CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201102029

Calcium–Amidoborane–Ammine Complexes: Thermal Decomposition of Model Systems

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Abstract: Hydrocarbon-soluble model systems for the calcium–amidoborane–ammine complex $Ca(NH_2BH_3)_2{\cdot}(NH_3)_2$ were prepared and structurally characterized. The following complexes were obtained by the reaction of RNH_2BH_3 (R = H, Me, *i*Pr, DIPP; DIPP = 2,6-diisopropylphenyl) with Ca(DIPP-nacnac)$(NH_2){\cdot}(NH_3)_2$ (DIPP-nacnac = DIPP–NC(Me)CHC(Me)N–DIPP): Ca(DIPP-nacnac)$(NH_2BH_3){\cdot}(NH_3)_2$, Ca(DIPP-nacnac)$(NH_2BH_3){\cdot}(NH_3)_3$, Ca(DIPP-nacnac)$[NH(Me)BH_3]{\cdot}(NH_3)_2$, Ca(DIPP-nacnac)$[NH(i\text{Pr})BH_3]{\cdot}(NH_3)_2$, and Ca(DIPP-nacnac)$[NH(DIPP)BH_3]{\cdot}NH_3$. The crystal structure of Ca(DIPP-nacnac)$(NH_2BH_3){\cdot}(NH_3)_3$ showed a $NH_2BH_3^-$ unit that was fully embedded in a network of BH···HN interactions (range: 1.97(4)–2.39(4) Å) that were mainly found between NH_3 ligands and BH_3 groups. In addition, there were N–H···C interactions between NH_3 ligands and the central carbon atom in the ligand. Solutions of these calcium–amidoborane–ammine complexes in benzene were heated stepwise to 60 °C and thermally decomposed. The following main conclusions can be drawn: 1) Competing protonation of the DIPP-nacnac anion by NH_3 was observed; 2) The NH_3 ligands were bound loosely to the Ca^{2+} ions and were partially eliminated upon heating. Crystal structures of $[Ca(DIPP\text{-}nacnac)(NH_2BH_3){\cdot}(NH_3)]_\infty$, Ca(DIPP-nacnac)$(NH_2BH_3){\cdot}(NH_3){\cdot}$(THF), and $[Ca(DIPP\text{-}nacnac)\{NH(i\text{Pr})BH_3\}]_2$ were obtained. 3) Independent of the nature of the substituent R in $NH(R)BH_3$, the formation of H_2 was observed at around 50 °C. 4) In all cases, the complex $[Ca(DIPP\text{-}nacnac)(NH_2)]_2$ was formed as a major product of thermal decomposition, and its dimeric nature was confirmed by single-crystal analysis. We proposed that thermal decomposition of calcium–amidoborane–ammine complexes goes through an intermediate calcium–hydride–ammine complex which eliminates hydrogen and $[Ca(DIPP\text{-}nacnac)(NH_2)]_2$. It is likely that the formation of metal amides is also an important reaction pathway for the decomposition of metal–amidoborane–ammine complexes in the solid state.

Keywords: alkaline earth metals · boranes · calcium · hydrogen storage · structure elucidation

Introduction

Ammonia–borane (NH_3BH_3) has been widely investigated as a hydrogen-storage material on account of its high hydrogen content (19.6 wt %).[1] However, the recently introduced early main-group metal–amidoboranes ($LiNH_2BH_3$, $NaNH_2BH_3$, and $Ca(NH_2BH_3)_2$)[2] are potentially more-advantageous; these compounds eliminate hydrogen at much lower temperatures, do not need an induction time, show less foaming, and generate hydrogen that is free of the highly undesirable fuel-cell poison: borazine.[3] However, replacing one of the hydrogen atoms in NH_3BH_3 with an early main-group metal also creates a mismatch between the number of hydridic BH and protic NH functionalities, thus reducing the potentially available hydrogen content from three to two equivalents of H_2 per storage molecule.

One way to circumvent this loss in capacity was found by serendipity. Chen and co-workers recently reported a new synthetic procedure for $Ca(NH_2BH_3)_2$ from $Ca(NH_2)_2$ and NH_3BH_3.[4] The product obtained was found to be the ammine complex $Ca(NH_2BH_3)_2{\cdot}(NH_3)_2$, which was formed by complexation of the NH_3 side-product to the Ca^{2+} center. Introduction of an NH_3 molecule gives a material of high hydrogen content (12.0 wt %) and restores the number of protic hydrogen atoms for reaction with hydridic BH units. Indeed, the solid-state structure of this ammine complex features an extended network of short $NH^{\delta+}\cdots H^{\delta-}B$ bridges that range from 1.927–2.358 Å, that is, shorter than the cut-off value of 2.4 Å (twice the van der Waals radius of H). Such interactions are common and were also found in the solid-state structure of NH_3BH_3.[5]

Heating the ammine complex $Ca(NH_2BH_3)_2{\cdot}(NH_3)_2$ under a flow of argon gave a loss of two equivalents of NH_3 at about 70 °C and, as observed previously for neat $Ca(NH_2BH_3)_2$),[2b] at above 120 °C H_2 started to be eliminated. The first step, loss of NH_3, is a reversible reaction and the

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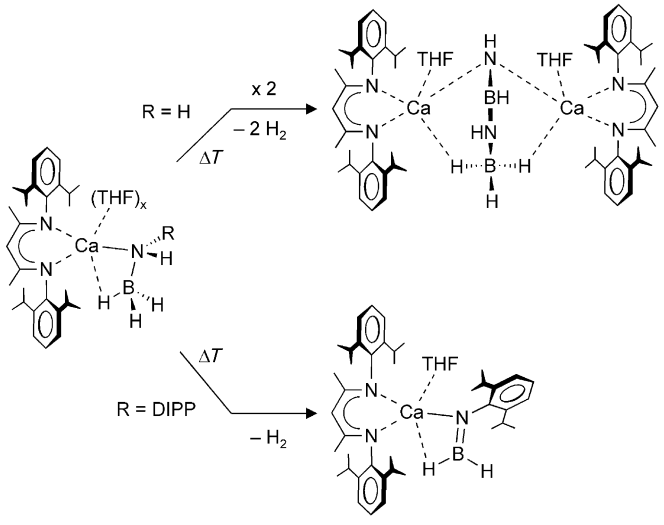
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102029.

ammine complex could be regenerated by reaction of $Ca(NH_2BH_3)_2$ with gaseous ammonia. The second step, loss of H_2, is irreversible.

However, heating the ammine complex $Ca(NH_2BH_3)_2 \cdot (NH_3)_2$ in a closed system at 70–80 °C already led to the elimination of considerable amounts of H_2. This significantly reduced temperature for H_2 formation was attributed to the combination of hydridic BH groups with NH units in NH_3. The latter should be more acidic than those in $NH_2BH_3^-$. Further heating led to elimination of nearly six equivalents of H_2 per molecule of the complex. These observations indicate that the NH_3 ligands are a source of hydrogen and play an important role in the desorption mechanism. Subsequent investigations on $Mg(NH_2BH_3)_2 \cdot NH_3$[6] and $Li(NH_2BH_3) \cdot NH_3$[7] support this role of NH_3 incorporation.

As these investigations are typically performed in the solid state, it is not straightforward to gain an insight into the intermediates and chemical processes involved during H_2 desorption. The amorphous residue with the formula $CaB_2N_2H_4$ has been analyzed by IR and NMR spectroscopy. It likely contains B in a BN_2 or BN_3 environment and imide or amide NH groups.[4]

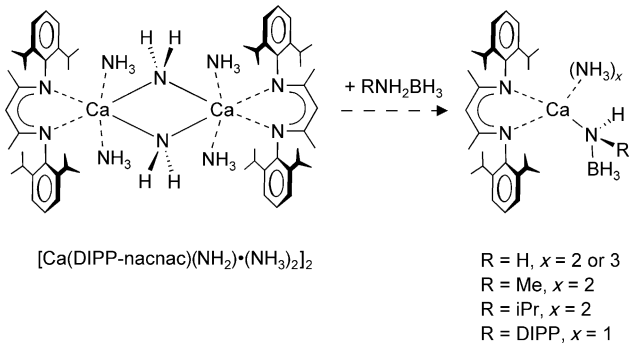
In our previous research, we demonstrated the importance of molecular models in unraveling the mechanism of hydrogen release in metal–amidoborane complexes. The use of the strongly coordinating, bulky β-diketiminate ligand, DIPP-nacnac (DIPP = 2,6-diisopropylphenyl, DIPP-nacnac = DIPP–NC(Me)CHC(Me)N–DIPP) enabled the isolation of unique species that play a role in H_2 desorption from metal–amidoborane storage materials (Scheme 1).[8–10] Herein, we report our investigation of calcium–amidoborane–ammine complexes and the role of NH_3 during thermal decomposition.



Scheme 1. Soluble model systems for calcium–amidoborane and isolated products after thermally promoted H_2 elimination.

Results

Syntheses and structures of calcium–amidoborane–ammine complexes: The key precursor in the synthesis of a large variety of calcium–amidoborane–ammonia adducts is our recently reported calcium–amide complex Ca(DIPP-nacnac)$(NH_2) \cdot (NH_3)_2$ that crystallizes as a dimer (Scheme 2).[11] De-



Scheme 2. Syntheses of model systems for calcium–amidoborane–ammine complexes.

protonation of a range of N-substituted ammonia boranes in toluene gave moderate yields of pure crystalline calcium–amidoborane complexes that contained between one and three neutral NH_3 ligands per calcium atom. The complexes with the smaller substituents (R = H, Me, *i*Pr) crystallized as bis-ammine adducts whereas the amidoborane complex with the larger DIPP-substituent crystallized with only one NH_3 ligand. When the synthesis of the complex with the smaller $NH_2BH_3^-$ anion was carried out in a sealed tube, even a tris-ammine complex was isolated. The latter complex is stable in the solid state but easily loses NH_3 upon solvation in an aromatic solvent. Although all complexes crystallized well and were conveniently obtained as pure crystalline solids, attempts to determine the crystal structures were in many cases frustrated by poor crystal quality or unresolved disorder in the crucial amidoborane parts of the molecule; we could only determine an accurate crystal structure for the tris-ammine complex Ca(DIPP-nacnac)$(NH_2BH_3) \cdot (NH_3)_3$. The remaining complexes were fully characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy.

The crystal structure of Ca(DIPP-nacnac)$(NH_2BH_3) \cdot (NH_3)_3$ is shown in Figure 1a and selected bond distances are summarized in Table 1. The asymmetric unit contained two unique molecules with comparable structures. The coordination geometries of the six-coordinate Ca^{2+} ions strongly deviated from a pure-octahedral geometry. This deviation was due in part to the predetermined small bite-angle of the DIPP-nacnac ligands (average: 77.17(5)°) but was also caused by an intramolecular non-classical NH···C hydrogen bonding between one of the NH_3 ligands and the DIPP-nacnac backbone: N5–H12···C3 2.63(3) Å (134(1)°) and N11–H28···C32 2.65(3) Å (136(1)°). These distances are con-

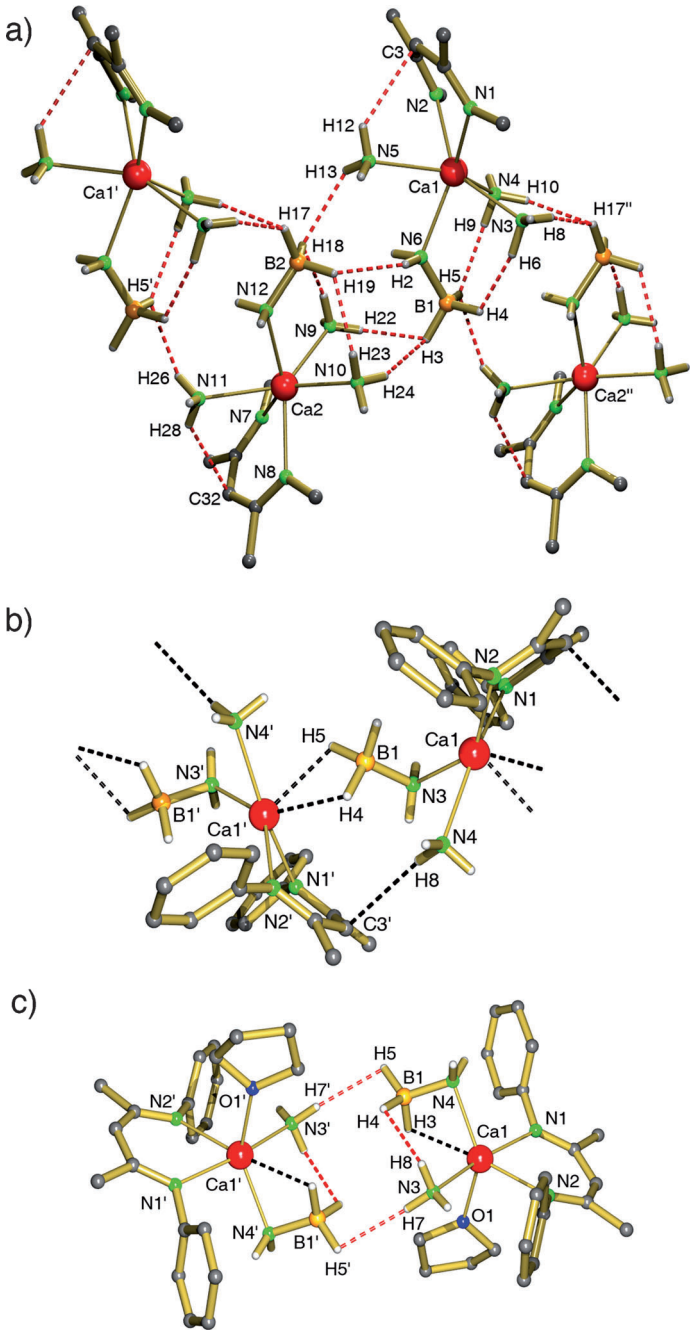


Figure 1. The crystal structures of a) Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)_3$, b) [Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)]_\infty$, and c) Ca(DIPP-nacnac)-(NH_2BH_3)·NH_3·THF; for clarity DIPP-substituents are only partially shown.

siderably shorter than the sum of the van der Waals radii of carbon and hydrogen (2.90 Å).

The main difference between the structure of the tris-ammine adduct Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)_3$ and the previously reported complex with THF, Ca(DIPP-nacnac)-(NH_2BH_3)·$(THF)_2$, is the coordination mode of the amidoborane ligand. Whereas in the latter THF complex, $NH_2BH_3^-$ coordinates side-on to the Ca^{2+} ion, that is, through an agostic BH···Ca^{2+} interaction (cf. Scheme 1), the

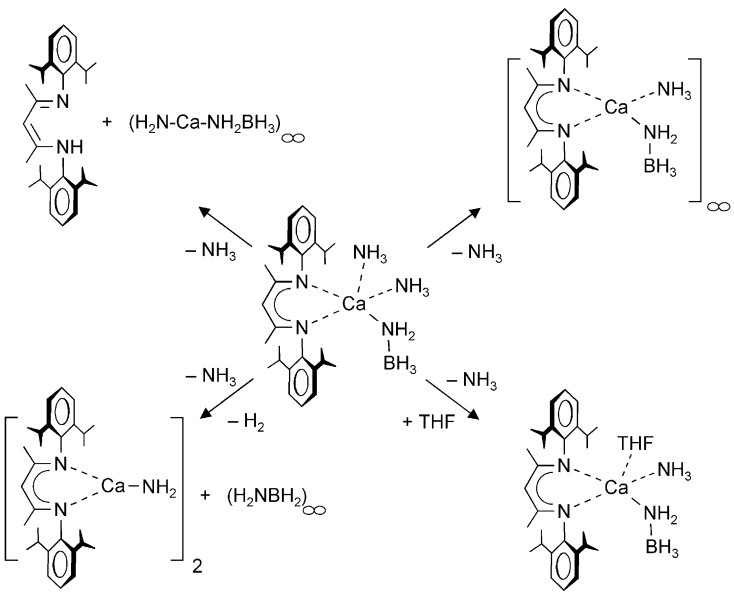
Table 1. Selected bond lengths for the crystal structures [Å].

Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)_3$					
Ca1–N1	2.449(1)	Ca2–N10	2.545(2)	H5···H9	2.14(4)
Ca1–N2	2.444(2)	Ca2–N11	2.509(2)	H8···H17″	1.97(4)
Ca1–N3	2.512(2)	Ca2–N12	2.528(2)	H10···H17″	2.30(4)
Ca1–N4	2.526(3)	B1–N6	1.555(3)	H12···C3	2.63(3)
Ca1–N5	2.557(2)	B2–N12	1.566(3)	H13···H18	2.39(4)
Ca1–N6	2.491(2)	H2···H19	2.24(5)	H18···H21	1.99(4)
Ca2–N7	2.465(2)	H3···H22	2.10(4)	H19···H23	2.21(4)
Ca2–N8	2.451(1)	H3···H24	2.16(4)	H26···H5′	2.29(4)
Ca2–N9	2.503(3)	H4···H6	2.04(4)	H28···C32	2.65(3)
[Ca(DIPP-nacnac)(NH_2BH_3)·$NH_3]_\infty$					
Ca–N1	2.056(1)	Ca–N4	2.417(2)	Ca1′···B1	2.916(2)
Ca–N2	2.074(1)	Ca1′···H4	2.36(2)	B1–N3	1.543(2)
Ca–N3	2.122(1)	Ca1′···H5	2.49(2)	H8···C3′	2.75(1)
Ca(DIPP-nacnac)(NH_2BH_3)·NH_3·THF					
Ca1–N1	2.418(1)	Ca1–N4	2.393(1)	Ca1···H3	2.22(2)
Ca1–N2	2.419(1)	Ca1–O1	2.350(1)	H4···H8	1.97(2)
Ca1–N3	2.524(1)	Ca1···B1	2.871(2)	H5···H7′	2.33(3)
[Ca(DIPP-nacnac)$(NH_2)]_2$					
Ca1–N1	2.345(1)	Ca1–N2	2.354(1)	Ca1–N3	2.378(1)
[Ca(DIPP-nacnac){NH(*i*Pr)BH_3}]$_2$					
Ca1–N1	2.313(2)	Ca1···H1′	2.27(3)	Ca1···B1	2.753(3)
Ca1–N2	2.338(2)	Ca1···H2′	2.28(3)	Ca1···B1′	2.710(4)
Ca1–N3	2.394(3)	Ca1···H2	2.44(3)	B1–N3	1.516(4)

$NH_2BH_3^-$ unit in the ammonia complex is fully embedded in a network of BH···HN interactions (1.97(4)–2.39(4) Å). These short distances are mainly found between the NH_3 ligand and the BH_3 groups but an intermolecular interaction between two amidoborane anions is also observed (H2···H19). Each hydridic $B^{\delta+}$–$H^{\delta-}$ unit has at least one interaction with a protic $N^{\delta-}$–$H^{\delta+}$ group.

Thermal decomposition of Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)_2$: As the tris-ammine complex Ca(DIPP-nacnac)-(NH_2BH_3)·$(NH_3)_3$ loses NH_3 upon solvation in aromatic solvents, the thermal decomposition of the less-crowded bis-ammine complex Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)_2$ was investigated (Scheme 3). A solution of the complex in C_6D_6 was slowly heated in 10 °C increments and monitored at regular intervals by ^{1}H NMR spectroscopy.

At 30 °C, traces of DIPP-nacnacH began to be formed. Stepwise heating to 60 °C accelerated the protonation of the DIPP-nacnac anion and caused precipitation of a white amorphous solid. This solid, which was also insoluble in polar solvents like THF, did not contain the DIPP-nacnac ligand and was probably polymeric $(H_2NCaNH_2BH_3)_\infty$. Protonation of the DIPP-nacnac anion by NH_3 was unexpected and seemed thermodynamically unfavorable: the pK_a value of NH_3 (41)[12] is substantially higher than the pK_a value of the β-diketimine DIPP-nacnacH (estimated at < 30). However, this reaction is possibly predetermined by a non-classical N–H···C interaction, as observed in the crystal structure of Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)_3$ (Figure 1 a). The subsequent precipitation of $(H_2NCaNH_2BH_3)_\infty$ forces the equilibrium to the side of the protonated ligand. The non-inno-



Scheme 3. Established routes for the thermal decomposition of Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)_2$.

cence of β-diketiminate ligands is well-documented. They can play a role in redox reactions,[13] act as nucleophiles[14] or electrophiles,[15] and react as an acid[16] or a base.[17] A similar protonation of the β-diketiminate ligand has been observed in $[Ca(DIPP\text{-}nacnac)(NH_2)\cdot(NH_3)_2]_2$. In the crystalline state at −20 °C, this complex is stable indefinitely. However, heating a solution of this complex in benzene to 60 °C gave rapid protonation of the DIPP-nacnac anion.

Although the protonation of the β-diketiminate ligand already started at an early stage, other products were isolated (Scheme 3). During the course of the heating process, not only amorphous insoluble calcium amides but also colorless crystals started to precipitate. These crystals redissolved at a later stage in the heating process. Their crystal structure showed a coordination polymer of the mono-ammine complex $[Ca(DIPP\text{-}nacnac)(NH_2BH_3)\cdot NH_3)]_\infty$ (Figure 1b, Table 1) in which the Ca^{2+} ion was chelated by the DIPP-nacnac ligand and solvated by a single NH_3 ligand. This orientation left ample space at the metal and caused the $NH_2BH_3^-$ anion to bridge between neighboring Ca^{2+} ions, thereby resulting in the formation of a one-dimensional coordination polymer. The NH_3 ligand was not involved in any NH···HB bonding interactions, but rather formed a non-classical NH···C bridge to the central carbon atom of the DIPP-nacnac ligand (2.75 Å; 162(1)°), similar to that observed in $Ca(DIPP\text{-}nacnac)(NH_2BH_3)\cdot(NH_3)_3$. This observation underscores the importance of such interactions.

As the loss of NH_3 resulted in the crystallization of the insoluble coordination polymer $[Ca(DIPP\text{-}nacnac)(NH_2BH_3)\cdot NH_3)]_\infty$, we attempted to keep the complex in solution by adding small quantities of THF (using THF as the solvent led to formation of the complex $Ca(DIPP\text{-}nacnac)(NH_2BH_3)\cdot(THF)_2$, the thermal decomposition of which had previously been investigated).[8] The addition of only two equivalents of THF led to the crystallization of a few crystals of $Ca(DIPP\text{-}nacnac)(NH_2BH_3)\cdot THF\cdot NH_3$. However, a larger-scale isolation of this complex could not be realized. Its crystal structure (Figure 1c, Table 1) shows a molecular unit that is bound to a symmetry-related unit through NH···HB interactions to form a centrosymmetric dimer. Apart from inter- and intramolecular NH···HB interactions, the amidoborane anion $NH_2BH_3^-$ was also involved in an agostic $BH\cdots Ca^{2+}$ interaction.

Thermal decomposition of a solution of $Ca(DIPPnacnac)(NH_2BH_3)\cdot(NH_3)_2$ in benzene lead, despite side-reactions such as protonation of the DIPP-nacnac anion and elimination of volatile NH3, to the release of H_2. At a temperature of approximately 50 °C, a sharp singlet at $\delta = 4.45$ ppm (H_2 in C_6D_6) was observed in the ^1H NMR spectrum. Separating the mother liquor from the deposit (formed during decomposition) and cooling the resulting clear solution gave crystals of $Ca(DIPP\text{-}nacnac)(NH_2)$. This donor-free complex crystallized as a centrosymmetric dimer with bridging NH_2^- ions (Figure 2, Table 1). The asymmetric unit contained two independent dimers with very similar structures. It is surprising that the dimer is free of additional coordinating donor ligands (like NH_3). Most dimeric $[Ca(DIPP\text{-}nacnac)(X)]_2$ complexes with small bridging X^- ions (H^-, OH^-) crystallize with donor solvents like THF or Et_2O.[11] Solvent-free dimers were only observed with larger bridging groups (X = C≡CPh,[18] NHBn,[19] $OCHPh_2$,[20] $OSiMe_3$[21]). The fact that this complex is free of donors demonstrates the relatively weak coordinating ability of the NH_3 ligand. The unusually low coordination number of four for Ca^{2+} ions gives rise to rather short ligand–metal bonds. The Ca–N bonds to the bridging NH_2^- ion (2.378(1) Å) are considerably shorter than those in dimeric $[Ca(DIPP\text{-}nacnac)(NH_2)\cdot(NH_3)_2]_2$ (2.439(1) Å). We found that donor-free $[Ca(DIPP\text{-}nacnac)(NH_2)]_2$ can also be isolated as a by-product in the synthesis of $[Ca(DIPP\text{-}nacnac)(NH_2)\cdot(NH_3)_2]_2$ (see the Experimental Section). The strongly basic complex $[Ca(DIPP\text{-}nacnac)(NH_2)]_2$ could be a convenient precursor for the synthesis of

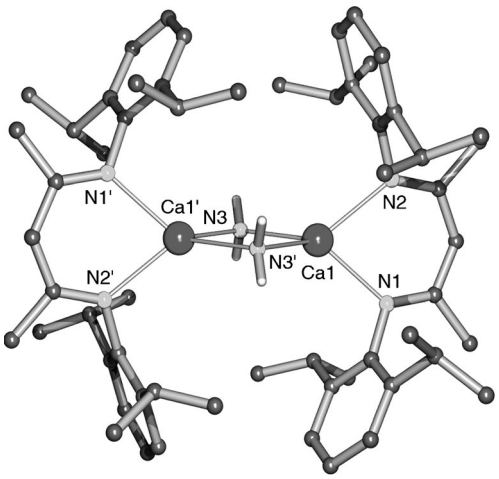


Figure 2. The crystal structure of $[Ca(DIPP\text{-}nacnac)(NH_2)]_2$.

various base-free Ca(DIPP-nacnac)(X) complexes. ^{1}H NMR monitoring of a thermally decomposed benzene solution of Ca(DIPP-nacnac)(NH_2BH_3)·(NH_3)$_2$ revealed that it contained at least 40% [Ca(DIPP-nacnac)(NH_2)]$_2$ (the remaining 60% is DIPP-nacnacH formed by ammonolysis). Therefore, this calcium–amide complex represents a major decomposition product.

Thermal decomposition of *N*-substituted calcium–amidoborane–ammine complexes: The complexes Ca(DIPP-nacnac)[NH(Me)BH_3]·(NH_3)$_2$, Ca(DIPP-nacnac)[NH(*i*Pr)BH_3]·(NH_3)$_2$, and Ca(DIPP-nacnac)[NH(DIPP)BH_3]·(NH_3)$_2$ were dissolved in C_6D_6, heated stepwise to 60°C and monitored by ^{1}H NMR spectroscopy at regular intervals. In all cases, the formation of DIPP-nacnacH was already observed at an early stage. The speed of ammonolysis is dependent on the size of the substituent, R. With the largest substituent (R = DIPP), protonation of the β-diketiminate anion already occurred at RT and was complete at this temperature after several hours. It is unclear why the steric bulk of the amidoborane anion influences the rate of ammonolysis but it might be explained by the fact that large ligands enforce close proximity of the DIPP-nacnac$^-$ and NH_3 ligands.

Loss of the NH_3 ligand was also an important side-reaction for this series of complexes. In one case, we crystallized donor-free Ca(DIPP-nacnac)[NH(*i*Pr)BH_3] from solution; its crystal structure revealed a dimeric complex that is held together by BH_3···Ca interactions (Figure 3, Table 1).

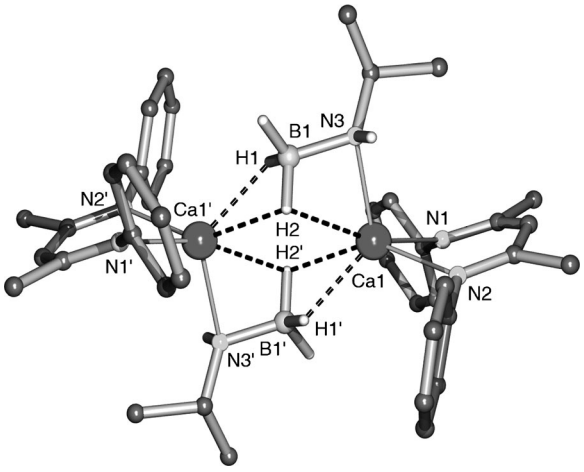


Figure 3. The crystal structure of [Ca(DIPP-nacnac){NH(*i*Pr)BH_3}]$_2$.

In all cases, a significantly large signal was found for molecular H_2 in the ^{1}H NMR spectra (δ = 4.45 ppm). In contrast to the THF adducts described earlier, the nature of the substituent does not influence the temperature for the onset of H_2 formation. Whereas for complexes of the form Ca(DIPP-nacnac)[NH(R)BH_3]·(THF)$_x$ the hydrogen-elimination temperature was highly dependent on the size of the substituent (R = H 20°C, Me 40°C, *i*Pr 100°C, and DIPP 120°C),[8,9] the corresponding ammine complexes all started to release hydrogen at the low temperature of 50°C. For comparison, the solid material Ca(NH_2BH_3)$_2$ releases hydrogen at a temperature of 120°C.[2b] This observation makes it likely that, in ammine complexes, H_2 is formed through a combination of a hydridic BH unit of the amidoborane ligand N(R)HBH_3^- and a protic NH unit of the NH_3 ligand. If it were the case that the N(R)HBH_3^- ligand was both the BH and NH source, a strong influence of the substituent R on nitrogen would be expected. In agreement with this observation is that, in all cases, the donor-free calcium–amide complex [Ca(DIPP-nacnac)(NH_2)]$_2$ was observed in the ^{1}H NMR spectra as the major product of thermal decomposition.

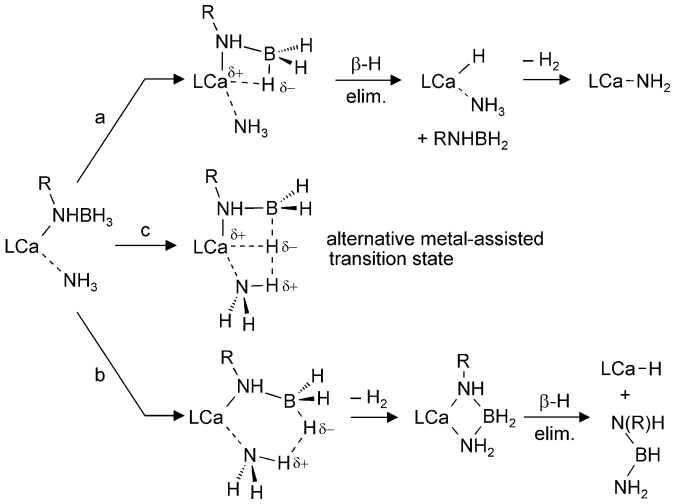
Discussion

Calcium–amidoborane–ammine complexes can be conveniently obtained by deprotonation of ammonia-boranes with a calcium base that contains NH_2^- and NH_3 ligands. The ammine ligands in these complexes are loosely bound and, over the course of our studies, crystal structures of complexes with a varying number (0–3) of ammine ligands were obtained. In general, the ammine-rich complexes, like Ca(DIPP-nacnac)(NH_2BH_3)·(NH_3)$_3$, showed interactions between the BH_3 group and NH_3 ligands, whereas the ammine-poor (or ammine-free) complexes showed BH_3···Ca^{2+} bonding interactions. In Ca(DIPP-nacnac)-(NH_2BH_3)·NH_3·THF, a combination of BH···HN and BH···Ca^{2+} interactions were found.

Investigations concerning the thermal decomposition of these complexes can be summarized by the following statements: 1) In all cases, thermal decomposition of β-diketiminate calcium–amidoborane–ammine complexes gave significant protonation of the DIPP-nacnac anion. This protonation is accompanied by the appearance of an insoluble white precipitate that is likely to be a coordination polymer, [H_2NCaNH(R)BH_3]$_\infty$. 2) The NH_3 ligands are only bound loosely to the Ca^{2+} ions and are easily eliminated upon heating. 3) The formation of H_2 is observed in all cases by the appearance of a characteristic singlet at 4.45 ppm in the ^{1}H NMR spectrum. The temperature for formation of H_2 in the presence of NH_3 (ca. 50°C) is much lower than that for Ca(NH_2BH_3)$_2$ (ca. 120°C)[2b] and is fully independent of the substituent (R) on nitrogen atom. Therefore, it is likely that the protic hydrogen atom is delivered by NH_3 and not by the NH group in the amidoborane anion. The nature of substituent R will have a large effect on the NH group in RNH_2BH_3 but a much smaller effect on the BH_3 unit. 4) In all cases, the complex [Ca(DIPP-nacnac)(NH_2)]$_2$ was formed as the major product of thermal decomposition. The fate of the concomitantly formed N(R)BH_2 is unknown but it likely polymerizes and is part of the insoluble precipitate. After complete decomposition, the solution only contained DIPP-nacnacH and [Ca(DIPP-nacnac)(NH_2)]$_2$ and, as deter-

mined by ^{11}B NMR spectroscopy, there were no major boron-containing compounds in solution.

The exact mechanism for the formation of [Ca(DIPP-nacnac)(NH_2)]$_2$ is unclear. For the thermal decomposition of magnesium amidoborane complexes, we have previously demonstrated that an intermediate metal–hydride species plays a key role in the mechanism.[10] Investigations on Group-2-metal-promoted hydrogen release in $NH(Me)_2BH_3$ by Hill and co-workers,[22] and recent calculations by Kim et al.[23] corroborate this observation. The most-likely mechanism is β-H elimination followed by deprotonation of NH_3 (route (a), Scheme 4). Route (b), the direct coupling of hydridic BH and protic NH groups (from the NH_3 ligand) should give a metallacycle with a H(R)N–BH_2–NH_2^- anion. This could, after β-H elimination, give a hydride complex (which would deprotonate NH_3) and H(R)N–BH–NH_2. As we did not observe any soluble boron-containing species, this route seems less likely. The decomposition of the complex with R = DIPP did not give H(DIPP)N–BH–N(DIPP)H, a stable and known compound that is formed quantitatively in the magnesium-catalyzed dehydrogenation of (DIPP)NH_2BH_3.[24] A possible alternative route could be an intermediate pathway between routes (a) and (b) in which the BH_3 hydride atom transfers onto the metal and reacts with the NH_3 ligand in one concerted step (route (c), Scheme 4). Such intricate details need to be explored by theoretical calculations.



Scheme 4. Possible mechanisms for the decomposition of calcium–amidoborane–ammine complexes (L = DIPP-nacnac). Transition state (c) is the intermediate to routes (a) and (b).

Although solution experiments are not necessarily representative of the situation in the solid-state, the repeated observation of [Ca(DIPP-nacnac)(NH_2)]$_2$ as one of the major products makes it plausible that the residues of solid-state decomposition of previously reported metal–amidoborane–ammine complexes also contain the NH_2^- ion. As the decomposition of $Ca(NH_2BH_3)_2$·$(NH_3)_2$ has been performed at temperatures of up to 300 °C, it is not likely that $Ca(NH_2)_2$ would survive in the residue: $Ca(NH_2)_2$ already decomposes readily to CaNH and NH_3 at 150 °C.[25] However, careful examination of the IR spectrum of the residue of thermally decomposed $Li(NH_2BH_3)_2$·NH_3 shows a large sharp signal at approximately 3260 cm^{-1} and a smaller one at approximately 3310 cm^{-1}.[7] These two signals are reminiscent of the symmetric and asymmetric N–H stretching frequencies in $LiNH_2$, respectively.[26] Likewise, the IR spectrum reported for the residue of thermally decomposed $Mg(NH_2BH_3)_2$·NH_3 showed larger and smaller IR signals at approximately 3280 and 3350 cm^{-1}, respectively.[6] The frequencies and intensities of these signals compare well to the IR spectrum of Mg$(NH_2)_2$ (3272 and 3326 cm^{-1}).[27] Therefore, it is likely that the NH_2^- ion also plays an important role in the mechanism and residue for the dehydrogenation of solid-state metal–amidoborane–ammine complexes.

Conclusion

In conclusion, the introduction of ammine ligands into calcium–amidoborane hydrogen-storage systems completely reroutes the course of thermal decomposition. The NH_3 ligand is actively involved in H_2 formation as a protic hydrogen source and thus restores the natural imbalance between protic and hydridic hydrogen atoms in metal–amidoborane complexes. Because the loss of NH_3 is also an important side-reaction, the hydrogen-production reaction of calcium amidoborane with NH_3 needs to be performed in a closed system. Therefore, it is questionable whether calcium–amidoborane–ammine complexes will be potentially useful for the generation of hydrogen. However, the recently reported magnesium–amidoborane–ammine complex [Mg$(NH_2BH_3)_2$]·NH_3,[6] contains a more-Lewis-acidic Mg^{2+} center, and therefore a more-strongly bound ammine ligand. Consequently, hydrogen produced by heating this material in an open system is only slightly contaminated with NH_3. Therefore, the concept of balancing the protic/hydridic hydrogen ratio by the introduction of NH_3 is still a promising technique, especially for systems containing more-Lewis-acidic metals.

Experimental Section

All experiments were carried out under an argon atmosphere using standard Schlenk-techniques and freshly dried solvents. The following starting materials have been prepared according to literature procedures: [Ca(DIPP-nacnac)$(NH_2)(NH_3)_2$]$_2$,[11] NH_3BH_3,[28] $MeNH_2BH_3$,[28] $iPrNH_2BH_3$,[9] and $DIPPNH_2BH_3$.[9]

Ca(DIPP-nacnac)(NH_2BH_3)·$(NH_3)_2$: [Ca(DIPP-nacnac)(NH_2)·$(NH_3)_2$]$_2$ (500 mg, 0.99 mmol) and NH_3BH_3 (30 mg 0.97 mmol) were dissolved in toluene (8.5 mL) using an ultrasound bath. After standing for 20 min at RT, precipitation of the product as colorless needles started. After 2 h, the crystalline product was separated from the mother liquor by decantation, washed with *n*-pentane (4 mL) and briefly dried under high vacuum (0.01 Torr). Yield: 240 mg, 0.46 mmol, 47 %; $^1H\{^{11}B\}$ NMR (500 MHz, [D_6]benzene, 20 °C): $\delta = -0.45$ (br q, $^3J(H,H) = 4.9$ Hz, 2H; NH_2), 0.21 (s, 6H; NH_3), 1.19 (d, $^3J(H,H) = 6.8$ Hz, 12H; *i*Pr), 1.22 (d, $^3J(H,H) = 6.8$ Hz,

12H; *i*Pr), 1.55 (br t, ^3J(H,H) = 4.9 Hz, 3H; BH_3), 1.72 (s, 6H; Me backbone), 3.21 (sept, ^3J(H,H) = 6.8 Hz, 4H; *i*Pr), 4.75 (s, 1H; backbone), 7.08 ppm (m, 6H; aryl); ^{13}C NMR (75 MHz, [D_6]benzene, 20 °C): δ = 24.8 (*i*Pr), 24.8 (Me backbone), 28.1 (*i*Pr), 93.6 (backbone), 123.7 (aryl), 124.0 (aryl), 141.6 (aryl), 148.8 (aryl), 164.8 ppm (backbone); ^{11}B NMR (160 MHz, [D_6]benzene, 20 °C): δ = −20.7 ppm (q, ^{1}J(B,H) = 85.5 Hz; BH_3); elemental analysis calcd (%) for $C_{29}H_{52}BCaN_5$ (521.65): C 66.77, H 10.05; found: C 65.43, H 9.66.

Ca(DIPP-nacnac)(NH_2BH_3)·(NH_3)$_3$: [Ca(DIPP-nacnac)(NH_2)·(NH_3)$_2$]$_2$ (60 mg, 0.12 mmol) and NH_3BH_3 (3.6 mg 0.12 mmol) were weighed into a J. Young NMR tube. Immediately after addition of [D_6]benzene (600 μL), the NMR tube was closed tight. Within 30 min, all of the NH_3BH_3 had dissolved completely. The resulting solution was slowly cooled to 8 °C. Crystals of Ca(DIPP-nacnac)(NH_2BH_3)·(NH_3)$_3$ were isolated in 85% yield (160 mg, 0.339 mmol). The structure was determined by X-ray diffraction (see below). The crystals dissolved in [D_6]benzene upon heating, which resulted in loss of one molecule of ammonia. Therefore, NMR analysis of this product is essentially the same as that for Ca(DIPP-nacnac)(NH_2BH_3)·(NH_3)$_2$.

Ca(DIPP-nacnac)[NH(Me)BH_3]·(NH_3)$_2$: [Ca(DIPP-nacnac)(NH_2)·(NH_3)$_2$]$_2$ (280 mg, 0.55 mmol) and NH_2(Me)BH_3 (25 mg 0.56 mmol) were dissolved in toluene (4 mL) using an ultrasound bath. After standing for a short period of time at RT, precipitation of the product as colorless needles started. After keeping the reaction mixture at RT for 2 h, it was slowly cooled overnight to −28 °C. Crystals were isolated by decantation, washed with cold *n*-pentane (2 mL) and briefly dried under a high vacuum (0.01 Torr). Yield: 180 mg, 0.37 mmol, 66%; ^{1}H{^{11}B} NMR (500 MHz, [D_6]benzene, 20 °C): δ = −0.49 (br s, 1H; NHMe), 0.24 (s, 6H; NH_3), 1.22 (d, ^3J(H,H) = 6.9 Hz, 24H; *i*Pr), 1.61 (br s, 3H; BH_3), 1.71 (s, 6H; Me backbone), 2.16 (br s, 3H; NHMe), 3.20 (sept, ^3J(H,H) = 6.9 Hz, 4H; *i*Pr), 4.73 (s, 1H; backbone), 7.10 ppm (m, 6H; aryl); ^{13}C NMR (75 MHz, [D_6]benzene, 20 °C): δ = 24.8 (*i*Pr), 24.9 (Me backbone), 28.3 (*i*Pr), 37.9 (NHMe), 93.3 (backbone), 123.9 (aryl), 124.1 (aryl), 141.6 (aryl), 148.7 (aryl), 165.0 ppm (backbone); ^{11}B NMR (160 MHz, [D_6]benzene, 20 °C): δ = −17.1 ppm (q, ^{1}J(B,H) = 85.4 Hz; BH_3); elemental analysis calcd (%) for $C_{30}H_{54}BCaN_5$ (535.67): C 67.27, H 10.16; found: C 67.53, H 9.90.

Ca(DIPP-nacnac)[NH(*i*Pr)BH_3]·(NH_3)$_2$: [Ca(DIPP-nacnac)(NH_2)·(NH_3)$_2$]$_2$ (500 mg, 0.98 mmol) and NH_2(*i*Pr)BH_3 (72 mg 0.98 mmol) were dissolved in toluene (10 mL) under slight heating. The clear solution was kept at RT for 2 h and then subsequently cooled slowly to −28 °C. The colorless needle-like crystals were isolated by decantation, washed with cold *n*-hexane (5 mL) and dried under high vacuum (0.01 Torr). Yield: 275 mg, 0.49 mmol, 50%; ^{1}H{^{11}B} NMR (500 MHz, [D_6]benzene, 20 °C): δ = −1.19 (br s, 1H; *i*PrNH), 0.08 (s, 6H; NH_3), 1.14 (d, ^3J(H,H) = 6.3 Hz; 6H, *i*PrNH), 1.22 (d, ^3J(H,H) = 6.9 Hz, 12H; *i*Pr), 1.24 (d, ^3J(H,H) = 6.9 Hz, 12H; *i*Pr), 1.70 (s, 6H; Me Backbone), 1.73 (br s, 3H; BH_3), 2.70 (sept, ^3J(H,H) = 6.3 Hz, 1H; (*i*Pr)NH), 3.27 (sept, ^3J(H,H) = 6.9 Hz, 4H; *i*Pr), 4.78 (s, 1H; backbone), 7.11 ppm (m, 6H; aryl); ^{13}C NMR (75 MHz, [D_6]benzene, 20 °C): δ = 24.6 (Me backbone), 24.7 (*i*Pr), 25.1 (*i*Pr), 26.0 (*i*PrNH), 28.2 (*i*Pr), 50.2 (*i*PrNH), 93.8 (backbone), 123.8 (aryl), 124.0 (aryl), 141.2 (aryl), 148.4 (aryl), 165.4 ppm (backbone); ^{11}B NMR (160 MHz, [D_6]benzene, 20 °C): δ = −18.8 ppm (q, ^1J(B,H) = 86.0 Hz; BH_3); elemental analysis calcd (%) for $C_{32}H_{58}BCaN_5$ (563.72): C 68.18, H 10.37; found: C 67.48, H 9.95.

Ca(DIPP-nacnac)[NH(DIPP)BH_3]·NH_3: [Ca(DIPP-nacnac)(NH_2)·(NH_3)$_2$]$_2$ (500 mg, 0.98 mmol) and NH_2(DIPP)BH_3 (187 mg, 0.98 mmol) were dissolved in toluene (10 mL). The clear solution was kept at RT for 2 h and subsequently concentrated to about 5 mL. Slow cooling to −28 °C gave thin needle-like crystals that were isolated by decantation, washed with cold *n*-hexane (5 mL) and briefly dried under high vacuum (0.01 Torr). Yield: 310 mg, 0.47 mmol, 48%. ^{1}H{^{11}B} NMR (500 MHz, [D_6]benzene, 20 °C): δ = 0.64 (s, 3H; NH_3), 1.09 (d, ^3J(H,H) = 6.6 Hz, 12H; *i*Pr in NH(DIPP)BH_3), 1.19 (d, ^3J(H,H) = 6.8 Hz, 12H; *i*Pr), 1.21 (d, ^3J(H,H) = 6.8 Hz, 12H; *i*Pr), 1.65 (s, 6H; Me backbone), 2.06 (br s, 3H; BH_3), 2.27 (sept, ^3J(H,H) = 6.6 Hz, 2H; *i*Pr in NH(DIPP)BH_3), 2.69 (br s, 1H; NH in NH(DIPP)BH_3), 3.16 (sept, ^3J(H,H) = 6.8 Hz, 4H; *i*Pr), 4.73 (s, 1H; backbone), 6.98 (m, 3H; aryl NH(DIPP)BH_3) 7.11 ppm (m, 6H; aryl); ^{13}C NMR (75 MHz, [D_6]benzene, 20 °C): δ = 24.2 (Me backbone), 24.2 (*i*Pr NH(DIPP)BH_3), 24.3 (*i*Pr), 24.9 (*i*Pr), 28.3 (*i*Pr), 29.1 (*i*Pr in NH(DIPP)BH_3), 93.3 (backbone), 121.1 (aryl in NH(DIPP)BH_3), 123.4 (aryl in NH(DIPP)BH_3), 124.0 (aryl), 125.0 (aryl), 132.2 (aryl in NH(DIPP)BH_3), 136.3 (aryl) 138.1 (aryl in NH(DIPP)BH_3), 141.5 (aryl), 166.0 ppm (backbone); ^{11}B NMR (160 MHz, [D_6]benzene, 20 °C): δ = −18.8 ppm (br s, BH_3); elemental analysis calcd (%) for $C_{41}H_{68}BCaN_5$ (681.89): C 72.21, H 10.05; found: C 71.86, H 9.93.

[Ca(DIPP-nacnac)(NH_2)]$_2$: This complex was isolated from the thermal decomposition of Ca(DIPP-nacnac)(NH_2BH_3)·(NH_3)$_2$ in benzene. However, it can be obtained more conveniently as a side-product in the synthesis of [Ca(DIPP-nacnac)(NH_2)·(NH_3)$_2$]$_2$. Ca(DIPP-nacnac)[N(SiMe$_3$)$_2$]·THF (4.00 g, 5.80 mmol) was dissolved in *n*-hexane (40 mL). Dry NH_3 was bubbled through the solution and, after a few minutes, a white precipitate started to form. This precipitate was isolated and dissolved in warm *n*-hexane (50 mL). Slowly cooling this solution to −27 °C gave crystals of [Ca(DIPP-nacnac)(NH_2)·(NH_3)$_2$]$_2$. Concentrated of the mother liquor to a volume of 10 mL followed by repeated cooling to −27 °C gave colorless crystals of [Ca(DIPP-nacnac)(NH_2)]$_2$. Yield: 0.82 g, 0.87 mmol, 30%; ^{1}H NMR (300 MHz, [D_6]benzene, 20 °C): δ = −1.20 (s, 4H; NH_2), 0.99 (d, ^3J(H,H) = 6.9 Hz, 24H; *i*Pr), 1.33 (d, ^3J(H,H) = 6.9 Hz, 24H; *i*Pr), 1.68 (s, 12H; Me backbone), 3.15 (sept, ^3J(H,H) = 6.9 Hz, 8H; *i*Pr), 4.81 (s, 2H; H backbone), 7.04–7.13 ppm (m, 12H; aryl); ^{13}C NMR (75 MHz, [D_6]benzene, 20 °C): δ = 24.5 (Me backbone), 25.0 (*i*Pr), 25.5 (*i*Pr), 28.2 (*i*Pr), 94.8 (backbone), 124.7 (aryl), 125.2 (aryl), 142.4 (aryl), 146.0 (aryl), 165.7 ppm (backbone); elemental analysis calcd (%) for $C_{58}H_{86}Ca_2N_6$ (947.49): C 73.52, H 9.15; found: C 72.82, H 9.19.

Thermal decomposition of calcium–amidoborane–ammine complexes in benzene solution: A typical procedure for thermal decomposition of a calcium–amidoborane complex is described. Ca(DIPP-nacnac)(NH_2BH_3)·(NH_3)$_2$ (30 mg, 0.058 mmol) was added to a J. Young NMR tube and subsequently dissolved in [D_6]benzene (0.6 mL). This solution was heated stepwise at 10 °C increments and the decomposition process was regularly monitored by ^{1}H NMR spectroscopy. Protonation of the DIPP-nacnac anion already started at 30 °C. At the same temperature, an amorphous colorless compound started to precipitate. This precipitate is also insoluble in polar solvents like THF and, although its exact composition could not be verified, it does not contain the DIPP-nacnac ligand. From 50 °C and above, the formation of H_2 was observed (^{1}H NMR signal at 4.43 ppm). At these temperatures, the formation of a crystalline product was also observed. Isolation and crystallographic characterization revealed the product Ca(DIPP-nacnac)(NH_2BH_3)·NH_3. These crystals slowly dissolved with time. This polymeric complex was insoluble in benzene but dissolved well in [D_8]THF in which it showed the same NMR data as reported earlier for Ca(DIPP-nacnac)(NH_2BH_3)·(THF)$_2$.[8] After heating at 60 °C for 6 days, the ^{1}H NMR spectrum did not change any more and only showed signals of DIPP-nacnacH and [Ca(DIPP-nacnac)(NH_2)]$_2$. The latter product can be crystallized by concentrating and cooling the solution (yield: 36%). The mother liquor did not give any signals in the ^{11}B NMR spectrum and is likely free of boron-containing products. The amorphous white precipitate is presumably a mixture of Ca(NH_2)(NH_2BH_3) and insoluble $B_xN_yH_z$ polymers. Thermolysis of the other complexes gave similar results; Ca(DIPP-nacnac)[NH(*i*Pr)BH_3]·(NH_3)$_2$ and a few crystals of the donor-free complex [Ca(DIPP-nacnac){NH(*i*Pr)BH_3}]$_2$ were isolated. The latter complex could not be prepared in larger quantities.

Crystal structure determination: Detailed information can be found in the Supporting Information. CCDC-832156 (Ca(DIPP-nacnac)(NH_2BH_3)·(NH_3)$_3$), CCDC-832157 ([Ca(DIPP-nacnac){NH(*i*Pr)BH_3}]$_2$), CCDC-832158 ([Ca(DIPP-nacnac)(NH_2BH_3)·NH_3]$_\infty$), CCDC-832159 (Ca(DIPP-nacnac)(NH_2BH_3)·NH_3·THF), CCDC-832160 ([Ca(DIPP-nacnac)(NH_2)]$_2$), 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.

Acknowledgements

We thank Prof. Dr. R. Boese and D. Bläser for the collection of the X-ray data and acknowledge the DFG for financial support.

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Received: July 1, 2011
Revised: September 21, 2011
Published online: January 16, 2012

