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

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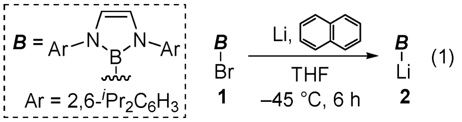
Boron-containing reagent made a great contribution in synthetic organic chemistry.[1] Examples are found in hydroboration chemistry,[2] Lewis acidic boron-mediated chemistry,[3] boron-enolate chemistry,[4] and recent Suzuki−Miyaura cross-coupling chemistry.[5] It should be mentioned that the boron atom 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**[10] 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]

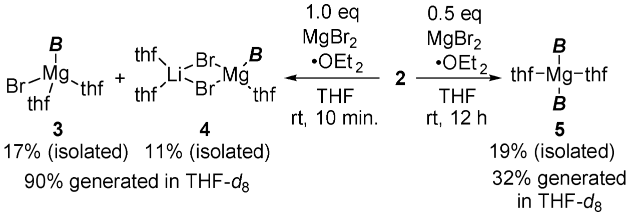


(1)

Borylmagnesiums were prepared by the transmetallation of boryllithium **2** with 1 or 0.5 equiv of $MgBr_2$•OEt_2 powder in THF at room temperature (Scheme 1). Recrystallization of the product from the reaction with 1.0 equiv of $MgBr_2$ 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 $MgBr_2$ 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 sp^2 boron atom and slightly distorted sp^3 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 radii[12] 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]$_2$[10] rather than those in the protonated hydroborane **6**. The results above indicate an ionic character of the B−Mg single bonds.

Scheme 1. Reaction of Boryllithium **2** with $MgBr_2$•OEt_2



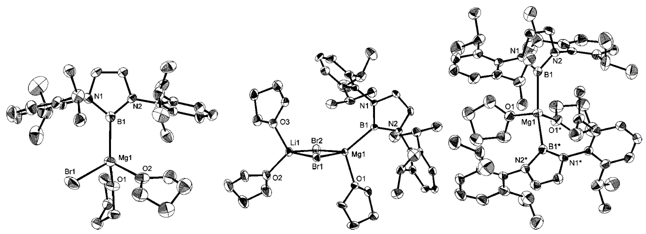


Figure 1. ORTEP drawings of **3** (left), **4** (center), and **5** (right).

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)

Dissolution of isolated crystals of **3** and **4** into THF-d_8 showed identical ^{1}H and ^{11}B NMR spectra (see Supporting Information) with appropriate integral ratio of free THF molecules which coordinated to magnesium in the crystal. Furthermore, the ^{7}Li NMR 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 ^{1}H NMR spectra. All of **3**−**5** showed a broad peak at δ_B 37.6 in their ^{11}B NMR spectra. These low-field shifted broad ^{11}B 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 $MgBr_2$•OEt_2 as follows. The reaction of **2** with 1.0 equiv of $MgBr_2$•OEt_2 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 ^{1}H 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 $MgBr_2$•OEt_2 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

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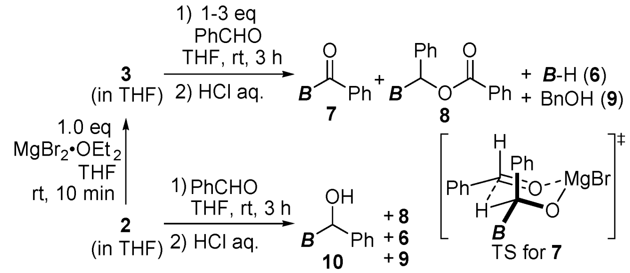
Table 2. Reaction of Borylmagnesium Bromide **3** or Boryllithium **2** with Benzaldehyde (yields are based on the amount of **1**)

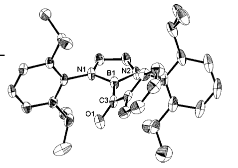


run	reactant	PhCHO (equiv)	**7** (%)[a]	**8** (%)[a]	**6** (%)[a]	**9** (%)[b]	**10** (%)[a]
1	**3**	1	18	18	56	27	0
2	**3**	2	34	24	32	47	0
3	**3**	3	22	40	16	55	0
4	**2**	1	0	0	6	0	81
5	**2**	3	0	51	10	50	0

[a] ^{1}H 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	$Ph_2C{=}O$
C-O bond	1.241(2) Å	1.222 Å
$\nu_{C=O}$ (KBr)	1618 cm^{-1}	1655 cm^{-1}
δ_C (C_6D_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 diaminoboryl 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 ^{13}C NMR peak (broadened by a quadrupolar ^{11}B 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 $MgBr_2$·OEt_2 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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