

Bis-BN Cyclohexane: A Remarkably Kinetically Stable Chemical Hydrogen Storage Material

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Supporting Information

ABSTRACT: A critical component for the successful development of fuel cell applications is hydrogen storage. For back-up power applications, where long storage periods under extreme temperatures are expected, the thermal stability of the storage material is particularly important. Here, we describe the development of an unusually kinetically stable chemical hydrogen storage material with a H₂ storage capacity of 4.7 wt%. The compound, which is the first reported parental BN isostere of cyclohexane featuring two BN units, is thermally stable up to 150 °C both in solution and as a neat material. Yet, it can be activated to rapidly desorb H₂ at room temperature in the presence of a catalyst without releasing other detectable volatile contaminants. We also disclose the isolation and characterization of two cage compounds with S₄ symmetry from the H₂ desorption reactions.

Hydrogen is currently being investigated as a potential energy carrier, with the principal drivers being (1) petroleum independence, i.e., hydrogen can be produced from a variety of non-petroleum-based sources, and (2) relatively high energy conversion efficiencies, i.e., H₂ can be efficiently converted to electrical energy and motive power using fuel cells.^{1–4} For example, a well-to-wheels analysis of various vehicular technologies indicated that proton exchange membrane (PEM, also referred to as polymer electrolyte membrane) fuel cell electrical vehicles can compare favorably to other vehicular technologies including battery electric, plug-in hybrid electric, hybrid electric, and conventional internal combustion vehicles in terms of CO₂ emission and petroleum energy usage.^{5,6} In addition to vehicular applications,^{7–9} potential early market applications for fuel cell power are being explored.¹⁰ In an analysis by Battelle,¹¹ back-up power (e.g., for telecommunications towers) has been identified among others as a potentially attractive market segment for PEM fuel cells.¹² The current technology in this area relies on lead-acid batteries and generators. Compared to those, fuel cells can potentially offer advantages with regard to run times, maintenance costs, and durability over a wider range of temperatures.

A critical component for the successful development of fuel cell applications is hydrogen storage.¹³ Important parameters

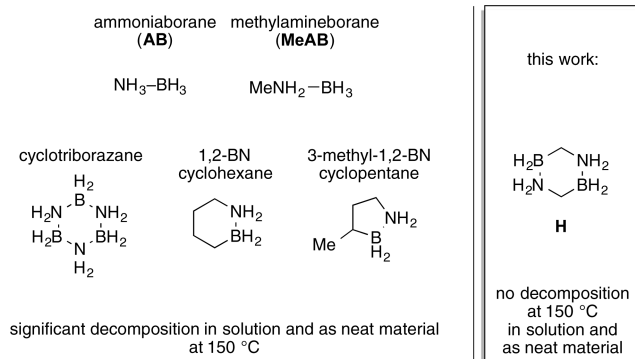


Figure 1. Thermal stability of amine-borane-based chemical hydrogen storage materials.

that need to be considered include storage capacity, cost, durability/operability, discharging rates, and fuel purity.¹⁴ For back-up power applications, where long storage periods under extreme temperatures are expected, thermal stability of the storage material is particularly important. On the other hand, fast and consistent hydrogen desorption without external energy input is also expected when back-up power is needed during power outages. A kinetically stable hydrogen storage material that can readily release hydrogen in the presence of a catalyst could meet those requirements.

Compressed hydrogen gas is the current state-of-the-art¹⁵ for vehicular and stationary applications, but it requires high pressures and/or cryogenic temperatures. To increase the storage density and mitigate the risks of dealing with compressed gas, numerous condensed-phase hydrogen storage approaches including metal hydrides,¹⁶ sorbent materials,¹⁷ and chemical hydrogen storage systems^{18,19} are currently under investigation. Amine-borane-based chemical hydrogen storage materials feature relatively high gravimetric storage capacities and facile H₂ desorption kinetics.²⁰ However, these materials typically are not stable at high temperatures. For instance, a significant rate of decomposition at temperatures equal to or below 150 °C is observed for ammonia borane (AB),^{21–23} various amine-boranes,²⁴ and the cyclic compounds cyclo-

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triborazane,^{25,26} 1,2-BN-cyclohexane,²⁷ and 3-methyl-1,2-BN-cyclopentane²⁸ (Figure 1).

We describe in this Communication the discovery of an unusually kinetically stable chemical hydrogen storage material (compound **H**, Figure 1) with a H₂ storage capacity of 4.7 wt%. Compound **H** is thermally stable up to 150 °C both in solution and as a neat material. Yet, it can be activated to rapidly desorb H₂ at room temperature in the presence of a catalyst without releasing other detectable volatile contaminants.

The Liu laboratory has been focusing on the development of BN isosteres of classic organic molecules^{27–31} to expand the chemical space of existing compounds for potential applications in biomedical research and materials science.³² In 2011, we reported the synthesis of 1,2-BN cyclohexane²⁷ and demonstrated that it readily and cleanly releases 2 equiv of hydrogen to form a trimer. In order to increase the storage capacity of 1,2-BN cyclohexane, we embarked on the synthesis of a bis-BN cyclohexane **H**. As can be seen from Figure 2, the synthesis of

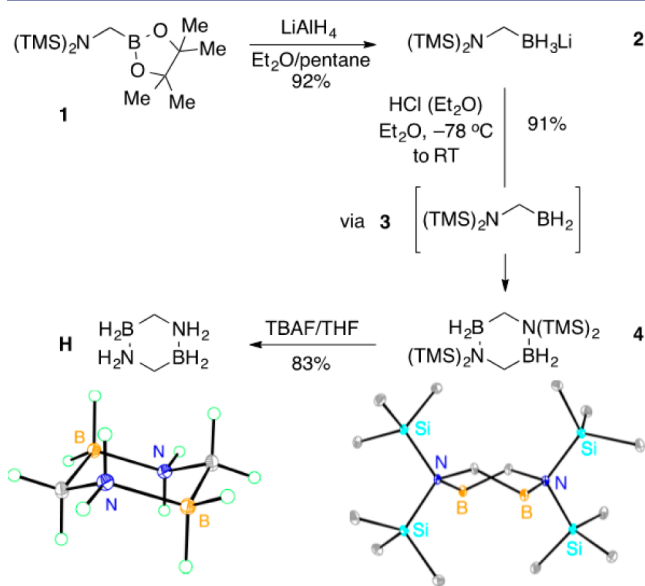


Figure 2. Synthesis of compound **H**.

compound **H** can be accomplished in three steps from the known aminomethylene boronate ester **1**.³³ Reduction of compound **1** with LiAlH₄ generates the lithium borohydride intermediate **2** in high yield. Subsequent treatment of **2** with one equivalent of anhydrous HCl produces the bis-(trimethylsilyl)aminomethyl borane **3**, which spontaneously dimerizes to form 1,1,4,4-tetra(trimethylsilyl)-1,4-diazonia-2,5-diboratacyclohexane **4** in 91% yield from **2**. The structure of **4** was unambiguously confirmed by single-crystal X-ray diffraction analysis, which shows a twist boat conformation as the ground state in the solid state (Figure 2). Removal of the trimethylsilyl groups in **4** was achieved with tetrabutylammonium fluoride, furnishing the target compound **H** in 69% overall yield from **1**. The identity of compound **H** was also unambiguously confirmed by its single-crystal X-ray structure, which shows a chair conformation that is also adopted by cyclohexane. To the best of our knowledge, compound **H** represents the first reported parental BN isostere of cyclohexane featuring two BN units.

Compound **H** is a crystalline solid that sublimates without decomposition at temperatures higher than 150 °C. As a comparison, 1,2-BN cyclohexane has a melting point of 75–77

°C, and the all-carbon cyclohexane melts between 4 and 7 °C. Cyclotriborazane sublimates at around 157 °C with decomposition.²⁶ ¹¹B and ¹H NMR analysis indicated that compound **H** does not decompose when kept on the bench for more than 18 months under ambient conditions. No noticeable change was brought about when **H** is heated in toluene at 150 °C in a sealed tube for 24 h. Under the same conditions, more than 50% of 1,2-BN cyclohexane decomposed, and AB, MeAB, and 3-methyl-1,2-BN-cyclopentane completely decomposed within 2 h (see Supporting Information). Similarly, it is reported that cyclotriborazane readily decomposes in solution at temperatures above 100 °C.²⁶

We also performed the thermal stability study of solid **H** by thermogravimetric analysis (TGA) accompanied by differential scanning calorimetry (DSC) experiment (Figure 3). At a

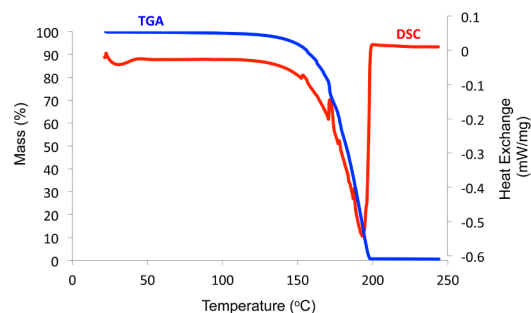


Figure 3. TGA (blue)/DSC (red) data of neat compound **H**.

heating rate of 1 °C/min, compound **H** undergoes an endothermic sublimation process in the range between 150 and 200 °C that is accompanied by total loss of weight. ¹¹B and ¹H NMR analysis indicated no decomposition during the sublimation process.

We then investigated the H₂ release of compound **H** under a variety of conditions. In view of the high thermal stability exhibited by **H**, we surmised that H₂ desorption will have to be mediated by an appropriate catalyst. We recently showed that simple base metal salts such as FeCl₂ and CoCl₂ are very efficient catalyst precursors for the dehydrogenation of 3-methyl-1,2-BN-cyclopentane.²⁸ However, these catalysts were ineffective in the dehydrogenation of compound **H**. When heated in the presence of CoCl₂ (10 mol%), compound **H** showed less than 20% conversion at 90 °C in THF for over 1.5 h. Similarly, no noticeable change was detected when FeCl₂ (10 mol%) was used under the same conditions (see Supporting Information). After a brief screening of catalysts, we determined that Pd/C was suitable in mediating the dehydrogenation process;³⁴ however, high temperatures (up to 150 °C) were necessary to achieve high conversion (see Supporting Information). Gratifyingly, the ruthenium complex previously used by Fagnou and co-workers³⁵ for the dehydrogenation of AB proved effective for the dehydrogenation of **H**. As can be seen from Figure 4, desorption of 2 equiv of H₂ from compound **H** (i.e., 4.7 wt% H₂) can be accomplished with 5 mol% [Ru] at room temperature in about 15 min. At 0.5 mol% catalyst loading, the release of 2 equiv of H₂ can be achieved in the same time frame at 65 °C. To probe the purity of the released H₂ gas, we performed residual gas analysis (RGA) of compound **H** in tetraglyme as the solvent using 2 mol% [Ru] catalyst at 65 °C. With the exception of minor tetraglyme background signals, H₂ is the only detectable volatile species (see Supporting Information).

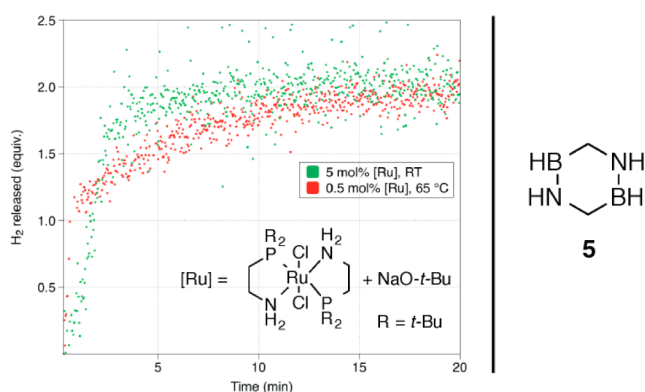


Figure 4. Automated volumetric buret measurements of H₂ release of compound **H** in the presence of the [Ru] catalyst.

In the process of screening various catalytic conditions for the dehydrogenation of **H**, we noticed a difference in the observed ¹¹B NMR spectra when using Pd/C or the [Ru] as the catalyst. While a doublet at 40.6 ppm (assigned to the BH of compound **5** (Figure 4, right)) was observed in the Pd/C-catalyzed dehydrogenation, the same signal was not found in [Ru]-catalyzed system. To further understand the details, we tried to optimize the reaction conditions to isolate and characterize the dehydrogenation products from the two catalytic systems. While some as of yet unidentified polymeric species^{36–38} were formed from both of the systems, we were able to intercept two distinct cage compounds in moderate to good yields from each of the reactions, respectively. When Pd/C was selected as the dehydrogenation catalyst, the resulting cage compound **6**, consisting of four six- and two four-membered rings, was produced as the only non-polymeric product presumably by the dimerization of two molecules of the non-isolable intermediate **5** (Figure 5, eq 1). In contrast, when [Ru] was employed as the catalyst, cage compound **7**,

consisting of four five- and two six-membered rings, was formed (Figure 5, eq 2). We were able to obtain single-crystal X-ray structures for both of the cage compounds, thus unambiguously confirming their structural assignments (Figure 5). Both cage compounds **6** and **7** belong to the point group *S*₄, which makes the nitrogen, boron, and carbon atoms equivalent in each of the molecules. Both of the cage compounds are air and moisture stable, and they can be purified by silica gel chromatography. Compound **7** does not convert to compound **6** when heated in toluene at 150 °C, with or without Pd/C. Similarly, cage compound **6** does not convert to **7** when subjected to the reaction conditions shown in Figure 5, eq 2.³⁹ The lack of interconversion between **6** and **7** suggests that their formation is kinetically controlled. G3MP2^{40–44} gas-phase calculations show that the formation of the six-four cage **6** from **H** is exergonic by –56.0 kcal/mol (Figure 5, eq 3), whereas the analogous reaction to form the six-five cage **7** is exergonic by –64.3 kcal/mol (Figure 5, eq 4). Thus, the six-five cage **7** is thermodynamically more stable than the six-four cage isomer **6** by 8 kcal/mol. It is worth noting that the higher temperature employed in eq 1 (Figure 5), which would seemingly favor the thermodynamic product, is actually producing the less thermodynamically stable cage isomer **6**.

In conclusion, we have developed the synthesis of compound **H**, which is the first parental BN isostere of cyclohexane featuring two BN units. Bis-BN cyclohexane **H** is a remarkably kinetically stable amine-borane, withstanding temperatures up to 150 °C both as a neat material and in solution. Yet, it can be activated to release 4.7 wt% of analytically pure H₂ at room temperature in 15 min in the presence of a catalyst. We have also intercepted and structurally characterized two cage compounds that might give insight into the possible structures of polymeric materials that were also formed during the H₂ desorption process. The kinetic stability exhibited by compound **H** and the ability to readily release its stored H₂ content upon exposure to a catalyst would make it a potentially suitable candidate for stationary fuel cell applications.

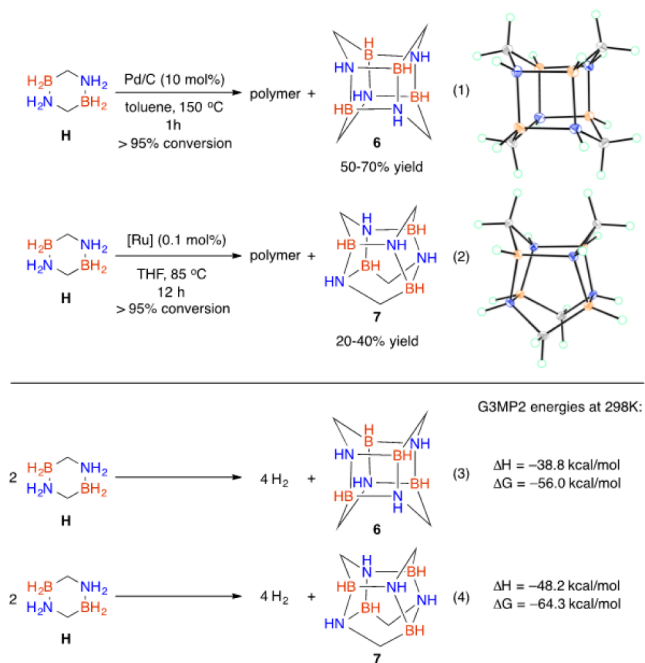


Figure 5. Isolation and characterization of cage compounds **6** and **7** and predicted energies for their formation.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures, spectroscopic data, additional computational details, complete ref 44, and crystallographic information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED IN PROOF

Sterically encumbered derivatives of compound **3** are predicted to behave like frustrated Lewis pairs.⁴⁵