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Base Metal Catalyzed Dehydrogenation of Ammonia−Borane for Chemical Hydrogen Storage

Richard J. Keaton, Johanna M. Blacquiere, and R. Tom Baker*

Chemistry Division, MS J582, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received October 2, 2006; E-mail: bakertom@lanl.gov

With greenhouse gas emissions affecting political and environmental climates, the need for alternative fuels has become abundantly clear. Hydrogen has emerged as a clean-burning option, and the U.S. Department of Energy (DOE) has set aggressive goals for development of on-board storage systems. Current technology (pressurized H_2) has safety, efficiency, and density shortcomings, requiring further research into hydrogen storage methodologies if a hydrogen economy is to become a reality.

Chemical hydrogen storage, in which (catalytic) chemical reactions release gaseous H_2 from hydrogen atoms covalently bound in a molecule, provides a promising future for hydrogen. To meet the DOE targets for overall system weight (9.0 wt % H by 2015),[1] practical hydrogen storage materials must be of low molecular weight and high chemical weight percent hydrogen. Given these criteria, the adduct ammonia−borane (H_3NBH_3, AB) is a leading candidate as a storage medium, with a molecular weight of 30.9 g/mol and a potential capacity of 19.6 wt % H_2. Containing both protic N−H and hydridic B−H hydrogens within the same molecule, AB appears ripe for dehydrogenation.

While solution[2,3] and solid state[4−6] thermal dehydrogenation of amine−boranes has been reported, as well as acid-catalyzed dehydrocoupling,[7] only recently have transition-metal-catalyzed dehydrogenation reactions been described in the literature. Manners reported that precious metal Rh, Ir, Pd, and Ru catalysts are active for amine−borane dehydrocoupling at room temperature with catalyst loadings as low as 0.5 mol %.[6] While the nature of the active species has been disputed,[8] the Rh-catalyzed reaction affords black solutions, with commensurate precipitate formation, and slow AB dehydrogenation at 45 °C to give a mixture of cyclotriborazane $(H_2NBH_2)_3$, borazine $(HNBH)_3$, and poly(iminoborane) $(HNBH)_n$. A subsequent paper by Manners details an early metal catalyst (presumably a Ti(II) species) for dehydrocoupling of dialkylamine−boranes but makes no mention of AB.[9] Finally, an Ir-pincer catalyst rapidly dehydrocouples AB to yield 1 equiv of H_2 and the insoluble cyclic amino−borane pentamer, $(H_2NBH_2)_5$.[10]

Our research has focused on development of additional metal complexes which are competent for the dehydrogenation of amine−boranes, with attention paid to greater catalyst stability and extension to cheaper and more abundant first row metals. With the knowledge that strongly donating ligands promote B−H bond activation,[11] trialkylphosphine and N-heterocyclic carbene (NHC) metal complexes were tested for their potential to enhance catalyst solubility, stability, and activity. We report here the first examples of AB dehydrogenation catalysts based on Ni−NHC complexes which afford long-lived catalysts with unprecedented extent of hydrogen release (>2.5 equiv or 18 chemical wt %).

To avoid significant decomposition of both the amine−borane starting material and the catalyst, NHC ligands were explored as alternatives to phosphines.[12] An active dehydrogenation catalyst was generated in situ by reaction of $Ni(cod)_2$ with 2 equiv of a suitable NHC ligand in C_6D_6.[13] This dark solution was then combined with a slurry of 10 equiv of AB in C_6D_6 or a solution in diglyme [bis(2-methoxyethyl)ether] at 60 °C. The resulting homogeneous[14] dark maroon solution evolved H_2 immediately.

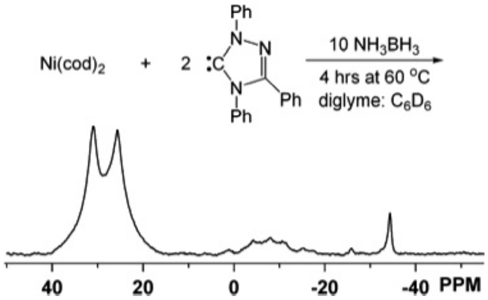

Figure 1. $^{11}B-\{^{1}H\}$ NMR spectrum in C_6D_6/diglyme from the reaction of 10 equiv of NH_3BH_3 with 1 and 2 equiv, respectively, of $Ni(cod)_2$ and Enders' NHC after 4 h at 60 °C. The signal at −36 ppm is attributable to the NHC−BH_3 adduct (ca. 2% of total B).

Inspection of the $^{11}B-\{^{1}H\}$ NMR spectrum of a 10 mol % Ni−NHC-catalyzed AB dehydrogenation experiment after 4 h at 60 °C (Figure 1) shows that all of the AB starting material (−22 ppm) has been consumed. The spectrum contains minor amounts of singly dehydrogenated four-coordinate boron atoms from 0 to −20 ppm and two broad resonances due to B−N cross-linked borazine units from 40 to 18 ppm.[15] Notably, formation of the latter species requires that more than 2 equiv of H_2 be released from AB. Quantification of the hydrogen evolved showed that 29 mL of H_2 was produced of a maximum 31 mL for 3 equiv of H_2, equating to 18 wt % H_2. For the Ni−NHC catalyst systems, borazine (30 ppm) is evident in the ^{11}B NMR (Figure S4) but does not build up in significant amounts because it is rapidly consumed by subsequent cross-linking. This is important because the rate of dehydrogenation of borazine, a volatile compound and potential poison of fuel cell catalysts, is at least on the order of consumption of the AB starting material for this Ni−NHC system.

To gauge which Ni−NHC-based system was the most active, the rate of AB dehydrogenation was studied with three different NHCs using ^{11}B NMR spectroscopy. Using the NHCs Idipp (*N*,*N′*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), Imes (*N*,*N′*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), and Enders' (1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene),[16] first-order rate constants for the disappearance of AB with 5 mol % of catalyst at 60 °C of 5.6, 7.3, and 64.6 × 10^{-3} min^{-1} were obtained, respectively, illustrating the greater activity of the Enders' NHC system. Control experiments show that the free NHCs exhibited similar rates at 60 °C to the uncatalyzed reaction, while $Ni(cod)_2$ showed lower activity (vs Ni−NHC systems) and nonlinear kinetics indicative of catalyst deactivation. To assess AB dehydrogenation rates with different metals, we compared the Ni−Enders' system to newly generated catalysts formed by addition of 2 equiv of Enders' NHC per metal to $[RuCl_2(p\text{-cymene})]_2$[17] and $[RhCl(coe)_2]_2$ (coe = *cis*-cyclooctene).[18] With 5 mol % catalyst loading, the Ni−

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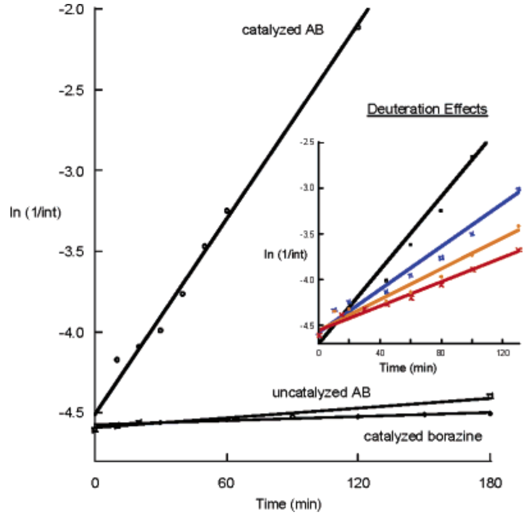

Figure 2. Dehydrogenation kinetics of 25 wt % AB or borazine solutions in diglyme at 60 °C with 1 mol % of Ni−Enders' NHC catalyst. Inset: Kinetics of dehydrogenation at 60 °C with 20:1 AB/Ni ratio for AB (black), NH_3BD_3 (blue), ND_3BH_3 (orange), and ND_3BD_3 (red).

Enders' catalyst system consumed AB twice as fast as Ru and four times faster than Rh.

In a dehydrogenation using high monomer concentrations, a 25 wt % solution of AB in diglyme was prepared and mixed with 1 mol % of the Ni−Enders' NHC catalyst generated in situ. At 60 °C, extensive H_2 release was observed and AB consumption was complete in 150 min. A first-order rate constant of 2.02×10^{-2} min^{-1} was obtained, which is a 20-fold increase in activity when compared to the uncatalyzed reaction (1.01×10^{-3} min^{-1}) (Figure 2). A similar experiment using borazine as the monomer showed poor activity for dehydrogenation (3.73×10^{-4} min^{-1}), suggesting that the catalytically active species formed during AB dehydrogenation is not formed starting with borazine alone.

To gain some insight into the initial steps of AB dehydrogenation, reaction rates with the Ni−Enders' NHC system were measured with appropriately deuterated AB samples (Figure 2 inset). A kinetic isotope effect (KIE) of 1.7 was determined for deuteration at boron, NH_3BD_3. A larger KIE (2.3) was found for deuteration at nitrogen, ND_3BH_3. Fully deuterated AB, ND_3BD_3, was shown to have the slowest rate of dehydrogenation, having an observed KIE of 3.0. These studies suggest that both an N−H and a B−H bond are being broken in the rate-determining step(s).

Although the detailed mechanism of metal-catalyzed AB dehydrogenation has not been discussed previously, a notable characteristic of metal-catalyzed dehydrogenation of substituted amine−boranes, such as Me_2HNBH_3 or t-BuH_2NBH_3, is initial production of the reactive amino−borane monomer, $RR'NBH_2$.[6,8,19] Although we have been unable to observe any Ni−H resonances by ^1H NMR during AB dehydrogenation nor any irreversible reaction of $Ni(NHC)_2$ with Me_3NBH_3, the most logical reaction pathway involves initial formation of a σ-complex,[20,21] B−H bond activation, and β-H elimination from the N−H bond (Figure 3). The implication from the observed isotope effects, then, is that the latter two steps have competitive rates (i.e., $k_1 \cong k_2$).

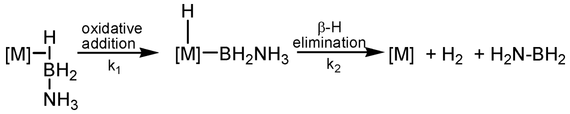

Figure 3. Proposed initial steps of metal-catalyzed AB dehydrogenation.

To our knowledge, this is the first example of active first row transition metal catalysts for the dehydrogenation of AB, a promising chemical hydrogen storage material. The Ni−NHC system exhibits an unprecedented extent of dehydrogenation to a soluble cross-linked borazine structure at 60 °C. Further work on mechanistic studies of dehydrogenation of substituted amine−boranes, cyclotriborazane, and borazine, as well as isolation and identification of subsequent products, is underway.

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Supporting Information Available: Details of dehydrogenation experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Dresselhaus, M., Crabtree, G., Buchanan, M., Eds. *Basic Energy Needs for the Hydrogen Economy*; Basic Energy Sciences, Office of Science, U.S. Department of Energy: Washington, DC, 2003.
(2) Wang, J. S.; Geanangel, R. A. *Inorg. Chim. Acta* **1988**, *148*, 185.
(3) Bluhm, M. E.; Bradley, M. G.; Butterick, R.; Kusari, U.; Sneddon, L. G. *J. Am. Chem. Soc.* **2006**, *128*, 7748.
(4) Wolf, G.; Baumann, J.; Baitalow, F.; Hoffmann, F. P. *Thermochim. Acta* **2000**, *343*, 19.
(5) Baitalow, F.; Baumann, J.; Wolf, G.; Jaenicke-Rössler, K.; Leitner, G. *Thermochim. Acta* **2002**, *391*, 159.
(6) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424.
(7) Stephens, F. H.; Baker, R. T. *Angew. Chem., Int. Ed.* **2006**, in press.
(8) Chen, Y.; Fulton, J. L.; Linehan, J. L.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254.
(9) Clark, T. J.; Russell, C. A.; Manners, I. *J. Am. Chem. Soc.* **2006**, *128*, 9582.
(10) Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048.
(11) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399.
(12) Investigation of AB dehydrogenation activity with Fe and Ni phosphine complexes shows extensive precipitation of black inactive solids and formation of phosphine−borane (see Figures S1 and S2).
(13) Arduengo, A. J., II; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391. While NMR spectroscopic evidence was obtained for $Ni(NHC)_2$ using Enders' carbene, isolated solid was only ca. 90% pure and very air sensitive so catalysts were generated in situ.
(14) In parallel experiments with and without added mercury, no difference in rate, selectivity, or extent of AB dehydrogenation was observed.
(15) Fazen, P. J.; Remsen, E. E.; Beck, J. S.; Carroll, P. J.; McGhie, A. R.; Sneddon, L. G. *Chem. Mater.* **1995**, *7*, 1942.
(16) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021.
(17) Poyatos, M.; Mas-Marzá, E.; Sanaú, M.; Peris, E. *Inorg. Chem* **2004**, *43*, 1793.
(18) Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, *19*, 1194.
(19) See example of Me_2HNBH_3 using a Cu−NHC catalyst in Supporting Information (Figure S3).
(20) Crestani, M. G.; Munoz-Hernandez, M.; Arevalo, A.; Acosta-Ramirez, A.; Garcia, J. J. *J. Am. Chem. Soc.* **2005**, *127*, 18066.
(21) Kawano, Y.; Haskiva, M.; Shimoi, M. *Organometallics* **2006**, *25*, 4420.

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