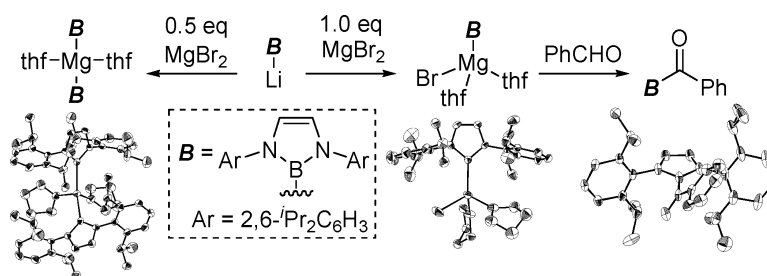


Synthesis, Structure of Borylmagnesium, and Its Reaction with Benzaldehyde to Form Benzoylborane

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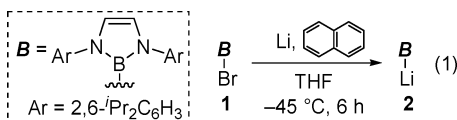
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Boron-containing reagent made a great contribution in synthetic organic chemistry.¹ Examples are found in hydroboration chemistry,² Lewis acidic boron-mediated chemistry,³ boron-enolate chemistry,⁴ and recent Suzuki–Miyaura cross-coupling chemistry.⁵ It should be mentioned that the boron atom is electrophilic in all cases. On the other hand, a boron-centered nucleophile has been a challenging target for organic chemists.⁶ Although there have been several reports about the generation of borylmetal species which may play a role as boron nucleophiles,^{7,8} the application of the boron nucleophiles is still limited.

A Grignard reagent, RMgX, is one of the most important reagents in organic chemistry since its discovery in 1900.⁹ From the viewpoint of synthetic chemistry, Grignard reagents are considered as carbanion equivalents because of the highly polarized carbon–magnesium bond. However, the corresponding borylmagnesium has never been reported. Our recent discovery of boryllithium **2** by the reduction of bromoborane **1** (eq 1, the diaminoboryl substituent is abbreviated as **B** unless otherwise noted) prompted us to synthesize borylmagnesium species. Herein, we report the chemistry of new anionic boron nucleophiles, borylmagnesium, containing the first example of a B–Mg single bond.¹¹



Borylmagnesiums were prepared by the transmetalation of boryllithium **2** with 1 or 0.5 equiv of MgBr₂·OEt₂ powder in THF at room temperature (Scheme 1). Recrystallization of the product from the reaction with 1.0 equiv of MgBr₂ gave a separable pair of crystals which consists of colorless **3** and pale yellow **4**. On the other hand, reaction with 0.5 equiv of MgBr₂ gave the corresponding bis(boryl)magnesium species **5** as yellow crystals. X-ray crystallographic analysis revealed the structures of these three molecules (Figure 1).

In the crystal structures, each of these molecules includes a nearly ideal sp² boron atom and slightly distorted sp³ magnesium atom with the first structurally characterized B–Mg single bonds.¹¹ All B–Mg bonds (Table 1) were slightly longer than the sum (2.24 Å) of covalent radii¹² of boron and magnesium atoms as was observed in the previously reported boryllithium [2·DME]₂.¹⁰ The elongation of the B–Mg bond can be attributed to the weakened Coulomb interaction due to the coordination of THF molecules.¹³ The B–N bonds and N–B–N angles of borylmagnesiums were closer to those in boryllithium [2·DME]₂¹⁰ rather than those in the protonated hydroborane **6**. The results above indicate an ionic character of the B–Mg single bonds.

Dissolution of isolated crystals of **3** and **4** into THF-*d*₈ showed identical ¹H and ¹¹B NMR spectra (see Supporting Information) with appropriate integral ratio of free THF molecules which coordinated to magnesium in the crystal. Furthermore, the ⁷Li NMR

Scheme 1. Reaction of Boryllithium **2** with MgBr₂·OEt₂

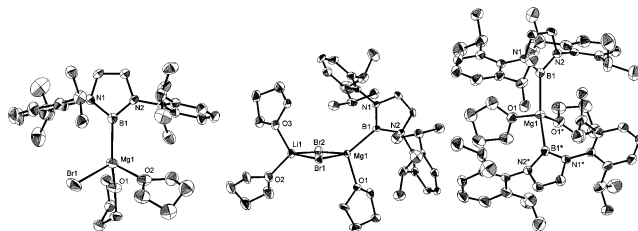
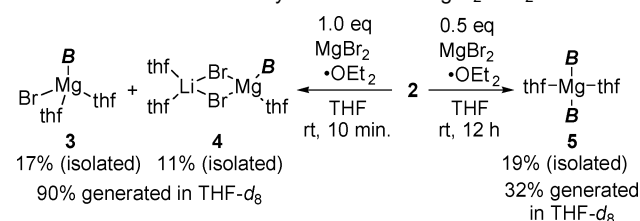


Figure 1. ORTEP drawings of **3** (left), **4** (center), and **5** (right).

Table 1. Structural Comparison between Borylmagnesiums and Related Compounds

	3	4	5	[2·DME] ₂	B–H (6)
B–Mg (Å)	2.281(6)	2.282(6) 1.453(6)	2.377(4)		
B–N (Å)	1.453(7) 1.465(7)	1.458(7) 1.464(7) 1.467(7)	1.471(5) 1.487(4)	1.465(4) 1.467(4)	1.418(3) 1.423(3)
N–B–N (°)	100.7(4)	100.5(4)	99.3(3)	99.2(2)	105.25(16)

chemical shift of **3** (δ_{Li} 0.4) was identical to that of LiBr in THF-*d*₈. That is, **4** may have a formula of **3** in THF solution even in the presence of LiBr. Bis(borylmagnesium) **5** could be easily distinguished from **3** and **4** by its ¹H NMR spectra. All of **3**–**5** showed a broad peak at δ_{B} 37.6 in their ¹¹B NMR spectra. These low-field shifted broad ¹¹B peaks also support the ionic character of B–Mg bonds in borylmagnesium species due to their paramagnetic contribution to shielding as was discussed about boryllithium.¹⁰ On the basis of the above characterization, we could estimate the reaction conversion of **2** with MgBr₂·OEt₂ as follows. The reaction of **2** with 1.0 equiv of MgBr₂·OEt₂ in THF-*d*₈ enabled us to confirm that 90% of **2** was converted to **3** in solution with 10% of hydroborane **6** as judged by ¹H NMR spectroscopy if 100% of **4** existed as **3** in solution (Scheme 1). On the other hand, only 32% of **2** was converted to **5** by the reaction of **2** with 0.5 equiv of MgBr₂·OEt₂ in THF-*d*₈ accompanied with 36% of hydroborane **6** and 32% of unreacted **2**.

The reaction of borylmagnesium bromide **3** generated from **2** in situ with 1–3 equiv of benzaldehyde was performed (Table 2, runs 1–3). These reactions afforded a mixture of benzoylborane **7**, boron-substituted ester **8**, and hydroborane **6**. Simultaneous formation of benzyl alcohol **9** suggests intermolecular hydride transfer from a magnesium borylbenzyloxide intermediate to an excess of

Table 2. Reaction of Borylmagnesium Bromide **3** or Boryllithium **2** with Benzaldehyde (yields are based on the amount of **1**)

run	reactant	PhCHO (equiv)	7 (%) ^a	8 (%) ^a	6 (%) ^a	9 (%) ^b	10 (%) ^a
1	3	1	18	18	56	27	0
2	3	2	34	24	32	47	0
3	3	3	22	40	16	55	0
4	2	1	0	0	6	0	81
5	2	3	0	51	10	50	0

^a ¹H NMR yield. ^b GC yield.**Table 3.** Properties of Acylborane **7** with a Reference Benzophenone and ORTEP Drawing of **7** (50% Thermal Ellipsoids, Hydrogen Atoms were Omitted for Clarity)

	7	Ph ₂ C=O
C–O bond	1.241(2) Å	1.222 Å
$\nu_{\text{C=O}}$ (KBr)	1618 cm ⁻¹	1655 cm ⁻¹
δ_{C} (C ₆ D ₆)	218.7 ppm	195.7 ppm

benzaldehyde probably via a six-membered ring transition state (see picture) as was reported for the magnesium–Oppenauer oxidation.¹⁴ It is noteworthy that no borylbenzylalcohol **10**¹⁰ was formed by the reaction of **3** with benzaldehyde (runs 1–3) in sharp contrast to the fact that **10** was obtained in 81% yield by the reaction of boryllithium **2** with 1 equiv of benzaldehyde (run 4). Addition of a second equivalent of benzaldehyde to **2** led to the intermolecular hydride transfer to form **8** (run 5) accompanied with the formation of **9**. Thus, the counter metal cation alters the reactivity of α -borylbenzyloxide.¹⁵

Benzoylborane **7** is the first example of a fully characterized acylborane.¹⁶ Alternatively, we could also synthesize **7** in a higher yield by the reaction of boryllithium **2** with benzoyl chloride. The σ -donor ability of the diamino-boryl substituent to the carbonyl group is indicated by (i) long C=O bond length in its X-ray structure,¹⁷ (ii) IR carbonyl absorption shifted to lower energy,¹⁸ and (iii) lower-field shifted ¹³C NMR peak (broadened by a quadrupolar ¹¹B nucleus) when compared to that of benzophenone (Table 3). The tendency is common to benzoylsilanes reported in the literature.¹⁹ In the solid state, the benzoyl plane was not coplanar with the boron plane (N–B–C=O torsion = 50.0(3)°).

In conclusion, the reaction of boryllithium **2** with 1.0 or 0.5 equiv of MgBr₂·OEt₂ provided borylmagnesium bromides **3** and **4** or bis-(boryl)magnesium **5**. Structures of **3**, **4**, and **5** in the crystals and solutions indicated the ionic character of the B–Mg bonds. The reactivity of borylmagnesium **3** with benzaldehyde was different from that of boryllithium **2**. Benzoylborane **7** was fully characterized as the first acylborane. Further studies on reactivity of borylmagnesiums **3**–**5** and benzoylborane **7** are now in progress.

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Supporting Information Available: All experimental procedures, spectroscopic data of new compounds, and CIF files of **3**–**5** and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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