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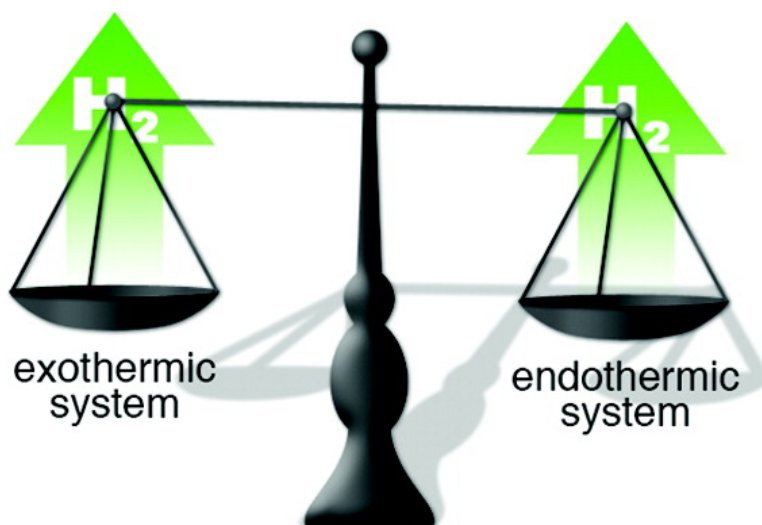# Production of H from Combined Endothermic and Exothermic Hydrogen Carriers

Dominik Wechsler, Yi Cui, Darrell Dean, Boyd Davis, and Philip G. Jessop

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Production of H$_2$ from Combined Endothermic and Exothermic Hydrogen Carriers

Dominik Wechsler,[†] Yi Cui,[†] Darrell Dean,[†] Boyd Davis,*[‡] and Philip G. Jessop*[†]

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6, and Queen's-RMC Fuel Cell Research Centre, 945 Princess Street, Second Floor, Kingston, Ontario, Canada K7L 5L9

Received September 2, 2008; E-mail: jessop@chem.queensu.ca; boyd.davis@mine.queensu.ca

Abstract: One of the major limitations to the use of fuel cell systems in vehicular transportation is the lack of hydrogen storage systems that have the required hydrogen storage density and moderate enthalpy of dehydrogenation. Organic liquid H$_2$ carriers that release H$_2$ endothermically are easier to handle with existing infrastructure because they are liquids, but they have low storage densities and their endothermicity consumes energy in the vehicle. On the other hand, inorganic solid H$_2$ carriers that release H$_2$ exothermically have greater storage densities but are unpumpable solids. This paper explores combinations of an endothermic carrier and an exothermic carrier, where the exothermic carrier provides some or all of the necessary heat required for dehydrogenation to the endothermic system, and the endothermic carrier serves as a solvent for the exothermic carrier. The two carriers can be either physically mixed or actually bonded to each other. To test the latter strategy, a number of chemically bound N-heterocycle:BH$_3$ adducts were synthesized and in turn tested for their ability to release H$_2$ by tandem hydrolysis of the BH$_3$ moiety and dehydrogenation of the heterocycle. To test the strategy of physically mixing two carriers, the hydrolysis of a variety of amine-boranes (H$_3$N:BH$_3$, Me$_2$HN:BH$_3$, Et$_3$N:BH$_3$) and the catalytic dehydrogenation of indoline were carried out together.

Introduction

Due to rising concerns about emissions of carbon dioxide and other pollutants from mobile emission sources such as vehicles, much attention is being paid to H$_2$ as a clean fuel and energy carrier.[1,2] While fuel cell technologies are advancing,[2,3] the development of hydrogen storage systems, beyond compressed hydrogen and low storage density metal hydrides, is being stymied by significant technological roadblocks. Currently, several hydrogen storage systems are being developed for vehicular transportation; these include physical systems involving compressed or adsorbed H$_2$ and chemical systems such as metal hydrides and organic liquids.[4-6] The chemical systems can be divided into those that release H$_2$ endothermically and those that release H$_2$ exothermically.

Endothermic carriers, such as cyclic hydrocarbons (e.g., cyclohexanes),[7-14] and N-heterocycles (e.g., piperidines),[15-21]

are organic liquids that can be dehydrogenated on-board (in the vehicle or device) and rehydrogenated off-board (i.e., in a factory). The use of liquids greatly facilitates the engineering because they are pumpable and, if they are to be used in vehicles, can be stored and delivered using existing infrastructure. Endothermicity is also desirable because it makes the reaction more controllable. However, one drawback for implementing these endothermic systems in vehicles is the large amount of energy that must be supplied within the vehicle to satisfy the enthalpy of dehydrogenation—this significantly detracts from the effective energy storage density. Naturally, the reverse hydrogenation reaction (off-board regeneration) releases large

† Queen's University.
‡ Queen's-RMC Fuel Cell Research Centre.
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amounts of energy, requiring the reaction vessels to be cooled to help dissipate the heat evolved.

Exothermic carriers, such as boron hydrides and metal hydrides (when the H_2 is released by hydrolysis), have the great advantages of significantly higher gravimetric hydrogen storage densities and not requiring heat to be supplied on-board. However, these carriers require more complicated on-board engineering because they are solids and because the exothermic release of hydrogen results in heat management issues and the risk of overheating or runaway reaction. The exothermic carriers are also much more difficult to regenerate. This causes a significant barrier to their use since it means that their cost of production is high, and therefore their potential applications are limited to niche high value products such as remote power and military devices. However, chemical methods for the regeneration of hydrolyzed $NaBH_4$, for example, have been reported.[22,23] An electrolytic method of directly reversing the hydrolysis with hydrogen gas has been proposed[24] and may be followed by others that would significantly reduce the overall cost of regeneration.

The energy content (enthalpy of combustion) of H_2 is 285.8 kJ/mol,[25] which is only partially converted to electrical energy by the polymer electrolyte membrane (PEM) fuel cell. PEM fuel cells used for transportation purposes have an electrical efficiency of 53−58% (151.5−165.8 kJ/mol H_2), while the remaining 42−47% (120.0−134.4 kJ/mol H_2) is released as heat (operating temperature 50−100 °C), which could possibly be used to provide some of the heat for the dehydrogenation of endothermic hydrogen carriers.[26]

A combination of an endothermic system and an exothermic system would combine the advantages of both systems. The energy released from the exothermic system would provide some or all of the energy required for the endothermic process. The liquid endothermic carrier would dissolve the solid exothermic carrier, eliminating the engineering difficulties associated with the use of a solid. The high hydrogen storage density of the exothermic system would increase the overall storage capacity of the combination relative to the low H_2 storage capacities of endothermic systems. In order for such a combined system to operate adequately, the endothermic and exothermic carriers must be chosen so that neither prevents the hydrogen release from the other nor renders it unstable to decomposition or premature H_2 release. The two carriers should also be miscible (if both are liquids) or the liquid carrier should dissolve the solid, so that the mixture is liquid from −40 °C to well above the temperature required for H_2 release.

In this paper, we describe the feasibility of combining a carrier that releases hydrogen by endothermic dehydrogenation with a carrier that releases hydrogen by exothermic hydrolysis. Two different approaches were considered for combining the two carriers: (a) chemical binding of one carrier to the other and (b) physical mixtures of the carriers. Ideally, the combined system would release H_2 at or below 100 °C to best match the temperature of operation of a PEM fuel cell operation. In all of
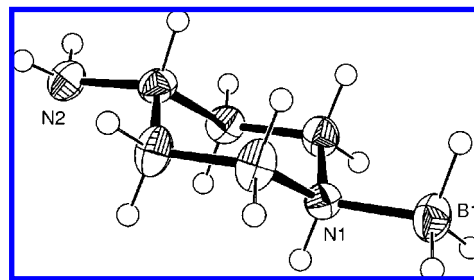

Figure 1. ORTEP diagram for **2a**, shown with 50% displacement ellipsoids.

this work, the endothermic carrier is a N-heterocycle and the exothermic carrier contains B−H bonds which release H_2 by exothermic hydrolysis. Specifically, combinations of N-heterocycles as the endothermic carrier with different amine-boranes as the exothermic carrier were evaluated.

Results and Discussion

Chemically Bound Nitrogen−Boron Complexes: Synthesis and Reactivity. Adducts of saturated N-heterocycles and BH_3 are advantageous because the two carriers are combined into one molecule; accidental phase separation of the two carriers is impossible, energy transfer from the exothermic to the endothermic carrier is facile, and the ratio of exothermic to endothermic carriers is fixed. Although there are many reports on using ammonia-borane and other amine-boranes[27−30] as hydrogen carriers, none of the reported amine-boranes have an endothermic hydrogen releasing portion. Several such compounds have now been synthesized and evaluated to determine whether these compounds can be hydrolyzed (exothermic portion) and dehydrogenated (endothermic portion) at 100 °C.

A significant potential disadvantage of binding BH_3 to N-heterocycles is the resulting loss of electron density from the heterocycle. Electron density strongly influences whether a compound is easily dehydrogenated. We have shown previously[16] that the substituents on N-heterocycles have a significant influence on the ability of dehydrogenation. Electron-donating substituents or conjugated substituents promote dehydrogenation, while electron-withdrawing substituents have the opposite effect.

4-Aminopiperidine served as the endothermic carrier for the first systems studied. Adducts of 4-aminopiperidine with two BH_3 molecules (**1a**) and with one BH_3 molecule (**2a**) were prepared (eq 1). An ORTEP[31] diagram of **2a** is shown in Figure 1. The nitrogen−boron bond distance (1.597(3) Å) agrees with similar compounds in the literature[32−34] exhibiting single bond character. The connectivity of **1a** was confirmed by standard NMR experiments (^{1}H, ^{13}C, ^{11}B, COSY, HSQC, and HMBC) as well as ^{1}H{^{11}B} and ^{1}H−^{1}H NOESY NMR experiments. In the ^{1}H{^{11}B} spectra (Figure 2), each of the boron moieties

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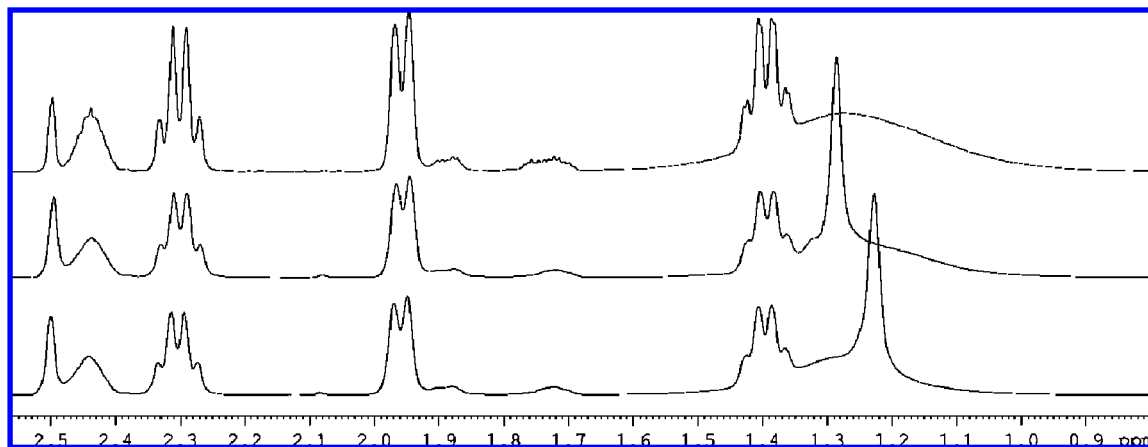
Figure 2. ¹H NMR spectrum of **1a** (top); ¹H{¹¹B} NMR spectra of **1a**, boron decoupled at −14.7 ppm (middle), and boron decoupled at −21.2 ppm (bottom).
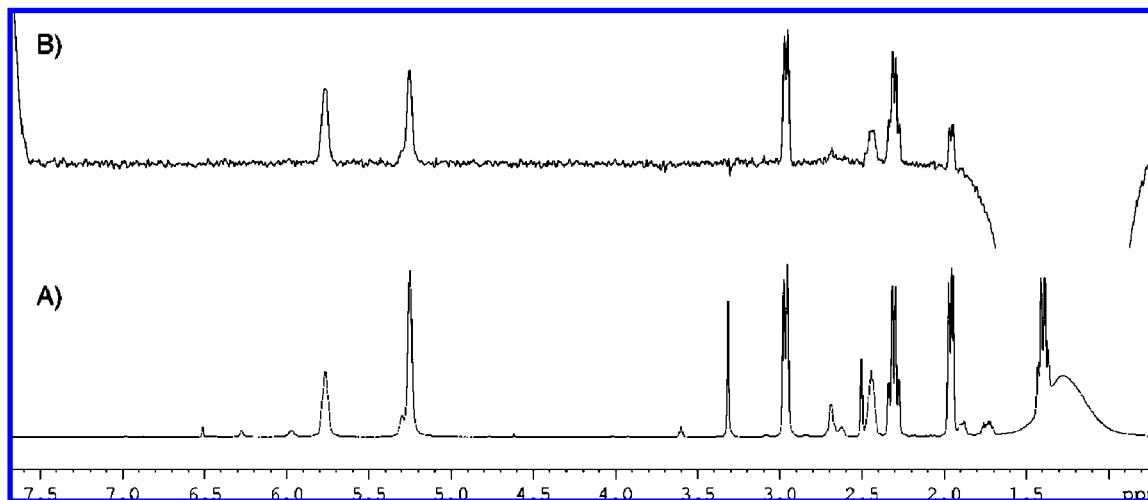

Figure 3. (A) The ¹H NMR spectrum of **1a**. (B) A cross-section slice of the ¹H−¹H NOESY NMR spectrum for **1a** was taken along the borane proton shift (1.3 ppm; NH−BH₃ and NH₂−BH₃) depicting any correlations to other protons within the molecule. As seen in the figure, the ¹H−¹H NOESY correlations correspond to the amine protons (5.8 [NH] and 5.2 ppm [NH₂]) as well as the other methylene protons within the molecule.

(attached to the NH [¹¹B NMR: δ −14.7] and NH₂ [¹¹B NMR: δ −21.2]) is decoupled individually, resulting in two separate singlets at 1.30 and 1.24 ppm, respectively. The structure was further confirmed by through-space ¹H−¹H NOESY correlations (see Supporting Information Figures S9 and S10 for ¹H−¹H NOESY NMR spectrum) between the methylene, amine, and the borane protons. A cross-section slice of the ¹H−¹H NOESY NMR spectrum along the borane proton shift was extracted and referenced to the ¹H NMR spectrum. Clear correlations are observed between the borane protons and the amine and methylene protons (Figure 3); this provides additional evidence besides the ¹H{¹¹B} NMR spectra for the presence of two distinct borane moieties.
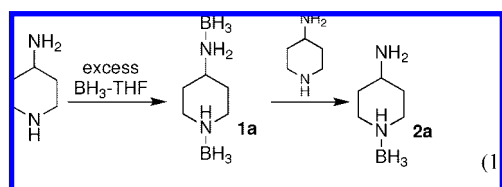
When **1a** is heated to 100 °C for 3 h in the presence of water and catalyst (Pd/silica), gas evolution is observed. Examination

of the resulting product by NMR spectroscopy showed a change in the boron chemical shifts, while the C–H protons have the same splitting pattern as the starting material with only a slight change in chemical shift. The boron chemical shifts of **1a** [¹¹B NMR: δ −14.5 (R₂NH:BH₃) and −20.8 (RNH₂:BH₃)] shifted downfield to a very broad singlet at about 10−11 ppm corresponding to a borate species, such as B(OH)₃ or BO₂⁻; Xu and co-workers have reported that such borate species exist in an equilibrium mixture.[35−37] For simplicity, only the boric acid derivative of **1a** (**1b**) is shown in eq 2. The change in the boron chemical shifts suggests complete borane hydrolysis, while the lack of proton chemical shifts in the olefinic and aromatic regions of the ¹H NMR spectrum confirms the complete absence of ring dehydrogenation. In contrast, the dehydrogenation of 4-aminopiperidine (without BH₃ groups attached) with Pd/SiO₂ occurs in 100% conversion over 0.5 h at 170 °C[16] and in 15% conversion over 3 h at 100 °C.

Reaction of **2a** with water under the same reaction conditions as **1a** showed only borane hydrolysis [¹¹B NMR: δ −14.5 (R₂NH:BH₃ of **2a**) shifted downfield to a very broad singlet at

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(36) Chandra, M.; Xu, Q. *J. Power Sources* **2006**, *159*, 855–860.
(37) Xu, Q.; Chandra, M. *J. Alloys Compd.* **2007**, *446−447*, 729–732.

$$(2)$$
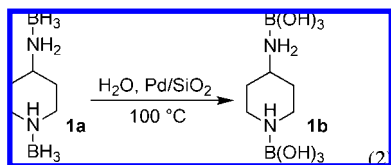
about 10.4 ppm], but again no dehydrogenation of the ring system was observed. For simplicity, only the boric acid form of **2a** (**2b**) is shown in eq 3. The dehydrogenation of the ring system seems to be unattainable at 100 °C when borane is attached. The lack of dehydrogenation indicates that the hydrolysis reaction is unable to provide enough energy to facilitate the dehydrogenation at this temperature and/or that the dehydrogenation is inhibited by electron density loss from the ring to the boron moiety.


$$(3)$$
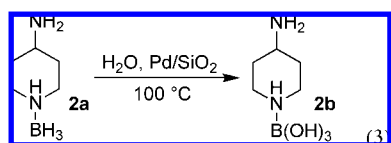
In order to determine whether the lack of dehydrogenation is due to the temperature used or to the presence of the electron-withdrawing borane moieties, the dehydrogenations of complexes **1b** and **2b** were explored in the presence of palladium on silica without water at elevated temperature (170 °C) in deuterated DMSO (solvent was added because the melting points of **1b** and **2b** are >220 °C). Even at 170 °C, no dehydrogenation was observed for either **1b** or **2b** over the course of 3 h, which is quite a contrast to the case of the parent molecule 4-aminopiperidine which completely dehydrogenates over the course of 0.5 h under similar conditions.

On the basis of the lack of dehydrogenation of **1b** and **2b** (vide supra), we wanted to determine if the type of boron moiety [BH_3 vs $B(OH)_3$] has an effect on the dehydrogenation of the ring. Therefore, the dehydrogenation of **1a** was explored under similar conditions but without the addition of water. The dehydrogenation of compound **1a** (melting point: >240 °C) was performed in triglyme or DMSO at 170 °C over several hours without any dehydrogenation of the ring (confirmed by the lack of proton chemical shifts in the olefinic and aromatic regions). However, the number of detectable amine protons in the ^1H NMR spectrum has gone from 3 (for compound **1a**) to 1, suggesting B−N dehydrocoupling. The product was not isolated or characterized.

The lack of observable dehydrogenation for the cyclic moieties of the boron complexes **1b** and **2b** at 170 °C suggests that, even though the hydrolysis reaction is exothermic, the coordinated boron moieties are sufficiently electron-withdrawing to increase the enthalpy of dehydrogenation and thereby prevent dehydrogenation.

Due to the lack of clean dehydrogenation of the ring moiety of 4-aminopiperidine in **1a,b** and **2a,b** even at elevated temperatures, the use of indoline was explored as an alternative endothermic carrier. Indoline has been shown to dehydrogenate fully over half an hour at 100−110 °C (eq 4).[17]

$$(4)$$
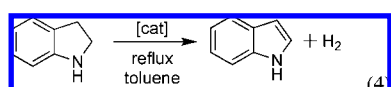
Compound **3** (the BH_3 adduct of indoline) was synthesized in a similar manner as **1a**. The connectivity of **3** was confirmed

by standard NMR experiments as well as $^1H\{^{11}B\}$ and $^1H-^1H$ NOESY NMR experiments. In the ^1H NMR spectrum of **3**, the borane protons appear as a broad apparent quartet (^1H NMR: δ 2.48, $^1J_{HB} = \sim90$ Hz, 3H, BH_3), while in the $^1H\{^{11}B\}$ spectrum, the quartet disappeared and was replaced by a singlet (Figure 4). The structure is further confirmed by through-space $^1H-^1H$ NOESY correlations (see Supporting Information Figures S14 and S15 for the $^1H-^1H$ NOESY NMR spectrum) between the C7−H, amine, and the borane protons. A cross-section slice of the $^1H-^1H$ NOESY NMR spectrum (Figure 5) was extracted along the C7 proton shift, showing any correlations toward other protons within the molecule. The correlations that are observed can be referenced to the ^1H NMR spectrum, providing evidence for the C7 proton being in close proximity to the amine and borane protons, confirming the proposed indoline-borane structure **3**.

The dehydrogenation and hydrolysis of **3** was performed using palladium on carbon in the presence of water at 100 °C over the course of 2 h. Analysis of the product mixture by ^1H and ^{11}B NMR spectroscopy showed good indoline dehydrogenation (71%) and complete borane hydrolysis (eq 5). The ^1H NMR spectrum of the major product (in DMSO-d_6) shows an NH peak at 11 ppm that clearly correlates, in the COSY spectrum, to the olefin hydrogens, demonstrating that the product retains an NH proton and therefore only a single bond between N and B. This reaction constitutes an example of H_2 release from both an endothermic carrier and an exothermic carrier, with the two carriers actually being chemically bonded to each other. The gravimetric hydrogen storage capacity of the system is 6.0% (not including the water, which we assume will be obtained from the exhaust of the fuel cell). The overall reaction is exothermic, however, because the enthalpy of BH_3 hydrolysis (approximately −156 kJ/mol)[36,37] added to the enthalpy of indoline dehydrogenation (52 kJ/mol for unsubstituted indoline)[38] gives a total of −104 or −26 kJ/mol H_2. Also, the dehydrogenation of **3** was incomplete, even though the parent compound indoline dehydrogenates completely in that time, in keeping with the suggestion that the boron moiety acts as an electron-withdrawing group, making the dehydrogenation more difficult.

$$(5)$$
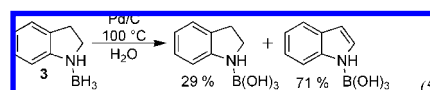
In order to avoid this problem, the boron moiety must not be bonded directly to the heterocycle. One method of separating the two moieties would be to have each in separate independent molecules, which is the strategy described in the next section.

Physical Combination of Endothermic/Exothermic Systems. In order to separate the borane moiety from the cyclic moiety, we explored physical combinations of boranes and indoline. This should avoid the inhibition problem described above (only partial dehydrogenation of indoline) as long as no borane transfer to indoline occurs.

Having two independent systems gives one the opportunity to adjust the ratio of the two systems; this is advantageous in

(38) ΔH_{rxn} for the dehydrogenation of indoline was calculated with Gaussian03[38a,b] using the B3LYP/6-311++G** basis set. (a) Frisch, M. J.; *Gaussian 03*, revision B.04; Gaussian Inc.: Wallingford, CT, 2004. (b) Dennington, R., II; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. *GaussView*, version 3.08; Semichem, Inc.: Shawnee Mission, KS, 2003.
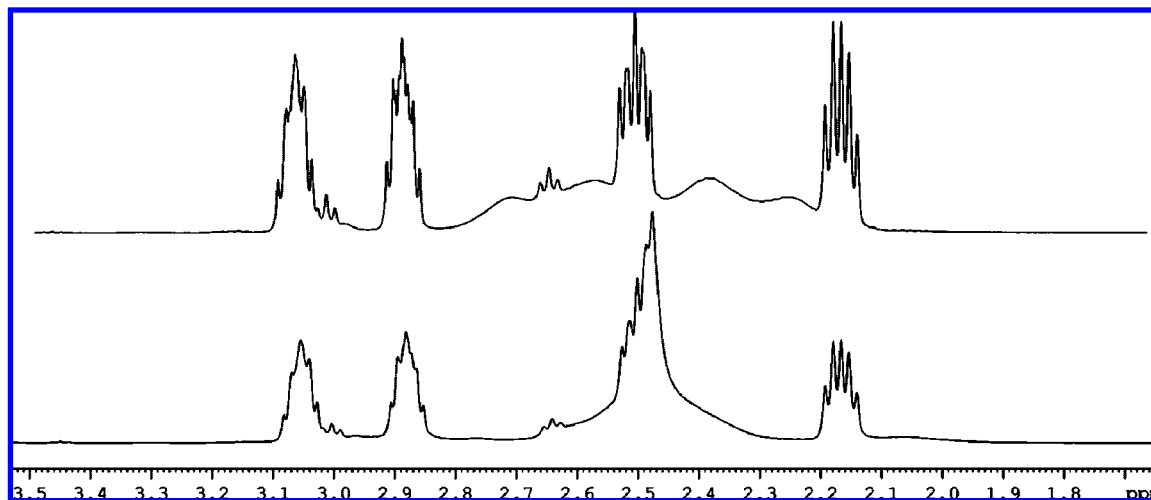
Figure 4. ^{1}H NMR spectrum of **3** (top) and ^{1}H$\{^{11}$B$\}$ NMR spectrum (bottom).
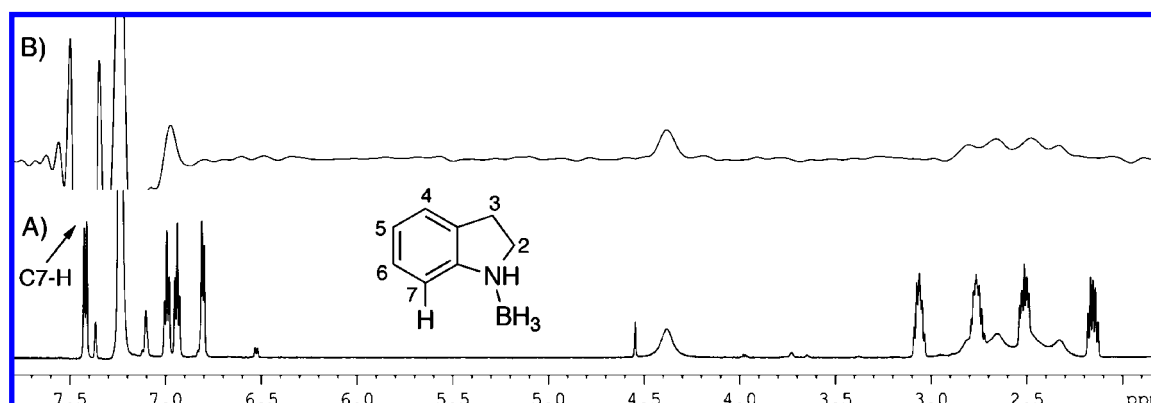

Figure 5. (A) ^{1}H NMR spectrum of **3** is shown as a reference spectrum. (B) Cross-section slice of the ^{1}H–^{1}H NOESY NMR spectrum for **3** was taken along the C7 proton shift (7.4 ppm) depicting any correlations to other protons within the molecule. As seen in the figure, the ^{1}H–^{1}H NOESY correlations correspond to the amine proton (4.4 ppm) and the broad "quartet" of the borane protons (2.9–2.2 ppm).

order to achieve an overall heat balance within the system. Because the exothermic and endothermic carriers that will be used in this system have different enthalpy values, a 1:1 ratio might not always be ideal for a heat balanced system. The first combination of carriers that was explored was the exothermic hydrolysis reaction of amine-boranes[2,39–42] (eq 6, e.g., H$_3$N: BH$_3$: $\Delta H_{rxn} = -156$ kJ/mol BH$_3$[36,37]) and the endothermic dehydrogenation of indoline (eq 4, $\Delta H = 52$ kJ/mol).[43] In order to achieve heat balance in this system, an indoline to amine-borane ratio of 3:1 would be required.
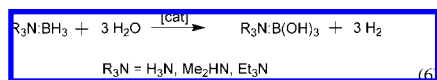
(39) Amendola, S. C.; Sharp-Goldman, S. L.; Janjua, M. S.; Spencer, N. C.; Kelly, M. T.; Petillo, P. J.; Binder, M. *Int. J. Hydrogen Energy* **2000**, *25*, 969–975.

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(43) ΔH_{rxn} for the dehydrogenation of indoline was calculated with Gaussian03[38a,b] using the B3LYP/6-311++G** basis set.

In order to avoid carrying any extra weight in the vehicle, we wanted to look at a solventless system. Fortunately, indoline is liquid at room temperature and has a boiling point of 220 °C, much higher than the dehydrogenation temperature and the PEM fuel cell operating temperature. On the other hand, the amine-boranes explored are not always liquid under the same conditions; therefore, the solubility of the amine-boranes in the endothermic carrier is of importance. The solubility of each amine-borane within indoline is part of the following discussion.

Utilization of Triethylamine-Borane. Triethylamine-borane (Et$_3$N:BH$_3$) was first examined because it is a liquid at room temperature and is fully miscible with indoline.

The reactivity of Et$_3$N:BH$_3$ (^{11}B NMR: $\delta = -13.6$ (q, $^1J_{BH}$ = 96 Hz)) was first explored in the absence of indoline. Triethylamine-borane is stable over palladium on carbon at 100 °C; no decomposition products are observed after 2 h (Table 1, entry 1). When water is added under the same conditions, gas and heat evolution is observed and the only product seen by NMR spectroscopy is the hydrolysis product Et$_3$N:B(OH)$_3$ (^{11}B NMR: δ 18; eq 7; Table 1, entry 2). Triethylamine-borane will also not hydrolyze at room temperature unless catalyst is added (Table 1, entries 5 and 3, respectively).
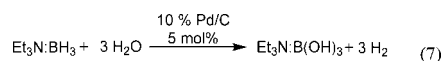
Table 1. Combinations of Indoline, Et$_3$NBH$_3$, Water, and Catalyst^a

entry	reagent equivalent			catalyst	% conv. of indoline	hydrolysis of BH$_3$
	indoline	Et$_3$N:BH$_3$	H$_2$O			
1	0	1	0	Pd/C		no change
2	0	1	3	Pd/C		complete
3^b	0	1	3	Pd/C		complete
4	0	1	3	none		complete
5^b	0	1	3	none		no change
6	1	0	0	none	0	
7	1	0	3	none	0	
8	1	0	0	Pd/C	>99	
9	1	0	3	Pd/C	>99	
10	1	1	0	none	0	no change
11	1	1	0	Pd/C	>99	no change
12	1	1	3	none	0	complete
13	1	1	3	Pd/C	>99	complete
14	3	1	3	Pd/C	>99	complete

^{a} Catalyst: 10% Pd/C at 5 mol % loading, time = 2 h, temp = 100 °C, under N$_2$ flow to remove produced hydrogen. ^{b} Reaction performed at room temperature.

In certain cases, additional boron-containing species were observed after the hydrolysis reaction was complete (^{11}B NMR: δ 19, 8, and 2). Xu and co-workers[35−37] have observed that there is an equilibrium process between B(OH)$_3$, BO$_2^-$, and other borate species which is dependent on small changes in the reaction conditions. The difference in chemical shift of the borate species can potentially be attributed to a change in available water equivalents and/or pH.

Indoline as the sole reagent in the absence of catalyst is stable at 100 °C even in the presence of water (Table 1, entries 6 and 7, respectively). However, in the presence of catalyst, indoline completely dehydrogenates, even in the presence of water (Table 1, entries 8 and 9, respectively).

Indoline and Et$_3$N:BH$_3$ do not react with each other at 100 °C (Table 1, entry 10). The hydrolysis of Et$_3$N:BH$_3$ at 100 °C is not inhibited by the presence of indoline (compare Table 1, entries 4 and 12). The catalytic dehydrogenation of indoline is not inhibited by the presence of Et$_3$N:BH$_3$ (Table 1, entries 8 and 11). This contrasts to the marked inhibition that was observed when BH$_3$ was bound directly to the endothermic carrier (vide supra). When all reagents (indoline, Et$_3$N:BH$_3$, catalyst, and water) are reacted together, both indoline dehydrogenation and borane hydrolysis are observed, showing that neither carrier system prevents the other from releasing its H$_2$ (Table 1, entries 13 and 14). This confirms that endothermic and exothermic hydrogen producing reactions can be operated together in the same system without one carrier significantly inhibiting or destabilizing the other.

In the current system, the BH$_3$ moiety remains bound to Et$_3$N, and no evidence of the borane transferring to the indoline is observed by NMR spectroscopy. No transfer was expected because triethylamine is a better Lewis base than indoline.

To the best of our knowledge, there have been only two reports[44,45] where the simultaneous occurrence of endothermic and exothermic dehydrogenation are described. Gelsey and co-workers[45] have first described the use of exothermic hydrolysis with H$_2$ release (NaBH$_4$ + H$_2$O) and an endothermic dehydrogenation (metal hydride), although the reactions were performed in separate chambers to avoid direct contact between the two

(44) Thorn, D. L.; Tumas, W.; Ott, K. C.; Burrell, A. K. US20070183967, 2007.
(45) Gelsey, J. U. S. Patent 7,108,933, Intel Corporation, 2006.

Table 2. Combinations of Indoline, Me$_2$HN:BH$_3$, Water, and Catalyst^a

entry	reagent equivalent			catalyst	% conv. of indoline	hydrolysis of BH$_3$
	indoline	Me$_2$H:NBH$_3$	H$_2$O			
1	0	1	3	none		partial (∼95%)
2^b	0	1	3	none		no change
3	0	1	3	Pd/C		complete
4^b	0	1	3	Pd/C		complete
5	1	1	0	none	0	shifted to 6 ppm
6	1	1	0	Pd/C	0	shifted to 6 ppm
7	1	1	3	none	0	partial (∼95%)
8	1	1	3	Pd/C	91	complete
9	3	1	3	Pd/C	>99	complete
10^c	3	1	3	Pd/C	72	complete

^{a} Catalyst: 10% Pd/C at 2 mol % loading, time = 2 h, temp = 100 °C, under N$_2$ flow to remove produced hydrogen. ^{b} Reaction performed at room temperature. ^{c} Reaction performed without N$_2$ flow.

carriers. Thorn and co-workers,[44] on the other hand, have reported the use of exothermic non-H$_2$-releasing reactions to supply the heat for the release of H$_2$ from endothermic carriers. However, the text of the patent briefly mentions the dehydrogenation of amine-borane using palladium or platinum (supported on carbon, etc.) combined with the dehydrogenation of decalin at 250−280 °C, without providing experimental data.

The advantages of our system are that (a) each hydrogen storage carrier can operate independently in a common chamber without inhibiting the ability of the other to produce hydrogen, (b) the reaction temperature is a moderate 100 °C, which is in the operating temperature range of a PEM fuel cell, and (c) the use of the endothermic carrier as a solvent to dissolve the exothermic carrier facilitates material handling.

The overall gravimetric hydrogen storage density of the current system at a 3:1 ratio of indoline to Et$_3$N:BH$_3$ (not counting water because it could be supplied from the fuel cell) is 2.5% (Et$_3$N:BH$_3$ is 5.2%; indoline is 1.7%). The estimated overall enthalpy is 0 kJ/mol at a 3:1 ratio, based upon the dehydrogenation enthalphy of indoline (52 kJ/mol H$_2$)[46] and the hydrolysis enthalpy of H$_3$N:BH$_3$ (−156 kJ/mol BH$_3$).[36,37] At a 1:1 mol ratio, the H$_2$ capacity and overall enthalpy are 3.4% and −104 kJ/mol, respectively. The feasibility of increasing the hydrogen storage density by replacing the triethylamine-borane with lower molecular weight boranes such as dimethylamine-borane (Me$_2$HN:BH$_3$) and H$_3$N:BH$_3$ will be described next.

Utilization of Dimethylamine-Borane. Dimethylamine-borane is a solid at room temperature but is completely soluble in indoline at room temperature at a 1:1 ratio. The reactivity of Me$_2$HN:BH$_3$ in the presence of catalyst or acid and absence of water has been summarized by Baker and co-workers.[30] Dimethylamine-borane does not undergo dehydrocoupling in the presence of a Lewis acid, but if a precious metal catalyst is implemented, dehydrocoupling occurs over several hours with gentle heating (26−45 °C).[30] We explored the reactivity of Me$_2$HN:BH$_3$ toward water in the absence of catalyst (Table 2, entries 1 and 2); at 100 °C, only partial hydrolysis (∼20%) is observed in 2 h, while at room temperature, no hydrolysis occurred. In the presence of catalyst (eq 8; Table 2, entries 3 and 4), complete hydrolysis is achieved at both 100 °C and room temperature.

When Me$_2$HN:BH$_3$ is mixed with indoline and heated to 100 °C in the absence or presence of catalyst, a new boron-

(46) ΔH$_{rxn}$ for the dehydrogenation of indoline was calculated with Gaussian03 using the B3LYP/6-311++G** basis set.

$$Me_2HN{:}BH_3 + 3\,H_2O \xrightarrow{\ Pd/C\ } Me_2HN{:}B(OH)_3 + 3\,H_2 \qquad (8)$$
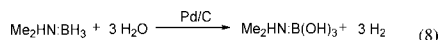
containing species is produced (^{11}B NMR: δ 6 ppm; Table 2, entries 5 and 6, respectively). No dehydrogenation of the indoline portion is observed even in the presence of catalyst (Table 2, entry 6), suggesting a new amine borane complex similar to compound **3** is formed. The identity of this boron-containing species is currently unknown and will be part of future examinations.

Combining all three reagents (Me$_2$HN:BH$_3$, indoline, and water) in the absence of catalyst results in partial borane hydrolysis (Table 2, entry 7 compared to entry 1). In the presence of catalyst, complete hydrolysis of the borane and good conversion of indoline are observed in 2 h (Table 2, entry 8, eq 9). When the indoline to borane ratio is increased to 3:1 (Table 2, entry 9), complete hydrolysis and dehydrogenation are observed. All of these experiments, thus far, were performed with N$_2$ gas flushing through the system to remove H$_2$ as it forms. Performing the reaction without N$_2$ gas flushing through the system, to allow the partial pressure of H$_2$ gas to build up, reduced the dehydrogenation of indoline to 72% conversion (entry 10 vs entry 9).

$$\text{(indoline)} + Me_2HN{:}BH_3 + 3\,H_2O \xrightarrow[\ 100\ ^\circ C\ ]{\ Pd/C\ } \text{(indole)} + Me_2HN{:}B(OH)_3 + 4\,H_2 \qquad (9)$$
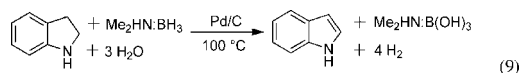
The overall hydrogen storage density of the current system at a 3:1 ratio of indoline to Me$_2$HN:BH$_3$ (not counting water because it would be supplied from the fuel cell) is 2.9% (Me$_2$HN:BH$_3$ is 11.4%; indoline is 1.7%). The estimated overall enthalpy is the same as for Et$_3$N:BH$_3$. At a 1:1 mol ratio, the H$_2$ capacity and overall enthalpy are 4.5% and −104 kJ/mol, respectively.

Utilization of Ammonia-Borane. Use of H$_3$N:BH$_3$ instead of Me$_2$HN:BH$_3$ would again result in increased hydrogen capacity. In this case, we were curious to see if the borane moiety of ammonia-borane (^{11}B NMR: δ −23.4 (q, $^1J_{BH}$ = 90 Hz)) would transfer to indoline (as in the case of Me$_2$HN:BH$_3$; Table 2, entries 5 and 6) and in turn inhibit its dehydrogenation. The stability and reactivity of ammonia-borane have been widely studied.[30] Unfortunately, ammonia-borane is a solid at room temperature and is not soluble in indoline at a 1:1 or 3:1 indoline to borane ratio until it is heated or in the presence of catalyst and undergoes hydrogen loss.

We explored the reactivity of H$_3$N:BH$_3$ toward water in the absence of catalyst (Table 3, entries 3 and 4); at 100 °C, only partial hydrolysis (∼75%) is observed in 2 h, while at room temperature, no hydrolysis occurred. In the presence of catalyst (Table 3, entries 1 and 2), complete hydrolysis is achieved at both 100 °C and room temperature.

Whenever indoline and ammonia-borane are combined in the absence of water, with or without catalyst, a shift to 25 ppm in the ^{11}B NMR is observed, suggesting the formation of a new boron-containing complex (Table 3, entries 5 and 6, respectively). The ^{1}H NMR spectra contained peaks matching those of indoline plus additional peaks corresponding to a BH$_3$ species. The ^{11}B NMR spectrum of this unknown borane-indoline adduct does not match that of compound **3**, suggesting that an ammonia-borane derivative is formed which in turn complexes with indoline. Although this adduct could not be identified, it is clear that its formation inhibits the dehydrogenation of indoline (compare Table 3, entry 6 with entry 10).

Table 3. Combinations of Indoline, H$_3$N:BH$_3$, Water, and Catalyst[a]

entry	reagent equivalent			catalyst	% conv. of indoline	hydrolysis of BH$_3$
	indoline	H$_3$N:BH$_3$	H$_2$O			
1	0	1	3	Pd/C		complete
2[b]	0	1	3	Pd/C		complete
3	0	1	3	none		partial (∼75%)
4[b]	0	1	3	none		no change
5	1	1	0	none	0	shift to 25 ppm
6	1	1	0	Pd/C	0	shift to 25 ppm
7	1	1	3	none	0	complete
8[c]	1	1	3[c]	Pd/C	66	complete
9	3	1	3	Pd/C	>99	complete
10	1	0	0	Pd/C	>99	

[a] Catalyst: 10% Pd/C at 2 mol % loading, time = 2 h, temp = 100 °C, under N$_2$ flow to remove produced hydrogen. [b] Reaction performed at room temperature. [c] Water was added to reaction after ∼30 min of heating.

When the reaction (Table 3, entry 6) was repeated with the addition of water in the absence of catalyst (Table 3, entry 7), complete hydrolysis of the borane but no borane-indoline adduct formation was observed.

Both the hydrolysis of H$_3$N:BH$_3$ and the dehydrogenation of indoline are observed when a mixture of all three reagents (indoline, water, and H$_3$N:BH$_3$) is exposed to palladium on carbon (Table 3, entry 9). This suggests that the hydrolysis reaction prevents or reverses adduct formation.

In order to determine the stability of the unknown indoline-borane adduct, we combined indoline and ammonia-borane with catalyst at 100 °C (as in Table 3, entry 6) for 1 h followed by the addition of water and continued heating at 100 °C for 2 h. The ^{1}H and ^{11}B NMR spectra were taken and showed complete borane hydrolysis as well as partial indoline dehydrogenation (Table 3, entry 8). This result suggests that once the BH$_3$ moiety is hydrolyzed the indoline dehydrogenation is no longer inhibited to the same extent.

The overall hydrogen storage density of the current system at a 3:1 ratio of indoline to H$_3$N:BH$_3$ (not counting water because it would be supplied from the fuel cell) is 3.1% (H$_3$N:BH$_3$ is 19.4%; indoline is 1.7%). At a 1:1 mol ratio, the H$_2$ capacity is 5.3%. The estimated overall enthalpy is the same as for Et$_3$N:BH$_3$ and Me$_2$HN:BH$_3$.

Increasing the overall hydrogen storage density by employing lower molecular weight amine-boranes only makes small improvements to the overall H$_2$ capacity because the amine-borane is only one-quarter of the weight of the system. Larger increases would be obtained by using a different endothermic system that has a higher hydrogen storage density; this will be part of future explorations.

Conclusion

In this paper, we explored the combination of two independent hydrogen storage systems to determine if any interactions occur between the two that might prevent H$_2$ release. Depending on the type of borane used, some interaction was observed in the absence of water, while in the presence of water, complete hydrolysis of the exothermic carrier (triethylamine-, dimethylamine-, and ammonia-borane) and complete dehydrogenation of the endothermic carrier (indoline) are observed. This shows that, under the right conditions, two hydrogen carriers can operate simultaneously in the same system without inhibiting each other. The ratio of the endothermic and exothermic systems can also be altered to achieve overall heat balance.

The system is not, however, without its disadvantages. Although the kinetics of the system have not been evaluated, it is clear that hydrogen release from the exothermic system is much faster than the hydrogen release from the endothermic system; ideally, the reactions would have comparable rates. Also, the borate hydrolysis products are not completely soluble in indoline, so that precipitation of the product onto the catalyst could, after some time, result in catalyst deactivation.

This work has also shown that a chemically bound exothermic carrier tends to inhibit the dehydrogenation of the endothermic carrier. In the case of compound **3**, only partial indoline dehydrogenation was observed in 2 h versus complete dehydrogenation for indoline in the absence of any borane. Therefore, the two moieties have to be separated to prevent this inhibition.

Future explorations will include a survey of other endothermic carriers to increase the hydrogen storage density of the overall system. Other exothermic carriers that would be more easily regenerated will also be part of future explorations. Finally, combinations of exothermic and endothermic carriers that have comparable rates of H_2 release will be sought.

Experimental Section

General Considerations. Manipulations of air-sensitive compounds were conducted in the absence of oxygen and water under an atmosphere of N_2, by use of standard Schlenk methods, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Indoline (Aldrich) was dried in vacuo at 80 °C for 2 h prior to use. Triethylamine-borane (Aldrich), 1 M BH_3−THF solution in THF (Aldrich or Alfa Aesar), 10% palladium on activated carbon (dry powder) (Strem Chemicals), hexanes (Fisher Scientific), and dimethylamine-borane (Alfa Aesar) were used as received. Ammonia-borane was synthesized via literature methods.[47] Tetrahydrofuran and diethyl ether were obtained from Fisher Scientific and passed through a double-column solvent purification system purchased from Innovative Technologies, Inc. prior to use. C_6D_6, CD_3OD, $CDCl_3$, and $(CD_3)_2SO$ were purchased from Cambridge Isotope Laboratories Inc. and used as received. ^1H, ^{13}C, and ^{11}B NMR spectra were collected at 300 K on a Bruker AV-400 spectrometer operating at 400.3, 100.7, and 128.4 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^1H and ^{13}C) or BF_3−Et_2O (for ^{11}B). ^1H and ^{13}C NMR chemical shift assignments were made on the basis of data obtained from ^{13}C, ^1H−^1H COSY, ^1H−^{13}C HSQC, and ^1H−^{13}C HMBC NMR experiments. $^1H\{^{11}B\}$ and ^1H−^1H NOESY NMR experiments for compounds **1a** and **3** were performed at 300 K on a Bruker AV-600 spectrometer at 600.2 MHz. Where reported, the ^{15}N chemical shifts were assigned on the basis of a ^1H−^{15}N HMBC NMR experiment run at 300 K on a Bruker AV-600 spectrometer operating at 60.8 MHz with chemical shifts reported in parts per million with respect to CH_3NO_2 at 381 ppm. Elemental analyses were attempted for compounds **1a,b**, **2a,b**, and **3**, but each sample returned lower than expected experimental values. This could be due to the formation of thermally stable borocarbides in boron-containing molecules during elemental analysis.[48] Mass spectroscopic techniques that could ionize these molecules without loss of BH_3 were not found.

Synthesis of 1a. A Schlenk flask was charged with a stir bar and 4-aminopiperidine (1.0 mL, 9.4 mmol) followed by the addition of 2−3 equiv of 1 M BH_3−THF in THF (25 mL, 25 mmol) and magnetically stirred for 16 h. The solvent was removed in vacuo, leaving behind a white solid. The solid was washed several times with distilled water and dried in vacuo, yielding **1a** as a white solid (1.04 g, 8.1 mmol, 86%): ^1H NMR (DMSO-d_6) δ 5.78 (br s, 1H,

NH), 5.26 (br s, 2H, NH_2), 2.96 (d, $^3J_{HH}$ = 12.1 Hz, 2H, C2−H and C6−H), 2.44 (m, 1H, C4−H), 2.30 (q, $^3J_{HH}$ = 11.1 Hz, 2H, C2−H and C6−H), 1.95 (d, $^3J_{HH}$ = 12.5 Hz, 2H, C3−H and C5−H), 1.39 (q of d, $^3J_{HH}$ = 13.0 Hz, J_{HH} = 3.5 Hz, 2H, C3−H and C5−H), 1.26 (br m, 6H, BH_3's); $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ 52.4 (C4), 51.0 (C2 and C6), 29.4 (C3 and C5); ^{11}B NMR (DMSO-d_6) δ −14.8 (br s, NH-BH_3), −21.4 (br s, NH_2-BH_3).

Synthesis of 1b. To a round-bottom flask equipped with a stir bar and condenser were added compound **1a** (0.039 g, 0.31 mmol) and distilled water (∼1 mL). The mixture was heated to 100 °C, and 5% palladium on silica (5 mol%) was added through the condenser. After gas evolution ceased, more water (3 mL) was added and the reaction mixture was filtered through diatomaceous earth to remove the heterogeneous catalyst and other insolubles. The filtrate was then dried in vacuo to remove any solvent and other volatiles, resulting in a white solid (0.047 g, 0.21−0.25 mmol, 68−81%; depending on $B(OH)_3$ or BO_2^-, respectively): ^1H NMR (D_2O) δ 3.31 (d, $^3J_{HH}$ = 13.2 Hz, 2H, C2−H and C6−H), 3.07 (m, 1H, C4−H), 2.86 (t of d, $^3J_{HH}$ = 13.0 Hz, J_{HH} = 2.9 Hz, 2H, C2−H and C6−H), 2.01 (d, $^3J_{HH}$ = 13.4 Hz, 2H, C3−H and C5−H), 1.52 (q of d, $^3J_{HH}$ = 14.0 Hz, J_{HH} = 4.1 Hz, 2H, C3−H and C5−H); $^{13}C\{^1H\}$ NMR (D_2O) δ 45.8 (C4), 42.7 (C2 and C6), 29.8 (C3 and C5); ^{11}B NMR (D_2O): δ 10.1 (br s).

Synthesis of 2a. To a round-bottom flask equipped with a condenser containing a magnetically stirred solution of **1a** (0.12 g, 0.94 mmol) in THF (3 mL) was added 4-aminopiperidine (0.10 mL, 0.94 mmol). The mixture was heated at 60 °C for 18 h. The solvent and other volatiles were removed in vacuo. Methanol (4 mL) was added, and the solution was filtered through diatomaceous earth. The filtrate was dried in vacuo, resulting in a white solid (0.16 g, 1.4 mmol, 72%): ^1H NMR (CD_3OD) δ 3.14 (d of d, $^3J_{HH}$ = 13.6 Hz, J_{HH} = 1.9 Hz, 2H, C2−H and C6−H), 2.78 (m, 1H, C4−H), 2.47 (apparent t, $^3J_{HH}$ = 13.4 Hz, 2H, C2−H and C6−H), 1.88 (d of d, $^3J_{HH}$ = 12.4 Hz, J_{HH} = 1.4 Hz, 2H, C3−H and C5−H), 1.39 (q of d, $^3J_{HH}$ = 11.4 Hz, J_{HH} = 4.0 Hz, 2H, C3−H and C5−H); $^{13}C\{^1H\}$ NMR (CD_3OD) δ 53.2 (C2 and C6), 48.5 (C4), 35.3 (C3 and C5); ^{11}B NMR (CD_3OD) δ −15.6 (apparent d, J_{BH} = 9.6 Hz); ^{15}N NMR (CD_3OD) δ 35 (NH), 38 (NH_2).

Synthesis of 2b. Ten percent palladium on carbon (0.054 g, 5 mol %, 0.051 mmol) was added to a round-bottom flask charged with a stir bar and **2a** (0.12 g, 1.0 mmol). Magnetic stirring was initiated, and distilled water (0.5 mL) was added, resulting in gas and heat evolution. The mixture was allowed to stir for 30 min followed by the addition of 2 mL of water and removal of the catalyst by filtration through diatomaceous earth. The filtrate was dried in vacuo, resulting in a pure white solid (0.12 g, 0.74−0.83 mmol, 73−83%; depending on $B(OH)_3$ or BO_2^-, respectively): ^1H NMR (CD_3OD) δ 3.19 (apparent d, $^3J_{HH}$ = 13.0 Hz, 2H, C2−H and C6−H), 2.97 (m, 1H, C4−H), 2.75 (t of d, $^3J_{HH}$ = 12.5 Hz, J_{HH} = 2.6 Hz, 2H, C2−H and C6−H), 1.97 (apparent d, $^3J_{HH}$ = 12.6 Hz, 2H, C3−H and C5−H), 1.46 (q of d, $^3J_{HH}$ = 12.1 Hz, J_{HH} = 4.0 Hz, 2H, C3−H and C5−H); $^{13}C\{^1H\}$ NMR (CD_3OD) δ 49.0 (C4), 45.2 (C2 and C6), 33.8 (C3 and C5); ^{11}B NMR (CD_3OD) δ 10.4 (br s); ^{15}N NMR (CD_3OD) δ 32 (NH), 36 (NH_2).

Synthesis of 3. To a Schlenk flask charged with a stir bar were added indoline (0.80 mL, 7.1 mmol) and 1 M BH_3−THF solution in THF (14.3 mL, 14.3 mmol) and stirred overnight (16 h). Solvent was removed in vacuo, leaving a yellow solid to which hexanes was added (3 mL). The hexanes dissolved the yellow impurity, leaving behind a white precipitate. The hexanes were decanted, and the remaining solid was washed several times with fresh hexanes (3 × 5 mL) followed by drying in vacuo, leaving behind a white solid (0.80 g, 6.0 mmol, 85%). Storage of compound **3** at low temperature is preferred to inhibit decomposition. It appears to be mildly pyrophoric in air. In solution under air, it degrades over hours: ^1H NMR (C_6D_6) δ 7.42 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C7−H), 6.94 (t, $^3J_{HH}$ = 7.3 Hz, 1H, C6−H), 6.88 (t, $^3J_{HH}$ = 7.2 Hz, 1H, C5−H), 6.75 (d, $^3J_{HH}$ = 7.3, C4−H), 5.01 (br s, 1H, NH), 3.07 (m, 1H, C2−H_2), 2.87 (m, 1H,

(47) Ramachandran, P. V.; Gagare, P. D. WO2007106459, 2007.
(48) Borda, P. P.; Legzdins, P. *Anal. Chem.* **1980**, *52*, 1777−1778.

C2−H), 2.50 (m, 1H, C3−H₂), 2.16 (m, 1H, C3−H₂), 2.49 (apparent q, $^1J_{HB}$ = ∼90 Hz, 3H, BH₃; partially underneath CH₂ peaks); ^{13}C{^{1}H} NMR (C₆D₆) δ 146.5 (C3a), 134.9 (C7a), 128.0 (C6), 127.7 (C5), 125.2 (C4), 120.3 (C7), 55.3 (C2), 29.0 (C3); ^{11}B NMR (C₆D₆) δ −13.8 (q, $^1J_{BH}$ = 91 Hz, BH₃).

Dehydrogenation and Hydrolysis of Indoline/R₃N:BH₃ (R = H or Et) Mixtures. The 1:1:3 reaction mixture of indoline, Et₃N: BH₃, and water is described here as the general protocol. For other reaction ratios, the same conditions were followed.

A round-bottom flask was charged with a stir bar, indoline (0.18 mL, 1.6 mmol), triethylamine-borane (0.24 mL, 1.6 mmol), distilled water (0.087 mL, 4.8 mmol), and 10% palladium on carbon (0.085 g, 0.08 mmol) and equipped with a condenser. The reaction mixture was immersed into a preheated oil bath (set at 100 °C) and stirred magnetically for 2 h under a N₂ flow for the duration of the experiment. In order to get efficient borane hydrolysis, vigorous stirring is required due to the insolubility of indoline and triethyl-amine-borane in water to produce consistent dispersion of the water throughout the reaction mixture. The reaction flask was then allowed to cool to room temperature, and the reaction mixture was extract with CDCl₃ followed by filtration through a small plug of diatomaceous earth to remove the remaining catalyst. The filtrate was analyzed by NMR spectroscopy, showing indole and hydro-lyzed triethylamine-borane.

Dehydrogenation and Hydrolysis of Indoline/Me₂HN:BH₃ Mixtures. The 3:1:3 reaction mixture of indoline, Me₂HN:BH₃, and water is described here as the general protocol. For other reaction ratios, the same reaction conditions were followed.

A 25 mL Schlenk tube was charged with a stir bar, indoline (0.34 mL, 3.0 mmol), dimethylamine-borane (0.059 g, 1.0 mmol), distilled water (0.054 mL, 3.0 mmol), and 10% palladium on carbon (0.064 g, 0.06 mmol). The tube was equipped with a condenser, immersed into a preheated oil bath, and stirred magnetically for 2 h at 100 °C under N₂ flow for the duration of the experiment. The reaction flask was then allowed to cool to room temperature, and the reaction mixture was extracted with CDCl₃ or CD₃OD and filtered through a small plug of Al₂O₃ powder to remove any remaining catalyst. The filtrate was analyzed by use of NMR spectroscopy.

Crystallographic Characterization of 2a. A crystal of the compound (colorless, plate-shaped, size 0.39 × 0.28 × 0.11 mm) was mounted on a glass fiber with grease and cooled to −93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 4.82−52.00°. No significant decay was observed during the data collection.

Data were processed on a PC using the Bruker AXS Crystal Structure Analysis Package:[49] Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2; data reduction: SAINT (Bruker, 2005) and XPREP (Bruker, 2005); program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL. Neutral atom scattering factors were taken from Cromer and Waber.[50] The crystal is orthorhombic space group *Pna*2₁, based on the systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-squares refinements minimizing the function $\sum w\,(F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms −CH₂ and =NH were calculated (C−H = 0.99 Å and N−H = 0.93 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(N,C)$. The −NH₂ and −BH₃ hydrogen atoms were located from difference Fourier maps and refined isotropically.

There are two molecules in the asymmetrical unit, and each molecule is hydrogen-bonded to its two neighboring molecules (N−H···NH₂ and H₂N···H−N), presenting a 1-D chain along the *b* axis. Additional crystallographic information is provided in the accompanying CIF.

Supporting Information Available: Single-crystal X-ray dif-fraction data in CIF format for **2a**. ^{13}C NMR spectra for **1a,b**, **2a,b**, and **3**. ^{1}H, ^{1}H{^{11}B}, and NOESY NMR spectra for **1a** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(49) *Bruker AXS Crystal Structure Analysis Package*; Bruker, 2000; *SHELXTL*, version 6.14; Bruker AXS Inc.: Madison, WI, 2005; *XPREP*, version 2005/2; Bruker AXS Inc.: Madison, WI, 2005; *SAINT*, version 7.23A; Bruker AXS Inc.: Madison,WI, 2006; *APEX2*, version 2.0-2; Bruker AXS Inc.: Madison, WI.

(50) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystal-lography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.2A.