

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

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[HIPTN₃N]Mo(N₂) (**MoN**₂) ([HIPTN₃N]³⁻ = [(HIPTNCH₂CH₂)₃N]³⁻ where HIPT = 3,5-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃) reacts with dihydrogen slowly (days) at 22 °C to yield [HIPTN₃N]MoH₂ (**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 **MoN**₂ and H₂ is proposed to be [HIPTN₃N]Mo (**Mo**). In contrast, **MoN**₂, **MoNH**₃, and **MoH**₂ are interconverted rapidly in the presence of H₂, N₂, and NH₃, and **MoH**₂ is the lowest energy of the three Mo compounds. Catalytic runs with **MoH**₂ as a catalyst suggest that it is competent for reduction of N₂ with protons and electrons under standard conditions. [HIPTN₃N]MoH₂ reacts rapidly with HD to yield a mixture of [HIPTN₃N]MoH₂, [HIPTN₃N]MoD₂, and [HIPTN₃N]MoHD, and rapidly catalyzes H/D exchange between H₂ and D₂. **MoH**₂ reacts readily with ethylene, PMe₃, and CO to yield monoadducts. Reduction of dinitrogen to ammonia in the presence of 32 equiv 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 1 equiv per dinitrogen reduced, is formed in the FeMo nitrogenase system at high pressures (e.g., 50 atm N₂).² Formation of 1 equiv of dihydrogen per 2 equiv 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 1 equiv of dihydrogen is formed at the

same site where dinitrogen is reduced and 1 equiv of dihydrogen *must* be formed for every dinitrogen reduced. What is known with certainty is that dihydrogen inhibits dinitrogen reduction.³ Furthermore, under a D₂ atmosphere 2 equiv of HD are formed during turnover of dinitrogen to ammonia, but no deuterium is incorporated into the solvent (H₂O) 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 [HIPTN₃N]³⁻ ligand ([HIPTN₃N]³⁻ = [(HIPTNCH₂CH₂)₃N]³⁻ where HIPT is 3,5-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃), examples being [HIPTN₃N]Mo(N₂), [HIPTN₃N]Mo–N=NH, and [HIPTN₃N]Mo(NH₃).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 [HIPTN₃N]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

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employ the full $[\text{HIPTN}_3\text{N}]^{3-}$ 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 $[\text{HIPTN}_3\text{N}]\text{Mo}(\text{N}_2)$ 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 equiv under the conditions employed, in large part because the $[\text{HIPTN}_3\text{N}]^{3-}$ 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 $[\text{HIPTN}_3\text{N}]\text{Mo}(\text{NH}_3)$ (MoNH_3) to MoN_2 via intermediate $\text{Mo}(\text{NH}_3)(\text{N}_2)$ and because the equilibrium constant for this equilibrium ($[\text{MoN}_2][\text{NH}_3]/[\text{MoNH}_3][\text{N}_2]$) is 0.1 in benzene at 22 °C.

Since dihydrogen is formed along with ammonia in the $[\text{HIPTN}_3\text{N}]\text{Mo}$ system we became interested in the dihydrogen chemistry of MoN_2 and of other $[\text{HIPTN}_3\text{N}]\text{Mo}$ derivatives that have been isolated and characterized. We also wanted to understand why MoH is as efficient a catalyst precursor as $[\text{HIPTN}_3\text{N}]\text{Mo}$ complexes that are proposed to lie on the catalytic pathway, for example, MoN_2 or $\text{Mo}-\text{N}=\text{NH}$.¹⁰ Selected reactions that involve dihydrogen and various $[\text{HIPTN}_3\text{N}]\text{Mo}$ complexes are reported here.

Results

Synthesis of $[\text{HIPTN}_3\text{N}]\text{Mo}(\text{H}_2)$. $[\text{HIPTN}_3\text{N}]\text{Mo}(\text{N}_2)$ (MoN_2) reacts with dihydrogen slowly (2–3 days at 22 °C in C_6D_6) in solution to yield $[\text{HIPTN}_3\text{N}]\text{Mo}(\text{H}_2)$ (MoH_2). By ¹H NMR after 48 h the resonances corresponding to MoN_2 are no longer visible if the atmosphere is removed and replaced with hydrogen after 24 h. Addition of dinitrogen to MoH_2 leads to slow reformation of MoN_2 . A magnetic susceptibility measurement on MoH_2 in solution (Evans method; $\mu_{\text{eff}} = 1.4\text{--}1.5 \mu_{\text{B}}$) is consistent with $S = 1/2$ and therefore with MoH_2 being either a d^1 or a low spin d^3 species. MoN_2 reacts with D_2 to yield MoD_2 at the same rate as MoN_2 reacts with H_2 . (A convenient method of distinguishing MoD_2 , MoH_2 , and MoHD is described later.) The ability to prepare MoD_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 MoHD from MoN_2 and HD resulted in formation of a 1:2:1 mixture of MoH_2 , MoHD , and MoD_2 . No IR absorption assignable to some IR active MoH or MoD mode could be found for either MoH_2 or MoD_2 in pentane at 22 °C. The absence of any readily observed MoH IR modes is more consistent with MoH_2 being a Mo(III) dihydrogen complex than a Mo(V) dihydride.¹¹

A persistent impurity present in early syntheses of MoH_2 turned out to be MoCl , traces of which are formed upon oxidation of $[\text{MoN}_2]^-$ with ZnCl_2 .¹² We found that oxidation of $[\text{MoN}_2]^-$ with zinc acetate instead of zinc chloride led to samples of MoN_2 that were free of MoCl , and therefore samples of MoH_2 that were free of MoCl . Unfortunately, we were not able to obtain crystals of MoH_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 $[\text{HIPTN}_3\text{N}]^{3-}$ 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 MoN_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 MoN_2 is ground to a fine powder and the atmosphere is refreshed periodically with dihydrogen. Even then, a trace ($\sim 1\%$) of MoN_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 toward traces of oxygen and water and toward dinitrogen, both in solution and in the solid phase. Even in the solid state samples of MoH_2 under dinitrogen at -30 °C slowly form some MoN_2 . MoH_2 also decomposes slowly in vacuo at approximately the same rate as it reacts with dinitrogen to yield MoN_2 . For example, after 3 days in vacuo virtually all of the original MoH_2 has decomposed. Attempts to crystallize and identify the decomposition product or products of MoH_2 have been unsuccessful. The final decomposition product does not react with dihydrogen to reform MoH_2 and no free ligand is found in NMR spectra of partially decomposed samples. Multiple attempts to obtain a satisfactory elemental analysis of MoH_2 failed. We conclude that MoH_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 MoH_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 MoH_2 into MoN_2 , and vice versa, no evidence for formation of a stable “naked” species, Mo , has yet been obtained. It should be noted that MoN_2 does *not* decompose to any significant degree in vacuo under conditions where MoH_2 does.

MoH_2 reacts readily with ethylene, CO, and PMe_3 . Addition of ethylene to MoH_2 results in formation of $\text{Mo}(\text{C}_2\text{H}_4)$,¹³ with only a trace of H_2 ($\sim 1\%$ in solution)

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and ethane (~33% in solution versus an internal standard) being observed, according to the NMR spectra of MoH_2 under an ethylene atmosphere (C_6D_6 , 22 °C, 12 h). (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 $\text{Mo}(\text{C}_2\text{H}_4)$ in C_6D_6 at 22 °C under a hydrogen atmosphere is unchanged for weeks, ethane must be formed when ethylene attacks MoH_2 . Formation of ethane is most readily explained in classic terms, that is, 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, that is, from a Mo(III) dihydrogen complex.

MoCO^{13} is formed immediately upon exposure of a solution of MoH_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 1 equiv, typically between 0.30 and 0.70 equiv, depending on the sample's history. However, when freshly prepared samples of MoH_2 in toluene were degassed and treated with CO, 0.95 ± 0.05 , 0.86 ± 0.08 , and 0.93 ± 0.02 equiv of H_2 were found in the atmosphere above the solution in three different experiments. Therefore MoH_2 clearly contains 1 equiv of hydrogen.

A solution of MoH_2 turned red after 1 h upon addition of trimethylphosphine, and red $\text{Mo}(\text{PMe}_3)$ was isolated in good yield (55% recrystallized) after 24 h. The NMR spectrum of $\text{Mo}(\text{PMe}_3)$ is very similar to that of MoN_2 and MoCO . Again less than 1 equiv of dihydrogen was found in the gas phase when typically prepared MoH_2 samples in toluene were treated with several equiv of PMe_3 .

The results of the reactions between MoH_2 and ethylene, CO, and PMe_3 suggest that only 1 equiv of dihydrogen is present in MoH_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 reso-

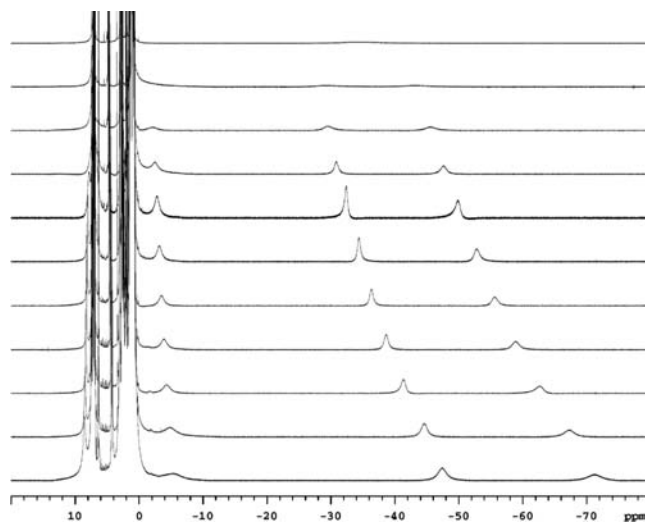


Figure 1. VT NMR stack plot of MoH_2 from -80 °C (bottom) to 20 °C (top) in steps of 10 °C.

nance 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 $[\text{MoNH}_3]^+$,¹² MoH ,¹² and MoMe .¹³ This behavior is also found for Mo(III) and Mo(IV) complexes that contain a $[\text{TMSN}_3\text{N}]^{3-}$ or $[\text{C}_6\text{F}_5\text{N}_3\text{N}]^{3-}$ ligand such as $[\text{TMSN}_3\text{N}]\text{MoMe}$ or $[\text{TMSN}_3\text{N}]\text{MoCl}$.^{17,18}

The value of ΔG^\ddagger 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 ($\Delta\nu_c$) at T_c , the temperature of coalescence. From $k_c = \pi\Delta\nu_c/\sqrt{2}$ at T_c and $k_c = k_B T/h \exp(-\Delta G^\ddagger/RT)$, a ΔG^\ddagger value of 11.7 kcal/mol was obtained. Values of ΔG^\ddagger for the C_3 to C_{3v} conversion in $[\text{TMSN}_3\text{N}]\text{MoMe}$ and $[\text{TMSN}_3\text{N}]\text{MoCl}$ were found to be 8.2 ± 0.2 kcal/mol and 9.2 ± 0.2 kcal/mol.¹⁹ For MoN_2 a value of $\Delta G^\ddagger = 8.5 \pm 0.4$ kcal/mol was found; the error is

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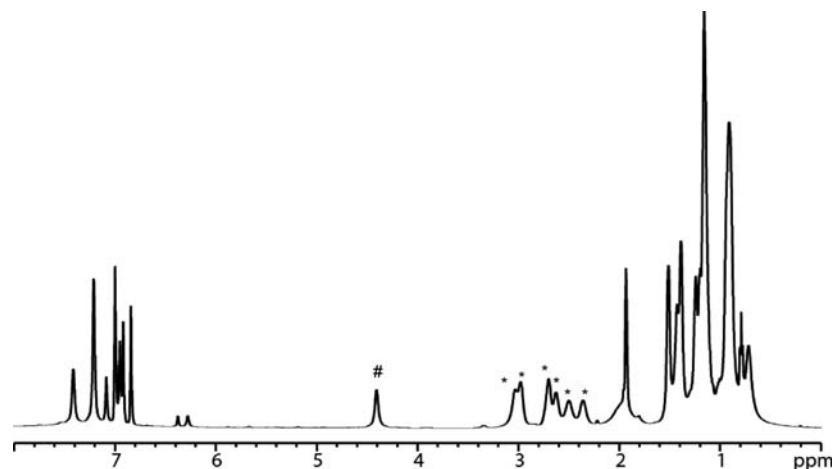


Figure 2. Proton NMR spectrum of MoH_2 at $-60\text{ }^\circ\text{C}$ in toluene- d_8 between 0 and 8 ppm. Only one resonance is observed for the HIPT H_p protons (#), which shifts with temperature. The presence of six isopropyl methine resonances (*) suggest that the six isopropyl groups in each HIPT group are inequivalent.

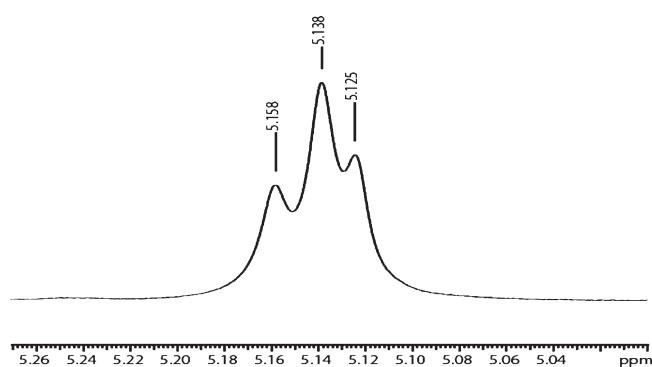


Figure 3. Resonances for the H_p protons in a 1:2:1 mixture of MoD_2 (at 5.158 ppm), MoHD (at 5.138 ppm), and MoH_2 (at 5.125 ppm) at $22\text{ }^\circ\text{C}$. (Relative intensities were determined through modeling using gNMR.).

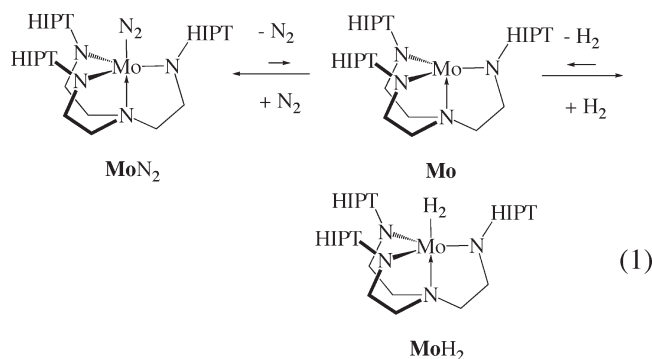
larger since the methylene resonances become relatively broad below T_c . For MoCl and MoCO no ΔG^\ddagger could be obtained because the backbone signals were too broad or disappear into the baseline below T_c .²⁰ The value of ΔG^\ddagger for the C_3 to C_{3v} conversion in MoH_2 is higher by ~ 2 kcal/mol 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 $22\text{ }^\circ\text{C}$ (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_6D_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

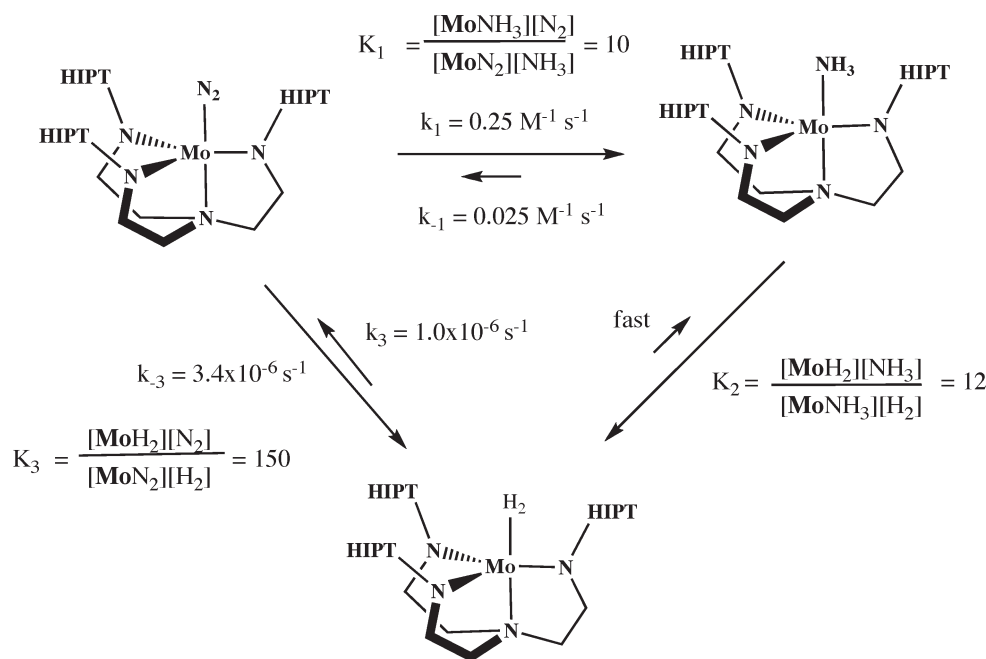
$3.4 \times 10^{-6}\text{ s}^{-1}$ ($t_{1/2} = 57\text{ h}$). Therefore, we propose that the exchange of N_2 for H_2 consists of rate-limiting loss of dinitrogen to yield unobservable trigonal monopyramidal Mo (eq 1). Formation of MoH_2 from MoN_2 appears to be slower than exchange of $^{15}\text{N}_2$ for N_2 in $\text{Mo}(^{15}\text{N}_2)$



($t_{1/2} = 35\text{ h}$) 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 ($t_{1/2} = 57\text{ h}$ vs 35 h) to be ascribable to an ^{15}N isotope effect, although the reaction of MoN_2 with $^{15}\text{N}_2$ has not been done. It should be noted that exchange of $^{15}\text{N}_2$ in $[\text{HTBTN}_3\text{N}]\text{Mo}(^{15}\text{N}_2)$ (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_{N_2} 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]- $[\text{BAR}_{\text{F}4}]$ ($\text{Ar}_{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) and collidine = 2,4,6- $\text{NC}_3\text{H}_2\text{Me}_3$) or CrCp^*_2 .

The reaction between MoH_2 and N_2 in C_6D_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 ($t_{1/2} = 8\text{ days}$). From a plot

(20) The coalescence temperatures for N_3NMo species other than MoH_2 lie between $-30\text{ }^\circ\text{C}$ and $-40\text{ }^\circ\text{C}$.

Scheme 1. Exchange Reactions Relating MoN_2 , MoNH_3 , and MoH_2 

of $\ln[\text{MoH}_2]$ versus time over a period of 6 days (five points) a value of $k_3 = 1.0 \times 10^{-6} \text{ s}^{-1}$ was obtained (cf. $k_{-3} = 3.4 \times 10^{-6} \text{ s}^{-1}$ for the reaction between MoN_2 and H_2). The equilibrium constant for the reaction of MoN_2 with hydrogen, $K_{\text{eq}} = K_3 = [\text{MoH}_2][\text{N}_2]/[\text{MoN}_2][\text{H}_2]$, was found to be ~ 150 in C_6D_6 at 22°C , that is, dihydrogen exchanges with dinitrogen in MoN_2 about $\sim 3\times$ 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 $[\text{MoH}_2]^+$, reduction of $[\text{MoH}_2]^+$ to MoH_2 , and conversion of MoH_2 to MoN_2 cannot be the mechanism by which MoH is drawn into a successful catalytic cycle 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 min, conversion of MoNH_3 to MoH_2 under one atmosphere of H_2 in C_6D_6 was more than 80% complete according to NMR spectra. The reverse reaction is also fast. Roughly 4 equiv of NH_3 (dried over a freshly prepared sodium mirror) were added to a C_6D_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, $K_{\text{eq}} (= K_2 = [\text{MoH}_2][\text{NH}_3]/[\text{MoNH}_3][\text{H}_2])$ for the reaction between MoNH_3 , and MoH_2 could be determined; K_2 was found to be ~ 12 in C_6D_6 at 22°C . Since $K_1 = [\text{MoNH}_3][\text{N}_2]/[\text{MoN}_2][\text{NH}_3] = 10$,¹⁶ K_3 (which equals K_1K_2) therefore should be ~ 120 , consistent with the measured value for K_3 (150; see above).

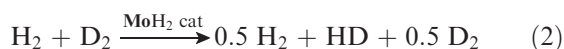
A 1:5 mixture of MoNH_3 and MoH_2 in C_6D_6 under 1 atm of dinitrogen was examined by proton NMR. Almost all MoNH_3 had disappeared after 5 min, and a 2:1 mixture of MoH_2 and MoN_2 was formed. This result is to be expected since a large excess of dinitrogen is present

and MoH_2 is the most stable of the three adducts. The relationships between MoN_2 , MoNH_3 , and MoH_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.

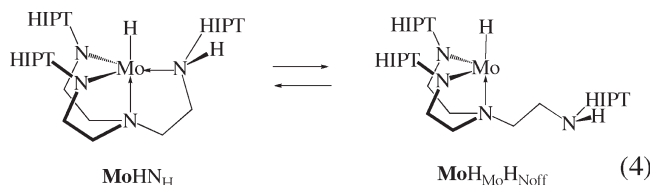
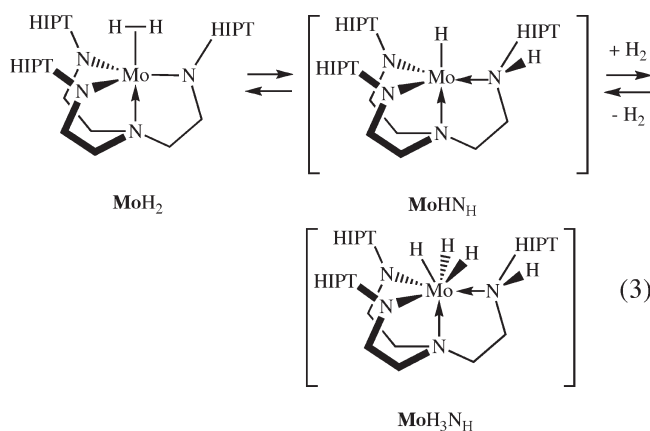
Catalytic runs with MoH_2 as a catalyst suggest that it is competent for reduction of N_2 with protons and electrons under standard conditions.⁴ Ammonia is formed in 52% yield (from N_2) relative to reducing equivalents added (cf. 60–65% yield from N_2 with other catalysts such as MoN_2 .) The lower 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, that is, ~ 1 equiv of dihydrogen is present from the beginning of the experiment. Both ammonia and dihydrogen remove MoN_2 from the system to yield MoNH_3 and MoH_2 . Therefore turnover to give ammonia (relative to dihydrogen) should slow as ammonia and dihydrogen are formed. Since the rate constants for $\text{MoH}_2 \rightarrow \text{MoNH}_3$ and $\text{MoNH}_3 \rightarrow \text{MoN}_2$ are of the order or faster than the time frame of the catalytic reduction (6 h), a catalytic reaction in which MoH_2 is present in the system is viable.

Catalytic runs employing $\text{Mo}\equiv\text{N}$ 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 1 equiv of ammonia from $\text{Mo}\equiv\text{N}$, but no ammonia from dinitrogen. Therefore we conclude that a large amount of dihydrogen (5% is approximately $32\times$ 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 (eq 2 and Figure 4). 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.



Exactly how H–H, D–D, and H–D scission (eq 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 eq 3; reversible oxidation of MoHN_H to a Mo(V) trihydride, MoH₃N_H, would then



result in H/D scrambling. This mechanism is sufficient to account for rapid exchange if MoHN_H is formed rapidly and reversibly from MoH₂ and if MoHN_H reacts rapidly and reversibly with H_xD_{2-x}. Dissociation of one arm in MoHN_H to give MoH_{Mo}H_{NoFF} (eq 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 H₂, D₂, and HD is not known.

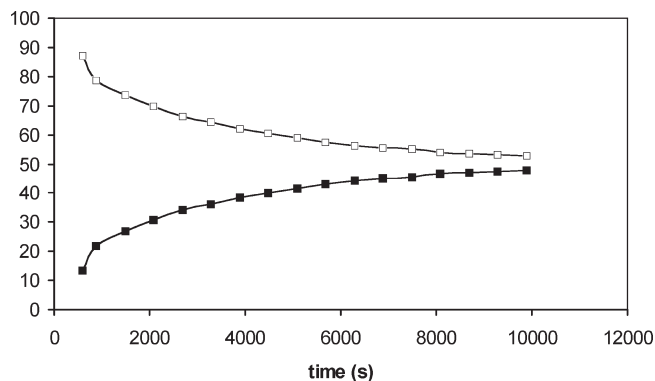


Figure 4. Conversion of a mixture of H₂ plus D₂ (□) into HD (■) in C₆D₆ in the presence of 0.1% MoH₂ as a catalyst in C₆D₆ (y axis = %).

In any case, we can at least have some confidence that heterolytic splitting of dihydrogen is a requirement for rapid H/D exchange, via either MoHN_H or MoH_{Mo}H_{NoFF}. Heterolytic splitting of dihydrogen or especially formation of MoH_{Mo}H_{NoFF} (eq 4) could plausibly be involved in processes that lead to decomposition of MoH₂ 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 MoH₂ in solution with a large excess of D₂ results in formation of MoD₂. The reaction does not depend upon the pressure of D₂ at the pressures explored (up to 4 atm) and has a half-life of ~24 h at one atmosphere of D₂ ($k = 8.0 \times 10^{-6} \text{ s}^{-1}$). 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 MoH₂ and N₂ proceeds with a first order $k_{-3} = 1.0 \times 10^{-6} \text{ s}^{-1}$, while the reaction between MoH₂ and D₂ to form MoD₂ proceeds with a first order $k = 8.0 \times 10^{-6} \text{ s}^{-1}$, Mo cannot be a common intermediate in the two reactions. In the presence of a large excess of D₂ only MoD₂ is formed from MoH₂ through mass action. We propose that formation of MoD₂ in a reaction between MoH₂ and a large amount of D₂ proceeds via a mechanism that is the same as that shown in eq 3.

A solution that contains MoH₂ and MoD₂ under argon yields MoHD after several days. Equilibrium is reached with a half reaction time of ~28 h for a 24 mM solution of total molybdenum species. The rate of MoHD formation from MoH₂ and MoD₂ 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 $k_{-1} = 6.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ can be derived for the disappearance of MoHD.²¹ One could propose that a reaction that is actually bimolecular in Mo is required, for example, MoH_{Mo}H_{NoFF} (eq 4) could form a {Mo(μ_2 -H)}₂ dimer, {MoH_{Mo}H_{NoFF}}₂, which would result in H/D exchange. The steric feasibility of forming {MoH_{Mo}H_{NoFF}}₂ is supported through molecular

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mechanics simulations (Spartan). It remains to be seen whether this “slow” H/D exchange reaction actually could take place via loss of some H₂ from MoH₂ (or D₂ from MoD₂) followed by HD exchange as shown in eq 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 MoH₂ is not secure, is that this relatively slow “background” H/D exchange reaction could involve products of decomposition of MoH₂. 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 MoN₂, MoNH₃, and MoH₂ are in ready equilibrium in the presence of H₂, N₂, and NH₃, with MoH₂ 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 MoNH₃ into MoH₂, which results in conversion of more MoN₂ into MoNH₃. Dihydrogen does not *directly* compete with dinitrogen for the Mo(III) center since interconversion of MoN₂ and MoH₂ 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 MoN₂ concentration decreases under catalytic conditions as NH₃ and H₂ are formed and therefore the degree to which turnover actually is inhibited by NH₃ and H₂. 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 MoH₂ is facile. Therefore if a catalytic dinitrogen reduction were to be carried out in the presence of a large amount of D₂ relative to Mo, dinitrogen reduction should be inhibited and twice as much HD should be formed as H₂ is formed in the absence of D₂. Both inhibition (by H₂ or D₂) and formation of HD (in the presence of D₂) 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 D₂ 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)]⁺,¹⁶ protonation of MoH to give [MoH₂]⁺, followed by reduction of [MoH₂]⁺ to MoH₂ is an insufficient explanation, since the direct reaction between MoH₂ and dinitrogen to give MoN₂ we now know is slow. Exchange of dihydrogen in [MoH₂]⁺ for dinitrogen to yield [MoN₂]⁺, followed by reduction of [MoN₂]⁺ to MoN₂ is still a viable option.

Reactions that involve H₂ or D₂ 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 D₂ to yield MoD and HD,¹⁶ while [(TMSNCH₂CH₂)₃N]WH was found to react slowly with H₂ to give isolable [(TMSNCH₂CH₂)₃N]WH₃.²² Finally, relatively slow H/D exchange in [(C₆F₅NCH₂CH₂)₃N]ReH₂ was observed upon

heating samples in solution under mixtures of H₂ and D₂.¹⁵ Exchange in the Re system was proposed to involve formation of intermediate 18 electron [(CH₂CH₂NC₆F₅)₂NCH₂CH₂NHC₆F₅]ReH, followed by dissociation of the amine donor in the CH₂CH₂NHC₆F₅ 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(CH₂CH₂NTMS)₂(CH₂CH₂NMe₂)]Mo(NNTMS)}-OTf produced structurally characterized [N(CH₂CH₂NTMS)₂(CH₂CH₂NMe₂)]Mo(CH₃)(NNTMS) in which the amine donor in the CH₂CH₂NMe₂ arm was not coordinated to the metal.²³ Experimental evidence suggests that an amido nitrogen in MoN₂ is protonated to give cationic {[HIPTNHC(CH₂CH₂)N(CH₂CH₂NHIPT)₂]MoN₂}⁺, which is much more susceptible to reduction to [(HIPTNHC(CH₂CH₂)N(CH₂CH₂NHIPT)₂]MoN₂, 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 MoN_{Mo}H_{N_{off}} at some stage (eq 2).

Splitting of dihydrogen heterolytically across a metal–ligand bond (often a Ru–N bond²⁴) 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 for moving 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 MoHN_H (eq 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 MoHN_H. Therefore, we still favor the proposal that MoH₂ is a Mo(III) dihydrogen complex, a Mo(V) dihydride, or something in between, and that MoHN_H can be formed in a rapid equilibrium. Formation of MoHN_H seems to be a likely contributor to the instability of MoH₂ 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 MoN₂ is known to be protonated and

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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) $\text{Mo}-\text{N}=\text{NH}$ is known to decompose slowly to MoH ;^{12a} (ii) $\text{Mo}=\text{NH}$ is known to decompose to yield a mixture of $\text{Mo}\equiv\text{N}$ and MoNH_2 ;¹⁶ (iii) [Hybrid] $\text{Mo}-\text{N}=\text{NH}$ species, in which the "hybrid" ligand is significantly smaller than $[\text{HIPTN}_3\text{N}]^{3-}$, 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] $\text{Mo}-^{15}\text{N}=\text{NH}$ species have been observed to exchange with N_2 to yield [Hybrid] $\text{Mo}-\text{N}=\text{NH}$ 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 Procedures. 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_6D_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. $\text{LiN}(\text{TMS})_2$ (sublimed) and $[\text{CoCp}^*_2]\text{PF}_6$ 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 $[\text{CoCp}^*_2]\text{PF}_6$ by reduction with crushed sodium and purified by sublimation.²⁹ $[\text{2,4,6-collidinium}]\text{BAR}_\text{F}$ was prepared in a procedure similar to $[\text{2,6-lutidinium}]\text{BAR}_\text{F}$. Syntheses of MoN_2 , MoH , MoCO , $\text{Mo}(\text{C}_2\text{H}_4)$, and $[\text{MoNH}_3]^+$ 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 $[\text{HIPTN}_3\text{N}]\text{MoH}_2$. MoN_2 (379 mg) was dissolved in 15 mL of 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 2 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 MoH_2 (60%): ^1H NMR (C_6D_6 , 20°C) δ 7.28 (s, 12H, 3,5,3'',5''-H), 5.15 (s, 3H, 2'-H), 2.98 (septet, $J_{\text{HH}} = 6.9$ Hz, 6H, 4,4''-CHMe₂), 2.88 (br septet, 12H, 2,6,2'',6''-CHMe₂), 1.39 (d, $J_{\text{HH}} = 6.9$ Hz, 36H, 4,4''-CH(CH₃)₂), 1.3 (very br s, 36H, 2,6,2'',6''-CH(CH₃)₂), 1.17 (br s, 36H, 6,2'',6''-CH(CH₃)₂). The 4',6''-H resonance has not been observed, and the NCH₂ signals are not observed at room tem-

perature because of coalescence. In spite of many attempts at elemental analysis of MoH_2 no satisfactory and repeatable results were obtained.

Alternative Synthesis of $[\text{HIPTN}_3\text{N}]\text{MoH}_2$. A sample of very finely crushed MoN_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 MoH_2 . The NMR spectrum of the material from this reaction is identical to that above. MoD_2 was prepared using the same procedure using D_2 instead of H_2 .

Quantitation of Hydrogen in $[\text{HIPTN}_3\text{N}]\text{MoH}_2$. A Schlenk flask of known volume is loaded with 31 mg of $[\text{HIPTN}_3\text{N}]\text{MoN}_2$ 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 min. The Schlenk flask containing the $[\text{HIPTN}_3\text{N}]\text{MoN}_2$ 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 min and isolated from one another. This procedure was repeated after 24 and 48 h. By ^1H NMR the resonances corresponding to MoN_2 are no longer visible within 48 h. After 72 h the sample of $[\text{HIPTN}_3\text{N}]\text{MoH}_2$ is frozen in liquid N_2 and purged with a flow of N_2 gas for 10 min. The solution was then removed from liquid N_2 and allowed to warm under a flow of N_2 gas for an additional 10 min. The sample was then sealed and 2.0 mL of CO was injected to form $[\text{HIPTN}_3\text{N}]\text{MoCO}$, and hydrogen was measured in the atmosphere after 5 min. Four GC measurements employing 20 μL samples yielded an average of 0.95 ± 0.05 equiv of H_2 per metal center. A run employing 36 mg of $[\text{HIPTN}_3\text{N}]\text{MoH}_2$ gave an average (four measurements) of 0.86 ± 0.08 equiv of H_2 , while a third employing 61 mg of $[\text{HIPTN}_3\text{N}]\text{MoH}_2$ gave an average of 0.93 ± 0.02 equiv of H_2 (five measurements).

Gas Chromatographic Quantitation of Hydrogen. An HP 6890 Series GC equipped with a 50 m \times 0.530 mm, 25 μm , HP Mole-Sieve 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 min. The sample volumes were corrected for the partial pressure of toluene and the volume of CO added.

Synthesis of $[\text{HIPTN}_3\text{N}]\text{Mo}(\text{PMe}_3)$. 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 $\text{Mo}(\text{PMe}_3)$ (55% yield): ^1H NMR (C_6D_6 , 20°C) δ 19.2 (br s, 9H, PMe_3), 15.8 (br s, 6H, NCH₂), 6.55 (s, 12H, 3,5,3'',5''-H), 2.43 (br septet, 6H, 4,4''-CHMe₂), 1.8 (br s, 36H, 2,6,2'',6''-CH(CH₃)₂), 0.94 (d, 36H, 4,4''-CH(CH₃)₂), 0.88 (br s, 15H, 2,6,2'',6''-CHMe₂ and 2'-H), 0.55 (br s, 36H, 2,6,2'',6''-CH(CH₃)₂), -7.3 (br s, 6H, 4',6''-H), -25.9 (br s, 6H, NCH₂). Anal. Calcd for $\text{C}_{117}\text{H}_{168}\text{MoN}_4\text{P}$: 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 glovebox 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 glovebox 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 overpressurize the side arm. The plug is

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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 min, and the Teflon stopper is then closed. After 10 min 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 [HIPTN₃N]MoN and 321 mg (0.325 mmol) of Collidinium{BAR₄} 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 equiv 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 equiv of H₂ versus Mo. Upon completion of the catalytic run and indophenol analysis an average of 0.87 equiv of ammonia were obtained relative to molybdenum, or 0 from dinitrogen.

In a second run 9.0 mL (0.400 mmol) of H₂ were added. The internal pressure increased by 12.3% and H₂ to give a N₂/H₂ mixture in which 11.6% consisted of dihydrogen, or 65 equiv of H₂ versus Mo. Upon completion and analysis of the catalytic run 0.89 equiv of ammonia were obtained relative to molybdenum, or 0 from dinitrogen (Figure 4).

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