

## Iridium-Catalyzed Dehydrogenation of Substituted Amine Boranes: Kinetics, Thermodynamics, and Implications for Hydrogen Storage

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Received June 24, 2008

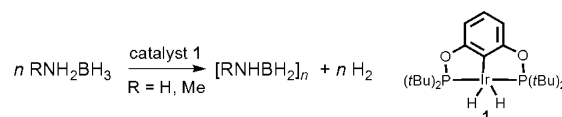
Dehydrogenation of amine boranes is catalyzed efficiently by the iridium pincer complex ( $\kappa^3$ -1,3-(OP<sup>t</sup>Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)Ir(H)<sub>2</sub> (**1**). With CH<sub>3</sub>NH<sub>2</sub>BH<sub>3</sub> (MeAB) and with AB/MeAB mixtures (AB = NH<sub>3</sub>BH<sub>3</sub>), the rapid release of 1 equiv of H<sub>2</sub> is observed to yield *soluble* oligomeric products at rates similar to those previously reported for the dehydrogenation of AB catalyzed by **1**.  $\Delta H$  for the dehydrogenation of AB, MeAB, and AB/MeAB mixtures has been determined by calorimetry. The experimental heats of reaction are compared to results from computational studies.

The widespread use of hydrogen fuel cells to power vehicles is one way to reduce the carbon footprint of the transportation sector.<sup>1,2</sup> A key obstacle to the development of this approach is the current lack of a safe and practical method for on-board storage of hydrogen. Storage of hydrogen in a chemical compound via a reversible chemical reaction is a promising strategy.<sup>3,4</sup> Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB) and related amine boranes have emerged as attractive candidates for hydrogen storage materials because of their high percentage by weight (wt %) of available hydrogen<sup>5</sup> and the potential reversibility of these dehydrogenation reactions.<sup>6</sup>

We have previously reported the rapid dehydrogenation of AB catalyzed by the iridium pincer complex (*t*-Bu<sup>POCOP</sup>)Ir(H)<sub>2</sub> (**1**) *t*-Bu<sup>POCOP</sup> = ( $\kappa^3$ -1,3-(OP<sup>t</sup>Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).<sup>7,8</sup> Catalyst **1** gives the fastest reported rate for the dehydrogenation of AB. However, upon release of 1 equiv of H<sub>2</sub>, the reaction yields a highly insoluble material previously identified<sup>9</sup> as the cyclic

pentamer [NH<sub>2</sub>BH<sub>2</sub>]<sub>5</sub> (**2**). In contrast, Rh complexes reported by Manners et al. catalyze the release of 2 equiv of H<sub>2</sub> from AB to produce borazine.<sup>10</sup> A Ni catalyst reported by Baker and co-workers promotes the release of 2.5 equiv of H<sub>2</sub> from AB.<sup>11</sup>

Soluble dehydrogenation products are desirable for engineering considerations in developing on-board hydrogen storage systems. Such products also have greater potential for the development of tandem catalysis methods that may allow for the release of additional equivalents of H<sub>2</sub> from the soluble products. Finally, soluble materials are more desirable when considering pathways for regenerating the parent amine borane complexes in order to form a comprehensive hydrogen storage system. We hypothesized that the dehydrogenation of substituted variants of AB catalyzed by **1** could result in soluble dehydrogenation products. The dehydrogenation of methylamine borane (CH<sub>3</sub>NH<sub>2</sub>BH<sub>3</sub>, MeAB) and AB/MeAB mixtures with **1** are reported herein.<sup>12</sup> The high activity of the Ir catalyst allowed us to measure the reaction enthalpies and evaluate the potential for direct regeneration of the dehydrogenated material.



In the previously reported Rh-catalyzed amine borane dehydrogenation reactions, Me<sub>2</sub>NHBH<sub>3</sub> was dehydrogenated more rapidly than AB.<sup>10,13–15</sup> In contrast, we found that dehydro-

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## COMMUNICATION

**Table 1.** First-Order Rate Constants ( $k_{\text{obs}}$ ) for Various Amine-Borane Substrates at Different Catalyst Loadings (298 K, THF)

substrate	catalyst loading (mol%)	$k_{\text{obs}}$ ( $10^{-3} \text{ s}^{-1}$ )
AB	0.5	11(2)
AB	1.0	22(3)
AB	2.0	38(6)
MeAB	0.5	13.4(7)
MeAB	1.0	30(5)
MeAB	2.0	55(3)
1:1 AB/MeAB	0.5	13(2)
1:1 AB/MeAB	1.0	26(6)
1:1 AB/MeAB	2.0	52(4)

generation of  $\text{Me}_2\text{NHBH}_3$  catalyzed by **1** is very slow, with less than 1 equiv of  $\text{H}_2$  released over 48 h. More rapid  $\text{H}_2$  loss was observed from MeAB.

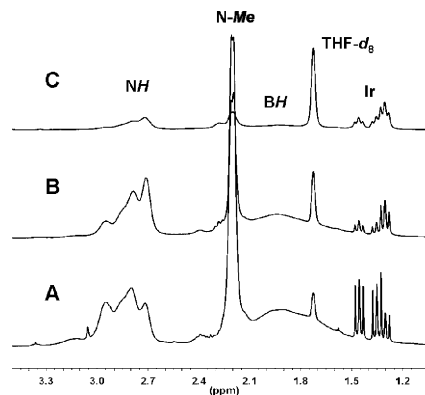
Under conditions analogous to those previously reported for AB dehydrogenation,<sup>7</sup> the addition of catalyst **1** to a THF solution of MeAB gave rapid evolution of 1 equiv of  $\text{H}_2$ . No further dehydrogenation was observed over 24 h. Dehydrogenation resumed immediately upon the introduction of additional MeAB. In contrast to the product obtained in analogous reactions with AB, the product of MeAB dehydrogenation was completely soluble.

With an initial concentration of 0.5 M MeAB in THF and 0.5 mol % catalyst loading at 298 K, the reaction was complete in ca. 13 min, with a measured first-order rate constant of  $k_{\text{obs}} = 13.4 \pm 0.7 \times 10^{-3} \text{ s}^{-1}$ . The reaction shows a linear dependence on catalyst loading (1.0 mol % catalyst,  $k_{\text{obs}} = 30 \pm 5 \times 10^{-3} \text{ s}^{-1}$ ; 2.0 mol % catalyst,  $k_{\text{obs}} = 55 \pm 3 \times 10^{-3} \text{ s}^{-1}$ ). Remarkably, the dehydrogenation rates are very similar to those found for the AB reaction (Table 1).

When the reaction was monitored by  $^1\text{H}$  NMR spectroscopy in  $\text{THF-}d_8$  (1.0 mol % **1**, 298 K), the resonances due to MeAB rapidly disappeared. New signals appeared, including two broad NH resonances at 3.21 ppm (1H) and 3.00 ppm (2H), a methyl resonance with a discernible shoulder at 2.21 ppm (9H), and a broad  $\text{BH}_2$  resonance at 1.76 ppm (6H). Also observed were ( $t\text{-Bu}$ ) $\text{POCOP}$ Ir $\text{H}_4$  (**3**) and ( $t\text{-Bu}$ ) $\text{POCOP}$ Ir( $\text{BH}_3$ )( $\text{H}_2$ ) (**4**), in agreement with the previous report.<sup>7,16</sup> Integration of the BN product signals versus the  $t\text{-Bu}$  signals of the various Ir species is consistent with all of the dehydrogenation products remaining in solution after  $\text{H}_2$  release.

Despite the relatively simple  $^1\text{H}$  NMR spectrum of the dehydrogenation product, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum reveals a large number of methyl resonances between 36 and 38 ppm. While these resonances are similar to those previously reported for the cyclic trimer  $[\text{MeNHBH}_2]_3$  (34–38 ppm),<sup>17</sup> they do not match any previously reported compound. The  $^{11}\text{B}$  NMR spectrum of the product contains a single broad resonance at  $-8.31$  ppm, whereas a sharp triplet is observed at  $-5.16$  ppm for  $[\text{MeNHBH}_2]_3$ .

Analysis of the product by electrospray ionization mass spectrometry (ESI-MS) shows numerous  $[\text{M} + \text{H}]^+$  peaks, with isotopic distribution patterns consistent with those of cyclic



**Figure 1.** Partial  $^1\text{H}$  NMR spectra of soluble dehydrogenation products (500 MHz,  $\text{THF-}d_8$ , 298 K) (A) 1:1 AB/MeAB, (B) 2:1 AB/MeAB, and (C) 5:1 AB/MeAB.

oligomers of the form  $[\text{MeNHBH}_2]_n$  ( $n = 2\text{--}20$ ) as well as acyclic oligomers  $[\text{MeNH}_2\text{BH}_2][\text{MeNHBH}_2]_n[\text{MeNH}_2]$  (with  $n = 4\text{--}48$ ).<sup>18</sup> Although ESI-MS is a “soft” technique, adjustment of instrument parameters to reduce any premature fragmentation resulted in no significant change to the spectra, suggesting that the mass spectrum represents a distribution of oligomers of varying length rather than fragmentation of a larger polymer. It is unclear from the mass spectrum whether the cyclic oligomers represent complete macrocycles or smaller cycles with linear branching. Similarly, it is unclear whether the noncyclic oligomers are branched or linear chains.

Because both AB and MeAB exhibit similar rates of dehydrogenation, we reasoned that dehydrogenation of AB/MeAB mixtures might result in products that incorporated both  $[\text{NH}_2\text{BH}_2]$  and  $[\text{MeNHBH}_2]$  fragments into the oligomeric structure. The composition of these mixtures could also be varied in order to obtain products that retain the solubility observed in the MeAB system while approaching the more desirable weight percent of hydrogen available in the AB system.

Upon addition of a THF solution of **1** to a THF solution of 1:1 AB/MeAB prepared under an atmosphere of argon, rapid evolution of 1 equiv of  $\text{H}_2$  was observed, along with a color change from red to pale yellow. The product of dehydrogenation was completely soluble. The rate of dehydrogenation was similar to that seen in the separate AB and MeAB reactions (Table 1).

The rapid disappearance of the AB and MeAB starting materials and the appearance of several new product resonances were observed by  $^1\text{H}$  NMR spectroscopy ( $\text{THF-}d_8$ ). The product resonances appear as two overlapping methyl signals at 2.20 and 2.21 ppm (3H), a broad BH resonance at 1.91 ppm, and a number of broad overlapping NH resonances of varying intensity between 2.72 and 3.13 ppm, which integrate to a total of three protons relative to the methyl protons (Figure 1). Integration versus the  $t\text{-Bu}$  resonances of the Ir species (**3** and **4**) confirms that all of the dehydrogenation product is in solution.

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(18) The product distributions described result from reactions carried out in dilute THF solutions. Recent observations by Manners and co-workers suggest that the use of concentrated amine borane solutions results in high-molecular-weight polymers (Manners, I. Private communication). See also: Staubitz, A.; Presa Soto, A.; Manners, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 6212.

Precipitation of **2** is not observed in this reaction, and the proton resonances do not match those of the MeAB dehydrogenation product.

In the  $^{11}\text{B}$  NMR spectrum, broad resonances at  $-8.7$  and  $-11.4$  ppm were observed, while the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum showed a broad resonance at  $36\text{--}37$  ppm. As with the soluble MeAB dehydrogenation product, the presence of broad resonances in both the  $^{13}\text{C}\{^1\text{H}\}$  and  $^{11}\text{B}$  NMR spectra is most consistent with various inequivalent boron and carbon environments, suggesting that similar mixtures of oligomers were formed from the 1:1 mixture of AB/MeAB.

Because the product of dehydrogenation of 1:1 mixtures of AB/MeAB remained in solution, subsequent reactions were carried out with increasing ratios of AB/MeAB in an attempt to form products that would remain soluble but would contain a higher weight percent of hydrogen. The addition of catalyst **1** to a 2:1 mixture of AB/MeAB in THF resulted in rapid evolution of 1 equiv of  $\text{H}_2$ , accompanied by precipitation of a white solid. The addition of **1** to a 5:1 mixture of AB/MeAB in THF proceeded in a similar fashion but produced significantly more solid. In each case, the IR spectrum of the insoluble product was consistent with the formation of **2**.<sup>9</sup>

These AB/MeAB reactions were repeated in THF- $d_8$  using the same total substrate concentration but varying ratios of AB/MeAB, and the reactions were monitored by  $^1\text{H}$  NMR spectroscopy (Figure 1). Regardless of the initial ratio of AB to MeAB, the signals observed in each spectrum are the same as those observed in the 1:1 AB/MeAB reaction, with the exception of what appears to be an additional methyl resonance observed at 2.28 ppm in the 5:1 reaction. Although the NH resonances have the same chemical shifts in each of the separate reactions, the signal intensities vary depending on the initial AB/MeAB ratio. Similarly, ESI-MS data show identical isotopic distribution patterns for each reaction but with varying intensities of the peaks.<sup>18</sup> The results from the different mixed AB/MeAB reactions suggest that the soluble product consists of oligomers of varying chain lengths, with the initial ratio of AB/MeAB determining which oligomers are formed preferentially.

For all three reactions, integration of the N–Me  $^1\text{H}$  NMR resonances confirms that all MeAB is incorporated into the soluble products. Notably, integration of the N–Me resonances versus the NH protons of the products from both the 2:1 and 5:1 AB/MeAB reactions is consistent with a 1:1 ratio of  $[\text{NH}_2\text{BH}_2]$  and  $[\text{MeNHBH}_2]$  fragments incorporated into the soluble product. This observation parallels the larger production of insoluble **2** as the ratio of AB to MeAB was increased.

ESI-MS spectra of the soluble products show isotopic distribution patterns consistent with cyclic compounds of the general formula  $[\text{NH}_2\text{BH}_2]_x[\text{MeNHBH}_2]_y$  and noncyclic oligomers of the general formula  $[\text{NH}_2\text{BH}_2]_x[\text{MeNHBH}_2]_y[\text{H}_2]$ . All observed distribution patterns can be described by formulas in which  $x$  and  $y$  do not differ by more than 3, which is consistent with the 1:1 ratio of N–Me versus NH  $^1\text{H}$  NMR signals. However, because isotopic distribution patterns in which the disparity between  $x$  and  $y > 3$  encompass mass ranges similar to those signals already described, larger differences cannot be ruled out.

Evaluation of the potential viability of hydrogen storage materials requires data for the thermodynamics of hydrogen release from the materials. There have been several computational investigations<sup>6,19–21</sup> of AB dehydrogenation, but experimental verification under relevant conditions has remained elusive. Wolf and co-workers have reported the enthalpy of AB dehydrogenation in the solid state, but no solution data are available.<sup>22</sup> The ability of **1** to catalyze rapid  $\text{H}_2$  loss allowed for the direct determination of the enthalpy of these reactions. The reaction enthalpy ( $\Delta H$ ) for AB dehydrogenation in THF at 303 K (2.5 mol % **1**) was found to be  $-6.7 \pm 0.6$  kcal mol<sup>-1</sup> by differential scanning calorimetry (DSC). For the dehydrogenation of MeAB and 1:1 AB/MeAB catalyzed by **1**,  $\Delta H$  values of  $-6.8 \pm 0.6$  and  $-6.7 \pm 0.1$  kcal mol<sup>-1</sup>, respectively, were determined. A value of  $\Delta H = -10.7$  kcal mol<sup>-1</sup> was calculated by Matus and co-workers for AB dehydrogenation to the cyclic trimer.<sup>21</sup> Thus, the results reported here provide experimental support for computational studies, suggesting that reversible hydrogen absorption and release under mild conditions using amine boranes may not be feasible. Alternate methods of regenerating the parent amine borane compounds from spent materials will be needed.

In summary, the iridium complex **1** is an efficient catalyst for the rapid dehydrogenation of MeAB and AB/MeAB mixtures. The rates of dehydrogenation are similar to those seen for AB dehydrogenation. The dehydrogenation reactions of both MeAB and mixtures of AB/MeAB with **1** result in *soluble* products. Dehydrogenation of MeAB results in a mixture of cyclic and noncyclic oligomers of varying chain lengths. The dehydrogenation of mixtures of AB and MeAB also yield multiple cyclic and noncyclic oligomeric products. The amount of AB incorporation appears limited to 1:1 relative to MeAB as evidenced by the observation of ca. 1:1 ratios of dehydrogenated  $[\text{NH}_2\text{BH}_2]$  and  $[\text{MeNHBH}_2]$  fragments and the additional formation of insoluble pentamer **2** with reactions where AB/MeAB ratios greater than 1:1 were employed. The measured exothermicity of the dehydrogenation reactions suggests that direct regeneration under mild conditions is not feasible.

**Acknowledgment.** This work was supported by the U.S. Department of Energy (DOE) as part of the Center of Excellence for Chemical Hydrogen Storage. PNNL is operated for the DOE by Battelle. Thanks to A. St. John, L. Kruse and M. Sadilek at UW for skilled technical assistance. Thanks to Abhi Karkamkar of PNNL for assistance with the calorimetry.

**Supporting Information Available:** Characterization of products, quantification of  $\text{H}_2$  evolved, DSC experimental details, and ESI-MS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC801161G

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