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Stoichiometric and Catalytic Reactivity of *tert*-Butylamine Borane with Calcium Silylamides

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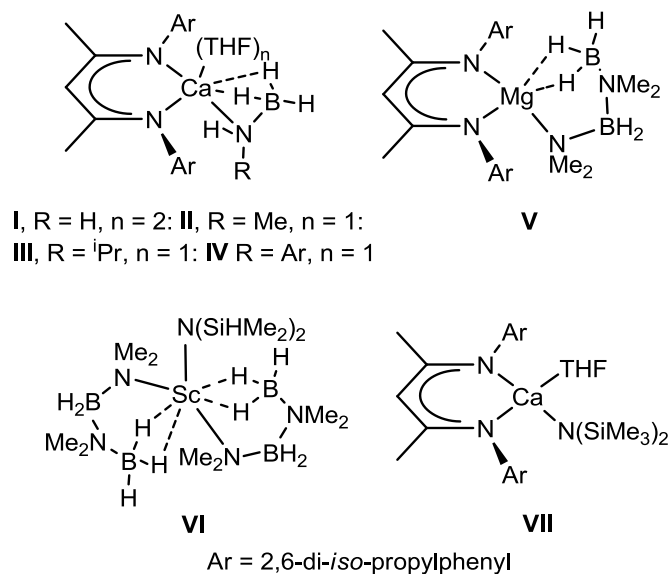
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Abstract

*The primary amine borane $t\text{-BuNH}_2\cdot\text{BH}_3$ reacts with a β -diketiminato-supported silylamido calcium complex with elimination of $\text{HN}(\text{SiMe}_3)_2$ and formation of the corresponding primary amidoborane complex in which the deprotonated amine borane is attached to the alkaline earth center via its nitrogen atom and anagostic interactions with the boron-bound hydrides. Catalytic dehydrocoupling reactions employed with this β -diketiminato pre-catalyst are found to be slow and complicated by protonation of the supporting ligand and the formation of a number of boron-containing products, all of which have been positively identified. In common with previous studies of group 2-catalyzed secondary amine borane dehydrogenation, the first formed major product of the catalysis is identified by solution NMR and solid-state single crystal X-ray studies to be a cyclic diborazane, $[\text{H}^t\text{BuN-BH}_2]_2$, the formation of which is accompanied by variable proportions of diamidoborane and aminoborane products. The active calcium species is also observed to be depleted during the catalysis due to the formation of hydrocarbon insoluble $[\text{Ca}(\text{BH}_4)_2\cdot\text{THF}]_\infty$, which has also been structurally characterized. Continued heating of these reactions results in the formation of cyclic trimeric 1,3,5-tri(*tert*-butyl)borazine which is proposed to form through the intermediacy of $[\text{H}^t\text{BuN-BH}_2]_2$ by an, as yet, undefined sequence of borazane dehydrogenation and ring expansion reactions.*

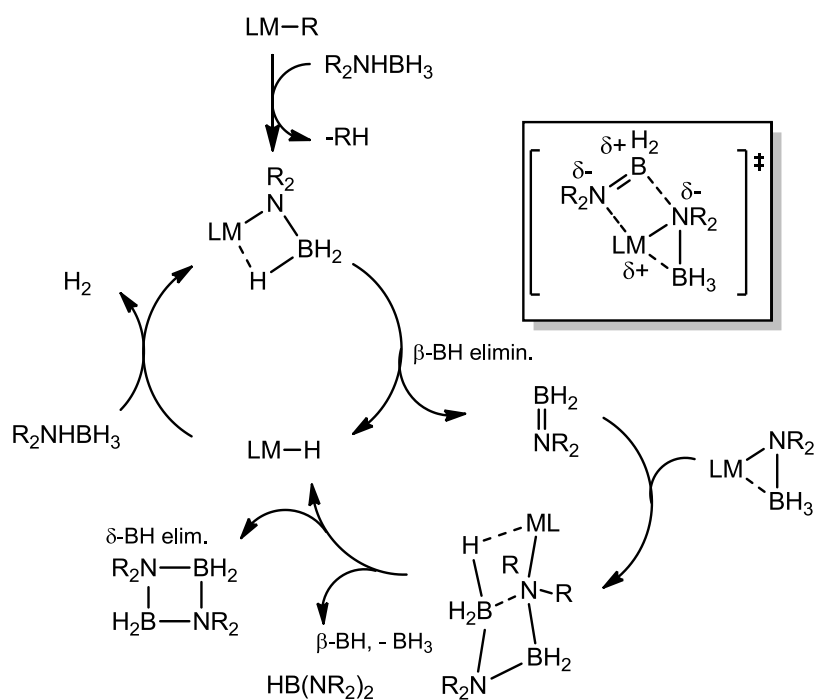
Introduction

The reactivity of ammonia borane (AB) and organo-amine boranes, $R_{3-n}NH_n.BH_3$ ($n = 2$ or 1), has received considerable recent attention because of their potential relevance to hydrogen fuel storage media.¹⁻⁹ Consequently, the homogeneous catalytic dehydrocoupling activity of a wealth of transition metal complexes, including those of Ti,^{10,11} V,¹² Cr,¹²⁻¹⁵ Mo,¹⁶ W,¹⁵⁻¹⁷ Mn,^{12,15} Re,^{18,19} Fe,²⁰⁻²² Ru,²³⁻²⁷ Rh,²⁸⁻⁴³ Ni,⁴⁴⁻⁴⁷ or Pd,⁴⁸⁻⁵⁰ has been explored.



Whereas many mechanistic interpretations of these catalyses require formal oxidation state changes to the transition metal center, a complementary class of amine borane dehydrocoupling catalyst^{51,52} has emerged from the use of effectively redox inactive d^0 complexes of the elements of groups 2 (Mg, Ca, Sr, Ba),⁵³⁻⁵⁷ 3 (Sc and Y)⁵⁸⁻⁶⁰ and 13.⁶¹⁻⁶⁴ Initial work by Harder and co-workers demonstrated that a β -diketiminato-supported calcium hydride reacts with AB and primary amine boranes through H_2 elimination to form the monomeric calcium amidoborane derivatives **I** – **IV**.^{65,66} Whereas subsequent B-N bond formation to provide dimeric calcium complexes of $\{RN-BH-NR-BH_3\}^{2-}$ ions was observed for compounds **I** - **III**, the greater steric demands of the primary aniline borane, $ArNH_2.BH_3$ (Ar = 2,6-di-*iso*-propylphenyl) allowed the isolation of a monomeric derivative containing the borylamido anion, $[ArN=BH_2]^-$. To the background of these observations, and in common with many previous studies of catalytic amine borane dehydrocoupling activity, our own efforts have concentrated on the group 2 and group 3-catalyzed dehydrocoupling of secondary amine boranes, $R_2NH.BH_3$, which, in containing a single (protic) N-H residue, were judged to be more amenable toward initial mechanistic analysis of the B-H bond

breaking and B-N bond forming steps.^{55,56} In several cases, we have observed that the ultimate products of the dehydrocoupling of secondary amine boranes by magnesium and calcium alkyls and silylamides, primarily cyclic dimeric borazanes of the form $[\text{R}_2\text{NBH}_2]_2$, occur via the intermediacy of coordination compounds containing complex anions of the general form $\{\text{NR}_2\text{BH}_2\text{NR}_2\text{BH}_3\}^-$ (see, for example, the magnesium and scandium compounds **V**⁵⁵ and **VI**⁵⁸). We have suggested that this process is predominantly metal-mediated and dependent upon the mechanism illustrated in Scheme 1,^{55,56,58,67-69} for which some supporting evidence has recently emerged from computational DFT studies.⁷⁰ Under this regime, the primary B-N bond forming reaction requires a sequence of metalated amidoborane β -hydride elimination and polarised $\text{R}_2\text{N}=\text{BH}_2$ insertion and δ -hydride elimination steps. Minor quantities of diamidoboranes, $(\text{R}_2\text{N})_2\text{BH}$, and tetrahydridoborate anions have also been observed in these catalytic systems and we have suggested that these species are the result of a further β -hydride elimination step,⁵⁷ which may occur in competition to the predominant δ -hydride elimination, from intermediate compounds containing the $\{\text{NR}_2\text{BH}_2\text{NR}_2\text{BH}_3\}^-$ anion.^{55,56,58} Although magnesium compounds such as **V** formed at room temperature, reactions of the calcium silylamide reagent **VII** with secondary amine boranes provided straightforward access to compounds containing amidoborane anions, $[\text{R}_2\text{NBH}_3]^-$. Based upon these observations it is qualitatively evident that the dehydrocoupling activity is dependent upon the identity of the metal employed and we have proposed that the ability of a particular d^0 metal centre to engage in dialkylamine borane dehydrocoupling is dictated by the charge density and resultant capacity for the cationic centre to mediate the individual reaction steps involved. Although the absolute reactivity derived from the use of calcium-based reagents is, thus, insufficient to provide any viable utility in amine borane dehydrocoupling, their slower kinetics are better suited to the monitoring and identification of reaction intermediates during the catalysis. Reactions of $\text{E}(\text{N}^i\text{Pr}_2)_3$ ($\text{E} = \text{Al}, \text{Ga}$) with the primary amine-borane, $t\text{-BuNH}_2\cdot\text{BH}_3$ have been reported to provide sequential dehydrogenation to the structurally characterized cyclic tri-borazane $[t\text{-BuNHBH}_2]_3$ and, ultimately, the borazine $[t\text{-BuNBH}]_3$.⁶³ As an extension to our studies of alkaline earth-mediated dehydrocoupling catalysis, we describe in this contribution an investigation of the reactivity of *tert*-butylamine borane which provides similar but contrasting reaction outcomes with the calcium reagents **VII** and $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ (**VIII**).



Scheme 1: Suggested mechanism for the group 2-centered dehydrocoupling of secondary amine boranes, $R_2NH.BH_3$.

Results and Discussion

The addition of **VII** to one equivalent of *t*-BuNH₂.BH₃ at room temperature resulted in the appearance of a single new quartet resonance in the resultant ¹¹B NMR spectrum at $\delta = -17.3$ ppm (¹J_{BH} = 80 Hz), assigned to the BH₃ unit of the β -diketiminato calcium *tert*-butylamidoborane **1**. These data are closely comparable to both Harder's parent calcium amidoborane **I** ($\delta = -19.6$ ppm, ¹J_{BH} = 84 Hz)⁶⁵ and the primary amidoborane derivatives **II** - **IV** (**II** $\delta = -15.8$ ppm, ¹J_{BH} = 87 Hz; **III** $\delta = -18.1$ ppm, ¹J_{BH} = 88 Hz; **IV** $\delta = -14.7$ ppm, ¹J_{BH} = 74 Hz) all of which contain an identical β -diketiminato ligand.⁶⁶ The solid-state structure of compound **1** was confirmed by an X-ray diffraction analysis performed on crystals isolated from a concentrated toluene solution at -30 °C. The results of this analysis are displayed in Figure 1 while selected bond length and angle data are provided in the figure caption and crystallographic parameters in Table S1.

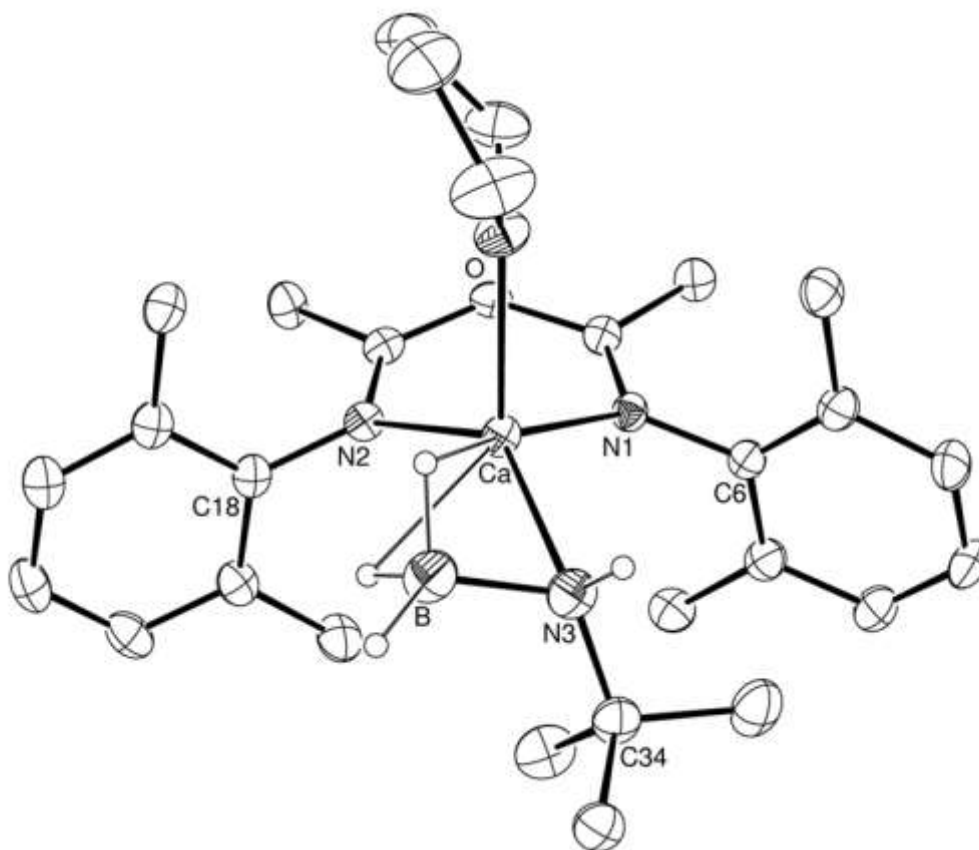
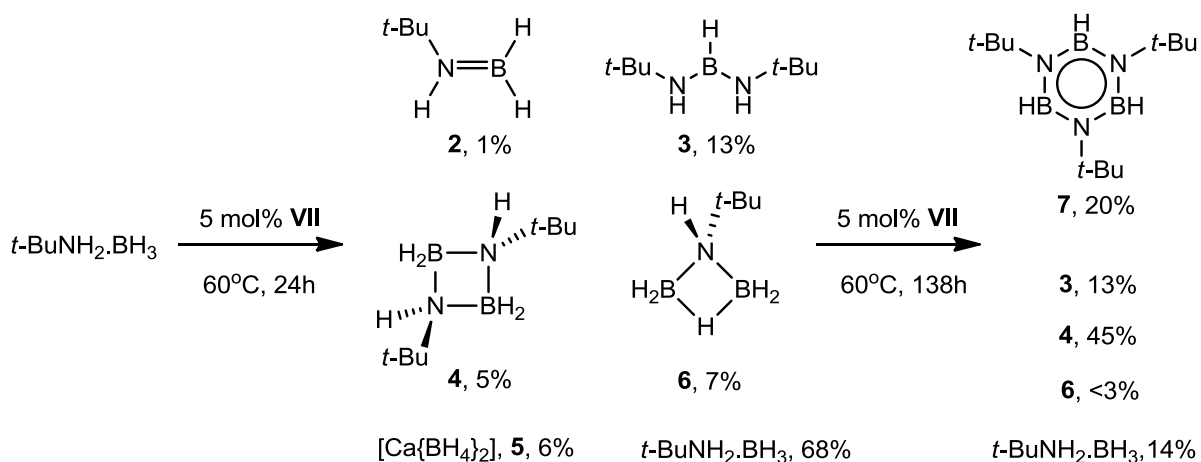


Figure 1: ORTEP representation of the solid-state structure of compound **1**. Thermal ellipsoids set at 30 % probability. Hydrogen atoms other than those bound to B or N(3) and *iso*-propyl methyl carbons are removed for clarity. Selected bond lengths (Å) and angles (°); Ca-N(1) 2.372(3), Ca-N(2) 2.370(3), Ca-N(3) 2.414(3), N(3)-B(1) 1.554(6), N(3)-C(34) 1.490(5), N(1)-Ca-N(2) 79.76(9), N(1)-Ca-N(3) 113.61(10), N(2)-Ca-N(3) 138.18(11), O-Ca-N(2) 103.85(9), O-Ca-N(1) 101.69(9), O-Ca-N(3) 111.09(11), Ca-N(3)-B 79.1(2).

The solid-state structure of **1** comprises a calcium center supported by the bidentate β -diketiminato ligand, the *tert*-butylamidoborane ligand, which is bound through its nitrogen atom and anagostic interactions with the boron-bound hydrides, and a molecule of THF. This coordination geometry is, thus, completely analogous to that described for the previously reported methyl- and *iso*-propylamido borane derivatives, **II** and **III**, respectively.^{65,66} The Ca-N(3) bond length of **1** [2.414(3) Å] is also closely comparable to that of **III** [2.406(4) Å] and **I** [2.399(2) Å], despite the higher formal coordination number of the ammonia borane derivative, but longer, however, than the methylamido borane species **II** [2.382(4) Å] and significantly shorter than the anilido borane derivative **IV** [2.460(2) Å].^{65,66} Although this variation may be rationalized as a consequence of the combined electronic effects and steric

requirements of the nitrogen-bound substituent, it is notable that the B-N(3) bond lengths across **1** and **I** - **IV** are effectively invariant [ranging from 1.581(4) to 1.587(4) Å].

Catalytic dehydrocoupling of *t*-BuNH₂.BH₃ was undertaken employing 5 mol % **VII**, the results of which are summarized in Scheme 2. Analysis of the ¹¹B NMR spectrum after heating at 60 °C for ca. 24 hours evidenced consumption of ca. 34 % of the starting *t*-BuNH₂.BH₃ and indicated the formation of several new boron-environments including a small quantity (ca. 1 %) of a species characterized by a deshielded triplet resonance at δ = 38.2 ppm (¹J_{BH} = 128 Hz), which was attributed to the aminoborane [H^tBuN=BH₂] (**2**). We suggest that compound **2** is the product of β-hydride elimination from compound **1** in a process analogous to that depicted in Scheme 1 for the d⁰-centered dehydrocoupling of secondary amine boranes. A further 13 % of the total observed ¹¹B NMR signals comprised a doublet species at δ = 29.1 ppm (¹J_{BH} = 126 Hz) assigned as the diamidoborane [HB(NH^tBu)₂] (**3**) and 5 % of a species manifested as a triplet resonance at δ = -6.1 ppm (¹J_{BH} = 109 Hz) which we assign as the BH₂ unit of the diborazane, [*t*-BuHN-BH₂]₂ (**4**) (*vide infra*), analogous to the cyclic product depicted in Scheme 1 and the primary product of numerous studies of secondary amine borane dehydrocoupling catalysis. Notably this observation demonstrates a distinctive divergence in reactivity from the observations of Wright and co-workers who observed the cyclic triborazane [*t*-BuNHBH₂]₃ (δ_{11B} = -5.1, ¹J_{BH} = 106 Hz) as the primary product of dehydrocoupling with aluminium and gallium amide pre-catalysts.⁶³ The ¹¹B NMR spectrum at this point in the reaction also evidenced the formation of (ca. 6 %) [BH₄]⁻ species (**5**) as a quintet resonance at δ = -30.6 ppm (¹J_{BH} = 82 Hz) and a partially obscured resonance integrating to ca. 7 % of the total boron species at δ = -22.8 ppm (**6**) which appeared as a 1:1:2:2:1:1 triplet of doublets (¹J_{BH} = 99 Hz and ²J_{BH} = 31 Hz). Although the identity of compound **6** could not be confirmed, Manners has reported the formation of small quantities of [H₂B(μ-H)(μ-NMe₂)BH₂] which also appears as a triplet of doublets resonance in ¹¹B NMR spectra at δ = -19 ppm (J_{BH} = 129 Hz, J_{BH} = 31 Hz) in FLP-induced dehydrocoupling reactions of Me₂NH.BH₃.⁷¹



Scheme 2: Products and product distribution observed by ^{11}B NMR spectroscopy during the dehydrocoupling of $t\text{-BuNH}_2\cdot\text{BH}_3$ catalyzed by 5 mol% **VII**.

Further heating of this reaction at 60°C for 138 hours provided ca. 86 % consumption of the initial $t\text{-BuNH}_2\cdot\text{BH}_3$ at which point analysis by ^{11}B NMR spectroscopy indicated a mixture of ca. 45 % $[t\text{-BuHN-BH}_2]_2$ **4**, 13 % $[\text{HB}(\text{NH}t\text{-Bu})_2]$ **3** and 20 % of a further new species (**7**) characterized by a broad singlet resonance at $\delta = 34.4$ ppm (Scheme 2). In common with Wright's earlier observations of group 13-centered dehydrocoupling of $t\text{-BuNH}_2\cdot\text{BH}_3$,⁶³ compound **7** was identified as the cyclic borazine, $[t\text{-BuN-BH}]_3$ (*vide infra*). Although, at this point in the reaction, the resonance attributed to $[\text{BH}_4]^-$ after ca. 24 hours heating had completely disappeared and the integration of the signal ascribed to species **6** had decreased to 3.2 %, the NMR spectra of the sample were not completely representative of the reaction outcome due to the formation of solid material, which crystallized directly from the reaction mixture after storage at -30°C . Mechanical separation of single crystals of compound **4** suitable for X-ray diffraction analysis provided the solid-state structure illustrated in Figure 2. Bond length and angle data are provided in the figure caption and details of the X-ray analysis are presented in Table S1.

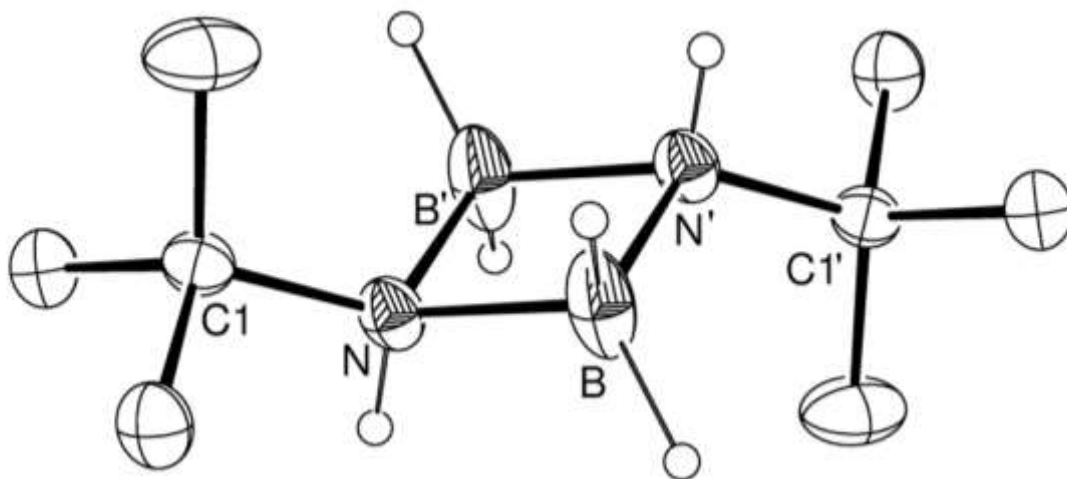


Figure 2: ORTEP representation of the solid-state structure of compound **4**. Thermal ellipsoids set at 30 % probability. Hydrogen atoms other than those bound to boron and nitrogen are removed for clarity. Selected bond lengths (Å) and angles (°); B-N 1.599(3), B-N' 1.600(3), N-C(1) 1.498(2), N-B-N' 92.13(15), B-N-C(1) 122.09(17). Symmetry transformations used to generate equivalent atoms ('): $-x+1, -y+1, -z+1$.

Compound **4** is a cyclo-borazane [*t*-BuHN-BH₂]₂ species and, as such, is the first crystallographically characterized cyclo-dimeric product of a dehydrogenated primary amine borane to be described. All previously reported products for transition-metal catalyzed dehydrocoupling of primary amine boranes have comprised higher oligomers,^{21,26,39,63,72} while all six crystallographically characterized species of similar N₂B₂ structure (**IX** – **XIV**, Figure 3),^{26,39,73-75} are compounds containing secondary amine-derived units. The B-N bond distances (1.599(3) and 1.600(3) Å) in the solid-state structure of **4** are identical to those reported for **IX** [1.594(4) Å],^{26,39} **X** [four in unit cell in range 1.584(5) – 1.609(5) Å],²⁶ **XI** [1.600 Å],⁷⁴ **XII** [1.616 Å],⁷⁵ and **XIII** [1.594(4) Å],⁷³ but are shorter in comparison to that of **XIV** [1.621 Å], which possesses more sterically demanding 2,6-dimethylpiperidinyl nitrogen-centered substituents.⁷⁴

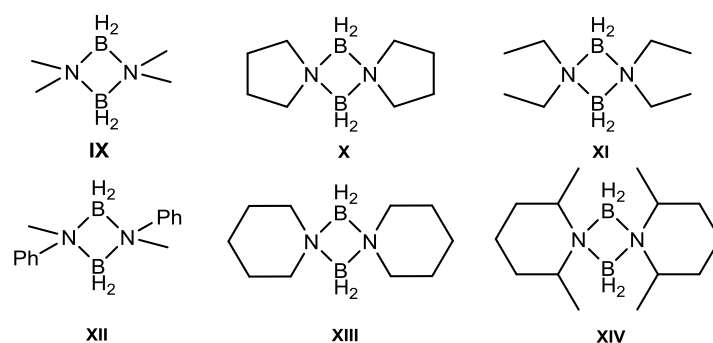


Figure 3: Previously reported crystallographically defined cyclo-dimeric species of the form $[RR'N-BH_2]$.^{26,39,73-75}

The formation of borohydride species during this reaction was also confirmed by a further single crystal X-ray diffraction analysis. Although the crystals diffracted weakly at high angles, leading to consequentially high residuals, the connectivity of the inorganic calcium tetrahydroborate (**5**) was unambiguous (Figure 4). Selected bond length and angle data and details of the X-ray analysis of compound **5** are provided in the figure caption and Table S1 respectively.

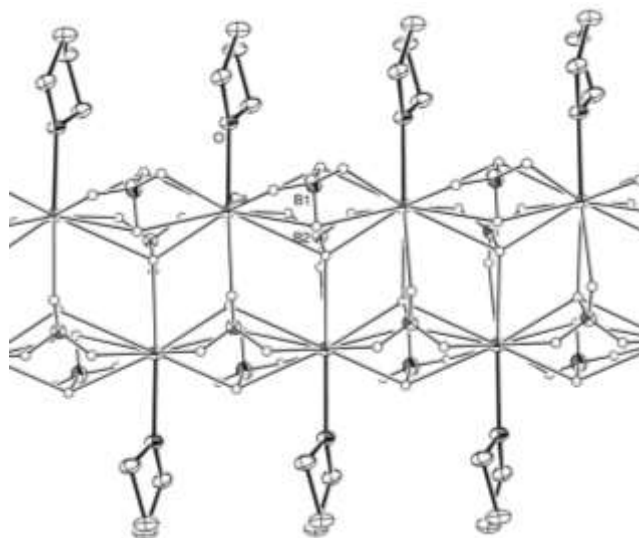


Figure 4: ORTEP representation of the solid-state structure of compound **5** illustrating the propagation of the infinite polymer. Thermal ellipsoids set at 30 % probability. Hydrogen atoms other than the boron-bound hydrides are removed for clarity. Selected bond lengths (Å) and angles (°); Ca-O 2.354(2), Ca-B(1) 2.799(5), Ca-B(1)' 2.749(5), Ca-B(2) 3.005(4), Ca-B(2)' 3.000(4), Ca-B(2)'' 2.958(4), O-Ca-B(1) 85.87(11), O-Ca-B(2) 92.64(9), B(1)-Ca-B(2) 81.01(12), Ca-B(1)'-Ca' 100.36(2).

The solid-state structure of **5** propagates as a double stranded one-dimensional calcium bis(tetrahydroborate) polymer whereby the coordination sphere of each calcium center is provided by bonding to five $[\text{BH}_4]^-$ units through anagostic interaction with the boron-bound hydrides and augmented by a molecule of THF. The B(1)-containing tetrahydroborate anion bridges between two adjacent calcium centers to form an infinite polymeric chain of calcium cations and borohydride anions while the B(2) containing anion is connected to a third calcium center of a second $[\text{Ca}(\text{BH}_4)_2\cdot\text{THF}]_n$ chain to provide the overall double stranded structure. Although the structure of **5** is similar to that of $[\text{Ca}(\text{BH}_4)_2\cdot\text{NH}_3]$ reported by Yu et al,⁷⁶ in that each calcium center was also supported by five $[\text{BH}_4]^-$ units and a single donor ligand, the differing steric demands of the THF donor enforce a transition away from the three-dimensional network structure of the previously reported compound. The Ca-B distances for $[\text{Ca}(\text{BH}_4)_2\cdot\text{NH}_3]$ are reported as averaging 2.95 Å whilst those for **5** are shorter for the Ca-B(1) bond distances and longer for Ca-B(2) bond distances, averaging 2.90 Å.⁷⁶

The formation of the toluene-insoluble compound **5** is indicative of β -diketiminato ligand protonation by this more reactive primary amine borane and the probable redundancy of this intended supporting ligand under catalytic conditions. The catalytic dehydrocoupling of *t*-BuNH₂.BH₃ was thus repeated using 5 mol % of the homoleptic calcium amide $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ **VIII**. Heating of this reaction at 70 °C for ca. 66 hours provided, by integration of the resultant ¹¹B NMR spectrum, ca. 31 % $[\textit{t}\text{-BuHN-BH}_2]_2$ **4**, 13 % $[\text{HB}(\text{N}\textit{t}\text{-BuH})_2]$ **3**, 3 % of the tentatively identified compound **6** and 44 % of the cyclic borazine, compound **7**, characterized as a broad resonance at $\delta = 34.4$ ppm and previously observed as the major product in the group 13-mediated dehydrocoupling of *t*-BuNH₂.BH₃.⁶³ On further heating of this sample the proportion of **4** decreased, falling to ca. 12 % after ca. 232 hours at 70 °C, whilst the relative proportions of **3** and **7** were observed to increase to 15 % and 67 % respectively. The ¹¹B NMR chemical shift data for species **7** produced in these dehydrocoupling reactions are comparable to literature values for the borazine compounds $[\text{MeN-BH}]_3$ ($\delta = 33.2$ ppm, $^1J_{\text{BH}} = 132$ Hz) and $[\text{PhN-BH}]_3$ ($\delta = 32.8$ ppm, br) both of which were produced by a rhodium-catalysed dehydrocoupling process from the respective primary amine boranes.²⁶ Storage of this reaction mixture at -30 °C yielded single crystals of the major reaction product **7** suitable for X-ray diffraction analysis. Although the crystals were poorly diffracting ($R1 = 0.1893$), the connectivity of the 1,3,5-tri(*tert*-butyl)borazine molecule, comprising a planar six-membered B₃N₃ ring, was unambiguous. The solid-state

structure of **7**, as the only *N*-alkyl borazine to be characterized by any X-ray method, is thus presented in Figure S1 and found to be completely analogous to 1,3,5-triphenylborazine and 1,3,5-tris(biphenyl-2-yl)borazine, the two previous *N*-aryl compounds to be structurally characterised.^{26,77-79}

In conclusion, these investigations indicate that although the ultimate outcome of the dehydrocoupling of *t*-BuNH₂.BH₃ by all of the group 2 and group 13 pre-catalysts reported thus far is effectively identical,⁶³ the observation of borazane intermediates of differing nuclearity is a first indication that the selection of the *s*- or *p*-block reagent can be used to modulate catalytic behavior and the nature of products formed. Whilst the species identified during the early period of the calcium-centered catalysis, the borazane **4** and the diamidoborane **3** along with minor quantities of the aminoborane **2**, are consistent with the gross features of the mechanism presented in Scheme 1, additional reaction pathways must operate to account for the formation of species such as **7**. Although beyond the scope of this initial qualitative investigation, any metal-mediated mechanism must account for both the further dehydrogenation of the borazane **4** and its effective ring expansion during the formation of the borazine **7**. Although further reaction sequences comprising a single further *t*-BuHN=BH₂ insertion reaction allied to N-H deprotonation and B-H elimination from **4** may be envisaged to enable the production of compound **7**, this is at present no more than unfounded conjecture. Further studies will, thus, investigate the role of the calcium species during the conversion of **4** to **7** and will extend this reactivity to the other members of the alkaline earth series. Irrespective of the the outcome of these investigations, the additional complexity introduced through elaborations of this dehydrocoupling reactivity to substrates containing two nitrogen-bound protons highlights the difficulties intrinsic to the development of any generalised mechanism for dehydrocoupling of amine boranes.

Experimental Section

All reactions 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 96.3 MHz (¹¹B). 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. C₆D₆ and d₈-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. *t*-BuNH₂.BH₃

was purchased from Sigma-Aldrich Ltd. and used without further purification. Compounds **VII** and **VIII** were synthesized by literature procedures.^{80,81} CHN microanalysis was performed by Mr Stephen Boyer of London Metropolitan University.

Synthesis of Compound 1. D₈-toluene (ca. 0.5 ml) was added to a solid mixture of **VII** (103.4 mg, 0.15 mmol) and *t*-BuH₂N.BH₃ (13.0 mg, 0.15 mmol) and the solution was sealed in a Youngs tap NMR tube before standing at room temperature for ca. 30 minutes. Analysis at this point indicated stoichiometric formation of compound **1**, which was isolated by crystallization from the reaction solution (0.06g, 64%) ¹H NMR (d₈-tol, 298 K) δ = 0.80 (s, 9H, N(CH₃)₃), 1.21 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.30 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.55 (s, 1H, NH), 1.65 (s, 6H, NC(CH₃)), 3.19 (m, 4H, CH(CH₃)₂), 4.75 (s, 1H, C-H), 6.95 – 7.16 (m, 6H, arom-H). ¹³C{¹H} NMR (d₈-tol, 298 K) δ = 25.1 (CH(CH₃)), 25.2 (CH(CH₃)), 25.4 (CH(CH₃)), 25.9 (CH(CH₃)), 28.8 (NC(CH₃)₃), 28.9 (NC(CH₃)), 31.4 (NC(CH₃)₃), 94.1 (CH), 124.3 (*m*-C₆H₃), 125.1 (*p*-C₆H₃), 141.9 (*o*-C₆H₃), 147.4 (*i*-C₆H₃), 166.3 (CN). ¹¹B NMR (d₈-tol, 298 K) δ = -17.3 (q, BH₃, ¹J_{BH} = 80 Hz). Anal. Calc. for C₃₇H₆₂BCaN₃O: C: 72.17; H: 10.15; N: 6.82 %. Found: C: 72.30; H: 10.06; N: 6.77 %.

Catalytic dehydrocoupling of *t*-BuNH₂.BH₃ with VII. D₈-toluene (0.5 ml) was added to a solid mixture of *t*-BuH₂N.BH₃ (87.0 mg, 1 mmol) and **VI** (29.4 mg, 0.05 mmol) and the solution sealed in a Youngs tap NMR before heating at 60 °C for a total of ca. 138 hours. ¹H NMR (C₆D₆, 298 K) δ = 0.98 (s, C(CH₃)₃ **4**), 1.00 (s, C(CH₃)₃ **4**), 1.02 (s, NH), 1.03 (s, NH), 1.14 (s, C(CH₃)₃ **3**), 1.20 (s, NH), 1.38 (s, C(CH₃)₃ **7**). ¹³C{¹H} NMR (C₆D₆, 298 K) δ = 27.3 (C(CH₃)₃ **4**), 27.6 (C(CH₃)₃ **4**), 33.7 (C(CH₃)₃ **3**), 34.4 (C(CH₃)₃ **7**). ¹¹B NMR (d₈-tol, 298 K) δ = -22.8 (td, ¹J_{BH} = 99Hz, ²J_{BH} = 31 Hz, BH₂(μ-H)BH₂ **6**), -6.1 (t, *J*_{BH} = 109 Hz, BH₂ **4**), 29.1 (d, *J*_{BH} = 126 Hz, BH **3**), 38.2 (t, *J*_{BH} = 128 Hz, BH₂ **2**). Approximate conversion by integration of ¹¹B NMR spectrum: 4.3 % **2**, 13.4 % **3**, 45.2 % **4**, 3.2 % **6**, 20.1 % **7**.

Single crystals of **4** suitable for X-ray diffraction analysis were isolated from a concentrated toluene solution at -30 °C. Anal. Calc. for C₈H₂₄B₂N₂: C: 56.55; H: 14.24; N: 16.49 %. Found: C: 56.67, 56.69; H: 14.34, 14.38; N: 16.58, 16.55 %.

X-ray diffraction analysis of crystalline precipitate yielded the solid-state structure of **5**. Accurate CHN microanalysis could not be obtained for this compound. Although compound **5** could not be solubilised, the ¹¹B NMR spectrum of the reaction mixture was observed to contain a quintet resonance at δ = -30.6 ppm, *J*_{BH} = 82 Hz, which is assigned to a solvated form of this compound.

Catalytic dehydrocoupling of *t*-BuNH₂.BH₃ with VIII: Synthesis of 7. D₈-toluene (0.5 ml) was added to a solid mixture of *t*-BuH₂N.BH₃ (87.0 mg, 1 mmol) and VIII (18 mg, 0.05 mmol) and the solution sealed in a Youngs tap NMR before heating at 70 °C for ca. 66 hours. ¹H NMR (C₆D₆, 298 K) δ = 1.28 (s, 1H, NH), 1.38 (s, 9H, C(CH₃)₃), ca. 5.1 (v. br. d, 1H, BH). ¹³C{¹H} NMR (C₆D₆, 298 K) δ = 34.4 (C(CH₃)₃). ¹¹B NMR (d₈-tol, 298 K) δ = 34.4 (br. s, BH). Although single crystals of 7 suitable for X-ray diffraction analysis were isolated from a concentrated toluene solution at -30 °C, they diffracted only weakly obviating full structural discussion. Anal. Calc. for C₁₂H₃₀B₃N₃: C: 57.92; H: 12.15; N: 16.89 %. Found: C: 57.90; H: 11.98; N: 16.82 %.

X-ray Crystallography

Data for compounds **1**, **4** and **5** were collected at 150 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystem, using graphite monochromated MoK_α radiation (λ= 0.71073 Å). Data were processed using the Nonius Software.⁸² Crystal parameters and details on data collection, solution and refinement for the complexes are provided in Table S1. Structure solution, followed by full-matrix least squares refinement was performed using the WINGX-1.70 suite of programs throughout.⁸³ The structure of **5** was refined taking 30 % of twinning with 180.0° rotation about the 1 0 0 direct lattice direction into account. All hydrogen atoms binding to B(1) and B(2) were located in the difference Fourier map and were freely refined.

Supporting Information

Crystallographic information files (CIF) for **1**, **4** and **5** and details of the X-ray analysis of compound **7**. This material is available free of charge at <http://pubs.acs.org>.

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References

1. Mueller, K.; Stark, K.; Mueller B.; Arlt, W. *Energy & Fuels*, **2012**, *26*, 3691.
2. Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613.
3. Smythe, N. C.; Gordon, J. C. *Eur. J. Inorg. Chem.* **2010**, 509.
4. Peng, B.; Chen, J. *Energy & Env. Sc.* **2008**, *1*, 479.
5. Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279.
6. Huang, Z.; Autrey, T. *Energy & Env. Sc.* **2012**, *5*, 9257.
7. Autrey, T.; Bowden, M.; Karkamkar, A. *Faraday Disc.* **2011**, *151*, 157.
8. Parvanov, V. M.; Schenter, G. K.; Hess, N. J.; Daemen, L. L.; Hartl, M.; Stowe, A. C.; Camaioni, D. M.; Autrey, T. *Dalton Trans.* **2008**, 4514.
9. Staubitz, A.; Robertson, A. P. M.; Manners, I. *Chem. Rev.* **2010**, *110*, 4079.
10. Clark, T. J.; Russell, C. A.; Manners, I. *J. Am. Chem. Soc.* **2006**, *128*, 9582.
11. Sloan, M. E.; Staubitz, A.; Clark, T. J.; Russell, C. A.; Lloyd-Jones, G. C.; Manners, I. *J. Am. Chem. Soc.* **2010**, *132*, 3831.
12. Kakizawa, T.; Kawano, Y.; Naganeyama, K.; Shimoi, M. *Chem. Lett.* **2011**, *40*, 171.
13. Bera, B.; Jagirdar, B. R. *Inorg. Chim. Acta* **2011**, *372*, 200.
14. Kawano, Y.; Uruichi, M.; Shimoi, M.; Taki, S.; Kawaguchi, T.; Kakizawa, T.; Ogino, H. *J. Am. Chem. Soc.* **2009**, *131*, 14946.
15. Kawano, Y.; Yamaguchi, K.; Miyake, S. Y.; Kakizawa, T.; Shimoi, M. *Chem.-Eur. J.* **2007**, *13*, 6920.
16. Kawano, Y.; Uruichi, M.; Shimoi, M.; Taki, S.; Kawaguchi, T.; Kakizawa, T.; Ogino, H. *J. Am. Chem. Soc.* **2009**, *131*, 14946.
17. Tian, R.; Mathey, F. *Chem.-Eur. J.* **2012**, *18*, 11210.
18. Jiang, Y.; Berke, H. *Chem. Commun.* **2007**, 3571.
19. Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. *Organometallics* **2009**, *28*, 5493.
20. Baker, R. T.; Gordon, J. C.; Hamilton, C. W.; Henson, N. J.; Lin, P. H.; Maguire, S.; Murugesu, M.; Scott, B. L.; Smythe, N. C. *J. Am. Chem. Soc.* **2012**, *134*, 5598.
21. Vance, J. R.; Robertson, A. P.; Lee, K.; Manners, I. *Chem.-Eur. J.* **2011**, *17*, 4099.
22. Miyazaki, T.; Tanabe, Y.; Yuki, M.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2011**, *30*, 2394.
23. Ledger, A. E. W.; Ellul, C. E.; Mahon, M. F.; Williams, J. M. J.; Whittlesey, M. K. *Chem.-Eur. J.* **2011**, *17*, 8704.
24. Blaquiere, N.; Diallo-Garcia, S.; Gorelsky, S. I.; Black, D. A.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 14034.
25. Friedrich, A.; Drees, M.; Schneider, S. *Chem.-Eur. J.* **2009**, *15*, 10339.

26. Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424.
27. Staubitz, A.; Sloan, M. E.; Robertson, A. P.; Friedrich, A.; Schneider, S.; Gates, P. J.; Schmedt auf der Günne, J.; Manners, I. *J. Am. Chem. Soc.* **2010**, *132*, 13332.
28. Alcaraz, G.; Chaplin, A. B.; Stevens, C. J.; Clot, E.; Vendier, L.; Weller, A. S.; Sabo-Etienne, S. *Organometallics* **2010**, *29*, 5591.
29. Chaplin, A. B.; Weller, A. S. *Inorg. Chem.* **2010**, *49*, 1111.
30. Douglas, T. M.; Chaplin, A. B.; Weller, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 14432.
31. Chaplin, A. B.; Weller, A. S. *Angew. Chem., Int. Edition*, 2010, **49**, 581-584.
32. Tang, C. Y.; Thompson, A. L.; Aldridge, S. *J. Am. Chem. Soc.* **2010**, *132*, 10578.
33. Butera, V.; Russo, N.; Sicilia, E. *Chem.-Eur. J.* **2011**, *17*, 14586.
34. Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776.
35. Sewell, L. J.; Chaplin, A. B.; Weller, A. S. *Dalton Trans.* **2011**, *40*, 7499.
36. Chen, Y. S.; Fulton, J. L.; Linehan, J. C.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254.
37. Douglas, T. M.; Chaplin, A. B.; Weller, A. S.; Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2009**, *131*, 15440.
38. Tang, C. Y.; Thompson, A. L.; Aldridge, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 921.
39. Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *Chem. Commun.* **2001**, 962.
40. Sloan, M. E.; Clark, T. J.; Manners, I. *Inorg. Chem.* **2009**, *48*, 2429.
41. Chaplin, A. B.; Weller, A. S. *Inorg. Chem.* **2010**, *49*, 1111.
42. Sewell, L. J.; Huertos, M. A.; Dickinson, M. E.; Weller, A. S.; Lloyd-Jones, G. C. *Inorg. Chem.* **2013**, *52*, 4509.
43. Sewell, L. J.; Lloyd-Jones, G. C.; Weller, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 3598.
44. Vogt, M.; de Bruin, B.; Berke, H.; Trincado, M.; Grützmacher, H. *Chem. Sci.* **2011**, *2*, 723.
45. Zimmerman, P. M.; Paul, A.; Zhang, Z.; Musgrave, C. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 2201.
46. Yang, Z.; Hall, M. B. *J. Organometal. Chem.* **2009**, *694*, 2831.
47. Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844.
48. Rossin, A.; Bottari, G.; Lozano-Vila, A. M.; Paneque, M.; Peruzzini, M.; Rossi, A.; Zanobini, F. *Dalton Trans.* **2013**, *42*, 3533.
49. Kim, S. K.; Han, W. S.; Kim, T. J.; Kim, T. Y.; Nam, S. W.; Mitoraj, M.; Piekoś, Ł.; Michalak, A.; Hwang, S. J.; Kang, S. O. *J. Am. Chem. Soc.* **2010**, *132*, 9954.
50. Hartmann, C. E.; Jurčík, V.; Songis, O.; Cazin, C. S. *Chem. Commun.* **2013**, *49*, 1005.
51. Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 8826.
52. Chapman, A. M.; Wass, D. F. *Dalton Trans.* **2012**, *41*, 9067.
53. Spielmann, J.; Bolte, M.; Harder, S. *Chem. Commun.* **2009**, 6934.
54. Harder, S.; Spielmann, J.; Tobey, B. *Chem.-Eur. J.* **2012**, *18*, 1984.

55. Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; MacDougall, D. J. *Chem.- Eur. J.* **2010**, *16*, 8508.
56. Hill, M. S.; Hodgson, M.; Liptrot, D. J.; Mahon, M. F. *Dalton Trans.* **2011**, *40*, 7783.
57. Harder, S.; Spielmann, J. *Chem. Commun.* **2011**, *47*, 11945.
58. Hill, M. S.; Kociok-Köhn, G.; Robinson, T. P. *Chem. Commun.* **2010**, *46*, 7587.
59. Lu, E.; Yuan, Y.; Chen, Y.; Xia, W. *ACS Catalysis* **2013**, *3*, 521.
60. Cui, P.; Spaniol, T. P.; Maron, L.; Okuda, J. *Chem.- Eur. J.* **2013**, *19*, 13437.
61. Cowley, H. J.; Holt, M. S.; Melen, R. L.; Rawson, J. M.; Wright, D. S. *Chem. Commun.* **2011**, *47*, 2682.
62. Less, R. J.; Melen, R. L.; Wright, D. S. *RSC Advances* **2012**, *2*, 2191.
63. Hansmann, M. M.; Melen, R. L.; Wright, D. S. *Chem. Sci.* **2011**, *2*, 1554.
64. Less, R. J.; Simmonds, H. R.; Dane, S. B. J.; Wright, D. S. *Dalton Trans.* **2013**, *42*, 6337.
65. Spielmann, J.; Jansen, G.; Bandmann, H.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6290.
66. Spielmann, J.; Harder, S. *J. Am. Chem. Soc.* **2009**, *131*, 5064.
67. Bellham, P.; Hill, M. S.; Liptrot, D. J.; MacDougall, D. J.; Mahon, M. F. *Chem. Commun.* **2011**, *47*, 9060.
68. Bellham, P.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J. *Dalton Trans.* **2013**, *42*, 737.
69. Bellham, P.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J. *Chem. Commun.* **2013**, *49*, 1960.
70. Butera, V.; Russo, N.; Sicilia, E. *Chem. Eur. J.* **2014**, *20*, in press, DOI: 0.1002/chem.201304329.
71. Whittell, G. R.; Balmond, E. I.; Robertson, A. P. M.; Patra, S. K.; Haddow, M. F.; Manners, I. *Eur. J. Inorg. Chem.* **2010**, 3967.
72. Staubitz, A.; Soto, P.; Manners, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 6212.
73. Maringgele, W.; Noltemeyer, M.; Teichgraber, J.; Meller, J. *Main Group Metal Chemistry*, **2000**, *23*, 735.
74. Maringgele, W.; Noltemeyer, M.; Schmidt, H. G.; Meller, J. *Main Group Metal Chemistry*, **1999**, *22*, 715.
75. Wrackmeyer, B.; Molla, E.; Thoma, P.; Klimkina, E. V.; Tok, O. L.; Bauer, T.; Kempe, R. Z. *Anorg. Allg. Chem.* **2011**, *637*, 401.
76. Tang, Z. W.; Tan, Y. B.; Gu, Q. F.; Yu, X. B. *J. Mater. Chem.* **2012**, *22*, 5312.
77. Biswas, S.; Muller, M.; Tonshoff, C.; Eichele, K.; Maichle-Mossmer, C.; Ruff, A.; Speiser, B.; Bettinger, H. F. *Eur. J. Org. Chem.* **2012**, 4634.
78. Sham, I. H. T.; Kwok, C. C.; Che, C. M.; Zhu, N. Y. *Chem. Commun.* **2005**, 3547.
79. Muller, M.; Maichle-Mossmer, C.; Bettinger, H.F. *Chem. Commun.* **2013**, *49*, 11773.
80. Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Chem. Commun.*, **2003**, 48.
81. Westerhausen, M. *Inorg. Chem.* **1991**, *30*, 96.

82. DENZO-SCALEPACK Otwinowski, Z.; Minor, W. "Processing of X-ray Diffraction Data Collected in Oscillation Mode", *Methods in Enzymology*, Volume 276: Macromolecular Crystallography, part A, p.307-326, **1997**, C.W. Carter, Jr. & R. M. Sweet, Eds., Academic Press.
83. Farrugia, L. J. *J. Appl. Cryst.* **1999**, 32, 837.

For Table of Contents:

Stoichiometric and Catalytic Reactivity of *tert*-Buylamine Borane with Calcium Silylamides

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