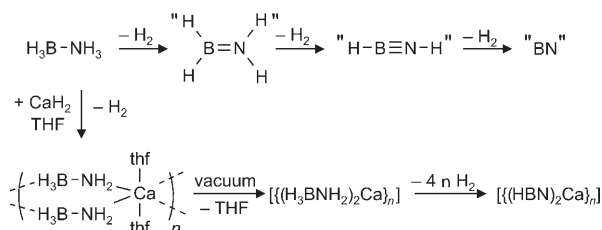


# Calcium Amidoborane Hydrogen Storage Materials: Crystal Structures of Decomposition Products\*\*

Jan Spielmann, Georg Jansen, Heinz Bandmann, and Sjoerd Harder\*

Dedicated to Professor Heinrich Nöth on the occasion of his 80th birthday

The safe and convenient storage of molecular hydrogen is a crucial target in the transition to a hydrogen-based energy economy.<sup>[1]</sup> Among the many different approaches to achieve this end,<sup>[2]</sup> one is that of chemical storage in ammonia–borane (NH<sub>3</sub>BH<sub>3</sub>).<sup>[3]</sup> This small molecule, with nearly 20 weight % hydrogen content, displays a hydrogen density easily exceeding that of liquid hydrogen. Ammonia–borane eliminates hydrogen by combining protic and hydridic hydrogen atoms, finally culminating in formation of ceramic boron nitride (BN) (Scheme 1).



**Scheme 1.** Dehydrogenation of ammonia–borane and the calcium amidoborane complex  $[\{\text{Ca}(\text{NH}_2\text{BH}_3)_2(\text{thf})_2\}_n]$ .

This process, which is only partially understood, is the subject of extensive theoretical<sup>[4]</sup> as well as thermodynamic<sup>[5]</sup> considerations. Whereas thermal dehydrogenation typically produces a myriad of intermediates, transition-metal-catalyzed reactions tend to be more selective.<sup>[6]</sup>

Recently several amidoborane complexes of early main group metals have been introduced as convenient high-capacity hydrogen-storage materials: LiNH<sub>2</sub>BH<sub>3</sub>, NaNH<sub>2</sub>BH<sub>3</sub>, and Ca(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub>.<sup>[7]</sup> These salt-like compounds show a number of advantages over neutral NH<sub>3</sub>BH<sub>3</sub>: 1) lower hydrogen release temperatures have been measured (90 °C for the lithium and sodium complexes and 120–170 °C for the calcium complex), 2) the hydrogen released is not contami-

nated with undesirable borazine by-products, 3) there is no induction period and also foaming, generally a serious problem, is not observed, and 4) the dehydrogenation process for the amidoborane complexes is much less exothermic (3–5 kJ mol<sup>-1</sup>)<sup>[7]</sup> than that for NH<sub>3</sub>BH<sub>3</sub> (22.5 kJ mol<sup>-1</sup>).<sup>[5b,c]</sup> The last point greatly facilitates the search for suitable regeneration routes, a prerequisite for a hydrogen storage material.

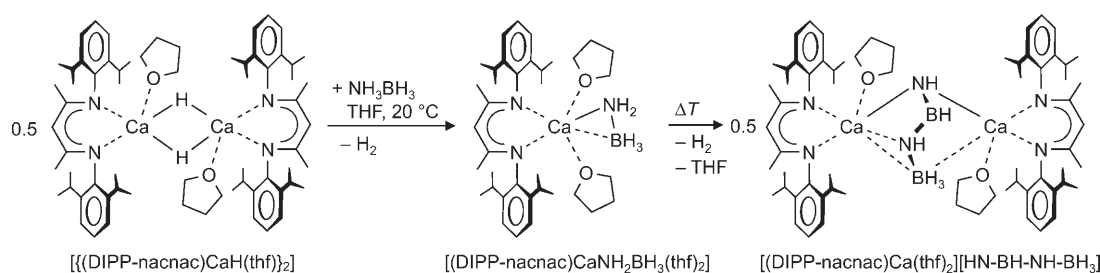
Group 1 and Group 2 metal–amidoborane complexes are easily accessible. For example, the calcium complex has been prepared by reaction of NH<sub>3</sub>BH<sub>3</sub> with CaH<sub>2</sub> in THF (Scheme 1).<sup>[7]</sup> Crystallization gave a coordination polymer,  $[\{\text{Ca}(\text{NH}_2\text{BH}_3)_2(\text{thf})_2\}_n]$ , which lost coordinated THF under vacuum. Whereas the precursor is well-defined, the decomposition product after hydrogen release has only been characterized by elemental analysis, as CaN<sub>2</sub>B<sub>2</sub>H<sub>2</sub>C<sub>0.2</sub>.<sup>[7a]</sup> The final product could be formally regarded as a  $\{\text{Ca}(\text{NBH}_2)_2\}$  complex, contaminated with some calcium carbide. Lack of crystallinity impedes structural analysis and only leaves room for speculation. For example, a polymeric network containing three-fold deprotonated borazine, Ca<sub>3</sub>[(BH)<sub>3</sub>N<sub>3</sub><sup>3-</sup>]<sub>2</sub>, could have been formed.<sup>[8]</sup> This hypothesis would explain the absence of borazine in the hydrogen released.

As difficulties in the characterization of intermediates and products are a general problem in solid state chemistry, we decided to investigate this intriguing reaction under homogeneous conditions. The hydrocarbon-soluble calcium hydride complex  $[\{(\text{DIPP-nacnac})\text{CaH}(\text{thf})_2\}_n]$  (Scheme 2)<sup>[9]</sup> allows investigation of calcium hydride reactivity at a molecular level.<sup>[10]</sup> The sterically encumbered β-diketiminato ligand, DIPP-nacnac ((2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC(Me)C(H)C(Me)N(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)), is essential for the stability of this heteroleptic complex. It prevents ligand exchange and formation of homoleptic species, such as  $[\text{Ca}(\text{DIPP-nacnac})_2]$  and polymeric, insoluble  $(\text{CaH}_2)_n$ . Reaction of this soluble form of calcium hydride with NH<sub>3</sub>BH<sub>3</sub> in toluene/THF gave clean formation of  $[(\text{DIPP-nacnac})\text{CaNH}_2\text{BH}_3(\text{thf})_2]$ , which crystallized as a monomer (Figure 1a). Use of the bulky DIPP-nacnac ligand seems to effectively prevent formation of coordination polymers with bridging B–N ligands. The side-on coordinated NH<sub>2</sub>BH<sub>3</sub> anion has, in contrast to NH<sub>3</sub>BH<sub>3</sub>,<sup>[11]</sup> an eclipsed conformation. This could be due to the short contact between Ca<sup>2+</sup> and a hydride atom (2.40(2) Å; observed and refined). The Ca–N (2.399(2) Å) and Ca···B contacts (2.867(4) Å) are significantly longer than those in  $[\{\text{Ca}(\text{NH}_2\text{BH}_3)_2(\text{thf})_2\}_n]$  (average values: 2.216(7) and 2.589(12) Å, respectively).<sup>[7a]</sup> This is due either to its side-on coordination mode or to the presence of the bulky DIPP-nacnac ligand.

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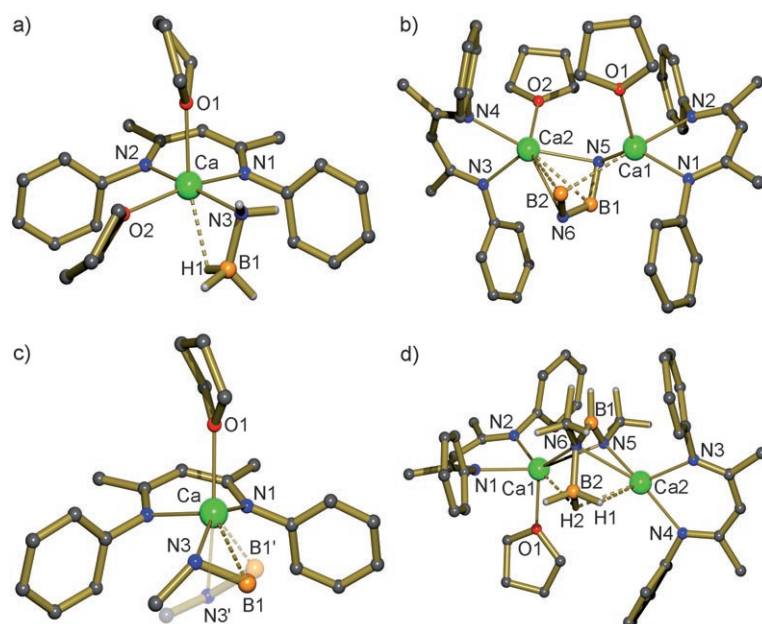
**Scheme 2.** Formation and dehydrogenation of  $[(\text{DIPP-nacnac})\text{CaNH}_2\text{BH}_3(\text{thf})_2]$ .

The amidoborane complex  $[(\text{DIPP-nacnac})\text{CaNH}_2\text{BH}_3(\text{thf})_2]$  easily loses one or more THF ligands. Crystals of the mono-thf complex could be obtained, for which we propose a dimeric structure in which the  $\text{NH}_2\text{BH}_3$  anions bridge adjacent  $\text{Ca}^{2+}$  ions in a similar manner to those in  $[\text{Ca}(\text{NH}_2\text{BH}_3)_2(\text{thf})_2]_n$  (Scheme 1). The presence of THF influences the dehydrogenation process. Dissolved in THF,  $[(\text{DIPP-nacnac})\text{CaNH}_2\text{BH}_3(\text{thf})_2]$  does not eliminate hydro-

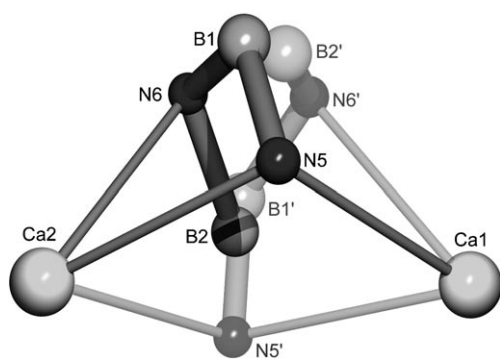
gen and is stable, even under reflux conditions. In a benzene solution, however, elimination of hydrogen starts at temperatures as low as  $20^\circ\text{C}$ . Monitoring by  $^1\text{H}$  and  $^{11}\text{B}$  NMR shows that, at the higher temperature of  $40^\circ\text{C}$ , decomposition is complete within 16 h ( $\text{H}_2$  has been positively detected in the  $^1\text{H}$  NMR spectrum at  $\delta = 4.45$  ppm). This observation suggests that hydrogen elimination from the  $\text{NH}_2\text{BH}_3$  anion is intermolecular (as has been observed for ammonia-boranes).<sup>[3c,d,6a]</sup> Low concentrations of THF allow for loss of THF ligands and dimerization, inducing intermolecular dehydrogenation. Also, the extremely low decomposition temperature in solution hints at an intermolecular process in which reactant mobility is essential.

Crystallization of the dehydrogenation product from hexane gave well-defined colorless single-crystals of a dimeric complex with terminally bound DIPP-nacnac and THF ligands (Figure 1b). The dianionic unit between the  $\text{Ca}^{2+}$  ions is disordered but could best be described as two partially occupied BNB fragments. Free unconstrained refinement of these units gave satisfying displacement factors and  $R$ -values (see Supporting Information for a detailed discussion). The two BNB units in the disorder model (Figure 2) are related to each other through the approximate (non-crystallographic)  $C_2$ -axis that can also be applied to the rest of the dimer. Both BNB units show short contacts between the terminal nitrogen atom (N5) and the  $\text{Ca}^{2+}$  ions ( $2.430(2)$ – $2.589(5)$  Å). The other nitrogen atom in the BNB chain is coordinated to only one of the  $\text{Ca}^{2+}$  ions: N6 to Ca1 ( $2.620(3)$  Å) and N6' to Ca2 ( $2.555(4)$  Å). Contacts between the boron atoms and calcium are somewhat longer (range:  $2.752(12)$ – $2.974(10)$  Å) but similar to that in  $[(\text{DIPP-nacnac})\text{CaNH}_2\text{BH}_3(\text{thf})_2]$ .

As disorder of the central  $[\text{BNBN}]^{2-}$  ion complicates localization of the hydrogen atoms, the nature of the bridging particle is debatable. The pattern in the B–N–B–N bond lengths, a rather long terminal B2–N6 bond ( $1.593(6)$  Å) followed by a short central N6–B1 bond ( $1.451(6)$  Å) and a somewhat shorter B1–N5 terminal bond ( $1.419(5)$  Å), hints to the dianion  $[\text{H}_3\text{B–NH–BH–NH}]^{2-}$ . The long B–N bond length compares well to that in  $\text{H}_3\text{B–NH}_2^-$ , whereas the two



**Figure 1.** a) Crystal structure of  $[(\text{DIPP-nacnac})\text{CaNH}_2\text{BH}_3(\text{thf})_2]$ ; only hydrogen atoms of the BN fragment (located and refined) are shown and *i*Pr groups have been omitted for clarity. Selected bond lengths [Å]: Ca–N1 2.424(2), Ca–N2 2.448(2), Ca–O1 2.378(2), Ca–O2 2.412(2), Ca–N3 2.399(2), Ca...B1 2.867(4), Ca...H1 2.40(2), B1–N3 1.581(4). b) Crystal structure of  $[(\text{DIPP-nacnac})\text{Ca}(\text{thf})_2][\text{HN-BH-NH-BH}_3]$ ; hydrogen atoms on the BNB fragment could not be located owing to disorder and *i*Pr groups have been omitted for clarity (Figure 2). Selected bond lengths [Å]: Ca1–N1 2.392(2), Ca1–N2 2.406(2), Ca1–O1 2.365(2), Ca2–N3 2.379(2), Ca2–N4 2.421(2), Ca2–O2 2.386(2). Bond lengths towards or within the BNB unit are summarized in Figure 3. c) Crystal structure of  $[(\text{DIPP-nacnac})\text{Ca}(\text{MeNHBH}_3)(\text{thf})]$ . *i*Pr groups have been omitted for clarity. The MeNHBH<sub>3</sub> fragment is disordered over two positions (56/44). Selected bond lengths [Å]: Ca–N1 2.352(2), Ca–N2 2.344(2), Ca–O1 2.364(2), average values: Ca–N3 2.382(4), Ca...B1 2.584(7), B1–N3 1.581(8). d) Crystal structure of  $[(\text{DIPP-nacnac})\text{Ca}(\text{thf})_{0.5}]_2[\text{MeN-BH-NMe-BH}_3]$ ; only hydrogen atoms on the BNB fragment (located and refined) are shown and *i*Pr groups have been omitted for clarity. Selected bond lengths [Å]: Ca1–N1 2.392(1), Ca1–N2 2.419(2), Ca1–O1 2.359(1), Ca2–N3 2.350(2), Ca2–N4 2.365(2), Ca1...H2 2.31(2), Ca2...H1 2.25(2), Ca2...H2 2.49(2); bond lengths towards or within the BNB unit are summarized in Figure 3.

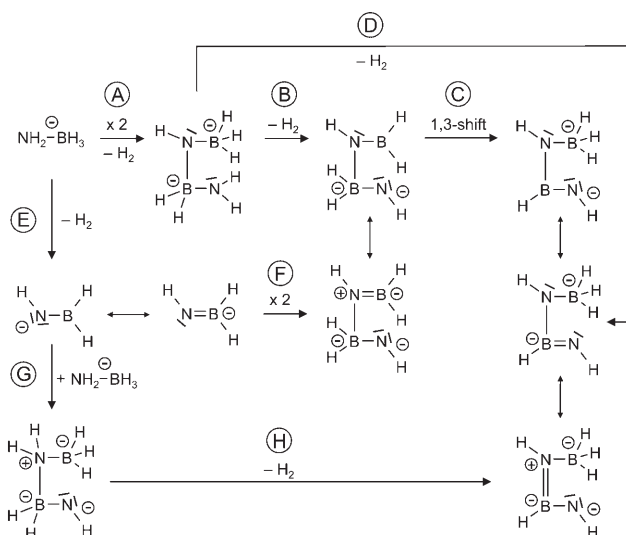


**Figure 2.** Partial structure of  $[(\text{DIPP-nacnac})\text{Ca}(\text{thf})_2][\text{HN-BH-NH-BH}_3]^{2-}$  showing the disorder model for the dianionic BNB unit (ratio 67/33; the fragment with lower site occupation,  $\text{N5}'\text{-B1}'\text{-N6}'\text{-B2}'$  is shown shaded).

shorter bonds are similar to the B–N bond lengths in borazine (1.436(2) Å)<sup>[12a]</sup> or the bora-amidinate anions ( $[\text{RN-BR}'\text{-NR}]^{2-}$ , 1.42–1.48 Å).<sup>[12b–d]</sup> Also the B–N–B (122.3(3)°) and N–B–N (115.7(3)°) angles are similar to those in borazine (122.9(1)° and 117.1(1)°, respectively).

The formation of the dianionic species can be rationalized by the various routes outlined in Scheme 3 ( $\text{Ca}^{2+}$  not shown). The most likely route (see above) is an intermolecular dehydrogenative dimerization (step A) followed by hydrogen elimination (step B). The latter species, with neighboring formal negative charges, converts, by a 1,3-hydride shift (step C), into the proposed product for which several resonance structures can be drawn. The A–B–C route avoids elimination of neighboring hydride and proton functionalities. Alternatively, route A–D circumvents the 1,3-hydride shift. Other possible, but less likely, routes start with intramolecular hydrogen loss from the parent amidoborane  $[\text{H}_2\text{N-BH}_3]^-$  to give  $[\text{HN-BH}_2]^-$  (step E). Hitherto, it is unclear whether the metal cation plays a role in the dehydrogenation step.

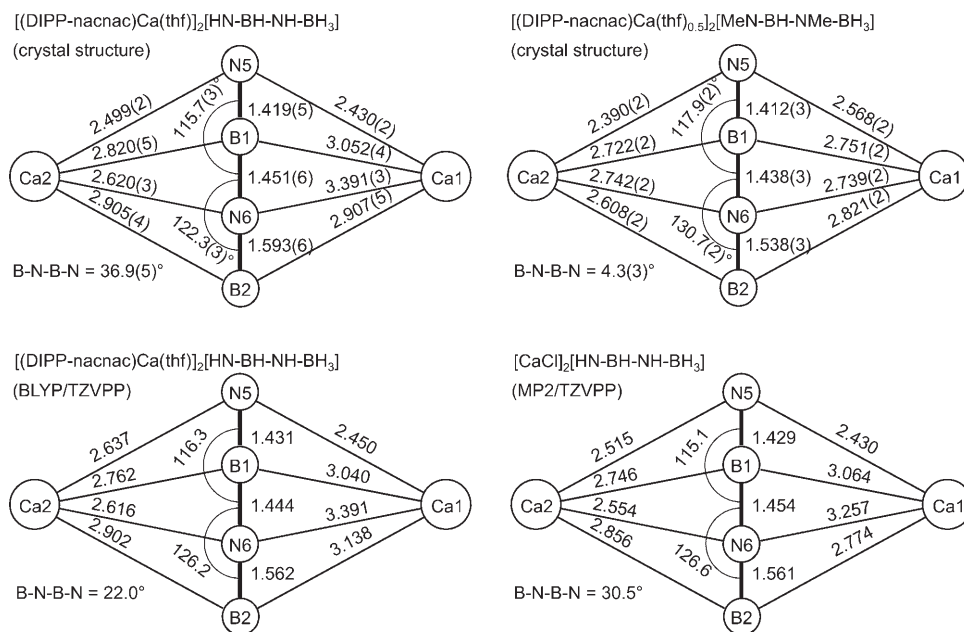
The proposed nature of the bridging species is further enforced by NMR analyses. The  $^{11}\text{B}$  NMR spectrum shows a 1:3:3:1 quartet, indicative for a  $\text{BH}_3$  group ( $\delta = -22.8$  ppm,  $J(\text{B,H}) = 83.3$  Hz). The BH group could not be located in the  $^{11}\text{B}$  NMR spectrum (even under variable temperatures), probably owing to quadrupole broadening. However, the group could be detected in the  $^1\text{H}$  NMR spectrum as a broad signal ( $\delta = 3.74$  ppm) which sharpens upon  $^{11}\text{B}$  decoupling. The  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum shows the  $\text{BH}_3$  group as a doublet, indicative of a neighboring NH



**Scheme 3.** Various proposed routes towards the  $[\text{HN-BH-NH-BH}_3]^{2-}$  ion.

group ( $\delta = 1.09$  ppm,  $J(\text{H,H}) = 4.4$  Hz). Two broadened singlets at  $\delta = 1.70$  ppm and 2.48 ppm are assigned to the NH groups which show weak coupling signals to the  $\text{BH}_3$  and BH units in the 2D  $^1\text{H}\text{-}^1\text{H}$  COSY( $^{11}\text{B}$ ) NMR spectrum (see Supporting Information).

Other evidence for the nature of the bridging BNB dianion comes from theoretical calculations. Optimization of a complete dimeric aggregate with a  $[\text{HN-BH-NH-BH}_3]^{2-}$  ion as the bridging unit reproduces the crystal structure in detail (BLYP/TZVPP, see Supporting Information for details). The calculated geometry of the central  $[\text{HN-BH-NH-BH}_3]^{2-}$  ion is very close to that in the crystal structure (Figure 3). The B...Ca and N–Ca bond lengths and the B–N–



**Figure 3.** Comparison of bond lengths, bond angles and torsion angles between crystal structures (top) and calculated structures (bottom).

B–N torsion angle are somewhat less well reproduced, to be expected on account of their much shallower potential surface. Calculations (MP2/TZVPP) on a model system in which the ligands at Ca have been replaced by  $\text{Cl}^-$ ,  $[\text{CaCl}]_2[\text{HN}-\text{BH}-\text{NH}-\text{BH}_3]$ , show a better fit for the B–N–B–N torsion angle (Figure 3). The alternative isomer,  $[\text{CaCl}]_2[\text{HN}-\text{BH}_2-\text{NH}-\text{BH}_2]$  (resulting from step B in Figure 3), is calculated to be  $28.3 \text{ kcal mol}^{-1}$  higher in energy (MP2/TZVPP + ZPE correction). The B–N–B–N bond pattern in the alternative isomer  $[\text{HN}-\text{BH}_2-\text{NH}-\text{BH}_2]^{2-}$  has two long bonds (HN–BH<sub>2</sub> 1.547 Å, BH<sub>2</sub>–NH 1.621 Å) and one short bond (NH–BH<sub>2</sub> 1.397 Å). This pattern does not fit the crystal structure.

Natural bond orbital analysis (BLYP/TZVPP) shows a high negative charge of  $-1.87$  at the central  $[\text{HN}-\text{BH}-\text{NH}-\text{BH}_3]^{2-}$  unit indicative of ionic bonding to both  $\text{Ca}^{2+}$  ions. NBO also supports  $[\text{HN}=\text{BH}-\text{NH}-\text{BH}_3]^{2-}$  as the dominant Lewis structure with following group charges: terminal NH  $-1.07$ , BH  $+0.44$ , internal NH  $-0.70$  and BH<sub>3</sub>  $-0.53$ . On account of the electronegativity difference between N and B, actual charges differ substantially from formal charges.

Most convincing proof for the bridging  $[\text{HN}-\text{BH}-\text{NH}-\text{BH}_3]^{2-}$  ion has been obtained by repeating the experiments above with the closely related N-methylated ammonia-borane:  $\text{MeNH}_2\text{BH}_2$ . By analogy, the methylated amidoborane  $[(\text{DIPP-nacnac})\text{Ca}(\text{MeNHBH}_3)(\text{thf})]$  could be obtained. It crystallizes as a monomeric complex in which the somewhat larger  $[\text{MeNHBH}_3]^-$  ion allows coordination of only one THF ligand (Figure 1c). This anion, which is disordered over two positions, is also coordinated side-on to the  $\text{Ca}^{2+}$  ion and shows Ca–N bonds of similar length (average:  $2.382(4) \text{ Å}$ ). The Ca···B contact of  $2.584(7)$  is much shorter than that observed for the  $\text{NH}_2\text{BH}_3$  anion ( $2.867(4) \text{ Å}$ ). This is likely due to the lower coordination number of  $\text{Ca}^{2+}$ , which also explains the shorter bonds to the DIPP-nacnac ligand. Though disorder of the  $[\text{MeNHBH}_3]^-$  ion prohibited localization of the hydrogen atoms, its nature has been confirmed by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy (see Supporting Information).

Dehydrogenation of  $[(\text{DIPP-nacnac})\text{Ca}(\text{MeNHBH}_3)(\text{thf})]$  proceeds at temperatures of  $40\text{--}60^\circ\text{C}$ , which is slightly higher than for the non-methylated amidoborane. The decomposition product crystallizes with similar cell parameters and the same space group as observed for  $[(\text{DIPP-nacnac})\text{Ca}(\text{thf})]_2[\text{HN}-\text{BH}-\text{NH}-\text{BH}_3]$ . Crystal structure analysis revealed a dimeric complex with terminal DIPP-nacnac ligands and a bridging  $[\text{MeNH}-\text{BH}-\text{NMe}-\text{BH}_3]^{2-}$  fragment. Owing to the increased steric bulk of this dianionic fragment, only one of the  $\text{Ca}^{2+}$  ions shows additional THF coordination. N-Methylation of the B–N–B–N dianion resulted in a well-ordered structure in which all the hydrogen atoms of the bridging fragment have been observed and could be refined isotropically. Thus, the dianion  $[\text{MeN}-\text{BH}-\text{N}(\text{Me})-\text{BH}_3]^{2-}$  has been unambiguously confirmed. In contrast to  $[\text{HN}-\text{BH}-\text{NH}-\text{BH}_3]^{2-}$ , the methylated fragment is nearly planar (torsion angle for B–N–B–N =  $4.3(3)^\circ$ ) but displays a similar pattern of B–N bond lengths (Figure 3). It asymmetrically bridges the two  $\text{Ca}^{2+}$  ions with shorter contacts to the least-coordinated  $\text{Ca}^{2+}$  ion (Ca2). NMR

analyses of the complex are comparable to those for the non-methylated decomposition product. The BH<sub>3</sub> group is visible in  $^1\text{H}$  and  $^{11}\text{B}$  spectra but the BH group can only be observed as a very broad signal in the  $^1\text{H}$  NMR spectrum (see Supporting Information).

The dianionic species,  $[\text{HN}-\text{BH}-\text{NH}-\text{BH}_3]^{2-}$  and  $[\text{MeN}-\text{BH}-\text{N}(\text{Me})-\text{BH}_3]^{2-}$ , are unique in BN-chemistry and are considered intermediates on the pathway to the fully dehydrogenated species “ $[\text{NBH}]^-$ ”. They could be envisioned as the triply deprotonated form of the recently proposed intermediate in acid-catalyzed dehydrogenation,  $[\text{H}_3\text{N}-\text{BH}-\text{NH}_2-\text{BH}_3]^+$ ,<sup>[3b]</sup> or as a boraamidinate dianion  $[\text{HN}-\text{BH}-\text{NH}]^{2-}$  bound to neutral BH<sub>3</sub>. The dianion  $[\text{HN}-\text{BH}-\text{NH}-\text{BH}_3]^{2-}$  is formally isoelectronic to the allylic dianion  $[\text{HC}-\text{CH}-\text{CH}-\text{CH}_3]^{2-}$ , a highly desirable but hitherto unrealized target in organic synthesis.<sup>[13]</sup>

In summary, we have shown that the hydrocarbon-soluble calcium hydride complex,  $[(\text{DIPP-nacnac})\text{CaH}(\text{thf})]_2$ , is a useful reagent for performing solid-state reactions at a molecular level, not only enabling a study of reaction intermediates by solution methods but also allowing the growth of single crystals that give valuable information on their structures. Although dehydrogenation processes in solution and in the solid state might follow different pathways, insight into the dehydrogenation process and its intermediates could be advantageous for the further development of high-performance solid-state hydrogen-storage materials. We are currently investigating further dehydrogenation products and anticipate that our solution models could also be very useful in investigations on the regeneration of hydrogen depleted products to amidoborane precursors.

## Experimental Section

All experiments were carried out under argon using standard Schlenk techniques and freshly dried degassed solvents. The following compounds have been prepared according to literature:  $[(\text{DIPP-nacnac})\text{CaH}(\text{thf})]_2$ ,<sup>[9]</sup>  $\text{H}_3\text{NBH}_3$ <sup>[14]</sup> and  $\text{MeH}_2\text{NBH}_3$ .<sup>[14]</sup>

General procedure for the preparation of calcium amidoborane complexes: A solution of the ammonia-borane (43 mg, 1.40 mmol) in THF (0.5 mL) was cooled to  $-20^\circ\text{C}$  and added dropwise with a syringe to a stirred solution of  $[(\text{DIPP-nacnac})\text{CaH}(\text{thf})]_2$  (767 mg, 0.72 mmol) in toluene (32 mL) at  $-20^\circ\text{C}$ . After the evolution of gas was complete, the solution was stirred for an additional hour at room temperature and the solvents were removed in vacuo. Slow cooling of a solution of the raw product in a 6:1 hexane/THF mixture to  $-30^\circ\text{C}$  gave colorless crystals of the calcium amidoborane complex.

$[(\text{DIPP-nacnac})\text{CaNH}_2\text{BH}_3(\text{thf})]_2$ : Yield: 630 mg, 0.997 mmol, 69%. Elemental analysis (%) calcd for  $\text{C}_{37}\text{H}_{62}\text{BCaN}_3\text{O}_2$  ( $M_r = 631.80$ ): C 70.34, H 9.89; found C 69.98, H 9.51. Recrystallization from toluene gave the mono-thf product,  $[(\text{DIPP-nacnac})\text{CaNH}_2\text{BH}_3(\text{thf})]$ .  $^1\text{H}$  NMR (300 MHz,  $[\text{D}_8]\text{toluene}$ ,  $20^\circ\text{C}$ ):  $\delta = -0.66$  (q (br),  $^3J(\text{H,H}) = 4.5 \text{ Hz}$ , 2H, NH<sub>2</sub>), 1.22 (d,  $^3J(\text{H,H}) = 6.8 \text{ Hz}$ , 12H, *i*Pr), 1.23 (d,  $^3J(\text{H,H}) = 6.8 \text{ Hz}$ , 12H, *i*Pr), 1.33 (t (br),  $^3J(\text{H,H}) = 4.5 \text{ Hz}$ , 3H, BH<sub>3</sub>), 1.43 (m, 4H, thf), 1.66 (s, 6H, Me backbone), 3.23 (sept,  $^3J(\text{H,H}) = 6.8 \text{ Hz}$ , 4H, *i*Pr), 3.55 (m, 4H, thf), 4.74 (s, 1H, H backbone) 7.05–7.13 ppm (m, 6H, H aryl).  $^{11}\text{B}$  NMR (160 MHz,  $[\text{D}_8]\text{toluene}$ ,  $20^\circ\text{C}$ ):  $\delta = -19.6 \text{ ppm}$  (q,  $^1J(\text{B,H}) = 84.0 \text{ Hz}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $[\text{D}_6]\text{benzene}$ ,  $20^\circ\text{C}$ ):  $\delta = 24.7$  (*i*Pr), 24.8 (*i*Pr), 25.2 (*i*Pr), 25.5 (Me backbone), 28.4 (thf), 69.0 (thf), 94.1 (backbone), 123.8 (Ar), 124.4 (Ar), 129.3 (Ar), 142.0 (Ar), 147.1 (Ar), 165.7 ppm (backbone).



[(DIPP-nacnac)Ca(MeNHBH<sub>3</sub>)(thf)]: Yield: 571 mg, 0.995 mmol, 69%. Elemental analysis (%) calcd for C<sub>34</sub>H<sub>56</sub>BCa<sub>2</sub>N<sub>3</sub>O (M<sub>r</sub> = 573.72): C 71.18, H 9.84; found C 70.74, H 9.54. <sup>1</sup>H{<sup>13</sup>B} NMR (500 MHz, [D<sub>6</sub>]benzene, 20°C): δ = −0.16 (m (br), 1H, NH), 1.23 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 12H, iPr), 1.26 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 12H, iPr), 1.31 (m, 4H, thf), 1.68 (s, 6H, Me backbone), 1.77 (m (br), 3H, BH<sub>3</sub>), 1.97 (d, <sup>3</sup>J(H,H) = 3.1 Hz, 3H, NMe), 3.22 (sept, <sup>3</sup>J(H,H) = 6.8 Hz, 4H, iPr), 3.68 (m, 4H, thf), 4.79 ppm (s, 1H, H backbone). <sup>11</sup>B NMR (160 MHz, [D<sub>6</sub>]benzene, 20°C): δ = −15.8 ppm (q, <sup>1</sup>J(B,H) = 87.2 Hz). <sup>13</sup>C NMR (75 MHz, [D<sub>6</sub>]benzene, 20°C): δ = 24.5 (iPr), 24.7 (iPr), 25.2 (iPr), 25.4 (Me backbone), 28.4 (thf), 37.1 (NMe), 69.7 (thf), 93.7 (backbone), 123.9 (Ar), 123.9 (Ar), 124.7 (Ar), 141.7 (Ar), 146.3 (Ar), 165.9 ppm (backbone).

Synthesis of [(DIPP-nacnac)Ca(thf)<sub>2</sub>][HN-BH-NH-BH<sub>3</sub>]: A solution of [(DIPP-nacnac)CaNH<sub>2</sub>BH<sub>3</sub>(thf)<sub>2</sub>] (105 mg, 0.17 mmol) in benzene (1.0 mL) was heated at 40°C for 16 h. The solvent was removed in vacuo and the raw product crystallized by slowly cooling a hexane solution to −30°C. Yield 40 mg 0.04 mmol, 43%. Elemental analysis (%) calcd for C<sub>66</sub>H<sub>104</sub>B<sub>2</sub>Ca<sub>2</sub>N<sub>6</sub>O<sub>2</sub> (M<sub>r</sub> = 1115.39): C 71.07, H 9.40; found C 70.66, H 9.28. <sup>1</sup>H{<sup>13</sup>B} NMR (500 MHz, [D<sub>8</sub>]toluene, 20°C): δ = 1.09 (d (br), <sup>3</sup>J(H,H) = 4.4 Hz, 3H, BH<sub>3</sub>), 1.15 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 12H, iPr), 1.16 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 24H, iPr), 1.20 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 12H, iPr), 1.43 (m, 8H, thf), 1.62 (s, 12H, Me backbone), 1.69 (s (br), 1H, NH), 2.48 (s (br), 1H, NH), 3.06 (sept, <sup>3</sup>J(H,H) = 6.8 Hz, 4H, iPr), 3.08 (sept, <sup>3</sup>J(H,H) = 6.8 Hz, 4H, iPr), 3.51 (m, 8H, thf), 3.74 (br, 1H, BH), 4.70 (s, 1H, H backbone), 6.99–7.07 ppm (m, 12H, aryl). <sup>11</sup>B NMR (160 MHz, [D<sub>8</sub>]toluene, 20°C): δ = −22.8 ppm (q, <sup>1</sup>J(B,H) = 83.3 Hz, BH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, [D<sub>8</sub>]toluene, 20°C): δ = 24.5 (iPr), 24.6 (iPr), 24.7 (iPr), 24.8 (iPr), 25.0 (iPr), 25.5 (Me backbone), 28.4 (thf), 69.4 (thf), 93.9 (backbone), 123.5 (Ar), 123.6 (Ar), 124.3 (Ar), 141.6 (Ar), 141.9 (Ar), 147.0 (Ar), 165.2 ppm (backbone).

Synthesis of [(DIPP-nacnac)Ca(thf)<sub>0.5</sub>]<sub>2</sub>[MeN-BH-NMe-BH<sub>3</sub>]: A solution of [(DIPP-nacnac)Ca(MeNHBH<sub>3</sub>)(thf)] (151 mg, 0.26 mmol) in benzene (10 mL) was stirred at room temperature overnight and then stirred for an additional 3 h at 60°C. The solvent was removed in vacuo and the raw product crystallized by slow cooling of a hexane solution to −30°C. Yield: 75 mg, 0.070 mmol, 54%. Elemental analysis (%) calcd for C<sub>64</sub>H<sub>100</sub>B<sub>2</sub>Ca<sub>2</sub>N<sub>6</sub>O (M<sub>r</sub> = 1071.30): C 71.75, H 9.41; found C 71.58, H 9.72. <sup>1</sup>H{<sup>13</sup>B} NMR (300 MHz, [D<sub>6</sub>]benzene, 20°C): δ = 1.16 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 12H, iPr), 1.17 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 24H, iPr), 1.19 (br, 3H, BH<sub>3</sub>), 1.28 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 12H, iPr), 1.34 (d, <sup>3</sup>J(H,H) = 6.8 Hz, 24H, iPr), 1.40 (m, 4H, thf), 1.59 (s, 3H, NMe), 1.61 (s, 12H, Me backbone), 2.21 (s, 3H, NMe), 3.10 (sept, <sup>3</sup>J(H,H) = 6.8 Hz, 4H, iPr), 3.11 (sept, <sup>3</sup>J(H,H) = 6.8 Hz, 4H, iPr), 3.53 (m, 4H, thf), 4.40 (br, 1H, BH), 4.78 (s, 2H, H backbone) 6.99–7.07 ppm (m, 12H, aryl). <sup>11</sup>B NMR (160 MHz, [D<sub>6</sub>]benzene, 20°C): δ = −19.8 ppm (q, <sup>1</sup>J(B,H) = 84.1 Hz, BH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, [D<sub>6</sub>]benzene, 20°C): δ = 24.5 (iPr), 24.6 (iPr), 24.9 (iPr), 24.9 (iPr), 25.0 (iPr), 25.6 (Me backbone), 28.6 (iPr), 28.7 (thf), 37.5 (NMe), 41.3 (NMe), 70.0 (thf), 94.5 (backbone), 123.8 (Ar), 124.1 (Ar), 124.6 (Ar), 141.7 (Ar), 142.2 (Ar), 147.2 (Ar), 165.9 ppm (backbone).

Crystal structure determinations: CCDC-685975, CCDC-685976, CCDC-685977, and CCDC-685978 contain 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. Structures were solved and refined with the programs SHELXS-97 and SHELXL-97, respectively.<sup>[15]</sup> Geometry calculations, graphic presentations and treatment of disordered cosolvent were performed using the program PLATON.<sup>[16]</sup>

[(DIPP-nacnac)CaNH<sub>2</sub>BH<sub>3</sub>(thf)<sub>2</sub>]: measurement at −100°C (Mo<sub>Kα</sub>), formula C<sub>37</sub>H<sub>62</sub>BCa<sub>2</sub>N<sub>3</sub>O<sub>2</sub>, monoclinic, space group P2<sub>1</sub>/n, a = 12.6798(7), b = 20.2834(12), c = 16.0721(9) Å, β = 103.694(3)°, V = 4016.1(4) Å<sup>3</sup>, Z = 4, ρ<sub>calc</sub> = 1.045 g cm<sup>−3</sup>, m (Mo<sub>Kα</sub>) = 0.188 mm<sup>−1</sup>, 63 129 measured reflections, 7315 independent (R<sub>int</sub> = 0.094), 5074 observed with I > 2σ(I), θ<sub>max</sub> = 25.4°, R = 0.0550, wR2 = 0.1498,

GOF = 1.11, 427 parameters, min/max residual electron density −0.38/+0.38 e Å<sup>−3</sup>. Hydrogen atoms in the NH<sub>2</sub>BH<sub>3</sub> anion were observed and were refined isotropically. Others were placed at calculated positions. One cocrystallized molecule of toluene was severely disordered and treated with the SQUEEZE procedure incorporated in PLATON.<sup>[16]</sup>

[(DIPP-nacnac)Ca(thf)<sub>2</sub>][H-BH-NH-BH<sub>3</sub>]: measurement at −100°C (Mo<sub>Kα</sub>), C<sub>66</sub>H<sub>98</sub>B<sub>2</sub>Ca<sub>2</sub>N<sub>6</sub>O<sub>2</sub>, monoclinic, space group P2<sub>1</sub>/n, a = 14.7695(6), b = 21.2212(8), c = 24.4116(10) Å, β = 97.038(2)°, V = 7593.6(5) Å<sup>3</sup>, Z = 4, ρ<sub>calc</sub> = 1.096 g cm<sup>−3</sup>, m (Mo<sub>Kα</sub>) = 0.189 mm<sup>−1</sup>, 177 697 measured reflections, 18 876 independent (R<sub>int</sub> = 0.073), 13 270 observed with I > 2σ(I), θ<sub>max</sub> = 28.3°, R = 0.0568, wR2 = 0.1731, GOF = 1.07, 729 parameters, min/max residual electron density −0.54/+0.86 e Å<sup>−3</sup>. Two cocrystallized molecules of THF showed severe disorder and were treated with SQUEEZE bypass method incorporated in the program PLATON.<sup>[16]</sup> Hydrogen atoms were placed on calculated positions. Hydrogen atoms could not be observed, owing to disorder of the central BNB<sup>2−</sup> unit (see Supporting Information). As not all hydrogen atoms in this fragment can be placed unambiguously at calculated positions, we have not included these in the final refinement.

[(DIPP-nacnac)Ca(MeNHBH<sub>3</sub>)(thf)]: measurement at −120°C (Mo<sub>Kα</sub>), formula C<sub>34</sub>H<sub>56</sub>BCa<sub>2</sub>N<sub>3</sub>O, monoclinic, space group P2<sub>1</sub>, a = 9.4088(9), b = 16.6084(16), c = 11.8063(12) Å, β = 109.186(5)°, V = 1742.4(3) Å<sup>3</sup>, Z = 2, ρ<sub>calc</sub> = 1.094 g cm<sup>−3</sup>, m (Mo<sub>Kα</sub>) = 0.208 mm<sup>−1</sup>, 28 095 measured reflections, 9973 independent (R<sub>int</sub> = 0.036), 8164 observed with I > 2σ(I), θ<sub>max</sub> = 30.6°, R = 0.0497, wR2 = 0.1267, GOF = 1.10, 369 parameters, min/max residual electron density −0.36/+0.55 e Å<sup>−3</sup>, Flack = −0.017(23). The MeNHBH<sub>3</sub> anion is disordered over two positions (ratio 56/44). All hydrogen atoms have been placed at calculated positions.

[(DIPP-nacnac)Ca(thf)<sub>0.5</sub>]<sub>2</sub>[MeN-BH-NMe-BH<sub>3</sub>]: measurement at −100°C (Mo<sub>Kα</sub>), formula C<sub>64</sub>H<sub>100</sub>B<sub>2</sub>Ca<sub>2</sub>N<sub>6</sub>O, monoclinic, space group P2<sub>1</sub>/n, a = 14.7448(4), b = 23.4653(6), c = 24.4447(6) Å, β = 95.750(1)°, V = 7726.6(4) Å<sup>3</sup>, Z = 4, ρ<sub>calc</sub> = 1.045 g cm<sup>−3</sup>, m (Mo<sub>Kα</sub>) = 0.183 mm<sup>−1</sup>, 175 365 measured reflections, 19 219 independent (R<sub>int</sub> = 0.048), 13 780 observed with I > 2σ(I), θ<sub>max</sub> = 28.3°, R = 0.0582, wR2 = 0.1643, GOF = 1.05, 736 parameter, min/max residual electron density −0.32/+0.38 e Å<sup>−3</sup>. Two cocrystallized molecules of THF showed severe disorder and were treated with SQUEEZE bypass method incorporated in the program PLATON.<sup>[16]</sup> Hydrogen atoms at the MeN-B(H)-N(Me)-BH<sub>3</sub> fragment have been located and were refined isotropically. All others were placed on calculated positions.

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