

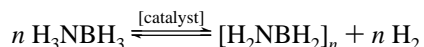
Efficient Catalysis of Ammonia Borane Dehydrogenation

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There are considerable challenges to be met in creating a "Hydrogen Economy".^{1,2} A key obstacle delaying the widespread use of hydrogen fuel cells to power automobiles is the development of a safe and practical method for storing hydrogen on board a vehicle. Chemical hydrogen storage, wherein hydrogen is stored in a chemical compound and released via a reversible chemical reaction, is a promising strategy.^{3,4} Ammonia borane (H_3NBH_3) and related amineborane compounds have emerged as particularly attractive candidates for hydrogen-storage materials due to their high percentage by weight of available hydrogen⁵ and the potential reversibility of hydrogen-release reactions.⁶ However, catalysts are needed to effect the release of hydrogen from amineborane compounds at efficient rates.



Catalysis of the dehydrogenation of ammonia borane and related substituted compounds (e.g. Me_2NHBH_3) by rhodium complexes was recently reported.⁷ The nature of the active catalytic species (heterogeneous rhodium colloids or rhodium clusters)^{8,9} presents a challenge for further optimization, as these systems are not sufficiently active to allow for efficient hydrogen release, particularly when H_3NBH_3 is the substrate.

Effective homogeneous catalysts for alkane dehydrogenation have been reported.^{10–12} Since amineboranes are isoelectronic with alkanes, we considered the application of such complexes to the problem of amineborane dehydrogenation. Herein we report that (POCOP)Ir(H)₂ (POCOP = $[\eta^3\text{-}1,3\text{-(OP}^t\text{Bu}_2)_2\text{C}_6\text{H}_3]$) (**1**),¹² is an exceptionally active catalyst for the dehydrogenation of NH_3BH_3 .

When **1** was added to a THF solution of ammonia borane, under an atmosphere of argon, vigorous evolution of gas was observed. Concurrent with this, the red color of **1** instantly faded to pale yellow, and a white solid precipitated. The progress of the reaction can be followed by monitoring the amount of hydrogen evolved. With an initial ammonia borane concentration of 0.5 M and a 0.5 mol % catalyst loading, quantitative conversion of ammonia borane and the release of one equivalent of hydrogen gas was observed within 14 min (Figure 1). After complete consumption of the substrate, gas evolution was immediately renewed upon addition of more ammonia borane.

During the course of the reaction, a white solid was deposited. The precipitate was insoluble in water and most common organic solvents. Solid-state ¹¹B NMR spectroscopy of this product gave a broad, symmetric resonance at ca. -18 ppm. The negative shift and approximately Gaussian appearance of this signal is characteristic of a species containing tetracoordinate boron atoms with near cubic symmetry,¹³ supporting a dehydrogenated product of the form $[\text{H}_2\text{NBH}_2]_n$. The IR spectrum and X-ray powder diffraction (XRD) pattern of the precipitate agree closely with data reported for the known cyclic pentamer, $[\text{H}_2\text{NBH}_2]_5$.¹⁴ The pentamer is formed in near quantitative yield.

The rate of the reaction is dependent on catalyst loading (Table S1). As shown in Figure 1, with the same initial ammonia borane

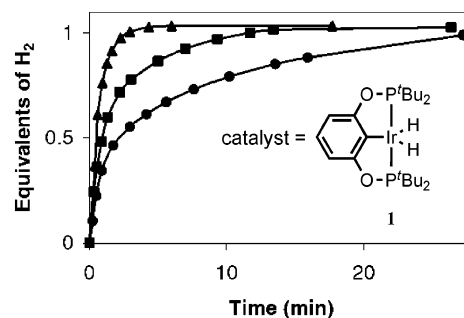


Figure 1. Amount of hydrogen gas evolved per mole of H_3NBH_3 using 0.25 mol % (●), 0.5 mol % (■), and 1.0 mol % (▲) of **1** as catalyst.

concentration, a 0.25 mol % catalyst loading increases the time required to consume the substrate to at least 30 min, while a 1.0 mol % catalyst loading reduces the time to ca. 4 min.

The catalytic activity of complex **1** in the dehydrogenation of ammonia borane is substantially higher than the current best reported catalyst.⁸ The rhodium-catalyzed reaction reported by Manners and co-workers required 2–4 days at 45 °C with a catalyst loading of 0.6 mol % to produce 2 equiv of hydrogen gas and borazine. By contrast, the reaction catalyzed by a comparable loading of the iridium catalyst **1** (0.5 mol %) is complete within 14 min at room temperature.

The dehydrogenation of H_3NBH_3 catalyzed by 0.5 mol % of **1** occurred at the same rate in the presence or absence of elemental mercury. This observation strongly suggests that the iridium catalyst remains homogeneous throughout the reaction. In comparison, elemental mercury completely inhibited a similar reaction that used the rhodium catalyst system, suggesting a heterogeneous environment for that catalyst.⁸

To investigate the fate of **1** in the dehydrogenation of H_3NBH_3 , the reaction was monitored by NMR spectroscopy. Signals for complex **1** disappeared immediately upon addition of H_3NBH_3 . The iridium species initially observed is the tetrahydride complex (POCOP)Ir(H)₄ (**2**),¹⁵ resulting from the reaction of **1** with H_2 generated by the reaction. At long reaction times, a new iridium hydride species (**3**) was observed. In addition to the phenyl resonances, the ¹H NMR spectrum for complex **3** exhibits two distinct virtual triplets for the *tert*-butyl groups, indicative of a low-symmetry structure. A sharp hydride resonance (1H) is observed at -20.7 ppm (t, $J_{\text{HP}} = 12$ Hz), along with two broad hydride resonances at -5.4 and -6.6 ppm (each 1H). Also observed is a broad resonance (2H) at 7.0 ppm. The ³¹P{¹H} NMR spectrum consists of a single resonance at 171.3 ppm. ¹¹B NMR spectroscopy revealed a single broad signal at 13.6 ppm. No signals for N–H protons were observed by ¹H NMR spectroscopy. Complex **3** was also prepared by reaction of **1** in THF with an excess of $\text{BH}_3 \cdot \text{THF}$, which affords complex **3** in good yield. In this reaction, no H_2 is evolved, consistent with formulation of **3** as a BH_3 adduct of **1**. When this preparation was carried out with $\text{BD}_3 \cdot \text{THF}$ and **1**-*d*₂, the resulting sample of **3**-*d*₅ gave a ¹H NMR spectrum lacking the

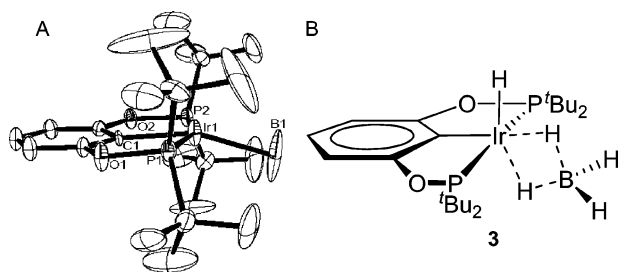


Figure 2. (A) ORTEP diagram for complex **3**, 50% thermal ellipsoids. Hydrogen atoms omitted. (B) Proposed structure of **3**.

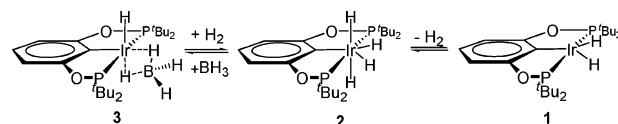
signals at -20.7 , -6.6 , -5.4 , and 7.0 ppm. Complex **3** was also prepared by the reaction of NaBH_4 with $(\text{POCOP})\text{IrHCl}$. Similarly, deuterium-enriched samples of complex **3** were prepared from NaBD_4 . A ^2H NMR spectrum of **3**- d_5 exhibited signals at -20.7 , -6.6 , -5.4 , and 7.0 ppm. The infrared spectrum of **3** exhibits bands at $2466(\text{s})$, $2441(\text{s})$, $2285(\text{s})$, and $2219\text{ cm}^{-1}(\text{m})$ attributed to B–H stretches. A band assigned to the Ir–H stretch is observed at $1930\text{ cm}^{-1}(\text{m})$. All of these data suggest that **3** is best formulated as a bidentate borohydride complex or as a BH_3 adduct of the electron deficient iridium dihydride complex.

The structure of complex **3** was determined by single-crystal X-ray diffraction, which confirmed that B–N bond cleavage had indeed occurred (Figure 2A). The POCOP ligand to metal interactions closely resemble the bond distances and angles reported previously for this ligand.¹⁵ A boron atom is coordinated to the metal center with an Ir–B bond distance of $2.185(9)\text{ \AA}$. This is somewhat longer than Ir–B bond lengths in other iridium boryl species, which are typically between 2.023 and 2.093 \AA ,^{16–18} but is very similar to the value of $2.214(4)\text{ \AA}$ reported for a dimeric Ir borohydride complex.¹⁹

Although the hydrogen atoms attached to boron and iridium could not be reliably located in the X-ray structure, ^1H NMR data for **3** indicate a low-symmetry structure. A structure such as the one depicted in Figure 2B is consistent with the NMR and IR data. However, the data do not distinguish between a bidentate borohydride complex and a σ complex of BH_3 , or a structure in between these two extremes where an Ir–H donates some electron density to the electron deficient boron atom.²⁰

A recent report by Manners and co-workers indicated that the presence of excess BH_3 poisoned their colloidal Rh catalyst, leading to complete inhibition of the dehydrocoupling reaction of Me_2NHBH_3 .²¹ This result prompted us to investigate the catalytic activity of **3** with respect to H_3NBH_3 dehydrogenation. Negligible reactivity was observed between **3** and H_3NBH_3 . In independent experiments we determined that **3** in THF reacts with hydrogen gas (30 psi) to regenerate the catalytically active tetrahydride species, **2**, along with $\text{BH}_3\cdot\text{THF}$. Degassing this solution of **2** produces **1**.

In summary, the iridium pincer complex **1** catalyzes the efficient release of hydrogen chemically stored in H_3NBH_3 at unprecedented rates under mild conditions. Although a dormant form of the catalyst is produced over time, the active species can be efficiently



regenerated in the presence of hydrogen. The dormant form of the catalyst apparently results from a novel reaction of BH_3 with an Ir hydride. The impressive rates and clean catalyst regeneration observed in this Ir pincer system under H_2 pressure represent a promising initial step toward the development of ammonia borane as a viable on-board hydrogen-storage medium.

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Supporting Information Available: Experimental details, including details of X-ray data collection; crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. The crystallographic data for **3** have been deposited (CCDC297267).

References

- Coontz, R.; Hanson, B. *Science* **2004**, *305*, 957.
- Crabtree, G. W.; Dresselhaus, M. S.; Buchanan, M. V. *Phys. Today* **2004**, *39*.
- U.S. DOE, "Hydrogen, Fuel Cells & Infrastructure Technologies Program" (<http://www.eere.energy.gov/hydrogenandfuelcells/storage>).
- The American Physical Society, "The Hydrogen Initiative" (http://www.aps.org/public_affairs/index.cfm).
- U.S. DOE, "Basic Research Needs for the Hydrogen Economy" (http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf).
- Dixon, D. A.; Gutowski, M. J. *Phys. Chem. A* **2005**, *109*, 5129.
- Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424.
- Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776.
- Chen, Y.; Fulton, J. L.; Linehan, J. C.; Autrey, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 3254.
- Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **1999**, 2443. Morales-Morales, D.; Redon, R.; Yung, C.; Jensen, C. M. *Inorg. Chim. Acta* **2004**, *357*, 2953.
- Krogh-Jespersen, K.; Czerw, M.; Summa, N.; Renkema, K. B.; Achord, P. D.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 11404.
- Göttker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804.
- Gervais, C.; Babonneau, F. *J. Organomet. Chem.* **2002**, *657*, 75.
- Böddeker, K. W.; Shore, S. G.; Bunting, R. K. *J. Am. Chem. Soc.* **1966**, *88*, 4396.
- Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766.
- 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.
- Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008.
- Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Can. J. Chem.* **1993**, *71*, 930.
- Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508.
- Lachaize, S.; Essalah, K.; Montiel-Palma, V.; Vendier, L.; Chaudret, B.; Barthelot, J.-C.; Sabo-Etienne, S. *Organometallics* **2005**, *24*, 2935.
- Jaska, C. A.; Clark, T. J.; Clendenning, S. B.; Grozea, D.; Turak, A.; Lu, Z.-H.; Manners, I. *J. Am. Chem. Soc.* **2005**, *127*, 5116.

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