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The Significance of Secondary Interactions during Alkaline Earth-promoted Dehydrogenation of Dialkylamine-Boranes[‡]

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Abstract

Reactions of anilidoimine magnesium *n*-butyl and calcium bis(trimethylsilyl)amide derivatives with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ at 25 °C resulted in the isolation of complexes containing $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ and $[\text{NMe}_2\text{BH}_3]^-$ anions respectively. Although onward reaction of the calcium species at 30 °C with a further equivalent of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ provided ca. 90% conversion of the coordinated dimethylamidoborane anion to $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$, this process also resulted in significant (ca. 25%) levels of competitive protonation of the anilidoimine spectator ligand. A similar reaction performed between a previously reported β -diketiminato calcium dimethylamidoborane and $\text{Me}_2\text{NH}\cdot\text{BH}_3$, however, provided clean conversion to a structurally characterised calcium $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ complex. Reaction of a more sterically congested β -diketiminato magnesium *n*-butyl reagent with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ has allowed the isolation of a magnesium derivative of the $[\text{NMe}_2\text{BH}_3]^-$ anion. The thermal stability of these compounds as well as previously reported magnesium and calcium amidoborane species indicate, in partial agreement with a recent DFT study, that all of these compounds are resistant to the β - and δ -hydride elimination reactions that have previously been implicated as the key B-N bond-forming and dehydrogenative steps in the group 2-catalysed dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$. In contrast to these observations, addition of stoichiometric quantities of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ to the various isolated group 2 amidoborane species was found to result in facile elimination of the cyclic borazane $[\text{Me}_2\text{N}-\text{BH}_2]_2$ which occurs with regeneration of the metallated amidoborane. On this basis, we suggest that the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ at group 2 centres takes place as a sequence of concerted proton-assisted steps during which B-H and N-H bond breaking plays an equally prominent role, with the efficacy of boron hydride protonolysis dictated by the relative polarising influence of the B-H to Mg/Ca interactions. Furthermore, we propose a modified mechanism for group 2-mediated dimethylamine borane dehydrocoupling that is dependent on the intermediacy of key derivatives of the $[\text{NMe}_2\cdot\text{BH}_3]^-$ and $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anions but does not require the formation of high energy alkaline earth hydride intermediates. Although these results are specifically focussed on the applications of alkaline earth species, this mechanistic insight is of redox-inactive main group element-based systems and to our understanding of hydrogen evolution from saline derivatives of ammonia borane.

Introduction

The chemistry of metallated amidoborane derivatives and their role in the catalytic heterodehydrocoupling of B-H and N-H functionalities has been significantly extended during the last decade. Although driven by an initial consideration of ammonia borane, $\text{H}_3\text{N}\cdot\text{BH}_3$ (AB), as a potential hydrogen storage material,¹ the metal-centred dehydrocoupling reactivity of primary and secondary organoamine derivatives ($\text{RH}_2\text{N}\cdot\text{BH}_3$ and $\text{R}_2\text{HN}\cdot\text{BH}_3$) has also impacted more broadly on other areas. For example, studies of dimethylamineborane, $\text{Me}_2\text{HN}\cdot\text{BH}_3$ (DMAB), alone have allowed the synthesis of novel B-N bonded polymeric materials and given rise to a plethora of new mechanistic information.² Although a majority of this attention has focussed on the use of redox-active mid- and late transition elements,³ the synthesis and chemistry of amidoborane derivatives of the typical main group elements and d^0 transition metal species has also received significant consideration.⁴ For *s*-block element derivatives, many of the B-H or N-H bond activation pathways open to redox active transition metals are inapplicable and the dehydrogenation of amine boranes must necessarily ensue by a sequence of heterolytic bond breaking and bond forming events. Initial reports demonstrated that the propensity toward hydrogen release of AB could be improved through replacement of a protonic hydrogen with a more electropositive alkaline earth (Ae) metal and the formation of metal amidoboranes, $\text{Ae}(\text{NH}_2\text{BH}_3)_2$ (Ae = Mg, Ca, Sr).⁵ These compounds exist as extended polymeric materials in the solid state, propagated through complex networks of primary metal to amide bonds and a multiplicity of secondary B-H $\cdots$ M and N-H $\cdots$ H-B hydrogen bonding interactions.⁵ While the structures and properties of these derivatives are directly relevant to hydrogen release from AB, their study can provide only limited insight into the molecular processes at play during dehydrogenation. More of our understanding of the amine borane dehydrocoupling activity of the group 2 elements has, thus, been informed by the isolation of well-defined molecular derivatives and to this end a number of groups have turned their attention to the synthesis of magnesium and calcium derivatives of primary and secondary amine boranes. Particularly prominent among these latter species are derivatives of β -diketiminate ligands such as compounds **1** - **3** (Scheme 1),^{4d,o} which display the common features of Ae $\cdots$ HB interactions but which are constrained to either mono- or di-nuclear constitutions by the presence of the sterically demanding spectator ligand. Under catalytic conditions, our own work has concentrated on the dehydrocoupling of secondary amine boranes, $\text{R}_2\text{NH}\cdot\text{BH}_3$ (R = Me, $\{(\text{CH}_2)_2\}_2$), by magnesium and calcium amidoborane derivatives such as **2** and **3**.^{4d,e} In these cases, the ultimate products of catalytic dehydrocoupling are cyclic borazanes of the form $[\text{R}_2\text{N}-\text{BH}_2]_2$ which are formed alongside minor amounts of diaminoboranes, $\text{HB}(\text{NR}_2)_2$, which have been deduced to form through the formation of isolable magnesium compounds such as **3** containing coordinated $[\text{H}_3\text{BNR}_2\text{BH}_2\text{R}_2\text{N}]^-$ anions. To account for these observations we have suggested that this process is predominantly metal-mediated and dependent upon the generalised mechanism illustrated in Scheme 1. Under this regime, the primary B-N bond forming reactions require a sequence of metallated amidoborane β -hydride elimination from species

akin to compound **2** (depicted as **A** in Scheme 1) and polarised $[R_2N=BH_2]$ (**B**) insertion to provide isolable intermediate species (**C**) such as compound **3**. The final borazane product (**D**) may then be generated by a proposed δ -hydride elimination step that occurs with formation of a catalytically competent alkaline earth hydride. We have suggested that the changing kinetic facility for the reactions is dictated by the charge density and resultant ability of the Ae^{2+} centre to polarise and activate a B-H bond of the ligated $[H_3BNR_2BH_2R_2N]^-$ anion, such that the dehydrocoupling activity describes a reactivity trend $Mg > Ca > Sr > Ba$.

Scheme 1: Structures of compounds **1** – **3** and the suggested mechanism for group 2-centred dehydrocoupling of secondary amine boranes, $R_2NH.BH_3$.

Although many of the gross features of this hypothesis were borne out by a subsequent DFT study provided by Sicilia and co-workers,⁶ their results have questioned the viability of several of the simple molecular processes depicted in Scheme 1. The model magnesium complex $[HC\{(Me)CN(C_6H_5)_2\}MgNMe_2BH_3]$ was computed to decompose by β -hydride elimination to produce $[HC\{(Me)CN(C_6H_5)_2\}MgH]$ and $[R_2N=BH_2]$. Although the insertion of this latter species into the Mg-N bond of $[HC\{(Me)CN(C_6H_5)_2\}MgNMe_2BH_3]$ was shown to ensue via an accessible free energy barrier of $16.5 \text{ kcal mol}^{-1}$, any subsequent δ -hydride elimination step required the traversal of a barrier of some 40 kcal mol^{-1} . This prohibitively high activation energy led the authors to conclude that the formation of the cyclic borazane product must necessarily transpire as an off-metal process through the exothermic ($4.2 \text{ kcal mol}^{-1}$) dimerisation of two $[R_2N=BH_2]$ fragments rather than through direct release from species similar to compound **3**.

As a counterpoint to these observations, further calculations performed on a calcium derivative analogous to compound **2.THF** demonstrated that even the initial β -hydride elimination step associated

with $[\text{Me}_2\text{N}=\text{BH}_2]$ production is unfeasible without the coordinative assistance of a second molecule of DMAB.⁶ In this instance intermolecular elimination of H_2 was deduced to occur as part of a concerted process to liberate $[\text{R}_2\text{N}=\text{BH}_2]$ and directly regenerate the initial calcium dimethylamidoborane species (Scheme 2). Although this route may again yield the cyclic borazane through an off-metal process, a necessary implication is a disavowal of any calcium species containing $[\text{H}_3\text{BNMe}_2\text{BH}_2\text{Me}_2\text{N}]^-$ anions or the intermediacy of molecular calcium hydride species.

Scheme 2: DFT computed concerted pathway allowing DMAB dehydrogenation at calcium.

Although the previously reported compound **3** and several closely related magnesium complexes are available to further test these hypotheses,^{4d} the calculated pathway summarised in Scheme 2 implies that analogous calcium derivatives containing the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion are effectively inaccessible. Similarly, no magnesium amidoborane derivatives containing the $[\text{H}_3\text{B}.\text{NMe}_2]^-$ anion are available for comparison to compounds such as **2**.THF. Both classes of compound, therefore, represent ‘missing links’ in our experimental understanding of group 2-centred amine borane dehydrogenation chemistry. In this contribution we describe our efforts to address these lacunae and provide our further observations with regard to the mechanism(s) of alkaline earth-promoted amine borane dehydrocoupling.

Results and Discussion

Synthesis of Anilidoimine derivatives: The synthesis of the β -diketiminate-supported compounds **2**.THF and **3** has previously been achieved by the direct reaction of DMAB with heteroleptic calcium bis(trimethylsilyl)amido and magnesium *n*-butyl precursors respectively.^{4d} Although some provisional (¹¹B NMR) spectroscopic evidence was accrued for the intermediacy of a mono amidoborane magnesium species, $[\text{HC}\{(\text{Me})\text{CN}(2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)_2\}\text{MgNMe}_2\text{BH}_3]$, *en route* to the magnesium compound **3**, all attempts to constrain the reaction to the 1:1 stoichiometry required for the isolation of this species have been unsuccessful. Sarazin and Carpentier have recently demonstrated the application

of Piers' anilidoimine ligand as an alternative platform to allow the synthesis of the Ca, Sr and Ba derivatives, $[\{\text{ArN}(o\text{-C}_6\text{H}_4)\text{C}(\text{H})=\text{NAr}\}\text{Ae}(\text{THF})_n\{\text{N}(\text{SiMe}_3)_2\}]$ ($\text{Ar}=2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$, $n=1$ $\text{Ae}=\text{Ca}$; $n=2$ $\text{Ae}=\text{Sr}$, Ba) which function as stable pre-catalytic species for a wider range of multiple bond heterofunctionalisation and cross-coupling based catalyses.⁷ To assess the suitability of this ligand system for the study of group 2-centred amine borane dehydrogenation we, thus, synthesised the previously unreported magnesium *n*-butyl derivative (**4**) from the reaction of *n*-Bu₂Mg and the parent aniline-imine ligand precursor, and the calcium bis(trimethylsilyl)amide derivative (**5**) (Scheme 3).

Scheme 3: Synthetic routes to the anilidoimine-supported magnesium and calcium derivatives, **6**, **7** and **8**.

In common with our previously reported attempts to synthesise magnesium derivatives of the dimethylamidoborane anion,^{4d,e} addition of a single molar equivalent of DMAB to a toluene solution of compound **4** at room temperature resulted in the consumption of approximately 50% of the magnesium *n*-butyl starting material to provide a new species (**6**), which was characterised by the appearance of quartet and triplet resonances of a similar intensity in the ¹¹B NMR spectrum at $\delta = -16.0$ ppm ($^1J_{\text{BH}} = 86$ Hz) and $\delta = 3.3$ ppm ($^1J_{\text{BH}} = 99$ Hz) respectively. The ¹¹B NMR signals associated with compound **6** are comparable with those observed for the previously described compound **3** ($\delta = -14.9$ ppm and $\delta = 4.1$ ppm respectively)^{4d} and are, thus, assigned to the {BH₃} and {BH₂} units of an anilidoimine supported magnesium $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ complex. The facile formation of compound **6** under these conditions, which could be prepared in effective stoichiometric yield through adjustment of the DMAB:**4** reaction stoichiometry to 2:1, indicates that the reactivity of the anilidoimine supported magnesium centre is as similarly non-discriminating for the stabilisation of the $[\text{H}_3\text{B}\cdot\text{NMe}_2]^-$ anion as the previously investigated β -diketiminato systems. The solid-state structure of compound **6** was confirmed by a single crystal X-ray diffraction analysis, obtained by crystallisation from a concentrated toluene solution at -30°C . The results of this analysis are shown in Figure 1, while details of the X-ray

data collection and refinement and selected bond length and angle data are presented in Tables 1 and 2 respectively.

Figure 1: ORTEP representation of the solid-state structure of compound **6**. Thermal ellipsoids set at 25% probability. Hydrogen atoms other than the boron-bound hydrides and 2,6-di-*iso*-propylphenylaniline *iso*-propyl methyl carbon atoms are removed for clarity.

The solid-state structure of **6** is broadly analogous to that of compound **3**, comprising a magnesium centre coordinated by the bidentate anilidoimine ligand and the nitrogen atom of the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion. The coordination of this latter ligand is augmented by further agostic-type interactions with the boron-bound hydrides of the $\{\text{BH}_3\}$ unit. Although the $\text{Mg}(1)\text{-N}(3)$, $\text{N}(3)\text{-B}(1)$, $\text{N}(4)\text{-B}(1)$ and $\text{N}(4)\text{-B}(2)$ bond distances within the amidoborane anion are effectively identical to those observed for compound **3**, the $\text{Mg}(1)\text{-N}(1)$ [2.089(2) Å] and $\text{Mg}(1)\text{-N}(2)$ [2.029(2) Å] bond distances emphasise the much greater anisobidenticity of the anilidoimine ligand in comparison to the previously employed β -diketiminato supporting environment [2.0531(13) and 2.0529(13) Å].

In contrast to this magnesium-centred reactivity, addition of an equimolar quantity of DMAB to compound **5** resulted in smooth conversion to a new species characterised by a single quartet resonance in the ^{11}B NMR spectrum at $\delta = -12.4$ ppm ($^1J_{\text{BH}} = 80$ Hz). This resonance was readily assigned to the $\{\text{BH}_3\}$ unit of a new calcium dimethylamidoborane derivative (**7**) by comparison to the corresponding signal observed in the previously reported β -diketiminato calcium species, compound **2**.THF ($\delta = -11.5$ ppm, $^1J_{\text{BH}} = 86$ Hz) (Scheme 3).^{4d} The solid-state structure of compound **7** was confirmed by a further single crystal X-ray diffraction analysis, the results of which are shown in Figure 2 with details of the analysis and selected bond length and angle data displayed in Tables 1 and 2

respectively. Aside from the change in ancillary ligand, the solid-state structure of **7** is effectively analogous to that of the previously described compound **2**.THF and merits no further detailed comment.

Figure 2: ORTEP representation of the solid-state structure of compound **7**. Thermal ellipsoids set at 25% probability. Hydrogen atoms other than the boron-bound hydrides and 2,6-di-*iso*-propylphenylaniline *iso*-propyl methyl carbons are removed for clarity.

Although compound **7** formed cleanly with precise adherence to the necessary 1:1 DMAB:**5** reaction stoichiometry, attempts to synthesise calcium species analogous to compound **6** by addition of two molar equivalents of DMAB to the bis(trimethylsilyl)amide precursor **5** were observed to result in protonation of the anilidoimine supporting ligand and the formation of toluene-insoluble material. A further reaction was, thus, attempted by careful heating of equimolar quantities of **7** and DMAB in *d*₈-toluene at 30°C for ca. 16 hours. Although this procedure also resulted in protonation of approximately 25% of the anilidoimine ligand, the resultant ¹¹B NMR spectrum displayed quartet and triplet resonances accounting for ca. 90% of the total signal intensity at $\delta = -11.2$ ppm ($^1J_{\text{BH}} = 89$ Hz) and $\delta = 1.8$ ppm ($^1J_{\text{BH}} = 96$ Hz). While these data were indicative of the formation of a new calcium complex (**8**) containing the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion (Scheme 3) and confirm the viability of the formation of its formation from the initial $[\text{NMe}_2\text{BH}_3]^-$ derivative (**7**), all attempts to crystallise and isolate this new species were unsuccessful.

Synthesis of β -diketiminato derivatives: In the light of the above noted issues of supporting ligand protonation we turned our attention to the previously reported β -diketiminato calcium amidoborane derivative **2**.THF, which has demonstrated its resistance to deleterious protonation by DMAB.^{4d}

Addition of one equivalent of DMAB to a toluene solution of compound **2**.THF and heating at 30°C for 72 hours did indeed result in the formation of a single new β -diketiminato species, compound **9**, which could be assigned as a derivative of the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion through the observation of quartet and triplet resonances at $\delta = -11.2$ ppm ($^1J_{\text{BH}} = 99$ Hz) and $\delta = 2.1$ ppm ($^1J_{\text{BH}} = 96$ Hz) respectively in the ^{11}B NMR spectrum (Scheme 4). These ^{11}B NMR chemical shifts are respectively downfield and upfield of the analogous resonances observed for the $\{\text{BH}_3\}$ and $\{\text{BH}_2\}$ units of the analogous β -diketiminato magnesium species (**3**) ($\delta = -14.9$ ppm and $\delta = 4.1$ ppm) but bear close comparison to the tentatively identified species (**8**) resulting from reaction of compound **5** and DMAB.

Scheme 4: Synthesis of compound **9**.

Single crystals of compound **9** suitable for X-ray diffraction analysis were isolated from a concentrated toluene solution at -30°C . The resultant solid-state structure is shown in Figure 3 while details of the analysis and selected bond length and angle data are provided in Tables 1 and 2. The structure of compound **9** is broadly analogous to that of its magnesium analogue (**3**) albeit with the coordination sphere of the larger calcium centre saturated through the addition of a single molecule of donor THF.^{4d} Although the calcium centre is similarly coordinated by the nitrogen and agostic-type interactions with the BH_3 -bound hydrides of the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion, Ca(1) also displays close contacts with the BH_2 unit (depicted as B(1) in Figure 3). We suggest that the persistence of this additional interaction in solution is the likely origin of the upfield shift associated with this boron nucleus in the ^{11}B NMR spectrum. As a structural consequence of this interaction, the bond angles along the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ ligand are distorted in comparison with the magnesium compounds **3** and **6** containing the identical moiety.

Figure 3: ORTEP representation of the solid-state structure of compound **9**. Thermal ellipsoids set at 25% probability. Hydrogen atoms other than the boron-bound hydrides and *iso*-propyl groups are removed for clarity.

Although we have previously presented limited spectroscopic evidence for the formation of a magnesium amidoborane, $[\text{HC}\{(\text{Me})\text{CN}(2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)_2\}\text{MgNMe}_2\text{BH}_3]$ (**10**),^{4d} analogous to compound **2**, this species, in common with the isolation of compound **6** described above, has been shown to react indiscriminately with a further equivalent of DMAB even at reduced reaction temperatures to form the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion. An alternative synthesis of compound **10** (Scheme 5) was thus attempted through a salt metathesis reaction between Jones' β -diketiminato-magnesium-iodide (**11**) and $[\text{K}(\text{NMe}_2\text{BH}_3)]$, which were prepared by literature procedures.⁸

Scheme 5: Attempted preparation of compound **10**.

The ^{11}B NMR spectrum of compound **10** comprised a single quartet resonance at $\delta = -11.8$ ppm ($^1J_{\text{BH}} = 91$ Hz) which bears close comparison to both of the calcium dimethylamidoborane derivatives, compounds **2**.THF ($\delta = -11.5$ ppm, $^1J_{\text{BH}} = 86$ Hz) and **7** ($\delta = -12.4$ ppm, $^1J_{\text{BH}} = 80.3$ Hz). Storage of solutions for attempted crystallisation of compound **10**, however, resulted in the formation of intractable and insoluble material preventing confirmation of this species by crystallographic and microanalytical elemental analysis.

Scheme 6: Synthesis of compound **13**.

In an attempt to improve the kinetic stability of such a β -diketiminato magnesium dimethylamidoborane we turned our attention to Chisholm's recently described $[\text{HC}\{(t\text{-Bu})\text{CN}(2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)_2\}\text{Mg}n\text{-Bu}]$ (**12**) which utilises a *tert*-butyl substituted variant of the β -diketiminato ligand to provide enhanced steric influence over the reactivity of the magnesium centre.⁹ Reaction of compound **12** with an equimolar quantity of DMAB at room temperature in benzene provided a single new compound (**13**) which displayed a quartet resonance at $\delta -15.4$ ($^1J_{\text{BH}} = 91$ Hz) in its ^{11}B NMR spectrum (Scheme 6). This value is comparable with the ^{11}B NMR chemical shifts (ca. $\delta -10$ ppm) arising from compounds **2**.THF and **7** and the solution data recorded for compound **10**.^{4d} The identity of compound **13** as a magnesium dimethylamidoborane derivative was confirmed through an X-ray diffraction analysis performed on a single crystal isolated from the benzene reaction solvent. The results of this analysis are shown in Figure 4 with details of the analysis and selected bond length and angle data provided in Tables 1 and 2 respectively.

Figure 4: ORTEP representation of the solid-state structure of compound **13**. Thermal ellipsoids set at 25% probability. Hydrogen atoms other than the boron-bound hydrides and 2,6-di-*iso*-propylphenylamine *iso*-propyl methyl carbons are removed for clarity.

The incorporation of the *tert*-butyl substituents in the β -diketiminato ligand of compound **13** has little effect on the Mg(1)-N(1) and Mg(1)-N(2) bond lengths and the N(1)-Mg(1)-N(2) angle about the magnesium centre when compared with the corresponding measurements of compound **3** and a variety of previously reported magnesium derivatives.⁴ The greater steric congestion imposed by the larger alkyl substituents is clearly apparent, however, by consideration of the Mg(1)-N(1)-C(12) [111.46(8)°] and Mg(1)-N(2)-C(24) [112.41(8)°] angles which are significantly compressed in comparison to the typical values observed in compounds supported by the less sterically demanding methyl-substituted β -diketiminato ligand (ca. 123°).⁴

Reactivity and stability of group 2 amidoborane derivatives

β -hydride elimination from magnesium and calcium dimethylamidoboranes: The thermal stabilities of the β -diketiminato magnesium and calcium dimethylamidoborane derivatives, compounds **13** and **2**.THF, were assessed by heating of NMR samples in d_8 -toluene at 80°C for 16 hours and monitoring by ^{11}B NMR spectroscopy. Neither species displayed any evidence of reaction or decomposition under these conditions, or after further heating at 100°C and 120°C for an additional 3 hours in each case. The notable thermal stability of the calcium species **2**.THF provides experimental corroboration of the earlier DFT study performed on this exact system, which indicated that our previously proposed β -hydride elimination step was energetically unfeasible.⁶ Although the barrier to β -hydride elimination for a magnesium dimethylamidoborane derivative has been computed to be viable (20 kcal mol⁻¹), this conclusion contradicts the notable thermal stability of compound **13**, albeit the isolation of this latter species is dependent upon the enhanced steric protection provided by the *tert*-butyl substituted β -diketiminato ligand. In a further experiment addition of a single molar equivalent of DMAB to a solution of compound **13** at room temperature induced the formation of $[\text{Me}_2\text{N-BH}_2]_2$ as the only observable new reaction product. This process took place without any apparent consumption of compound **13** which remained in solution in an approximate 2:1 ratio with respect to the cyclic borazane. Notably, no evidence for the intermediacy of a magnesium hydride or any species containing the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion could be observed.

Their assessment of the calcium species **2**.THF led Sicilia and co-workers to propose the alternative ‘DMAB assisted’ pathway summarised in Scheme 2, the natural consequence of which is not only the preclusion of any calcium hydride formation but also the production and catalytic relevance of calcium species such as compound **9** containing the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion.⁶ As described above, addition of an additional equivalent of DMAB to the β -diketiminato or anilidoimine calcium dimethylamidoborane derivatives, compounds **2**.THF and **7** respectively, results in dehydrogenation and formation of the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion within the coordination sphere of the group 2 element. Careful monitoring of these reactions by ^{11}B NMR spectroscopy failed to detect any further

intermediates, most notably the aminoborane $[\text{Me}_2\text{N}=\text{BH}_2]$, which has previously been observed during the dehydrocoupling of DMAB by group 2 reagents under catalytic conditions.^{4d,e}

As detailed above, the stoichiometric reaction between compound **2**.THF and DMAB to form compound **9** was observed to proceed in practicable timescales at 30 – 35°C. For temperatures above 35 °C borazane formation became significant (*vide infra*), whilst study of reactions performed at temperatures below 30°C was precluded by impracticably slow reaction rates. Kinetic (¹¹B) NMR-scale studies of the reaction between compound **2**.THF and DMAB, $\text{Me}_2\text{NH}.\text{BD}_3$ and $\text{Me}_2\text{ND}.\text{BH}_3$ were, thus, undertaken at 35°C to further elucidate the nature of this process. Although the increase in concentration of compound **9** could not be modelled by any simple 0, 1st nor 2nd order kinetic data plots, the consumption of DMAB, and that of its *B*- and *N*-deuterated analogues conformed to well behaved 2nd order kinetics (Figure 5).

Figure 5: Second order kinetic data plots for the consumption of DMAB (diamonds,◇), $\text{Me}_2\text{NH}.\text{BD}_3$ (crosses, ×) and $\text{Me}_2\text{ND}.\text{BH}_3$ (triangles△) for the stoichiometric reaction with compound **2**.THF at 35°C.

The data presented in Figure 5 illustrate that the reaction of compound **2**.THF with the *N*-deuterated and *B*-deuterated amine boranes proceeded at a slower, but similar, rate in comparison to per-protio DMAB. The resultant $k_{\text{H}}/k_{\text{D}}$ values of 1.4 for N-H/D and 1.6 for B-H/D highlight, therefore, that both N-H/B-H bond breaking/forming are of comparable significance during the rate determining step (RDS) of the reaction.

In the light of these observations, the notable thermal stability of compound **13** and its facile reactivity with DMAB, we infer that our initial suggestion of β -hydride elimination with resultant group 2 hydride and $[\text{Me}_2\text{N}=\text{BH}_2]$ formation is most likely incorrect. Although the second order consumption

of the amine borane during the reaction of compound **2**. THF with DMAB defies any simple interpretation, we now propose that dihydrogen elimination occurs as part of a concerted process assisted by the protic DMAB reagent. This behaviour is somewhat reminiscent of that depicted in Scheme 2, however, we suggest that the generated aminoborane, $[\text{Me}_2\text{N}=\text{BH}_2]$, does not leave the coordination sphere of the group 2 metal and that B-N bond formation to generate the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion occurs concurrently as part of a concerted process such as that depicted in Scheme 7. We, furthermore, deduce that the minor quantities of free $[\text{Me}_2\text{N}=\text{BH}_2]$ detected under catalytic conditions are possibly a result of competitive but unrelated reactivity and,^{4d,e} in this manner, the relative facility for the formation of the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion is a consequence of the differing polarising capabilities of the Mg and Ca centres on the hydridic B-H unit.

Scheme 7: Proposed concerted pathway to dehydrogenative $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion formation.

δ -hydride elimination from magnesium and calcium $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ derivatives: The availability of the analogous magnesium and calcium derivatives of the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion, compounds **3** and **9**, provides an opportunity to assess the viability and relative efficacy of the proposed δ -hydride elimination step depicted as the primary route to the cyclic borazane $[\text{Me}_2\text{N}-\text{BH}_2]_2$ in Scheme 1. We have reported previously that heating of **3** at 60 °C for 16 hours in toluene solution provides limited (ca. 20%) conversion to $[\text{Me}_2\text{N}-\text{BH}_2]_2$ along with tentative evidence for the simultaneous formation of the β -diketiminato magnesium hydride $[\text{HC}\{(\text{Me})\text{CN}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_2\}_2\text{MgH}]_2$.^{4d,10} We have repeated this experiment and now believe this observation to be erroneous and that any conversion to $[\text{Me}_2\text{N}-\text{BH}_2]_2$ observed at that time was due to the presence of small quantities of DMAB which had been carried over from the initial synthesis. To ensure complete reaction of the amine borane starting material upon conversion to compound **3** a sub-stoichiometric quantity (1.9 equivalents) of DMAB was reacted with $[\text{HC}\{(\text{Me})\text{CN}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_2\}_2\text{MgH}-\text{Bu}]$. The resultant solution, which displayed signals in its ^{11}B and ^1H NMR spectra consistent with the formation of **3** along with a small residual quantity of the organomagnesium starting material, was then heated at 100 °C for 3 hours. Although this procedure induced very minor changes in the subsequent NMR spectra no evidence for the formation of $[\text{Me}_2\text{N}-\text{BH}_2]_2$ or the magnesium hydride $[\text{HC}\{(\text{Me})\text{CN}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)_2\}_2\text{MgH}]_2$ was observed as a result of thermally induced β -hydride elimination. In stark contrast to these observations, addition of a further two molar equivalents of DMAB to this sample at room temperature induced a visible bubbling within the NMR tube. Periodic monitoring of this reaction by ^{11}B and ^1H NMR spectroscopy over a 72

hour period at room temperature indicated that this process occurred with the production of the cyclic borazane without any apparent consumption of compound **3**. The observation of a singlet resonance at δ 4.49 ppm in the ^1H NMR spectrum also confirmed the presence of molecular H_2 as the other product of the reaction, which we now suggest was previously mistakenly assigned as the Mg-H resonance of $[\text{HC}\{(\text{Me})\text{CN}(2,6\text{-}i\text{-Pr}_2\text{-C}_6\text{H}_3)_2\}\text{MgH}]_2$.^{4d} On the basis of these observations we propose that $[\text{Me}_2\text{N-BH}_2]_2$ is indeed formed via a δ -hydride elimination reaction of compound **3**. In agreement with the calculations of Sicilia and co-workers,⁶ however, we deduce that the thermal activation of this process is energetically inaccessible and again requires the assistance of one or more molecules of the protic DMAB substrate, in a manner effectively analogous to that depicted for the β -hydride elimination step shown in Scheme 7. In further support of this hypothesis, although addition of a range of protic secondary amines to solutions of compound **3** were similarly noted to yield $[\text{Me}_2\text{N-BH}_2]_2$ at room temperature, no reaction was observed to occur with the aprotic tertiary amine borane, $\text{Me}_3\text{N.BH}_3$. The calcium species (**9**) was observed to behave similarly. Although this compound was thermally stable in d_8 -toluene solution up to temperatures in excess of 70°C , addition of further equivalents of DMAB under these conditions was observed to result in the production of $[\text{Me}_2\text{N-BH}_2]_2$ which was detected along with variable quantities of compounds **2.THF** and **9**. We suggest that the minor amounts of $\text{HB}(\text{NMe}_2)_2$ observed during the catalytic dehydrocoupling of DMAB by magnesium and calcium species may be similarly rationalised as a consequence of β -hydride elimination from the coordinated BH_2 unit of the $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anion (e.g. labelled as B(1) in Figure 3).

Conclusions

On the basis of the empirical observations described above it is possible to delineate a number of modifications and refinements to the mechanism for amine borane dehydrocoupling shown in Scheme 1. Although these deductions relate solely to solution processes mediated by the alkaline earth elements magnesium and calcium we suggest that they may carry broader potential relevance to a range of related reactivities derived from other redox-inactive metal centres and to the solid-state decomposition of saline ammonia borane derivatives.⁵

Scheme 8: Proposed ‘proton-assisted’ pathway to alkaline earth mediated DMAB dehydrocoupling.

In disagreement with the computational deductions of Sicilia and co-workers,⁶ we continue to advocate that the mechanism of DMAB dehydrocoupling ensues through a common mechanism for derivatives of both magnesium and calcium. Although we also infer that derivatives of both the $[\text{NMe}_2\text{BH}_2]^-$ and $[\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3]^-$ anions are central intermediates during these reactions, we deduce that hydride elimination in every case is necessarily induced by secondary interactions with further molecules of the DMAB substrate.

Although the revised mechanism shown in Scheme 8 undoubtedly remains an oversimplification, a number of salient features may be articulated at a meaningful level of confidence. Neither of the proposed β - or δ -hydride elimination steps results in the generation of an alkaline earth hydride intermediate. Rather, each of these processes is proton assisted by the interaction of the relevant intermediates with one or more equivalents of the DMAB substrate. This reactivity occurs concurrently with the heterolytic elimination of H_2 with the relevant barrier to dehydrogenative boron-nitrogen bond formation dictated by the relative polarising influence of the alkaline earth centre in question. We are continuing to study these processes and related chemistry and suggest that the proposals presented in this contribution are worthy of further experimental and theoretical investigation.

† Electronic supplementary information (ESI) available: Experimental procedures and characterisation data for all new compounds. . Crystallographic data for compounds **6**, **7**, **9** and **13** are available as CCDC 1488814-1488817 respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXX

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Table 1: Single crystal X-ray diffraction analysis of compounds **6**, **7**, **9** and **13**

Compound	6	7	9	13
Empirical formula	C ₃₅ H ₅₆ B ₂ MgN ₄	C ₃₇ H ₅₆ BCaN ₃ O	C ₃₇ H ₆₆ B ₂ CaN ₄ O	C ₄₃ H ₆₈ BMgN ₃
Formula weight	578.76	609.73	644.63	662.12
Temperature/K	150(2)	150.15	150.15	173.15
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>Pbca</i>
<i>a</i> /Å	11.8779(2)	10.3026(5)	12.3115(2)	18.6055(4)
<i>b</i> /Å	15.2518(3)	31.9329(16)	18.1303(3)	19.4729(4)
<i>c</i> /Å	38.9205(8)	11.9820(5)	18.4090(3)	22.3867(5)
α /°	90	90	90	90
β /°	90	110.693(3)	100.9010(10)	90
γ /°	90	90	90	90
<i>U</i> /Å ³	7050.8(2)	3687.7(3)	4034.95(12)	8110.8(3)
<i>Z</i>	8	4	4	8
ρ_{calc} /cm ³	1.090	1.098	1.061	1.084
μ /mm ⁻¹	0.079	0.200	0.186	0.076
<i>F</i> (000)	2528.0	1328.0	1416.0	2912.0
Crystal size/mm ³	0.5 × 0.25 × 0.15	0.5 × 0.25 × 0.25	0.7 × 0.6 × 0.5	0.41 × 0.20 × 0.19
2 θ range for data collection/°	6.036 to 50.01	7.654 to 50.726	7.366 to 55.014	6.88 to 54.96
Index ranges	-14 ≤ <i>h</i> ≤ 14, -18 ≤ <i>k</i> ≤ 18, -46 ≤ <i>l</i> ≤ 46	-12 ≤ <i>h</i> ≤ 11, -38 ≤ <i>k</i> ≤ 38, -12 ≤ <i>l</i> ≤ 14	-15 ≤ <i>h</i> ≤ 15, -23 ≤ <i>k</i> ≤ 23, -23 ≤ <i>l</i> ≤ 23	-23 ≤ <i>h</i> ≤ 24, -25 ≤ <i>k</i> ≤ 13, -29 ≤ <i>l</i> ≤ 18
Reflections collected	47170	24515	57988	25897
Independent reflections, <i>R</i> _{int}	6150, 0.1699	5846, 0.0552	9193, 0.0549	9277, 0.0284
Data/restraints/parameters	6150/0/411	5846/0/410	9193/0/458	9277/12/502
Goodness-of-fit on <i>F</i> ²	1.015	1.062	1.036	1.017
Final <i>R</i> 1, <i>wR</i> 2[<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0662, 0.1315	0.0529, 0.1020	0.0396, 0.1030	0.0433, 0.0989
Final <i>R</i> 1, <i>wR</i> 2[all data]	0.1310, 0.1570	0.0994, 0.1169	0.0562, 0.1145	0.0714, 0.1135
Largest diff. peak/hole / e Å ⁻³	0.28, -0.29	0.29, -0.19	0.24, -0.20	0.27, -0.22

Table 2: Selected bond lengths (Å) and angles (°) for compounds **6**, **7**, **9** and **13**.

	6^a	7^b	9^b	13^a
Ae(1)-N(1)	2.089(2)	2.317(2)	2.4008(11)	2.0350(12)
Ae(1)-N(2)	2.029(2)	2.388(2)	2.3694(11)	2.0341(11)
Ae(1)-O(1)	-	2.3575(19)	2.4086(10)	-
Ae(1)-N(3)	2.088(2)	2.382(2)	2.4758(11)	2.0886(13)
N(3)-B(1)	1.587(4)	1.537(5)	1.550(2)	1.538(12)
N(4)-B(1)	1.613(4)	-	1.598(2)	-
N(4)-B(2)	1.558(4)	-	1.587(2)	-
N(1)-Ae(1)-N(2)	92.05(9)	76.16(7)	78.42(4)	96.11(5)
N(2)-Ae(1)-N(3)	128.46(10)	110.21(8)	103.06(4)	129.15(5)
N(1)-Ae(1)-N(3)	116.89(9)	120.34(8)	130.76(4)	129.59(5)
Ae(1)-N(3)-B(1)	100.93(18)	79.03(19)	88.53(8)	76.6(4)
N(3)-B(1)-N(4)	114.2(2)	101.65(7) ^c	117.14(12)	-
B(1)-N(4)-B(2)	112.3(2)	98.61(7) ^d	112.91(10)	-

^a Ae(1) = Mg; ^b Ae(1) = Ca; ^c N(1)-Ae(1)-O(1); ^d N(2)-Ae(1)-O(1)

References

1. (a) F. H. Stephens, V. Pons and R. T. Baker, *Dalton Trans.* 2007, 2613; (b) B. Peng and J. Chen, *Energy & Env. Sci.* 2008, **1**, 479; (c) V. M. Parvanov, G. K. Schenter, N. J. Hess, L. L. Daemen, M. Hartl, A. C. Stowe, D. M. Camaioni and T. Autrey, *Dalton Trans.* 2008, 4514; (d) C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.* 2009, **38**, 279; (e) N. C. Smythe and J. C. Gordon, *Eur. J. Inorg. Chem.* 2010, 509; (f) T. Autrey, M. Bowden and A. Karkamkar, *Faraday Disc.* 2011, **151**, 157; (g) Z. Huang and T. Autrey, *Energy & Env. Sci.* 2012, **5**, 9257; (h) A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.* 2010, **110**, 4079.
2. See, for example, (a) H. C. Johnson, E. M. Leita, G. R. Whittell, I. Manners, G. C. Lloyd-Jones and A. S. Weller, *J. Am. Chem. Soc.* 2014, **136**, 9078; (b) A. Kumar, N. A. Beattie, S. D. Pike, S. A. Macgregor and A. S. Weller, *Angew. Chem., Int. Ed.*, 2016, **55**, 6651.
3. See, for example, (a) T. J. Clark, C. A. Russell and I. Manners, *J. Am. Chem. Soc.* 2006, **128**, 9582; (b) M. E. Sloan, A. Staubitz, T. J. Clark, C. A. Russell, G. C. Lloyd-Jones and I. Manners, *J. Am. Chem. Soc.* 2010, **132**, 3831; (c) Y. Kawano, M. Uruichi, M. Shimoi, S. Taki, T. Kawaguchi, T. Kakizawa and H. Ogino, *J. Am. Chem. Soc.* 2009, **131**, 14946; (d) R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P. H. Lin, S. Maguire, M. Murugesu, B. L. Scott and N. C. Smythe, *J. Am. Chem. Soc.* 2012, **134**, 5598; (e) J. R. Vance, A. P. Robertson, K. Lee and I. Manners, *Chem. Eur. J.* 2011, **17**, 4099; (f) T. Miyazaki, Y. Tanabe, M. Yuki, Y. Miyake and Y. Nishibayashi, *Organometallics* 2011, **30**, 2394; (g) A. E. W. Ledger, C. E. Ellul, M. F. Mahon, J. M. J. Williams and M. K. Whittlesey, *Chem. Eur. J.* 2011, **17**, 8704; (h) N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black and K. Fagnou, *J. Am. Chem. Soc.* 2008, **130**, 14034; (i) A. Friedrich, M. Drees and S. Schneider, *Chem. Eur. J.* 2009, **15**, 10339; (j) C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *J. Am. Chem. Soc.* 2003, **125**, 9424; (k) A. Staubitz, M. E. Sloan, A. P. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Gnne and I. Manners, *J. Am. Chem. Soc.* 2010, **132**, 13332; (l) G. Alcaraz, A. B. Chaplin, C. J. Stevens, E. Clot, L. Vendier, A. S. Weller, S. Sabo-Etienne, *Organometallics* 2010, **29**, 5591.
4. For a recent review, see, (a) T. E. Stennett and S. Harder, *Chem. Soc. Rev.* 2016, **45**, 1112; see also (b) J. Spielmann, M. Bolte and S. Harder, *Chem. Commun.* 2009, 6934; (c) J. Spielmann, M. Bolte and S. Harder, *Chem. Commun.* 2009, 6934; (d) D. J. Liptrot, M. S. Hill, M. F. Mahon and D. J. MacDougall, *Chem. Eur. J.* 2010, **16**, 8508; (e) M. S. Hill, M. Hodgson, D. J. Liptrot and M. F. Mahon, *Dalton Trans.* 2011, **40**, 7783; (f) S. Harder and J. Spielmann, *Chem. Commun.* 2011, **47**, 11945; (g) M. S. Hill, G. Kociok-Khn and T. P. Robinson, *Chem. Commun.* 2010, **46**, 7587; (h) E. Lu, Y. Yuan, Y. Chen and W. Xia, *ACS Catalysis* 2013, **3**, 521; (i) P. Cui, T. P. Spaniol, L. Maron and J. Okuda, *J. Chem. Eur. J.* 2013, **19**, 13437; (j) H. J. Cowley, M. S. Holt, R. L. Melen, J. M. Rawson and D. S. Wright, *Chem. Commun.* 2011, **47**, 2682; (k) R. J. Less, R. L. Melen and D. S. Wright, *RSC Advances* **2012**, **2**, 2191; (l) M. M. Hansmann, R. L. Melen and D. S. Wright, *Chem. Sci.* 2011, **2**, 1554; (m) R. J. Less, H. R. Simmonds, S. B. J. Dane and D. S.

- Wright, *Dalton Trans.* 2013, **42**, 6337; (n) R. J. Less, R. Garcia-Rodriguez, H. R. Simmonds, L. K. Allen, A. D. Bond, and D. S. Wright, *Chem. Commun.* 2016, **52**, 3650; (o) J. Spielmann, G. Jansen, H. Bandmann and S. Harder, *S. Angew. Chem., Int. Ed.* 2008, **47**, 6290; (p) J. Spielmann and S. Harder, *J. Am. Chem. Soc.* 2009, **131**, 5064; (q) P. Bellham, M. S. Hill, D. J. Liptrot, D. J. MacDougall and M. F. Mahon, *Chem. Commun.* 2011, **47**, 9060; (r) P. Bellham, M. S. Hill, G. Kociok-Köhn and D. J. Liptrot, *Dalton Trans.* 2013, **42**, 737; (s) P. Bellham, M. S. Hill, G. Kociok-Köhn and D. J. Liptrot, *Chem. Commun.* 2013, **49**, 1960; (t) P. Bellham, M. S. Hill and G. Kociok-Köhn, *Organometallics* 2015, **33**, 5716; (u) P. Bellham, M. S. Hill and G. Kociok-Köhn, *Dalton Trans.* 2015, **44**, 12078; (v) J. Spielmann, D. F.-J. Piesnik and S. Harder, *Chem. Eur. J.* 2010, **16**, 8307; (w) J. Spielmann, M. Bolte and S. Harder, *Chem. Commun.* 2009, 6934; (x) J. Spielmann and S. Harder, *Dalton Trans.* 2011, **40**, 8314; (y) C. Jones, S. J. Bonyhady, S. Nembemma and A. Stasch, *Eur. J. Inorg. Chem.* 2012, 2596; (z) S. Harder, J. Spielmann and B. Tobey, *Chem.-Eur. J.* 2012, **18**, 1984; (aa) K. A. Erickson, J. P. W. Stelmach, N. T. Mucha and R. Waterman, *Organometallics* 2015, **34**, 4693.
5. (a) H. V. K. Diyabalanage, R. P. Shrestha, T. A. Semelsberger, B. L. Scott, M. E. Bowden, B. L. Davis and A. K. Burrell, *Angew. Chem., Int. Ed.*, 2007, **46**, 8995; (b) Z. Xiong, C. K. Yong, G. Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards and W. I. F. David, *Nature Mater.*, 2008, **7**, 138; (c) Q. Zhang, C. Tang, C. Fang, F. Fang, D. Sun, L. Ouyang and M. Zhu, *J. Phys. Chem. C*, 2010, **114**, 1709; (d) H. V. K. Diyabalanage, T. Nakagawa, R. P. Shrestha, T. A. Semelsberger, B. L. Davis, B. L. Scott, A. K. Burrell, W. I. F. David, K. R. Ryan, M. O. Jones and P. P. Edwards, *J. Am. Chem. Soc.*, 2010, **96**, 4; (e) K. Wang, J. G. Zhang, T. T. Man, M. Wu and C. C. Chen, *Chem. Asian J.*, 2013, **8**, 1076; (f) D. Y. Kim, N. Jiten Singh, H. M. Lee and K. S. Kim, *Chem. Eur. J.*, 2009, **15**, 5598; (g) G. Xia, X. Yu, Y. Guo, Z. Wu, C. Yang, U. Liu and S. Dou, *Chem. Eur. J.*, 2010, **16**, 3763; (h) K. Shimoda, Y. Zhang, T. Ichikawa, H. Miyaoka and Y. Kojima, *J. Mater. Chem.*, 2011, **21**, 2609; (i) A. T. Luedtke and T. Autrey, *Inorg. Chem.*, 2010, **49**, 3905; (j) Y. S. Chua, G. Wu, Z. Xiong, T. He and P. Chen, *Chem. Mater.*, 2009, **21**, 4899; (k) W. Li, L. Miao, R. H. Scheicher, Z. Xiong, G. Wu, C. M. Araujo, A. Blomqvist, R. Ahuja, Y. Feng and P. Chen, *Dalton Trans.*, 2012, **41**, 4754; (l) H. Wu, W. Zhou, F. E. Pinkerton, M. S. Meyer, Q. Yao, S. Gadipelli, T. J. Udovic, T. Yildirim and J. J. Rush, *Chem. Commun.*, 2011, **47**, 4102; (m) G. Xia, Y. Tan, X. Chen, Z. Guo, H. Liu and X. Yu, *J. Mater. Chem. A*, 2013, **1**, 1810; (n) Y. S. Chua, W. Li, G. Wu, Z. Xiong and P. Chen, *Chem. Mater.* 2012, **24**, 3574; (o) Y. S. Chua, G. Wu, Z. Xiong, A. Karkamar, J. Guo, M. Jian, M. W. Wong, T. Autrey and P. Chen, *Chem. Commun.* 2010, **46**, 5752; (p) Y. S. Chua, H. Wu, W. Zhou, T. J. Udovic, G. Wu, Z. Xiong, M. W. Wong and P. Chen, *Inorg. Chem.* 2012, **51**, 1599.
6. V. Butera, N. Russo and E. Sicilia, *Chem., Eur. J.* 2014, **20**, 5967.

7. (a) B. Liu, T. Roisnel, J. F. Carpentier, and Y. Sarazin, *Angew. Chem., Int. Ed.* 2012, **51**, 4943; (b) B. Liu, T. Roisnel, J. F. Carpentier, and Y. Sarazin, *Chem., Eur. J.* 2013, **19**, 13445; (c) C. Bellini, J. F. Carpentier, S. Tobisch, and Y. Sarazin, *Angew. Chem., Int. Ed.* 2015, **54**, 7679.
8. (a) J. Prust, K. Most, I. Muller, E. Alexopoulos, A. Stasch, I. Uson and H. W. Roesky, *Z. Anorg. Allg. Chem.* 2001, **627**, 2032; (b) D. J. Wolstenholme, J. Flogeras, F. N. Che, A. Decken and G. S. McGrady, *J. Am. Chem. Soc.*, 2013, **135**, 2439; (c) C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2003, **125**, 9424.
9. V. Balasanthiran, M. H. Chisholm, K. Choojun, C. B. Durr and P. M. Wambua, *Polyhedron*, 2016, **103**, 235.
10. S. P. Green, C. Jones and A. Stasch, *Angew. Chem., Int. Ed.*, 2008, **47**, 9079.
11. P. G. Hayes, G. C. Welch, D. J. H. Emslie, C. L. Noack, W. E. Piers and M. Parvez, *Organometallics* 2003, **22**, 1577.
12. A. L. Vangeet, *Anal. Chem.*, 1968, **40**, 2227.

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