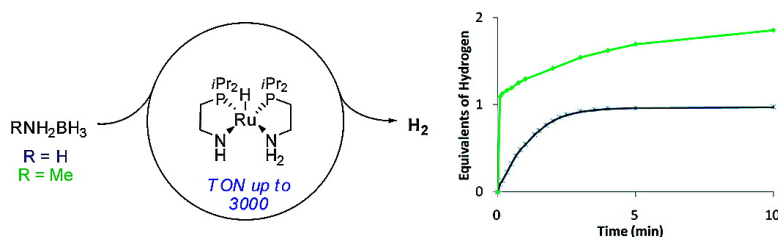Communication

# Ruthenium-Catalyzed Dehydrogenation of Ammonia Boranes

Nicole Blaquiere, Sarah Diallo-Garcia, Serge I. Gorelsky, Daniel A. Black, and Keith Fagnou

## More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

# Ruthenium-Catalyzed Dehydrogenation of Ammonia Boranes

Nicole Blaquiere, Sarah Diallo-Garcia, Serge I. Gorelsky, Daniel A. Black, and Keith Fagnou*

*Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie,
Ottawa, Ontario, K1N 6N5, Canada*

Received June 4, 2008; E-mail: keith.fagnou@uottawa.ca

Ammonia borane (AB), which has a very high hydrogen content by weight (19.6%), is attracting attention as a means of achieving efficient chemical hydrogen storage.[1,2] Heating AB in the solid state,[3] ionic liquids[4] or the presence of acid[5] has been shown to induce the release of >1.0 equiv of $H_2$ over the course of several hours, and transition metal complexes of Rh,[6] Ni,[7] and Ir[8] have been shown to catalyze $H_2$ release under mild conditions. Notably, the Ni catalysts described by Baker release up to 2.8 equiv of $H_2$,[7] an observation that has prompted a more detailed evaluation of their reaction mechanism.[9a] When considering strategies for dehydrogenation, AB is often compared to ethane.[10] Computational predictions provide little mechanistic support for this analogy, however,[9,11] and in terms of local dipoles and reactivity AB may better be compared to methanol. Drawing from this analogy, we have discovered that ruthenium catalysts, originally developed for alcohol redox processes,[12] will induce the release of 1 equiv of $H_2$ from AB (up to 1.0 system wt %) within 5 min at room temperature with as little at 0.03 mol% Ru. Furthermore, 2 equiv of $H_2$ is rapidly released from highly concentrated (11 M) MeAB solutions at 22 °C (ambient temperature), providing 3.0 system wt % hydrogen release. We have also found that by using an AB/MeAB mixture at 50 °C, up to 3.6 system wt % $H_2$ can be released with 0.1 mol % Ru.

An evaluation of several alcohol oxidation/reduction catalysts provided promising leads with complexes **1** to **6** (Figure 1).[13] In these studies, the precatalysts (0.1 mol%) were activated via treatment with KO'Bu (3 mol%)[13c] in THF under inert atmosphere to generate the active ruthenium amide species prior to the addition of AB to the reaction vessel.[14] Complexes **1** and **2** are particularly reactive even at 0.03 mol% Ru.[14] Optimal outcomes are observed at high [AB] (5.0 M), an important parameter for maximal gravimetric $H_2$ density. In reactions with AB, we note the formation of an insoluble precipitate, which has been identified as the same polymeric aminoborane species obtained by Goldberg[8] and Manners.[15]

The dehydrogenation of methylammonia-borane (MeAB) was also evaluated.[6] Under conditions similar to those employed for AB dehydrogenation, 0.5 mol% **1** induced the release of up to 2.0 equiv of $H_2$ from MeAB in ~10 min (Figure 2).[16] These reactions are characterized by a very rapid release of the first equivalent of $H_2$ (occurring in less than 10 s), generating poly(N-methylaminoborane).[15] This is followed by a slower release of the second equivalent over ~10 min.[17] Since no insoluble precipitate is observed, more concentrated conditions (11 M [MeAB]) may be employed, increasing the system % $H_2$ to 3% (1.9 equiv of $H_2$ released). To further maximize the gravimetric $H_2$ density, AB−MeAB mixtures were evaluated.[18] Initial results using a 1:1
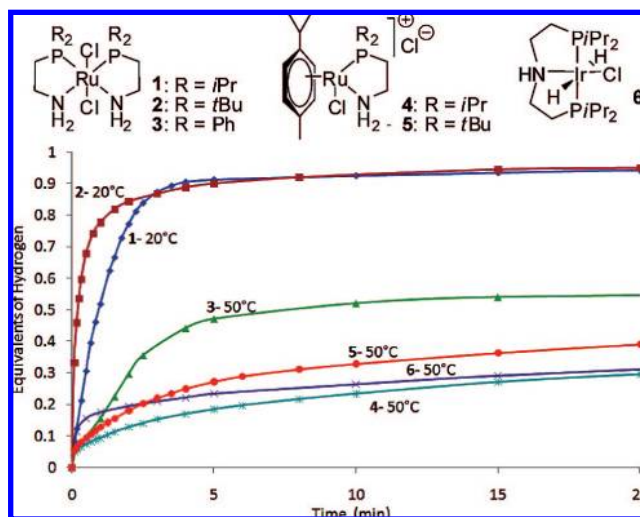


**Figure 1.** $H_2$ release from AB with 0.1 mol % catalyst **1**−**6** after activation with KO'Bu.
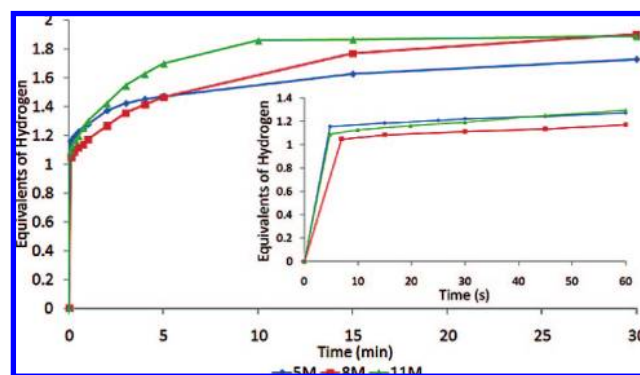


**Figure 2.** $H_2$ release from MeAB with 0.5 mol % **1** after activation with KO'Bu.

AB/MeAB mixture at 50 °C indicate that 3.6 system wt % $H_2$ release can be achieved with 0.1 mol% **1** under solvent-free conditions.[16]

As a preliminary probe into the reaction mechanism, the viability of a reaction pathway similar to that involved in alcohol oxidation/reduction was evaluated by density functional theory calculations at the B3LYP level (Scheme 1).[16,19] Ru-catalyzed alcohol oxidation has been shown to involve an outer sphere hydrogen transfer mechanism between the alcohol and an amide ligand on the Ru metal.[12,13,20] Along a similar pathway, we determined that AB binding to Ru-hydride **7** is energetically favored, giving **8** (a species very close in structure to known ruthenium borohydride hydrogena-

**Scheme 1.** Catalytic Cycle for Dehydrogenation of AB with the Ru Catalyst in THF and Gas Phase from DFT Calculations[a][16]
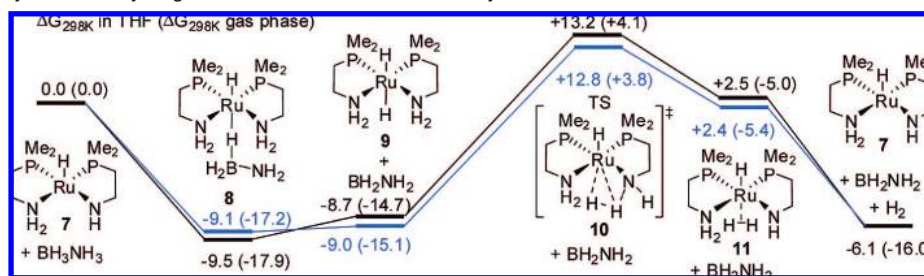


[a] Black and blue lines indicate different conformers of the P,N ligands of the Ru species. Reported values are in kcal/mol.

**Scheme 2.** Reduction of Ketones and Imines Using PyrAB as the Source of $H_2$
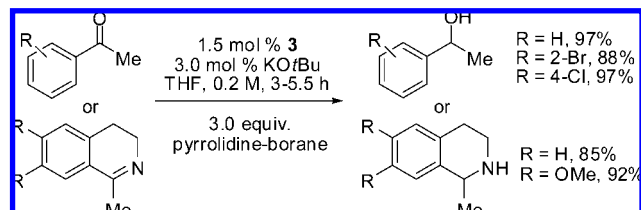


tion precatalysts).[21] AB dehydrogenation at **8** to form dihydride **9** is slightly endothermic; however, a reaction coordinate scan in forward and reverse directions revealed that this step does not have a kinetic barrier in gas phase calculations. The largest kinetic barrier from these calculations involves the formation of dihydrogen complex **11** via transition state **10** that can subsequently dissociate $H_2$ to regenerate catalyst **7**. The intermediacy of a species similar to dihydride **9** is further supported through the successful coupling of AB dehydrogenation with C=O, C=N hydrogenation (*vide infra*) since Ru-dihydrides are known to mediate $H_2$ delivery to these functional groups.

We have also determined that AB-ketone/imine transfer hydrogenation may be achieved.[22] Superior outcomes are observed with precatalyst **3**, which is less reactive than **1** in hydrogen release processes. Use of pyrrolidine borane (PyrAB) in conjunction with 1.5 mol% precatalyst **3** and 3 mol% KO′Bu efficiently induces the hydrogenation of several organic substrates (Scheme 2).[16] In each instance, no detectable background reduction was observed in the absence of Ru catalyst over the same reaction time.

Significant challenges remain in the development of chemical hydrogen storage. The full potential of AB will only be attained by increasing the amount of $H_2$ released to well over 1.0 equiv and by solving the important problem of regenerating AB from the waste products;[23] however, the exceptionally low catalyst loadings, mild reaction conditions, rapid release of $H_2$, and high concentration achievable by this system represent a new opportunity for approaching hydrogen storage/release goals.[24]

**Supporting Information Available:** Experimental procedures, additional information, computational details, and DFT structures. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

(1) Amos, W. A. *Costs of Storing and Transporting Hydrogen*; National Renewable Energy Laboratory, U.S. DOE: Golden, CO, 1998.
(2) (a) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613. (b) Marder, T. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8116.
(3) (a) Hu, M. G.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1978**, *23*, 249. (b) Sit, V.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1987**, *113*, 379. (c) Wolf, G.; Baumann, J.; Baitalow, F.; Hoffmann, F. P. *Thermochim. Acta* **2000**, *343*, 19. (d) Baitalow, F.; Baumann, J.; Wolf, G.; Jaenicke-Rößler, K.; Leitner, G. *Thermochim. Acta* **2002**, *391*, 159.
(4) Bluhm, M. E.; Bradley, M. G.; Butterick, R., III.; Kusari, U.; Sneddon, L. G. *J. Am. Chem. Soc.* **2006**, *128*, 7748.
(5) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 746.
(6) (a) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424. (b) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 2698. (c) Clark, T. J.; Russell, C. A.; Manners, I. *J. Am. Chem. Soc.* **2006**, *128*, 9582.
(7) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844.
(8) Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048.
(9) (a) Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2008**, *130*, 1798. (b) Ankan, P.; Musgrave, C. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8153.
(10) Liu, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2007**, *47*, 242.
(11) Peyerimhoff, S. D.; Buenker, R. J. *J. Chem. Phys.* **1968**, *49*, 312.
(12) (a) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.
(13) (a) Tianshu, L.; Churlaud, R.; Lough, A. J.; Abdur-Rashid, K.; Morris, R. H. *Organometallics* **2004**, *23*, 6239. (b) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104. (c) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201.
(14) Control reactions run with AB and 10 mol % KO′Bu in the absence of catalyst eliminated the possibility of base-enabled dehydrogenation.
(15) Staubitz, A.; Presa Soto, A.; Manners, I. *Angew. Chem., Int. Ed.* **2008**, *47*, Early View.
(16) See Supporting Information for experimental and computational details.
(17) ^{1}H, ^{13}C, and ^{11}B NMR revealed the presence of a complex reaction mixture. See Supporting Information.
(18) Lane, C. F. U. S. DOE Hydrogen Program; *2007 Annual Progress Report*, Section IV.B.5j, 2007.
(19) Homogenous catalysis was confirmed, as the addition of mercury to the reaction medium had no effect on $H_2$ evolution.
(20) (a) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931. (b) Sandoval, C. A.; Ohkuma, T.; Muñiz, K.; Noyori, R. *J. Am. Chem. Soc.* **2003**, *125*, 13490. (c) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40. (d) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew, Chem, Int. Ed. Engl.* **1997**, *36*, 285.
(21) (a) Guo, R.; Morris, R. H.; Song, D. *J. Am. Chem. Soc.* **2005**, *127*, 516. (b) Ohkuma, T.; Koizumi, M.; Muñiz, K.; Hilt, G.; Kabuto, C.; Noyori, R. *J. Am. Chem. Soc.* **2002**, *124*, 6508.
(22) For uncatalyzed reductions using amine-boranes, see: (a) Uyeda, C.; Biscoe, M.; LePlae, P.; Breslow, R. *Tetrahedron Lett.* **2006**, *47*, 127. (b) Allwood, B. L.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *Chem. Commun.* **1984**, *22*, 1461 For the catalyzed transfer hydrogenation of alkenes, see: (c) Clark, T. J.; Lee, K.; Manners, I. *Chem.—Eur. J.* **2006**, *12*, 8634. (d) Jiang, Y.; Berke, H. *Chem. Commun.* **2007**, 3571.
(23) For theoretical studies on the properties of AB and its decomposition products, see: Caetano, M. R.; Gerbrand, C. *J. Chem. Phys.* **2007**, *126*, 184703. For studies on regeneration of AB: (b) Hausdorf, S.; Baitalow, F.; Wolf, G.; Mertens, F. O. R. L. *Int. J. Hydr. Energy* **2008**, *33*, 608. (c) Sneddon, L. G. U.S. DOE Hydrogen Program; *2007 Annual Progress Report*, Section IV.B.5e, 2007.
(24) Just prior to the submission of this manuscript we became aware of similar work being performed independently at Kanata Chemical Technologies (Dr. Abdur-Rashid) using similar catalysts.

JA804235T