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Group 2 Promoted Hydrogen Release from $NMe_2H{\cdot}BH_3$: Intermediates and Catalysis

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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 $Me_2NH{\cdot}BH_3$. Reactions of either magnesium dialkyls or the β-diketiminate complex $[HC\{(Me)CN(Dipp)\}_2Mg\textit{n}Bu]$ with four or two equivalents of Me_2NHBH_3, respectively, produce compounds containing the $[H_3BNMe_2BH_2Me_2N]^-$ 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 $[(H_2BNMe_2)_2]$ 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 $H_2B{=}NMe_2$ 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.

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

Introduction

Driven by the possible use of ammonia–borane ($H_3N{\cdot}BH_3$) 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 $MeNH_2{\cdot}BH_3$ 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 σ-borane complexes)[7] and/or B−N reductive elimination as pathways toward amidoborane formation.[1c] Keller demonstrated in the 1970s that more complex amidoboranes could be prepared by a combination of R_2N- for H exchange and H_2 elimination from the interaction of either lithium primary amides and B_2H_6 or alkali metal hydrides and amine–boranes.[8] 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 $H_3N{\cdot}BH_3$ dehydrogenation by initial nitrogen deprotonation to form $[H_3BNH_2]^-$ and subsequent anionic dehydropolymerization.[9] Although hydrogen release may be promoted by solid-state ball milling with MgH_2, and conversion of $H_3N{\cdot}BH_3$ to the crystallographically characterized calcium amidotrihydoborates $[Ca(NH_2BH_3)_2(thf)_n]$ ($n=0$, 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 σ-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

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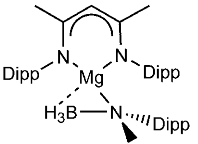
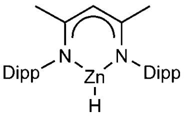
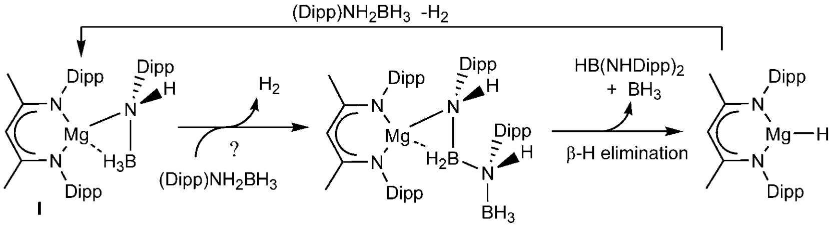
amidoborane derivatives of both $H_3N{\cdot}BH_3$ itself and BH_3 adducts of primary amines and anilines.[13] In these cases further thermally induced B−N formation apparently occurred via the intermediacy of dimeric calcium complexes of the complex dianions $[RN\text{-}BH\text{-}NR\text{-}BH_3]^{2-}$ (R = H; Me; *i*Pr). In cases in which dimerization was not possible, unimolecular H_2 elimination provided species containing coordinated imidoborane anions. Most recently, the same group reported that di-*n*-butyl magnesium or a β-diketiminate-supported magnesium silylamide are capable of the catalytic dehydrocoupling of the primary anilino–borane, $(Dipp)NH_2BH_3$ (Dipp = 2,6-di-iso-propylphenyl), via the intermediacy of a structurally characterized magnesium anilido species, $[HC\{(Me)CN(Dipp)\}_2Mg\{NH(Dipp)BH_3\}]$ (**I**), in the case of the heteroleptic derivative.[6a] The only dehydrocoupled product to be fully characterized was $[HB\{NH(Dipp)\}_2]$, proposed to be the result of β-hydride elimination and BH_3 evolution from a more complex, but unidentified, species derived from **I** containing an additional B−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 B−N bond formation and concurrent H_2 elimination to provide the complex intermediate $[(Dipp)NHBH_2NH(Dipp)BH_3]^-$ 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 ammonia–borane $(Dipp)NH_2BH_3$.[6a]



I



II



Scheme 1.

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 secondary amine–boranes, $R_2NH{\cdot}BH_3$, in the expectation that extra substitution of the amine will provide more mechanistically amenable intermediates. In this submission we describe our initial observations of reactions of Group 2 metal alkyls and amides with Me_2NHBH_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 $Me_2NH{\cdot}BH_3$ and either di-*n*-butyl magnesium or the more crowded alkyl derivative $[Mg\{CH(SiMe_3)_2\}_2(thf)_2]$ in THF produced a steady stream of bubbles and evidence of immediate protonation of all the alkyl residues by ^1H NMR spectroscopy. The corresponding proton-coupled ^{11}B NMR spectra revealed the complete disappearance of a resonance attributable to the $Me_2NH{\cdot}BH_3$ starting material (δ_{11B} 11.9 ppm, $^1J_{HB} = 97.3$ Hz) and evidence of two new boron environments observed at 4.0 and −15.3 ppm, which appeared as triplet ($^1J_{HB} = 102$ Hz) and quartet ($^1J_{HB} = 89$ Hz) signals, respectively. The origin of these observations was revealed by a single-crystal X-ray diffraction analysis performed upon crystals of compound **1** 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 **1** is a discrete magnesium complex in which the magnesium coordination sphere is composed of a molecule of THF and two borylamido anions, $[H_3BNMe_2BH_2Me_2N]^-$. These latter ligands may be considered as the deprotonated form of $H_3BNMe_2BH_2Me_2NH$ (**III**),[15] the product of a single dehydrocoupling reaction between two Me_2NHBH_3 molecules. Although **III** has previously been postulated as a key intermediate in the catalytic dehydrocoupling of $Me_2NH{\cdot}BH_3$ and the dianionic species $[H_3BNHBHNH]^{2-}$ has been identified from the calcium-induced dehydrocouping of ammonia–borane itself,[3a,4e,h,i,12a] to the best of our knowledge, the ligand within compound **1** is the first example of this particular anion to be crystallographically characterized. The primary interactions between the $[H_3BNMe_2BH_2Me_2N]^-$ ions and magnesium are provided by the formally deprotonated nitrogen atom of each ligand. The observed bond lengths (Mg1−N1 2.1649(11), Mg1−N3 2.1684(11) Å) are considerably longer than those observed between magnesium and the anilidoborane anion within **I** (Mg−N 2.083(4) Å), but are only slightly elongated in comparison to those within $Mg(Me_2C_5H_3BNMe_2)_2$ (Mg−N 2.140(3), 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-

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

	1	**2**	**4**
formula	$C_{12}H_{42}B_4MgN_4O$	$C_{33}H_{58}B_2MgN_4$	$C_{35}H_{58}BCaN_3O$
M_r [g mol^{-1}]	326.05	556.76	587.73
crystal system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$Pnma$
a [Å]	9.4110(2)	11.890(3)	18.4020(2)
b [Å]	9.8350(2)	15.0550(4)	19.9490(3)
c [Å]	13.1350(3)	19.3270(3)	10.1400(1)
α [°]	103.802(1)	90	90
β [°]	94.767(1)	91.311(1)	90
γ [°]	111.340(1)	90	90
V [Å^3]	1080.11(4)	3458.70(14)	3722.41(8)
Z	2	4	4
μ [mm^{-1}]	0.086	0.078	0.196
ρ [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/R_{int}	21626/6299/ 0.0484	48225/7861/ 0.0533	51539/3369/ 0.0465
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0467, 0.1197	0.0524, 0.1335	0.0621, 0.1642
R_1[a], wR_2[b] (all data)	0.0712, 0.1338	0.0825, 0.1514	0.0740, 0.1800

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

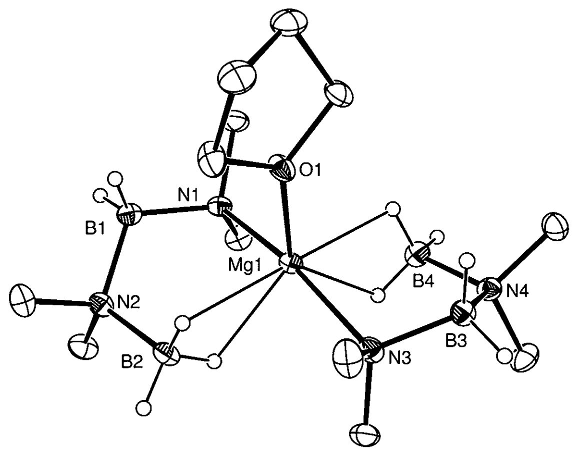


Figure 1. ORTEP representation of compound **1** (50 % probability ellipsoids). H atoms except for those bonded to boron are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N1 2.1649(11), Mg1–N3 2.1684(11), Mg1–O1 2.0838(9), Mg1–H2D 2.12, Mg1–H4D 2.11, Mg1–H2E 2.16, Mg1–H4E 2.16, N1–B1 1.5647(17), B1–N2 1.6145(17), N2–B2 1.5762(17), N3–B3 1.5646(17), B3–N4 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).

graphically characterized species **III** (B1–N1: **1** 1.5647(17), **III** 1.599(2); B1–N2: **1** 1.6145(17), **III** 1.589(2); B2–N2: **1** 1.5762(17), **III** 1.600(2) Å).[15] Although the B–N bond lengths across the -NHBHNH- unit of the bridging and calcium-coordinated dianionic species, $[H_3BNHBHNH]^{2-}$, (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" $-BH_3$ component of both anions are significantly shortened within **1** (B2–N2: 1.5762(17) and B3–N3: 1.5646(17) versus 1.593(6) Å).[13] 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 $^1H\{^{11}B\}$ NMR spectrum between 228 K and 288 K provided evidence for two independent fluxional processes in [D$_8$]toluene. At temperatures below 258 K, the resonances associated with the BH_2 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 ($\Delta G^{\ddagger} = 44.1$ kJ mol^{-1}) at temperatures above 258 K. The resonances associated with the BH_3 units of compound **1** also displayed a rather more complex decoalescence 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 $\delta_H = 2.33$ ppm, $\Delta G^{\ddagger} = 42.4$ kJ mol^{-1}; for $\delta_H = 2.23$ ppm, $\Delta G^{\ddagger} = 46.6$ kJ mol^{-1}) effectively identical to that deduced for the boron-centered unit within the limits the of experimental observations.

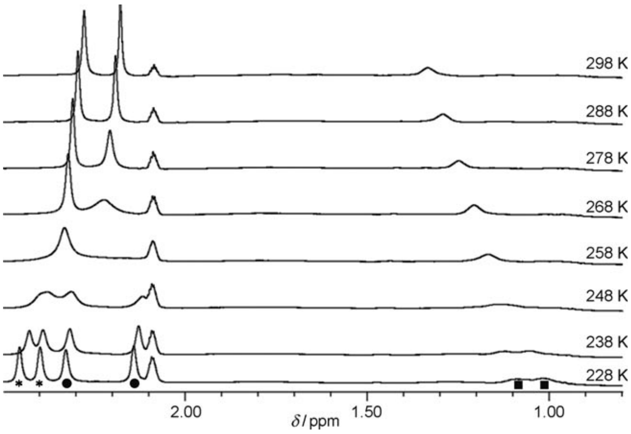
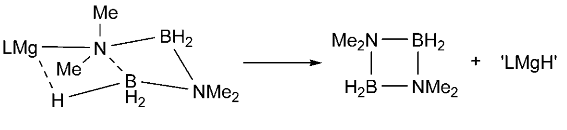


Figure 2. Variable-temperature $^1H\{^{11}B\}$ NMR spectra of the $-NMe_2$ and $-BH_2$ regions of compound **1** recorded 228–288 K. Exchanging partners described in text are indicated by * ($\Delta G^{\ddagger} = 42.4$ kJ mol^{-1}), ● ($\Delta G^{\ddagger} = 46.6$ kJ mol^{-1}) and ■ ($\Delta G^{\ddagger} = 44.1$ kJ mol^{-1}) symbols.

Heating a solution of compound **1** in C_6D_6 to 60 °C, monitored by ^{11}B NMR spectroscopy over the course of four days, resulted in the disappearance of the signals attributed to the $[H_3BNMe_2BH_2Me_2N]^-$ ligand and the appearance of a new triplet signal centered at $\delta_{11B} = 5.2$ ppm ($^1J_{HB} = 108$ Hz). This species was identified as the cyclic dimer

$[H_2BNMe_2]_2$ 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)]. In support of this hypothesis, no evidence for the formation of the BH_4^- ion, a necessary consequence of the previously described β-hydride- and BH_3-elimination based chemistry reported for primary anilidoborane dehydrocoupling was observed.[6]



(1)

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 $[H_3BNMe_2BH_2Me_2N]^-$ ion. A reaction of the β-diketiminate complex [HC{(Me)CN-(Dipp)}$_2$Mg*n*Bu] with two equivalents of $Me_2NH{\cdot}BH_3$ resulted in the formation of a single compound (**2**), which displayed a similar but broadened ^{11}B NMR ($\delta = 4.1$, -14.9 ppm) spectrum to those recorded for compound **1**. The identity of compound **2** was confirmed by a combination of multinuclear NMR spectroscopy, elemental analysis and a single-crystal X-ray diffraction experiment, the results of which are illustrated in Figure 3. Details of the analysis are given in Table 1, while selected bond length and angle data are provided in the figure caption. Compound **2** contains a pseudo-four-coordinate magnesium center, in which the coordination sphere of the alkaline earth element is provided by the bidentate β-diketiminate ligand and a chelated $[H_3BNMe_2BH_2Me_2N]^-$ ion identical to that observed in the homoleptic species, compound **1**. The amidoborane ligand binds to the magnesium in an exactly analogous manner in both compounds **1** and **2**. The presence of the sterically demanding β-diketiminate ligand and the reduced formal coordination number of the magnesium center in compound **2** produce only minor adjustments to the bond lengths and angles around the six-membered MgNBNBH heterocycle. Although compound **2** proved to be more thermally robust, NMR monitoring of a sample heated to 60 °C for 16 h also resulted in the production (ca. 20 % conversion) of $[(H_2BNMe_2)_2]$. Of more significance, however, was the concurrent production of a small quantity of Jones' recently reported dimeric magnesium hydride [{HC{(Me)CN-(Dipp)}$_2$MgH(thf)}$_2$],[16] identified by comparison to the ^{1}H NMR literature data and again indicative of a reaction pathway analogous to the β-hydride elimination illustrated in Scheme 1, but involving the δ-located BH_3 unit within the chelated anion of **2**.

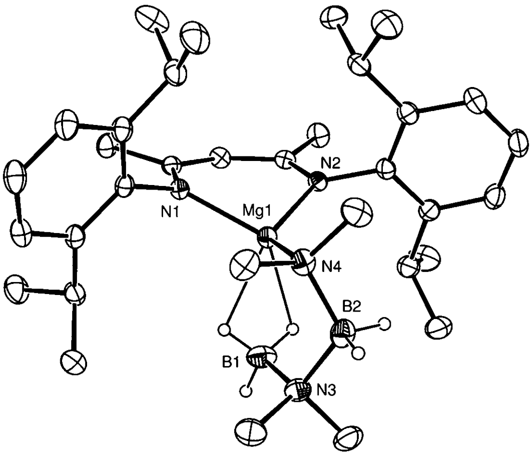
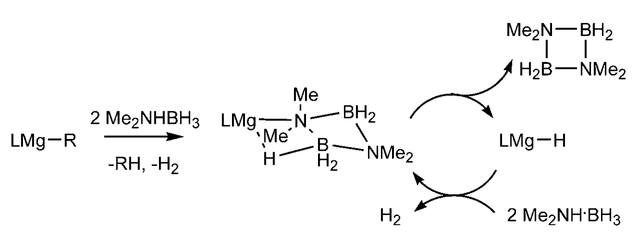


Figure 3. ORTEP representation of compound **2** (50 % probability ellipsoids). Minor disordered component and hydrogen atoms (except for those bonded to boron) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N1 2.0531(13), Mg1–N2 2.0529(13), Mg1–N4 2.0929(14), N4–B2 1.586(3), B2–N3 1.620(3), N3–B1 1.570(3); N2-Mg1-N1 94.92(5), N2-Mg1-N4 123.27(6), N1-Mg1-N4 121.51(6), B1-N3-B2 110.83(15), N4-B2-N3 114.18(17), B2-N4-Mg1 105.19(12).

Irrespective of the mode of formation of the intermediate $[H_3BNMe_2BH_2Me_2N]^-$ ion (see below), the apparent production of a hydrido species indicated that the dehydrocoupling of Me_2NHBH_3 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.



Scheme 2.

To test this hypothesis, the catalytic dehydrocoupling reaction of $Me_2NH{\cdot}BH_3$ utilizing 5 mol % [Mg{CH(SiMe$_3$)$_2$}$_2$-(thf)$_2$] as catalyst in C_6D_6 was attempted at 60 °C and monitored by ^{11}B NMR spectroscopy. Although quite slow, the catalytic dehydrocoupling protocol illustrated by Scheme 2 provided clean and selective conversion to the dimerized species $[(H_2BNMe_2)_2]$ over the course of 72 h. A number of notable features were also apparent from inspection of the ^{11}B NMR spectra recorded during the dehydrocoupling process (Figure 4). The presence of a BH_2 unit of an intermediate analogous to the Mg-coordinated $[H_3BNMe_2BH_2Me_2N]^-$ species observed in the well-defined compounds **1** and **2** was inferred from the presence of a low intensity triplet at about 4 ppm ($^1J_{HB} = 101$ Hz) throughout the reaction. An additional quartet resonance at approximately -9 ppm ($^1J_{HB} = 92$ Hz) was not assigned to the corresponding BH_3 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 ^{11}B-^{11}B correlation

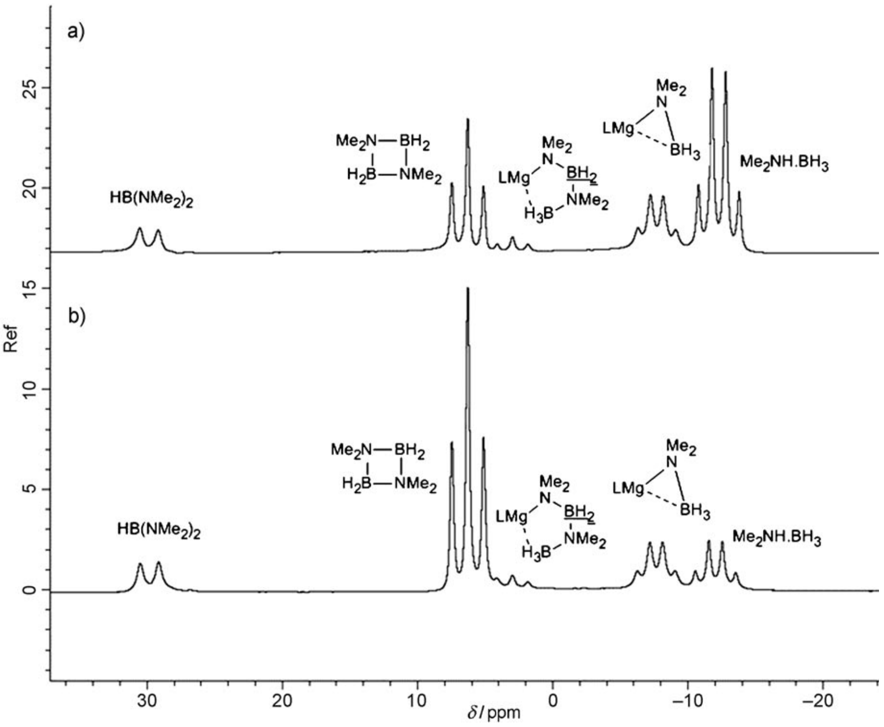


Figure 4. ^{11}B NMR spectra of the catalytic dehydrocoupling of $Me_2NH{\cdot}BH_3$ catalyzed by 5 mol% [Mg{CH(SiMe$_3$)$_2$}$_2$(thf)$_2$] at 60°C recorded after a) 48 h and b) 72 h.

experiment, this low intensity signal is proposed to be obscured by the quartet resonance of the $Me_2NH{\cdot}BH_3$ starting material and it is notable that Weller and co-workers have recently made similar deductions during studies of the Rh-catalyzed dehydrocoupling of the same substrate.[4i] Having tentatively assigned a similar downfield triplet resonance to the trimerized species [$(H_2BNMe_2)_3$] in their original communication,[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 $Me_2NH{\cdot}BH_3$ starting material. The diaminoborane $HB(NMe_2)_2$ was also observed at early stages of, and throughout, the course of the reaction. Although the reaction of $HB(NMe_2)_2$ with diborane has been reported to result in longer chain amine–boranes,[8b] 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 $[H_3BNMe_2BH_2Me_2N]^-$ ion followed by loss of BH_3.[17] A similar β-hydride elimination has been proposed to occur during the magnesium-catalyzed production of [HB{NH(Dipp)}$_2$] from (Dipp)NH_2BH_3.[6a] 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_2H_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$_3$)$_2$}$_2$(thf)$_n$] (**3**, M = Ca, n = 2), which can function as basic derivatives for the exploration of heavier alkaline earth reaction chemistry.[18] Accordingly, NMR monitoring of reactions of compound **3** with either two or four molar equivalents of $Me_2NH{\cdot}BH_3$ 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 $[H_3BNMe_2BH_2Me_2N]^-$ 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 $Me_2NH{\cdot}BH_3$ 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 ($^1J_{HB}$ = 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$_3$)$_2$}$_n$],[11b] (Ca−N 2.383 Å) and those within Harder's similarly mononuclear β-diketiminato calcium primary isopropylamido and anilido derivatives, [HC{(Me)CN(Dipp)}$_2$Ca{NH(R)BH$_3$}(thf)] (R = iPr, 2.406(4); R = 2,6-iPr$_2$C$_6$H$_3$, 2.460(2) Å).[13b] Although the parent amidoborane species [HC{(Me)CN(Dipp)}$_2$Ca{NH$_2$BH$_3$}(thf)$_2$] was report-

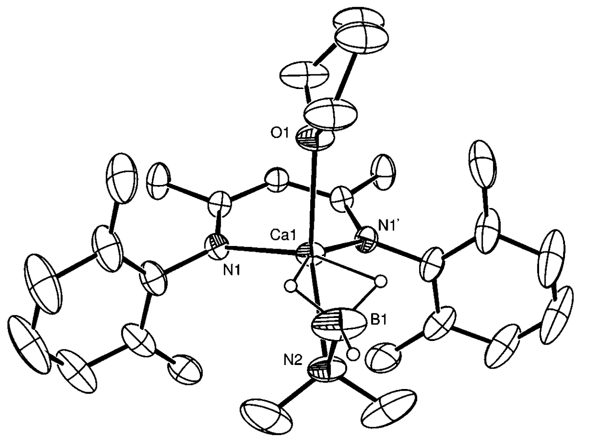
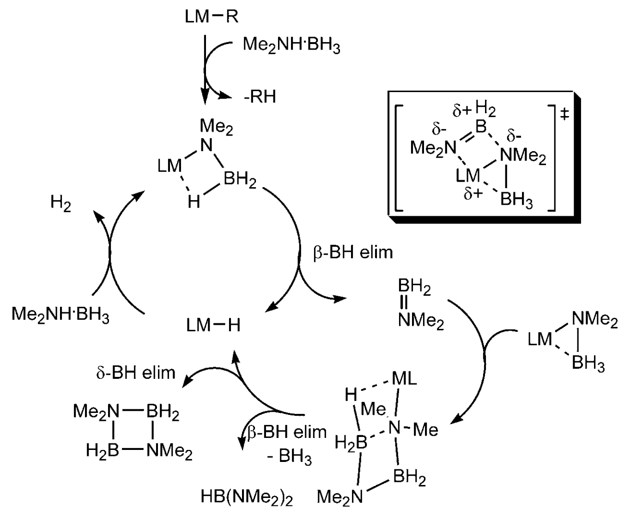


Figure 5. ORTEP representation of compound **4** (25% probability ellipsoids). Isopropyl methyl carbons and H atoms except for those bonded to boron are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ca1−N1 2.335(17), Ca1−N2 2.375(3), N2−B1 1.497(6), Ca1−O1 2.352(2); N1-Ca1-N1′ 81.71(8), 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, $-y+\frac{1}{2}$, z.



Scheme 3.

ed to be highly unstable,[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_6D_6 heated to 80 °C for 4 h evidenced <10% decomposition. Although small quantities of $HB(NMe_2)_2$ were again apparent, perhaps significantly, a low intensity resonance at about 36 ppm was also observed, which may be assigned to monomeric $Me_2N{=}BH_2$.[4a,i] Careful inspection of the ^1H NMR spectrum of this thermal reaction also provided evidence for the formation of the known β-diketiminato calcium hydride $[[HC\{(Me)CN(Dipp)\}_2CaH(thf)]_2$,[19] and we thus tentatively suggest that compound **4** undergoes a thermally induced β-hydride elimination/intramolecular σ-bond metathesis process under these conditions. Although $[(H_2BNMe_2)_2]$ was not observed under these conditions, preliminary observations of stoichiometric and catalytic reactions of both $[HC\{(Me)CN(Dipp)\}_2Ca\{N(SiMe_3)_2\}(thf)]$ and the calcium dialkyl compound **3** with $Me_2NH{\cdot}BH_3$ provided ^{11}B NMR spectra similar to those illustrated in Figure 4 and evidence for $[(H_2BNMe_2)_2]$ formation by a common and sequential protonolysis-metathesis pathway.

The observation of $Me_2N{=}BH_2$ during the course of these reactions and the highly specific formation of $[H_3BNMe_2BH_2Me_2N]^-$ ions observed during the course of these d^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 $Me_2NH{\cdot}BH_3$ dehydrocoupling illustrated in Scheme 3.[20] Under this regime, catalytic B−N bond formation and turnover is dependent upon production and insertion of the unsaturated (and polarized) species $Me_2N{=}BH_2$ (transition state, inset Scheme 3) to form a key catalytic intermediate containing the $[H_3BNMe_2BH_2Me_2N]^-$ ion. Subsequent formation of the amidoborane products, $[(H_2BNMe_2)_2]$ and $HB(NMe_2)_2$, is then dictated by the relative energetics of two possible intramolecular B−H/M−N σ-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_2 release from lithium and magnesium amidoboranes,[1,6a,21] the course of these d^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 σ-bond metathesis and insertion of unsaturated units.[22] The contrast between the activity of the Mg- and Ca-based systems indicates that the suitability of a particular d^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 (^{13}C), 96.3 MHz (^{11}B). Variable-temperature ^1H NMR data were recorded on a Bruker AV400 spectrometer. The spectra were referenced relative to residual solvent resonances or an external $BF_3.OEt_2$ standard (^{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_6D_6 and $[D_8]$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 in *n*-heptane) and $Me_2NH{\cdot}BH_3$ were purchased from Sigma–Aldrich and used without further purification. Group 2 metal bis(trimethylsilyl)alkyls,[18] the ligand precursor DippNC(Me)CHC(Me)NHDipp,[23] $[HC\{(Me)CN(Dipp)\}_2Mg\textit{n}Bu]$[24] and $[HC\{(Me)CN(Dipp)\}_2Ca\{N(SiMe_3)_2\}(thf)]$[25] were synthesized by literature procedures. CHN microanalysis was performed by Mr Stephen Boyer of London Metropolitan University.

Synthesis of $[Mg\{N(CH_3)_2BH_2N(CH_3)_2BH_3\}_2(thf)]$ (1): A solution of $\textit{n}Bu_2Mg$ (1.45 mL of 1.0 M solution, 1.45 mmol in *n*-heptane diluted with ca. 10 mL *n*-hexane) was added at room temperature to $Me_2NH{\cdot}BH_3$ (0.34 g, 5.78 mmol). After gas evolution had ceased, the solution was stirred overnight before in vacuo removal of volatiles. Crystallization of the resultant colorless solid from hexane resulted in the isolation of compound **1** as colorless crystals suitable for an X-ray diffraction analysis (70%). Despite repeated attempts accurate microanalytical data could not be obtained for this compound. $^1H\{^{11}B\}$ NMR (C_6D_6, 298 K): δ = 1.20–1.25 (m, 4H; THF), 1.70 (s, 6H; BH_3), 2.07 (s, 4H; BH_2), 2.23 (s, 12H; CH_3, splits into 2×s 2.12, 2.31 ppm at 228 K, each 6H), 2.33 (s, 12H; CH_3, splits into 2×s 2.40, 2.43 ppm at 228 K, each 6H), 3.76 ppm (m, 4H; THF); $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ = 25.3 (THF), 46.1 (CH_3), 52.8 (CH_3), 71.0 ppm (THF); ^{11}B NMR (C_6D_6, 298 K): δ = 4.2 (t, $^1J_{HB}$ = 102 Hz, BH_2), −15.0 ppm (q, $^1J_{HB}$ = 89 Hz, BH_3).

Synthesis of $[HC\{(Me)CN(Dipp)\}_2Mg\{N(CH_3)_2BH_2N(CH_3)_2BH_3\}]$ (2): Toluene (15 mL) was added at room temperature to a mixture of solid $[HC\{(Me)CN(Dipp)\}_2Mg\textit{n}Bu]$ (0.15 g, 0.3 mmol) and $Me_2NH{\cdot}BH_3$ (0.034 g, 0.6 mmol). The resultant solution was stirred overnight before in vacuo removal of all volatiles. Compound **2** was isolated as colorless crystals by crystallization from hexane solution at 5 °C (60%). Elemental analysis calcd (%) for $C_{33}H_{58}B_2MgN_4$: C 71.17, H 10.51, N 10.06; found: C 71.12, H 10.59, N 10.06; $^1H\{^{11}B\}$ NMR (C_6D_6, 298 K): δ = 1.16 (d, J = 6.9 Hz, 12H; $CH(CH_3)$), 1.22 $CH(CH_3)$), 1.32 (brs, 3H; BH_3), 1.49 (brs, 2H; BH_2), 1.67 (s, 6H; NCH_3), 1.82 (s, 6H; NCH_3), 2.14 (s, 6H; $NCCH_3$), 3.31–3.34 (m, 4H; $CH(CH_3)$), 4.77 (s, 1H; $C_\gamma H$), 7.10–7.20 ppm (m, 6H; Ar); $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ = 23.8 ($CH(CH_3)$), 24.9 ($CH(CH_3)$), 25.6 ($CH(CH_3)$), 29.0 ($NC(CH_3)$), 45.4 (NCH_3), 52.0 (NCH_3), 95.3 (CH), 123.9 (m-C_6H_3), 126.1 (p-C_6H_3), 143.1 (o-C_6H_3), 146.2 (i-C_6H_3), 169.8 ppm (CN); ^{11}B NMR (C_6D_6, 298 K): δ = 4.1 (br. unresolved m, BH_2), −14.5 ppm (unresolved m, BH_3).

Synthesis of $[HC\{(Me)CN(Dipp)\}_2Ca\{N(CH_3)_2BH_3\}(thf)]$ (4): Hexane (15 mL) was added at room temperature to a mixture of solid $[HC\{(Me)CN(Dipp)\}_2Ca\{N(SiMe_3)_2\}(thf)]$ (0.10 g, 0.3 mmol) and $Me_2NH{\cdot}BH_3$ (0.034 g, 0.6 mmol). The reaction mixture was stirred for 1 h at room temperature. Crystals suitable for X-ray analysis were isolated after concentration of the solution (72%). Elemental analysis calcd (%) for $C_{35}H_{58}BCaN_3O$: C 71.52, H 9.95, N 7.15; found: C 71.49, H 10.03, N 7.10; $^1H\{^{11}B\}$ NMR (C_6D_6, 298 K): δ = 1.21 (d, J = 7.0 Hz, 12H; $CH(CH_3)$), 1.29 (d, J = 7.0 Hz, ca. 16H; $CH(CH_3)$ coincident with THF), 1.65 (brs, 3H; BH_3), 1.67 (s, 6H; NCH_3), 1.95 (s, 6H; $NCCH_3$), 3.23–3.26 (m, 4H; $CH(CH_3)$), 4.77 (s, 1H; $C_\gamma H$), 7.10–7.20 ppm (m, 6H; Ar); $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ = 24.8 ($CH(CH_3)$), 25.1 ($CH(CH_3)$), 25.7 ($CH(CH_3)$), 25.9 (THF), 28.8 ($NC(CH_3)$), 47.1 (NCH_3), 70.4 (THF), 93.9 (CH), 124.3 (m-C_6H_3), 124.5 (p-C_6H_3), 142.0 (o-C_6H_3), 146.6 (i-C_6H_3), 166.3 ppm (CN); ^{11}B NMR (C_6D_6, 298 K): δ = −11.5 ppm (q, $^1J_{HB}$ = 86 Hz, BH_3).

Crystallographic data: Data for **1** and **2** were collected on a Nonius Kappa CCD diffractometer at 150(2) K (**4** 240 K), using graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Data were processed using the Nonius Software.[26] Structure solution, followed by full-matrix least-squares refinement was performed using the programme suite X-SEED throughout.[27] For **2** C1, C2, C3, C4, and B1 were disordered over two sites in an 80:20 ratio. The 80% fractions were refined anisotropically. N−C distances were restrained to be similar where disorder of the carbon was present. Hydrogens attached to boron atoms were included at calculated positions, which coincided closely with residual electron density evident in the penultimate difference Fourier Map. For **4** data were collected at 240 K, as the crystal underwent a phase transition at 150 K. Data were truncated to a θ value of 25° due to a fall off in diffraction at higher resolution. H1a and H1b were located and refined subject to being similar distances from B1. The asymmetric unit consists of half of a molecule with atoms Ca1, O1, N2, B1, C17, and C20 located on a mirror plane intrinsic to the space group. This necessarily means that C18 and C19 are disordered over two positions in a 50:50 ratio. Atoms C17 to C20 were refined anisotropically subject to having similar ADP restraints.

CCDC-753081 (**1**), 753082 (**2**), and 753083 (**4**) 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.

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