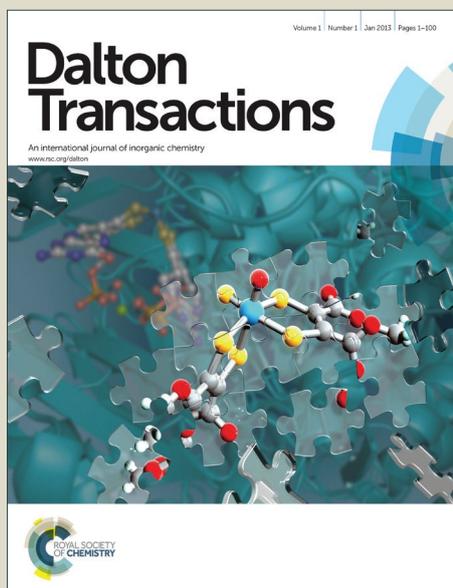


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Dehydrogenation of Ammonia Borane through the Third Equivalent of Hydrogen

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Ammonia Borane (AB) has high hydrogen density (19.6 wt. %), and can, in principle, release up to 3 equivalents of H₂ under mild catalytic conditions. A limited number of catalysts are capable of non-hydrolytic dehydrogenation of AB beyond 2 equivalents of H₂ under mild conditions, but none of these is shown directly to derivatise borazine, the product formed after 2 equivalents of H₂ are released. We present here a high productivity ruthenium-based catalyst for non-hydrolytic AB dehydrogenation that is capable of borazine dehydrogenation, and thus exhibits among the highest H₂ productivity reported to date for anhydrous AB dehydrogenation. At 1 mol% loading, (phen)Ru(OAc)₂(CO)₂ (**1**) effects AB dehydrogenation through 2.7 equivalents of H₂ at 70°C, is robust through multiple charges of AB, and is water and air stable. We further demonstrate that catalyst **1** has the ability both to dehydrogenate borazine in isolation and dehydrogenate AB itself. This is important, both because borazine derivatisation is productivity-limiting in AB dehydrogenation and because borazine is a fuel cell poison that is commonly released in H₂ production from this medium.

Introduction

Dehydrogenation of ammonia borane (AB, H₃N-BH₃) has been studied extensively as an approach for high-capacity hydrogen storage, because AB has high hydrogen density (19.6 wt%) and the ability to release H₂ under mild conditions.¹ Although catalytic hydrolysis is well known and efficient for H₂ production from AB,² non-hydrolytic dehydrogenation is a more desirable approach, because it (1) enables more facile re-reduction of dehydrogenated spent fuel and (2) minimizes evolution of ammonia, a hydrogen fuel cell poison, in the eluent gas stream.^{4, 1b} Several transition metal catalysts are active for non-hydrolytic AB dehydrogenation, including complexes of iron,⁵ molybdenum,⁶ iridium,⁷ rhodium,⁸ nickel,⁹ palladium,¹⁰ and ruthenium.^{11, 12} Catalyst systems reported to date fit one of two classes:¹³ (1) those that release 1 equivalent of hydrogen quickly^{14, 7} and (2) those that release 2 or more equivalents slowly.^{9, 10a, 12, 15} The latter are known to proceed through (or stop at) borazine, N₃B₃H₆, as an intermediate with its subsequent conversion to polyborazylene as a slow step in the overall mechanism of hydrogen evolution.¹⁶ This is problematic because (1) slow borazine derivatization limits H₂ productivity,¹² (2) borazine, which boils at 55 °C, is poisonous to fuel cells, and (3) borazine is known to coordinate metals¹⁷ and deactivate some AB dehydrogenation catalysts.¹⁶

Maximizing the H₂ release efficiency is highly desirable, and

only a few catalysts achieved a high release extent of 2.5 equivalents or greater (Figure 1). Currently, Baker's nickel-based system supported by Ender's carbene is the highest extent of H₂ release from AB reported to date. The Guan Fe-POCOP catalyst uses inexpensive iron but dehydrogenates fairly slowly and reacts through 2.5 equiv. H₂. The Agapie Mo catalyst has the same productivity, and is limited by air and water sensitivity. Further, Wegner has recently presented a metal-free catalyst that is capable of releasing ca. 2.5 equiv. of H₂. Despite high extent of H₂ release observed with these catalytic systems, no study of direct borazine consumption was reported with any of them, and borazine remains a significant constituent of the reactive medium at the end of the AB dehydrogenation reaction for each.

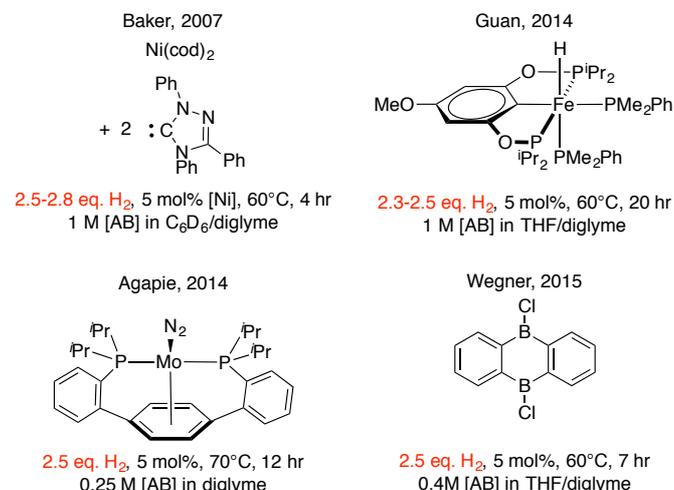


Fig. 1 Catalysts that dehydrogenate AB over 2.5 equiv.

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In the absence of a catalyst, borazine undergoes slow dehydrogenative BN cross-linking (48-60 hours at 70 °C under reduced pressure with periodic degassing) to polyborazylene.¹⁸ This rate is insufficient to prevent borazine accumulation under catalytic hydrogen evolution conditions. Thus, there is a desire to find a catalyst system that will dehydrogenate borazine at a rate faster than (or commensurate with) the rate at which it reacts with ammonia borane itself. No such system has yet to be reported. We report here the reactivity of ruthenium complex **1** (Figure 2) with AB to produce H₂ gas with high efficiency. **1** and its isomers are known to catalyse hydrogenation of ketones, olefins, and alkynes¹⁹ and hydroformylate olefins,²⁰ but its reactivity with AB has not been studied. **1** not only dehydrogenates AB, but also reacts with borazine to form polyborazylene, therefore exceeding the extent of dehydrogenation available with other systems and decreasing the amount of fuel cell poison in the gaseous eluent stream as less volatile polyborazylene. In addition to decreasing the accumulation of borazine in the dehydrogenation reactor, conditions based on **1** yield unusually high productivity, 2.7 equivalents of H₂ at mild reaction temperature, and are air and water tolerant.

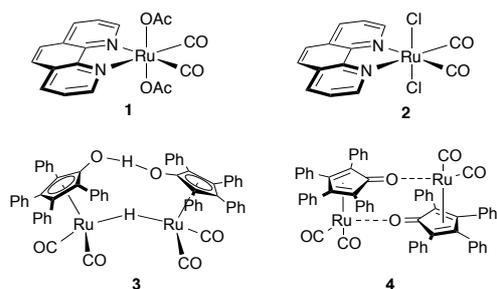


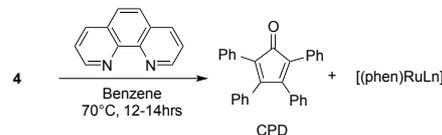
Fig. 2 Ru catalysts for AB dehydrogenation. (phen)Ru(OAc)₂(CO)₂ (**1**), (phen)RuCl₂(CO)₂ (**2**), Shvo's catalyst (**3**), Shvo oxidised form dimer (**4**).

Results and Discussion

Catalyst Development

We have previously demonstrated that the Shvo catalyst can lose its tetraphenylcyclopentadienone (CPD) ligand from the metal centre in the presence of bidentate nitrogen ligands such as 1,10-phenanthroline (phen) shown in Scheme 1.²¹ We suspect that the species produced by the expulsion of the CPD ligand contributes to the increase in rate of AB dehydrogenation. This species potentially consists of a ruthenium centre supported by two carbonyl ligands and the bidentate bis(nitrogen) ligand. We therefore investigated ruthenium scaffolds composed of these constituents. Whereas these square planar ruthenium complexes are not stable to isolation, we generate analogous compounds in situ. We reasoned that treatment of the known complex (phen)RuCl₂(CO)₂ (**2**)²² with TIOF and ammonia borane would generate a reactive (phen)Ru(CO)₂-based fragment.²¹ While 10% of **2** with 2 equivalents of TIOF will liberate 2.5-2.7 equivalents of H₂ from AB, the high loading of metals (both Ru

and Ti) is undesirable. Further, this reaction is not as effective at lower catalyst loadings. We eliminated the usage of thallium by replacing the chlorine ligands with acetates (**1**, Figure 2)^{22b} with the expectation that acetate groups should dissociate easily from the metal centre in the presence of an excess of boron with this dissociation driven by the strength of boron-acetate bonds.



Scheme 1. Ruthenium dimer **4** loses CPD in the presence of bidentate nitrogen ligands such as phen.

Reactivity of **1** with AB

1 dehydrogenates AB efficiently at low catalyst loading, down to 1 mol%, producing 2.4–2.7 equiv. of hydrogen, as shown in Figure 3. The catalyst system is robust, capable of producing a similarly high extent of H₂ release (2.6, 2.5, 2.4) in each of the multiple AB reloadings. Further, we compared the rates of catalytic reactions prepared in the glove box under nitrogen atmosphere and an analogous sample of **1** suspended in solvent and immersed in an ultrasonic bath in open air for 20 minutes before AB addition. We find that exposure of the catalyst to air and water in the atmosphere neither slows nor accelerates dehydrogenation; rather, these runs have analogous rates (Supplementary Information).

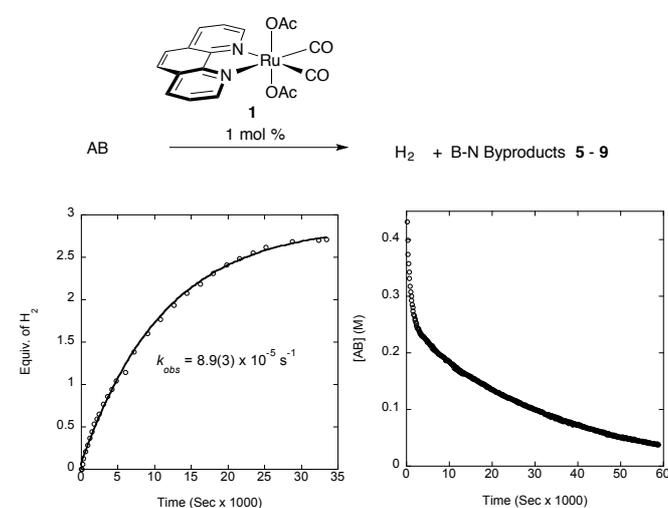
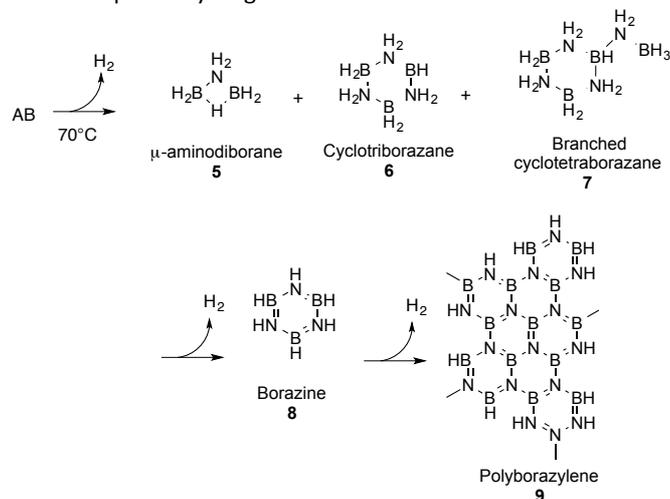


Fig. 3 Left: H₂ production from 1% of **1** at 70°C in diglyme releasing 2.7 equiv. Right: ¹¹B kinetic profile of the consumption of AB catalyzed by 1% of **1** in 2:1 diglyme/benzene-d₆.

Reactivity of **1** with Borazine

Treatment of AB with **1** results in the formation of a family of AB dehydrogenation products (Scheme 2) that has homology to those formed when the dehydrogenation is conducted with the Shvo catalyst (**3**),¹⁶ except that the reaction does not stop at borazine, but goes on to

polyborazylene materials (**9**). Borazine (**8**) is the exclusive boron-nitrogen material formed when **3** is used as the catalyst, and it is the principal material that accumulates after two equivalents of H₂ are produced. We expect that the Shvo system can not derivatise borazine because it is restricted to an outer sphere hydrogen transfer mechanism.



Scheme 2. Typical BN byproducts seen in AB dehydrogenation reactions.

Unlike **3** and its derivatives,²¹ **1** reacts with isolated borazine at 70 °C, yielding polyborazylene as the major byproduct. We can observe this directly by ¹¹B NMR (Figure 4). In this experiment, borazine was isolated by a vacuum transfer of the volatiles in a spent **3**-catalysed AB dehydrogenation reaction.^{12a} After the transfer of borazine and solvents into a J-Young NMR tube preloaded with **1**, a ¹¹B NMR spectrum was taken, and the solution was heated to 70 °C (see experimental section for further details). After heating for 24 hours, borazine (31 ppm) was converted, ca. 70%, relative to the external ¹¹B standard (0 ppm) to give signals consistent with cross-linked polyborazylene and other unsaturated B-N byproducts. These are indicated by broad signals in the ¹¹B NMR spectra from 24–34 ppm. Visual inspection of the NMR tube after the reaction shows insoluble, gelatine-like, white material, which is consistent with the formation of polymeric B-N species and accounts for the loss in integration of ¹¹B products observed by NMR. In contrast, the background thermal decomposition reaction under these conditions gives only ca. 15% after 24 hours (see Supplementary Information).

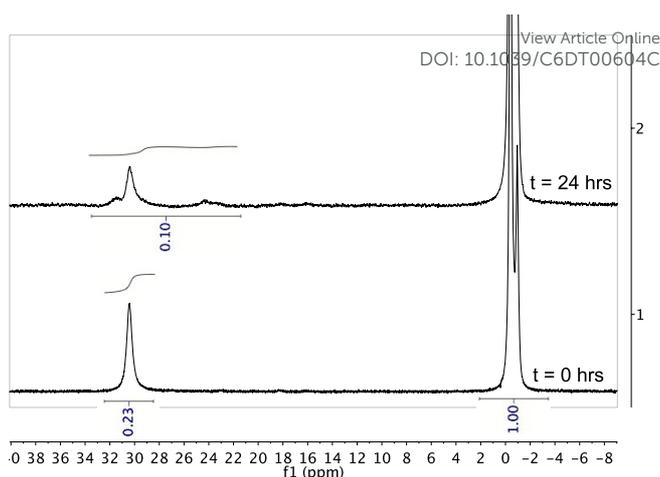


Fig. 4 Reaction of **1** with borazine (**8**) in 2:1 diglyme/benzene-*d*₆. Bottom: initial ¹¹B spectrum of **1** and borazine at room temperature. Top: ¹¹B spectrum of **1** and borazine after 24 hrs at 70 °C. Boron external standard BF₃-OEt₂ is at 0 ppm, and borazine is the only boron species present in the bottom spectrum at 31 ppm. In the top spectrum, borazine peak height has decreased and other broad boron species that are indicative of polyborazylene appear after 24 hrs. Areas under the peaks are integrated relative to the external standard BF₃-OEt₂ peak set to 1.00.

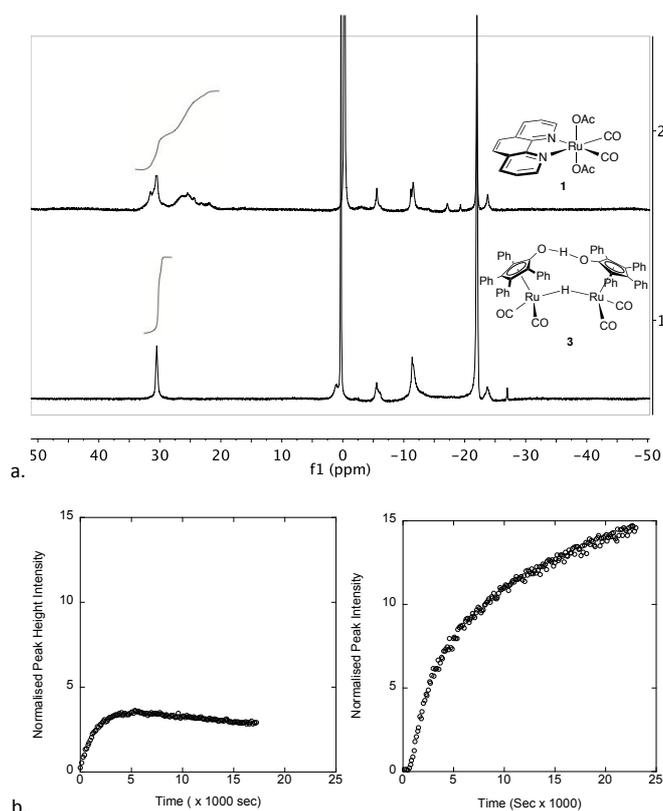


Fig. 5 a. Comparison of end-of-reaction ¹¹B NMR spectra under representative conditions. Top: AB dehydrogenation catalysed by 10% Ru atom of **1** after 1.75 hours in 2:1 diglyme/benzene-*d*₆ at 70 °C. Bottom: AB dehydrogenation catalysed by 10% Ru atom of **3** after 1.75 hours in 2:1 diglyme/benzene-*d*₆ at 70 °C. Note the larger proportion of polyborazylene in the top spectra (24–34 ppm) compared to the bottom spectra. Boron standard (BF₃-OEt₂ inset tube) is at 0 ppm. Areas under the peaks are integrated relative to the external standard BF₃-OEt₂ peak set to 1.00. b. Peak height of borazine over time catalysed by 10% Ru atom of **1** (left) and **3** (right).

Reaction Intermediates

We observe by ^{11}B NMR that reactions catalysed by **1** generate boron intermediates common in AB dehydrogenation reactions with catalysts outlined in Figure 1, which include μ -aminodiborane (**5**), cyclotriborazane (**6**), aminoborane cyclic tetramer (**7**), and borazine (**8**) (Scheme 2). However, at 1% loading of **1**, we observe the appearance of polyborazylene (**9**) as early as the first 20 minutes into AB consumption, along with intermediates **6-8**. This suggests that as borazine is produced, another mechanism is concurrently dehydrogenating it into polyborazylene. The borazine concentration builds steadily until approximately 50% of AB is consumed, and then the growth of the borazine peak tapers off followed by its conversion to polyborazylene. When we compare ^{11}B NMR spectra of **1**-catalysed AB dehydrogenation (10 mol% Ru atom loading) with our previously-reported reaction catalysed by the same loading of **3**,^{12a} we observe less borazine (31 ppm) build-up and more polyborazylene (24-34 ppm) in the reaction catalysed by **1** (Figure 5a). Plotting normalized peak height of borazine against time for reactions catalysed by 10 mol % of **1** and **3** (Figure 5b), we observe the decrease of borazine over time with **1**, while the borazine peak rises in the reaction catalysed by **3**.

Homogeneity

In order to probe the homogeneity or heterogeneity of the dehydrogenation catalysis, we conducted several tests. We added ca. 100 μL of elemental mercury to the reaction conducted at 10% catalyst loading and monitored AB consumption via ^{11}B kinetics in a mercury drop test of homogeneity. While there was a small drop in rate, the reaction proceeded similarly to the parent reaction, completing in approximately the same amount of time (Figure 6). This result suggests homogeneous catalysis, even though there are observable heterogeneous materials in the reaction. We therefore suspect that we have a homogeneous active species working in a heterogeneous suspension.

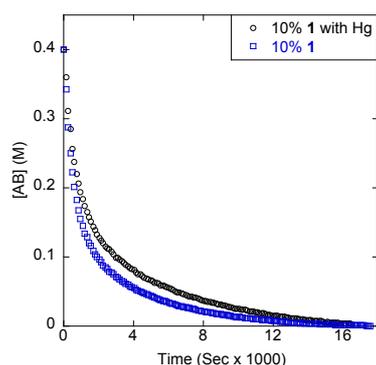


Fig. 6 Hg addition homogeneity test in 2:1 diglyme/benzene- d_6 at 70°C. Black circles: 10 mol% of **1** with Hg. Blue squares: 10% of **1**.

Conclusions

In summary we present here a high productivity non-hydrolytic ammonia borane dehydrogenation system releasing

up to 2.7 equiv. of H_2 at low catalyst loading. It has desirable kinetic properties, air and water tolerance, and reusability. We also show that this catalyst has reactivity with borazine itself, thus minimizing borazine concentration in the gas eluent stream of the H_2 generation reactor.

Experimental

All air and water sensitive procedures were carried out either in a Vacuum Atmosphere glove box under nitrogen (0.5-10 ppm O_2 for all manipulations) or using standard Schlenk techniques under nitrogen. Deuterated NMR solvents were purchased from Cambridge Isotopes Laboratories. Benzene- d_6 and diethylene glycol dimethyl ether (diglyme, Alfa Aesar) were dried over sodium benzophenone ketyl and distilled prior to use. Ammonia borane (NH_3BH_3 , AB) was purchased from Sigma Aldrich and used under N_2 atmosphere only without further purifications. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Pressure Chemical Co. and used without further purifications. Shvo's catalyst (**3**) was purchased from Strem Chemicals and used without further purifications. Acetic acid was purchased from EMD Millipore and used without further purification. Formic acid, 1,10-phenanthroline, and silver acetate were purchased from Alfa Aesar and used without further purification. $[\text{RuCl}_2(\text{CO})_2]_n$, $(\text{phen})\text{RuCl}_2(\text{CO})_2$ (**2**) and $(\text{phen})\text{Ru}(\text{OAc})_2(\text{CO})_2$ (**1**) were synthesized according to literature procedures (more details in the Supplementary Information).²³ ^1H and ^{11}B NMR spectra were obtained on Varian 600 MHz (600 MHz in ^1H , 192 MHz in ^{11}B), 500 MHz, and 400 MHz spectrometers with chemical shifts reported in units of ppm. All ^1H chemical shifts were referenced to the residual ^1H solvent (relative to TMS). All ^{11}B chemical shifts were referenced to a $\text{BF}_3\text{-OEt}_2$ in diglyme in a co-axial external standard (0 ppm). ^{11}B spectra are phased, baseline corrected, and backwards linear predicted 3-8 points. NMR spectra were taken in 8" J-Young tubes (Wilmad) with Teflon valve plugs. FTIR were taken on KBr salt plate, or KBr pellet on a Bruker Vertex 80 FTIR.

Hydrogen Quantification

In a typical reaction, 7.7 mg AB (0.25 mmol) was combined with catalyst (1-10 mol%) in a 2 mL Schlenk bomb equipped with a Teflon stir bar while in a glove box under nitrogen. Diglyme (0.6 mL) was added to the flask to create a light yellow mixture. The eudiometer was constructed as follows: The side arm of the valve was connected to a piece of Tygon tubing, which was connected to a 3-way valve. Center of the 3-way valve was connected to the Schlenk line to allow vacuum and nitrogen purge of the apparatus. The last valve was connected to Tygon tubing that was adapted to 20 gauge (0.03") Teflon tubing with a needle. The tubing was threaded through open end of a burette that was sealed with a Teflon stopcock on the other end. The burette was filled with water. The entire apparatus was then inverted into a 500 mL Erlenmeyer filled with water and clamped onto a metal ring stand. Opening the 3-way-valve to the Schlenk line and the bomb (reaction still closed and wrapped in foil at room

temperature), the space in the 3-way valve and tubing was vacuumed and refilled with N₂ for 5 minutes twice and then opening all 3 valves to the line, N₂ purge was conducted through out the burette for 10 minutes. Then the 3-way valve was turned so that only the bomb and the side connected to the burette were open, and N₂ was turned off. The water in the burette was pulled upwards by a pipette filler bulb and the initial volume was recorded. The bomb was then submerged into a 70 °C oil bath for 2 minutes to allow the temperature of the system to equilibrate. The reactor's valve was opened to release gas from the reactor headspace while heating in a regulated oil bath. The volume of liberated gas was recorded periodically until gas evolution ceased. Liberated hydrogen was quantified by recording its volume displacement in the eudiometer. Reaction proceeds from initial yellow to gray, to black suspension.

Kinetic Profiles of AB Dehydrogenation Recorded via ¹¹B NMR

In a typical reaction, 7.7 mg of AB was combined with catalyst (1.0 – 10.0 mol%) in a J-Young NMR tube while in a glove box under nitrogen. The AB concentration and catalyst concentrations may be varied. Diglyme (0.4 mL) and benzene-*d*₆ (0.2 mL) were added to the tube. The sample tube was immediately inserted into a temperature-equilibrated (70 °C), pre-shimmed, and pre-locked NMR, and the kinetic monitoring commenced. Disappearance of AB in the solution was monitored by the relative integration of its characteristic peak in the ¹¹B spectrum (–22 ppm) and the BF₃-OEt₂ (0 ppm) standard. The acquisition involved a 1.84 s pulse sequence in which 16,384 complex points were recorded, followed by 1 s relaxation delay. To eliminate B–O peaks from the borosilicate NMR tube and probe, the ¹¹B FIDs were processed with backward linear prediction. *Safety note: caution should be used when carrying out these reactions, as the release of hydrogen can lead to sudden pressurization of reaction vessels.*

Reactivity of **1** with Borazine

Borazine was generated in a J. Young NMR tube by the reaction of Shvo's catalyst (6.7 mg, 2.5%, 0.0062 mmol) with AB (7.7 mg, 0.25 mmol) in 2:1 diglyme/benzene-*d*₆ (0.4 mL and 0.2 mL respectively) in a 70°C oil bath for 16-20 hours.^{12a,16} The NMR tube was connected via a flame-dried U-tube to another J. Young NMR tube containing **1** (1.2 mg, 0.0025 mmol), diglyme (0.4 mL), and ¹¹B external standard. The volatiles (H₂, borazine, benzene-*d*₆) were transferred under static vacuum while the borazine-containing tube was heated gently with a heat gun while the receiving tube was submerged in liquid N₂ until all of the ca. 0.2 mL of benzene was transferred to the receiving tube. The J. Young valves were closed and the U-tube system was flushed with N₂. While the N₂ line was closed and the U-tube is under N₂, the receiving tube was opened briefly to return it to atmospheric pressure. ¹H and ¹¹B NMR spectra were taken, and then the borazine-containing tube was submerged in a 70 °C oil bath for 24 hours. Peak heights relative to the external standard (BF₃-OEt₂ in diglyme (0 ppm)) were compared since polyborazylene and borazine peaks

overlap in the ¹¹B spectrum and integrations could not be done accurately. The procedure for the borazine background reaction was the same, except for the absence of **1** in the receiving tube (See Supplementary Information for graphical representation).

Catalyst Reuse Reactions

To test the reusability of catalyst **1**, we studied the production of H₂ gas by eudiometry for successive runs with 1.0 mol% catalyst. For run 1, we added 7.7 mg AB, 1.2 mg **1**, and 0.6 mL diglyme to a 2 mL Schlenk flask equipped with a small stir bar. The reaction was heated at 70 °C in a regulated oil bath and reaction progress monitored by displacement of water by H₂ gas in an inverted 50 mL burette. For successive runs, we added 7.7 mg AB and 0.2 mL diglyme and repeated the reaction at 70 °C. Pseudo-first order rate constants for H₂ productions over these runs are 12.1, 10.8, and 7.0 x 10⁻⁵ s⁻¹.

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Robust, water and air stable catalyst (phen)Ru(OAc)₂(CO)₂ dehydrogenates ammonia borane through 2.7 equivalents of H₂ and derivatises fuel cell poison borazine.

