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Accounts

Recent Developments of Boryl Anions: Boron Analogues of Carbanion

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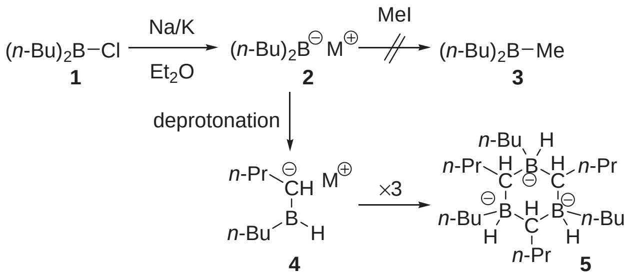
This account reviews the chemistry of "boryl anion." Boryl anions can be classified with their metallic counterpart, such as Li, Mg, Cu, and Zn in a similar manner to the classification of carbanions. The early attempts to generate boryl anions by reductive dehalogenation of haloboranes with alkali metal or photolysis of tetraphenylborate compounds had no modern spectroscopic identification of the reactive "boryl anion." Recent developments of base-stabilized boryl anion, base–$BH_2^-M^+$ (base = NEt_3 or PCy_3, M = K or Li), and generation of borylcopper species, "pinBCuL," have opened a new area of organoboron chemistry. Recently, we have synthesized a lithium salt of boryl anion, boryllithium, which reacted with electrophiles as a boron nucleophile. Based on the high reactivity of boryllithium, transmetallation to other metals enables synthesis of a series of borylmetals, such as borylmagnesium, borylcopper, and borylzinc species. All of these compounds were isolated and structurally characterized to have an sp^2 boron atom. Reactivity with organic electrophiles could confirm that they behaved as boron nucleophiles.

Carbanions are one of the most important components in synthetic organic chemistry. They act as a carbon nucleophile in organic reactions to construct a carbon–carbon bond because of the highly polarized carbon–metal bonds ($C^{\delta-}$–$M^{\delta+}$).[1] The properties of polar carbon–metal bonds in carbanion species depend on its metallic counterpart, such as lithium, magnesium, copper, and zinc. In contrast to the rich chemistry of carbanion, there have been limited examples for "boryl anion," which may play as a boron nucleophile. In general, boron-containing reagents have been used as electrophiles in organic chemistry. Examples of boron electrophiles are found in hydroboration chemistry,[2,3] Lewis acidic boron-mediated chemistry,[4] boron–enolate chemistry,[5] and recent Suzuki–Miyaura cross-coupling chemistry.[6–8] Therefore, boryl anion, a boron-centered anionic nucleophile, has been a challenging target in boron chemistry.[9] In this account, history and recent development of nucleophilic "boryl anion" possessing Li, Mg, Cu, or Zn as its counter cation are reviewed.

Early Attempts to Prepare the Boryl Anion

In 1952, Auten and Kraus reported a reduction of $(n\text{-Bu})_2BCl$ (**1**) with Na/K alloy (Scheme 1, top) to generate the corresponding boryl anion, $(n\text{-Bu})_2B^-M^+$ (**2**: M = Na or K).[10] They claimed that **2** was trapped with methyl iodide to form $(n\text{-Bu})_2BMe$ (**3**). However, they had no modern spectroscopic characterization of the substituted product **3**. After 24 years had passed, Smith and Swaminathan reported that **2** had rearranged to the corresponding boron-stabilized carbanion **4** through an intramolecular deprotonation of the butyl group by an anionic boron center (Scheme 1, bottom), and that **4** aggregated to form a cyclic trimer **5**.[11] In 1975, Eisch et al. reported photolysis of $Ph_4B^-Na^+$ (**6**) in the presence of diphenylacetylene followed by treatment with acetic acid to afford *cis*-stilbene (Scheme 2, top).[12,13] The authors assumed transient $Ph_2B^-Na^+$ (**7**), which reacted with diphenylacetylene to form boranuidacyclopropene **8**, and then **8** was protonated to give *cis*-stilbene under the reaction conditions. Two years later, Schuster et al. doubted the formation of $Ph_2B^-Na^+$ (**7**) because they considered another mechanism for the formation of biphenyl in the photolysis of **6** (Scheme 2, bottom).[14–16] In the mechanism, they assumed an excitation of Ph_4B^- anion in **6** by irradiation of light at 256 nm to afford a biradical species **9** and the following rearrangement to form a bicyclic intermediate **10a**,[17] whose derivative **10b** with one more phenyl group was structurally characterized by X-ray crystallography. Recently, Weber et al. have tried to reduce bromoborane **11** containing diazaborole skeleton (Scheme 3).[18] Alkaline metal reduction of **11** in toluene-d_8 afforded deuterioborane **14**



Scheme 1. Reduction of dialkylchloroborane **1**.

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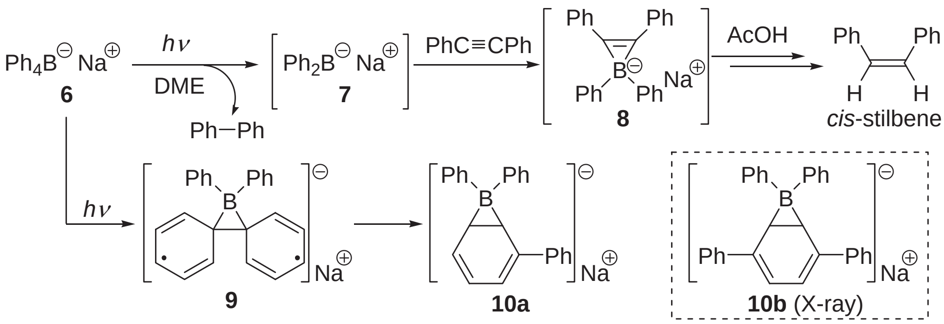
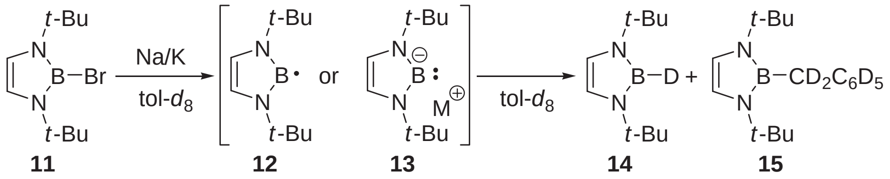
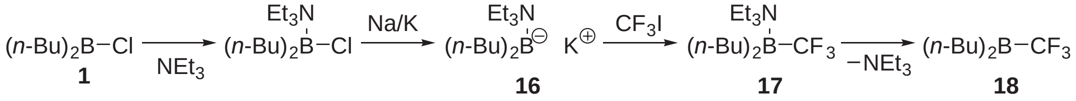


Scheme 2. Photolysis of sodium tetraphenylborate **6**.



Scheme 3. Reduction of bromoborane **11**.

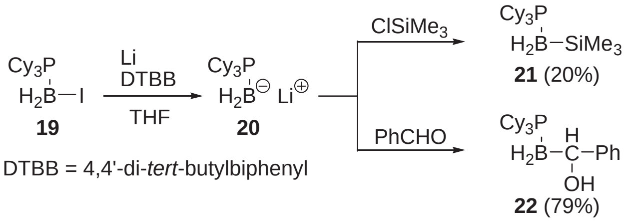


Scheme 4. Reduction of NEt_3-stabilized dialkylchloroborane **1** followed by a reaction with CF_3I.

and (d_7-benzyl)borane **15** in 1:1 ratio. They have mentioned the possibility of two intermediates, boryl radical **12** and boryl anion **13**. Unfortunately, no spectroscopic characterization of these reactive intermediates **12** and **13** appeared in the report. Thus, there have been no reports for a direct observation of boryl anion until recently.

Base-Stabilized Boryl Anion Having an sp^3 Boron Atom

According to the electronic structure of boryl anion, where the central boron atom has formally six electrons, a violation of the Lewis Octet rule would make synthesis of boryl anion more difficult (vide infra). One can expect that filling the vacant p-orbital of boron with Lewis base makes the boron atom sp^3, similar to carbon, to provide a good strategy for preparation of nucleophilic boryl anions as carbanion can be made from haloalkanes. In 1967, Parsons et al. reported a reduction of $(n\text{-Bu})_2BCl$ (**1**) with Na/K alloy in triethylamine to form the transient $(n\text{-Bu})_2B^-K^+\cdot NEt_3$ (**16**).[19] The first base-stabilized boryl anion **16** was reported to react with CF_3I to afford the corresponding substituted product, $(n\text{-Bu})_2BCF_3\cdot NEt_3$ (**17**), followed by deamination to form a base-free borane $(n\text{-Bu})_2BCF_3$ (**18**) in 30% yield based on the starting **1** (Scheme 4). However, it is generally difficult for CF_3I to accept a hard nucleophile, such as carbanion, to proceed by S_N2 reaction because of the steric and electronic repulsion between nucleophile and CF_3 moiety at the backside of the C–I bond.[20] Therefore, there may be an ambiguity for the formation of **17** by S_N2 reaction of boryl anion. 26 years later, Schmidbaur et al.[21] and Imamoto and Hikosaka[22] independently reported formation of a phosphine-stabilized boryl anion, $Cy_3P–BH_2Li$ (**20**, Cy = cyclohexyl), by reduction of **19** with lithium 4,4′-di-*tert*-butylbiphenylide (Scheme 5). Trapping of **20** with $ClSiMe_3$ or other various organic electrophiles gave the corresponding substituted or added products, such as $Cy_3P–BH_2SiMe_3$ (**21**) and $Cy_3P–BH_2CH(OH)Ph$ (**22**). Trimethylsilyl adduct **21** was characterized by X-ray crystallographic analysis to confirm the formation of a B–Si bond. Although these results are the first examples of nucleophilic boron reagent, there is no spectroscopic information of a nucleophilic boron reagent itself.



Scheme 5. Generation of Cy_3P-stabilized boryl anion **20** and its trapping with electrophiles.

Rational Design for Boryl Anion

A parent boryl anion, $^-BH_2$, has been calculated to have singlet ground state[23] in contrast to the well-understood parent carbene, CH_2, possessing triplet ground state.[24] Complexation of boryl anion with alkali metal cation was proven to lead to thermal stability of boryl anion.[23] 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

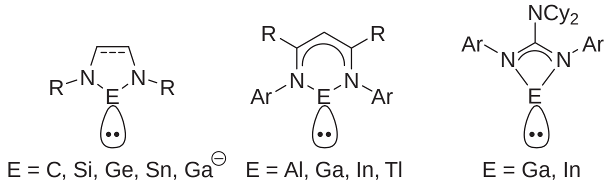
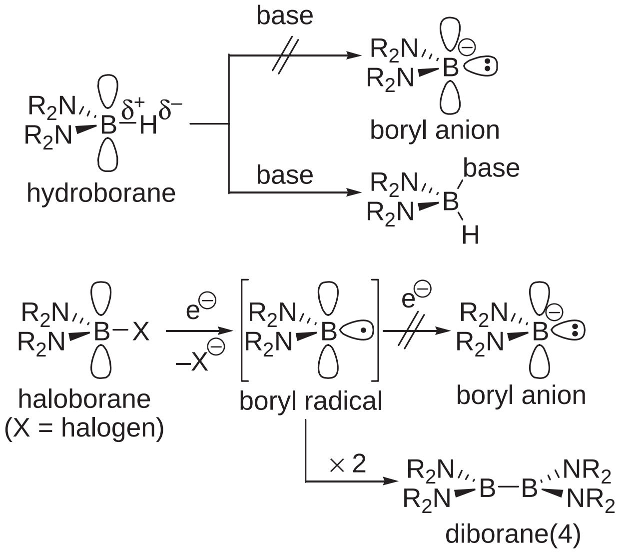


Figure 1. Monomeric low-valent group 14 and 13 element compounds with N-heterocyclic skeleton.

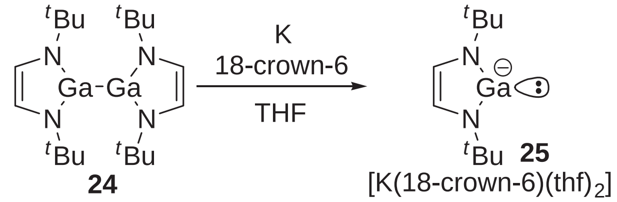


Scheme 6. Two conceivable pathways to synthesize the boryl anion.

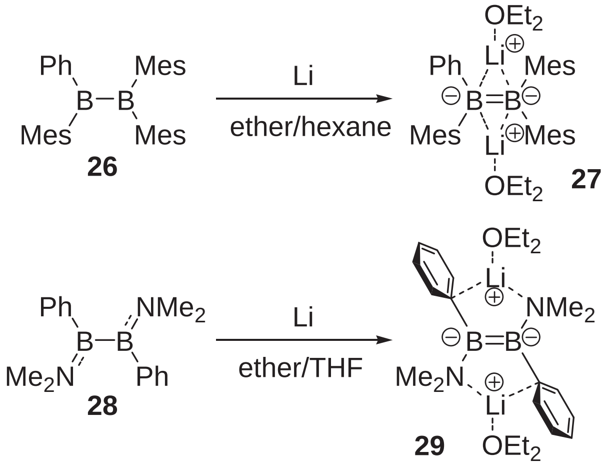
p-orbital of the boron atom in $LiB(NH_2)_2$ and $LiB(OH)_2$.[23] Consideration the established chemistry of low-valent main group elements, such as group 14 (C,[25–28] Si,[29,30] Ge,[31] and Sn[32]) and 13 (Al,[33] Ga,[34–38] In,[38–40] and Tl[40,41]), being isoelectronic to boryl anion with a four-, five-, or six-membered N-heterocyclic skeleton (Figure 1) inspired us to introduce five-membered ring diamino substituents to stabilize the boryl anion, containing low-valent boron(I) atom, with strong support from theoretical calculation.[42,43]

Why is It Difficult to Prepare Boryl Anion?

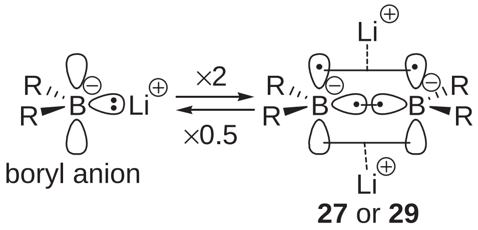
Analogous consideration to carbanion chemistry would enable imagination of two simple methods to prepare boryl anions (Scheme 6). The first one is deprotonation of hydroborane with base. However, hydrogen atoms in hydroborane are usually polarized negative, behaving as a hydride because of the lower electronegativity of boron atom (Pauling, 2.04)[44] than that of hydrogen (2.20). Additionally, a vacant p-orbital on the boron atom can accept a lone pair of the base to form Lewis acid–base adduct. Therefore, it is difficult to deprotonate hydroborane using a conventional base. The second method is reductive dehalogenation of haloborane with alkali metal reductant. However, reduction of haloborane generally leads to formation of diborane(4) species having a B–B single bond via dimerization of boryl radical intermediate generated by a single electron transfer followed by a loss of halide.[45] In fact, the most famous diborane(4) reagent, bis(pinacolato)-diborane(4) **23**, is usually synthesized by this dimerization method.[46,47] Additionally, bromine-substituted diazaborole compound **11** was reduced to form the corresponding diborane(4) species, even **11** has bulky *t*-butyl groups on its nitrogen atoms.[18]



Scheme 7. Synthesis of gallyl anion **25** by reductive cleavage of a Ga–Ga bond.

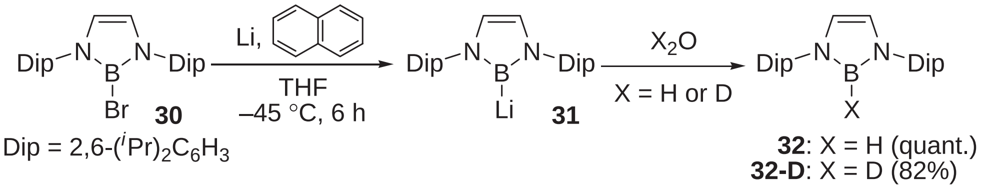


Scheme 8. Syntheses of dianionic diborane(4) species **27** and **29** with B=B double bond.



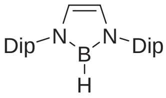
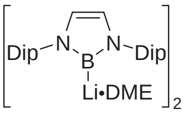
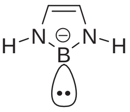
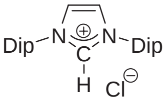
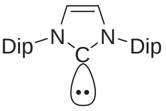
Scheme 9. Relationship between boryl anion and dianionic diborane(4) compounds **27** and **29**.

On the other hand, syntheses of gallyl anion derivatives[35–37] have been performed by reductive cleavage of the Ga–Ga single bond of digallane(4) species having five-membered N-heterocycle containing gallium (Scheme 7). In the case of boron, reduction of diborane(4), possessing a B–B single bond, is known to afford the corresponding singly or doubly reduced mono- or di-anionic diborane(4) species to form π interaction between two boron atoms without any cleavage of the B–B single bond (Scheme 8).[48–50] Ether-coordinated lithium cations in **27** and **29** were located over the B=B π-bond. These can be considered a dimer of desired boryl anion where each lone pair on the boryl anion was shared by the two boron atoms (Scheme 9). That is, reduction of a B–B single bond is not suitable for the synthesis of boryl anion because the B=B



Scheme 10. Synthesis of boryllithium **31**.

Table 1. Structural Comparison of Boryllithium **31** with Related Compounds [Dip = 2,6-(^{i}Pr)$_2$C$_6$H$_3$]

	 **32**	 [**31**–DME]$_2$	 **33**	 **34**	 **35**
B–N or C–N/Å	1.418(3) 1.423(3)	1.465(4) 1.467(4)	1.475	1.341 1.338	1.364 1.369
N–B–N or N–C–N/°	105.25(16)	99.2(2)	97.72	107.6	101.4

π-bond may be stronger than the π-bonds made from heavy main group elements.[51]

This situation prompted us to prepare a boryl anion as a lithium salt by reductive dehalogenation of haloborane possessing a well-studied diazaborole ring[52,53] and bulkier substituents than *t*-butyl group.

Boryllithium: sp^2 Boryl Anion

The bromoborane **30** was successfully reduced to the boryllithium **31** by the use of a combination of lithium powder and naphthalene in THF at $-45\,^\circ$C (Scheme 10).[54–56] The reaction of **31** with water quantitatively gave a hydroborane **32**, which could be independently synthesized by reaction of **30** with LiAlH$_4$.[57] Treatment of **31** with D_2O afforded the corresponding deuterioborane **32-D** in 82% yield, which indicates that **32** was mostly generated from the reaction of **31** with water rather than with the solvents or ligand backbone.

The use of 1,2-dimethoxyethane (DME) as a reaction solvent in place of THF enabled crystallization of boryllithium **31** with an included DME molecule. The structure of boryllithium **31**–DME was confirmed by X-ray crystallographic analysis with thermally unstable single crystals obtained from a hexane solution of **31**–DME at $-45\,^\circ$C (Figure 2). The solid-state structure of **31**–DME reveals a B–Li bond of 2.291(6) Å, which is 8.5% longer than the sum of the covalent radii (2.11 Å) of boron and lithium atoms.[44] A cocrystallized DME coordinates to the lithium atom, and one of the two DME oxygen atoms bridges to the other lithium atom to form a dimeric structure. Structural comparison of **31**–DME with related compounds (Table 1) shows that the two B–N bond lengths (1.465(4) and 1.467(4) Å) in **31**–DME are longer than those (1.418(3) and 1.423(3) Å) in the hydroborane **32**, and the angle of N1–B1–N2 (99.2(2)°) in **31**–DME is smaller than that in **32** (105.25(16)°). These B–N lengths and the N–B–N angle in **31**–DME are closer to those in the previously calculated free boryl anion **33** (B–N = 1.475 Å; N–B–N = 97.72°)[42] than to those in **32**, consistent with a highly polarized B–Li bond and anionic character of the boron center in **31**. The structural change from **32** to **31**–DME is similar to that from the corresponding imidazolium salt **34** to singlet carbene **35**.[58] Although the central dihydrodiazaborole ring in **31**–DME is planar, the lithium atom is slightly above (0.2481 Å) the mean plane of the dihydrodiazaborole ring. The N1–B1–Li1 (136.1(2)°) and N2–B1–Li1 (123.9(2)°) angles apparently differ, although the sum of the angles (359.2°) around the central boron atom shows a planarity characteristic of an sp^2-hybridized boron atom. These local distortions from ideal sp^2 hybridization of the central boron atom, without significant distortion of the whole dihydrodiazaborole ring, may reflect an ionic character of the B–Li bond as observed for C–Li bond in 2,3,4,5-F$_4$C$_6$HLi(thf)$_3$.[59]

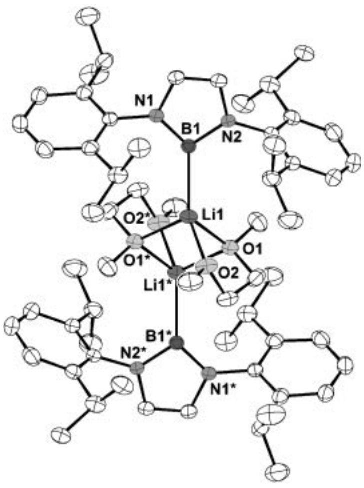


Figure 2. ORTEP drawing of [**31**–DME]$_2$ (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; half of the whole structure constitutes an asymmetric unit where numbers with asterisks are in the second asymmetric unit; only the major portions of disordered isopropyl groups are illustrated).

The boryllithium compound **31**–DME was also spectroscopically characterized in THF-d_8 solution, although 7% of **31** decomposed to the corresponding hydroborane **32** during sample preparation. In the ^{1}H NMR spectrum of **31**–DME in THF-d_8, the DME molecule was found to dissociate from the lithium atom in solution (free DME resonances were observed at 3.42 and 3.26 ppm). Instead, THF molecules appeared to coordinate to the lithium atom in THF-d_8 solution; preparation of **31** from **30** in THF-d_8 produced identical NMR spectra. The ^{11}B NMR spectrum of **31** showed a resonance at 45.4 ppm with a large half-width of $h_{1/2} = 535$ Hz. The lower field shift and larger half-width of this peak relative to those of hydroborane **32** (δ_B 22.9 ppm, $h_{1/2} = 379$ Hz) can be attributed to the paramagnetic contribution to nuclear shielding by the low-lying transition from an sp^2 lone pair of the boryl anion to the π^* orbital on the dihydrodiazaborole ring, as was reported for the isoelectronic singlet diaminocarbene.[60] Absence of splitting in the proton-coupled ^{11}B NMR spectrum of **31** confirmed that there is no B–H bond, whereas a ^{11}B–^{1}H coupling constant of 154 Hz was detected for **32**. The ^{7}Li NMR spectrum of **31** showed a broad singlet peak at 0.46 ppm with a half-width of $h_{1/2} = 36$ Hz; the large half-width may originate from the interaction of the lithium with the quadruple boron nucleus.[61] Thus, the NMR spectroscopy of boryllithium **31** also indicates that the central boron atom has an anionic character with a highly polarized B–Li bond in solution.

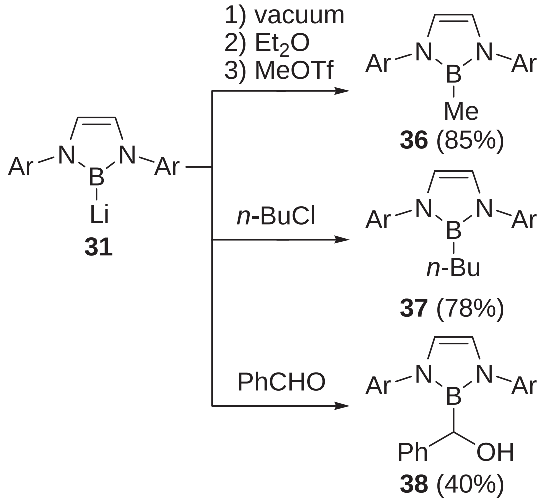
After removing excess lithium from the THF solution, boryllithium **31** was shown to react with a variety of electrophiles (Scheme 11). In ether, compound **31** reacted with MeOTf to give the substituted product methylborane **36** in 85% yield. The reaction with 1-chlorobutane in THF gave *n*-butylborane **37** in 78% yield. Boryllithium **31** also attacked the carbonyl group of benzaldehyde to afford the corresponding adduct, α-borylbenzyl alcohol **38** in 40% isolated yield.[62] Thus, we have successfully demonstrated that boryllithium **31** behaves as a base or a nucleophile.

Borylmagnesium: Boron Derivative of Grignard Reagent

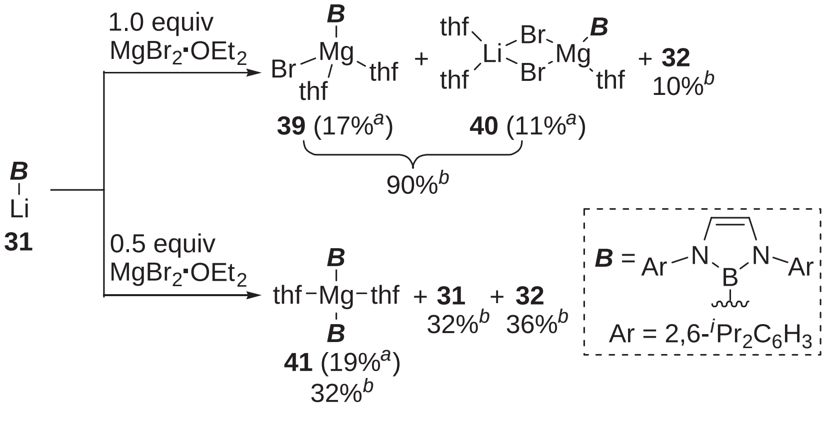
Borylmagnesiums were prepared by the transmetallation of boryllithium **31** with 1 or 0.5 equiv of $MgBr_2 \cdot OEt_2$ powder in THF at room temperature (Scheme 12).[63] Recrystallization of the product from the reaction with 1.0 equiv of $MgBr_2 \cdot OEt_2$ gave a separable pair of crystals which consists of colorless **39** and pale yellow **40**. On the other hand, reaction with 0.5 equiv of $MgBr_2 \cdot OEt_2$ gave the corresponding diborylmagnesium species **41** as yellow crystals. X-ray crystallographic analysis revealed the structures of these three molecules (Figures 3–5).

In the crystal structures, each of these molecules **39**–**41** includes a nearly ideal sp^2 boron atom and four-coordinate magnesium atom with the first structurally characterized B–Mg single bonds.[64–71] All B–Mg bonds (Table 2) were slightly longer than the sum (2.24 Å) of covalent radii[44] of boron and magnesium atoms as was observed in boryllithium **31**–DME. The B–N bonds and N–B–N angles of borylmagnesiums **39**–**41** were closer to those in boryllithium **31**–DME rather than those in the protonated hydroborane **32**. The results above indicate an ionic character of the B–Mg single bonds.

Dissolution of isolated crystals of **39** and **40** into THF-d_8 showed identical ^{1}H and ^{11}B NMR spectra with appropriate integral ratio of free THF molecules which coordinated to magnesium in the crystal. Furthermore, the ^{7}Li NMR chemical shift of **39** (δ_{Li} 0.4) was identical to that of LiBr in THF-d_8. That is, **40** may have a formula of **39** in THF solution even in the presence of LiBr. Diborylmagnesium **41** could be easily distinguished from **39** and **40** by its ^{1}H NMR spectrum. All of **39**–**41** showed a broad signal with a peak at δ_B 37.6 in their



Scheme 11. Reaction of boryllithium **31** with electrophiles.



Scheme 12. Syntheses of borylmagnesium compounds **39**–**41** from boryllithium **31** (^{a}isolated yield, ^{b}NMR yield calculated from ^{1}H NMR in THF-d_8).

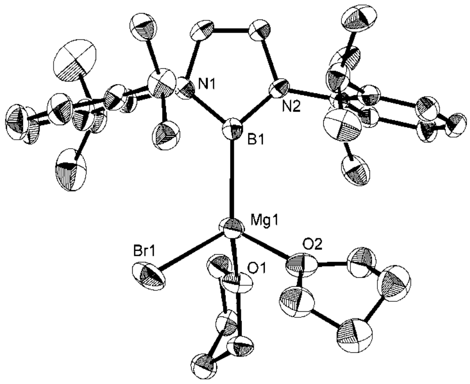


Figure 3. ORTEP drawing of **39** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; only the major portions of disordered isopropyl groups and THF molecules are illustrated). Reprinted with permission from Ref. 63 Copyright (2007) American Chemical Society.

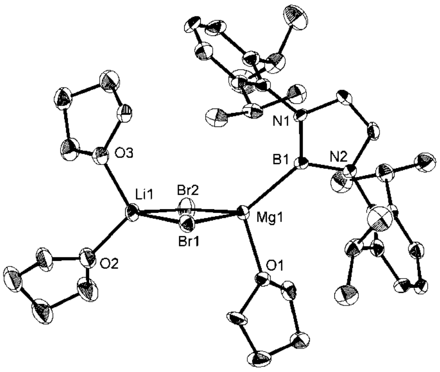


Figure 4. ORTEP drawing of **40** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; one of two independent molecules is shown; only the major portions of disordered isopropyl groups are illustrated). Reprinted with permission from Ref. 63 Copyright (2007) American Chemical Society.

^{11}B NMR spectra. These low-field shifted broad ^{11}B signals also support the ionic character of B–Mg bonds in borylmagnesium species due to their paramagnetic contribution to shielding as was discussed with boryllithium. On the basis of the above characterization, we could estimate the reaction conversion of **31** with $MgBr_2{\cdot}OEt_2$ as follows. The reaction of **31** with 1.0 equiv of $MgBr_2{\cdot}OEt_2$ in THF-d_8 enabled us to confirm that 90% of **31** was converted to **39** in solution with 10% of hydroborane **32** as judged by ^{1}H NMR spectroscopy if 100% of **40** existed as **39** in solution (Scheme 12). On the other hand, only 32% of **31** was converted to **41** by the reaction of **31** with 0.5 equiv of $MgBr_2{\cdot}OEt_2$ in THF-d_8 accompanied by 36% of hydroborane **32** and 32% of unreacted **31**.

The reaction of borylmagnesium bromide **39** generated from **31** in situ with 1–3 equiv of benzaldehyde was performed (Table 3, Runs 1–3). These reactions afforded a mixture of benzoylborane **42**, boron-substituted ester **43**, and hydroborane **32**. Simultaneous formation of benzyl alcohol **44** suggests intermolecular hydride transfer from a magnesium borylbenzyloxide intermediate to an excess of benzaldehyde probably via a six-membered ring transition state (see picture) as was reported for the magnesium-Oppenauer oxidation.[72,73] It is noteworthy that no borylbenzylalcohol **38** was formed by the reaction of **39** with benzaldehyde (Runs 1–3) in sharp contrast to the fact that **38** was obtained in 81% yield by the reaction of boryllithium **31** with 1 equiv of benzaldehyde (Run 4). Addition of a second equivalent of benzaldehyde to **31** led to an intermolecular hydride transfer to form **43** (Run 5) accompanied with the formation of benzyl alcohol **44**. Thus, the counter metal cation alters the reactivity of α-borylbenzyloxide intermediate.

Benzoylborane **42** is the first example of a fully characterized acylborane.[74] Alternatively, we could also synthesize **42** in a higher yield by the reaction of boryllithium **31** 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,[75] (ii) IR carbonyl

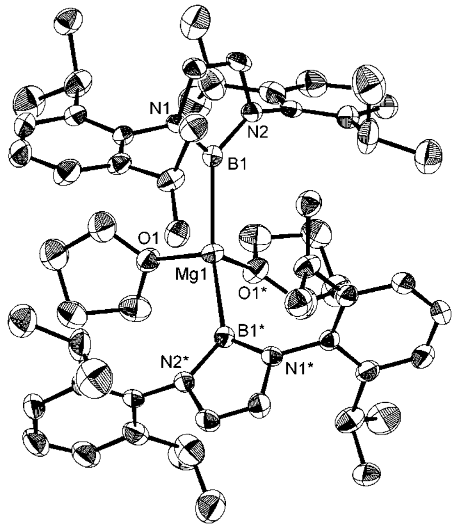


Figure 5. ORTEP drawing of **41** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; half of the whole structure constitutes an asymmetric unit where numbers with asterisks are in the second asymmetric unit; only the major portions of disordered isopropyl groups and THF molecules are illustrated). Reprinted with permission from Ref. 63 Copyright (2007) American Chemical Society.

Table 2. Structural Comparison between Borylmagnesiums **39**–**41** and Related Compounds[a]

	39	**40**	**41**	**31**–DME	**32**
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)

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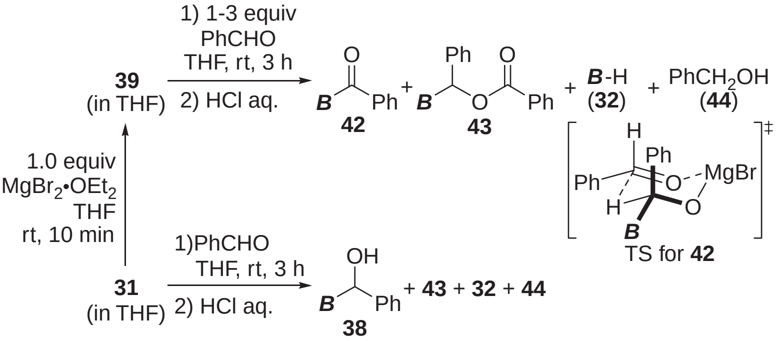
Table 3. Reactions of Boryllithium **31** and Borylmagnesium **39** with Benzaldehyde[a)]



Run	Reactant	PhCHO (equiv)	**42**/%[b)]	**43**/%[b)]	**32**/%[b)]	**44**/%[c)]	**38**/%[b)]
1	**39**	1	18	18	56	27	0
2	**39**	2	34	24	32	47	0
3	**39**	3	22	40	16	55	0
4	**31**	1	0	0	6	0	81
5	**31**	3	0	51	10	50	0

a) Reprinted with permission from Ref. 63 Copyright (2007) American Chemical Society. b) ^{1}H NMR yield. c) GC yield.

Table 4. Properties of Acylborane **42** with a Reference Benzophenone and ORTEP Drawing of **42** (50% Thermal Ellipsoids, Hydrogen Atoms were Omitted for Clarity)[a)]

	42	$Ph_2C=O$
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

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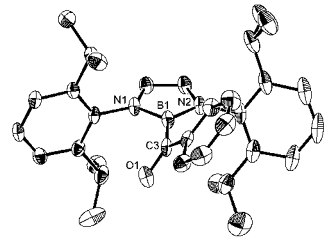
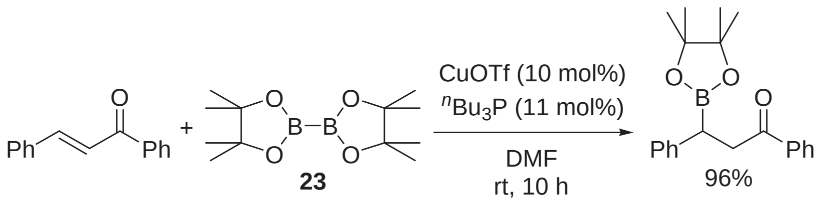


absorption shifted to lower energy,[76] and (iii) lower-field shifted ^{13}C NMR peak (broadened by a quadrupolar ^{11}B nucleus) when compared to that of benzophenone (Table 4). This tendency is common to benzoylsilanes reported in the literature.[77,78] In the solid state, the benzoyl plane was not coplanar with the boron plane (N–B–C–O torsion = 50.0(3)°).

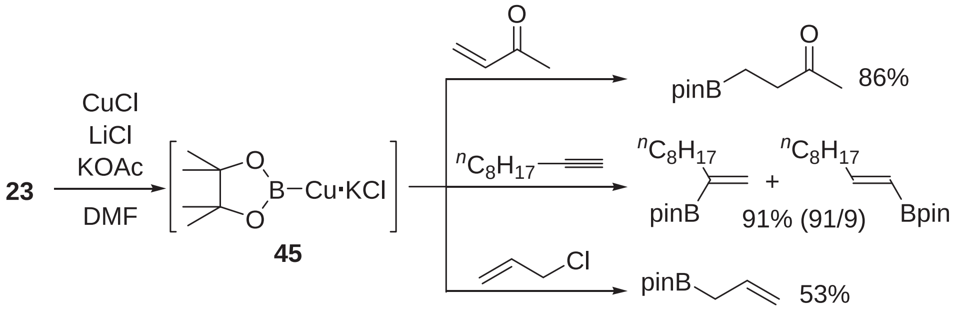
Borylcopper Generated from Diboron: Catalytic Borylation of Organic Electrophiles

In 2000, Cu-mediated β-borylation of α,β-unsaturated ketones was reported by Ito, Hosomi, et al.[79] Mixing bis(pinacolato)diborane(4) (**23**) and α,β-unsaturated ketone in the presence of a catalytic amount of CuOTf and $(n\text{-Bu})_3$P in DMF gave the corresponding conjugate adduct in up to 96% yield (Scheme 13). In the same year, Miyaura, Ishiyama, and co-worker reported formation of borylcopper species **45** by mixing **23** and CuCl in the presence of LiCl and KOAc, where the resulting borylcopper species could undergo β-borylation of α,β-unsaturated carbonyls, monoborylation of alkynes, and substitution of allyl chloride (Scheme 14).[80,81] They have mentioned that acetate anion played a crucial role for transmetallation of (pinacolato)boryl group from **23** to copper salt to form the borylcopper species **45**. Addition of MeOH to the Miyaura–Ishiyama system was reported to accelerate the reaction (Scheme 15).[82] They have expanded this reaction to an asymmetric version using ferrocene-based chiral diphosphine ligands (Scheme 16).[82,83] The Miyaura–Ishiyama β-borylation system has also been widely applied to construct a complex skeleton of the natural products and to synthesis of borylated amino acids.[84–86] Most recently, DFT calculation on the conjugate addition proved the β-attack of boron nucleophile to form copper enolate intermediate.[87]

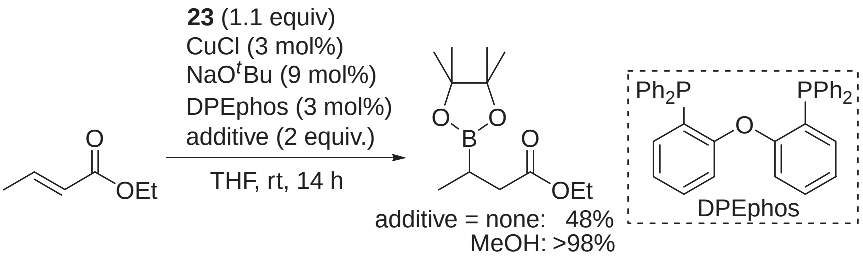
On the other hand, Ito, Sawamura, and co-worker reported a catalytic substitution reaction of allylic carbonate with **23** in the presence of Cu(O^{t}Bu) and Xantphos (Scheme 17).[88] The S$_N$2′ product was obtained in good yield and E selectivity, and the regiochemistry of optically pure allylic substrates could control the stereochemistry of the resulting C–B bond. Key steps of the catalytic cycle are the rapid generation of borylcopper species **46** from Cu(O^{t}Bu) and **23** and regenerating of copper alkoxide from copper carbonate by loss of CO_2 (Scheme 18). This reaction was expanded to an enantioselective reaction[89] (Scheme 19) using P chiral diphosphine ligand, (*R*,*R*)-QuinoxP*, developed by Imamoto et al.[90] The resulting chiral allylboronate could react with aldehyde in good yield and stereoselectivity to give the corresponding allylic alcohol with high ee. The above two types of reactions were successfully combined for a reaction of methyl acrylate having a 1-acetoxyethyl group to afford the corresponding ester-substituted homoallyl borates (Scheme 20). Introduction of chiral auxiliary to the ester-substituted boronate induced a highly diastereoselective allylation of benzaldehyde and the following



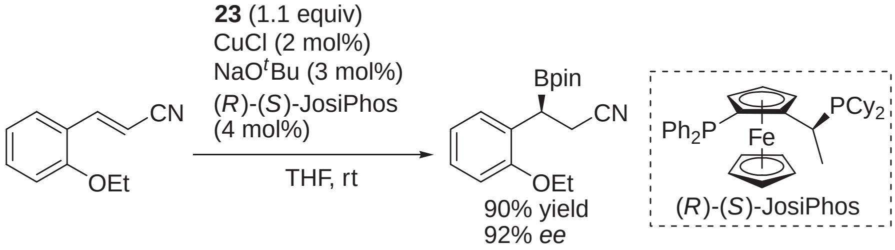
Scheme 13. The first example of copper-catalyzed β-borylation of α,β-unsaturated carbonyl compound using diborane(4) **23**.



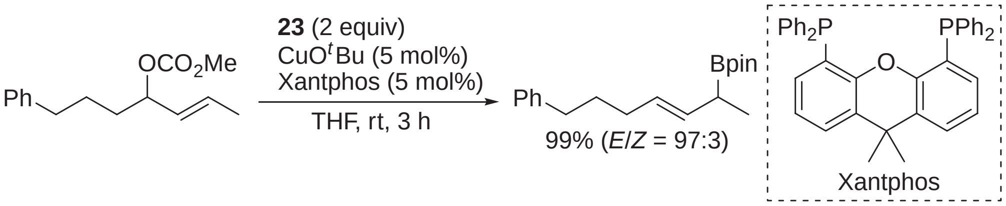
Scheme 14. Formation of borylcopper species **45** in situ from diborane(4) **23** and reactions with various organic electrophiles.



Scheme 15. Acceleration effect on addition of MeOH for Cu-catalyzed β-borylation of α,β-unsaturated carbonyl compound.



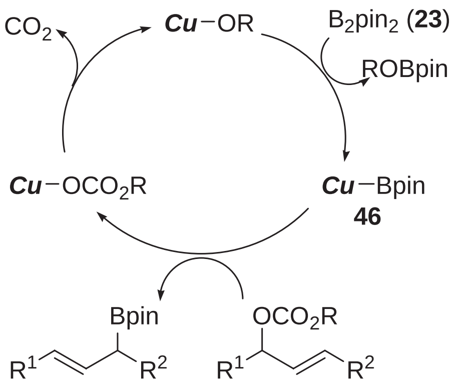
Scheme 16. Asymmetric β-borylation of electron-deficient alkenes.



Scheme 17. Copper-catalyzed S_N2' borylation of allylic carbonate.

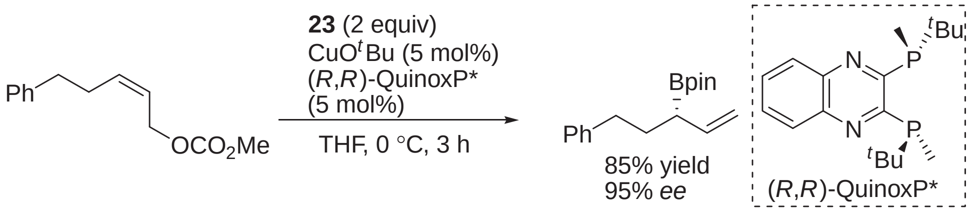
acid-catalyzed cyclization gave the corresponding lactone.[91]

Recently, isolation of borylcopper species, IPrCuBpin (**47**, IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, pin = pinacolato), prepared from IPrCu(O^{t}Bu) and diborane(4) **23** has been reported (Scheme 21).[92] The isolated borylcopper complex **47** catalyzed reduction of CO_2 with **23** (eq 1) and diboration of aldehydes (eq 2).[92,93] However, stoichiometric reaction of **47** with CO_2 or benzaldehyde afforded no insertion product which should have a metal–oxygen and boron–carbon bond. Theoretical calculation revealed the mechanisms of these reactions as follows (Scheme 22).[94,95] Boryl ligand in a model complex, L–Cu–***B***, possessing an NHC ligand

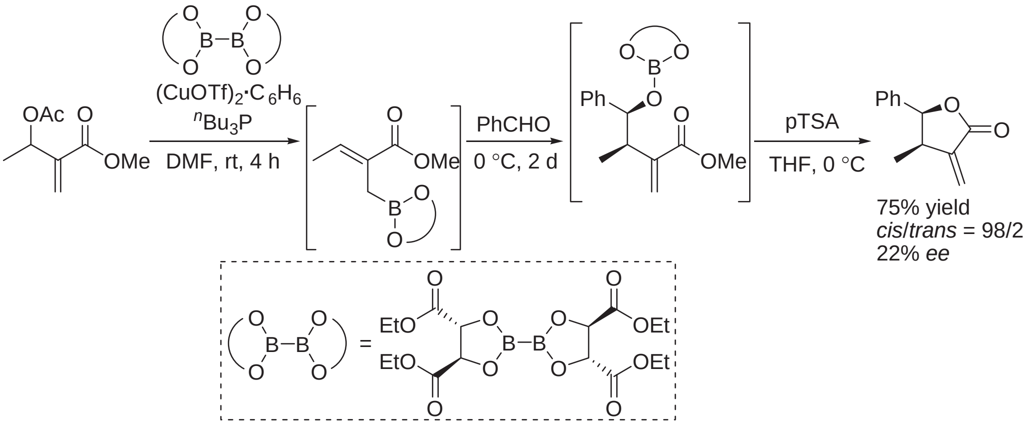


Scheme 18. Proposed catalytic cycle for Scheme 17.

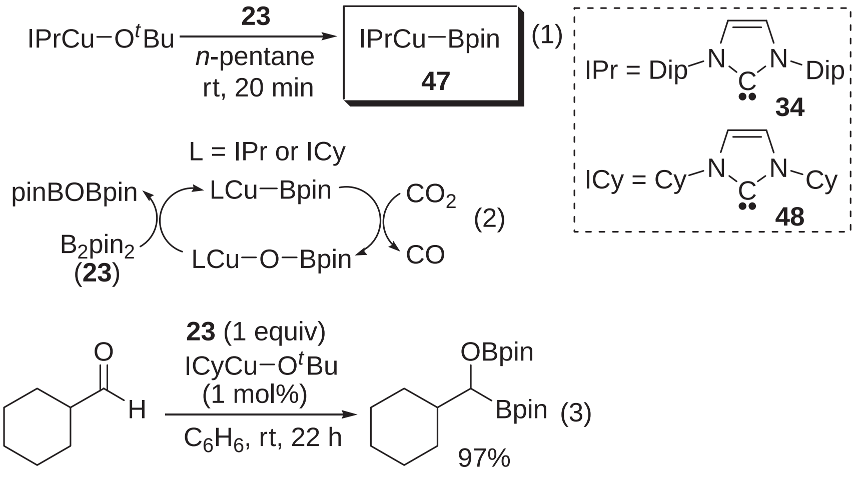
attacked a C=O double bond of CO_2 to form copper borylcarboxylate complex **49** via **TS1**. After change in orientation of the boryl group, boron–oxygen interaction in **TS2** led to an elimination of carbon monoxide to form the corresponding copper boronate complex. In the reaction of L–Cu–***B*** species with formaldehyde, boryl ligand also attacked the carbonyl carbon to form borylalkoxide complex **50** through **TS3**. The following isomerization induced by boron–oxygen interaction to give the corresponding boroxymethylcopper complex via **TS4** in the absence of diborane(4) reagent. Addition of diborane(4) to copper borylalkoxide led to an σ-bond metathesis reaction to afford diborylated aldehyde molecule with a reproduction of NHC-ligated borylcopper complex.



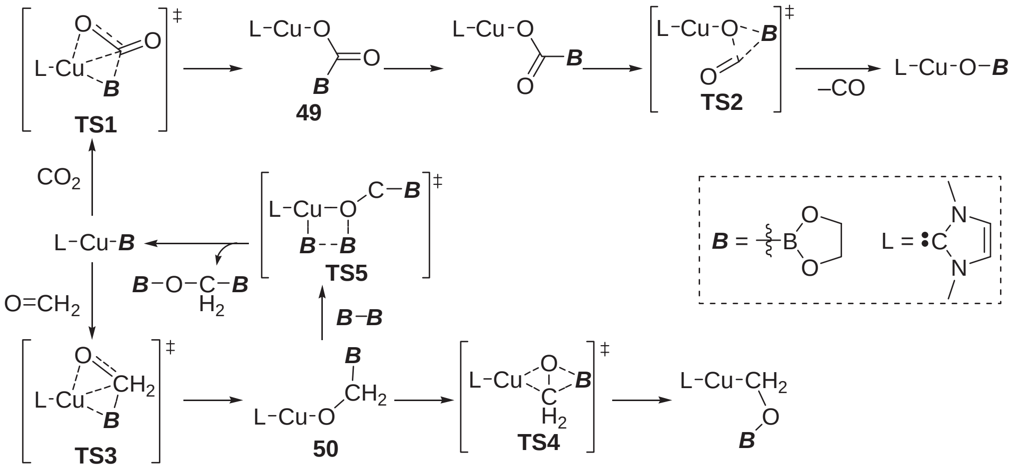
Scheme 19. Asymmetric S_N2' borylation of allylic carbonate.



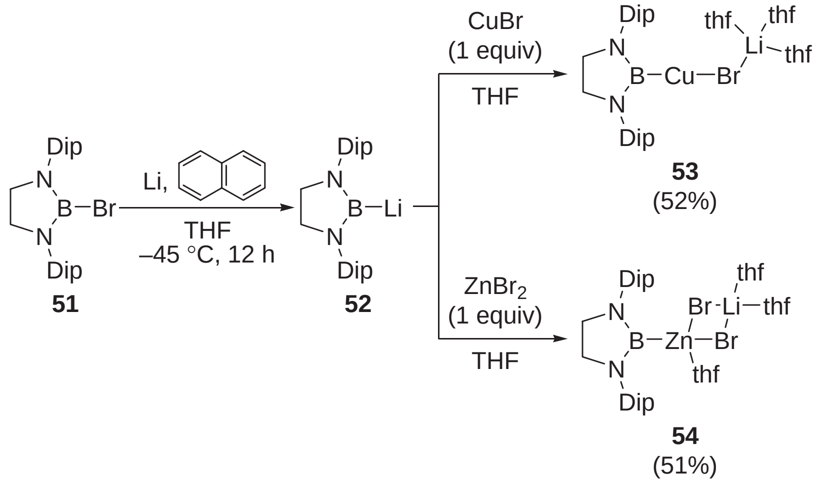
Scheme 20. A sequential borylation, allylation, and lactonization.



Scheme 21. Synthesis of isolable borylcopper **47** and catalytic activity of borylcopper derivatives.



Scheme 22. Calculated reaction pathway for carbonyl-insertion to borylcopper species.



Scheme 23. Synthesis of borylbromocuprate **53** and boryldibromozincate **54** from boryllithium **52**. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.

Borylcopper and Borylzinc Generated from Boryllithium: Formation of Boryl "ate" Complexes

Borylcuprate and borylzincate were synthesized by the transmetallation of boryllithium **52**, which was prepared from bromoborane **51**,[96] with 1 equiv of CuBr and $ZnBr_2$, respectively.[97] Recrystallization of the product from pentane gave crystals of lithium borylbromocuprate **53** and lithium boryldibromozincate **54** in 52 and 51% isolated yields (Scheme 23).

Two ate complexes **53** and **54** were spectroscopically and structurally characterized. The ^{11}B NMR spectrum showed a broad signal at 45 ppm for **53** or at 41 ppm for **54**. These values are comparable to that of boryllithium **52** (52 ppm). The molecular structures of **53** and **54** were determined by X-ray structural analysis (Figures 6 and 7). The first borylcuprate **53** contained a B–Cu–Br–Li chain with three THF molecules coordinating to the lithium atom.[98,99] The B–Cu bond length of **53** [1.983 Å (av.)] is similar to that of carbene–borylcopper complex **56** [Figure 8, 1.983(3) Å][96] and rather shorter than that of **47** [2.002(3) Å].[92] The B–Cu–Br angle of **53** (172.0°

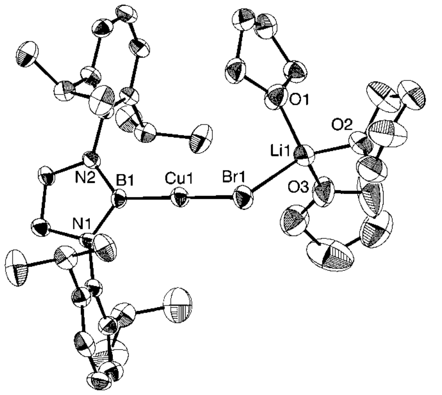


Figure 6. ORTEP drawing of **53** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; one of two independent molecules is shown; only the major portions of disordered isopropyl groups and THF molecules are illustrated). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.

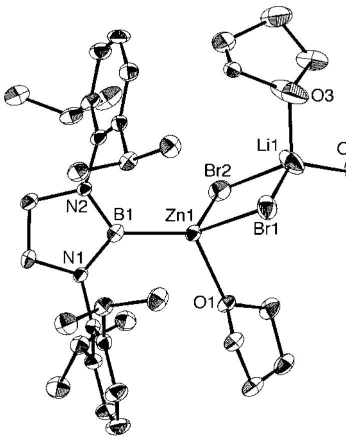
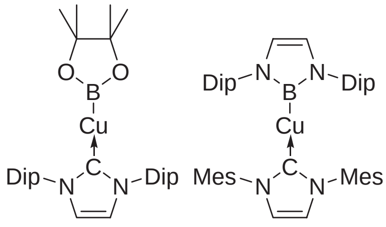


Figure 7. ORTEP drawing of **54** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; only the major portion of disordered THF molecules is illustrated). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.

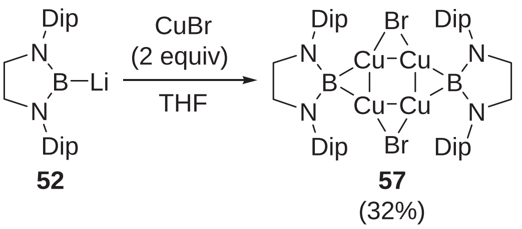


47 **56**

Figure 8. Reference borylcopper compounds. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.

(av.)) is slightly bent as was observed for the B–Cu–C angle of **47** (168.07(16)°),[92] whereas that of **56** was almost linear (179.41(15)°).[96] This difference may come from the less-bulky bridging bromide ligand on the central copper atom in **53** compared to carbene ligand in **47**. Lithium boryldibromozincate **54**[100,101] is the first example containing a 2c–2e B–Zn bond, and the B–Zn bond length (2.075(5) Å) is slightly shorter[102] than the sum of covalent radii (2.13 Å)[44] of boron and zinc atoms, and than the shortest B–Zn bond length (2.15(2) Å) among the previously reported multicenter–multielectron B–Zn bond.[103–108]

Tetranuclear copper(I) complex **57** was formed in 32% yield by changing the stoichiometry of CuBr (2 equiv) to boryllithium **52** (Scheme 24). The ^{11}B NMR spectrum of **57** showed a broad signal at 38 ppm, which is slightly shifted to higher field compared to that of **53** (45 ppm). The molecular structure of **57** obtained from crystallographic analysis is shown in Figure 9.[109] In the structure of **57**, each of the two bromine atoms and two boron atoms bridged two Cu atoms in an alternating fashion.[110] The longer B–Cu bond lengths in **57** (2.093(4) and 2.073(5) Å) than 2c–2e B–Cu bond lengths in **53** may reflect a bridging situation of boryl ligand as were observed for precedent bridging boryl complexes.[111–114]



Scheme 24. Synthesis of boryl-bridged tetranuclear copper complex **57**. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.

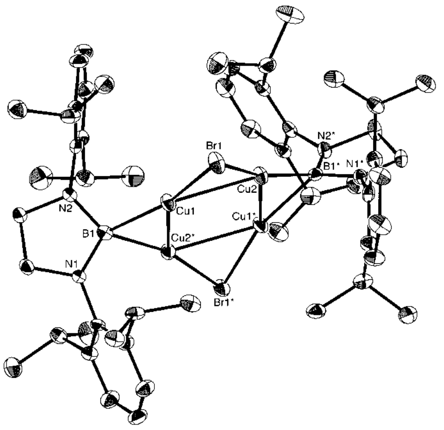
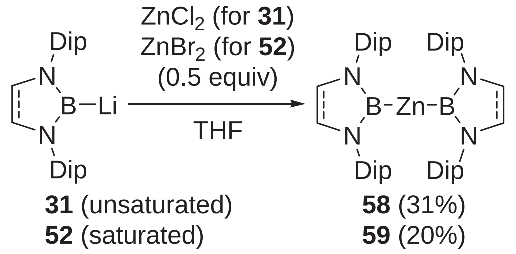


Figure 9. ORTEP drawing of **57** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; half of the whole structure constitutes an asymmetric unit where numbers with asterisks are in the second asymmetric unit; only the major portion of disordered bromine atoms is illustrated). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.



Scheme 25. Synthesis of diborylzinc species **58** and **59**. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.

Solvent-free diborylzinc species **58** and **59** were obtained as a colorless crystalline solid in 31 or 20% yield by an addition of 0.5 equiv of zinc halide to boryllithiums **31** or **52** (Scheme 25). The ^{11}B NMR spectra of these diborylzinc species showed a broadened signal at 32 ppm for **58** or at 38 ppm for **59**. The ^{1}H and ^{13}C NMR signals of **58** and **59** were slightly shifted from those of diborylmagnesium species **41**.[63]

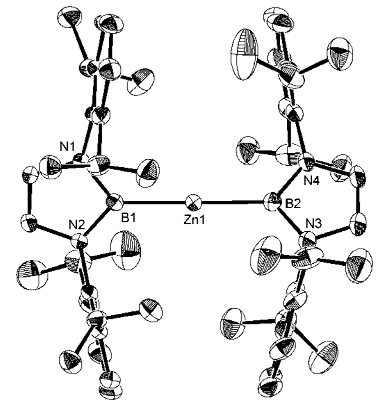
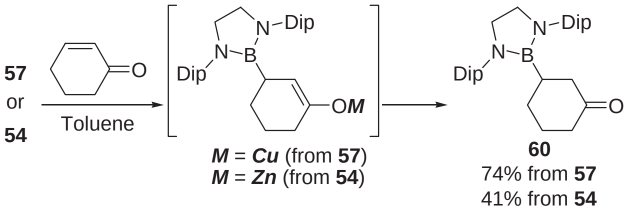


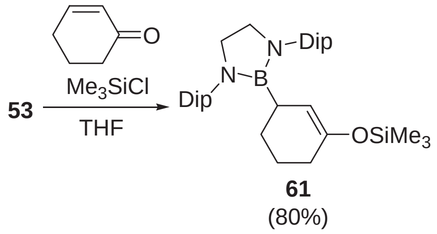
Figure 10. ORTEP drawing of **58** (50% thermal ellipsoids, hydrogen atoms are omitted for clarity; only the major portion of disordered bromine atoms is illustrated). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.



Scheme 26. Reactions of **57** or **54** with 2-cyclohexen-1-one. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.

X-ray crystallography (Figure 10 for **58**. See Ref. 97 for **59**) revealed that diborylzincs **58** and **59** had two-coordinate linear structures[115] where the B–Zn–B angles were 178.50(11)° for **58** and 177.41(11)° for **59**, the values being similar to most of the reported dialkyl- or diarylzinc species.[116–129] It should be noted that **58** and **59** are the first homoleptic borylmetal species.[130] The B–Zn bond distances (2.052(3) and 2.053(3) Å for **58**) are slightly shorter than that (2.075(5) Å) in boryldibromozincate **54**. Saturation of C–C bond in the boron-containing 5-membered ring led to longer B–Zn bond (2.088(3) and 2.087(3) Å for **59**).[131]

To investigate the reactivity of borylcopper and -zinc compounds as boron nucleophiles, borylcopper **57** and borylzincate **54** were allowed to react with an α,β-unsaturated ketone. Thus, the reaction of **57** or **54** with 2-cyclohexen-1-one gave the corresponding conjugate addition product, 3-borylcyclohexan-1-one **60** in 74 and 41% yield after hydrolysis (Scheme 26). In the case of **54**, one can expect that the lithium atom may act as a Lewis acid to achieve the conjugate addition.[132] In contrast, the reaction of boryllithium **52** with 2-cyclohexen-1-one led only protonation of **52** (as judged by ^{1}H NMR) to form the corresponding hydroborane [HB(NDipCH$_2$)$_2$ (**61**)] instead of the 1,2- or 1,4-addition product. The regioselectivity of the addition is the same as those of organo-cuprates,[133,134] -zincates,[135–140] and transient borylcopper species.[76–81] Trapping the copper enolate intermediate generated from **53** and 2-cyclohexen-1-one with trimethylsilyl chloride afforded γ-siloxyallylborane **61** in 80% yield (Scheme 27). The γ-siloxyallylborane **61** is a silicon enolate, and is concurrently an allylborane. Multi-step syntheses of such γ-siloxyallylboranes and their application to organic synthesis have been reported.[141–145] It should be noted that transition-metal-catalyzed silaboration of an α,β-unsaturated ketone affords complementary products, γ-boroxyallylsilane.[146–149]



Scheme 27. Synthesis of γ-siloxyallylborane **61** from **53**. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced from Ref. 97 with permission.

Conclusion and Outlook

We have reviewed the history of "boryl anion." Although the early attempts to generate a boryl anion all failed, the approach to occupy the vacant p-orbital of the boron atom with Lewis base succeeded to generate the corresponding base-stabilized boryl anion, in which the sp^3 boron center reacts with electrophiles. Modern catalyst technology also utilized the nucleophilic borylcopper species generated in situ for reaction with electron-deficient olefins, allylic esters, and aldehydes. The recent development of low-valent main group element compounds with N-containing heterocycles enabled us to synthesize and isolate the boryl anion, boryllithium, with the sp^2 boron center. Spectroscopic and crystallographic analysis of the resulting boryllithium confirmed the ionic character of the B–Li bond. The nucleophilicity of the boryllithium has been confirmed by reaction with organic electrophiles such as methyl triflate, 1-chlorobutane, and benzaldehyde. Transmetallation of boryllithium to other metals such as magnesium, copper, and zinc led to formation of the corresponding borylmetals, which can be also considered as boryl anions. The reactivity of these resulting borylmetals toward carbonyl compounds is similar to those of carbanionic species. Now we have a family of boryl anion as boron derivatives of carbanionic species such as organolithium, organomagnesium, organocopper, and organozinc in hand. In the future, many applications of these boryl anions is anticipated, such as new B–C bond formation, new boron-main group element linkage, and new transition metal boryl complexes.

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102 This is in contrast to boryllithium **31** and -magnesiums **39** and **41**, where the B–M (M = Li or Mg) bond is longer than the sum of covalent radii, probably due to the difference in polarity of boron–metal bond.

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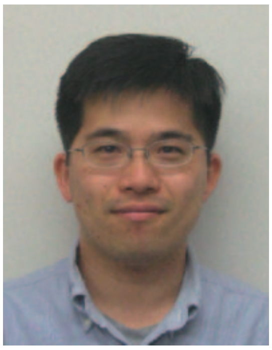

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