

Catalytic Reduction of Dinitrogen via Hydroboration

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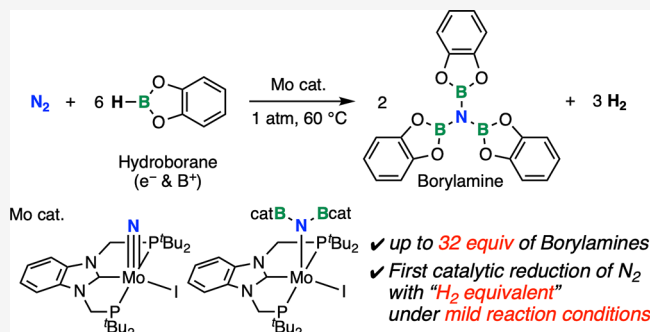


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ABSTRACT: The conversion of dinitrogen (N_2) into ammonia (NH_3) or other nitrogenous compounds under mild conditions remains highly desirable, given the extremely harsh conditions required by the typically employed Haber–Bosch process, which reacts N_2 with dihydrogen (H_2) to produce NH_3 . However, the catalytic conversion of N_2 using H_2 or related compounds containing H–E bonds (where E represents a general element) as reductants under mild conditions has remained elusive. Herein, we report the catalytic reduction of N_2 via hydroboration, wherein N_2 (1 atm) reacts with catecholborane in the presence of molybdenum–nitride complexes bearing PCP-type pincer ligands as catalysts at 60 °C, yielding up to 32 equiv of borylamines based on the molybdenum atom. The catalytic reaction proceeds through three successive 1,2-additions of hydroborane to the molybdenum–nitrogen bond, disproportionation of the molybdenum–hydride complex, and regeneration of the molybdenum–nitride complex via cleavage of the nitrogen–nitrogen triple bond. The catalytic reduction of N_2 with a “ H_2 equivalent” under mild reaction conditions represents a notable advance toward the development of ideal nitrogen fixation systems.



INTRODUCTION

Dinitrogen (N_2) is an abundant resource, accounting for 78% of the Earth's atmosphere. However, given the extremely low reactivity of N_2 , converting N_2 into ammonia (NH_3) or other nitrogenous compounds used as fertilizers, medicines, or energy carriers is challenging.^{1–3} The Haber–Bosch process is currently the most widely used industrial method capable of this conversion. In this process, N_2 is reduced by dihydrogen (H_2) to produce NH_3 in the presence of iron-based heterogeneous catalysts (Figure 1a). However, despite being well-established, the Haber–Bosch process requires extremely harsh reaction conditions (150–250 atm, 400–500 °C) and consumes a large amount of energy, which limits its practicality. For instance, they are not suitable for the on-demand production of NH_3 in flexible quantities and locations. Therefore, novel synthetic strategies for converting N_2 into nitrogenous compounds under milder conditions are being sought as next-generation nitrogen fixation methods.

Notably, homogeneous catalysts based on transition-metal complexes offer a promising approach for activating N_2 under considerably milder conditions than heterogeneous catalysts.^{4–17} Our research group, along with others, has developed catalytic reactions for producing NH_3 from N_2 using suitable one-electron reductants and proton sources under mild conditions.^{18–29} In particular, we established a method for the catalytic reduction of atmospheric pressure of N_2 using samarium diiodide (SmI_2) as a one-electron reductant and water or alcohol as proton sources. This reaction, conducted in

the presence of molybdenum complexes bearing pincer-type ligands as catalysts under ambient reaction conditions, afforded up to 60,000 equiv of NH_3 based on the molybdenum atom (Figure 1b).^{24,25} In this system, molybdenum–nitride complexes are formed as key reactive intermediates via the cleavage of the nitrogen–nitrogen bond in N_2 . Subsequent reduction and protonation afforded NH_3 alongside regenerated nitride complexes.

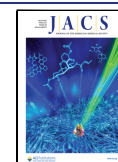
Thus, the reduction of N_2 into NH_3 using a combination of one-electron reductants and proton sources has gained increasing attention in recent years. In addition, reduction of N_2 with one-electron reductants and carbon-, silyl-, and boryl-centered electrophiles to produce cyanate anion,¹⁵ silylamines,¹⁶ and borylamines,^{17,30} respectively, has been developed using transition-metal complexes as catalysts. Unfortunately, however, the use of both one-electron reductants and electrophiles currently remains the only viable strategy for catalytic N_2 conversion under mild conditions. In stark contrast, the catalytic hydrogenation of N_2 under mild reaction conditions—where H_2 serves both as a reductant and a proton source—remains a formidable challenge.^{31,32} As a step toward addressing this

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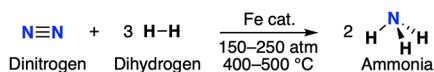
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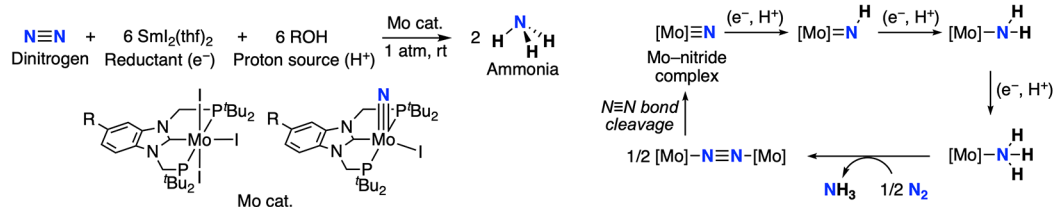
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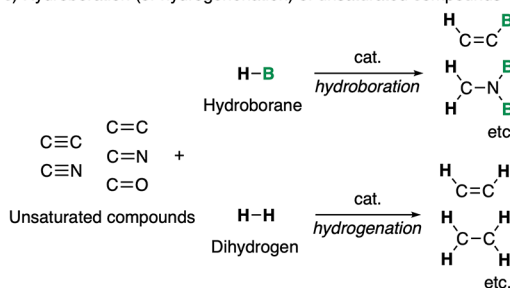
a) The Haber-Bosch process (hydrogenation of N_2 under harsh conditions)



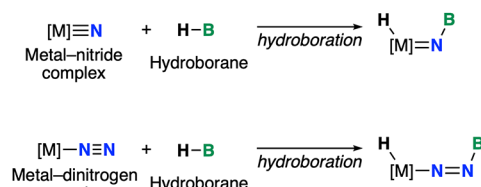
b) Catalytic reduction of N_2 with e^- and H^+ (previous work)



c) Hydroboration (or hydrogenation) of unsaturated compounds



d) Stoichiometric reaction of N_2 with hydroboranes



e) Catalytic reduction of N_2 via hydroboration (this work)

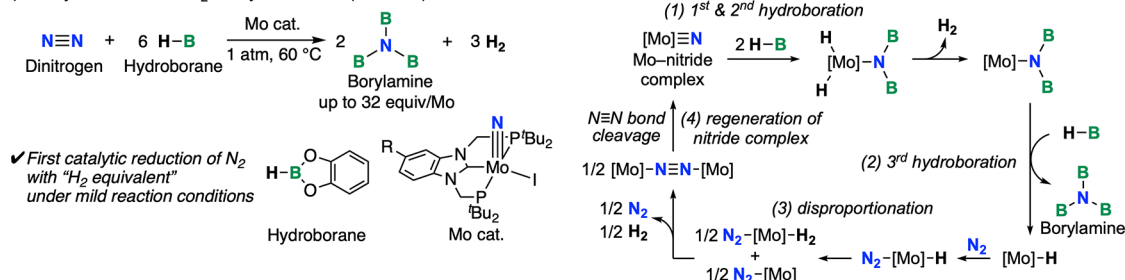


Figure 1. Research background and catalytic N_2 reduction via hydroboration.

challenge, we considered hydroboration, which is a process closely related to hydrogenation. Hydroboration—the 1,2-addition of a hydrogen–boron bond to multiple bonds in a manner analogous to hydrogenation—is a well-established, versatile method for functionalizing unsaturated compounds (Figure 1c).^{33–39} In the presence of transition-metal complexes as catalysts, a wide range of unsaturated compounds containing carbon–carbon or carbon–heteroatom multiple bonds can undergo hydroboration. Given the strong driving force for boron–nitrogen bond formation, we hypothesize that hydroboranes could be applied to the conversion of the nitrogen–nitrogen triple bond in the presence of suitable catalysts.

Our group and that of Mézailles independently reported stoichiometric reactions of molybdenum–nitride complexes, derived from N_2 , with hydroboranes. These reactions resulted in the 1,2-addition of hydrogen–boron bond to molybdenum–nitrogen triple bond, forming the corresponding molybdenum–borylimide–hydride complexes (Figure 1d).^{40–42} Further treatment with excess hydroborane afforded borylamine products. It is worth noting that the reaction of a molybdenum–nitride complex bearing a PNP-type pincer ligand with an excess amount of catecholborane (HBcat) at 80 °C under an atmospheric pressure of N_2 afforded up to 2 equiv of borylamines.⁴⁰ Isotope labeling experiments suggested that

half of the produced borylamines were derived from N_2 , while the other half from the nitride ligand. These findings demonstrate that the superstoichiometric reaction to convert N_2 via hydroboration can be achieved using the molybdenum complex. However, only (super)stoichiometric reactions of nitride^{40–42} or dinitrogen^{43–46} complexes with hydroboranes have been reported to date, while the catalytic conversion of N_2 via hydroboration is yet to be achieved. Herein, we report the catalytic reduction of N_2 via hydroboration using molybdenum–nitride complexes as catalysts. The reaction of an atmospheric pressure of N_2 with catecholborane (HBcat) in the presence of a catalytic amount of molybdenum complexes bearing PCP-type pincer ligands at 60 °C afforded up to 32 equiv of borylamines based on the catalyst, along with H_2 . Mechanistic studies revealed that this catalytic reduction involves three successive 1,2-additions of hydroborane to the molybdenum–nitrogen triple bond to generate borylamines, the disproportionation of a molybdenum–hydride complex, and the regeneration of the molybdenum–nitride complex via the cleavage of the nitrogen–nitrogen triple bond (Figure 1e). Notably, hydroborane acts as a reductant and a borylating reagent in this system, which is reminiscent of the dual role of H_2 (as a reductant and a proton source) in N_2 hydrogenation.

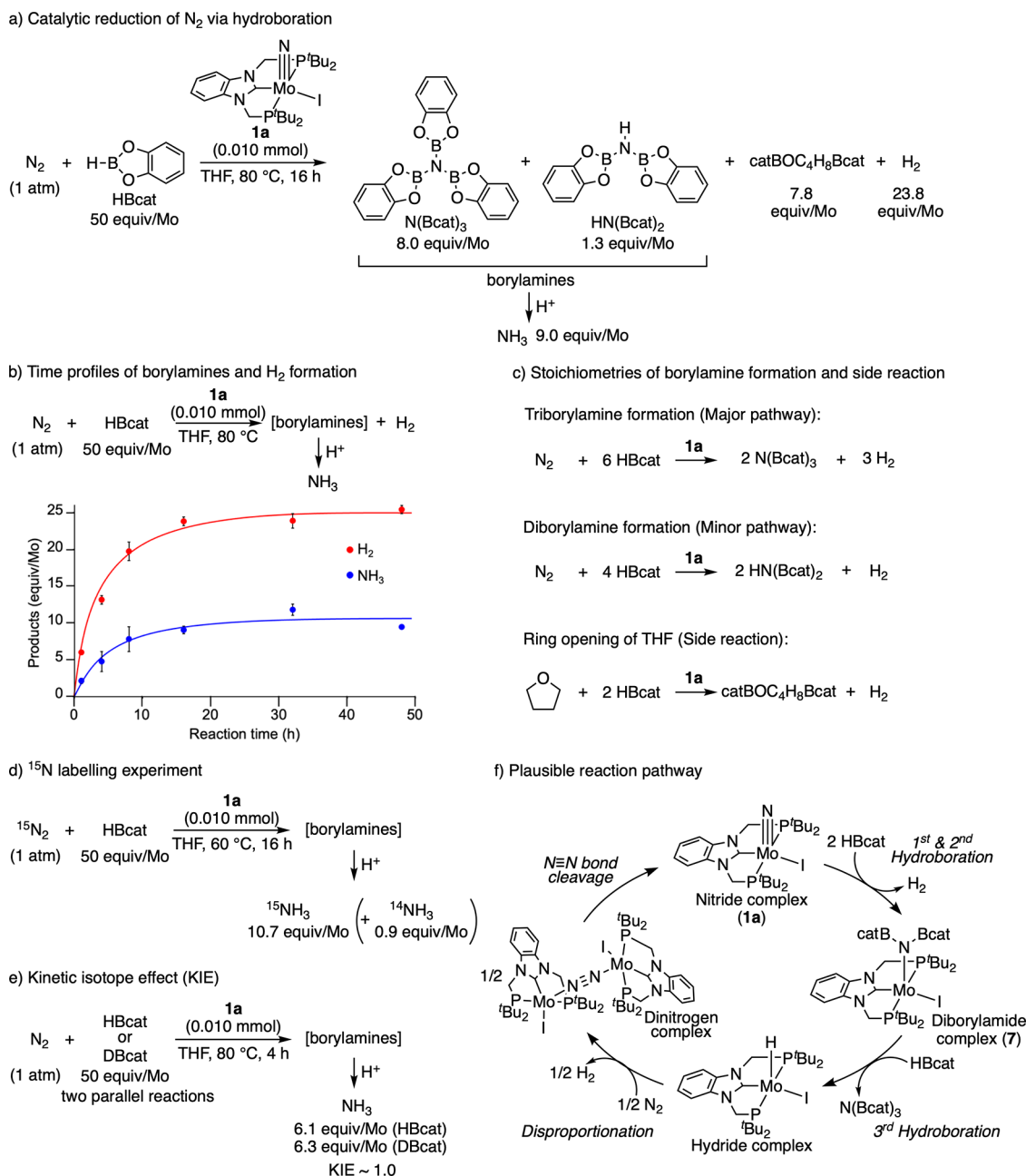


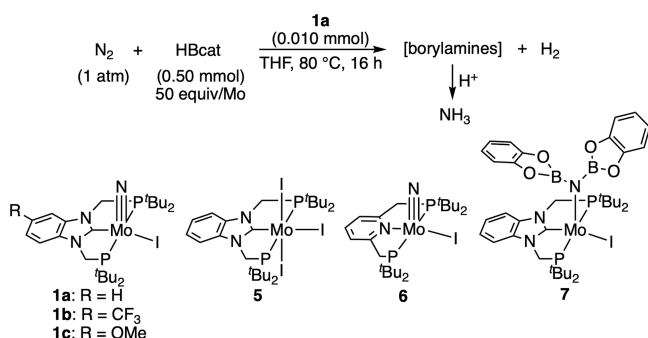
Figure 2. Catalytic reduction of dinitrogen with catecholborane. (a) Catalytic reduction of N₂ via hydroboration. (b) Time profiles of borylamine and H₂ formation. (c) Stoichiometries of borylamine formation and side reaction. (d) Catalytic reduction under an ¹⁵N₂ atmosphere to produce ¹⁵NH₃. (e) Kinetic isotope effect using HBcat or deuterated catecholborane (DBcat). (f) Plausible reaction pathway to afford triborylamine from N₂.

RESULTS AND DISCUSSION

Reaction Development. First, we examined the reaction of an atmospheric pressure of N₂ with 50 equiv of HBcat in tetrahydrofuran (THF) at 80 °C for 16 h in the presence of a catalytic amount of a molybdenum–nitride complex bearing a PCP-type pincer ligand (**1a**). This reaction afforded 9.0 equiv of NH₃ based on the molybdenum atom after protonolysis of the reaction mixture. Meanwhile, no hydrazine was detected. We also confirmed the generation of 23.8 equiv of dihydrogen (H₂) based on the molybdenum atom after the reaction by gas chromatography (Figure 2a and Table 1, Entry 1). Control experiments conducted in the absence of N₂, HBcat, or catalyst **1a** gave less than a stoichiometric amount of NH₃ after protonolysis, indicating that all three components are essential

to this reaction system (Table 1, Entries 2–4). Figure 2b presents time profiles of NH₃ and H₂ formation from the reaction of an atmospheric pressure of N₂ with HBcat in THF at 80 °C in the presence of **1a**. It was revealed that NH₃ and H₂ were generated in parallel without an induction period and that their formation was complete within approximately 16 h.

NH₃ formation in the catalytic reactions mentioned above suggests that borylamines were initially produced via the reduction of N₂ with hydroborane under catalytic conditions and subsequently converted to NH₃ by protonolysis. To support this hypothesis, we investigated the products of the catalytic reaction prior to protonolysis in detail. Notably, the ¹H and ¹¹B{¹H} nuclear magnetic resonance (NMR) spectra of the reaction mixture indicated the consumption of HBcat and the

Table 1. Reduction of Dinitrogen via Hydroboration

entry	deviations from standard conditions	NH ₃ (equiv/Mo)	NH ₃ (%) ^a	H ₂ (equiv/Mo)	H ₂ (%) ^a
1 ^b	none	9.0 ± 0.5	54	23.8 ± 0.6	94
2	without catalyst		0		3
3	under 1 atm of argon	0.8	5	23.1	92
4	without HBcat	0.5		0	0
5	HBpin instead of HBcat	0.9	6	1.0	4
6	BH ₃ ·THF instead of HBcat	0.5	3	10.9	43
7 ^b	room temperature	2.2 ± 0.1	13	3.5 ± 0.3	14
8 ^b	60 °C	11.7 ± 0.7	69	23.4 ± 0.1	93
9	toluene, 60 °C	3.6	21	6.5	26
10 ^b	1,4-dioxane, 60 °C	11.6 ± 0.5	69	17.9 ± 0.0	72
11 ^b	2-MeTHF, 60 °C	13.5 ± 0.5	81	24.3 ± 1.1	97
12	5 instead of 1a, 2-MeTHF, 60 °C	0.1	1	2.4	10
13	6 instead of 1a, 2-MeTHF, 60 °C	2.1	12	4.9	19
14	1b instead of 1a, 2-MeTHF, 60 °C	3.9	23	7.6	30
15 ^b	1c instead of 1a, 2-MeTHF, 60 °C	16.1 ± 0.2	96	22.6 ± 0.5	90
16 ^{b,c}	1c instead of 1a, 2-MeTHF, 60 °C, 32 h	32.0 ± 1.7	96	46.8 ± 0.1	94
17 ^b	7 instead of 1a	9.9 ± 2.4	59	27.5 ± 0.3	>99

^aYield based on the following equation: N₂ + 6 HBcat → 2 N(Bcat)₃ + 3 H₂. ^bData were the mean of multiple individual experiments (at least 2) with error bars representing standard deviation. ^cAnother HBcat (0.5 mmol) was added after 16 h.

formation of new boryl-containing products, which may correspond to the borylamines (Figures S23 and S24). After repeated attempts, we successfully isolated triborylamine N(Bcat)₃ (2) from the reaction mixture through recrystallization. The formation of triborylamine 2 was further confirmed by X-ray diffraction analysis, which revealed a crystal structure identical to that reported previously.⁴⁷ A comparison of the ¹H and ¹¹B{¹H} NMR spectra of the reaction mixture (Figures S23 and S24) with those of isolated compound 2 (Figures S3 and S4) revealed that 2 is the primary borylamine product (8.0 equiv/Mo) in the catalytic reaction. Although we were unable to isolate additional products directly from the reaction mixture, we separately synthesized diborylamine HN(Bcat)₂ (3)⁴⁸ and confirmed its formation in 1.3 equiv as a minor borylamine product. We also observed that a non-negligible amount of catBC₄H₈OBcat (4, 7.8 equiv) was formed via the ring-opening of THF. We separately confirmed that 4 is the main product from the reaction conducted in the presence of 1a under an Ar atmosphere (Figure S25, same reaction conditions as those in Table 1, Entry 3). In contrast, 4 was not formed in the absence of

1a, indicating that the ring-opening process is catalyzed by the molybdenum species. ¹H NMR analysis with an internal standard revealed that 2, 3, and 4 were produced in 8.0, 1.3, and 7.8 equiv based on the molybdenum atom, respectively (Figures 2a and S23 and S24). One thing to note is that the total amount of the produced borylamines (9.3 equiv/Mo) closely corresponds to the amount of NH₃ formed after protonolysis (9.0 equiv/Mo), indicating that the borylamines were quantitatively converted to NH₃ upon acid treatment.

Based on the above results, the aforementioned reaction system can be described as a combination of the following three reactions (Figure 2c): (A) The reaction of N₂ with three equiv of HBcat, producing triborylamine 2 as the major product. (B) The reaction of N₂ with two equiv of HBcat, producing diborylamine 3 as a minor product. (C) Ring-opening of THF, producing boryl ether 4, as a side reaction that does not involve N₂. Each of the three reactions is accompanied by the formation of H₂. Additionally, we separately confirmed that the reaction of diborylamine 3 with HBcat in THF at 60 °C under an Ar atmosphere did not afford triborylamine 2, regardless of the presence of molybdenum complex 1a. The results suggest that the in situ conversion of diborylamine 3, formed via reaction (B), into triborylamine 2 does not occur under catalytic conditions and can be excluded as a potential pathway to give 2.

Then, we proceeded to optimize the reaction conditions. First, we examined other commonly used hydroboranes, such as HBpin (Table 1, Entry 5) and BH₃·THF (Table 1, Entry 6). However, these reactions yielded less than stoichiometric amounts of NH₃ after protonolysis, indicating that the catechol moiety plays a crucial role in this reaction system. We assume that the catechol moiety imparts suitable Lewis acidity and steric hindrance at the boron center compared to those of its pinacol counterpart. Next, we optimized the reaction temperature and found that the reaction at 60 °C afforded the best result, likely owing to the suppression of the ring-opening of THF as a side reaction (Table 1, Entries 1, 7, and 8). We also investigated the effect of the solvent on the catalytic reaction. While the reaction in toluene (Table 1, Entry 9) afforded only a small amount of NH₃, reactions in dioxane (Table 1, Entry 10) and 2-MeTHF (Table 1, Entry 11) at 60 °C gave better results than those in THF. We then evaluated various molybdenum catalysts under the optimized conditions (in 2-MeTHF, at 60 °C). Catalytic reactions using a molybdenum triiodide complex bearing a PCP-type pincer ligand (5, Table 1, Entry 12) and the molybdenum–nitride complex bearing a PNP-type pincer ligand (6, Table 1, Entry 13) afforded only substoichiometric or slightly above-stoichiometric amounts of NH₃. Note that the catalytic reaction in the presence of 6 in 2-MeTHF at 60 °C (Table 1, Entry 13) resulted in the formation of a slightly above-stoichiometric amount of NH₃ in a similar manner to that in THF at 80 °C in our previous report.⁴⁰ We consider that the difference in catalytic activities between molybdenum–nitride complexes bearing PCP- and PNP-type pincer ligands can be attributed to their relative stability under catalytic conditions. It is well-known that the *N*-heterocyclic carbene binds to a transition metal center more strongly than pyridine.^{49,50} Also, our previous studies suggested that the PCP-type ligands hardly dissociate from the metal center during catalytic NH₃ formation, in contrast to the PNP-type ligand.⁵¹ These differences clearly explain the reason why the molybdenum complex bearing the PCP-type ligand is superior to that with the PNP-type ligand. Next, we examined the effect of substituents on the PCP-type pincer ligand. Catalytic reactions using molybdenum–nitride

complexes bearing trifluoromethyl- and methoxy-substituted PCP-type ligands (**1b** and **1c**, Table 1, Entries 14 and 15) gave 3.9 and 16.1 equiv of NH_3 after protonolysis, respectively. These findings suggest that the electron-donating substituent on the PCP-type ligand substantially enhances the catalytic activity. This trend contrasts with that observed in our previous study on the catalytic synthesis of NH_3 using one-electron reductants and proton sources in the presence of molybdenum catalysts, wherein introducing an electron-withdrawing group on the PCP-type pincer ligand improved catalytic activity.²⁵ Finally, the reaction of an atmospheric pressure of N_2 with 100 equiv of HBcat (added in two portions) in the presence of a catalytic amount of **1c** in 2-MeTHF at 60 °C for 32 h afforded 32.0 equiv of NH_3 based on the catalyst after protonolysis (Table 1, Entry 16).

To further confirm the origin of the nitrogen atom in NH_3 , we carried out isotope-labeling experiments using $^{15}\text{N}_2$ gas (Figure 2d). Notably, reacting an atmospheric pressure of $^{15}\text{N}_2$ with HBcat in THF at 60 °C in the presence of nitride complex **1a** afforded 10.7 equiv of $^{15}\text{NH}_3$, along with 0.9 equiv of $^{14}\text{NH}_3$ derived from the nitride ligand (Figure S26). This result provides unambiguous proof of the nitrogen atom's origin. We also performed the isotope-labeling experiments using deuterated catecholborane (DBcat) (Figure 2e). The reaction afforded 6.3 equiv of NH_3 after protonolysis (6.1 equiv when HBcat was used), and the kinetic isotope effect (KIE) was calculated to be ~ 1.0 ; this suggests that cleavage of the boron–hydrogen bond is not involved in the rate-determining step of the catalytic reaction.

Isolation and Reactivity of the Diborylamide Complex.

Next, we carried out stoichiometric reactions to investigate the underlying reaction pathway. Specifically, the reaction of molybdenum–nitride complex **1a** with 2.1 equiv of HBcat in THF- d_8 at room temperature afforded diborylamide complex (**7**) in 85% NMR yield, along with H_2 in 67% yield and a trace amount of $\text{HN}(\text{Bcat})_2$ (Figure 3a). Complex **7** was isolated and characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR as well as X-ray analysis. In particular, the X-ray crystallographic analysis of **7** revealed that its molybdenum center adopts a distorted square pyramidal geometry and that two boron–nitrogen bonds are formed on the nitride ligand (Figures 3b and S31). The molybdenum–nitrogen bond length increased substantially from 1.66 Å in nitride complex **1a**²⁵ to 2.07 Å in diborylamide complex **7**, indicating that a molybdenum–nitrogen triple bond was converted to a single bond. In sharp contrast to Mézailles' recent report⁴¹ on the reaction of a molybdenum–nitride complex bearing a PPP-type pincer ligand with $\text{BH}_3\cdot\text{SMe}_2$, complex **7** does not contain hydride ligands, owing to their elimination as H_2 . ^1H NMR spectroscopy (Figure S12), Fourier transform infrared spectroscopy (Figure S27), and electrospray ionization time-of-flight mass spectrometry measurements (Figure S28) support the absence of a hydride ligand in complex **7**. The single-bond character of the molybdenum–nitrogen bond in **7**, along with the absence of a hydride ligand, suggests that the molybdenum center was formally reduced from (IV) to (II).

The reactivity of diborylamide complex **7** was next examined. Treatment of complex **7** with 1.0 equiv of HBcat in THF- d_8 at 60 °C for 16 h under an Ar atmosphere afforded $\text{N}(\text{Bcat})_3$ and $\text{HN}(\text{Bcat})_2$ in 43% and 10% yields, respectively, along with H_2 in 34% yield (Figure 3c). This result suggests that the diborylamide ligand ($[\text{N}(\text{Bcat})_2]^-$) on complex **7** reacted with HBcat to afford free borylamines. Moreover, the catalytic reaction of N_2 in the

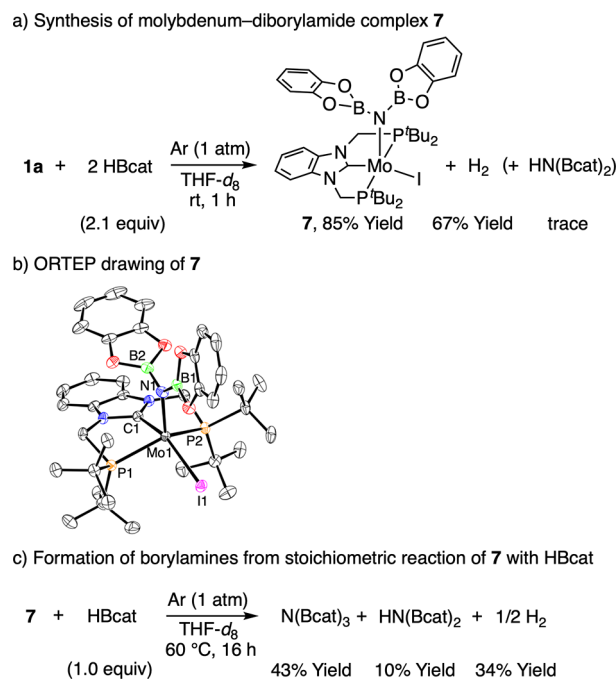


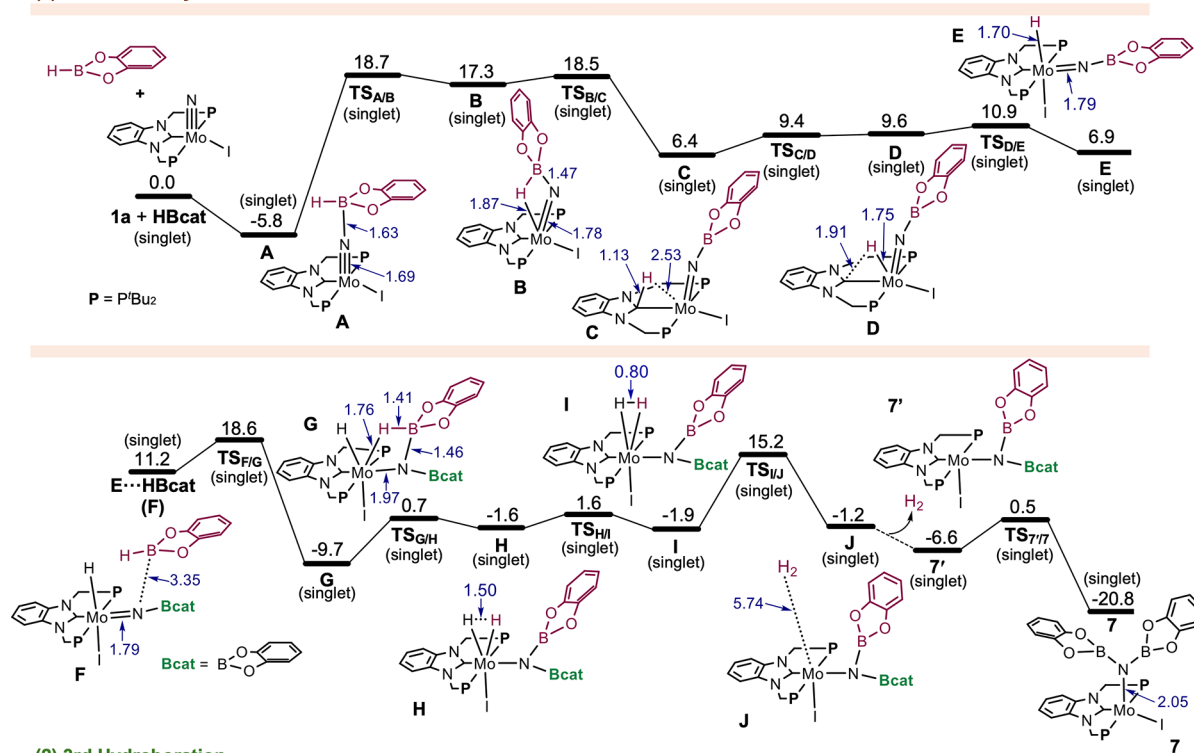
Figure 3. Stoichiometric reactions of molybdenum complexes with catecholborane. (a) Synthesis of molybdenum–diborylamide complex **7** from the reaction of molybdenum–nitride complex **1a** with two equiv of catecholborane under argon atmosphere. (b) ORTEP drawing of complex **7**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. (c) Formation of borylamines from the reaction of complex **7** with one equiv of catecholborane under argon atmosphere.

presence of complex **7** afforded 9.9 equiv of NH_3 based on the molybdenum atom after protonolysis, a value comparable to that obtained when complex **1a** was used (Table 1, Entry 17). These findings suggest that complex **7** serves as a reactive intermediate in the catalytic N_2 reduction via hydroboration, leading to the formation of borylamines.

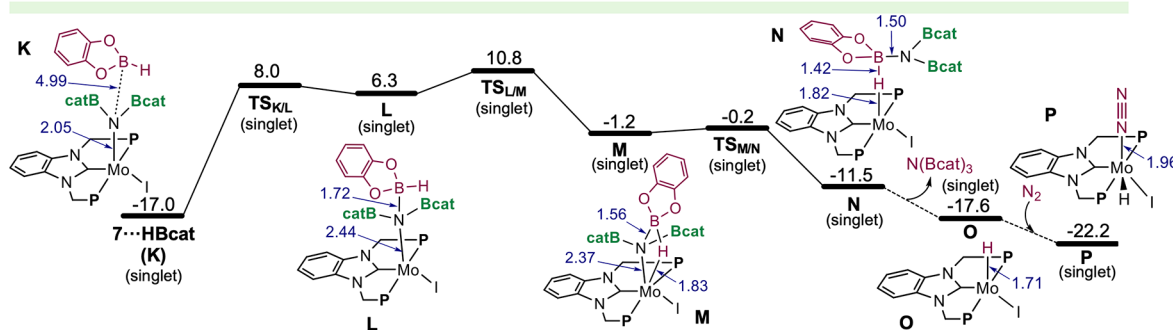
Density Functional Theory (DFT) calculations. DFT calculations were performed to further elucidate the reaction mechanism underlying the formation of $\text{N}(\text{Bcat})_3$ as the primary product. Based on the experimental findings, complex **7** was considered a key intermediate in the proposed catalytic cycle illustrated in Figure 2f. Figure 4 presents the free-energy profiles at 333 K calculated for the $\text{N}(\text{Bcat})_3$ formation catalyzed by **1a**. The optimized structures of the intermediates and transition states are provided in Figures S32–S41. The aforementioned catalytic cycle comprises four sequential steps: (1) Hydroboration of molybdenum–nitride complex **1a** by two molecules of HBcat yields diborylamide–dihydride complex **H**, which releases H_2 to generate **7**. (2) Hydroboration of **7** by HBcat yields $\text{N}(\text{Bcat})_3$ alongside the five-coordinate hydride intermediate **O**. Coordination of an N_2 molecule to **O** generates hydride– N_2 complex **P**. (3) Disproportionation of two molecules of **P** yields the dihydride– N_2 complex **T** and the N_2 complex **V**. Release of H_2 from **T** yields a second molecule of **V**. (4) Coupling of two molecules of **V** forms the N_2 -bridged dimolybdenum intermediate **X**. Finally, splitting of the bridging N_2 ligand of **X** regenerates two molecules of **1a**.

In step (1), a molecule of HBcat attacks the nitride ligand of **1a** to form intermediate **A** without an activation barrier. Intermediate **B**, which features a four-membered Mo–N–B–H ring, forms endergonically ($\Delta G_{333} = 23.1$ kcal/mol) with a

(1) 1st and 2nd hydroborations



(2) 3rd Hydroboration



(3) Disproportionation

(4) Regeneration of 1a

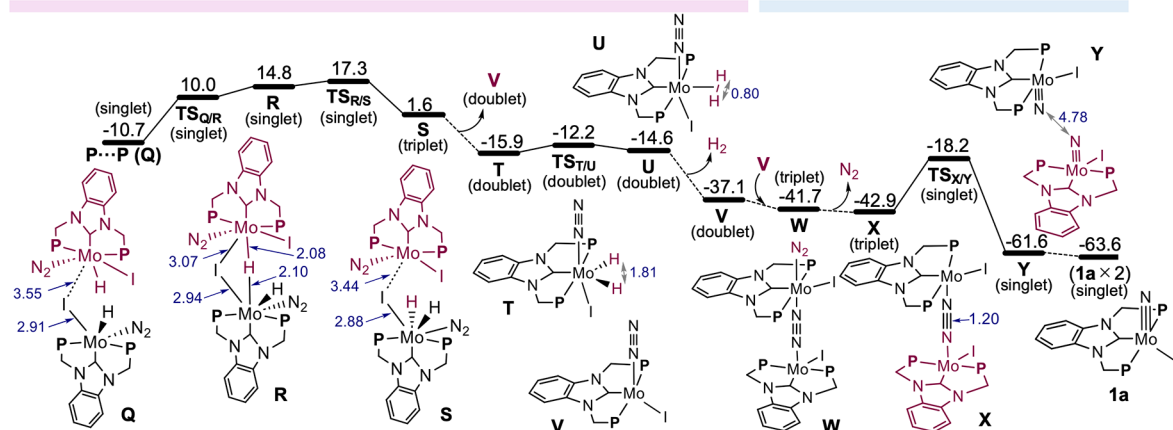


Figure 4. Theoretically proposed reaction pathway for molybdenum-catalyzed triborylamine formation. Free energy profiles at 333 K (ΔG_{333} in kcal/mol) for the whole catalytic process including three successive hydroborations of **1a**, disproportionation, and regeneration of **1a** (see more details in the Supporting Information). Optimized structures of intermediates and their selected interatomic distances in Å are presented.

relatively high activation free energy ($\Delta G_{333}^{\ddagger} = 24.5$ kcal/mol). Subsequent cleavage of the B–H bond in HBCat generates borylimide–hydride intermediate E. Computational analysis of this intermediate formation indicates that the hydrogen atom

transfers from the boron atom to the molybdenum atom via the carbene carbon atom of the PCP ligand ($\text{B} \rightarrow \text{C} \rightarrow \text{D}$). Overall, the first hydroboration ($\mathbf{1a} + \text{HBcat} \rightarrow \mathbf{E}$) is endergonic by 6.9 kcal/mol. A second HBcat molecule then attacks the imide

ligand of **E**, forming intermediate **G**. In the optimized structure of **G**, the hydrogen atom from HBcat is shared between the boron and molybdenum atoms. Cleavage of the B–H bond in **G** produces intermediate **H**, followed by the dissociation of an H₂ molecule via dihydrogen complex **I**.⁵² Release of H₂ from **I** yields diborylamide complex **7'**, an isomer of **7**. Subsequently, isomerization of **7'** to **7** proceeds smoothly ($\Delta G_{333} = -14.2$ kcal/mol and $\Delta G_{333}^{\ddagger} = 7.1$ kcal/mol). Overall, the second hydroboration (**F** → **7** + H₂) is highly exergonic by 32.0 kcal/mol.

In step (2), a third molecule of HBcat attacks the amide ligand of complex **7**, forming adduct **L**. This HBcat addition is endergonic ($\Delta G_{333} = 23.3$ kcal/mol) and proceeds with an activation free energy of 25.0 kcal/mol. Among the three hydroboration steps, this step has the highest activation barrier, likely owing to the steric hindrance from the bulky N(Bcat)₂ ligand. Subsequently, **L** undergoes Mo–N bond cleavage and Mo–H bond formation, producing intermediate **N** via **M**. Intermediate **M** adopts a four-membered Mo–N–B–H ring structure. Cleavage of the B–H bond in **N** leads to the formation of N(Bcat)₃ and intermediate **O**. Finally, coordinatively unsaturated intermediate **O** accepts an N₂ molecule to form **P**. This process is critical for the subsequent disproportionation reaction. Overall, step (2), described as **K** + N₂ → **P** + N(Bcat)₃, is exergonic by 5.2 kcal/mol.

In step (3), two molecules of **P** engage in a disproportionation reaction, during which the hydride ligand of **P** is eliminated as an H₂ molecule. The reaction begins with the formation of intermediate **Q**, which occurs without an activation barrier. The hydride ligand on one molybdenum center is then shared with the other, resulting in intermediate **R**. This is followed by full hydride transfer to the second molybdenum center, yielding intermediate **S**. The hydride transfer (**Q** → **R** → **S**) is endergonic ($\Delta G_{333} = 12.3$ kcal/mol) and proceeds with the highest activation free energy in the proposed catalytic cycle ($\Delta G_{333}^{\ddagger} = 28.0$ kcal/mol). This result indicates the involvement of the hydride transfer process in the rate-limiting step. This may explain the experimentally observed substituent effect, where the electron-donating substituent on the PCP-type ligand increases the electron density on the hydride ligand and thereby promotes the efficient hydride transfer. Subsequently, intermediate **S** undergoes cleavage to form **T** and **V** with $\Delta G_{333} = -17.5$ kcal/mol. Overall, the disproportionation reaction (**P** + **P** → **T** + **V**) is exergonic by 5.2 kcal/mol. Finally, intermediate **T** promptly releases H₂ to generate an additional molecule of **V** (**T** → **U** → **V** + H₂) with $\Delta G_{333} = -21.2$ kcal/mol and $\Delta G_{333}^{\ddagger} = 3.7$ kcal/mol.

In step (4), complex **1a** is regenerated from two molecules of **V**. These molecules form the N₂-bridged dimolybdenum intermediate **W**, which then readily loses an N₂ ligand at the *trans* position of the bridging N₂ ligand to afford **X** ($\Delta G_{333} = -5.8$ kcal/mol). Finally, cleavage of the bridging N₂ ligand of **X** regenerates two molecules of **1a**, completing the catalytic cycle ($\Delta G_{333} = -20.7$ kcal/mol; $\Delta G_{333}^{\ddagger} = 24.7$ kcal/mol; **X** → **Y** → **1a** + **1a**).

The rate-limiting step of the cycle is the disproportionation reaction, which proceeds with the highest activation free energy of 28.0 kcal/mol. Nevertheless, the overall reaction in one catalytic cycle (3HBcat + 1/2N₂ → N(Bcat)₃ + 3/2H₂) is highly exergonic, with a net ΔG_{333} of 42.9 kcal/mol, calculated as the sum of ΔG_{333} (**1a** + 3HBcat + N₂ → **P** + N(Bcat)₃ + H₂) and 1/2 ΔG_{333} (**P** + **P** → **1a** + **1a** + N₂ + H₂). Thus, this proposed mechanism supports the feasibility of the catalytic reaction under experimental thermal conditions.

CONCLUSIONS

In conclusion, we report the catalytic reduction of N₂ via hydroboration under mild conditions in the presence of molybdenum–nitride complexes bearing PCP-type pincer ligands as catalysts. The reaction of an atmospheric pressure of N₂ with catecholborane (HBcat) in the presence of the molybdenum catalyst in 2-MeTHF at 60 °C for 32 h afforded up to 32 equiv of borylamines based on the catalyst, along with H₂. Mechanistic investigations, including DFT calculations, revealed that the reduction proceeds through key steps: (1) three successive 1,2-additions of hydroborane to the molybdenum–nitrogen triple bond, (2) disproportionation of the molybdenum–hydride complex, and (3) regeneration of the molybdenum–nitride complex via cleavage of the nitrogen–nitrogen triple bond. Remarkably, the present reaction system enables catalytic conversion of N₂ without the need for strong one-electron reductants such as alkali metals, metallocenes, or samarium diiodide, which are typically required in the previous reaction systems using transition-metal complexes as catalysts.^{18–26} In our approach, hydroborane functions both as a reductant and as a borylating reagent, playing a role analogous to that of H₂ in the hydrogenation of N₂. Accordingly, hydroborane can be regarded as a “H₂ equivalent” in our reaction system. These findings offer valuable insight into the development of more sustainable and atom-economical strategies for catalytic reduction of N₂ using H₂ or its “equivalents” such as hydrosilanes.^{40,53}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.Sc07294>.

Experimental procedures, spectra of compounds, and computational details (PDF)

DFT-optimized geometries (XYZ)

Accession Codes

Deposition Numbers 2423562–2423564 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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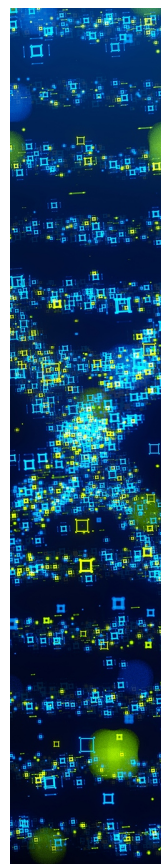
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As shown in the proposed reaction pathway toward $N(Bcat)_3$ in Figure 4, complex **7** forms via H_2 elimination from diborylamide–dihydrogen complex **1**. If N–H bond formation from intermediate **1** takes place instead of H_2 elimination, formation of $HN(Bcat)_2$, together with iodo–hydride complex **O**, can be rationalized. Importantly, generated **O** again serves as an active species toward formation of borylamines.

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