Magnesium Boryl Reactivity with 9-BBN and Ph₃B: Rational B−B′ Bond Formation and Diborane Isomerization

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Abstract: *Reactions of a magnesium-based pinacolatoboryl nucleophile with the electrophilic organoboranes, 9-BBN and Ph₃B, provide facile B−B′ single bond formation. Although the Ph₃B derivative is thermally stable, when heated, the unsymmetrical diborane(5) anion derived from 9-BBN is found to isomerize to two regioisomeric species via a proposed mechanism involving dehydroboration of the borabicyclo-[3.3.1]nonane and syn-diboration of the resultant alkenyl carbocycle.*

The aptitude of carbon for homocatenation is unsurpassed. In contrast, our ability to generate homonuclear E−E bonds between other p-block elements is at a much more primitive stage of development. Although, for example, boron catenation is common in boron hydride cluster chemistry,[1] only limited methods are available for the formation of electron-precise (2c–2e) B−B single bonds.[2] The generation of B−B bonds within synthetically important diborane(4) molecules such as bis(pinacolato)diborane (B₂pin₂), for example, is dependent on the reductive coupling of a haloborane by an alkali metal.[3] Although there have been recent advances in both the metal-templated coupling of borylene units[4] and catalytic[5] and stoichiometric[2,6] B−H dehydrocoupling, of more relevance to the current work are Yamashita and Nozaki's reports of the lithium boryltrihydroborate (**1**)[7] and the triborane(5) derivative (**2**).[8] In processes reminiscent of classical nucleophilic alkylation reactions, compounds **1** and **2** were synthesized from the nucleophilic lithium boryl anion (**3**)[9] and the boron electrophiles, BH₃·THF and BF₃·OEt₂, respectively.

The isolation of the boron nucleophile (**3**) itself, however, requires strongly reducing and problematic reaction conditions and is dependent on the high degree of kinetic stabilization provided by sterically demanding substituents about the boron center.[10] While diborane adducts such as **4** have also been shown to act as viable surrogates for boron nucleophiles,[11,12] we have reported that terminal magnesium boryl species may be generated by activation of the B−B bond

Dipp = 2,6-*i*-Pr₂C₆H₃

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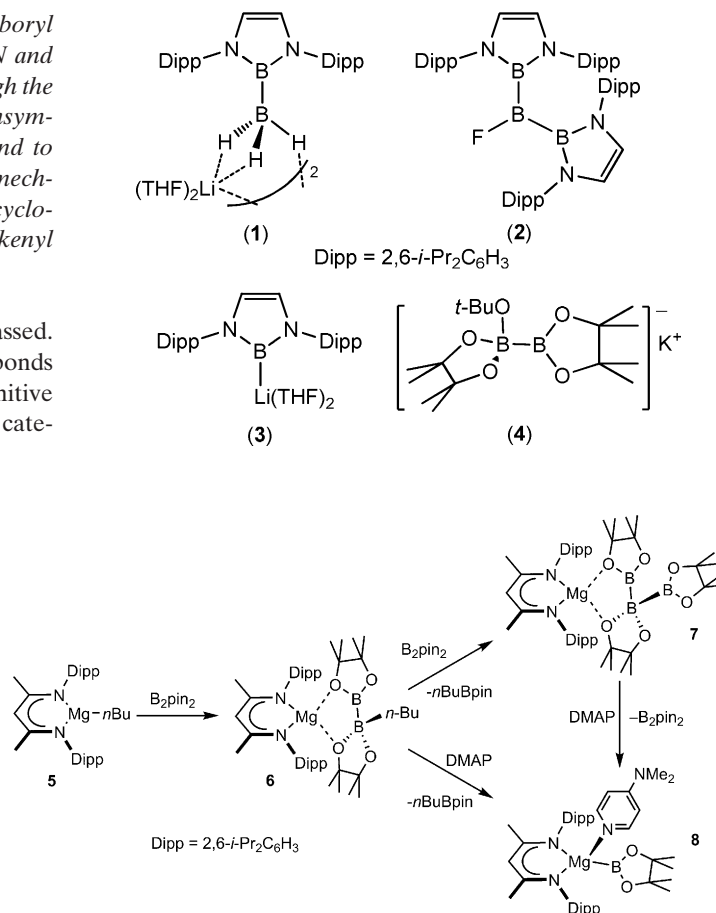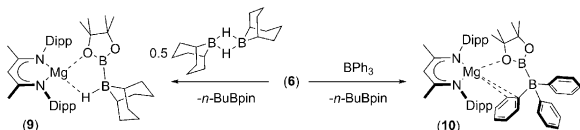
Scheme 1. Synthesis of compounds **6**–**8**.

of B₂pin₂ within the coordination sphere of magnesium (Scheme 1).[13] Treatment of compound **5** with one equivalent of B₂pin₂ provided complex **6** in which one of the boron centers of the diborane had been quaternized by addition of the *n*-butyl group. Addition of further equivalents of B₂pin₂ resulted in the displacement of *n*-BuBpin and the formation of an unusual derivative (**7**) of the catenated triboron [B₃pin₃]⁻ anion. Subsequent treatment of **6** or **7** with 2-dimethylaminopyridine (DMAP) provided the magnesium derivative (**8**) containing a terminal [Bpin]⁻ anion. While compound **8** performs as a well behaved boron centered nucleophile in reactions with both halogenated and non-halogenated organic electrophiles,[13] the formation of compound **7** highlights the potential of these systems for the generation of molecules containing electron precise B−B σ bonds. Herein, we extend our study of these magnesium-centered boron nucleophiles to their reactivity with the

organoboranes 9-borabicyclo[3.3.1]nonane (9-BBN) and Ph$_3$B.

The easily generated [pinB-Bpin(*n*-Bu)]$^-$ anion of compound **6** is reminiscent of nucleophilic boron surrogates such as **4**. Samples of compound **6** were thus reacted with 0.5 molar equivalents of the 9-BBN dimer and an equimolar quantity of Ph$_3$B. The resultant ^{1}H NMR spectra revealed the formation of the β-diketiminato magnesium compounds, **9** and **10**, for the 9-BBN- and Ph$_3$B-based reactions, respectively (Scheme 2).

Scheme 2. Synthesis of compounds **9** and **10**.

The ^{11}B NMR spectra of both reactions provided evidence for the production of *n*-BuBpin ($\delta = 34.2$ ppm), while resonances at δ −22.8 ppm (**9**) and −14.6 ppm (**10**) were consistent with the generation of new four-coordinate boron environments. After removal of volatiles, the *n*-BuBpin by-product was readily separated from samples of both **9** and **10** by washing of the colorless solids with *n*-hexane. In both cases, crystallization from toluene solutions at −35°C provided samples suitable for single-crystal X-ray diffraction analysis (Figure 1). These experiments revealed that both compounds **9** and **10** were magnesium derivatives of unsymmetrical B(sp^2)−B(sp^3) anions comprising bonds constructed from a {Bpin} unit and half an equivalent of the 9-BBN dimer (**9**) and BPh$_3$ (**10**), respectively.

The {pinB-BR$_2$X}$^-$ anions of both compounds **9** and **10** are reminiscent of the boron-containing anion of compound **1** and confirm that **6** provides a viable source of the [Bpin]$^-$ nucleophile.[7] The B1−B2 bond lengths (**9**, 1.7203(18); **10**, 1.718(7) Å) are otherwise unremarkable and are comparable to previously reported B(sp^2)−B(sp^3) bonds.[12] The most notable features of compound **9** are the significant interactions of H2 and H40, attached to B2 and C40, respectively, which were located and refined without restraints (Mg1−H2 1.900(15), Mg1−H40 2.220(15) Å), and the magnesium atom. Similarly, the magnesium center of compound **10** displays close contacts between the (C36) *ipso* and the (C37) *ortho* carbons of one of the boron-bound phenyl substituents (Mg1−C36 2.544(5), Mg1−C37 2.410(5) Å).

We have previously described a number of catalytic systems derived from compound **5** in which pinacolborane is utilized as a reagent for either the hydroboration of polarized multiple bonds or as the hydridic coupling partner during heterodehydrocoupling with organic amines.[14] In all cases, the liberation of the borylated products was deduced to occur through the assembly of isolable hydridoborate intermediates which undergo subsequent boron-to-magnesium hydride elimination as the product-forming step of the catalysis. To assess the potential for similar hydride or phenyl elimination, samples of **9** and **10** in [D$_8$]toluene were heated at 110°C. Although compound **10** proved to be completely stable, after
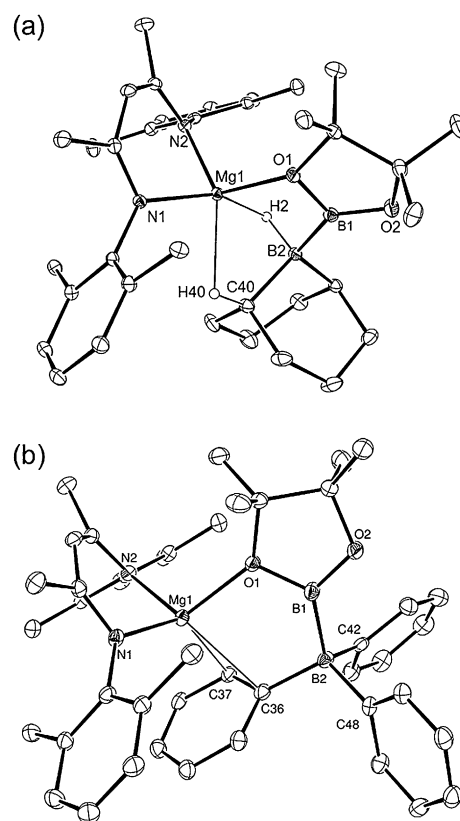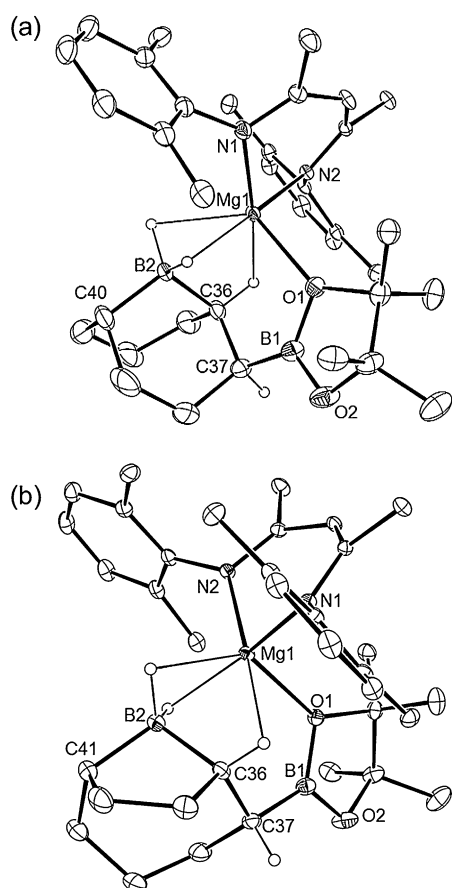

Figure 1. ORTEP representations of a) **9**; b) **10** (ellipsoids set at 25% probability). Isopropyl methyl groups and hydrogen atoms except H2 and H40 (**9**) are removed for clarity.[18] Selected bond lengths [Å] and angles [°]: (**9**) Mg1−N1 2.0556(10), Mg1−N2 2.0488(10), Mg1−O1 2.0719(9), B1−B2 1.7203(18); N2-Mg1-N1 94.95(4), B1-O1-Mg1 93.15-(7), O1-B1-B2 116.68(10); (**10**) Mg1−O1 2.059(3), Mg−N1 2.043(4), Mg1−N2 2.037(4), Mg1−C36 2.544(5), Mg1−C37 2.410(5), B1−B2 1.718(7), C36−B2 1.647(7), C42−B2 1.649(7), C48−B2 1.630(7); N2-Mg1-N1 96.40(14), O1-B1-B2 125.2(4), O2-B1-O1 108.1(4), O2-B1-B2 126.6(4), C36-B2-B1 109.3(4), C42-B2-B1 106.6(4), C48-B2-B1 114.4(4).

three days under these conditions the initial sample of **9** had been entirely consumed with the production of two new β-diketiminato magnesium derivatives, compounds **11** and **12**, in a respective 1:0.7 ratio. Although the ^{1}H and ^{13}C{^{1}H} NMR spectra of the resultant mixture of compounds were otherwise uninformative, the ^{11}B NMR spectrum displayed two resonances at δ−14.6 and −19.5 ppm, consistent with the formation of two differentiated four-coordinate boron environments.

Compounds **11** and **12** were identified by fractional crystallization from a saturated toluene solution at −35°C and mechanical separation of individual single crystals suitable for X-ray diffraction analysis (Figure 2). Both compounds crystallized with near identical monoclinic ($P2_1/n$) unit cells and, although neither compound contains a direct B−B bond, were identified to be constitutional isomers of compound **9**. In each case a {Bpin} unit appears to have replaced a C−H bond of a methylene group adjacent to the carbon center attached to the bridgehead boron atom (B2) of the original 9-BBN reagent. These latter atoms, while still four-coordinate, now comprise diorganoborohydride residues in both compounds and the structures of **11** and **12** differ only

Figure 2. ORTEP representations of a) **11**; b) **12** (ellipsoids set at 25% probability). Isopropyl methyl groups and hydrogen atoms except those attached to B2, C36, and C37 are removed for clarity.[18] Selected bond lengths [Å] and angles [°]: (**11**) N1–Mg1 2.066(3), N2–Mg1 2.061(2), O1–B1 1.408(5), O2–B1 1.348(5), C37–B1 1.568(5), C36–B2 1.628(5), C40–B2 1.594(5); N2-Mg1-N1 95.40(10), O2-B1-O1 111.8(3), C36-C37-B1 111.4(3), C40-B2-C36 104.9(3); (**12**) N1–Mg1 2.0684(13), N2–Mg1 2.0399(13), O1–B1 1.405(2), O2–B1 1.356(2), C37–B1 1.561-(3), C36–B2 1.661(2), C41–B2 1.618(3); N2-Mg1-N1 95.67(5), O2-B1-O1 111.81(16), C36-C37-B1 112.20(14), C41-B2-C36 102.24(14).

in the constitution of their respective bicyclic [3.3.1] (**11**) and [4.2.1] (**12**) ring systems; whereas the initial six-membered rings of 9-BBN are retained in **11**, the bicycle has isomerized to a combination of five- and seven-membered rings in **12**. In both cases the borohydride anion binds to the magnesium center through a combination of O1−Mg1 and B2-μ_2-H$_2$-Mg1 bridging interactions augmented by a further close contact with the C−H bond of the C36-containing methine unit.

Yalpani and co-workers have previously demonstrated that the isomerization of 9-borabicyclo[3.3.1]nonane to 9-borabicyclo[4.2.1]nonane may be thermally induced at temperatures > 150°C.[15] A similar metal-mediated rearrangement has also been observed during the attempted hydroboration of a zirconocene-coordinated diphenylacetylene by 9-BBN.[16] These earlier reports have suggested such isomerization proceeds through a sequence of de-hydroboration and intramolecular re-hydroboration to provide the two possible regioisomers. We thus suggest that the synthesis of compounds **11** and **12** ensues through a similar process and the
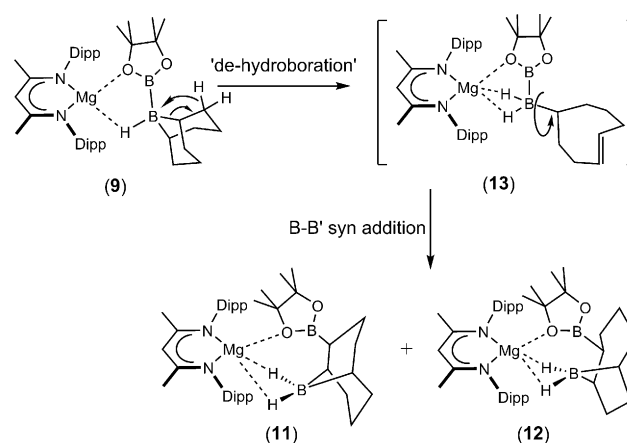
Scheme 3. Proposed route to compounds **11** and **12**.

formation of a common but unobservable borohydride intermediate (**13**), which is the result of thermally induced de-hydroboration (Scheme 3). Subsequent intramolecular *syn*-diboration of the alkenyl carbocycle with the unsymmetrical B−B′ bond then takes place to form both of the crystallographically characterized regioisomers, **11** and **12**.

The validity of these proposals was supported by density functional theory (DFT) calculations. Both borohydride derivatives, **11** and **12**, are exergonic relative to structure **9**, with free energies of −6.7 kcal mol^{-1} and −5.1 kcal mol^{-1} respectively, confirming the experimental generation of these species under the applied reaction conditions. The route through intermediate **13** was much more difficult to identify computationally, which is due to the conformational flexibility of the cyclooctenyl ring. A range of intermediates were optimized, ranging in free energy from +19.4 to 31.7 kcal mol^{-1}. This conformational freedom also militated against the location of any meaningful transition state for either of the subsequent proposed diboration steps to form compounds **11** and **12**, despite multiple attempts.

In summary, the easily accessed magnesium boryl equivalent **6** reacts with the electrophilic boron centers of 9-BBN and Ph$_3$B to provide anions with electron precise (2c–2e) B−B single bonds. Liberation of the neutral diborane(4) molecule has yet to be achieved. These observations, however, indicate that the reaction of compounds such as **6** with boron reagents containing more labile leaving groups should provide a practicable means to achieve B−B bond formation and facile access to synthetically useful unsymmetrical diboranes.[17]

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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[18] CCDC 1575641, 1575642, 1575643, and 1575645 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.