



The Complex Reactivity of β -Diketiminato Magnesium(I) Dimers Towards Pinacolborane: Implications for Catalysis

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**The Complex Reactivity of β -Diketiminato Magnesium(I) Dimers Towards Pinacolborane:
Implications for Catalysis**

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Abstract

Reactions between the borane, HBpin (pin = pinacolato), and three magnesium(I) dimers, $[\{(\text{ArNacnac})\text{Mg}-\}_2]$ ($\text{ArNacnac} = [(\text{ArNCMe})_2\text{CH}]^-$; Ar = xylyl (Xyl), mesityl (Mes) or 2,6-diethylphenyl (Dep)), have been carried out in 2:1, 5:1 and 20:1 ratios. In all cases, NMR spectroscopic studies have revealed complex mixtures of many known and novel products from these reactions. From extracts of the crude reaction mixtures, low yields of ten compounds, representing six different types of complexes between β -diketiminato magnesium fragments and boron containing ligands, have been isolated and crystallographically characterised. These include unprecedented examples of compounds in which the γ -carbon of the β -diketiminato ligand has been activated by boron hydride fragments. In addition, boryloxide (OBpin), borate ($[\text{B}(\text{pin})_2]^-$ or $[(\text{pin})_2\text{BH}_2]^-$), B–O bond ruptured $[\text{pinBH}_2]^-$, a diborane(5) dianion, or BH_3 have been shown to be incorporated into the isolated complexes. The complexity of the products of the reported reactions are discussed in light of recently published patents and papers which report that magnesium(I) dimers act as efficient catalysts, or as pre-catalysts to well defined catalysts, for the hydroboration of a variety of unsaturated substrates by HBpin. Our results strongly suggest that magnesium(I) dimers are not catalysts in these reactions, and that there are many more potential (pre-)catalysts that are generated in these reactions, than have previously been reported.

Introduction

Since the turn of the millennium considerable progress has been made in the field of organic transformations catalysed by alkaline-earth metal complexes.¹ This has been driven in large part by the high natural abundance of the lighter group 2 metals (magnesium and calcium), their low toxicity, and their cheap cost compared to the expensive and toxic noble metals conventionally employed in similar catalytic protocols.² Many of the recent advances in this area have come from

the groups of Hill, Harder and Okuda, who have utilised isolated, or *in situ* generated, molecular calcium and magnesium hydride compounds, e.g. **1** and **2** (Figure 1), as, for example, highly efficient catalysts for hydroelementations of a variety of unsaturated substrates.³ Compounds **1** and **2** are typically thermally stable, resistant to redistribution reactions, and can be readily prepared by σ -bond metathesis reactions between β -diketiminato metal alkyls or amides, and hydride sources, e.g. PhSiH_3 .^{4,5}

Our own interests in group 2 metal chemistry lie largely with magnesium(I), e.g. **3**, and magnesium(II) hydride complexes, e.g. **1** ($M = \text{Mg}$), both of which we have extensively studied as reagents for catalytically relevant small molecule activations and hydromagnesiations.⁶ With respect to catalysis itself, we have begun to explore the potential of magnesium(I) compounds in oxidative addition/reductive elimination based catalytic processes. Although this may seem a formidable task, we have recently shown that compounds such as **3** can oxidatively add across alkenes, and these reactions are readily reversible at room temperature.⁷ The resulting 1,2-dimagnesioethanes have been shown to be powerful reagents for small molecule activations and organometallic transformations in their own right.

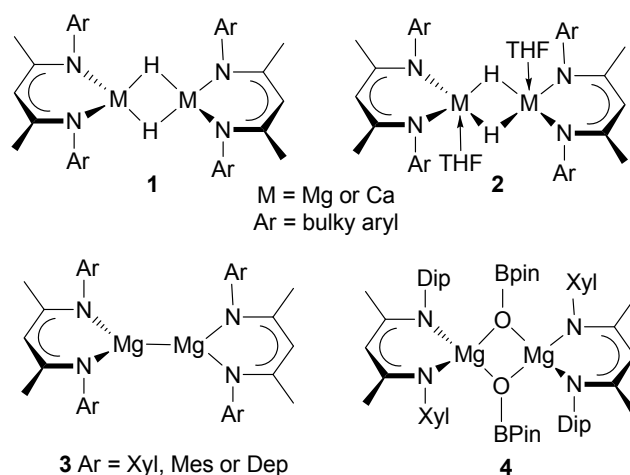


Figure 1. Catalytically active magnesium and calcium hydride complexes, **1** and **2**; examples of previously reported magnesium(I) dimers, **3**; and an unsymmetrical magnesium boryloxide compound, **4** (xylyl (Xyl), mesityl (Mes), 2,6-diethylphenyl (Dep), or 2,6-diisopropylphenyl (Dip)).

In addition to this work, in a series of patents Ma and co-workers have reported that one of our magnesium(I) compounds (**3** Ar = Xyl), and unsymmetrical analogues developed by themselves, act as efficient catalysts for the hydroboration of, for example, aldehydes, ketones, alkynes and isocyanates, using pinacolborane (HBpin).⁸⁻¹⁰ The implication here is that the magnesium(I) compounds are returned after these catalysed reactions are complete, and therefore they display no net reaction with the substrate or pinacolborane. Intriguingly, in a subsequent publication Ma reports that, at least in alkyne hydroborations, an unsymmetrical magnesium(I) compound, [$\{(\text{Dip}^{\text{Xyl}}\text{Nacnac})\text{Mg}-\}_2$], is in fact a pre-catalyst, initially yielding the dimeric boryloxide bridged complex, **4**, *via* decomposition of pinacolborane.¹¹ Compound **4** itself is identified as a pre-catalyst, and is said to react further with HBpin to yield a magnesium hydride, *cf.* **1** (M = Mg), which is the true catalyst in the reaction. This result is akin to previous work on magnesium hydride catalysed transformations of isocyanates involving HBpin, described by Hill and co-workers.¹² Surprisingly, however, Ma reports that **4** can be formed in moderate isolated yield (36%) by reaction of the unsymmetrical magnesium(I) dimer with a *ca.* 10 fold excess of both HBpin and phenylacetylene after heating at 90 °C for 12 hours, i.e. essentially under the catalytic conditions they employed for alkyne hydroboration reactions. The fact that **4** is apparently not converted to the corresponding magnesium hydride under these forcing conditions made us wonder if **4** does in fact act as a pre-catalyst in their hydroboration reactions.

Coincidentally to Ma's patents and report on the magnesium(I) catalysed and pre-catalysed hydroborations of unsaturates, we were exploring reactions of a series of magnesium(I) dimers with HBpin under various stoichiometries. We found that all reactions led to complex mixtures of many products, a number of which we were able to isolate in low yields, and characterise crystallographically. Although limited spectroscopic data could be obtained on these, we believed it worthwhile to report our results here, as these suggest that magnesium(I) dimers are not catalysts in the hydroboration of unsaturates, and that anyone of a number of products of the reactions of magnesium(I) dimers with HBpin could be acting as (pre-)catalysts or stoichiometric reactants in those hydroboration reactions.

Results and Discussion

So as to ascertain the stability of magnesium(I) dimers in the presence of various excess stoichiometries of HBpin, and thus the likelihood of such dimers potentially acting as catalysts for the hydroboration of unsaturates, toluene solutions of three magnesium(I) dimers, **3** (Ar = Xyl, Mes or Dep), were treated with either 2, 5 or 20 equivalents of HBpin at room temperature. After stirring the reaction mixtures overnight,¹³ volatiles were removed *in vacuo*, and ¹H and ¹¹B{¹H} NMR spectra of C₆D₆ solutions of the residues obtained (see Figure 2 for a representative ¹¹B{¹H} NMR spectrum and the ESI for all other spectra). In all cases, complex mixtures of many products were obtained, which seemingly did not include the magnesium(I) dimer starting material, or the β-diketiminato magnesium hydride complexes, [^{Ar}NacnacMg(μ-H)₂],¹⁴ which are akin to the magnesium hydride proposed by Ma and co-workers as the active catalyst in their later paper on the hydroboration of alkynes.¹¹ That said, it is not without the realms of possibility that magnesium hydrides [^{Ar}NacnacMg(μ-H)₂] are initially formed in the reactions described here, but these subsequently react with other components of the reaction mixture (see below). Of note is the fact that when the above reactions between [^{Ar}NacnacMg-₂] and HBpin were carried out in 1:1 stoichiometries, similar product mixtures were obtained, but some unreacted magnesium(I) dimer was returned, in addition to small quantities of the homoleptic complexes, [Mg(^{Ar}Nacnac)₂].^{4a}

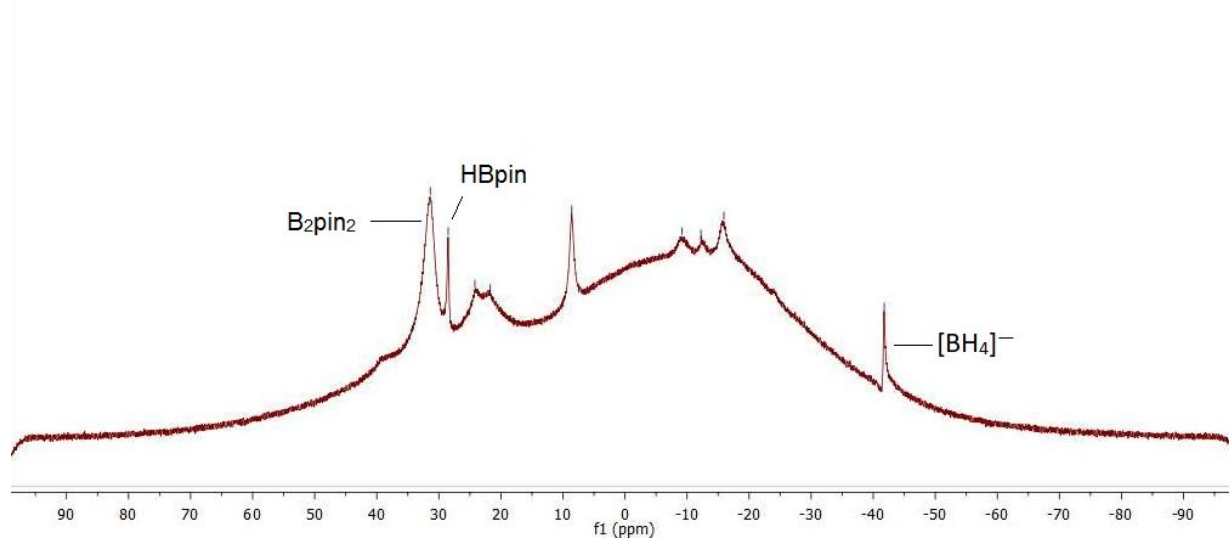


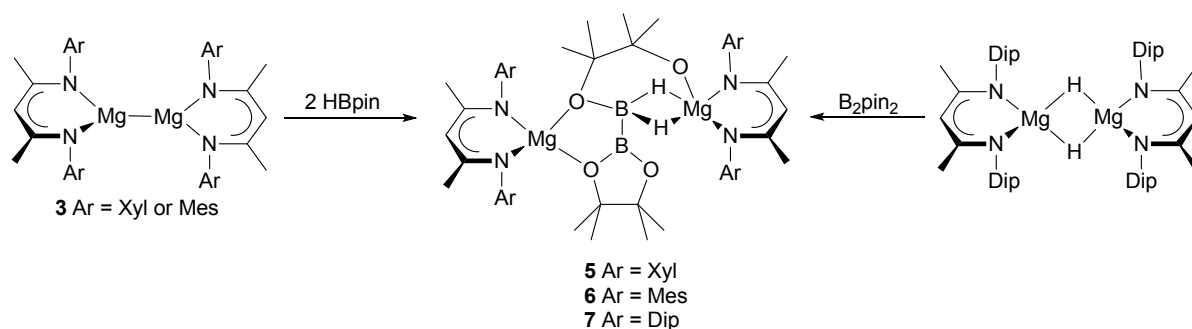
Figure 2. ¹¹B{¹H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between **3** (Ar = Mes) and 20 equivalents of HBpin.

Examination of the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of all the reaction mixtures (see ESI and Figure 2) allowed the assignment of several known boron containing species. Firstly, and not surprisingly, small amounts of residual HBpin were present, having not been completely removed during work-up. In most of the reactions the major product was B_2pin_2 , identified by a strong broad resonance centred at *ca.* δ 31.8 ppm. Indeed, from several reactions, this diborane crystallised from the reaction solution, and was structurally authenticated by X-ray crystallography. It can be speculated that B_2pin_2 is generated in these reactions by reduction of HBpin by the magnesium(I) dimer, generating transient $[\{(\text{ArNacnac})\text{Mg}(\mu\text{-H})\}_2]$, which reacts further with other components of the mixture. The only other signals in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of the reaction mixtures that can be assigned with any confidence are resonances at quite high field (*ca.* δ -41 to -42 ppm) which likely correspond to species incorporating the $[\text{BH}_4]^-$ anion.¹⁵ These signals are typically more intense in the reactions involving larger excesses of HBpin. Although it cannot be sure what the mechanism of formation of $[\text{BH}_4]^-$ is in these reactions, it is of note that the anion has previously been detected as a product of reactions between a β -diketiminato calcium hydride, **2** ($\text{M} = \text{Ca}$, $\text{Ar} = \text{Dip}$), and the borane HBcat (cat = catecholato), which is closely related to HBpin.¹⁶ Moreover, $[\text{BH}_4]^-$ salts are well known to reduce reactive unsaturates such as carbonyls, in the absence of catalysts.¹⁷ This raises the question as to whether tetrahydridoborate is acting, at least to some extent, as an *in situ* generated stoichiometric reductant in the supposedly magnesium(I) catalysed reductions reported by Ma (e.g. hydroborations of aldehydes and ketones catalysed by **3** $\text{Ar} = \text{Xyl}$ ⁸).

As mentioned above, the complexity of reactions between magnesium(I) dimers and HBpin makes it difficult, if not impossible, to determine what the catalytically active product(s) of these reactions is(are), if there are any at all. Notwithstanding this complexity, we have isolated a number of interesting, mechanistically informative, but low yielding, boron containing complexes from the reactions, the X-ray crystal structures and limited spectroscopic data of which we describe below. We believe these results can act as an aid to researchers who might wish to carry out similar chemistry.

(i) Isolated products from the reactions of magnesium(I) dimers with 2 equivalents of HBpin

The non-volatile residues from the 2:1 reactions of HBpin with **3** (Ar = Xyl or Mes) were extracted with hexane and the extracts stored at -30 °C overnight, to yield a few crystals of compounds **5** and **6** respectively (Scheme 1). It is interesting to note that the complexes are analogues of complex **7**, which was previously reported by Hill and co-workers to be generated from the reaction of [$\{(\text{DipNacnac})\text{Mg}(\mu\text{-H})\}_2$] with B_2pin_2 .¹⁸ The similarities here provide good circumstantial evidence that **5** and **6** are formed by reaction of B_2pin_2 with [$\{(\text{ArNacnac})\text{Mg}(\mu\text{-H})\}_2$] (Ar = Xyl or Mes), which are confirmed products and postulated transients, respectively, in the reactions between **3** (Ar = Xyl or Mes) and HBpin. If this is the case the B-B bond of the diborane is retained, whilst rupture of one of the Bpin fragments occurs upon transfer of two hydrides to the diborane by the magnesium hydride species.



Scheme 1. Synthesis of compounds **5** and **6**, and previously reported synthesis of **7**.

Although no spectroscopic data could be obtained for **5** and **6** due to their very low yields, X-ray crystal structure determinations of both were carried out. The quality of the diffraction data for **6** was too low to include details of its crystal structure here, but its gross molecular framework is unambiguous, and the compound is isostructural to **5** (and **7**). The molecular structure of **5** is depicted in Figure 3. The hydride ligands of the compound were located from difference maps and refined isotropically, which allows formulation of the compound as incorporating a dihydro-diborane(5) dianion which bridges two cationic ($\text{XylNacnac})\text{Mg}^+$ fragments. The only specific

precedent for compounds **5** and **6** lies with **7**, the metrical parameters of the central core of which are similar to those of **5** (e.g. the B-B distance in **7** = 1.713(2) Å¹⁸). The Mg···B distances in **5** are not consistent with bonding interactions, as they are significantly outside normal Mg–B distances in, for example, magnesium boryl complexes.¹⁹

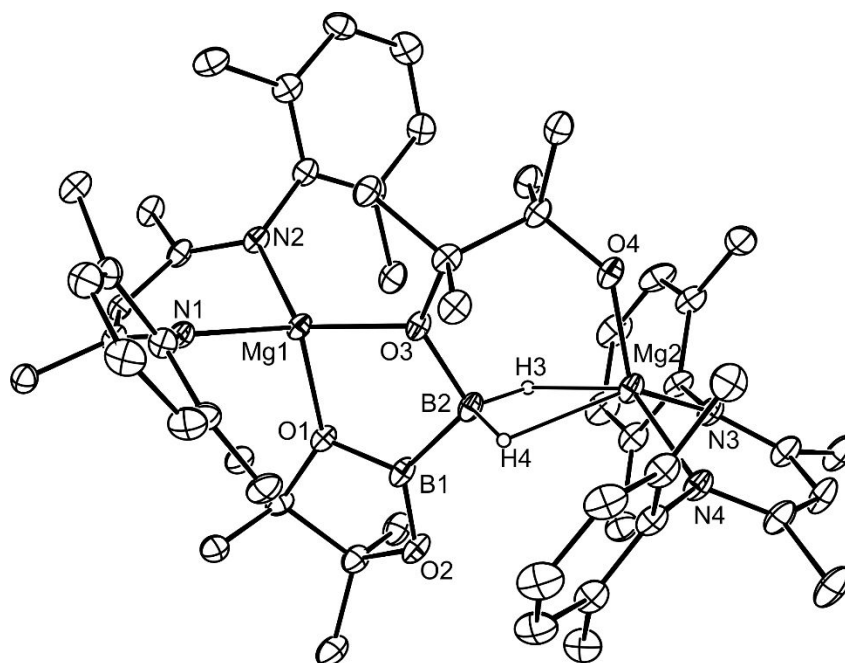


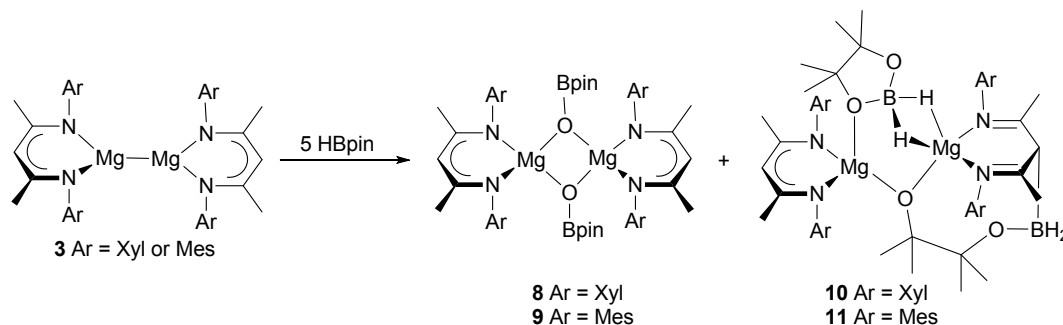
Figure 3. Molecular structure of **5** (25% thermal ellipsoids are shown; hydrogen atoms, except hydrides, omitted). Selected bond lengths (Å) and angles (°): Mg(1)-O(3) 1.955(4), Mg(1)-O(1) 2.049(4), B(1)-B(2) 1.725(9), Mg(2)-O(4) 1.860(4), Mg(2)-H(3) 1.97(5), Mg(2)-H(4) 2.09(5), B(2)-O(3) 1.521(6), B(2)-H(3) 1.20(5), B(2)-H(4) 1.10(5), N(2)-Mg(1)-N(1) 94.80(16), O(3)-Mg(1)-O(1) 91.91(14), N(4)-Mg(2)-N(3) 90.85(17), H(3)-Mg(2)-H(4) 53.5(19), O(3)-B(2)-B(1) 108.2(4), H(3)-B(2)-H(4) 105(3).

(ii) Isolated products from the reactions of magnesium(I) dimers with 5 equivalents of HBpin

The residues from the 5:1 reactions of HBpin with **3** (Ar = Xyl or Mes) were again extracted with hexane and the extracts stored at -30 °C overnight, to yield the colourless crystalline compounds **8-11** (Scheme 2). The first crop of crystals from each reaction (*viz.* **8** and **9**) were isolated in very low yields (5% and 3% respectively), while the second crops largely comprised **10** and **11**, which were obtained in markedly higher isolated yields (27% and 32% respectively). In line

with these yields is the fact that signals for both compounds were observed in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of the crude reaction mixtures that yielded them.

The low yielding boryloxide complexes, **8** and **9**, are direct analogues of Ma's unsymmetrical analogue, **4**,¹¹ and an example, $[\{(\text{DipNacnac})\text{Mg}(\mu\text{-OBpin})\}_2]$, reported by Hill and co-workers.¹² It cannot be sure how **8** and **9** were formed, but it is worth noting that Ma suggests the bridging oxide in **4** results from decomposition of pinacolborane, which seems a reasonable proposition. It is also noteworthy that we found **8** and **9** to be unreactive towards excess HBpin, at least at room temperature. To the best of our knowledge, the higher yielding products, **10** and **11**, have no precedent in the literature. Their formation can be speculated as occurring *via* reaction of *in situ* generated $[\{(\text{ArNacnac})\text{Mg}(\mu\text{-H})\}_2]$ with two equivalents of HBpin, with subsequent B–O bond rupture of one of the resultant H_2Bpin units, leading to a "dangling" Lewis acidic OBH_2 moiety, which is attacked by the nucleophilic γ -carbon of the Nacnac backbone. Although such Nacnac γ -carbon functionalisations are relatively common,²⁰ this is the first example involving boron.



Scheme 2. Synthesis of compounds **8-11**.

Limited spectroscopic data could be obtained for the boryloxide compounds **8** and **9**, but their ^1H NMR spectra are consistent with their solid state structures. No signals could be observed in their $^{11}\text{B}\{^1\text{H}\}$ NMR spectra, presumably due to the low mass of sample available for these experiments, and their relatively poor solubility in non-coordinating deuterated solvents. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **10** and **11** are complicated due to the unsymmetrical nature of these compounds, but again, are reminiscent of them retaining their solid state structures in solution. Of

particular note are signals at $\delta = 3.27$ ppm for **10** and $\delta = 3.30$ ppm for **11**, which were assigned to the borylated γ -CH units in the compounds. Moreover, The $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of each show two signals (**10**: $\delta -0.32$ ppm and -9.32 ppm; **11**: $\delta -0.22$ ppm and -9.34 ppm) which lie in the normal region for 4-coordinate boron.²¹ Two broad bands in the FTIR spectrum of each compound (**10**: $\nu = 2312$ cm^{-1} and 2116 cm^{-1} ; **11**: $\nu = 2293$ cm^{-1} and 2120 cm^{-1}) were assigned to B–H stretching modes. It is presumed that the higher wavenumber bands in each spectrum are associated with the terminal BH_2 fragments.

The X-ray crystal structures of all compounds **8-11** were determined, and as it was found that the pairs **8** and **9**, and **10** and **11**, are essentially isostructural, only the structures of **8** and **10** are depicted in Figure 4. Full crystallographic details of the other two compounds can be found in the ESI. The structures of **8** and **9** show them to be boryloxide bridged dimers which are very similar to previously reported **4**¹¹ and $[\{(\text{DipNacnac})\text{Mg}(\mu\text{-OBpin})\}_2]$.¹² The structures of **10** and **11** are more novel, and reveal them to be unsymmetrical dimetallic systems in which the two magnesium centres are bridged by a $[\text{H}_2\text{Bpin}]^-$ anion which coordinates one Mg centre through a dative O–Mg bond, and the other centre through two crystallographically refined bridging hydrides. The other ligand that bridges the Mg centres is essentially a B–O bond cleaved version of H_2Bpin , in which the cleaved O-centre bridges the Mg atoms, while the OBH_2 fragment has been attacked by the backbone γ -C centre of one Nacnac ligand. This leads to a loss of electronic delocalisation within that ligand, which is reflected in the bond lengths within its N_2C_3 backbone. Both of the B centres in the complexes have distorted tetrahedral geometries with B–C and/or B–O bond lengths in the normal ranges.²²

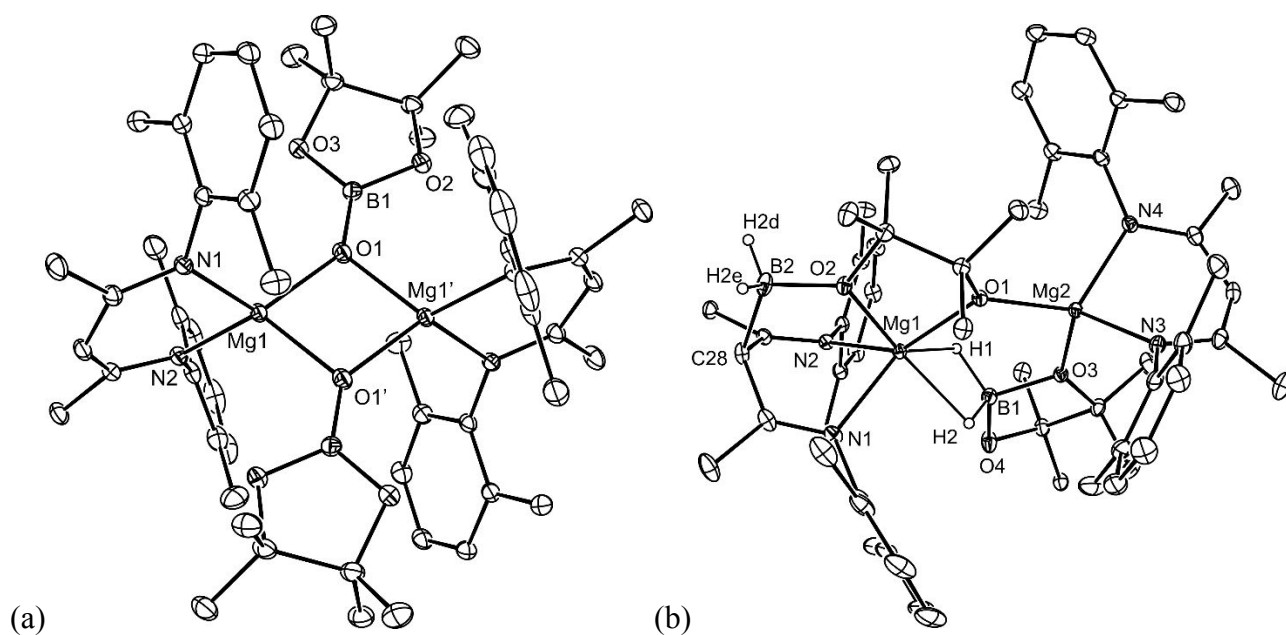
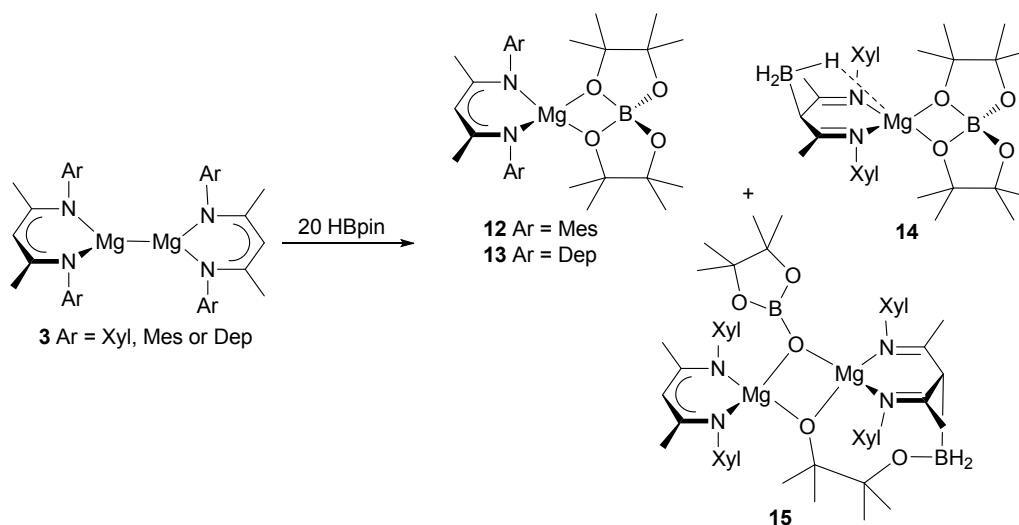


Figure 4. Molecular structures of (a) **8** and (b) **10** (25% thermal ellipsoids are shown; hydrogen atoms, except hydrides, omitted). Selected bond lengths (Å) and angles (°) for **8**: Mg(1)-O(1) 1.9605(13), Mg(1)-O(1') 1.9886(14), Mg(1)-N(1) 2.0234(15), Mg(1)-N(2) 2.0307(15), O(1)-B(1) 1.318(2), O(1)-Mg(1)-O(1') 82.51(6), N(1)-Mg(1)-N(2) 94.49(6), Mg(1)-O(1)-Mg(1') 97.49(6). Selected bond lengths (Å) and angles (°) for **10**: Mg(1)-O(1) 2.0095(10), Mg(1)-O(2) 2.0175(11), Mg(1)-H(1) 2.020(17), Mg(1)-H(2) 2.013(19), O(1)-Mg(2) 1.9496(11), B(1)-H(1) 1.182(17), B(1)-H(2) 1.199(18), Mg(2)-O(3) 2.0086(11), O(2)-B(2) 1.502(2), B(2)-C(28) 1.697(3), Mg(1)-O(1) 2.0095(10), Mg(1)-O(2) 2.0175(11), Mg(1)-H(1) 2.020(17), Mg(1)-H(2) 2.013(19), O(1)-Mg(2) 1.9496(11), B(1)-H(1) 1.182(17), B(1)-H(2) 1.199(18), Mg(2)-O(3) 2.0086(11), O(2)-B(2) 1.502(2), B(2)-C(28) 1.697(3), O(1)-Mg(1)-O(2) 80.67(4), H(1)-Mg(1)-H(2) 56.2(7), Mg(2)-O(1)-Mg(1) 124.16(5), H(1)-B(1)-H(2) 105.9(12), O(1)-Mg(2)-O(3) 100.93(4), O(2)-B(2)-C(28) 106.20(12).

(iii) Isolated products from the reactions of magnesium(I) dimers with 20 equivalents of HBpin

In order to more closely mimic the ratio of HBpin to magnesium(I) dimer that has been utilised previously in catalytic studies, reactions between the three magnesium(I) compounds and 20 fold excesses of the borane were carried out at room temperature. In all cases the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of the crude product mixtures were complex, but roughly resembled those for the 5:1

reactions. Despite this, compounds isolated from those previous reactions could not be isolated here. Instead, three different compound types (compounds **12-15**) were isolated as colourless crystals in very low yields (Scheme 3).



Scheme 3. Synthesis of compounds **12-15**.

The very low yields of **12-15** precluded the acquisition of meaningful spectroscopic data, but all compounds were crystallographically characterised. Compounds **12** and **13** are isostructural, so only the molecular structure of **12** is depicted in Figure 5, in addition to the structures of **14** and **15**. Complexes **12** and **13** can be formulated as contact ion pairs between $[(\text{Nacnac})\text{Mg}]^+$ cations and the borate anion $[\text{B}(\text{pin})_2]^-$. To the best of our knowledge these are the first examples of complexes between this borate and group 2 metals, though a potassium salt of $[\text{B}(\text{pin})_2]^-$ has been reported.²³ It cannot be sure how **12** and **13** are formed, but it is pertinent that Harder and co-workers have suggested the closely related borate $[\text{B}(\text{cat})_2]^-$ can be generated *via* decomposition of the borane HBcat with the calcium hydride complex, $[\{(\text{Dip}^i\text{Nacnac})\text{Ca}(\text{THF})(\mu\text{-H})\}_2]$.¹⁶ A similar process could be in operation here, namely decomposition of HBpin by the likely transiently generated complexes $[\{(\text{Ar}^i\text{Nacnac})\text{Mg}(\mu\text{-H})\}_2]$ (Ar = Mes or Dep). The metrical parameters within the crystal structures of **12** and **13** are unexceptional and do not warrant further comment.

Compound **14** is somewhat similar to **12** and **13**, except that its backbone γ -carbon centre has been activated, presumably by nucleophilic attack of that carbon on an *in situ* generated BH_3

complex or B_2H_6 . The observation of $[BH_4]^-$ in the spectrum of the reaction mixture that gave **14** makes the transient generation of BH_3 seem reasonable. If that is the case, BH_3 is a potent hydroboration reagent, and its participation in the previously reported magnesium(I) (pre-)catalysed hydroborations of substrates cannot be ruled out. The formulation of **14** as an alkyl/trihydroborate complex is confirmed by the location of all hydrides from difference maps, and their unrestrained isotropic refinement. Both boron centres of the complex have distorted tetrahedral geometries, as does the now saturated backbone γ -carbon of the ^{Xy}l Nacnac ligand. In line with this is electronic localisation of the two C=N double bonds of the ligand, as indicated by the lengths of those bonds.

The molecular structure of compound **15** reveals it to be structurally similar to **10** and **11**, in that a ruptured Bpin unit coordinates both Mg centres through a bridging oxygen, whilst its OBH_2 fragment has been attacked by the backbone γ -carbon of one ^{Xy}l Nacnac ligand, leading to loss of electronic delocalisation within the backbone of that ligand. The difference with **10** and **11** is that in those compounds the other bridging ligand is the $[pinBH_2]^-$ anion, while in **15** it is a boryloxide, similar to that found in **8** and **9**.

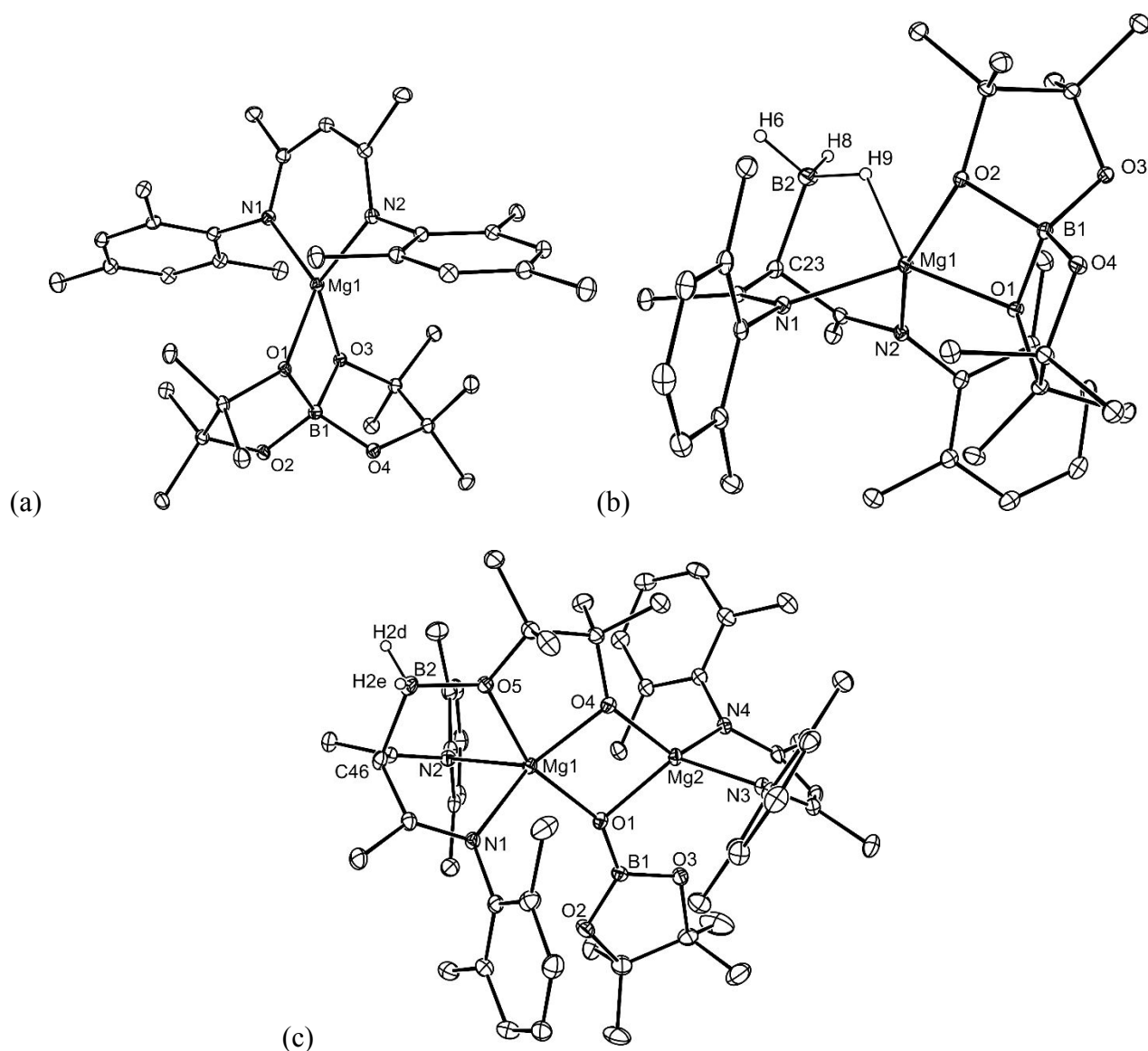


Figure 5. Molecular structures of (a) **12**, (b) **14** and (c) **15** (25% thermal ellipsoids are shown; hydrogen atoms, except hydrides, omitted). Selected bond lengths (Å) and angles (°) for **12**: Mg(1)-O(3) 2.0126(15), Mg(1)-O(1) 2.0145(15), O(1)-B(1) 1.528(2), B(1)-O(2) 1.433(2), B(1)-O(4) 1.443(2), B(1)-O(3) 1.526(2), O(3)-Mg(1)-O(1) 70.89(6), O(2)-B(1)-O(4) 111.18(16), O(3)-B(1)-O(1) 99.79(14). Selected bond lengths (Å) and angles (°) for **14**: Mg(1)-O(1) 1.9941(13), Mg(1)-O(2) 2.0737(12), Mg(1)-H(9) 1.99(3), B(2)-C(23) 1.680(2), B(2)-H(9) 1.20(3), B(2)-H(6) 1.14(3), B(2)-H(8) 1.17(3), Mg(1)-O(1) 1.9941(13), Mg(1)-O(2) 2.0737(12), Mg(1)-H(9) 1.99(3), B(2)-C(23) 1.680(2), B(2)-H(9) 1.20(3), B(2)-H(6) 1.14(3), B(2)-H(8) 1.17(3), O(1)-Mg(1)-O(2) 69.23(5), N(1)-Mg(1)-N(2) 89.24(6), C(23)-B(2)-H(9) 109.6(11). Selected bond lengths (Å) and angles (°) for **15**: Mg(1)-O(4) 1.993(2), Mg(1)-O(1) 2.004(2), Mg(1)-O(5) 2.065(2), O(1)-Mg(2) 2.012(2), Mg(2)-O(4) 1.926(2), B(2)-O(5) 1.496(4), B(2)-C(46) 1.690(5), Mg(1)-O(4) 1.993(2),

Mg(1)-O(1) 2.004(2), Mg(1)-O(5) 2.065(2), O(1)-Mg(2) 2.012(2), Mg(2)-O(4) 1.926(2), B(2)-O(5) 1.496(4), B(2)-C(46) 1.690(5), O(4)-Mg(1)-O(1) 80.95(9), O(4)-Mg(1)-O(5) 77.79(9), O(4)-Mg(2)-O(1) 82.37(9), O(5)-B(2)-C(46) 106.0(2).

Conclusion

In summary, reactions between the borane, HBpin, and three magnesium(I) dimers have been carried out in 2:1, 5:1 and 20:1 ratios. In all cases, the NMR spectroscopic studies have revealed complex mixtures of many products from these reactions. Several known compounds have been identified by $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy in these mixtures, e.g. B_2pin_2 and $[\text{BH}_4]^-$, while low yields of ten compounds, representing six different compound types, have been crystallised from extracts of the reaction mixtures. The crystallographic characterisation of all of these further highlights the complexity of the product mixtures derived from reactions between magnesium(I) dimers and HBpin. These results are important in light of recently published patents and papers which report that magnesium(I) dimers act as efficient catalysts in their own right, or as pre-catalysts on the way to well defined catalysts, for the hydroboration of a variety of unsaturated substrates by HBpin. Although we did not attempt magnesium catalysed unsaturated substrate hydroborations in this study, or did we examine reactions between magnesium(I) dimers and excesses of relevant unsaturates,²⁴ our results clearly show that caution must be used when assigning the nature of the catalyst in reactions involving magnesium(I) dimers and excess HBpin. Indeed, it is certain that magnesium(I) compounds do not act as catalysts in the previously reported hydroborations. Moreover, while compounds such as **4**, that arise from treating magnesium(I) dimers with HBpin, might play some part as pre-catalysts in hydroboration, we have shown that there are many other potential (pre-)catalysts that are generated in these reactions.

Electronic supplementary information (ESI) available: Experimental procedures and characterisation data for all new compounds. Crystal data, details of data collections and refinements. CCDC numbers: 1902608-1902616. For ESI and crystallographic data in CIF format see DOI: 10.xxxxxxx

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References

1. Selected reviews: (a) M. S. Hill, D. J. Liptrot, C. Weetman, *Chem. Soc. Rev.*, 2016, **45**, 972; (b) M. R. Crimmin, M. S. Hill in "Alkaline Earth Metal Compounds: Oddities and Applications", *Top. Organomet. Chem.*, vol. 45 (S. Harder ed.), Springer, Berlin, 2012, pp. 191-242; (c) S. Kobayashi, Y. Yamashita, *Acc. Chem. Res.*, 2011, **44**, 58; (d) S. Harder, *Chem. Rev.*, 2010, **110**, 3852; (e) D. Mukherjee, D. Schuhknecht, J. Okuda, *Angew. Chem. Int. Ed.*, 2018, **57**, 9590; (f) K. Revunova, G. I. Nikonov, *Dalton Trans.*, 2015, **44**, 840; (g) C. C. Chong, R. Kinjo, *ACS Catal.*, 2015, **5**, 3238.
2. A. Yaroshevsky, *Geochem. Int.*, 2006, **44**, 48.
3. Selected recent references: (a) A. S. S. Wilson, C. Dinoi, M. S. Hill, M. F. Mahon, L. Maron, *Angew. Chem. Int.*, 2018, **57**, 15500; (b) H. Bauer, K. Thum, M. Alonso, C. Fischer, S. Harder, *Angew. Chem. Int. Ed.*, 2019, **58**, 4248; (c) H. Bauer, M. Alonso, C. Fischer, B. Rösch, H. Elsen, S. Harder, *Angew. Chem. Int. Ed.*, 2018, **57**, 15177; (d) D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.*, 2017, **56**, 12367.
4. (a) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* 2010, **16**, 938; (b) S. P. Green, C. Jones, A. Stasch, *Angew. Chem. Int. Ed.* 2008, **47**,

- 9079; (c) S. Harder, J. Brettar, *Angew. Chem. Int. Ed.* 2006, **45**, 3474; (d) A. S. S. Wilson, M. S. Hill, M. F. Mahon, C. Dinoi, L. Maron, *Science*, 2017, **358**, 1168.
5. For an excellent review on magnesium hydride complexes and their synthesis, see: D. Mukherjee, J. Okuda, *Angew. Chem. Int. Ed.*, 2018, **56**, 1458.
6. (a) C. Jones, *Nat. Rev. Chem.*, 2017, **1**, 0059; (b) A. Stasch, C. Jones, *Dalton Trans.*, 2011, **40**, 5659.
7. (a) A. J. Boutland, A. Carroll, C. A. Lamsfus, A. Stasch, L. Maron, C. Jones, *J. Am. Chem. Soc.*, 2017, **139**, 18190; (b) D. Dange, A. R. Gair, D. D. L. Jones, M. Juckel, S. Aldridge, C. Jones, *Chem. Sci.*, 2019, **10**, 3208.
8. (a) M. Ma, W. Wang, K. Lu, W. Yao, CN Pat., 107602595, 2018; (b) W. Yao, M. Ma, X. Shen, J. Li, CN Pat., 107556196, 2018; (c) M. Ma, H. Hua, X. Shen, J. Li, CN Pat., 108191891, 2018; (d) M. Ma, W. Wang, M. Luo, Q. Xiao, L. Xu, CN Pat., 108358959, 2018;
9. The same group has also reported the related magnesium(I) catalysed silylcyanation (using Me_3SiCN) of carbonyls using **3** (Ar = Xyl). (a) M. Ma, W. Wang, W. Yao, CN Pat., 107556195, 2018; (b) W. Wang, M. Luo, S. A. Pullarkat, M. Ma, *Chem. Commun.*, 2018, **54**, 3042.
10. With regard to the reports detailed in ref. 9, we have previously shown that magnesium(I) dimers rapidly, and irreversibly, reductively couple or cleave Me_3SiCN . M. Ma, A. Stasch, C. Jones, *Chem. Eur. J.*, 2012, **18**, 10669.
11. J. Li, M. Luo, X. Sheng, H. Hua, W. Yao, S. A. Pullarkat, L. Xu, M. Ma, *Org. Chem. Front.*, 2018, **5**, 3538.
12. Y. Tang, M. D. Anker, J. Fang, M. F. Mahon, L. Maron, C. Weetman, M. S. Hill, *Chem. Sci.*, 2017, **8**, 3529.
13. Although stirred overnight, initial monitoring of the reactions by NMR spectroscopy showed complete consumption of the magnesium(I) starting material within minutes, and the formation of complex product mixtures.

14. (a) R. Lalrempuia, C. E. Kefalidis, S. J. Bonyhady, B. Schwarze, L. Maron, A. Stasch, C. Jones, *J. Am. Chem. Soc.*, 2015, **137**, 8944; (b) S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones, A. Stasch, *Nat. Chem.*, 2010, **2**, 865.
15. These signals were significantly broadened in the ^{11}B NMR spectra, relative to those in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra, but resolution into a quintet was not observed. We presume this is due to the $[\text{BH}_4]^-$ anion being associated with one or more magnesium containing cations in non-coordinating C_6D_6 solutions.
16. S. Harder, J. Spielmann, *J. Organomet. Chem.*, 2012, **698**, 7.
17. L. Banfi, E. Narisano, R. Riva, E. W. Baxter, "Lithium Borohydride" e-EROS Encyclopedia of Reagents for Organic Synthesis, Wiley, Hoboken, 2001.
18. A.-F. Pécharman, M. S. Hill, M. F. Mahon, *Dalton Trans.*, 2018, **47**, 7300.
19. (a) A.-F. Pécharman, A. L. Colebatch, M. S. Hill, C. L. McMullin, M. F. Mahon, C. Weetman, *Nat. Chem.*, 2017, **8**, 15022; (b) M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *J. Am. Chem. Soc.*, 2007, **129**, 9570.
20. See for example: A. J. Boutland, I. Pernik, A. Stasch, C. Jones, *Chem. Eur. J.*, 2015, **21**, 15749.
21. H. Nöth, B. Wrackmeyer, "Nuclear Magnetic Resonance Spectroscopy of Boron Compounds", No. 14 in the series "NMR-Basic Principles and Progress", P. Diehl, E. Fluck, R. Kosfeld (eds.), Springer Verlag, Berlin, 1978.
22. As determined from a survey of the Cambridge Crystallographic Database, March, 2019.
23. S. Pietsch, E. C. Neeve, D. C. Apperley, R. Bertermann, F. Mo, D. Qiu, M. S. Cheung, L. Dang, J. Wang, U. Radius, C. Kleeberg, Z. Lin, T. B. Marder, *Chem. Eur. J.*, 2015, **21**, 7082.
24. It is important to note that we have previously shown that magnesium(I) dimers rapidly reduce stoichiometric amounts of ketones, alkynes and isocyanates, and these reactions are irreversible. See refs 7 and 10, and C. Jones, L. McDyre, D. M. Murphy, A. Stasch, *Chem. Commun.*, 2010, **46**, 1151.

Graphical Abstract

**The Complex Reactivity of β -Diketiminato Magnesium(I) Dimers Towards Pinacolborane:
Implications for Catalysis****Dafydd D. L. Jones, Aidan Matthews and Cameron Jones***

Reactions of three β -diketiminato magnesium(I) dimers with various excesses of pinacolborane are complex, yielding mixtures of many known and new products, including ten structurally characterised magnesium-boron containing complexes (e.g. see picture). These results bring into question mechanisms recently proposed for the hydroboration of unsaturated substrates, involving magnesium(I) dimers as catalysts or pre-catalysts.

