Diborane heterolysis: breaking and making B–B bonds at magnesium†

Anne-Frédérique Pécharman, Michael S. Hill† and Mary F. Mahon

Reaction of the dimeric β-diketiminato magnesium hydride ([BDI]MgH₂ (BDI = HC{(Me)CN-2,6-i-Pr₂C₆H₃}₂) with bis-pinacolatodiborane (B₂pin₂) resulted in B–O bond activation and formation of a magnesium complex of an unusual borylborohydride anion. In contrast, similar treatment of the mono-nuclear organomagnesium ([BDI]Mg(n-Bu)) with 4,4',4',6,6'-hexamethyl-2,2'-bi(1,3,2-dioxaborinan) (B₆hex₂) provided a B(sp²)–B(sp³) diborane anion, [(hex)BB(n-Bu)/hex]^−, with a constitution which is analogous to that formed in the previously reported reaction with bis(pinacolato)diboron (B₂pin₂). Subsequent addition of 4-dimethylaminopyridine to a solution of this compound induced alkylborane displacement and provided a magnesium boryl derivative containing a terminal Mg–B(hex) interaction (Mg–B 2.319(3) Å), a result which reinforces the generality of this approach for the synthesis of boryl anions by B–B bond heterolysis. Further studies of the reactivity of the initially formed B(sp²)–B(sp³) anions with diborane small molecules also resulted in alkylborane displacement and the production of triboron anions, which are propagated by contiguous and electron precise (2c–2e) B–B–B interactions.

Introduction

The selective installation of boryl (–BX₃) units into organic molecules is an important capability in contemporary chemical synthesis. The resultant C–B bonds provide a straightforward means to introduce further functionality, either through oxidation or their use in catalytic C–C bond formation through the application of Suzuki–Miyaura protocols.1–3 Boryl moieties are conventionally transferred to an organic substrate by a variety of routes (e.g. alkene hydroboration) which are reliant upon the Lewis acidic and electrophilic behaviour of the electrophilic boron centre in reaction with an organic nucleophile. Although boryl ligands can be generated by oxidative addition of B–X (B = H, B or halide) bonds to transition metals,4,5 Yamashita and Nozaki’s seminal report of the lithium boryl, [HCN(BH₂)₂BLi(DME)] (1, Dipp = 2,6-di-isopropylphenyl, DME = dimethoxyethane, Scheme 1) was widely recognised as the first true boron-centred nucleophile.5,6 The isolation of compound 1 requires strongly reducing and inconvenient reaction conditions, however, and its isolation is also crucially dependent on the high degree of kinetic stabilisation provided by sterically demanding substituents about the boron centre. While compound 1 has since been shown to display broad applicability in boron-to-element bond forming reactions with a palette of organic and metal-centred electrophiles,7–15 this latter structural feature dictates that some of these transformations display only limited specificity. Reactions of compound 1 with organohalides, RX (X = Cl, Br), for example, not only provide the expected products of nucleophilic substitution, [[HCN(Dipp)]₂B-X], but also suffer from competitive halogen abstraction to give [[HCN(Dipp)]₂B-X].16,17

While a wide variety of alternative boron-centred nucleophiles have been described since the report of 1,18–36 a majority of routes to these species still require an alkali metal reduction step. With these issues in mind, we have recently reported that terminal magnesium boryl species may be easily generated by heterolysis of the B–B bond of commercially available bis(pinacolato)diborane (B₂pin₂) within the coordination sphere of a β-diketiminato magnesium derivative (Scheme 1).37 Treatment of the magnesium n-butyl complex, [[BDI]Mg(n-Bu)] (2) (BDI = HC{(Me)CN-2,6-i-Pr₂C₆H₃}₂) with one equivalent of B₂pin₂ provided compound 3, which contains a diborane-derived anion in which one of the boron centres has been quaternised. This anion is strongly reminiscent of the variety of B(sp²)–B(sp³) adducts of B₂pin₂ with neutral or anionic donors that have been shown to act as viable sources of nucleophilic {Bpin} units.38–40 With this reactivity in mind, we have very recently shown that the {Bpin} moiety of compound 3 may be utilised to form electron-precise B–B bonds through reactions with the boron electrophiles Ph₃B and borabicyclo[3.3.1]nonane (9-BBN) albeit, in common with the previously men-

†Electronic supplementary information (ESI) available: Experimental procedures and characterisation data of compounds 7–12 respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt01451e
toned B(sp3)–B(sp3) adducts, these compounds are synthesized without the explicit generation of boryl anions. Reaction of compound 3 with an additional equivalent of B₂pin₂ also resulted in the displacement of n-BuBpin and the formation of an unusual derivative (4) of the catenated triboron [B₃pin₃]⁺ anion, while treatment of either 3 or 4 with 4-dimethylaminopyridine (DMAP) provided a magnesium complex (5) which does contain the terminal [Bpin]⁻ anion (Scheme 1). Initial assessment of the reactivity of compound 5 with both iodomethane and with non-halogenated organic electrophiles provided completely specific B–C bond formation and a definitive demonstration of its potential as a source of the [Bpin]⁻ nucleophile. In this contribution we continue to explore the generality of these routes to magnesium boryl equivalents and catena-triborane anions.

Results and discussion

The molecular magnesium hydride [[(BDI)MgH]₂ (6)] has played a central role in our development of a suite of catalytic bond activation processes. We, thus, carried out the reaction of compound 6 with B₂pin₂. Although the reaction performed in d₅-toluene required brief heating to ensure the formation of a homogeneous solution, inspection of the resultant ¹H and ¹³C {¹H} NMR spectra revealed the emergence of two new sets of β-diketiminate ligand environments, which had been formed in a strict 1 : 1 ratio by relative integration. Although the corresponding ¹¹B{¹H} NMR spectrum was broad and uninformative, the origin of these observations was resolved through the isolation of single crystals from the reaction solution. The resultant X-ray diffraction analysis revealed that compound 7 is the result of formal addition of both hydrides of the dimeric magnesium reagent (6) to a single boron centre within B₂pin₂ (Fig. 1). This process ensues with retention of the B–B bond and ring opening of one of the pinacolato boron heterocycles through rupture of the B₂–O₄ bond. The resultant diborane(5) anion bridges unsymmetrically between the two magnesium centres of the dimer, with consequent disruption of the C₂ᵥ symmetry of the hydride precursor (6) that was apparent in the NMR spectra of 7. The new diborane anion coordinates to Mg1 through O1 and O3, which remain bound to B1 and B2, respectively, and to Mg2 via coordination by the now formal alkoxydonor O4 and µ₂-BH₂-Mg bridging interactions. Although the specific constitution of this diborane anion is unprecedented, the B1–B2 distance [1.713(2) Å] is closely comparable to the similar linkages within previously reported B(sp³)–B(sp³) bonded compounds.

We suggest that the B–O bond activation observed in the synthesis of compound 7 is a possible consequence of the initial dimeric structure of the hydride derivative 6. With this in mind, we returned our attention to the mononuclear magnesium n-butyl reagent, 2, to further investigate the generality of the synthetic approach illustrated for B₂pin₂ in Scheme 1. Reaction of an equimolar quantity of 2 with the alternative, but still commercially available, diborane reagent 4,4′,4′,6,6′-...
hexamethyl-2,2′-bi(1,3,2-dioxaborinane) (B\textsubscript{2}hex\textsubscript{2}) provided the colourless compound 8 after work-up in high (>90%) yield (Scheme 2). Although the \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra of 8 were complex, the corresponding \textsuperscript{11}B{\textsuperscript{1}H} NMR spectrum of 8 was reminiscent of that observed for compound 3 in comprising two broad resonances at δ 30.5 and 4.0 ppm, consistent with the presence of three- and four-coordinate boron, respectively. This supposition was confirmed through the isolation of single crystals from n-hexane solution at −35 °C. The structure of compound 9, shown in Fig. 2(b), is comparable to that of 5 and confirms the generality of the straightforward magnesium-centred B–B activation for the synthesis of terminally bound boryl anions. Like 5, compound 9 is a four-coordinate magnesium derivative with three of the magnesium to ligand contacts provided by the nitrogen atoms of the β-diketiminate ligand and a single undentate DMAP ligand and with the final coordination site occupied by the sp\textsuperscript{2} boron donor. The Mg1–B1 distance [2.319(3) Å] of compound 9 is effectively identical to that determined for 5 [2.324(2) Å] and lies within the range observed in three reported magnesium derivatives synthesised by reactions of compound 1 with MgBr\textsubscript{2} [2.281(6)–2.377(4) Å].\textsuperscript{7}

Although a complete study of the behaviour of compounds 8 and 9 towards organic electrophiles will be described elsewhere, these structural and spectroscopic observations suggest the reactivity of both compounds should be comparable to those of the previously reported derivatives, 3 and 5. The facile reaction of compound 3 with B\textsubscript{2}pin\textsubscript{2} to provide the triboron anion of compound 4 prompted us to assess the generality of this reaction to provide unusual homocatenated triboron species. Accordingly, toluene solutions of compound 3 were

![Scheme 2](image_url)

**Scheme 2** Synthesis of compounds 8 and 9.

![Fig. 2](image_url)

**Fig. 2** ORTEP representations (25% probability ellipsoids) of (a) compound 8 and (b) compound 9. Isopropyl methyl groups are removed for clarity. Selected bond lengths (Å) and angles (°): (8) Mg1–O1 2.0466(14), Mg1–O3 1.9378(16), Mg1–N1 2.0550(16), Mg1–N2 2.0524(16), B1–B2 1.738(4), O1–Mg1–N1 118.56(7), O1–Mg1–N2 109.95(7), N2–Mg1–N1 94.34(7); (9) Mg1–N1 2.0832(19), Mg1–N2 2.0744(19), Mg1–N3 2.1422(18), Mg1–B1 2.319(3), N1–Mg1–N3 102.94(7), N1–Mg1–B1 133.12(8), N2–Mg1–N1 91.26(7), N2–Mg1–N3 106.23(7), N2–Mg1–B1 114.33(9), N3–Mg1–B1 106.09(8).
treated with equimolar quantities of B\textsubscript{2}hex\textsubscript{2} and 5,5,5′,5′-tetramethyl-2,2′-bi(1,3,2-dioxaborinane) (B\textsubscript{2}neo\textsubscript{2}), respectively (Scheme 3). Examination of the resultant \textsuperscript{1}H NMR spectra after 2 hours at 40 °C evidenced, in both cases, the formation of two new β-diketiminato magnesium complexes, compounds 10 and 11. Both of the corresponding \textsuperscript{11}B{\textsuperscript{1}H} NMR spectra were also observed to contain resonances at δ 34.2 ppm, consistent with elimination of \textit{n}-BuBpin, which appeared alongside those employed in the synthesis of compounds 10 and 11. Initial inspection of the resultant \textsuperscript{1}H and \textsuperscript{11}B NMR spectra indicated the generation of a single reaction product (12), which was anticipated to be the result of formal \textit{n}-BuB(hex) elimination to form a magnesium complex of the catenated [pinB(Bpin)B(hex)]\textit{n}−anion. Work up and crystallisation of compound 12, however, revealed that this process had produced an isomeric form of the anticipated triborane anion (Scheme 4). The resultant single crystal X-ray analysis (Fig. 4) identified a triboron anion in which the central sp\textsuperscript{3} boron centre is provided by a \{B\textsubscript{2}neo\textsubscript{2}\} moiety rather than through retention of the entire \{B\textsubscript{2}pin\textsubscript{2}\} unit. Although it has not been possible to determine whether this apparent cross metathesis process occurs during or subsequent to the displacement of the \textit{n}-Bu(hex) by-product, we suggest that the ultimate structure adopted by 12 may be dictated by kinetic factors and the...

![Scheme 3: Synthesis of compounds 10 and 11.](image)

![Fig. 3: ORTEP representation of (a) compound 10 and (b) compound 11 (25% probability ellipsoids). Isopropyl methyl groups are removed for clarity.](image)

![Scheme 4: Synthesis of compound 12.](image)
The relative steric demands of the boron-bound pinacolato and glycolato chelates and suggests that these species are prone to B-B exchange equilibria in which the ultimate product is determined by kinetic factors. The significance of these observations will become apparent during the future elaboration of this chemistry and our further studies of the onward reactivity of these readily available sources of nucleophilic boron with a range of organic and inorganic electrophiles.

**Conflicts of interest**

There are no conflicts of interest to declare.

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**References**

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