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Hydrogen Storage

Calcium Amidotrihydroborate: A Hydrogen Storage Material[**]

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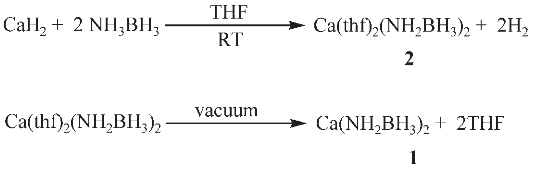
The promise of the hydrogen economy, while great, will only be realized when many major scientific challenges are overcome. One of primary challenges is the need to find a safe and economic method for storing and transporting H_2. Conventional storage systems include classical high-pressure tanks, insulated liquid-hydrogen systems, and storage in hydrocarbons.[1] Chemical methods, such as the use of metal hydrides (for example, MgH_2),[2] imides (such as $LiNH_2$),[3] organic frameworks (Zn_4O(1,4-benzenedicarboxylate)),[4,5] alkali-metal tetrahydroboride (such as $LiBH_4$),[6] alanates (for example, $NaAlH_4$),[7] and chemical hydrides all show promise. There are several advantages of chemical H_2 storage over compressed H_2; an important advantage is that the H_2 density available in chemical systems significantly outweighs even liquid H_2.

Among the potential candidates for effective chemical H_2 storage, ammonia–borane (NH_3BH_3) has garnered much interest owing to its ideal combination of low molecular weight and high H_2 storage capacity of 19.6 weight %, which exceeds the current capacity of gasoline.[8–15] The chemical nature of the NH_3BH_3 molecule, with both hydridic and protic hydrogen atoms in close proximity, provides a unique environment for the release of H_2. Ultimately, NH_3BH_3 can be dehydrogenated completely, forming ceramic BN, but only at temperatures in excess of 500 °C.[15–19] Recently, catalytic hydrogen release from NH_3BH_3 has also achieved significant attention.[11,20–23]

Herein we report a derivative of NH_3BH_3, $Ca(NH_2BH_3)_2$ (**1**), in which a new covalent bond between the nitrogen atom of NH_3BH_3 and calcium has been formed. Compound **1** has thermal properties that differ significantly from solid NH_3BH_3, and undergoes loss of H_2 without significant foaming, which is a common problem with NH_3BH_3. The H_2 loss from **1** is also not as exothermic as in ammonia–borane, and the steady release of H_2 in the solid state is spread over much wider temperature and time ranges (see Supporting Information).

The reaction of NH_3BH_3 with calcium hydride in THF leads to calcium amidotrihydroborate as the bis(thf) adduct (**2**) in excellent yield (Scheme 1). Compound **2** loses THF once it is removed from solution, giving **1**. In most samples of **1**, small amounts of THF are still detected, yet the amounts present are well below stoichiometric ratios. Calcium amidotrihydroborate is relatively stable in air, with no observable decomposition over two days in the solid state or in solution.



$$CaH_2 + 2\,NH_3BH_3 \xrightarrow[RT]{THF} Ca(thf)_2(NH_2BH_3)_2 + 2H_2$$

2

$$Ca(thf)_2(NH_2BH_3)_2 \xrightarrow{vacuum} Ca(NH_2BH_3)_2 + 2THF$$

1

Scheme 1. Synthesis of **1** from calcium hydride and ammonia–borane.

The boron chemical shift in NH_3BH_3, **1**, and **2** are effectively identical in the ^{11}B NMR spectrum, with the only difference being the B–H coupling constants ($^1J_{BH} = 93.0$ Hz for NH_3BH_3 and $^1J_{BH} = 86.0$ Hz for **1**). The characteristic differences between **1** and **2** are observed in the ^1H NMR spectrum. Two signals are observed for **1** in [D$_8$]THF, namely a quartet at $\delta = 1.39$ ppm and a broad singlet at $\delta = -0.64$ ppm, corresponding to BH_3 and NH_2 protons, respectively. On the other hand, the ^1H NMR of **2** in C_6D_6 shows two multiplets, at $\delta = 3.58$ ppm and 1.38 ppm, indicating the presence of thf ligands, in addition to two broad peaks corresponding to the BH_3 and NH_2 protons (at about $\delta = 1.22$ ppm and 0.88 ppm, respectively).

In the single-crystal X-ray analysis (Figure 1) of the crystals obtained from a THF/hexane mixture containing **1**, two thf ligands coordinate to each $Ca(NH_2BH_3)_2$ molecule, forming **2**. Intermolecular interactions of 2.368 Å are observed between the Ca^{II} ion and hydridic hydrogens of BH_3. This gives rise to an extended structure with a chain-like arrangement in the solid state structure of **2**.

The thermal properties of **1** are of primary importance if it is to be useful as a H_2 storage material. The thermal gravimetric analysis (TGA) of **1** shows several weight-loss events (Figure 2). The initial loss, which begins at 70 °C, is attributed to THF. This loss was also observed at this temperature by mass spectrometry (MS). The amount of THF that remains in **1** varies depending on the surface area of the sample. Elemental analysis of a typical sample of **1**, dried

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Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

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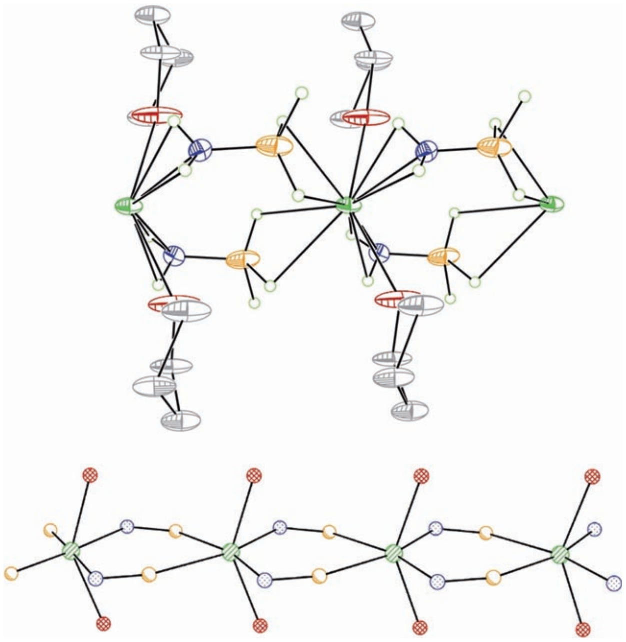

Figure 1. X-ray crystal structure of **2**, with thermal ellipsoids set at 35 % probability, and hydrogen atoms attached to thf carbon atoms omitted for clarity. A section of the chain (top) showing interactions involving the hydrogen atoms from the NH_2BH_3 unit, and (bottom) the full chain with hydrogen and carbon atoms omitted for clarity. B yellow, Ca green, O red, N blue, C gray, H small green open circles. Selected distances (Å): Ca(1)⋯Ca(1a) = 3.147(6), Ca(1)-B(1) = 2.349(12), Ca(1)-B(1a) = 2.829(13), Ca(1)-N(1) = 2.069(7), Ca(1)-N(1b) = 2.362(7), Ca(1)-O(1) = 2.438(4). Symmetry operations: a: $-x+1, -y, -z+1$; b: $-x+1, -y, -z$.

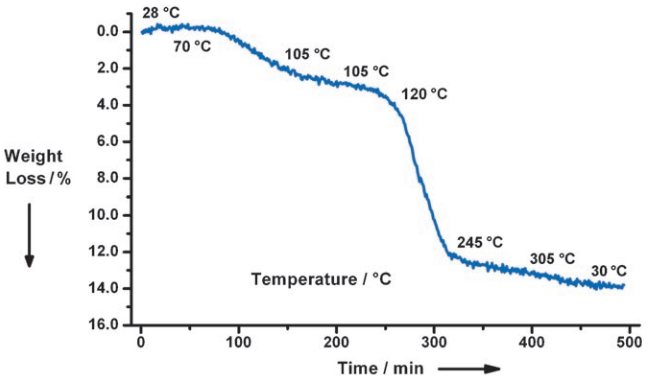

Figure 2. Thermogravimetric analysis of **1**; initial loss of THF begins at 70 °C. THF loss is also accompanied by a small release of H_2 before the major hydrogen release begins at 120 °C.

under a stream of argon, shows less than 10 % THF remaining. Upon heating to 120 °C, the onset of the most significant mass loss is observed. Analysis of the mass loss was carried out by mass spectrometry, and hydrogen was quantified below 170 °C by calibrated gas chromatography (GC; Figure 3). The majority of the mass loss is hydrogen gas. Small amounts of ammonia and borazine can be detected, but these contribute to less than 0.1 % of the weight change below

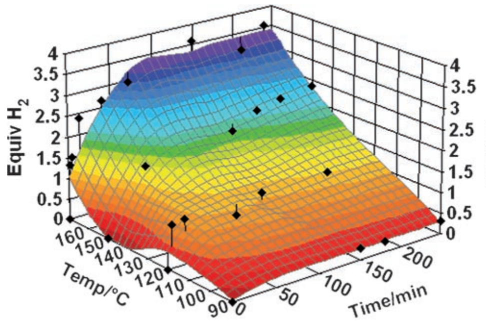

Figure 3. Thermal hydrogen-release profile for **1**. The colored surface is fitted to the black data points.

170 °C. A small amount of hydrogen release (< 0.3 equivalents of H_2) is observed at 90 °C. However, prolonged heating at 90 °C does not result in further release of hydrogen or any other detectible mass loss (for thermal gravimetric analysis and differential scanning calorimetry results, see the Supporting Information). GC experiments indicate that 1.1 equivalents of H_2 can be released from **1** at 120 °C, 2.4 equivalents at 150 °C, and (3.6 ± 0.2) equivalents at 170 °C. This is a 90 % yield at 170 °C based upon the four equivalents of H_2 expected from the combination of four protic ($-NH_2-$) and four of the six hydridic ($-BH_3$) hydrogen atoms, and corresponds to a gravimetric concentration of 7.2 weight % H_2. Both the rate and volume of H_2 release for **1** varies with temperature, which is in contrast to solid NH_3BH_3, where any temperature above 120 °C results in the release of about two equivalents of H_2. This is presumably a consequence of the endothermic hydrogen release from **1**, which was estimated to have an enthalpy of 3.5 kJ mol^{-1} after accounting for the overlapping THF endotherm in the DSC trace (Supporting Information). Hydrogen release from NH_3BH_3 is exothermic with an enthalpy of -22.5 kJ mol^{-1} for the release of the first equivalent of H_2.[17,18]

After about four equivalents of hydrogen are released from **1** by the facile combination of the boron hydrogen atoms and ammonia hydrogen atoms, the remaining hydrogen atoms in the residue ascribed to be $Ca(NBH)_2$ must be lost in an alternative mechanism at higher temperatures. As the sample is heated to from 170–245 °C, more hydrogen release is observed by mass spectrometry. Elemental analysis of the residue that remained after heating **1** to 170 °C indicates an elemental composition of $CaN_2B_2H_2C_{0.2}$. Elemental analysis of samples heated to greater than 245 °C show steady loss of nitrogen. Unfortunately, the residue that is formed as **1** is heated is amorphous and X-ray data cannot be obtained. Further studies on the high temperature decomposition of the residue formed after hydrogen release from **1** are underway.

In summary, we have described a straightforward route to obtain the calcium derivative of ammonia borane, which possesses different thermal properties that ammonia–borane and has a lower propensity for borazine release. As a potential hydrogen storage material, **1** offers some advantages in that the thermal hydrogen release does not suffer from the induction period present in ammonia–borane.

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Experimental Section

1: Ammonia–borane (0.20 g, 6.48 mmol) was dissolved in tetrahydrofuran (30.0 mL). This mixture was slowly added to a suspension of calcium hydride (0.14 g, 3.24 mmol) in tetrahydrofuran (20.0 mL) and allowed to stir overnight. The solvents were removed under vacuum to obtain the white solid product, $Ca(NH_2BH_3)_2$ (0.31 g). X-ray quality crystals of the THF adduct **2** were obtained from a THF/hexane solution of **2** at −22 °C. Compound **1** was obtained by vacuum-drying **2** overnight at room temperature. Yield of **1**: 96 %; m.p.: 98–100 °C (dec); ^{1}H NMR (300.13 MHz, [D$_8$]THF, 22 °C, TMS): $\delta = 1.39$ (q, ^1J(H,B) = 86.0 Hz, 3H, BH_3), −0.64 ppm (br.s, 2H, NH_2); ^{11}B NMR (96.29 MHz, [D$_8$]THF, 22 °C): $\delta = -23.62$ ppm (q, ^1J(B,H) = 86.0 Hz, BH$_3$); IR (neat): $\tilde{\nu} = 2977.7$ & 2879.6 (N-H), 2196.7 & 2146.2 (B-H), 1533.0, 1459.8, 1260.6, 1168.1, 1041.8, 1010.5, 917.2, 884.6, 816.5, 671.9, 607.7, 597.0 cm^{-1}.

Compound **1** was weighed into glass vials in an argon-filled glove box and crimp sealed. The vials were heated isothermally in a stainless steel reactor vessel preheated to set temperatures for set durations of time. After quenching the reaction by cooling to 0 °C, the gaseous contents were analyzed by GC at 35 °C. Calibration curves were constructed using the ratio of the areas of Ar and H_2 peaks in the chromatograph of standards having a known concentration. Percentage conversion of **1** to H_2, and consequently the number of equivalents of H_2 released, were calculated from these calibration curves. No other gaseous species were detected by GC in the quenched samples. TGA of **1** was carried out in N_2. The temperature range for TGA was 30–305 °C at a ramp rate of 0.5–1 °C min^{-1}. Mass spectrometry (MS) of was carried out using a Pfeiffer quadrupole spectrometer. The heated stainless steel capillary inlet was positioned in a stream of argon flowing across the sample, which was heated at 1 °C min^{-1}.

Crystal Data for **2**: $C_8H_{26}B_2CaN_2O_2$, $M_r = 244.01$, orthorhombic, $a = 7.910(2)$, $b = 17.570(4)$, $c = 4.6700(9)$ Å, $V = 649.0(2)$ Å^3, $T = 120$ K, space group $Pnnm$ (No. 58), $Z = 2$, $\rho_{\text{calcd}} = 1.249$ g cm^{-3}, $\mu(\text{Mo}_{K\alpha}) = 0.47$ mm^{-1}, 4461 reflections measured ($2\theta_{\max} = 50.0°$), and 681 unique ($R_{\text{int.}} = 0.0889$). The final residuals were $R(I > 2\sigma$; all data) = 0.0906; 0.1161, and $wR(I > 2\sigma$; all data) = 0.2729; 0.2835, with residual electron density = 0.484 e Å^{-3}. The data were collected on a Bruker D8, with APEX II CCD detector using ω scans. The structure was solved using Direct Methods (SHELXS-97), and refined on F^2 (SHELXL-97). The chain structure was disordered over two positions, and each atom was refined at one-half normal occupancy. The hydrogen atom positions were found on the difference map, and refined with fixed isotropic temperature factors (0.10 Å^2). The amine hydrogen atom positions were restrained. All non-hydrogen atoms were refined anisotropically. CCDC-646993 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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