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Hydrogen Elimination in Bulky Calcium Amidoborane Complexes: Isolation of a Calcium Borylamide Complex

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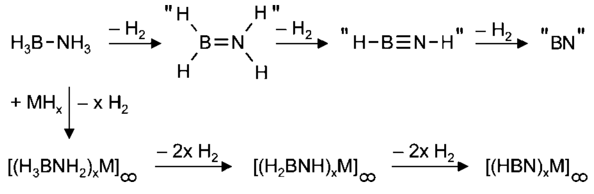
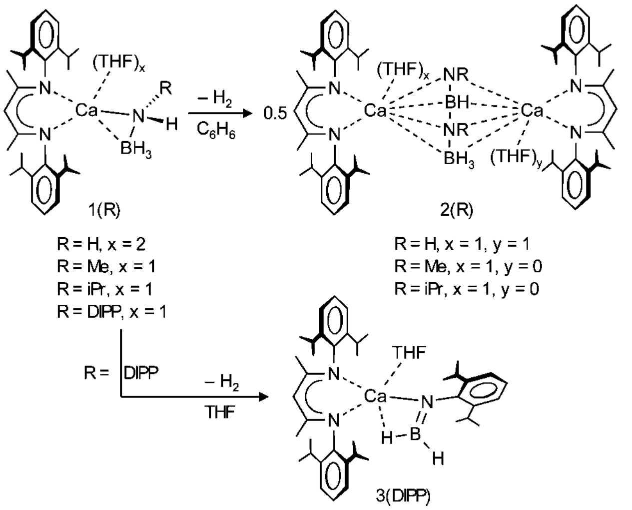
Ammonia−borane (NH_3BH_3, Scheme 1) is currently receiving enormous attention as a hydrogen storage material.[1] It is neither flammable nor explosive, features an extremely high hydrogen content of 19.6 w %, and, calculated by volume (146 g of H_2/L), far exceeds the storage capacities of liquid hydrogen (70 g/L at 20 K).[1a] Despite these advantages, there are also some major drawbacks among which are a relatively high hydrogen release window (120−450 °C) and the nonreversibility of the dehydrogenation reaction (hitherto only a chemical route for regeneration of BN to NH_3BH_3 is known).[2] The recently introduced metal amidoboranes (Scheme 1, M = Li, Na,[3a] or Ca[3b]) seem to be even more promising and show many advantages over NH_3BH_3: (i) lower hydrogen release temperatures (90−170 °C), (ii) no emission of the volatile side-product borazine, (iii) no induction period for hydrogen release, (iv) no foaming during hydrogen release, and (v) the dehydrogenation process is much less exothermic (3−5 kJ·mol^{-1}) than that for NH_3BH_3 (22−28 kJ·mol^{-1}).[4c,d] The latter aspect is promising for the development of convenient regeneration routes with molecular hydrogen.

Scheme 1



Although the mechanism for dehydrogenation of ammonia−borane is widely investigated,[4] hydrogen release in metal amidoborane salts is much less understood. We recently prepared defined calcium amidoborane complexes, **1(H)** and **1(Me)**, which dissolve well in apolar solvents.[5] These solubilized calcium amidoborane complexes already release hydrogen at 20−40 °C.[6] The homogeneous conditions also allowed characterization of the soluble dehydrogenation products **2(H)** and **2(Me)** by NMR and single crystal structure determination. In both cases, hydrogen release resulted in the formation of the hitherto unseen dianion: $(RN-BH-NR-BH_3)^{2-}$ (R = H or Me). This dianionic species can formally be regarded as a donor−acceptor complex of a boraamidinate (bam) ligand $(RN-BH-NR)^{2-}$ with BH_3.[7]

Pressurizing a solution of the dimeric dehydrogenation products **2(H)** and **2(Me)** with 100 bar of hydrogen did not result in regeneration of the amidoborane complexes **1(H)** and **1(Me)**, respectively. The newly formed B−N bond likely prevents such a conversion. To prevent dimerization by B−N bond formation, we prepared more sterically hindered calcium amidoborane complexes and investigated their structures and decomposition products.



Reaction of the soluble calcium hydride complex [DIPP-nacnacCaH·(THF)]$_2$ (DIPP-nacnac = CH{(CMe)(2,6-iPr$_2C_6H_3$N)}$_2$) with (iPr)NH_2BH_3 gave **1(*i*Pr)** in 76% crystalline yield. The more sterically hindered amidoborane complex **1(DIPP)** was prepared by reaction of DIPP-nacnacCaN$(SiMe_3)_2$·(THF) with (DIPP)NH_2BH_3 (DIPP = 2,6-iPr$_2$ C_6H_3) in 82% crystalline yield. Both crystallize as monomeric complexes with coordination of one additional THF ligand (Figure 1). The $RNHBH_3^-$ ions show the typical side-on coordination also observed in **1(H)** and **1(Me)**.[5] Increasing the steric bulk of the substituent R on nitrogen results in slight elongation of the N−Ca bond distance, shortening of the BH_3···Ca contact, and linearization of the angle R−N−Ca (Table 1). Although the B−N bond lengths are unaffected by the substituent R, an increase in bulk has a drastic influence on the stability of these calcium amidoborane complexes (Table 1). In C_6D_6, **1(*i*Pr)** releases hydrogen at 100 °C. **1(DIPP)** even needs a temperature of 120 °C, and ligand exchange to homoleptic species becomes a problem. Changing the solvent from benzene to THF, however, prevents this side reaction.

Table 1. Selected Bond Distances (Å), Angles (deg), and Decomposition Temperatures (°C) for Complexes **1(R)**

complex	1(H)[5]	1(Me)[5,a]	1(iPr)[a]	1(DIPP)
Ca−N	2.399(2)	2.382(4)	2.406(4)	2.460(2)
Ca···B	2.867(4)	2.584(7)	2.614(6)	2.570(3)
B−N	1.581(4)	1.581(8)	1.582(7)	1.587(4)
R−N−Ca	120(2)	125.8(3)	130.7(4)	147.6(2)
T_{decomp}	20	40	100	120

[a] The amidoborane unit is disordered; average values are given.

Decomposition of **1(*i*Pr)** gave the dimeric product **2(*i*Pr)** in 53% crystalline yield (Figure 2a). Similar to **2(H)** and **2(Me)**, the B−N bond lengths within the unit iPrN−BH−N(iPr)−BH_3^{2-} show the typical pattern: short (N6−B1 1.394(3) Å), intermediate (B1−N5 1.478(3) Å), and long (N5−B2 1.542(3) Å). In contrast to the

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structures of **2(H)** and **2(Me)**, the terminal nitrogen atom N6 in **2(*i*Pr)** does not bridge both Ca^{2+} ions but is only connected to Ca2 and N5 binds to Ca1.

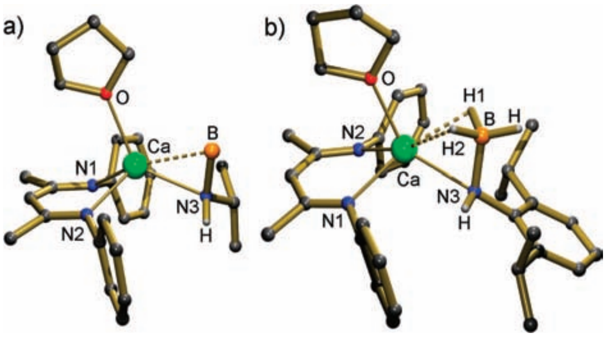

Figure 1. (a) Crystal structures of (a) **1(*i*Pr)** (hydrogen atoms on BH_3 could not be located due to disorder) and (b) **1(DIPP)**. The *i*Pr groups on the bidentate ligand and most hydrogen atoms are omitted for clarity. Selected bond distances (Å) in addition to those in Table 1: (a) Ca−N1 2.348(2), Ca−N2 2.356(2), Ca−O 2.362(2); (b) Ca−N1 2.345(2), Ca−N2 2.350(2), Ca−O 2.370(2), Ca···H1 2.27(3). Ca···H2 2.41(3).

Whereas the *i*Pr substituent still allows formation of the NBNB chain, the DIPP substituent is bulky enough to prevent such dimerization. Decomposition of **1(DIPP)** gave the monomeric product **3(DIPP)** in 71% crystalline yield. The crystal structure (Figure 2b) shows decomposition into a borylamide, $H_2B-(R)N^-$, with resonance structure $H_2B^-{=}N(R)$, that is edge-on coordinated to Ca^{2+}. The *p*-type lone pair on the N atom is perfectly shielded by the *i*Pr-substituents in the *ortho*-position. As lithium borylamides with small substituents on B normally show high reactivity,[8a] this shielding is responsible for the stability of **3(DIPP)**. Bulky groups on N also prevent the dimerization of $i\mathrm{Pr}_2N{=}BH_2$.[6a] The B−N bond length 1.353(3) Å in **3(DIPP)** is slightly smaller than those in substituted lithium borylamide complexes $LiN(R){=}BR'_2$ (1.383(4)−1.386(7) Å)[8a,b] or in an $(aryl)_2B{=}NH_2$ adduct (1.375(8) Å).[8b]

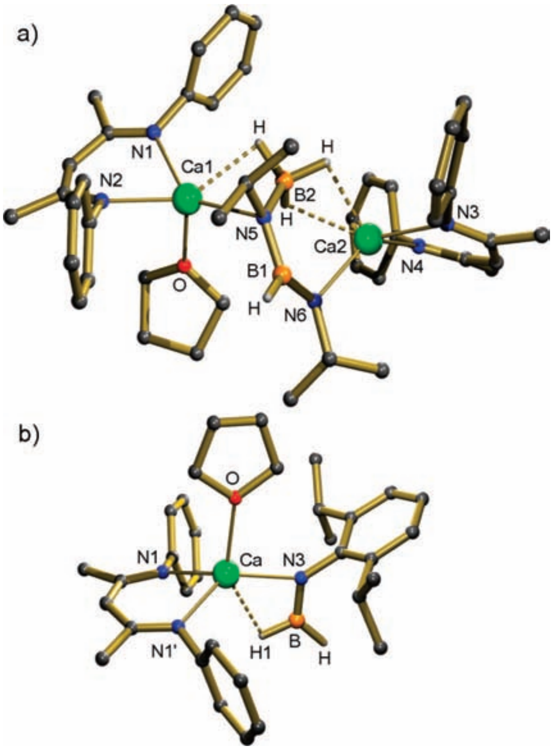

Figure 2. (a) Crystal structures of (a) **2(iPr)** and (b) **3(DIPP)**. The *i*Pr groups on the bidentate ligand and most hydrogen atoms are omitted for clarity. Selected bond distances (Å): (a) Ca1−N1 2.369(2), Ca1−N2 2.342(2), Ca1−N5 2.490(2), Ca1···B2 2.620(3), Ca1−O 2.319(2), Ca2−N3 2.357(2), Ca2−N4 2.352(2), Ca2−N6 2.283(2), Ca2···B2 2.701(3); (b) Ca−N1 2.343(1), Ca−N3 2.302(2), Ca···B 2.760(2), Ca−O 2.342(1), Ca···H1 2.38(2).

The anionic BN-fragment in **3(DIPP)** could be seen as a donor/acceptor pair that, similar to a frustrated Lewis pair,[9] might be able to activate molecular hydrogen. As a recent calculational study shows that hydrogenation of $R_2NBR'_2$ to $R_2HNBHR'_2$ is favored for substrates with electron-rich N and electron-poor B atoms,[10] hydrogenation of $H_2B(R)N^-$ might thermodynamically indeed be feasible. However, preliminary attempts to hydrogenate **3(DIPP)** to **1(DIPP)** have not been successful so far (H_2: 1−100 bar, temperature: 20−100 °C). This could either be due to a substantial $B{=}N$ π-bond energy[11] or might have a kinetic origin. We currently study the catalytic hydrogenation of metal complexes containing the $(DIPP)N{=}BH_2^-$ ligand and evaluate substituent effects on N and B.

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Supporting Information Available: Synthetic procedures, analyses and crystallographic data for **1(*i*Pr)**, **1(DIPP)**, **2(*i*Pr)** and **3(DIPP)** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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