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

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Abstract

$\text{[HIPTN}_3\text{N}]\text{Mo(N}_2\text{)}$ ($\text{MoN}_2$) ($\text{[HIPTN}_3\text{N}]^3^-$ 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 $\text{[HIPTN}_3\text{N}]\text{MoH}_2$ ($\text{MoH}_2$), a compound whose properties are most consistent with it being a dihydrogen complex of Mo(III). The intermediate in the slow reaction between $\text{MoN}_2$, $\text{MoNH}_3$, and $\text{MoH}_2$ is proposed to be $\text{[HIPTN}_3\text{N}]\text{Mo}$ ($\text{Mo}$). In contrast, $\text{MoN}_2$, $\text{MoNH}_3$, and $\text{MoH}_2$ are interconverted rapidly in the presence of $\text{H}_2$, $\text{N}_2$, and $\text{NH}_3$, and $\text{MoH}_2$ is the lowest energy of the three Mo compounds. Catalytic runs with $\text{MoH}_2$ as a catalyst suggest that it is competent for reduction of $\text{N}_2$ with protons and electrons under standard conditions. $\text{[HIPTN}_3\text{N}]\text{MoH}_2$ reacts rapidly with HD to yield a mixture of $\text{[HIPTN}_3\text{N}]\text{MoH}_2$, $\text{[HIPTN}_3\text{N}]\text{MoD}_2$, and $\text{[HIPTN}_3\text{N}]\text{MoHD}$, and rapidly catalyzes H/D exchange between $\text{H}_2$ and $\text{D}_2$. $\text{MoH}_2$ 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. 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 $\text{N}_2$). 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%. 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. Furthermore, under a $\text{D}_2$ atmosphere two equivalents of HD are formed during turnover of dinitrogen to ammonia, but no deuterium is incorporated into the solvent ($\text{H}_2\text{O}$) or into the ammonia formed. In 2003 it was shown that dinitrogen can be reduced catalytically to ammonia with protons and electrons by molybdenum complexes that contain the $\text{[HIPTN}_3\text{N}]^{3^-}$ ligand ($\text{[HIPTN}_3\text{N}]^{3^-} = \text{[HIPTNCH}_2\text{CH}_2\text{N}]^3^-$ where HIPT is 3,5-(2,4,6-i-Pr$^3$C$_6$H$_2$)$_2$C$_6$H$_3$), examples being $\text{[HIPTN}_3\text{N}]\text{Mo(N}_2\text{)}$, $\text{[HIPTN}_3\text{N}]\text{Mo-N=NH}$, and $\text{[HIPTN}_3\text{N}]\text{Mo(NH}_3\text{)}$. 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. In the $\text{[HIPTN}_3\text{N}]\text{Mo}$ 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.
experimental results in various triamidoamine molybdenum systems are now strongly supported by numerous theoretical studies, the most relevant being studies that employ the full [HIPTN₃N]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 [HIPTN₃N]Mo(N₂) 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 [HIPTN₃N]Mo(N₂) forms dihydrogen. The amount of ammonia increases from 63 % at 1 atm (15 psi) to 71 % 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 [HIPTN₃N]Mo(N₂) forms dihydrogen. The amount of ammonia increases from 63 % at 1 atm (15 psi) to 71 % at pressures above 30 psi.

Since dihydrogen is formed along with ammonia in the [HIPTN₃N]Mo system we became interested in the dihydrogen chemistry of MoN₂ and of other [HIPTN₃N]Mo derivatives that have been isolated and characterized. We also wanted to understand why MoH is as efficient a catalyst precursor as [HIPTN₃N]Mo complexes that are proposed to lie on the catalytic pathway, e.g., MoN₂ or Mo-N=NH.¹⁰ Selected reactions that involve dihydrogen and various [HIPTN₃N]Mo complexes are reported here.

Results
Synthesis of [HIPTN₃N]Mo(H₂)

[HIPTN₃N]Mo(N₂) reacts with dihydrogen slowly (2–3 days at 22 °C in CsD₆) in solution to yield [HIPTN₃N]Mo(H₂) (MoH₂). By ¹H NMR after 48 hours the resonances corresponding to MoN₂ are no longer visible if the atmosphere is removed and replaced with hydrogen after 24 hours. Addition of dinitrogen to MoH₂ leads to slow reformation of MoN₂. A magnetic susceptibility measurement on MoH₂ in solution (Evans method; μeff = 1.4–1.5 BM) is consistent with S = ½ and therefore with MoH₂ being either a d¹ or a low spin d³ species. MoN₂ reacts with D₂ to yield MoD₂ at the same rate as MoN₂ reacts with H₂. (A convenient method of distinguishing MoD₂, MoH₂, and MoHD is described later.) The ability to prepare MoD₂ 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 MoHD from MoN₂ and HD resulted in formation of a 1:2:1 mixture of MoH₂, MoHD and MoD₂. No IR absorption assignable to some IR active MoH or MoD mode could be found for either MoH₂ or MoD₂ in pentane at 22°C. The absence of any readily observed MoH IR modes is more consistent with MoH₂ being a Mo(III) dihydrogen complex than a Mo(V) dihydride.¹¹

A persistent impurity present in early syntheses of MoH₂ turned out to be MoCl, traces of which are formed upon oxidation of [MoN₂]⁻ with ZnCl₂.¹² We found that oxidation of [MoN₂]⁻ with zinc acetate instead of zinc chloride led to samples of MoN₂ that were free of MoCl, and therefore samples of MoH₂ that were free of MoCl. Unfortunately, we were not able to obtain crystals of MoH₂ suitable for a complete X-ray structural study. Crystals obtained from a dilute pentane solution diffraction poorly, although it was clear from the preliminary structural solution that the [HIPTN₃N]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.

MoH₂ also can be prepared by heating solid samples of MoN₂ 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 MoN₂ is ground to a fine powder and the atmosphere is refreshed.

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periodically with dihydrogen. Even then, a trace (~1 %) of MoN₂ (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.

MoH₂ 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 MoH₂ under dinitrogen at -30 °C slowly form some MoN₂. MoH₂ also decomposes slowly in vacuo at approximately the same rate as it reacts with dinitrogen to yield MoN₂. For example, after three days in vacuo virtually all of the original MoH₂ has decomposed. Attempts to crystallize and identify the decomposition product or products of MoH₂ have been unsuccessful. The final decomposition product does not react with dihydrogen to reform MoH₂ and no free ligand is found in NMR spectra of partially decomposed samples. Multiple attempts to obtain a satisfactory elemental analysis of MoH₂ failed. We conclude that MoH₂ 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 MoH₂ 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 H₄ 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 MoH₂ into MoN₂, and vice versa, no evidence for formation of a stable “naked” species, Mo, has yet been obtained. It should be noted that MoN₂ does not decompose to any significant degree in vacuo under conditions where MoH₂ does.

MoH₂ reacts readily with ethylene, CO, and PMe₃. Addition of ethylene to MoH₂ results in formation of Mo(C₂H₄)₁₃ with only a trace of H₂ (~ 1% in solution) and ethane (~33% in solution versus an internal standard) being observed, according the NMR spectra of MoH₂ under an ethylene atmosphere (C₆D₆, 22 °C, 12h). (The amounts of H₂ 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(C₂H₄) in C₆D₆ at 22 °C under a hydrogen atmosphere is unchanged for weeks, ethane must be formed when ethylene attacks MoH₂. 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.

MoCO₁₃ is formed immediately upon exposure of a solution of MoH₂ (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 MoH₂ in toluene were degassed and treated with CO, 0.95±0.05, 0.86±0.08, and 0.93±0.02 equivalents of H₂ were found in the atmosphere above the solution in three different experiments. Therefore MoH₂ clearly contains one equivalent of hydrogen.

A solution of MoH₂ turned red after one hour upon addition of trimethylphosphine and red Mo(PMe₃) was isolated in good yield (55% recrystallized) after 24 hours. The NMR spectrum of Mo(PMe₃) is very similar to that of MoN₂ and MoCO. Again less than one equivalent of dihydrogen was found in the gas phase when typically prepared MoH₂ samples in toluene were treated with several equivalents of PMe₃.

The results of the reactions between MoH₂ and ethylene, CO, and PMe₃ suggest that only one equivalent of dihydrogen is present in MoH₂. 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 PMe₃ on MoH₂. None of these results settles the question concerning whether MoH₂ is a dihydrogen complex or a classic dihydride, something in between, or something else entirely. (See later.)

The variable temperature NMR spectrum of MoH₂ 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 C₃ conformation at low temperature, a known property of triamidoamine complexes. 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 C₃ configurations of the ligand backbone to yield two backbone methylene resonances in a molecule with C₃ᵥ symmetry on the NMR time scale. 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 C₃ᵥ 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 MoN₂, MoCO, and MoNH₃ and Mo(IV) species such as MoCl₃, [MoNH₃]⁺, MoH, and MoMe. This behavior is also found for Mo(III) and Mo(IV) complexes that contain a [TMSN₃]⁻ or [C₆F₅N₃]⁻ ligand such as [TMSN₃]MoMe or [TMSN₃]MoCl.

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 C₃ to C₃ᵥ conversion in [TMSN₃]MoMe and [TMSN₃]MoCl were found to be 8.2 ± 0.2 kcal/mol and 9.2 ± 0.2 kcal/mol. For MoN₂ 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.

In the process of exploring MoH₂, MoHD, and MoD₂ species we noticed that the H_p protons could be observed (at 500 MHz) at 5.158 ppm for MoD₂, 5.138 ppm for MoHD, and 5.125 ppm for MoH₂ at 22 °C (Figure 3). Observation of only one MoHD resonance is consistent with a species that has C₃ᵥ symmetry on the NMR time scale.

Cyclic voltammetry studies on MoH₂ in PhF revealed no oxidation or reduction wave for MoH₂ between +1 and −2.8 V.

Details of reactions involving MoN₂ or MoH₂

The reaction between MoN₂ and H₂ in C₆D₆ 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 H₂ pressure in this range. The rate constant (kₚ, Scheme 1) was found to be 3.4 × 10⁻⁶ s⁻¹ (t½ = 57 h). Therefore, we propose that the exchange of N₂ for H₂ consists of rate-limiting loss of dinitrogen to yield unobservable trigonal monopyramidal Mo (equation...
Formation of MoH₂ from Mo₂N₂ appears to be slower than exchange of ¹⁵N₂ for N₂ in Mo (¹⁵N₂) (t₁/₂ = 35 h) in the presence of a large excess of normal N₂, a reaction that also is not pressure dependent and is proposed to take place via formation of intermediate Mo.¹³ One would not expect such a discrepancy (t₁/₂ = 57 h vs. 35 h) to be ascribable to an ¹⁵N isotope effect, although the reaction of Mo₂N₂ with ¹⁵N₂ has not been done. It should be noted that exchange of ¹⁵N₂ in [HTBTN₃]Mo(¹⁵N₂) (HTBT = hexa-t-butylterphenyl) is slower by a factor of 20 than what it is in Mo¹⁵N₂,¹⁰ even though the νN₂ 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 Mo₂N₂ with H₂ proceeds via the Mo intermediate.

The rate of reaction of Mo₂N₂ with H₂ is the same in the presence of [Collidinium][BARF₄] (ArF = 3,5-(CF₃)₂C₆H₃ and collidine = 2,4,6-NC₆H₂Me₃) or CrCp*₂.

The reaction between MoH₂ and N₂ in C₆D₆ 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 MoH₂ and N₂ does not depend on N₂ pressure, and the rate limiting step therefore is loss of H₂ from MoH₂. The reaction between MoH₂ and N₂ is relatively slow (t₁/₂ = 8 days). From a plot of ln[MoH₂] versus time over a period of six days (five points) a value of k₃ = 1.0 × 10⁻⁶ s⁻¹ was obtained (cf. k₃ = 3.4 × 10⁻⁶ s⁻¹ for the reaction between MoN₂ and H₂). The equilibrium constant for the reaction of MoN₂ with hydrogen, Kₑ₀ = K₃ = [MoH₂][N₂]/[Mo₂N₂][H₂], was found to be ~150 in C₆D₆ at 22 °C, i.e., dinitrogen exchanges with dihydrogen in MoN₂ about ~3x faster than dinitrogen exchanges with dihydrogen in MoH₂. Since the equilibrium between Mo₂N₂, MoH₂, N₂, and H₂ is reached relatively slowly (days) at one atmosphere, direct interconversion of MoN₂ and MoH₂ almost certainly can be neglected during the time of a typical catalytic reduction of N₂ (6 h).³ᵃ These results suggest also that protonation of MoH to give [MoH₂]⁺, reduction of [MoH₂]⁺ to MoH₂, and conversion of MoH₂ to Mo₂N₂ cannot be the mechanism by which MoH is drawn into a successful catalytic for dinitrogen reduction.¹⁰

In contrast to the slow reaction between Mo₂N₂ and H₂ (and vice versa), MoNH₃ reacts with H₂ within minutes to yield MoH₂. After 10 minutes, conversion of MoNH₃ to MoH₂ under one atmosphere of H₂ in C₆D₆ was more than 80% complete according to NMR spectra. The reverse reaction is also fast. Roughly 4 equivalents of NH₃ (dried over a freshly prepared soda mirror) were added to a C₆D₆ solution of MoH₂ from which all N₂ had been removed. Since the concentrations of NH₃, H₂, MoNH₃, and MoH₂ can all be determined in solution, Kₙₒ = K₉ = [MoH₂][NH₃]/[MoNH₃][H₂] for the reaction between MoNH₃ and MoH₂ could be determined: K₉ was found to be ~12 in C₆D₆ at 22 °C. Since K₁ = [MoNH₂][N₂]/[Mo₂N₂] [NH₃] = 10,¹⁶ K₉ (which equals K₁K₂) therefore should be ~120, consistent with the measured value for K₉ (150; see above).
A 1:5 mixture of MoNH₃ and MoH₂ in C₆D₆ under 1 atm of dinitrogen was examined by proton NMR. Almost all MoNH₃ had disappeared after five minutes and a 2:1 mixture of MoH₂ and MoN₂ was formed. This result is to be expected since a large excess of dinitrogen is present and MoH₂ is the most stable of the three adducts. The relationships between MoN₂, MoNH₃, and MoH₂ 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 MoH₂ as a catalyst suggest that it is competent for reduction of N₂ with protons and electrons under standard conditions. Ammonia is formed in 52% yield (from N₂) relative to reducing equivalents added (cf. 60–65% yield from N₂ with other catalysts such as MoN₂.) 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 MoN₂ from the system to yield MoNH₃ and MoH₂. Therefore turnover to give ammonia (relative to dihydrogen) should slow as ammonia and dihydrogen are formed. Since the rate constants for MoH₂→MoNH₃ and MoNH₃→MoN₂ are of the order or faster than the time frame of the catalytic reduction (6 hours), a catalytic reaction in which MoH₂ 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 D₂

When a solution that contains 0.1% of MoH₂ is placed under a 1:1 mixture of H₂ and D₂, an equilibrium 1:2:1 ratio of H₂, HD, and D₂ is formed in 2 h (equation 2). When a solution of MoH₂ is exposed to a large excess of HD a 1:2:1 ratio of H₂, HD, and D₂ also forms rapidly. This fast H/D exchange process is the reason why it is not possible to obtain the MoHD complex; only a mixture of MoH₂, MoHD, and MoD₂ is formed, as noted earlier. An attempt to prepare MoHD from MoN₂ and HD in the solid phase also yielded a 1:2:1 mixture of MoH₂, MoHD, and MoD₂, but relatively inefficiently; one week at 60 °C was required when starting from MoN₂.

\[
H₂ + D₂ \xrightarrow{\text{MoH₂ cat}} 0.5 H₂ + HD + 0.5 D₂
\]

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 "MoH₄" species, since the last remaining orbital of the three available to bind H₂ 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 MoH₂ in equation 3; reversible oxidation of MoHNH to a Mo(V) trihydride, MoH₃N₃H₁ would then
result in H/D scrambling. This mechanism is sufficient to account for rapid exchange if
MoHN\(_2\) is formed rapidly and reversibly from MoH\(_2\) and if MoHN\(_2\) reacts rapidly and
reversibly with H\(_x\)D\(_{2-x}\). Dissociation of one arm in MoHN\(_2\) to give MoHM\(_6\)H\(_{\text{off}}\) (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 MoHM\(_6\)H\(_{\text{off}}\)
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\(_2\) or MoHM\(_6\)H\(_{\text{off}}\).
Heterolytic splitting of dihydrogen or especially formation of MoHM\(_6\)H\(_{\text{off}}\) (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\(_2\) 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 × 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\(_{-3}\) = 1.0×10\(^{-6}\) s\(^{-1}\), while the reaction
between MoH\(_2\) and D\(_2\) to form MoD\(_2\) proceeds with a first order k = 8.0 × 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 MoH$_2$ and MoD$_2$ under argon yields MoHD 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 MoHD formation from MoH$_2$ and MoD$_2$ was found to increase as the molybdenum concentration increased. If we assume that the reaction exchange 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 MoHD.

One could propose that a reaction that is actually bimolecular in Mo is required, e.g., MoH$_2$MoH$_{Noff}$ (equation 4) could form a (Mo(μ$_2$-H)$_2$)$_2$ dimer, (MoH$_2$MoH$_{Noff}$)$_2$, which would result in H/D exchange. The steric feasibility of forming (MoH$_2$MoH$_{Noff}$)$_2$ 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 MoH$_2$ (or D$_2$ from MoD$_2$) 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 MoH$_2$ is not secure, is that this relatively slow “background” H/D exchange reaction could involve products of decomposition of MoH$_2$. 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 MoN$_2$, MoNH$_3$, and MoH$_2$ are in ready equilibrium in the presence of H$_2$, N$_2$, and NH$_3$, with MoH$_2$ 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 MoNH$_3$ into MoH$_2$, which results in conversion of more MoN$_2$ into MoNH$_3$. Dihydrogen does not directly compete with dinitrogen for the Mo(III) center since interconversion of MoN$_2$ and MoH$_2$ 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 MoN$_2$ 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 disastrous problem.

The second important finding is that H/D exchange at MoH$_2$ 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.

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 MoH functions as a catalyst precursor has not been settled as a consequence of the studies reported here. Since MoH is known to react with lutidinium to yield [Mo(Lut)]$^+$, protonation of MoH to give [MoH$_2$]$^+$, followed by reduction of [MoH$_2$]$^+$ to MoH$_2$ is an insufficient explanation, since the direct reaction between MoH$_2$ and dinitrogen to give MoN$_2$ we now know is slow. Exchange of dihydrogen in [MoH$_2$]$^+$ for dinitrogen to yield [MoN$_2$]$^+$, followed by reduction of [MoN$_2$]$^+$ to MoN$_2$ 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, MoH was found to react slowly with D$_2$ to yield MoD and HD, 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$_3$. Finally, relatively slow H/D exchange in [(C$_5$F$_3$NCH$_2$CH$_2$)$_3$N]ReH$_2$ was observed upon heating samples in solution under mixtures of H$_2$ and D$_2$. Exchange in the Re system was proposed to involve formation of intermediate.
18 electron \([\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_3]_2\text{NCH}_2\text{CH}_2\text{NHC}_6\text{F}_3\)ReH, followed by dissociation of the amine donor in the CH\(_2\)CH\(_2\)NHC\(_6\)F\(_3\) 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 \([\text{N}(\text{HIPTNHCH}_2\text{CH}_2\text{NMe}_2)]\text{Mo(NNTMS)}\)OTf produced structurally characterized \([\text{N}(\text{CH}_2\text{CH}_2\text{NNTMS})_2(\text{CH}_2\text{CH}_2\text{NMe}_2)]\text{Mo(Ch}_2\text{)(NNTMS)}\) 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\(\text{N}_2\) is protonated to give cationic \([[\text{HIPTNHCH}_2\text{CH}_2\text{N}](\text{HIPTNCH}_2\text{CH}_2\text{NMe}_2)]\text{Mo(NNTMS)}\)\(^{6}\), which is much more susceptible to reduction to \([\text{HIPTNHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NHIPT)}_2]\text{MoN}_2\), 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\(\text{N}_6\text{H}_{\text{offset}}\) 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(amide) 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\(_{\text{amido}}\) bond to form Mo\(\text{H}_2\) (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\(\text{H}_2\). Therefore, we still favor the proposal that Mo\(\text{H}_2\) is a Mo(III) dihydrogen complex, a Mo(V) dihydride, or something in between, and that Mo\(\text{H}_2\) can be formed in a rapid equilibrium. Formation of Mo\(\text{H}_2\) seems to be a likely contributor to the instability of Mo\(\text{H}_2\) 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\(\text{N}_2\) 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 MoH;\(^{12a}\) (ii) Mo-NH is known to decompose to yield a mixture of Mo-N and Mo\(\text{NH}_2\);\(^{16}\) (iii) [Hybrid]Mo-N=NH species, in which the “hybrid” ligand is significantly smaller than [HIPT\(\text{N}_2\)]\(^{3}\), 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]Mo\(\text{NH}_2\) species are formed; (iv) [Hybrid]Mo-O\(\text{N}_2\) 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]Mo\(\text{NH}_2\).\(^{28}\) 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-pump-thaw degassed three times if necessary; THF, heptane and C\(_6\)D\(_6\) were distilled from a dark purple
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Na/benzophenone ketyl solutions; PhF was distilled from P₂O₅ under N₂ and THF-d₈ was used as received; all dried and deoxygenated solvents were stored over molecular sieves in a nitrogen or argon-filled glovebox. Li[N(TMS)]₂ (sublimed) and [CoCp*₂]PF₆ 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]PF₆ by reduction with crushed sodium and purified by sublimation.²⁹ [2,4,6-collidinium]BAr₆ was prepared in a procedure similar to [2,6-lutidinium]BAr₆. Syntheses of MoN₂, MoH₂, MoCO, Mo(C₂H₄) and [MoNH₃]⁺ have been published.¹²,¹³,¹⁶ All metal complexes were stored in the dark, under N₂ 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 [HIPTN₃N]MoH₂

MoN₂ (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. H₂ 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 H₂. 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 MoH₂ (60%): ¹H NMR (C₆D₆, 20°C) 6.78 (s, 12H, 3.5,3.5″-H), 5.15 (s, 3H, 2′'-H), 2.98 (septet, JHH = 6.9 Hz, 6H, 4,4″-CHMe₂), 2.88 (br septet, 12H, 2,6,2′,6′-CHMe₂), 1.39 (d, JHH = 6.9 Hz, 36H, 3,5,3″-Me), 1.3 (very br s, 36H, 2,6,2′,6′-CH(CH₃)₂). The 4,6″-H resonance has not been observed, and the NCH₂ signals are not observed at room temperature due to coalescence. In spite of many attempts at elemental analysis of MoH₂ no satisfactory and repeatable results were obtained.

Alternative synthesis of [HIPTN₃N]MoH₂

A sample of very finely crushed MoN₂ was evacuated and placed under an H₂ atmosphere. The solid sample was heated at 60 °C for a week, during which time the atmosphere was refreshed several times with H₂, leading to formation of MoH₂. The NMR spectrum of the material from this reaction is identical to that above. MoD₂ was prepared using the same procedure using D₂ instead of H₂.

Quantitation of hydrogen in [HIPTN₃N]MoH₂

A Schlenk flask of known volume is loaded with 31 mg of [HIPTN₃N]MoN₂ 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 H₂ and frozen in liquid N₂ for 20 minutes. The Schlenk flask containing the [HIPTN₃N]MoN₂ solution is freeze/pump/thaw degassed and connected to the Schlenk bomb containing H₂ still immersed in liquid N₂. The two are allowed to equilibrate for 10 minutes and isolated from one another. The is repeated after 24 and 48 hours. By ¹H NMR the resonances corresponding to MoN₂ are no longer visible within 48 hours. After 72 hours the sample of [HIPTN₃N]MoH₂ is frozen in liquid N₂ and purged with a flow of N₂ gas for 10 minutes. The solution was then removed from liquid N₂ and allowed to warm under a flow of N₂ gas for an additional 10 minutes. The sample was then sealed and 2.0 mL of CO was injected to form [HIPTN₃N]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 H₂ per metal center. A run employing 36 mg of [HIPTN₃N]MoH₂ gave an average (four measurements) of 0.86 ± 0.08 equivalents of H₂, while a third employing 61 mg of [HIPTN₃N]MoH₂ gave an average of 0.93 ± 0.02 equivalents of H₂ (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 H₂. 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 (N₂) at 8 psi or 5 mL/min. Under these conditions with sample volumes of 20 μL, H₂ 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 [HIPTN₃N]Mo(PMe₃)

MoH₂ (220 mg) was dissolved in toluene and treated with a slight excess (30 μL) of PMe₃. 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(PMe₃) (55% yield):

1H NMR (C₆D₆, 20 °C) δ 19.2 (br s, 9H, PMe₃), 15.8 (br s, 6H, NC₆H₂), 6.55 (s, 12H, 3,5,3″,5″-H), 2.43 (br septet, 6H, 4,4″-CH₂Me₂), 1.8 (br s, 36H, 2,6,2″,6″-CH(C₆H₃)₂), 0.94 (d, 36H, 4,4″-CH₂Me₂), −7.3 (br s, 6H, 4′,6′-H), −25.9 (br s, 6H, NC₆H₂). Anal. Calcd for C₁₁₇H₁₆₈MoN₄P: 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 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 N₂ 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 H₂ drawn from a flask under a constant H₂ purge. The syringe is locked and brought to the catalytic apparatus where it is opened and H₂ 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 H₂ 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. Analysis of ammonia is also done by the previously reported indophenol method.

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 [HIPTN₃N]MoN and 321 mg (0.325 mmol) of Collidinium {BAr′₄} with 1.0 mL of heptane is added. The syringe barrel is then loaded with 81 mg (0.249 mmol) of Cp₂*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 N₂ was added to the system as described above. Addition of 4.5 mL of N₂ 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 H₂ were added. Addition of 4.5 mL (0.200 mmol) of H₂ increased the internal pressure of the apparatus by 6.3%, and H₂ accounted for 6.3% of the N₂/H₂ mixture, or 32 equivalents of H₂ 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.

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20. The coalescence temperatures for N₃NMo species other than MoH₂ lie between −30 °C and −40 °C.

21. Moore JW, Pearson RG. Kinetics and Mechanism (3). 3. John Wiley & SonsNew York1981(b) From the equilibrium rate law, ln \{x[a+(a+b)xe_]e_xe]/x\} = kt(2ab−(a+b)xe)/xe, where x equals the amounts of MoH₂ and MoD₂, 2x equals the amount of HDH that is formed, a is the starting concentration of MoH₂, b is the starting concentration MoD₂, and xe is x at equilibrium. ν₁ = k₁[MoH₂][MoD₂] and ν₋₁ = k₋₁[MoHD]², k₋₁ = 6.8 × 10⁻⁴ M⁻¹ s⁻¹ was determined. Since \( K = [\text{MoHD}]² /[\text{MoH₂}] [\text{MoD₂}] = 4 \), k₁/k₋₁, k₁ = 2.7 × 10⁻³ M⁻¹ s⁻¹.


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 MoH₂ at −60 °C in toluene-d₈ between 0 and 8 ppm. Only one resonance is observed for the HIPT Hₚ 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\textsubscript{p} protons in a 1:2:1 mixture of MoD\textsubscript{2} (at 5.158 ppm), MoHD (at 5.138 ppm), and MoH\textsubscript{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 = %).
Scheme 1.
Exchange reactions relating MoN₂, MoNH₃, and MoH₂.