

Molybdenum Catalyzed Ammonia Borane Dehydrogenation: Oxidation State Specific Mechanisms

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Supporting Information

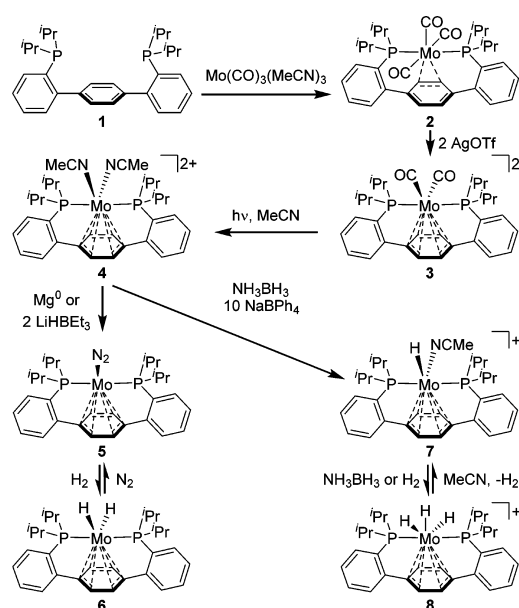
ABSTRACT: Though numerous catalysts for the dehydrogenation of ammonia borane (AB) are known, those that release >2 equiv of H₂ are uncommon. Herein, we report the synthesis of Mo complexes supported by a *para*-terphenyl diphosphine ligand, **1**, displaying metal–arene interactions. Both a Mo⁰ N₂ complex, **5**, and a Mo^{II} bis(acetonitrile) complex, **4**, exhibit high levels of AB dehydrogenation, releasing over 2.0 equiv of H₂. The reaction rate, extent of dehydrogenation, and reaction mechanism vary as a function of the precatalyst oxidation state. Several Mo hydrides (Mo^{II}(H)₂, [Mo^{II}(H)]⁺, and [Mo^{IV}(H)₃]⁺) relevant to AB chemistry were characterized.

There has been significant interest in transitioning from petroleum-based fuels to a “hydrogen economy,” with respect to both green energy and increased energy security.¹ A limitation to the implementation of hydrogen (H₂) in transportation is its low energy density and complications arising from compressed gas storage.^{1a,2} Numerous forms of chemical H₂ storage from metal hydrides^{1a} to metal organic frameworks³ have been explored. A forerunner in this field is ammonia borane (AB, NH₃BH₃), a compound with a substantial gravimetric storage capability of 19.6 wt % H₂ when dehydrogenated through the third equivalent (equiv).⁴ AB shows promise for reversible H₂ storage, with work toward efficient regeneration ongoing.⁵

Various AB dehydrogenation catalysts, including frustrated Lewis pairs⁶ and ionic liquids,⁷ have been investigated. Metal-based catalysts show the most potential for controlling both the rate and extent of H₂ release² and have demonstrated high activities in the cases of Ir,⁸ Ru,⁹ and Pd.¹⁰ Extensive H₂ release is less common due to NH₂BH₂ oligomerization,¹¹ but examples are known for Ni (*ca.* 2.7 equiv),¹² Fe (*ca.* 1.7 equiv),¹³ Pd (*ca.* 2.0 equiv),¹⁰ Rh (*ca.* 2.0 equiv),¹⁴ and Ru (*ca.* 2.3 equiv) (Table S1).¹⁵ These catalysts either employ expensive metals (Ru¹⁵ and Pd¹⁰) or suffer from instability (Pd,¹⁰ Fe,¹³ and Ni¹⁶). We report here the first examples of AB dehydrogenation catalysts based on Mo, an abundant and inexpensive metal. Our systems have demonstrated distinct behavior dependent on oxidation state, with isolated Mo⁰, Mo^{II}, and Mo^{IV} complexes capable of releasing over 2 equiv of H₂ from AB under moderate conditions.

Transition metals ligated by *para*-terphenyl diphosphine **1** (Scheme 1) have been studied for new types of reactivity.¹⁷ Mo complexes supported by diphosphine **1** were targeted to take advantage of the pendant arene acting as a versatile and

Scheme 1. Synthesis of Mo *para*-Terphenyl Diphosphine Complexes



hemilabile ligand for supporting different metal oxidation states and binding modes. Heating **1** in the presence of Mo(CO)₃(MeCN)₃ cleanly afforded the Mo *para*-terphenyl diphosphine complex **2** (Scheme 1). Through single crystal X-ray diffraction (XRD) analysis, η²-arene binding was observed with partial disruption of aromaticity in the central ring (Figure 1).

Targeting open Mo coordination sites, decarbonylation was pursued. Oxidation of **2** with 2 equiv of silver trifluoromethanesulfonate liberated one of the carbonyl ligands, increasing the hapticity of the Mo–arene interaction and maintaining an 18-electron configuration at the metal. Compound **3** exhibits a uniform elongation of the arene C–C bonds in the solid state (Figure 1), consistent with η⁶-binding.

Irradiation of **3** with UV light at –78 °C in the presence of acetonitrile afforded a deep purple complex lacking C–O stretching bands in the IR spectrum. XRD confirmed complete decarbonylation to the η⁶-arene-bis(acetonitrile) complex **4** (Figure 1). Stirring **4** vigorously over Mg⁰ under an N₂ atmosphere afforded the Mo⁰ dinitrogen complex, **5** (Scheme 1). The same species can be accessed upon treatment of **4** with

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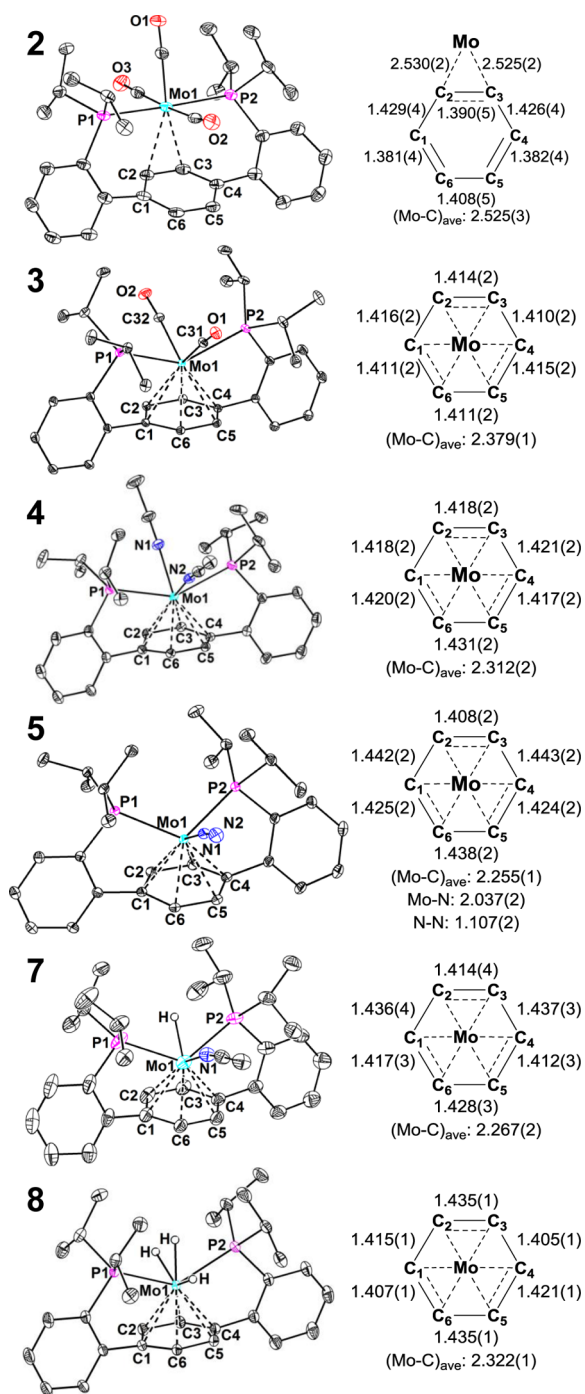


Figure 1. Solid-state structures of 2–5 and 7–8. Selected bond distances are reported in Å. Solvent molecules, counteranions, and select hydrogen atoms are omitted for clarity.

LiHBEt₃, albeit in lower yield. The ¹H NMR spectrum displayed two central arene signals at 4.3 and 4.0 ppm, suggesting a *pseudo*-C_s symmetric structure in solution, similar to the solid state. The average Mo–C distances (Å) in 5 (2.255(1)) are shorter than those in 3 (2.379(1)) and 4 (2.312(2)), consistent with increased δ -backbonding from Mo⁰ compared to Mo^{II} (Figure 1).¹⁸ The N–N IR stretching frequency, 2020 cm^{−1}, is similar to previously characterized (C₆H₅Me)Mo(PPh₃)₂N₂ (2000 cm^{−1}).¹⁹ Compounds 2–5 demonstrate the ability of diphosphine 1 to support Mo in multiple binding modes and oxidation states.

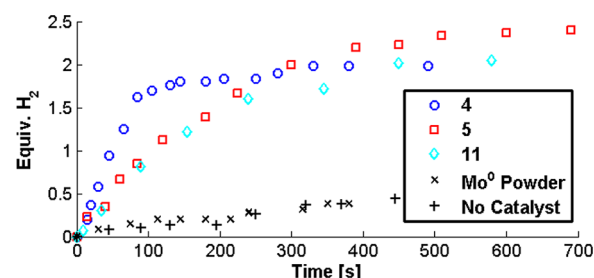


Figure 2. Eudiometry of AB dehydrogenation catalyzed by 4, 5, and 11. Mo⁰ powder and catalyst-free controls are included for reference.

With a precedent for base–metal catalysts effecting extensive H₂ release,¹² the reactivity of complex 5 with AB was tested. Addition of 1 equiv of AB led to partial conversion to a new species over several hours at room temperature. Although X-ray quality crystals have not been obtained, the ¹H NMR spectrum for this compound displays a single central arene signal at 4.81 ppm, indicating *pseudo*-C_{2v} symmetry, and a triplet at −4.10 ppm integrating to two protons, consistent with a Mo dihydride, 6. Complex 6 was independently synthesized via addition of H₂ to complex 5. Under excess N₂, 6 quantitatively reverts to 5, suggesting 6 as an intermediate in the LiHBEt₃ induced formation of 5 from 4. The T₁(min) (78 ms, 233 K, C₇D₈, 500 MHz; Figure S23) of 6 is inconsistent with a dihydrogen complex (T₁(min) ca. 20 ms), but is shorter than a typical dihydride relaxation, suggesting intermediate character.²⁰ The hydride-deuteride isotopolog, 6-HD, displays coupling (*J*_{HD} = 10.75 Hz, Figure S24) consistent with an H–D distance of 1.25²¹ to 1.36²² Å, further supporting this assignment. The Mo center in 6 is more electron rich than that of a similar Mo–dihydrogen complex bearing arene and CO ligands,^{20h} facilitating conversion toward a dihydride structure.

Extending this stoichiometric reaction to a catalytic system, a 0.25 M AB solution in diglyme was treated with 5 mol % 5 at 70 °C and gas evolution was monitored via eudiometry (Figure S30). This system produced 2.5 equiv of H₂ within 15 h, with the first 2 equiv liberated in 6.5 h (Figure 2). Such extensive H₂ release, 2.5 equiv, is rare.¹² Dehydrogenation attempts with Mo⁰ powder showed no change from the uncatalyzed control, and in the presence of elemental mercury, catalysis still proceeds (Figure S30),²³ consistent with homogeneous catalysis.²⁴ Analysis of the final reaction mixture by ¹¹B NMR spectroscopy showed a broad signal at 30 ppm corresponding to polyborazylene (PB),^{11,25} in agreement with production of >2 equiv of H₂.

Other Mo⁰ complexes were tested for AB dehydrogenation activity for comparison (Table S1). Mo(N₂)₂(dppe)₂, 9, proved ineffective, releasing less H₂ than the control and instead forming the stable tetrahydride complex Mo(dppe)₂(H)₄.²⁶ A pyridine-diphosphine-supported N₂ complex, 10,²⁷ showed similar dehydrogenation activity to 5, though it ultimately provided less H₂ (Figure S32). Reports of efficient dehydrogenative coupling of amino boranes by group 6 metal carbonyl species under thermo- or photolytic conditions²⁸ prompted the investigation of Mo(1,3,5-trimethylbenzene)(CO)₃, 11,²⁹ which demonstrated a similar initial rate of AB dehydrogenation to 5, but yielded less H₂ (Figure 2). Overall, precatalyst 5 is superior to other Mo⁰ species in terms of rate and extent of AB dehydrogenation (Table S1).

For comparison, catalytic trials were performed with Mo^{II} compound 4 under the aforementioned conditions, resulting in

the release of 2 equiv of H_2 in 8.5 h (Figure 2). Though complex **4** provided less extensive H_2 release, the initial rate was significantly faster than that of **5**. Similar to **5**, addition of elemental mercury had no effect on the rate of dehydrogenation (Figure S30). The Mo oxidation state (Mo^0 vs Mo^{II}) significantly affects the efficacy of the dehydrogenation catalysis, a phenomenon also observed for Fe-based systems.¹³

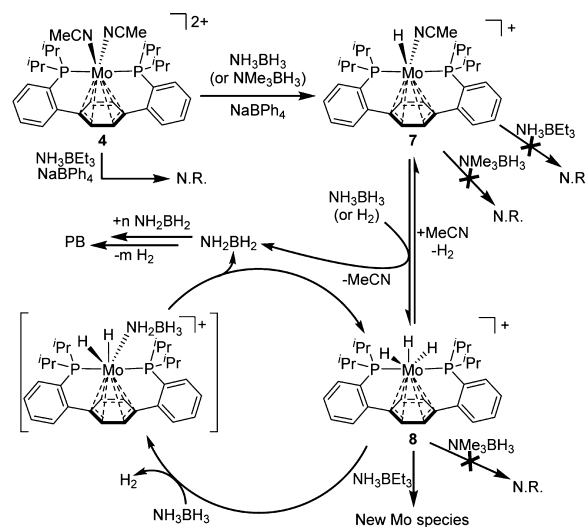
Interest in the disparate rate and extent of H_2 release catalyzed by **4** and **5** prompted a closer investigation of their respective reactivity. Monitoring stoichiometric reactions of **4** with AB at 70 °C showed the formation of a single new species with a peak at 92 ppm in the ^{31}P NMR spectrum. ^1H NMR spectroscopy displayed two central arene signals suggesting *pseudo-C_s* symmetry and a triplet with a relative integration of one at -0.5 ppm, consistent with a Mo monohydride (Scheme 1). XRD analysis confirmed the structure as a cationic Mo^{II} hydride, **7**, with an acetonitrile ligand completing the metal coordination sphere (Figure 1).

Treatment of **7** with AB resulted in partial conversion to another species (Scheme 1). The ^1H NMR spectrum of the mixture showed a new hydridic triplet at -4.6 ppm, integrating to three protons with respect to a single central arene peak at 5.6 ppm, suggesting a more oxidized and symmetric complex: the Mo^{IV} trihydride cation, **8**. Selective ^1H decoupling of the ^{31}P NMR spectrum (Figure S21) and independent synthesis via treating **7** with H_2 further supported this assignment. The hydridic resonance of **8** has a $T_1(\text{min})$ of 235 ms at 223 K (CD_2Cl_2 , 500 MHz; Figure S23), on the order of reported $\text{Mo}(\text{H})_3$ complexes, indicating classical trihydride character.^{20d,e,30} Precipitation in the absence of acetonitrile allows for the isolation of **8**. Acetonitrile promotes H_2 loss and the formation of **7**, with an equilibrium constant (K_{eq}) of 0.3 at 25 °C, as determined from solution concentrations.

Both hydrides **7** and **8** were observed in catalytic AB dehydrogenation by **4**, within 20 min, via ^{31}P NMR spectroscopy. Consumption of AB was observed in the ^{11}B NMR spectrum concurrent with the initial appearance of new signals at -20 and -12 ppm (B-(cyclo-diborazanyl)aminoborohydride, BCDB, Figure S26)¹¹ followed by two resonances near 30 ppm appearing after 45 min (borazine and PB).^{25,31} These observations suggest generation of NH_2BH_2 as a dehydrogenation intermediate on the way to borazine and PB.^{11,25} The formation of NH_2BH_2 was corroborated by cyclohexene trapping (Figure S26). Catalysis in the presence of excess cyclohexene afforded a major peak by ^{11}B NMR spectroscopy at 47 ppm, assigned to the hydroborylation product.¹¹

The terminus of activation was investigated using substituted amine–borane adducts.^{9c} Compound **4** reacts with NMe_3BH_3 to form **7** (Scheme 2) and not with Et_3BNH_3 , suggesting B–H activation as an initial step. This is reminiscent of the reaction of **4** with LiHBEt_3 (Scheme 1). Reactions of the isolated monohydride **7** with these AB analogs at 70 °C showed no change after 12 h even in the presence of excess substrate, providing no insight as to the site of reactivity with AB. Analogous experiments with **8** (Scheme 2) show reaction with Et_3BNH_3 , but not NMe_3BH_3 , in agreement with protic N–H hydrogens reacting with Mo^{IV} –H moieties. Catalytic trials with **4**, **7**, and **8** show that all are kinetically competent. Monitoring the rate of AB consumption by ^{11}B NMR showed first-order kinetics through three half-lives. Isotope effects of 1.7, 1.6, and 3.3 were determined for ND_3BH_3 , NH_3BD_3 , and ND_3BD_3 dehydrogenation by **4**, respectively (Figure S41). Though this may be consistent with H_2 evolution as the rate-determining step, the observed equilibrium between **8** and H_2 and potential H/D

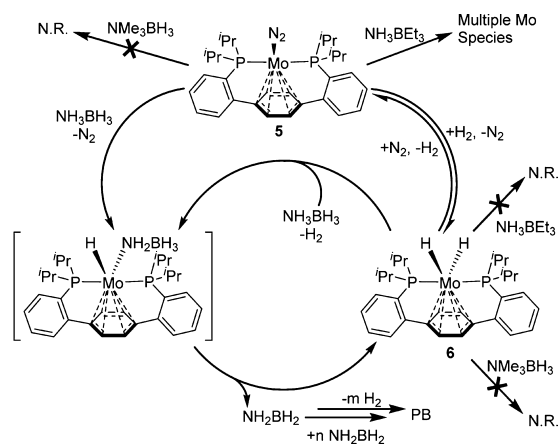
Scheme 2. Proposed Mechanism for Mo^{II} -Initiated Catalytic AB Dehydrogenation



scrambling complicate the interpretation of these data. A mechanism consistent with the present findings involves initiation from precatalyst **4** to generate Mo^{II} -monohydride **7**. Reaction of **7** with AB leads to Mo^{IV} -trihydride **8** and NH_2BH_2 , which can undergo further dehydrogenation events.¹¹ Activation of AB by **8** can occur directly at the N terminus with subsequent release of H_2 or via initial H_2 release followed by reaction with AB.

Similar studies of the catalytic behavior of **5** demonstrated the formation of **6** and disappearance of **5** within minutes. The ^{11}B NMR spectrum showed the consumption of AB and the appearance of the intermediate BCDB. Borazine and PB were observed, in accordance with dehydrogenation past 1 equiv. Unlike complex **4**, precatalyst **5** reacts with Et_3BNH_3 , albeit not cleanly. Complex **6**, isolated under argon, did not react with either terminus blocked substrate but did demonstrate AB dehydrogenation catalysis. The kinetics of AB dehydrogenation initiated by **5** were complicated, likely due to H_2 inhibition. A catalytic cycle consistent with these results involves reaction of **5** with AB via oxidative addition of an N–H bond (Scheme 3). Dihydride **6** may be accessible via β -hydride elimination, releasing NH_2BH_2 . Complex **6** could eliminate H_2 followed by

Scheme 3. Proposed Mechanism for Mo^0 -Initiated Catalytic AB Dehydrogenation



reaction with AB. Alternatively, **6** may react with AB directly and release H₂. In both instances, 1 equiv of H₂ is generated in an on-metal process, with the remainder derived from dehydro-oligomerization of NH₂BH₂. Although NH₂BH₂ is generated from both **4** and **5**, the difference in dehydrogenation extent is presently not well understood. It may be due to further metal-based reactivity of AB dehydrogenation products, in accordance with disparate byproduct distributions.

In summary, a series of Mo complexes have been shown to effectively catalyze the extensive dehydrogenation of AB, releasing ca. 2 equiv of H₂ in four cases. The Mo⁰ compound **5** is a rare example of a transition metal precatalyst capable of dehydrogenating AB through 2.5 equiv of H₂. These well-defined systems supported by the *para*-terphenyl diphosphine ligand, **1**, have been studied mechanistically and exhibit different reaction pathways as a function of metal oxidation state. A series of isolated Mo-hydrides (Mo^{II}(H)₂, [Mo^{II}(H)]⁺, and [Mo^{IV}-(H)₃]⁺) were found to support catalysis for the dehydrogenation of AB. Elucidation of the respective mechanisms and investigation of additional Mo-based AB dehydrogenation catalysts are ongoing.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, characterization data, crystallographic details (CIF), and full eudiometric data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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