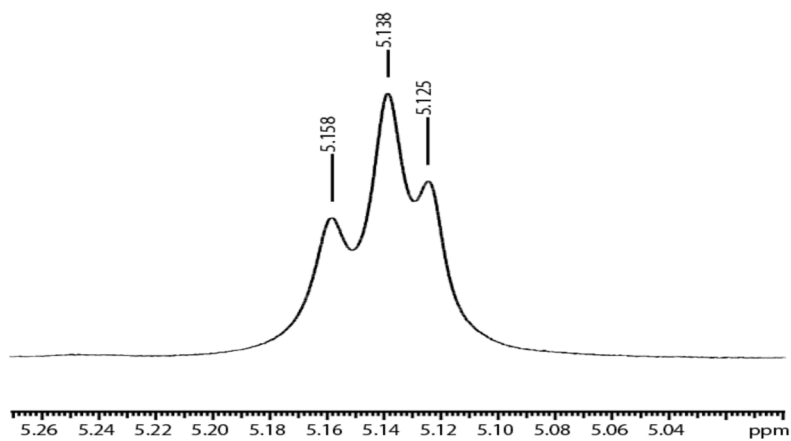
Figure 3.
Resonances for the H_p protons in a 1: 2: 1 mixture of **Mo**D$_2$ (at 5.158 ppm), **Mo**HD (at 5.138 ppm), and **Mo**H$_2$ (at 5.125 ppm) at 22 °C. (Relative intensities were determined through modeling using gNMR.)
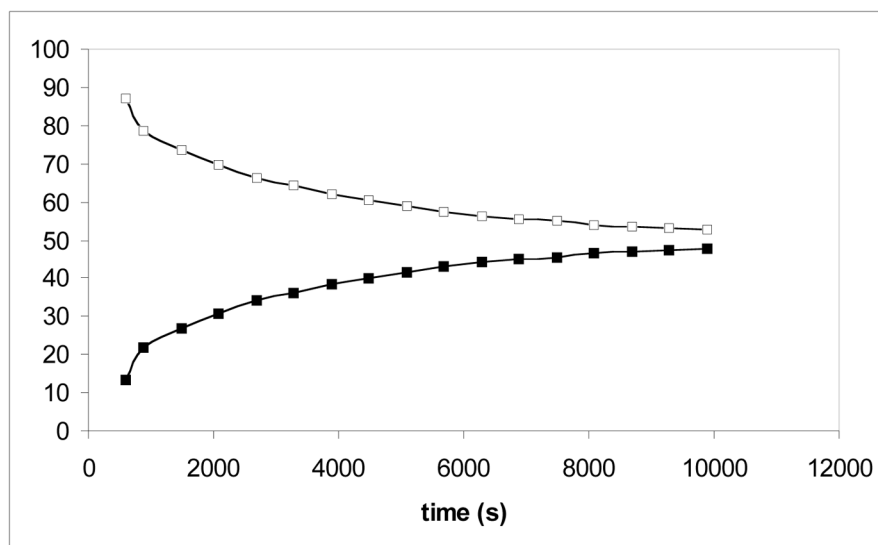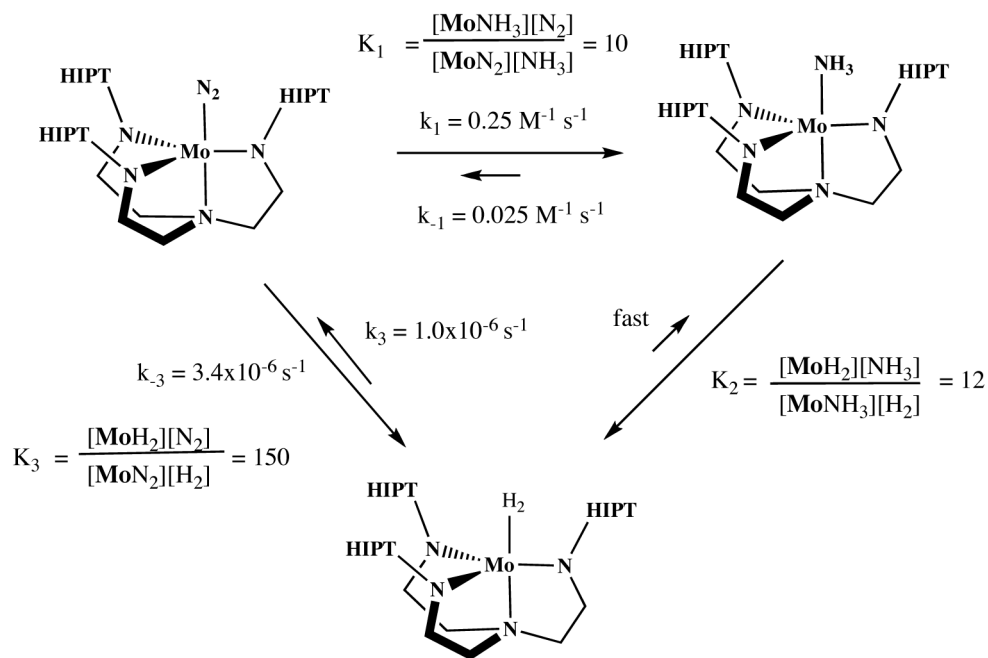
Figure 4.
Conversion of a mixture of H2 plus D2 (□) into HD (■) in C6D6 in the presence of 0.1 %
MoH2 as a catalyst in C6D6 (y axis = %).

$$K_1 = \frac{[\text{MoNH}_3][\text{N}_2]}{[\text{MoN}_2][\text{NH}_3]} = 10$$

$$k_1 = 0.25\ \text{M}^{-1}\ \text{s}^{-1}$$

$$k_{-1} = 0.025\ \text{M}^{-1}\ \text{s}^{-1}$$

$$k_3 = 1.0 \times 10^{-6}\ \text{s}^{-1}$$

fast

$$k_{-3} = 3.4 \times 10^{-6}\ \text{s}^{-1}$$

$$K_2 = \frac{[\text{MoH}_2][\text{NH}_3]}{[\text{MoNH}_3][\text{H}_2]} = 12$$

$$K_3 = \frac{[\text{MoH}_2][\text{N}_2]}{[\text{MoN}_2][\text{H}_2]} = 150$$

Scheme 1.

Exchange reactions relating **MoN$_2$**, **MoNH$_3$**, and **MoH$_2$**.