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Award Accounts

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Creation of Nucleophilic Boryl Anions and Their Properties

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A series of anionic boron compounds, possessing a polarized boron–metal bond, were synthesized and structurally characterized. Detailed analyses of these boryl anions using NMR spectroscopy, X-ray crystallography, reactivity with electrophiles, and DFT calculations revealed that these compounds have anionic and nucleophilic character on the boron center in contrast to conventional boron-containing molecules with a Lewis acidic character. Some applications of boryl anions toward organic synthesis, organometallic chemistry, and main group chemistry are also described.

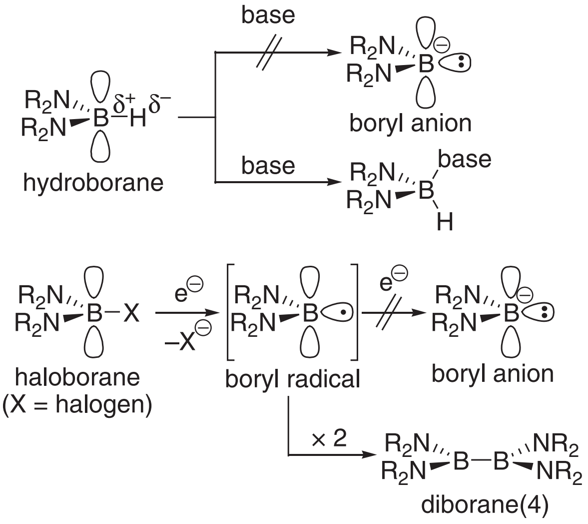
1. Introduction

Boron is a group 13 element in the 2nd period, located to the left of carbon in the periodic table. Since boron has three valence electrons, neutral boron molecules generally have a vacant p-orbital on the boron center. This nature of boron characterizes chemistry of boron compounds as electron-deficient species in organic and inorganic chemistry. For example, Lewis acidity of boron-containing compounds has been widely utilized for organic chemistry, such as hydroboration chemistry,[1] Lewis acidic boron-mediated chemistry,[2] boron–enolate chemistry,[3] and recent Suzuki–Miyaura cross-coupling chemistry.[4] Recently, some organic molecules containing boron as a key element are involved in a large area of material science.[5] To synthesize these types of boron-containing compounds, a boron-containing chemical bond should be constructed. In general, the electron-deficiency of boron atom allows introduction of a nucleophile to the boron-containing reagent to form a boron–nucleophile bond. However, there have been limited examples of "boryl anions," which may act as a boron nucleophile. In this account, the author describes recent efforts in the field of boryl anions.[6]

2. Design for Boryl Anion

A parent boryl anion, $^{-}BH_2$, has been calculated to have singlet ground state[7] in contrast to the well-understood parent carbene, CH_2, possessing triplet ground state.[8] Complexation of boryl anion with alkali metal cation was proven to lead to thermal stability of the anion.[7] Substitution of hydrogen atoms in $^{-}BH_2$ with electronegative heteroatoms, such as nitrogen and oxygen, was also effective for thermal stabilization because of an inductive effect of the heteroatom and an orbital overlap between a lone pair of the heteroatom and the vacant p-orbital of the boron atom in $LiB(NH_2)_2$ and $LiB(OH)_2$.[7] Well-established chemistry of *N*-heterocyclic carbene,[9] isoelectronic to boryl anion, prompted us to use five-membered ring diamino substituents for stabilization of boryl anion as theoretical calculations suggested.[10]

Two classic methodologies for preparation of carbanions are not applicable for boryl anions (Scheme 1). Deprotonation of hydroborane with base is usually difficult because of negatively-polarized hydrogen atom due to the lower electronegativity of boron (Pauling, 2.04)[11] than that of hydrogen (2.20). One can also expect the vacant p-orbital on the boron atom to accept the base to form Lewis acid–base adduct. Reductive cleavage of a B–halogen bond in haloborane is also not applicable because of the formation of diborane(4) species having a B–B single bond via dimerization of boryl radical



Scheme 1. Two conceivable pathways to synthesize the boryl anion.

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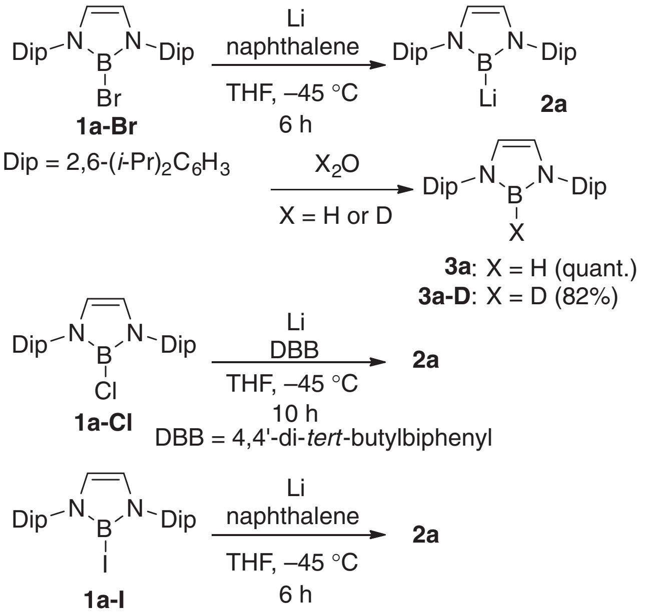


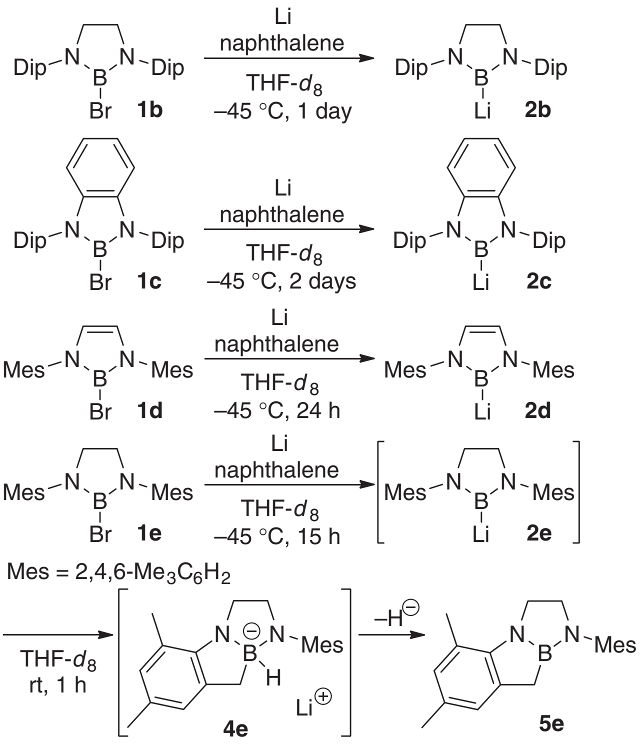
Scheme 2. Synthesis of boryllithium **2a**.

intermediate.[12] To avoid this dimerization of radical intermediate, bulky substituents on nitrogen atoms would be effective.

3. Chemistry of Boryl Anions

3.1 Boryllithium. 3.1.1 Syntheses of Boryllithiums: The bromoborane **1a-Br**, possessing two bulky 2,6-diisopropylphenyl groups, was successfully reduced to the boryllithium **2a** by the use of a combination of lithium powder and naphthalene in THF at −45 °C (Scheme 2).[13] The reaction of **2a** with water quantitatively gave a hydroborane **3a**, which could be independently synthesized by reaction of **1a-Br** with $LiAlH_4$. Treatment of **2a** with D_2O afforded the corresponding deuterioborane **3a-D** in 82% yield, indicating that **3a** was mostly generated from the reaction of **2a** with water rather than with the solvents or ligand backbone. Chloroborane **1a-Cl** and iodoborane **1a-I** could also be a precursor for boryllithium **2a**, although reduction of **1a-Cl** required stronger reductant Li–DBB.[14]

Effects of the five-membered ring structure and substituents on the nitrogen atoms were studied by using various bromoborane precursors **1b**–**1e** (Scheme 3).[14] Compound **1b** containing a C–C single bond in the five-membered ring structure, **1c** possessing a benzoannulated five-membered ring, and **1d** having relatively small mesityl ($2,4,6\text{-}Me_3C_6H_2$) groups, were successfully reduced to the corresponding boryllithium species **2b**–**2d** in quantitative yield as confirmed by their ^1H NMR spectra. Bromoborane **1e** with C–C single bond and mesityl groups could also be reduced to boryllithium **2e**, characterized by ^1H NMR spectrum at −45 °C, however, elevating temperature of the solution to room temperature, a cyclic hydroborate **4e** with C–H bond cleavage was found to be generated. The cyclic borate **4e** gradually decomposed to form neutral alkylborane **5e** with loss of hydride from the borate center.



Scheme 3. Generation of boryllithium derivatives from various bromoboranes **1b**–**1e**.

3.1.2 Structures of Boryllithium: By cooling hexane solutions of boryllithium **2a**–**2c** prepared in THF or DME solvent, several single crystals of (**2a**•dme)$_2$, **2a**•(thf)$_2$, **2b**•(thf)$_2$, and **2c**•(thf)$_2$ were obtained.[13–15] The obtained crystal structures are illustrated in Figure 1 and selected structural parameters of them are summarized in Table 1 with those of reference compounds, calculated free boryl anions opt-**6a**–**6c**, hydroboranes **3a**–**3c**, *N*-heterocyclic carbenes having the same skeleton **6**,[16] **8**,[17] **10**,[18] and their precursors, imidazolium salts **7**,[16] **9**,[17] **11**.[18] In (**2a**•dme)$_2$, DME molecules chelated to the central lithium atom, and one of two oxygen atoms bridging two lithium atoms to form a dimeric structure. Compound **2a** was also crystallized as **2a**•(thf)$_2$, contained two THF molecules coordinating to the lithium atom. Boryllithiums **2b**•(thf)$_2$ and **2c**•(thf)$_2$, which have a saturated C–C bond or a benzannulated C=C bond in the five-membered ring, have THF-coordinated structure similar to the case of **2a**•(thf)$_2$. Apparently, there is a 2c–2e B(sp^2)–Li bond in all crystal structures to show that the products were boryllithiums. The B–Li bond lengths [2.291(6) Å in (**2a**•dme)$_2$; 2.276(5) Å in **2a**•(thf)$_2$; 2.271(4) Å in **2b**•(thf)$_2$; 2.218(9) Å in **2c**•(thf)$_2$] were 8.5, 7.9, 7.6, and 5.1% longer than the sum of the covalent radii (2.11 Å)[11] for boron and lithium. A similar elongation of the C–Li bond was observed in the crystal structure of $2,3,4,5\text{-}C_6HF_4Li\cdot(thf)_3$.[19] In the five-membered ring, the B–N bond lengths [1.465(4) and 1.467(4) Å in (**2a**•dme)$_2$; 1.474(3) and 1.480(4) Å in **2a**•(thf)$_2$; 1.4547(18) Å in **2b**•(thf)$_2$; 1.474(4) Å in **2c**•(thf)$_2$] and the N–B–N angles [99.2(2)° in (**2a**•dme)$_2$; 98.7(2)° in **2a**•(thf)$_2$; 101.89(16)° in **2b**•(thf)$_2$; 100.0(3)° in **2c**•(thf)$_2$] are closer to those in the calculated free boryl anions opt-**6a**–**6c** rather than the hydroboranes **3a**–**3c**. This tendency indicates these boryllithiums have an anionic character. The relationships between structures of boryllithiums and hydroboranes are quite similar to that between structures of *N*-

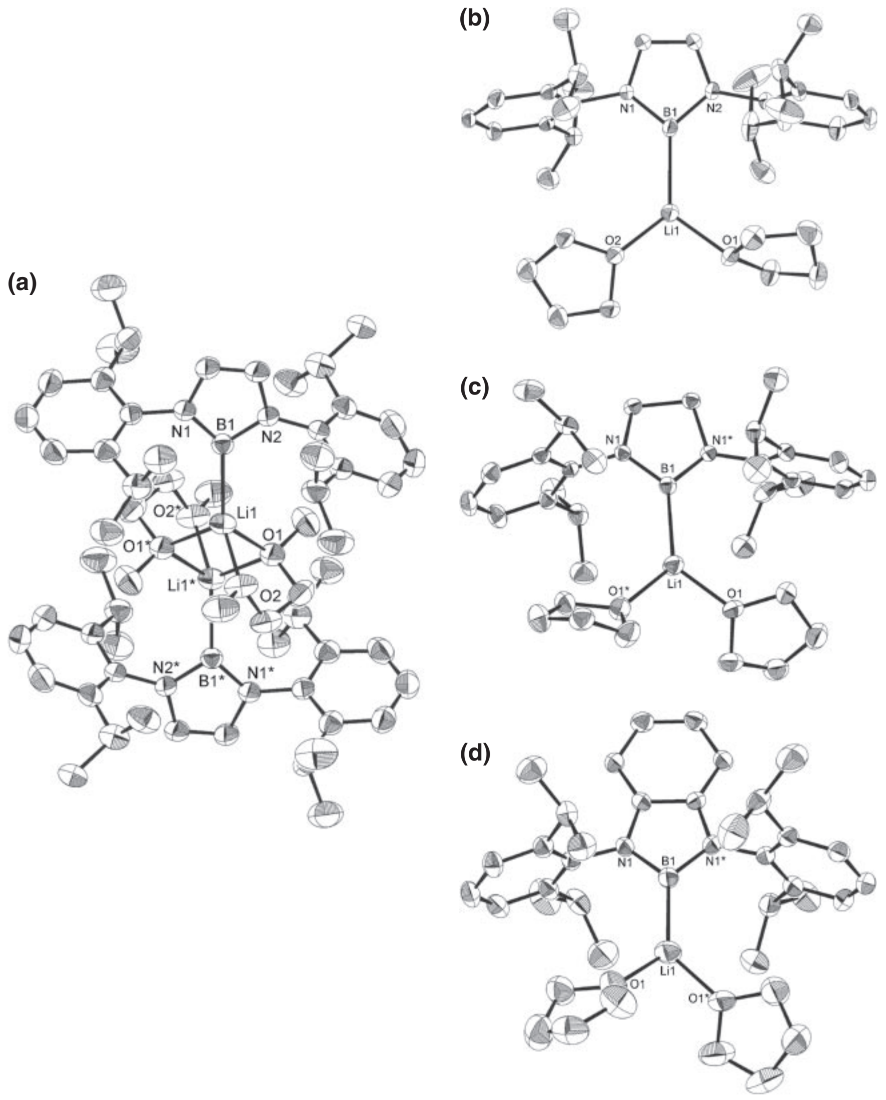


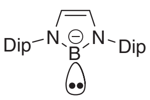
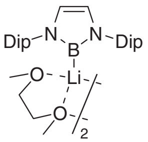
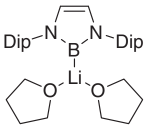
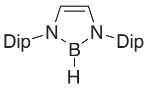
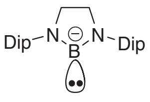
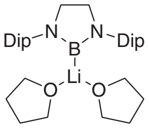
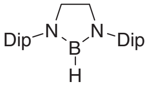
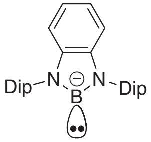
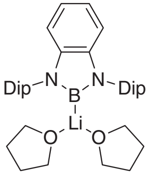
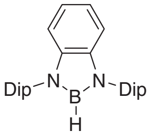
Figure 1. ORTEP drawings of boryllithium derivatives ($\mathbf{2a}\cdot\mathrm{dme})_2$ (a), $\mathbf{2a}\cdot(\mathrm{thf})_2$ (b), $\mathbf{2b}\cdot(\mathrm{thf})_2$ (c), and $\mathbf{2c}\cdot(\mathrm{thf})_2$ (d).

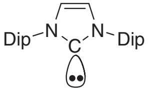
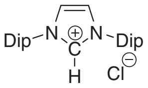
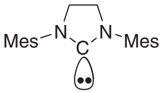
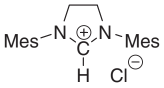
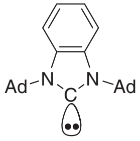
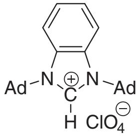
heterocyclic carbenes **6**,[16] **8**,[17] **10**[18] and imidazolium salts **7**,[16] **9**,[17] **11**,[18] which are protonated compounds of *N*-heterocyclic carbenes.

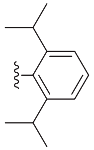
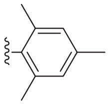
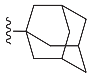
3.1.3 Spectroscopic Study of Boryllithiums: To clarify the solution structure of boryllithium, several spectroscopic studies were performed. Dissolution of single crystals of ($\mathbf{2a}\cdot\mathrm{dme})_2$ and $\mathbf{2a}\cdot(\mathrm{thf})_2$ into THF-d_8 gave identical ^{1}H, ^{13}C, and ^{11}B NMR spectra consisting of signals assignable to the *N*,*N*′-diaryldiazaborole moiety in **2a**. The solvent molecules, which originally coordinated to the central lithium atom in the solid state, were observed in solution [free DME (1 equiv) or THF (2 equiv) molecules were detected], indicating that **2a** forms a THF-d_8 solvated structure. In the ^{11}B NMR spectra, the chemical shift and half-width of the signal were the same as those observed for the reaction mixture (δ_B 45.4, $\nu_{1/2} = 535$ Hz). This signal shifted from that in hydroborane **3a** (δ_B 22.9, $\nu_{1/2} = 379$ Hz). This downfield shift was also observed for carbene **6** (δ_C 220.6 in C_6D_6)[16] in comparison with imidazolium salt **7** (δ_C 139.9 in DMSO-d_6),[14] possessing the same aromatic substituent on the nitrogen atoms as boryllithium **2a** and hydroborane **3a**. Accordingly, the boron center in boryllithium can be considered to have a lone pair. The other boryllithiums **2b**–**2e** also showed a broadened and downfield-shifted ^{11}B NMR signal (δ_B 51.9 for **2b**, δ_B 52.1 for **2c**, δ_B 45.0 for **2d**, δ_B 52.4 for **2e**). Isolation of single crystals of boryllithium enabled us to remove cogenerated lithium bromide for the measurement of the ^{7}Li NMR spectra. In each ^{7}Li NMR spectrum of $\mathbf{2a}\cdot(\mathrm{thf})_2$, $\mathbf{2b}\cdot(\mathrm{thf})_2$, and $\mathbf{2c}\cdot(\mathrm{thf})_2$, a broad signal [$\delta_{Li}$ 0.46, $\nu_{1/2} = 36$ Hz for $\mathbf{2a}\cdot(\mathrm{thf})_2$; δ_{Li} 0.68, $\nu_{1/2} = 35$ Hz for $\mathbf{2b}\cdot(\mathrm{thf})_2$; δ_{Li} 0.44, $\nu_{1/2} = 50$ Hz for $\mathbf{2c}\cdot(\mathrm{thf})_2$] was observed in contrast to that of the reference compound, LiCl in D_2O, which shows a very sharp signal (1.2 Hz). The significant broadening may originate from the interaction between the lithium atom with the quadrupolar boron nucleus.[20]

The ^{11}B NMR signal of **2a** (δ_B 45.4 at 20 °C) in THF or methylcyclohexane-d_{14} reversibly shifted to a higher field (δ_B 38.5) at −100 °C (Figure 2). In the methylcyclohexane-d_{14} solution, THF molecules coordinated to the central Li atom were observed at 1.47 and 3.19 ppm in the ^{1}H NMR spectrum as broadened signals, which could be distinguished from those of free THF molecules (1.74 and 3.61 ppm). Although it is

Table 1. Structural Parameters of Boryllithium Derivatives and Reference Compounds[a)]

	Compound									
	 opt-**6a**	 (**2a**·dme)$_2$	 **2a**·(thf)$_2$	 **3a**	 opt-**6b**	 **2b**·(thf)$_2$	 **3b**	 opt-**6c**	 **2c**·(thf)$_2$	 **3c**
B–Li/Å		2.291(6)	2.276(5)			2.271(4)			2.218(9)	
B–N/Å	1.496	1.465(4) 1.467(4)	1.474(3) 1.480(4)	1.418(3) 1.423(3)	1.473	1.4547(18)	1.405(3) 1.407(3)	1.503	1.474(4)	1.420(3) 1.428(3)
N–B–N/°	97.79	99.2(2)	98.7(2)	98.7(2)	100.90	101.89(16)	109.11(17)	98.36	100.0(3)	106.64(19)

	Compound					
	 **6**	 **7**	 **8**	 **9**	 **10**	 **11**
C–N/Å	1.365(3) 1.369(3)	1.341(4) 1.339(4)	1.352(4) 1.346(6)	1.352(4) 1.346(6)	1.374(4) 1.372(4)	1.374(4) 1.372(4)
N–C–N/°	101.4(2)	107.6(3)	104.7(3)	113.1(4)	103.8(2)	112.2(3)

a) Dip: , Mes: , Ad: .

difficult to clarify the origin of the reversible chemical shift change, there are two possible reasons: (i) the dissociation/association equilibrium of THF molecules to the lithium atom to induce a change in B–Li bond strength and (ii) changing aggregation state of boryllithium as observed for the alkyllithium species. It is difficult to consider the latter situation for aggregation because of bulky substituents on the nitrogen atoms in **2a**. On the other hand, the direction of the σ_{22} component of the chemical shielding tensor on *N*-heterocyclic carbene **12** has been calculated to be along with the lone pair of the central carbon (Figure 3).[21] By analogy with carbene, boryllithium **2a** may have a similar σ_{22} component along the B–Li bond, which can be affected by a change in solvation by THF molecules.

3.1.4 Theoretical Study to Elucidate the Anionic Character of Boryllithiums: To understand the characteristic B–Li bond, DFT calculations were performed. Using the crystal structure of **2a**•(thf)$_2$ as an initial structure, an optimized structure, opt-**2a**•(thf)$_2$, was obtained with no imaginary frequency in the vibrational analysis at the B3LYP/6-31+G* level.[22] The structural parameters and calculated ^{11}B NMR chemical shifts[23] of opt-**2a**•(thf)$_2$ (GIAO/B3LYP/6-311++G**) are summarized in Table 2 with two reference compounds, free boryl anion opt-**6a** and hydroborane opt-**3a**.[24] The calculated structural parameters and ^{11}B NMR chemical shift of opt-**2a**•(thf)$_2$ are close to the experimentally obtained values for **2a**•(thf)$_2$ (X-ray structure and δ_B 45.4), indicating that **2a**•(thf)$_2$ retains its structure in solution. The HOMOs of the free phenyl anion (Ph$^-$), free boryl anion opt-**6a**, opt-**2a**•(thf)$_2$, and opt-**3a** are shown in Figure 4. Two free anions, Ph$^-$ and opt-**6a**, have similar shapes of the HOMO, reflecting the lone-pair character of the central carbon and boron atom, respectively. Complexation of opt-**6a** with Li and solvation of two THF molecules to form opt-**2a**•(thf)$_2$ did not affect the lone-pair character of the HOMO. This result also suggested a polar character of the B–Li bond. On the other hand, the HOMO of hydroborane opt-**3a** corresponds to the π-orbital of the electron-rich boron-containing heterocycle. In other words, the localization of electrons in an ionic B–Li bond to the boron center made the lone pair become the HOMO over the π-orbital of diazaborole, indicating high reactivity of boryllithium as a nucleophile at the boron center. This similarity prompted us to compare the ionic nature of B–Li and C–Li[25] bonds by AIM analysis.[26] Small ρ(r) values (0.02889 $e/a_0{}^3$) and positive

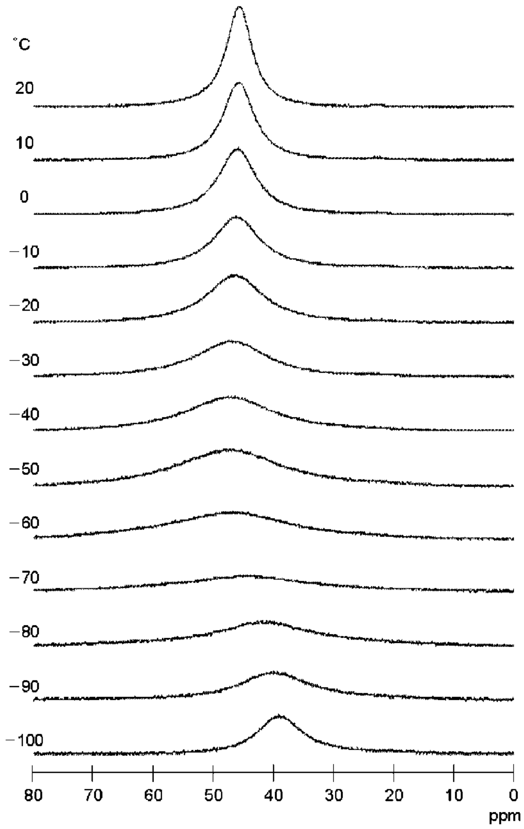
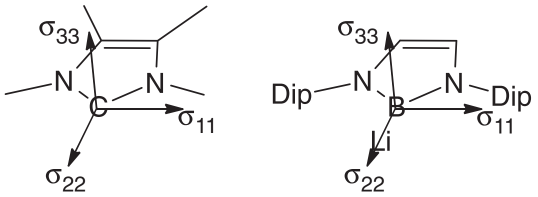


Figure 2. The ^{11}B NMR spectra of single crystals of **2a**•(thf)$_2$ dissolved in THF solution from 20 to −100 °C.



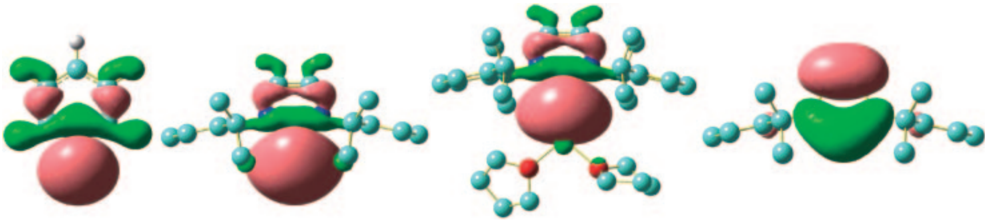
12

2a

Figure 3. Shielding tensor primary component orientations in carbene **12** and boryllithium **2a**.

Table 2. Structural Parameters (Å and °) and Calculated ^{11}B NMR Chemical Shift (ppm) for Optimized Boryllithium and Related Compounds with Experimentally Obtained Values

	opt-**6a**	opt-**2a**•(thf)$_2$	opt-**3a**	**2a**•(thf)$_2$ (exp)
B–Li	—	2.268	—	2.276(5)
B–N	1.495	1.481	1.436	1.474(3) 1.480(4)
N–B–N	97.74	99.22	105.28	98.7(2)
δ_B	51.3	41.4	19.6	45.4

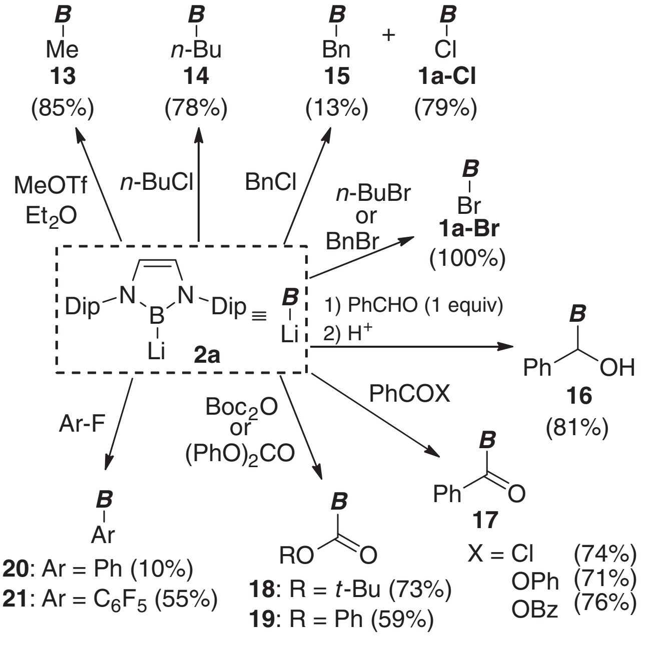


Ph$^-$ opt-**6a** opt-**2a**·(thf)$_2$ opt-**3a**

Figure 4. HOMOs of calculated boryllithium and reference compounds.

$\nabla^2\rho(r)$ values ($0.08409\,e/a_0{}^5$) at the bond critical point of the B–Li bond in opt-**2a**•(thf)$_2$ as alkyllithiums were calculated to have a polar C–Li bond.[27] This result clearly indicates a similar bonding character of the B–Li bond in boryllithium **2a** to that of the C–Li bond in alkyllithium.

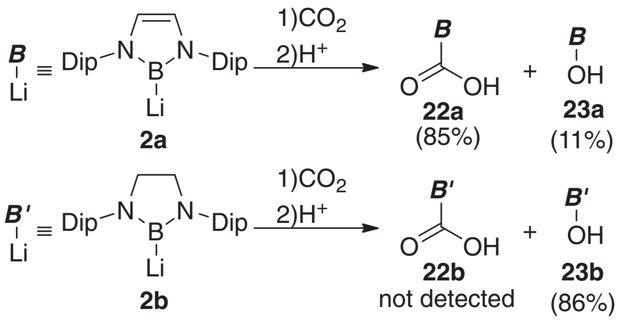
Reactivity of boryllithium **2a** with general organic electrophiles was studied (Scheme 4). Reactions with methyl trifluoromethanesulfonate, 1-chlorobutane, or benzyl chloride to form corresponding alkylborane derivatives **13**, **14**, and **15**, but in the case of benzyl chloride, the chlorination product **1a-Cl** was also generated as a major compound, probably due to the halophilic attack or single electron transfer from **2a** to benzyl chloride including a radical chain reaction. Reaction with more reactive *n*-butyl bromide or benzyl bromide afforded the bromoborane **1a-Br** as the sole product. The reaction with 1 equiv of benzaldehyde followed by protonation formed α-borylbenzyl alcohol **16** in 81% yield.[28,29] The reaction with benzoyl chloride, phenyl benzoate, and benzoic anhydride gave a substituted product benzoylborane **17** in good yields. The reaction with carbonates afforded the corresponding borylcarboxylate ester products, **18** and **19**, for both *t*-Bu and Ph groups. Boryllithium **2a** also reacted with fluoroarenes. The reaction with PhF yielded phenylborane **20** in a low yield because the reaction is slower than the decomposition of boryllithium. However, the reaction with C_6F_6 afforded a pentafluorophenylborane **21** in a moderate yield within a shorter reaction time.[30]



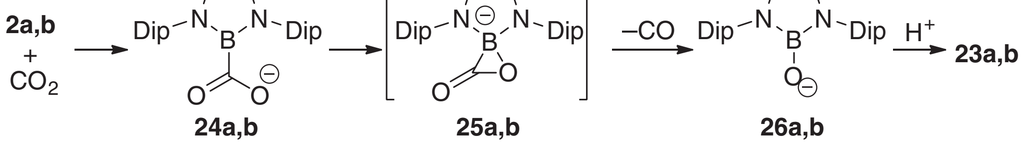
Scheme 4. Reactions of boryllithium **2a** with various electrophiles.

Reaction of boryllithium **2a** with carbon dioxide followed by protonation gave a borylcarboxylic acid, **22a**, in a high yield with a small amount of by-product, hydroxyborane **23a** (Scheme 5). On the other hand, a reaction of **2b** with CO_2 did not give any borylcarboxylic acid **22b**, instead, hydroxyborane **23b** was found as the sole product. A plausible mechanism for the formation of these unexpected products, hydroxyboranes **23a** and **23b**, is shown in Scheme 6. The reaction of the boryl anion with CO_2 formed the corresponding borylcarboxylate anion **24**, the negatively charged carboxylate oxygen directly interacted with a vacant p-orbital of the boron atom to form the three-membered ring transition state **25**, and the following loss of carbon monoxide gave the boronate anion **26** which can be protonated to afford the hydroxyboranes **23a** and **23b**. A similar reaction pathway was reported in the computational study[35o] of Cu-catalyzed deoxygenation of carbon dioxide in the presence of a diborane(4) reagent.[35m] The lower reactivity of borylcarboxylate **24a** in the rearrangement may be explained by a loss of aromaticity in the transition state **25a** that would destabilize the transition state more than the corresponding **25b**.

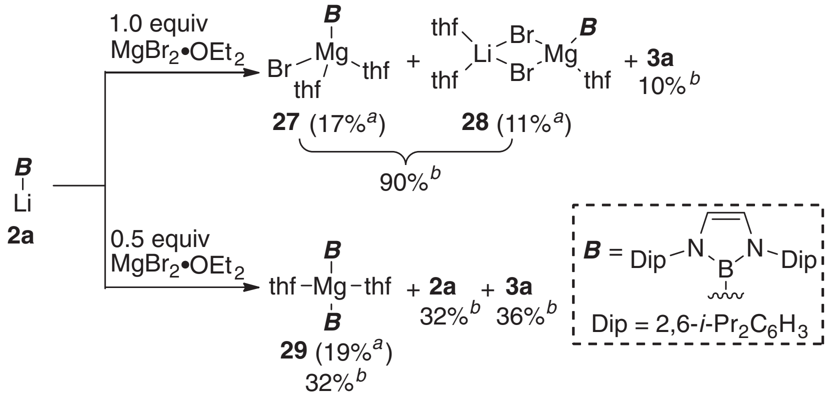
3.2 Borylmagnesium. A boron derivative of Grignard reagent, borylmagnesium, could also be prepared by a transmetallation of boryllithium **2a** with $MgBr_2{\cdot}OEt_2$ (Scheme 7).[31] Recrystallization from a reaction solution using 1.0 equiv of $MgBr_2{\cdot}OEt_2$ gave a separable pair of crystals, consisting of colorless borylmagnesium bromide **27** and pale yellow borylmagnesium bromide–LiBr adduct **28**. On the other hand, by a reaction with 0.5 equiv of $MgBr_2{\cdot}OEt_2$, diborylmagnesium **29** was isolated as yellow crystals. X-ray crystallographic analysis (Figure 5) revealed that each of these molecules **27**–**29** have a nearly ideal sp^2 boron atom and four-coordinate magnesium atom, where THF molecule occupied open coordination sites. The observed B–Mg contact is the first structurally characterized B–Mg single bond. All B–Mg bond lengths (Table 3) were longer than the sum (2.24 Å) of covalent radii of boron and magnesium atoms. The B–N bonds and N–B–N angles of borylmagnesiums **27**–**29** were closer to



Scheme 5. Reactions of boryllithiums **2a** and **2b** with CO_2.



Scheme 6. A plausible mechanism for the formation of hydroxyboranes **23a** and **23b**.



Scheme 7. Syntheses of borylmagnesium compounds **27**–**29** from boryllithium **2a** ([a]isolated yield, [b]NMR yield calculated from ^{1}H NMR spectrum in THF-d_8).

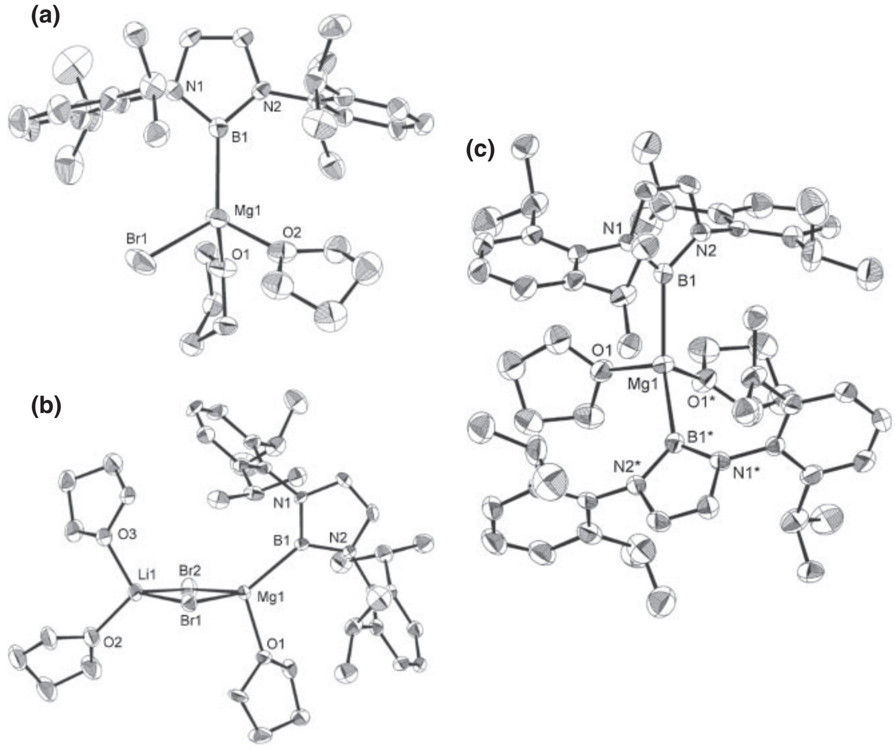


Figure 5. Structures of borylmagnesium derivatives **27** (a), **28** (b), and **29** (c) (50% thermal ellipsoids: hydrogen atoms, minor part of disordered isopropyl groups and THF molecules, and one of two independent molecules for **28** are omitted for clarity: half of the whole structure constitutes an asymmetric unit where numbers with asterisks are in the second asymmetric unit for **29**).

Table 3. Structural Comparison between Borylmagnesium Derivatives **27**–**29** and Reference Compounds

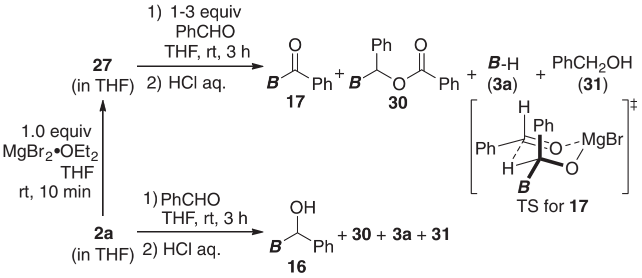
	27	28	29	2a	3a
B–Mg/Å	2.281(6)	2.282(6)	2.377(4)		
B–N/Å	1.453(7)	1.453(6)	1.471(5)	1.465(4)	1.418(3)
	1.465(7)	1.458(7)	1.487(4)	1.467(4)	1.423(3)
		1.464(7)			
		1.467(7)			
N–B–N/°	100.7(4)	100.5(4)	99.3(3)	99.2(2)	105.25(16)

those in boryllithium **2a** rather than those in the protonated hydroborane **3a**, indicating an anionic character of the boron center.

The isolated crystals of **27** and **28** was dissolved into THF-d_8 to show identical ^{1}H and ^{11}B NMR spectra with appropriate integral ratio of free THF molecules which originally coordinated to magnesium in the crystal. Furthermore, the ^{7}Li NMR chemical shift of **28** (δ_{Li} 0.4) was identical to that observed for THF-d_8 solution of LiBr. That is, LiBr may dissociate from **28** to be **27** in THF solution. Diborylmagnesium **29** showed a different ^{1}H NMR spectrum than those of **27** and **28**. All of **27**–**29** showed a broad signal around δ_{B} 37.6 in their ^{11}B NMR spectra. These downfield-shifted broad ^{11}B signals also support the ionic character of B–Mg bonds in borylmagnesium species as was discussed with boryllithium. According to the above observation, the reaction conversion of **2a** with $MgBr_2{\cdot}OEt_2$ could be estimated as follows. The ^{1}H NMR monitoring for the reaction of **2a** with 1.0 equiv of $MgBr_2{\cdot}OEt_2$ in THF-d_8 showed that 90% of **2a** was converted to **27** in solution with 10% of hydroborane **3a**. On the other hand, only 32% of **2a** was converted to **29** in the case of the reaction with 0.5 equiv of $MgBr_2{\cdot}OEt_2$, accompanied with 36% of hydroborane **3a** and 32% of unreacted **2a**.

Reactions of borylmagnesium bromide **27** with 1–3 equiv of benzaldehyde were performed (Table 4, Runs 1–3). These reactions afforded a mixture of benzoylborane **17**, boron-substituted benzyl ester **30**, and hydroborane **3a**. Simultaneous formation of benzyl alcohol (**31**) suggests an intermolecular hydride transfer from a magnesium borylbenzyloxide intermediate, formed by a nucleophilic addition of **27** to benzaldehyde, to an excess amount of benzaldehyde probably via a six-membered ring transition state (see picture) as was reported for the magnesium-Oppenauer oxidation.[32] It is noteworthy that no α-borylbenzyl alcohol **16** was formed (Runs 1–3) in sharp contrast to the fact that **16** was obtained in 81% yield by a reaction of boryllithium **2a** with 1 equiv of benzaldehyde (Run 4). Addition of a second equivalent of benzaldehyde to **2a** led to an intermolecular hydride transfer to form **30** (Run 5) accompanied with the formation of benzyl alcohol (**31**). Thus, the counter metal cation affects the reactivity of α-borylbenzyloxide intermediate.

Table 4. Reaction of Boryllithium **2a** and Borylmagnesium **27** with Benzaldehyde

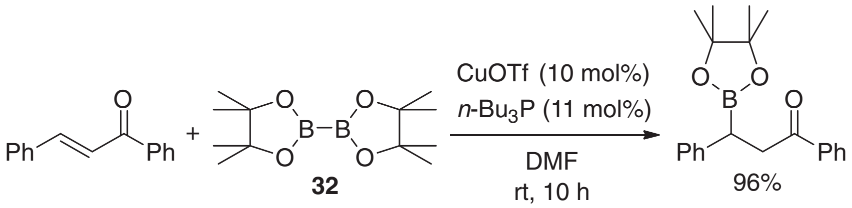


Run	Reactant	PhCHO /equiv	**17**/%[a]	**30**/%[a]	**3a**/%[a]	**31**/%[b]	**16**/%[a]
1	**27**	1	18	18	56	27	0
2	**27**	2	34	24	32	47	0
3	**27**	3	22	40	16	55	0
4	**2a**	1	0	0	6	0	81
5	**2a**	3	0	51	10	50	0

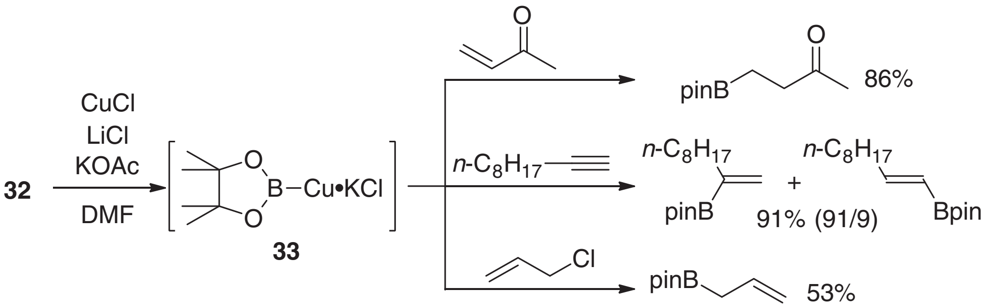
a) ^{1}H NMR yield. b) GC yield.

3.3 Borylcopper and Borylzinc. In 2000, Cu-catalyzed β-borylation of α,β-unsaturated ketones using bis(pinacolato)-diborane(4) (**32**) was reported by Ito and Hosomi (Scheme 8).[33] On the other hand, Miyaura and Ishiyama suggested that mixing **32** and CuCl in the presence of LiCl and KOAc gave borylcopper species **33**, where the resulting **33** could undergo β-borylation of α,β-unsaturated carbonyls, monoborylation of alkynes, and substitution of allyl chloride (Scheme 9).[34] After these discoveries, there have been many reports of improved borylation using borylcopper species[35] and some review articles summarized these works.[36] Recently, borylcopper species, IPrCuBpin (**34**), was successfully isolated from a reaction of IPrCu(Ot-Bu) with diborane(4) **32** (Scheme 10, eq 1).[35m] The isolated borylcopper complex **34** could catalyze reduction of CO_2 with **32** to CO (eq 2) and its derivative ICyCu–Ot-Bu was effective for 1,2-diboration of aldehydes (eq 3).[35m,35n]

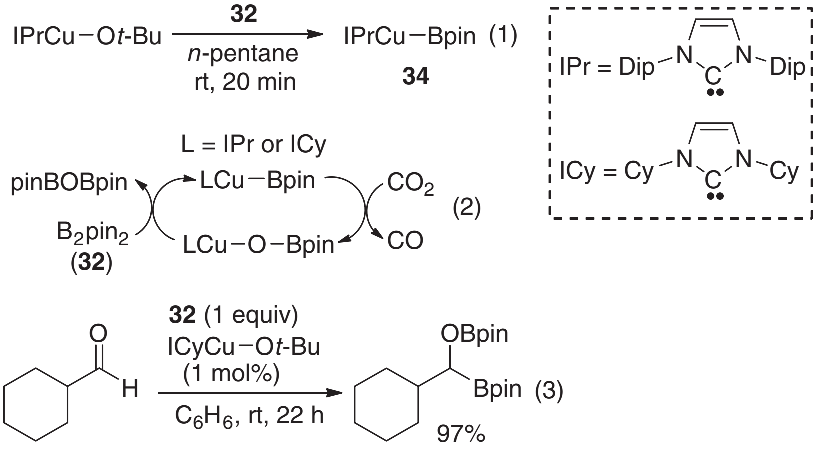
Recently, we reported syntheses of borylcuprate and borylzincate by the transmetallation of boryllithium **2b** with 1 equiv of CuBr and $ZnBr_2$.[37] Recrystallization from a pentane solution of the reaction mixture gave crystalline lithium borylbromocuprate **35** and lithium dibromoborylzincate **36** in 52 and 51% isolated yields (Scheme 11). The broad signals at δ_B 45 (**35**) or at δ_B 41 (**36**) in their ^{11}B NMR spectra are comparable to that of boryllithium **2b** (δ_B 52). The crystallographically characterized structures of **35** and **36** are illustrated in Figure 6. The first borylcuprate **35** contained B–Cu–Br–Li linkage with three THF molecules coordinating to Li.[38,39] The B–Cu bond lengths of **35** [1.983 Å (av.)] are shorter than that of



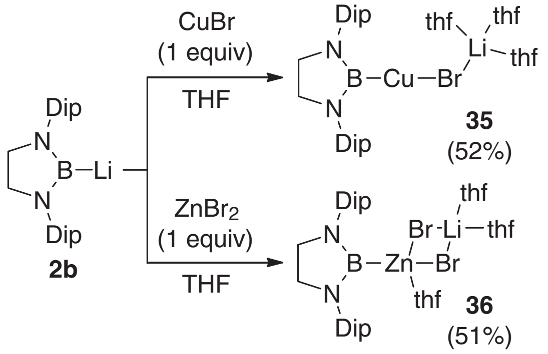
Scheme 8. The first example of copper-catalyzed β-borylation of α,β-unsaturated carbonyl compound using diborane(4) **32**.



Scheme 9. Formation of borylcopper species **33** in situ from diborane(4) **32** and reactions with various organic electrophiles.



Scheme 10. Synthesis of isolable borylcopper **34** and catalytic activity of borylcopper derivatives.



Scheme 11. Syntheses of borylbromocuprate **35** and boryldibromozincate **36**.

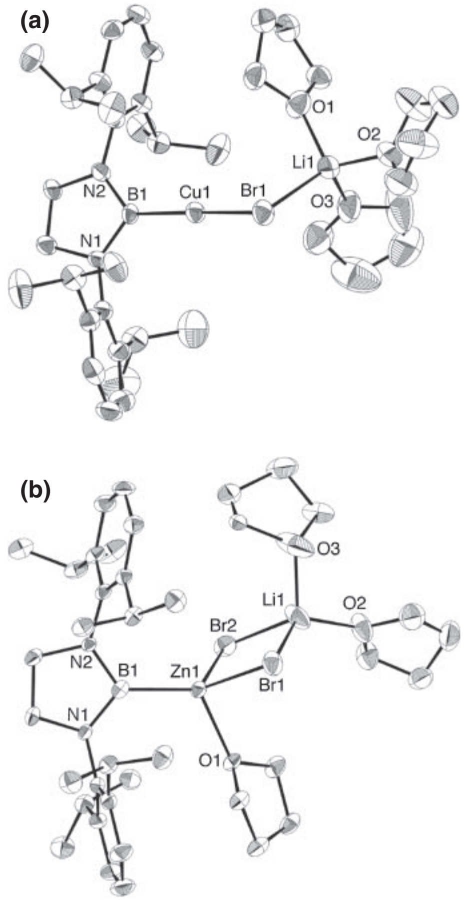


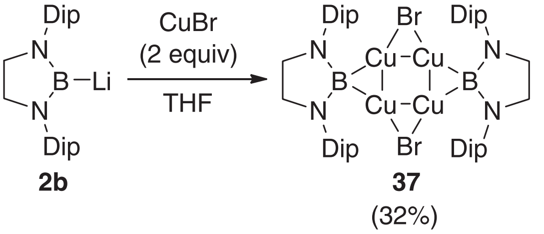
Figure 6. Structures of borylbromocuprate **35** (a) and boryldibromozincate **36** (b) (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; one of two independent molecules is shown for **35**; only the major portions of disordered isopropyl groups and THF molecules are illustrated).

34 [2.002(3) Å].[35m] The B–Cu–Br angles of **35** [172.0° (av.)] are close to linear to constitute a two-coordinate copper center as was observed for the B–Cu–C angle of **34** [179.41(15)°].[35m] In the structure of lithium dibromoborylzincate **36**,[40] the length of B–Zn bond [2.075(5) Å], the first example of a 2c–2e B–Zn bond, is slightly shorter[41] than the sum of covalent radii (2.13 Å)[11] of boron and zinc atoms.

A reaction of boryllithium **2b** with CuBr (2 equiv) gave tetranuclear copper(I) complex **37** in 32% yield (Scheme 12). The ^{11}B NMR signal of **37** resonated at δ_B 38, which was slightly shifted to higher field than that of **35** (δ_B 45). In the crystal structure of **37** (Figure 7), each of the two bromine atoms and two boron atoms bridged two Cu atoms in an alternating fashion.[42] The B–Cu bond lengths in **37** [2.093(4) and 2.073(5) Å] are longer than 2c–2e B–Cu bond lengths [1.983 Å (av.)] in **35**, probably due to a bridging situation of boryl ligand.[43]

Addition of zinc halide (0.5 equiv) to boryllithiums **2a** and **2b** gave solvent-free diborylzinc species **38a** and **38b** as a colorless crystalline solid in 31 or 20% yield (Scheme 13). These diborylzinc species showed a broad signal at δ_B 32 (**38a**) and 38 (**38b**). In the solid state (Figure 8 for **38a**) diborylzincs **38a** and **38b** had two-coordinate linear structures[44] with almost linear B–Zn–B angles [178.50(11)° for **38a**, 177.41(11)° for **38b**]. It should be noted that these are the first homoleptic borylmetal species. The B–Zn bond distances [2.052(3) and 2.053(3) Å for **38a**; 2.088(3) and 2.087(3) Å for **38b**] are similar to that (2.075(5) Å) in boryldibromozincate **36**.

Borylcopper **37** and borylzincate **36** were reacted with 2-cyclohexen-1-one to give the corresponding conjugate adduct, 3-borylcyclohexan-1-one **39** in 74 and 41% yield



Scheme 12. Synthesis of boryl-bridged tetranuclear copper complex **37**.

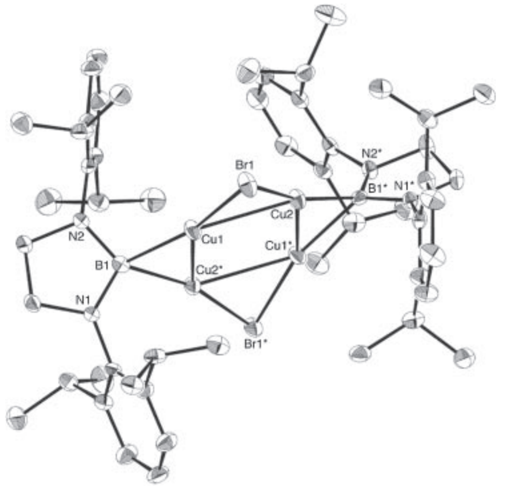
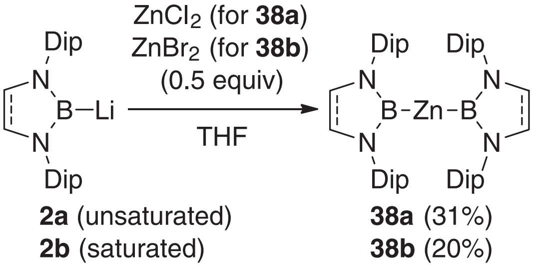


Figure 7. ORTEP drawing of **37** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; half of the whole structure constitutes an asymmetric unit where numbers with asterisks are in the second asymmetric unit; only the major portion of disordered bromine atoms is illustrated).



Scheme 13. Synthesis of diborylzinc species **38a** and **38b**.

(Scheme 14). In contrast, the reaction of boryllithium **2b** with 2-cyclohexen-1-one led to a formation of protonated hydroborane **3b**, instead of the 1,2- or 1,4-adduct. Trapping the copper enolate intermediate generated from **35** and 2-cyclohexen-1-one with chlorotrimethylsilane afforded γ-siloxyallylborane **40** in 80% yield.

4. Application of Boryl Anions

The nucleophilicity of boryl anions could also be applied to several fields of chemistry, such as organic synthesis, organometallic chemistry, and main group chemistry. The following paragraphs show some examples for application of boryl anions.

4.1 One-Pot "Carboboration" of Alkyne Using Borylcyanocuprate. Transmetallation of boryl anion from boryllithium **2a** to copper cyanide was effective to form lithium borylcyanocuprate **41** (Scheme 15).[45] X-ray crystallographic analysis revealed a monomeric linear structure of B–Cu–C≡N–Li linkage in **41** with three THF molecules coordinating to lithium atom (Figure 9). The relatively long Cu–C bond of 1.906(7) Å in **41** compared to that of $\mathrm{2,6\text{-}Mes_2C_6H_3CuCNLi(thf)_3}$ (1.869(4) Å)[46] reflects a strong *trans*-influence of boryl ligand on the copper center.[47] On the contrary, C≡N length of 1.147(7) Å in **41** was close to that [1.159(5) Å] in $\mathrm{2,6\text{-}Mes_2C_6H_3CuCNLi(thf)_3}$, indicating the boryl ligand mainly works as a σ-donor, not a π-donor. The ^{1}H and ^{13}C NMR spectra of **41** indicated its solution structure with C_{2v} symmetry

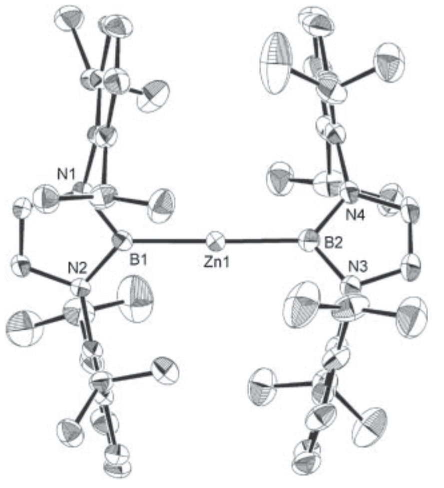
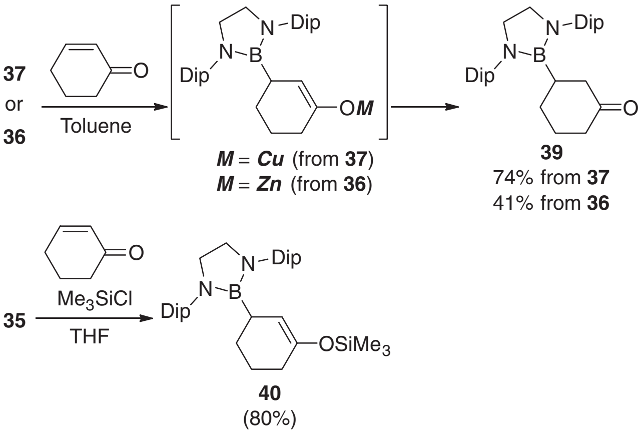
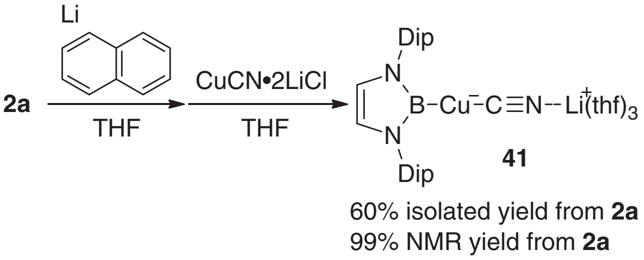


Figure 8. ORTEP drawing of **38a** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; only the major portion of disordered bromine atoms is illustrated).



Scheme 14. Reactions of borylcopper and borylzinc species with 2-cyclohexen-1-one.



Scheme 15. Synthesis of lithium borylcyanocuprate **41**.

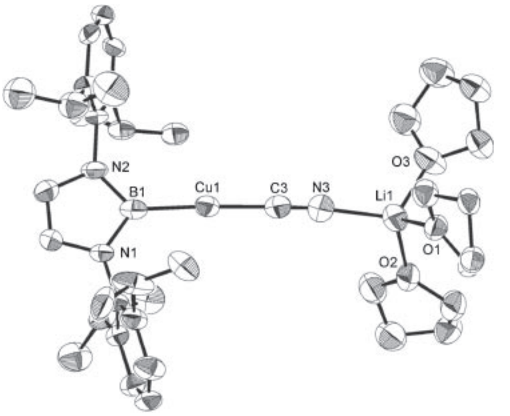
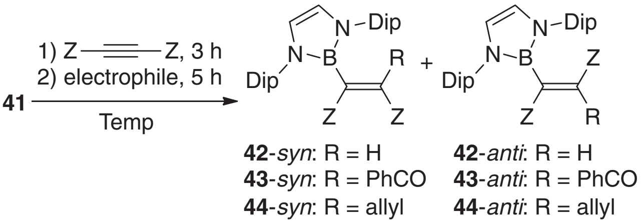


Figure 9. ORTEP drawing of **41** (50% thermal ellipsoids, hydrogen atoms and minor parts of disordered Dip moieties and THF molecules).

Table 5. Application of Lithium Borylcyanocuprate **41** for Carboboration of DEAD ($Z = CO_2Et$)

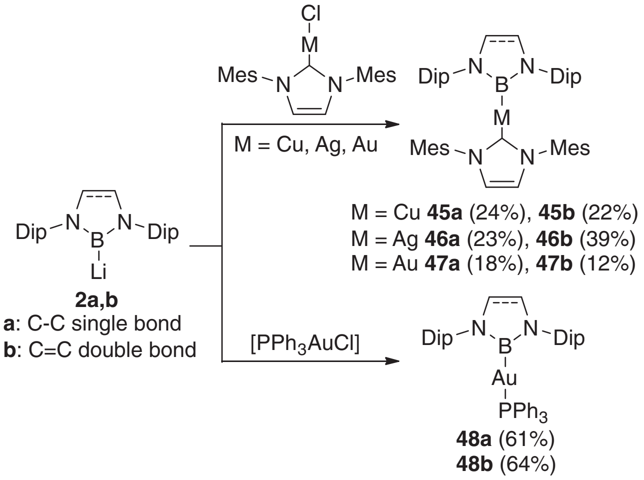


Entry	Electrophile	Temp/°C	Products (Yield[a]/%)	*syn*/*anti*
1	PhCOCl	−78	**42**-*syn* (48), **42**-*anti* (32)	60/40
2	PhCOCl	RT	**43**-*anti* (71)	1/99>
3	allylBr	−78	**44**-*syn* (93)	99>/1
4	allylBr	RT	**44**-*syn* (36), **44**-*anti* (60)	38/62

a) Isolated yield based on the added DEAD.

of boryl moiety with free rotation of N3–Li1 bond. Resonance in ^{11}B NMR spectra showed a broad signal at δ_B 38.6 which is close to those of known borylcopper species.[35m,35n,37]

Reaction of in situ generated **41** with DEAD (diethyl acetylenedicarboxylate), followed by treatment with benzoyl chloride or allyl bromide at −78 °C or room temperature, gave carboborated products, tetrasubstituted alkenylboranes (Table 5). At low temperature, reaction with benzoyl chloride afforded a mixture of hydroborated products, **42**-*syn* and **42**-*anti*, in 48% and 32% yields (Entry 1), indicating that the boryl-substituted alkenylcuprate intermediate did not react with benzoyl chloride at −78 °C. Reaction at room temperature afforded **43**-*anti* in 71% yield with a selectivity of *syn*/*anti* = 1/99> (Entry 2). Changing electrophile to allyl bromide at −78 °C gave **44**-*syn* in 93% yield, accompanied by a trace amount of *anti*-adduct **44**-*anti* (Entry 3). By elevating temperature to room temperature, a mixture of **44**-*syn* and **44**-*anti* were obtained in 36% and 60% yield (Entry 4). Obtained products here could be formally considered carboborated products from DEAD. Formation of *syn*- and *anti*-isomers may be explained by isomerization between *syn*- and *anti*-borylalkenylcuprate adducts via a copper allenolate intermediate as was suggested by NMR spectroscopic analysis[48] and theoretical calculations.[49]



Scheme 16. Syntheses of group-11 metal boryl complexes **45**–**47** using boryllithiums **2a** and **2b**.

Table 6. Selected Bond Lengths in **45**–**48** and Reference Compounds Obtained from X-ray Crystallographic Analysis [IMes: *N*,*N*′-Bis(2,4,6-trimethylphenyl)imidazole-2-ylidene]

Complexes	M–B/Å	M–C(P)/Å
45a	1.980(2)	1.918(2)
45b	1.983(3)	1.915(3)
46a	2.118(2)	2.1207(18)
46b	2.122(4)	2.124(4)
47a	2.074(4)	2.078(4)
47b	2.069(3)	2.070(3)
48a	2.076(6)	2.3469(13)
48b	2.086(5)	2.3574(11)
[IMesAgCl]		2.056(7)
[IMesAuCl]		1.998(5)
[PPh_3AuCl]		2.235(3)
[PPh_3AuPh]		2.296(2)
[PPh_3AuMe]		2.279(8)

4.2 “Nucleophilic” Borylation Methodology to Prepare Transition-Metal Boryl Complex Using Boryllithium. 4.2.1 Group 11 Borylmetal Complexes: Methods for the syntheses of transition-metal boryl complexes are generally limited to the following three methodologies:[50] (i) salt elimination reaction through the reaction of anionic metal carbonyls with haloborane;[51] (ii) oxidative addition of boron–heteroatom bond to low-valent transition metals;[52] and (iii) σ bond metathesis reaction between alkylmetal complexes and hydroborane in the presence of light[53] or oxygen-substituted metal complexes and diborane.[34b,35h,35m] Nucleophilic borylation using boryllithium would be a new methodology for the synthesis of transition-metal boryl complexes.

Carbene- or PPh_3-substituted group 11 metal chlorides were treated with boryllithiums **2a** and **2b** to give the corresponding borylmetal complexes **45**–**48** (Scheme 16).[54] All complexes were characterized by spectroscopic, elemental, and X-ray analyses and were shown to have a linear, two-coordinate structure (structural parameters are listed in Table 6, representative crystal structure is shown in Figure 10 for **46a**).

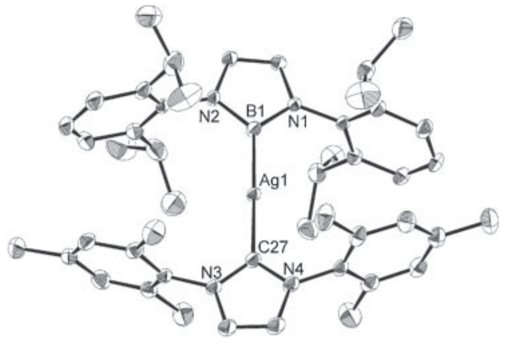
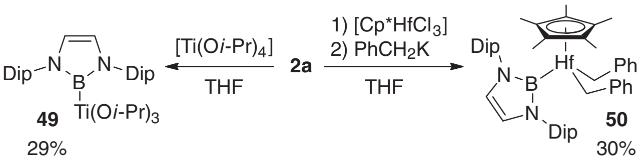


Figure 10. ORTEP drawing of **46a** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity).



Scheme 17. Syntheses of group 4 borylmetal complexes **49** and **50**.

Complexes **46**–**48** are the first examples of fully-characterized borylsilver and borylgold complexes having a 2c–2e M–B bond. The stronger *trans*-influence of a boryl ligand[47] than that of a chloride ligand is demonstrated by smaller Ag–^{13}C coupling constants $^1J_{\text{C–Ag}}$ in **46a** [81, 88 Hz (to ^{107}Ag, ^{109}Ag)] and **46b** (83, 95 Hz) than those (234, 270 Hz) in IMesAgCl.[55] X-ray crystallographic analyses further support the large *trans*-influence of boryl ligands by the following two facts: (i) the M–C$_{\text{carbene}}$ bonds in **46** and **47** are longer than those of reference IMesMCl complexes (M = Ag[55] and Au[56]); and (ii) the Au–P bonds in **48a** and **48b** are longer than those in a series of PPh$_3$-ligated Au(I) complexes[57] which have an additional anionic ligand Cl$^-$, Ph$^-$, or Me$^-$.

4.2.2 Group 4 Borylmetal Complexes: The three conventional methodologies (vide supra) are not applicable to the syntheses of group 4 boryl complexes, because (i) anionic group 4 metal complexes have no nucleophilicity on the metal center due to d^0 electron configuration, (ii) low-valent group 4 metal complexes are not easily available as a precursor, and (iii) a Lewis acidic boron reagent may abstract an anionic ligand from group 4 metal complexes to form a borate complex rather than σ bond metathesis. Therefore, our nucleophilic boryl anion may solve this problem for preparation of group 4 boryl complex.

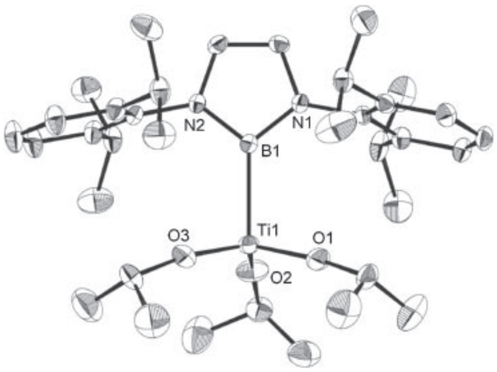


Figure 11. ORTEP drawing of **49** (50% thermal ellipsoids. Hydrogen atoms and minor parts of disordered isopropoxide groups are omitted for clarity).

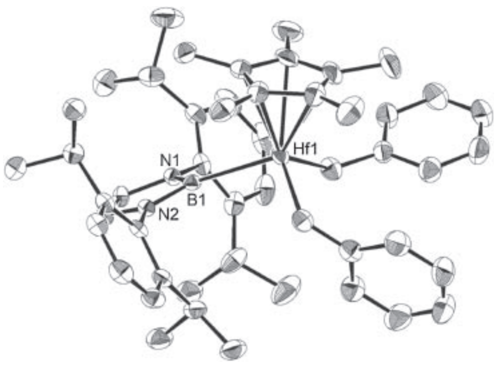
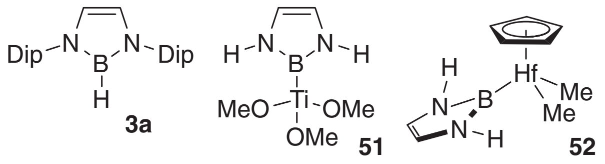


Figure 12. ORTEP drawing of **50** (50% thermal ellipsoids. Hydrogen atoms are omitted for clarity).

Table 7. Selected Bond Distances (Å) and Angles (°) of **49**, **50**, and Reference Molecules **3a**, **51**, and **52**



	Compound				
	49	**50**	**3a**	**51**	**52**
B–metal	2.258(2)	2.497(4)		2.226	2.394
B–N	1.446(3)	1.458(4)	1.418(3)	1.442	1.451
	1.447(3)	1.477(4)	1.423(3)		1.453
N–B–N	102.85(16)	100.6(3)	105.25(16)	102.2	100.9

A reaction of boryllithium **2a** with [Ti(O*i*-Pr)$_4$] gave boryltitanium triisopropoxide **49** (Scheme 17).[58] Sequential reaction of boryllithium **2a** with [Cp*HfCl$_3$] and benzylpotassium gave [HfCp*(boryl)(CH$_2$Ph)$_2$] (**50**).[59] Complexes **49** and **50** are the first examples of group 4 metal boryl complexes.[60] In the ^{1}H NMR spectrum of **49**, each of six methyl groups of three isopropoxide ligands and four methyl groups of Dip moieties are equivalent, respectively. Borylhafnium **50** has two distinct methyl protons of isopropyl groups and two geminal protons on a benzylic carbon were separately observed. A broad ^{11}B signal was observed at the typical region for borylmetal complexes for both cases (δ_B 38.2 for **49**, δ_B 70.0 for **50**). Crystallographic studies of **49** and **50** revealed a distorted tetrahedral structure of **49** and a typical three-leg piano stool structure of **50** (Figures 11 and 12, Table 7). Both B–M bonds in **49** and **50** are slightly longer than the sum of covalent radii of each atom (B–Ti: 2.20 Å, B–Hf: 2.32 Å).[11] Remarkably short Ti–O bonds (av. 1.758 Å) and large Ti–O–C angles (av. 164.9°) in **49** reflected pπ–dπ interaction between titanium and oxygen atoms.[61] Two Hf–benzylic carbon bonds (av. 2.219 Å) and five Hf–C(Cp*) bonds (av. 2.494 Å) in **3** are similar to those observed in conventional Cp*Hf–alkyl complexes.[62]

To elucidate the nature of group 4 transition metal–boron bonds, DFT studies were conducted. The structural parameters

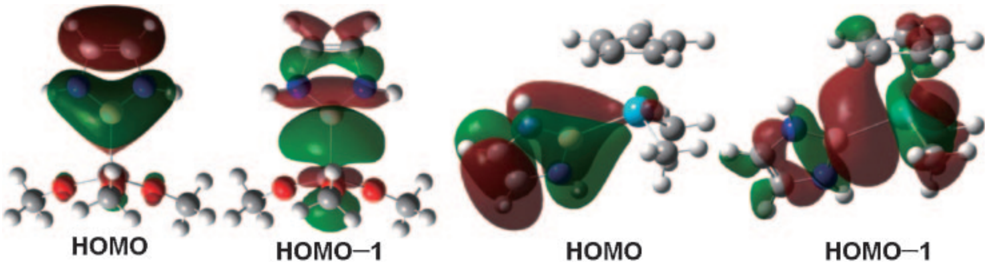
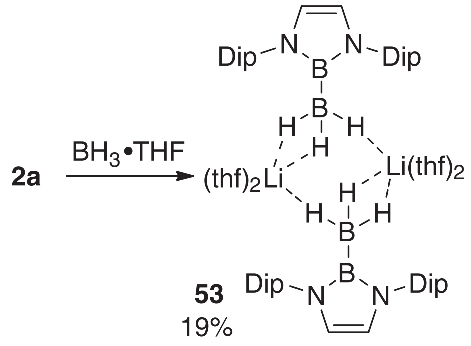


Figure 13. HOMO and HOMO−1 for model complexes **51** and **52**.



Scheme 18. Synthesis of boryltrihydroborate **53**.

of model complexes **51** and **52** were close to those of **49** and **50** (Table 7). Both **51** and **52** have similar HOMO character as a π-orbital of diazaborole ring (Figure 13), like hydroborane **3a** (Figure 4).[14,15] The shape of HOMO−1 seems to be similar to the HOMO of boryllithium **2a**, which has lone pair character on the central boron atom.[14,15]

An admixture of **50** with $Ph_3CB(C_6F_5)_4$ in toluene could polymerize ethylene to form a linear polyethylene (TOF = $110\,kg_{PE}\,mol_{Hf}^{-1}\,h^{-1}$, $M_n = 4800$, PDI = 2.1, 2 branches/1000C). The present system was also active for polymerization of hex-1-ene to afford an atactic poly(hex-1-ene) (TOF = $21\,kg_{PHex}\,mol_{Hf}^{-1}\,h^{-1}$, $M_n = 3100$, PDI = 2.2). Activities of **50**/$Ph_3CB(C_6F_5)_4$ toward polymerization were comparable to those of previously reported hafnium half-sandwich complex derived catalyst systems.[63]

4.3 Boron Compounds Possessing Boryl Substituents Introduced by Boryllithium. 4.3.1 Boryl-Substituted Hydroborate: A New Radical Hydrogen Donor: Tetrahydroborates (BH_4^-), often called borohydrides, are parents of an exceptionally important class of reagents in both organic and inorganic chemistry.[1] These reagents are used as reductants, as precursors for all kinds of interesting main group and organometallic compounds, and as hydrogen storage reagents, among other applications. Countless substituted borohydrides are known, with one or more hydrogen atoms replaced by carbon, oxygen, nitrogen, or other atoms.[64] However, simple boron-substituted borohydrides appear to be unknown. Boryl anions may provide a useful method to prepare them.

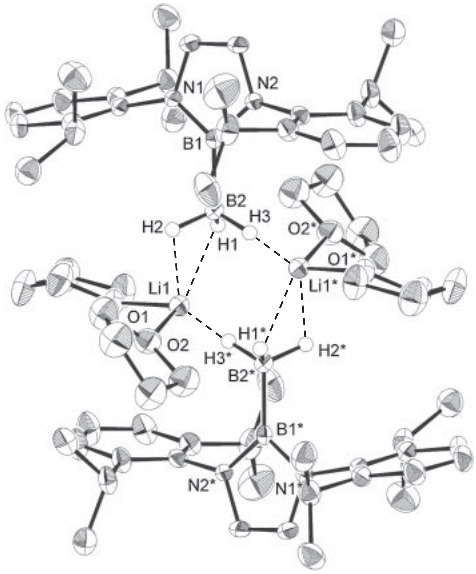
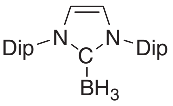


Figure 14. ORTEP drawing of boryltrihydroborate **53** (50% thermal ellipsoids. One half of the whole structure is the asymmetric unit. Asterisks on atomic labels show the other half. Disordered THF molecules and all hydrogen atoms except the hydroborate hydrogens are omitted for clarity.).

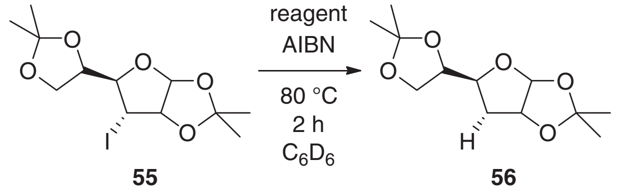
Table 8. Comparison of Selected NMR Spectroscopic Values of **53** with Reference Compounds[a)]

Compound	δ_H	δ_B	$^1J_{BH}$	δ_{Li}	$\nu_{1/2(Li)}$
53	−0.98, br	37.1, −44.7	broad	−0.73	11
$LiBH_4$	−0.52, quadruplet	−42.0, quintet	81	−0.53	18
 $IPr\text{-}BH_3$ (**54**)	0.52, br	−36.2	89	—	—

a) Solvent is THF-d_8, chemical shifts are in ppm, J and $\nu_{1/2}$ are in Hz.

Reaction of boryllithium **2a** with $BH_3{\cdot}THF$ gave a colorless, crystalline lithium boryltrihydroborate **53** in 19% isolated yield (Scheme 18[65] and Figure 14). Comparison of representative spectroscopic data between **53** and reference compounds, $LiBH_4$ and $IPr\text{-}BH_3$ (**54**) are summarized in Table 8. The ^1H NMR spectrum of **53** in THF-d_8 shows a broad signal, assignable to three hydrogen atoms of the trihydroborate moiety at relatively upfield of δ_H −0.98. The signal became sharper in $^1H\{^{11}B\}$ decoupled NMR spectrum to show ^1H–^{11}B coupling. A similar broadened signal was also observed in the spectrum of **54** (δ_H 0.52). In contrast to **53** and **54**, $LiBH_4$ showed a sharp quadruplet signal coupled with ^{11}B ($I = 3/2$, $J = 81$ Hz) and a satellite septuplet signal coupled with ^{10}B

Table 9. Reduction of Secondary Alkyl Iodide with **53**, $LiBH_4$, and **54**



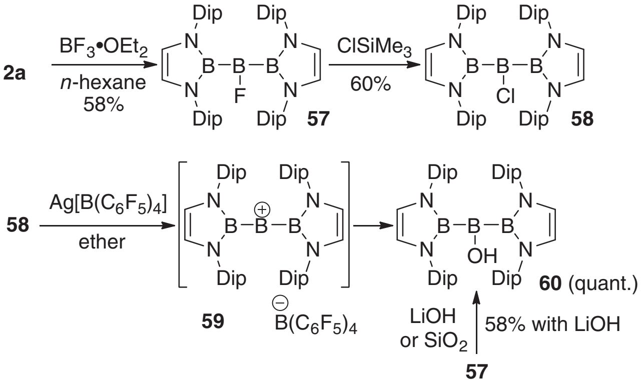
Entry	Reagent	Conv. **55**/%	Yield$^{a)}$/%
1	**53**	78	73
2	$LiBH_4$	≈0	—
3	**54**	37	65

a) Isolated yield of **55** and **56** (inseparable).

($I = 3$, $J = 27$ Hz) at δ_H −0.52. The difference in sharpness between the signals of **53** and $LiBH_4$ probably comes from the symmetry of molecules, which can affect the quadrupolar interaction. Compared to **54**, the upfield-shifted BH_3 signal of **53** may reflect the negative charge.

The hindered secondary alkyl iodide **55**, which may resist S_N2 substitution, was subjected to radical reduction with **53**, $LiBH_4$, and **54** as a reductant (Table 9). These reactions were conducted in C_6D_6 with AIBN for a fixed time of 2 h. The precursor **55** and the product **56** were inseparable, but their combined isolated yields were good in each case. In this sequence of reactions, **53** provided the best result, giving 78% conversion to **56** (Entry 1). In contrast, **54** gave 37% conversion (Entry 3) and $LiBH_4$ gave no conversion, possibly due to its low solubility (Entry 2). Thus, **53** is the best hydrogen donor for radical reduction among three reagents, probably due to its high solubility in hydrocarbon solvent and the small bond dissociation energy for B–H bonds.

4.3.2 Preparation of Linear Triborane(5)s Using Boryllithium: "Catenation" is a word describing the ability of an element to construct a long chain structure involving covalent bonds.[66] Many examples of catenation can be found as concecutive C–C bonds in organic chemistry and Si–Si bonds in polysilane chemistry. On the contrary, boron, one of the closest neighbors to carbon in the periodic table, does not show catenation. In general, compounds containing multiple boron atoms tend to form a multinuclear structure through sharing the electrons by three or more orbitals as found in B_2H_6 and polyborane structure because of the electron deficiency of boron atom.[67] In the literature, only three types of examples for catenated boranes have been reported as triborane(5), tetraborane(6), and hexaborane(8).[68,69]



Scheme 19. Syntheses of triborane(5)s **57**, **58**, and **60**.

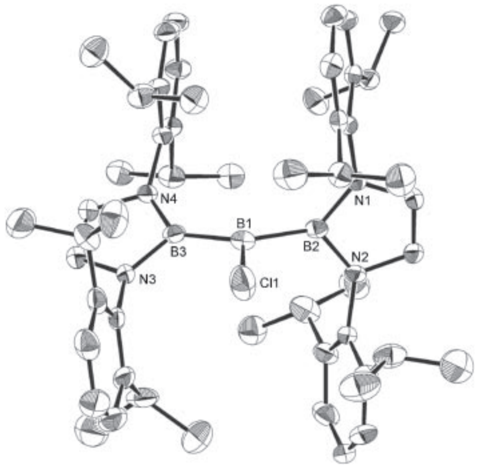


Figure 15. ORTEP drawing of **58** (hydrogen atoms, minor parts of disordered isopropyl groups, and cocrystallized THF molecule were omitted for clarity).

Simple mixing of boryllithium **2a**, generated in THF, with $BF_3 \cdot OEt_2$ in hexane gave fluorotriborane(5) **57** in 58% yield (Scheme 19).[70] Resonances in ^{1}H and ^{13}C NMR spectrum of **57** showed a highly symmetric pattern with two distinct methyl, one methyne, one backbone CH, and two aromatic signals. In the ^{11}B NMR spectrum of **57**, two signals at δ_B 83 and 25 were observed. The former signal could be assigned to the central boron atom from the integral ratio of two signals, although no ^{11}B–^{19}F coupling was observed probably due to significant broadening of the signal. It should be noted that the signal of the central boron atom appeared at significantly lower-field than that observed in the reported pentakis(dimethylamino)-triborane(5) (δ_B 60.2).[68b] This remarkable shift of ^{11}B resonance may be due to less-effective overlap of p orbitals along the B–F bond in **57** compared to the B–N bond in the previously reported triborane(5) compounds. Subsequent halogen exchange reaction of **57** could be achieved by treatment with $ClSiMe_3$ to give the chlorinated triborane(5) **58** in 60% yield. The crystal structure of **58** is illustrated in Figure 15. Treatment of chlorotriborane **58** with $Ag[B(C_6F_5)_4]$ in ether led to formation of white precipitate and hydroxytriborane(5) **60**. It may be assumed that a cationic intermediate **59** was generated by an absorption of chloride with silver cation to precipitate AgCl. The diborylboryl cation **59** may be distinguished from the previously reported example of isolated boryl cations,[71] where the cationic boron center has one or two heteroatom(s) to gain a stabilization by pπ–pπ interaction between the boron and heteroatom(s). The lack of pπ–pπ stabilization may give anomalous instability to **59** to induce the further reaction of **59** with ether.

5. Conclusion

This account reviewed the author's contribution to the chemistry of boryl anion. Spectroscopic and crystallographic analysis of boryllithium confirmed the ionic character of the

B–Li bond. The nucleophilicity of boryllithium has been confirmed by reactions with organic electrophiles. Transmetallation of boryllithium to other metals such as magnesium, copper, and zinc led to formation of the corresponding borylmetals, which can also be considered to be boryl anions. The reactivity of these resulting borylmetals toward carbonyl compounds is similar to those of carbanionic species. Applications of boryl anions toward organic syntheses, transition-metal chemistry, and main group chemistry are also described.

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