Group 2 Promoted Hydrogen Release from NMe$_2$H·BH$_3$: Intermediates and Catalysis

David J. Liptrot, Michael S. Hill,* Mary F. Mahon, and Dugald J. MacDougall$^{[a]}$

Abstract: Both homo- and heteroleptic alkyl and amide complexes of the Group 2 elements Mg and Ca are shown to be active for the catalytic dehydrocoupling of Me$_2$NH·BH$_3$. Reactions of either magnesium dialkyls or the β-diketiminate complex [HC{(Me)CN(Dipp)}$_2$MgBu] with four or two equivalents of Me$_2$NH·BH$_3$, respectively, produce compounds containing the [H$_3$BNMe$_2$BH$_2$Me$_2$N]$^+$ ion, which coordinates to the magnesium centers through Mg–N and Mg–HB interactions in both the solution and solid states. Thermolysis of these compounds at 60°C produces the cyclic product [[H$_3$BNMe$_2$]$_2$] and, it is proposed, magnesium hydrido species by an unprecedented δ-hydride elimination process. Calcium-based species, although less reactive than their magnesium-based counterparts, are found to engage in similar dehydrocoupling reactivity and to produce a similar distribution of products under thermally promoted catalytic conditions. A mechanism for these observations is presented that involves initial production and insertion of H$_2$B=NM$_2$ into polarized M–N bonds as the major B–N bond-forming step. The efficacy of this insertion and subsequent β- or δ-hydride elimination steps is proposed to be dependent upon the charge density and polarizing capability of the participating Group 2 center, providing a rationale for the observed differences in reactivity between magnesium and calcium.

Introduction

Driven by the possible use of ammonia–borane (H$_3$N·BH$_3$) as a chemical storage medium for H$_2$,$^{[1]}$ the formation of boron–nitrogen σ bonds by the catalytic dehydrocoupling of amine–boranes is currently receiving a great deal of attention.$^{[2]}$ Manners, for example, has reported that dehydrocoupling of Me$_2$NH·BH$_3$ to oligomeric or polymeric compounds may be effected by both homo- and heterogeneous Group 9 species.$^{[3]}$ Exemplified by this work, most progress has been based around the study of mid or late transition metals and relatively little attention has been directed toward d$^0$ species of the early transition metals (Groups 3–5) or metals of Groups 1 and 2.$^{[4]–[6]}$ In contrast to the reactivity derived from low oxidation state or more electron-rich catalytic centers, these series of metals must necessarily preclude the possibility of B–H oxidative addition (via B–H·borane complexes)$^{[7]}$ and/or B–N reductive elimination as pathways toward amidoborane formation.$^{[8]}$ Keller demonstrated in the 1970s that more complex amidoboranes could be prepared by a combination of R$_3$N– for H exchange and H$_2$ elimination from the interaction of either lithium primary amides and B$_2$H$_6$ or alkali metal hydrides and amine–boranes.$^{[9]}$ A recent report by Sneddon and co-workers has highlighted the ability of the strong, non-nucleophilic base bis(dimethylamino)naphthalene and the Group 1 derivatives lithium and potassium triethylborohydride to effect H$_2$N·BH$_3$ dehydrogenation by initial nitrogen deprotonation to form [H$_3$BNH$_2$]$^-$ and subsequent anionic dehydropropolimerization.$^{[9]}$ Although hydrogen release may be promoted by solid-state ball milling with MgH$_2$, and conversion of H$_2$N·BH$_3$ to the crystallographically characterized calcium amidotrihydroborates [Ca(NH$^+$BH$_3$)$_n$(thf)$_m$] ($n=0, 1, 2$) has been reported to result in significantly reduced hydrogen release temperatures, these solid-state reactions are, necessarily, mechanistically uncertain.$^{[10,11]}$ Two years ago we reported that o-bond metathesis reactions of β-diketiminato calcium amides with the secondary organoborane 9-BBN (9-borobicyclo[3.3.1]nonane) result in the formation of B–N bonded species and a calcium hydride as the reaction products.$^{[12]}$ More recently, Harder has reported that sequential H$_2$ elimination can be induced from β-diketiminato calcium...

Keywords: boranes · calcium · dehydrocoupling · magnesium · structure elucidation

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DOI: 10.1002/chem.201000127
amidoborane derivatives of both $\text{H}_2\text{N}·\text{BH}_3$ itself and $\text{BH}_3$ adducts of primary amines and anilines.$^{[13]}$ In these cases further thermally induced $\text{B}–\text{N}$ formation apparently occurred via the intermediacy of dimeric calcium complexes of the complex dianions $[\text{RN}·\text{BH}·\text{NR}·\text{BH}_3]^-$ ($\text{R} = \text{H}; \text{Me}; \text{iPr}$). In cases in which dimerization was not possible, unimolecular $\text{H}_2$ elimination provided species containing coordinated imidoborane anions. Most recently, the same group reported that di-$n$-butyl magnesium or a $\beta$-diketiminato-supported magnesium silylamide are capable of the catalytic dehydrocoupling of the primary anilino–borane, $(\text{Dipp})\text{NH}_2\text{BH}_3$ (Dipp = 2,6-di-iso-propylphenyl), via the intermediacy of a structurally characterized magnesium anilido species, $[\text{HC}·(\text{Me})\text{CN}(\text{Dipp})]_2\text{Mg}[\text{NH}(\text{Dipp})\text{BH}_3]$ (I), in the case of the heteroleptic derivative.$^{[6]}$ The only dehydrocoupled product to be fully characterized was $[\text{HB}[\text{NH}(\text{Dipp})]]_2$, proposed to be the result of $\text{B}$-hydride elimination and $\text{BH}_3$ evolution from a more complex, but unidentified, species derived from I containing an additional $\text{B}–\text{N}$ linkage (Scheme 1). Although sound precedent has been provided for the intermediacy of a resultant magnesium hydride by the same authors’ isolation of a tetrahydridoborane magnesium species from this reaction and their synthesis of the zinc hydride II via an analogous zinc primary amidoborane derivative,$^{[6a,b]}$ no rationale was developed for the mechanism of $\text{B}–\text{N}$ bond formation and concurrent $\text{H}_2$ elimination to provide the complex intermediate $[(\text{Dipp})\text{NH}·\text{BH}·\text{NH}·(\text{Dipp})\text{BH}_3]$ ion during the dehydrocoupling reaction (Scheme 1). Rather, these authors suggested that this central step simply occurs by a mechanistically undefined reaction of the isolated magnesium amidoborane with the acidic amonma–borane $(\text{Dipp})\text{NH}_2\text{BH}_3$.$^{[6a]}

Following the example of Manners and coworkers,$^{[5]}$ we have initiated a program of study of the reactions of Group 2 metal alkyls and amides with $\text{Me}_2\text{NHBH}_3$ and propose a mechanism that accounts for the observed reactivity of these more substituted amine-containing substrates.

**Results and Discussion**

A reaction between four equivalents of $\text{Me}_2\text{NH}·\text{BH}_3$ and either di-$n$-butyl magnesium or the more crowded alkyl derivative $[\text{Mg}[\text{CH}·(\text{SiMe}_3)_2]_2(\text{thf})]$ in THF produced a steady stream of bubbles and evidence of immediate protonation of all the alkyl residues by $\text{^1H NMR}$ spectroscopy. The corresponding proton-coupled $\text{^11B NMR}$ spectra revealed the complete disappearance of a resonance attributable to the $\text{Me}_2\text{NH}·\text{BH}_3$ starting material ($\delta_{\text{^11B}} = 11.9$ ppm, $\text{J}_{\text{BH}} = 97.3$ Hz) and evidence of two new boron environments observed at 4.0 and $–15.3$ ppm, which appeared as triplet ($\text{J}_{\text{BH}} = 102$ Hz) and quartet ($\text{J}_{\text{BH}} = 89$ Hz) signals, respectively. The origin of these observations was revealed by a single-crystal X-ray diffraction analysis performed upon crystals of compound I isolated from hexane. Details of this X-ray analysis are given in Table 1 and selected bond length and angle data are provided in the caption to Figure 1. As shown in Figure 1, compound I is a discrete magnesium complex in which the magnesium coordination sphere is composed of a molecule of THF and two borylamido anions, $[\text{HBNMe}_2\text{BH}_2\text{Me}_2\text{N}]^–$. These latter ligands may be considered as the deprotonated form of $\text{H}_2\text{BNMe}_2\text{BH}_2\text{Me}_2\text{N}$ (II).$^{[15]}$ The product of a single dehydrocoupling reaction between two $\text{Me}_2\text{NHBH}_3$ molecules. Although II has previously been postulated as a key intermediate in the catalytic dehydrocoupling of $\text{Me}_2\text{NH}·\text{BH}_3$ and the dianionic species $[\text{HBNBHBNH}]^{2–}$ has been identified from the calcium-induced dehydrocoupling of ammonia–borane itself,$^{[13a,4c,12a]}$ to the best of our knowledge, the ligand within compound I is the first example of this particular anion to be crystallographically characterized. The primary interactions between the $[\text{HBNMe}_2\text{BH}_2\text{Me}_2\text{N}]^–$ ions and magnesium are provided by the formally deprotonated nitrogen atom of each ligand. The observed bond lengths ($\text{Mg}–\text{N} = 2.1649(11)$, $\text{Mg}–\text{N} = 2.1684(11)$ Å) are considerably longer than those observed between magnesium and the anilidoborane anion within I ($\text{Mg}–\text{N} = 2.083(4)$ Å), but are only slightly elongated in comparison to those within $\text{Mg}·\text{Me}_2\text{C}_2\text{H}_2\text{BNMe}_3$ ($\text{Mg}–\text{N} = 2.140(5)$, $2.142(3)$ Å), in which the three-coordinate boron center forms part of a delocalized boratabenzene fragment.$^{[14]}$ Coordination to magnesium evidently produces only minor perturbations to the boron–nitrogen bond lengths of the chelated anion in comparison to the crystallo-

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Table 1. Crystallographic data for compounds 1, 2, and 4.

|     | 1         | 2         | 4         |
|-----|-----------|-----------|-----------|
| formula | C_{6}H_{12}B_{2}MgN_{2}O | C_{6}H_{6}B_{2}MgN_{2} | C_{6}H_{6}B_{2}CaN_{2}O |
| M_{r} [g mol⁻¹] | 326.05 | 556.76 | 587.73 |
| crystal system | triclinic | monoclinic | orthorhombic |
| space group | P_{1} | P_{2}_{1}/a | P_{n} |
| α [Å] | 9.4110(2) | 11.890(3) | 18.402(2) |
| β [Å] | 8.350(2) | 15.050(4) | 19.940(3) |
| γ [Å] | 13.1350(3) | 19.3270(3) | 10.1400(1) |
| α [°] | 103.802(1) | 90 | 90 |
| β [°] | 111.340(1) | 90 | 90 |
| γ [°] | 94.767(1) | 91.311(1) | 90 |
| Z | 2 | 4 | 4 |
| μ [mm⁻¹] | 0.086 | 0.078 | 0.196 |
| μ [g cm⁻³] | 1.003 | 1.069 | 1.049 |
| θ range [°] | 3.65–30.22 | 3.69–27.45 | 3.66–25.03 |
| measured/independent reflections | 21626/629/ | 48225/786/ | 51539/336/ |
| F_{o} wR_{2} [I > 2σ(I)] | 0.0484 | 0.0533 | 0.0465 |
| F_{o} wR_{2} (all data) | 0.0712, 0.1338 | 0.0825, 0.1514 | 0.0740, 0.1800 |

[a] R_{1} = Σ||F_{o}||–|F_{c}||/Σ||F_{c}||; [b] wR_{2} = [Σ[w(F_{o}²−F_{c}²)²]^{1/2}/Σ[w(F_{c}²)]^{1/2}]^{1/2}.

Figure 1. ORTEP representation of compound 1 (50% probability ellipsoids). H atoms except for those bonded to boron are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N1 2.1649(11), Mg1–N3 2.1684(11), Mg1–O1 2.0839(3), Mg1–H2D 2.12, Mg1–H4D 2.11, Mg1–H2E 2.16, Mg1–H4E 2.16, N1–B1 1.5647(17), B1–N2 1.6131(17), N4–B4 1.5731(18), O1–Mg1–N1 97.60(4), O1–Mg1–N3 97.27(4), N1–Mg1–N3 165.13(4).

Figure 2. Variable-temperature ¹H{¹¹B} NMR spectra of the –NMe₂ and –BH₃ regions of compound 1 recorded 228–288 K. Exchanging partners described in text are indicated by * (ΔG° = 42.4 kJ mol⁻¹), ● (ΔG° = 46.6 kJ mol⁻¹) and ▲ (ΔG° = 44.1 kJ mol⁻¹) symbols.

Figure 3. Variable-temperature ¹H{¹¹B} NMR spectra of the –NMe₂ and –BH₃ regions of compound 2 recorded 228–288 K. Exchanging partners described in text are indicated by * (ΔG° = 42.4 kJ mol⁻¹), ● (ΔG° = 46.6 kJ mol⁻¹) and ▲ (ΔG° = 44.1 kJ mol⁻¹) symbols.

Figure 4. Variable-temperature ¹H{¹¹B} NMR spectra of the –NMe₂ and –BH₃ regions of compound 3 recorded 228–288 K. Exchanging partners described in text are indicated by * (ΔG° = 42.4 kJ mol⁻¹), ● (ΔG° = 46.6 kJ mol⁻¹) and ▲ (ΔG° = 44.1 kJ mol⁻¹) symbols.

Figure 5. Variable-temperature ¹H{¹¹B} NMR spectra of the –NMe₂ and –BH₃ regions of compound 4 recorded 228–288 K. Exchanging partners described in text are indicated by * (ΔG° = 42.4 kJ mol⁻¹), ● (ΔG° = 46.6 kJ mol⁻¹) and ▲ (ΔG° = 44.1 kJ mol⁻¹) symbols.

graphically characterized species III (B–N1: 1 1.5647(17), III 1.599(2); B–N2: 1 1.6145(17), III 1.589(2); B–N2: 1 1.5762(17), III 1.600(2) Å). Although the B–N bond lengths across the -NHBBNH- unit of the bridging and calcium-coordinated dianionic species, [H₂B₂(HBBH₂)₂]⁻, (CaNH–BH: 1.419(5); NH–BH(NH): 1.451(6) Å) were greatly shortened in comparison to the relevant B–N bond lengths within the structure of 1, the bond lengths to the “terminal” –BH₃ component of both anions are significantly shortened within 1 (B–N2: 1 1.5762(17) and B3–N3: 1.5646(17) versus 1.593(6) Å). These variations are likely to be a result of both the widely differing charge distribution across the two NBNB moieties, as well as the reduced number of metal-to-ligand contacts within the strictly mononuclear species 1. Monitoring of the B–H region of the ¹H{¹¹B} NMR spectrum between 228 K and 288 K provided evidence for two independent fluxional processes in [D₃]toluene. At temperatures below 258 K, the resonances associated with the BH₃ unit of the ligand backbone occupy diastereotopic environments, most likely owing to the maintenance of a conformation of the chelated ligand similar to that observed in the solid state (Figure 2). The coalescence of these resonances is possibly indicative of either rapid coordination/de-coordination of the THF co-ligand or a facile conformational interconversion process (ΔG° = 44.1 kJ mol⁻¹) at temperatures above 258 K. The resonances associated with the BH₃ units of compound 1 also displayed a rather more complex decoupling event at low temperature (<248 K), suggestive of a low-energy conformational change, possibly involving the rapid coordination and de-coordination of terminal and Mg-bound hydrides. Although a value for T_c could not be accurately determined for this latter event, both processes indicate that the coordination of the NBNB–H chelate to magnesium is, to some extent, retained in toluene. The occurrence of these processes was rather more clearly defined through monitoring of the N–Me region of the same series of variable temperature spectra (Figure 2). Again two fluxional events were apparent at temperatures below 258 K and provided free energies of activation for both processes (for ΔH = −2.33 ppm, ΔG° = 42.4 kJ mol⁻¹; for ΔH = −2.23 ppm, ΔG° = 46.6 kJ mol⁻¹) effectively identical to that deduced for the boron-centered unit within the limits of the experimental observations.

Heating a solution of compound 1 in C₆D₆ to 60°C, monitored by ¹¹B NMR spectroscopy over the course of four days, resulted in the disappearance of the signals attributed to the [H₂B₂(Me₂)BH₂Me₂]⁻ ligand and the appearance of a new triplet signal centered at δ = 5.2 ppm (J_HH = 108 Hz). This species was identified as the cyclic dimer.
[H₂BNMe₂]₂ by comparison to literature data.[5a] Although no Mg–H resonance could be observed, we propose that this species is produced by means of an intramolecular σ-bond metathesis and an effective δ-hydride elimination (Eq. 1).[5a] In support of this hypothesis, no evidence for the formation of the BH₄⁻ ion, a necessary consequence of the previously described δ-hydride- and BH₃-elimination based chemistry reported for primary anilidoborane dehydrocoupling was observed.[5a]

In an attempt to extend the generality of this chemistry and to provide a positive means of identification of the proposed magnesium hydride produced by this process we sought to synthesize a potentially more tractable magnesium species containing the [H₂BNMe₂BH₂Me₂N]⁺ ion. A reaction of the β-diketiminate complex [HC{(Me)CN-(Dipp)}₂MgH][(Dipp)MgH(thf)]₆[16] identified by comparison to the ¹H NMR literature data and again indicative of a reaction pathway analogous to the δ-hydride elimination illustrated in Scheme 1, but involving the δ-located BH₃ unit within the chelated anion of 2.

Irrespective of the mode of formation of the intermediate [H₂BNMe₂BH₂Me₂N]⁺ ion (see below), the apparent production of a hydrido species indicated that the dehydrocoupling of Me₂NHₓBH₃ at a Group 2 center may be extended to a viable catalytic regime by the consecutive protonolysis/σ-bond metathesis mechanism illustrated in Scheme 2.

To test this hypothesis, the catalytic dehydrocoupling reaction of Me₂NHₓBH₃ utilizing 5 mol% [Mg(CH(SiMe₃)₂)]₂(thf)₃ as catalyst in C₆D₆ was attempted at 60°C and monitored by ¹¹B NMR spectroscopy. Although quite slow, the catalytic dehydrocoupling protocol illustrated by Scheme 2 provided clean and selective conversion to the dimerized species [([H₂BNMe₂]₂)] over the course of 72 h. A number of notable features were also apparent from inspection of the ¹¹B NMR spectra recorded during the dehydrocoupling process (Figure 4). The presence of a BH₃ unit of an intermediate analogous to the Mg-coordinated [H₂BNMe₂BH₂Me₂N]⁺ species observed in the well-defined compounds 1 and 2 was inferred from the presence of a low intensity triplet at about 9 ppm (J₃= 92 Hz) was not assigned to the corresponding BH₃ component of the anion, on the basis of the signal intensity and the lower field chemical shift compared to those observed in either 1 or 2. Rather, on the basis of a ¹¹B-¹³B correlation...
experiment, this low intensity signal is proposed to be obscured by the quartet resonance of the Me$_2$NH$_2$-BH$_3$ starting material and it is notable that Weller and co-workers have recently made similar deductions during studies of theRh-catalyzed dehydrocoupling of the same substrate.\cite{40} Having tentatively assigned a similar downfield triplet resonance to the trimerized species [(H$_2$BNMe$_2$)$_3$] in their original communication,\cite{4e} this group later revised their assignment of this resonance as arising from the BH$_2$ unit of the neutral product III. Through comparison to the deshielded environments observed for heavier metal derivatives of the same ligands (see below), the more intense downfield signal at −9 ppm is proposed to arise from a magnesium-coordinated anion derived by deprotonation of a single equivalent of the Me$_2$NH-BH$_3$ starting material. The dianinoborane HB-(NMMe)$_2$ was also observed at early stages of, and throughout, the course of the reaction. Although the reaction of HB(NMMe)$_2$ with diborane has been reported to result in longer chain amine–borane derivatives,\cite{49} this species was not consumed and our supposition is that this species is formed through a parallel but less significant reaction pathway involving elimination of a β-hydride from the coordinated [H$_2$BNMe$_2$BH$_2$Me$_2$N]~$^-$ ion followed by loss of BH$_3$~\cite{27} A similar β-hydride elimination has been proposed to occur during the magnesium-catalyzed production of [HB(H-Dipp)]$^-$ from (Dipp)NH$_2$BH$_3$~\cite{49} Although in this last case the occurrence of BH$_3$ elimination was supported by the isolation of a magnesium tetrahydridoborate, we have observed no evidence for this process and assume that BH$_3$ is displaced as B$_2$H$_6$ and one of the, as yet, unmonitored gaseous by-products.

We have recently reported a series of homoleptic Group 2 bis(trimethylsilyl)methyl derivatives of the form [M(CH-(SiMe$_3$)$_2$)(thf)]$_n$ (M = Ca, n = 2), which can function as basic derivatives for the exploration of heavier alkaline earth reaction chemistry.\cite{33} Accordingly, NMR monitoring of reactions of compound 3 with either two or four molar equivalents of Me$_2$NH-BH$_3$ produced immediate and complete protonation of the bis(trimethylsilyl)methyl ligands and the appearance of a single new resonance in the $^{11}$B NMR spectrum at −11.3 ppm. No triplet resonance assignable to the appearance of a [H$_2$BNMe$_2$BH$_2$Me$_2$N]~$^+$ ion, such as that observed in compounds 1 and 2, was observed at room temperature. Although no tractable single products have yet been isolated from this reaction, a further stoichiometric reaction between the β-diketiminate calcium amide [HC(Me)CN(Dipp)]$_2$Ca[N(SiMe$_3$)$_2$](thf)] and Me$_2$NH-BH$_3$ provided a significant insight into these observations. This reaction provided smooth access at room temperature to the simple amidoborane derivative [HC(Me)CN(Dipp)]$_2$Ca[NMe$_2$BH$_3$](thf)] (4), irrespective of the presence of an excess of the amine–borane reagent. Compound 4 provided a quartet resonance at −11.5 ppm ($^{11}$J$_{BB}$ = 86 Hz) in its $^{11}$B NMR spectrum and has been fully characterized by multinuclear NMR spectroscopy, elemental analysis, and a single-crystal X-ray structural analysis, the results of which are shown in Figure 5. Details of the crystallographic analysis are given in Table 1 and selected bond length and angle data are provided in the caption to the figure. The centrosymmetric structure consists of a mononuclear calcium complex in which the primary coordination to the metal is provided by the κ$^2$-N,N’-β-diketiminate and the κ$^2$-N,BH dimethylamidoborane ligands, augmented by a molecule of THF.

The Ca–N distances to the amidoborane unit (Ca1–N2, 2.375(3) Å) of 4 are comparable to those observed in both the polymeric calcium amidoborane derivative, [[Ca(NH$_2$BH$_2$)$_2$]$_3$]$_{118}$ (Ca–N 2.383 Å) and those within Harder’s similarly mononuclear β-diketiminate calcium primary isopropylamido and anilido derivatives, [HC(Me)CN(Dipp)]$_2$Ca[NH(R)BH$_2$](thf)] (R = iPr, 2.406(4); R = 2,6-iPr$_2$C$_6$H$_3$, 2.460(2) Å).\cite{13b} Although the parent amidoborane species [HC(Me)CN(Dipp)]$_2$Ca[NH$_2$BH$_3$](thf)] was report-
ed to be highly unstable,\textsuperscript{[13a]} like these last two derivatives, compound 4 displayed notable thermal stability at elevated temperatures and monitoring of a sample of compound 4 in C\textsubscript{6}D\textsubscript{6} heated to 80°C for 4 h evidenced <10% decomposition. Although small quantities of HB(NMe\textsubscript{2})\textsubscript{2} were again apparent, perhaps significantly, a low intensity resonance at about 36 ppm was also observed, which may be assigned to monomeric Me\textsubscript{2}N=BH\textsubscript{3}.\textsuperscript{[4a,i]} Careful inspection of the \textsuperscript{1}H NMR spectrum of this thermal reaction also provided evidence for the formation of the known β-diketiminato calcium hydride [HC[(Me)CN(Dipp)]\textsubscript{2}CaH(thf)]\textsubscript{2},\textsuperscript{[19]} and we thus tentatively suggest that compound 4 undergoes a thermally induced β-hydride elimination/intramolecular α-bond metathesis process under these conditions. Although [H\textsubscript{2}BNMe\textsubscript{2}]\textsubscript{2} was not observed under these conditions, preliminary observations of stoichiometric and catalytic reactions of both HC[(Me)CN(Dipp)]\textsubscript{2}Ca[N(SiMe\textsubscript{3})\textsubscript{2}](thf) and the calcium dialkyl compound 3 with Me\textsubscript{2}NH-BH\textsubscript{3} provided \textsuperscript{11}B NMR spectra similar to those illustrated in Figure 4 and evidence for [H\textsubscript{2}BNMe\textsubscript{2}]\textsubscript{2} formation by a common and sequential protonolysis-metathesis pathway.

The observation of Me\textsubscript{2}N=BH\textsubscript{3} during the course of these reactions and the highly specific formation of [H\textsubscript{2}BNMe\textsubscript{2}BH\textsubscript{2}Me\textsubscript{2}]\textsuperscript{+} ions observed during the course of these d\textsubscript{0}-catalyzed reactions alongside the apparent metal hydride formation from amidoborane elimination from both dimerized and non-dimerized amidoborane anions leads us to suggest the preliminary mechanism for catalytic Me\textsubscript{2}NH-BH\textsubscript{3} dehydrocoupling illustrated in Scheme 3.\textsuperscript{[28]} Under this regime, catalytic B–N bond formation and turnover is entirely upon production and insertion of the unsaturated (and polarized) species Me\textsubscript{2}N=BH\textsubscript{3} (transition state, inset Scheme 3) to form a key catalytic intermediate containing the [H\textsubscript{2}BNMe\textsubscript{2}BH\textsubscript{2}Me\textsubscript{2}]\textsuperscript{+} ion. Subsequent formation of the amidoborane products, [(H\textsubscript{2}BNMe\textsubscript{2})\textsubscript{2}] and HB(NMe\textsubscript{2})\textsubscript{2}, is then dictated by the relative energetics of two possible intramolecular B–HM–N α-bond metathesis (or δ-hydride versus β-hydride elimination) steps.

Although the individual species implicated in the mechanism summarized in Scheme 3 are similar to those postulated during transition-metal-catalyzed dehydrocoupling of amine–boranes and that recently proposed for H\textsubscript{2} release from lithium and magnesium amidoboranes,\textsuperscript{[1,6a,21]} the course of these d\textsubscript{0}-catalyzed reactions raises several issues suitable for more widespread exploration. We have previously described the effect of cation radius and charge density of Group 2 cations on the relative efficacy of metal-substituent bonds toward both polarized α-bond metathesis and insertion of unsaturated units.\textsuperscript{[22]} The contrast between the activity of the Mg- and Ca-based systems indicates that the suitability of a particular d\textsubscript{0} cation toward amine–borane dehydrocoupling may be dictated by similar considerations. We are continuing to explore this possibility for a greater range of Group 2 species and to extend this study to similarly redox-inactive centers of increasing charge density and polarizing power.

**Experimental Section**

**General experimental procedures:** All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox. NMR spectra were collected on a Bruker AV300 spectrometer operating at 75.5 MHz (\textsuperscript{1}H), 96.3 MHz (\textsuperscript{11}B). Variable-temperature \textsuperscript{1}H NMR data were recorded on a Bruker AV400 spectrometer. The spectra were referenced relative to residual solvent resonances or an external BF\textsubscript{3}OEt\textsubscript{3} standard (\textsuperscript{11}B). Solvents (toluene, THF; hexane) were dried by passage through a commercially available (Innovative Technologies) solvent purification system, under nitrogen and stored in ampoules over molecular sieves. C\textsubscript{4}D\textsubscript{0} and [D\textsubscript{2}]toluene were purchased from Goss Scientific Instruments and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. Di-n-butylmagnesium (1.0 M solution

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Figure 5. ORTEP representation of compound 4 (25% probability ellipsoids). Isopropyl methyl carbons and H atoms except for those bonded to boron are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ca1–N1 2.335(17), Ca1–N2 2.375(3), N2–B1 1.497(6), Ca1–O1 2.352(2); N1–Ca1–N1’ 81.71(8), N1–Ca1–O1 101.92(6), N1–Ca1–N2 113.99(7), O1–Ca1–N2 131.64(1). Symmetry transformations used to generate equivalent atoms: x, −y+1, z.
were truncated to a value of 25° due to a fall off in diffraction at higher resolution. H1a and H1b were located and refined subject to being similar in C distances were restrained to be similar where disorder of the carbon 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 the Nuffield Foundation for the provision of a summer studentship.

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Received: January 18, 2010
Published online: June 11, 2010