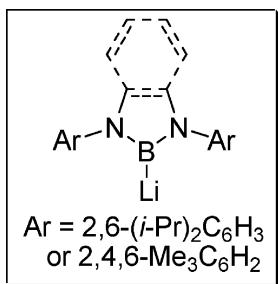


Chemistry of Boryllithium: Synthesis, Structure, and Reactivity

Yasutomo Segawa, Yuta Suzuki, Makoto Yamashita, and Kyoko Nozaki

J. Am. Chem. Soc., **2008**, 130 (47), 16069-16079 • DOI: 10.1021/ja8057919 • Publication Date (Web): 04 November 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



Synthesis & Structure

Bonding property

Reaction as nucleophile

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Chemistry of Boryllithium: Synthesis, Structure, and Reactivity

Yasutomo Segawa, Yuta Suzuki, Makoto Yamashita,* and Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo 7-3-1, Hongo, Bunkyo-ku, 113-8656 Tokyo, Japan

Received July 24, 2008; E-mail: makotoy@chembio.t.u-tokyo.ac.jp; nozaki@chembio.t.u-tokyo.ac.jp

Abstract: A series of lithium salts of boryl anion, boryllithiums, were synthesized and characterized by NMR spectroscopy and crystallographic analysis. In addition to the parent boryllithium compound **35a**, structural modification of boryllithium, using saturated C–C and benzannulated C=C backbones in the five-membered ring and mesityl groups on the nitrogen atoms, also allowed generation of the corresponding boryllithium. The solid state structures of boryllithium showed that the boron–lithium bond is polarized where the boron atom is anionic in all **(35a·DME)₂**, **35a·(THF)₂**, **35b·(THF)₂**, and **35c·(THF)₂** when compared to the structures of hydroborane **38a–c** and optimized free boryl anion **opt-46a–c**. Dissolution of the isolated single crystals of **(35a·DME)₂** and **35a·(THF)₂** in THF-*d*₈ showed that the boron–lithium bond remained in solution and free DME or THF molecules were observed. Temperature-dependent ¹¹B NMR chemical shift changes of **35a** were observed in THF-*d*₈ or methylcyclohexane-*d*₁₄, suggesting a change of chemical shift anisotropy around the boron center. The HOMO of **opt-35a·(THF)₂** had a lone pair character on the boron atom, as observed for phenyllithium, whereas the HOMO of hydroborane **38a** corresponds to the π-orbital of the boron-containing five-membered heterocycle. The polarity of the B–Li bond, estimated by AIM analysis, was similar to that of alkylolithium. Boryllithiums **35a** and **35b** behave as a base or a boron nucleophile in reaction with organic electrophiles via deprotonation, S_N2-type substitution, halogen–metal exchange or electron-transfer, 1,2-addition to a carbonyl group, and S_NAr reaction. In the case of the reaction with CO₂, intramolecular cyclization followed by CO elimination from borylcarboxylate anion and subsequent protonation gave hydroxyboranes **64a** and **64b**. The characters of the carbonyl groups in the borylcarbonyl compounds **60a**, **60b**, **61**, **62**, and **63a**, which were obtained from the reaction of boryllithiums **35a** and **35b**, were investigated by X-ray crystallography, IR, and ¹³C NMR spectroscopy to show that the boryl substituent weakened the C=O bond when compared to carbon substituted analogues.

Introduction

Lithium salts of the second row *p*-block elements, LiF, LiOH, LiNH₂, and CH₃Li,¹ are widely used as anionic nucleophiles in organic and inorganic syntheses. However, the corresponding lithium salts of boron, boryllithium, have not been synthesized or characterized yet.² Boryllithium may be considered as a boryl anion in which the boron center has an anionic charge because of the wide difference between the electronegativities of boron (2.04) and lithium (0.96).³ In conventional boron chemistry, boron-containing reagents are usually considered as electrophiles, because of their vacant *p*-orbital at the boron center and the low-electronegativity of the boron atom. Therefore, using boryllithium as a boron nucleophile in synthetic chemistry may lead to the “umpolung” concept. Unlike other lithium salts of *p*-block elements, the boron atom in boryllithium has only six valence electrons without satisfaction of the octet rule, where

the boron atom can be considered as an isoelectronic analog of singlet carbene.

Since 1952, there have been several reports on alkali metal salts of boryl anion as a proposed intermediate (Scheme 1). Auten and Kraus reported reduction of (*n*-Bu)₂BCl (**1**) using a sodium–potassium alloy to generate the corresponding boryl anion, (*n*-Bu)₂B[−]M⁺ (**2**, M = Na or K),⁴ which could be trapped with methyl iodide to form (*n*-Bu)₂BMe (**3**). However, modern spectroscopic characterization of the methylated product was not available then. After 24 years, Smith reported that **2** had rearranged to the corresponding boron-stabilized carbanion **4** through deprotonation of the alkyl group by an anionic boron center, and then **4** aggregated to form a cyclic trimer **5** with a characterization of the hydroborate moiety by IR spectroscopy.⁵ Diphenylboryl anion **7** was proposed in the photolysis of tetraphenylborate **6**, based on the formation of biphenyl.⁶ However, Schuster proved that irradiation of **6** produce a biradical species, which rearranged to the cyclic borate **8** possessing a three-membered ring, followed by protonation to

(1) Wakefield, B. J. *Organolithium methods*; Academic Press: London, 1988.

(2) Nöth, H. In *Science of Synthesis*; Kaufmann, D. E., Matteson, D. S., Eds.; Georg Thieme Verlag: Stuttgart-New York, 2005; Vol. 6, pp 139–178.

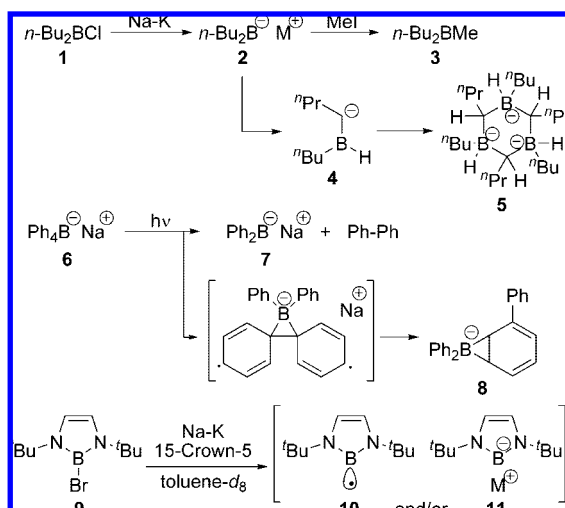
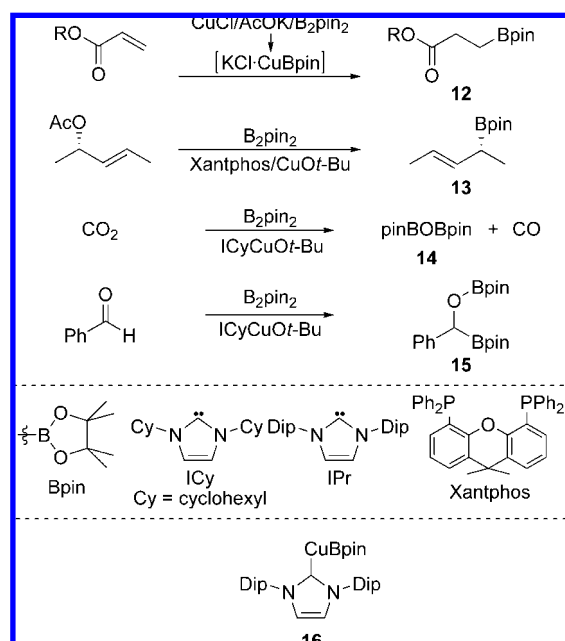
(3) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: New York, 1998.

(4) Auten, R. W.; Kraus, C. A. *J. Am. Chem. Soc.* **1952**, *74*, 3398–3401.

(5) Smith, K.; Swaminathan, K. *J. Chem. Soc., Dalton Trans.* **1976**, 2297–2300.

(6) Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Searle, R.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1967**, *89*, 5153–5157.

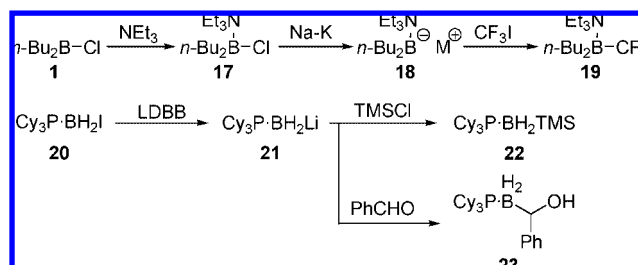
Scheme 1. Proposed Boryl Anions as Intermediates

Scheme 2. Reaction of Borylcopper as Boron Nucleophiles (Dip = 2,6-(*i*-Pr)₂C₆H₃; Cy = cyclohexyl)

form biphenyl.⁷ Recently, Weber et al. investigated the reaction of bromodihydrodiazaborole **9** with alkali metals in toluene-*d*₈.⁸ In that report, they mentioned that the intermediate of the reduction of sodium–potassium alloy would be boryl radical **10** or boryl anion **11**.

Some previously reported boron compounds which reacted as boron nucleophiles are shown in Schemes 2 and 3. The catalyst systems Cu(I)/diborane(4) reagent/oxygen ligand could mediate nucleophilic borylation of α,β -unsaturated carbonyl compounds (conjugate addition to form β -borylester **12**),⁹ allyl carbonate (S_N2' reaction to form allylborane **13**),¹⁰ CO₂ (reduction to form **14**), and benzaldehyde (1,2-diboration to form α -borylbenzyl borate **15**).^{11,12} Although most of these “nucleophilic” boron reagents have not been characterized well, a borylcopper complex, IPrCuBpin (**16**), possessing an *N*-hetero-

Scheme 3. Reaction of Base-Stabilized Boryl Anion as Boron Nucleophiles



cyclic carbene, was isolated recently.^{11a} The other case is a “base-stabilized boryl anion”; that is, triethylamine- or tricyclohexylphosphine-coordinated haloborane could be reduced using an alkali metal to form the corresponding sp³ boryl anion species with the coordination of the Lewis base to the boron atom. These species reacted with electrophiles such as CF₃I, TMSCl, and benzaldehyde in a nucleophilic manner to generate trifluoromethylborane (**19**), trimethylsilylborane (**22**), and α -borylbenzyl alcohol (**23**), respectively.^{13–15}

Boryllithium is also considered as a low-valent boron(I) species. Accessible low-valent group-14 element compounds (carbene (**24**),¹⁶ silylene (**25**),¹⁷ germylene (**26**),¹⁸ and stannylene (**27**)¹⁹) and their isoelectronic species, anionic group-13 element compounds (gallyl anion (**28**)^{20,21}), with a five-membered ring structure are shown in Figure 1. As shown in Scheme 4, gallyl anion **28** could be prepared by a reduction of the corresponding

- (9) (a) Takahashi, K.; Ishiyama, T.; Miyaura, N. *Chem. Lett.* **2000**, 29, 982–983. (b) Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2001**, 625, 47–53. (c) Canesi, S.; Bouchu, D.; Ciufolini, M. A. *Angew. Chem., Int. Ed.* **2004**, 43, 4336–4338. (d) Kabalka, G. W.; Wu, Z. Z.; Yao, M. L.; Natarajan, N. *Appl. Radiat. Isot.* **2004**, 61, 1111–1115. (e) Ciufolini, M. A.; Canesi, S.; Ousmer, M.; Braun, N. A. *Tetrahedron* **2006**, 62, 5318–5337. (f) Mun, S.; Lee, J. E.; Yun, J. *Org. Lett.* **2006**, 8, 4887–4889. (g) Lee, J.-E.; Yun, J. *Angew. Chem., Int. Ed.* **2008**, 47, 145–147. (h) Dang, L.; Lin, Z.; Marder, T. B. *Organometallics* **2008**, 27, 4443–4454.
- (10) (a) Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, 127, 16034–16035. (b) Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *J. Am. Chem. Soc.* **2007**, 129, 14856–14857.
- (11) (a) Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, 127, 17196–17197. (b) Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. *J. Am. Chem. Soc.* **2006**, 128, 11036–11037. (c) Zhao, H.; Lin, Z.; Marder, T. B. *J. Am. Chem. Soc.* **2006**, 128, 15637–15643. (d) Zhao, H.; Dang, L.; Marder, T. B.; Lin, Z. *J. Am. Chem. Soc.* **2008**, 130, 5586–5594.
- (12) Most recently, asymmetric synthesis of α -amino boronate esters from aldimines was reported; see: (a) Beenan, M. A.; An, C.; Ellman, J. A. *J. Am. Chem. Soc.* **2008**, 130, 5586–5594. 1,2-Diboration of aldimine using Pt catalyst has already been known, although the mechanism is unclear. (b) Mann, G.; John, K. D.; Baker, R. T. *Org. Lett.* **2000**, 2, 2105–2108.
- (13) (a) Parsons, T. D.; Self, J. M.; Schaad, L. H. *J. Am. Chem. Soc.* **1967**, 89, 3446–3448. However, it is generally difficult when CF₃I accepts a hard nucleophile, such as carbanion, for the S_N2 reaction to proceed because of the steric and electronic repulsion between the nucleophile and the CF₃ moiety at the backside of the C–I bond. See: (b) Uemoto, T. *Chem. Rev.* **1996**, 96, 1757–1778.
- (14) Blumenthal, A.; Bissinger, P.; Schmidbauer, H. *J. Organomet. Chem.* **1993**, 462, 107–110.
- (15) Imamoto, T.; Hikosaka, T. *J. Org. Chem.* **1994**, 59, 6753–6759.
- (16) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, 361–363.
- (17) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, 116, 2691–2692.
- (18) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F. R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 1485–1488.
- (19) Gans-Eichler, T.; Gudat, D.; Nieger, M. *Angew. Chem., Int. Ed.* **2002**, 41, 1888–1891.

(7) Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, 52, 2117–2122.
 (8) Weber, L.; Schnieder, M.; Lonneck, P. *J. Chem. Soc., Dalton Trans.* **2001**, 3459–3464.

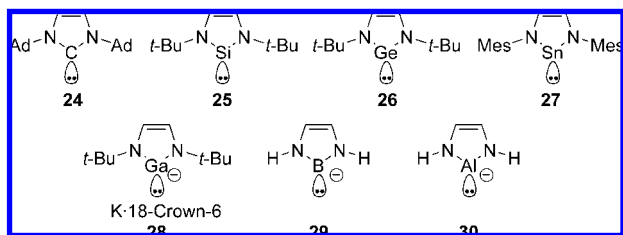
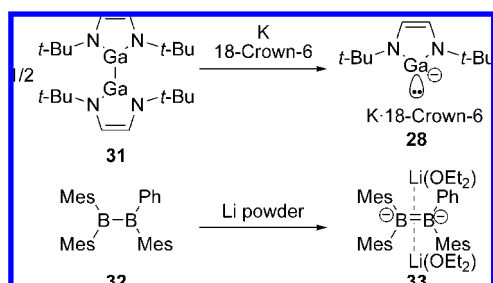
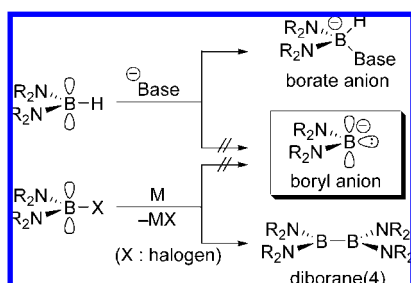


Figure 1. Low-valent group-14 and -13 element compounds possessing a five-membered *N*-containing heterocycle (Mes = 2,4,6-Me₃C₆H₃).

Scheme 4. Synthesis of Gallyl Anion and Diborane(4) Dianion



Scheme 5. Strategy for Generating a Boryl Anion



digallane(4) **31**; however, the reduction of the diborane(4) species **32** led to the formation of isolable diborane(4) dianion 2Li·(Mes)₂BB(Mes)Ph (**33**), having a B=B double bond character with π -coordination to lithium cations. Dianionic **33**

can be considered as a dimer of boryl anion, sharing four electrons between two boron atoms. The reason why boryl anion does not form from the diborane(4) dianion is that the second-row elements can form a stronger π -bond than the heavier main group elements, such as gallium.²³ A higher reactivity of boryl anion than that of the anionic heavier group-13 element compounds was also indicated by a computational study,^{24,25} which showed the higher HOMO energy of the boryl anion **29** than that of the anionic aluminum(I) species **30**.²⁵

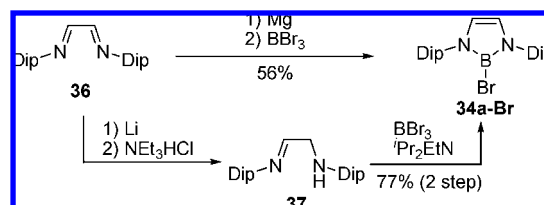
Some problems can be expected in the synthesis of boryllithium (Scheme 5). The general methods for generating organolithium compounds are deprotonation from a C–H bond and reductive dehalogenation from a C–halogen bond, but both involve difficulties in generating boryllithium. In the reaction of boryl-H with a base, it is difficult to deprotonate because the hydrogen atom usually has a hydride character, since the electronegativity of hydrogen atom is higher than that of boron atom (H: 2.20, B: 2.04).³ Furthermore, the generation of a Lewis acid–base adduct occurs in favor of deprotonation. Meanwhile, one-electron reduction of a halogen–boron bond generates a boryl radical, which is rapidly dimerized to form diborane(4) species before the second electron transfer occurs to form boryllithium.^{8,26}

Recently, we reported the synthesis of boryllithium by reduction of an *N*-heterocyclic bromoborane precursor possessing bulky 2,6-diisopropylphenyl groups on the nitrogen atoms.^{27,28} Herein, we report a further systematic study on the chemistry of boryllithium, which includes the synthesis of boryllithium from various precursors, modification of the boryllithium skeleton, solid state structures, the bonding properties of the boron–lithium bond with theoretical calculation, a broader study on their reactivity with organic electrophiles, and the carbonyl properties of the resulting borylcarbonyl compounds.

Results and Discussion

Generation of Boryllithium. Bromoborane **34a-Br** was chosen as the precursor of the corresponding boryllithium **35a**. In our previous study, **34a-Br** was synthesized by reduction of *N,N'*-diaryldiimine (**36**)²⁹ with Mg followed by an addition of BBr₃ (Scheme 6). We have also explored a more scalable procedure

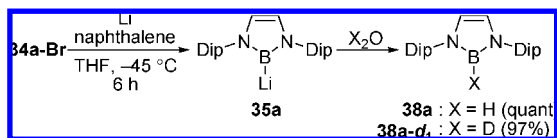
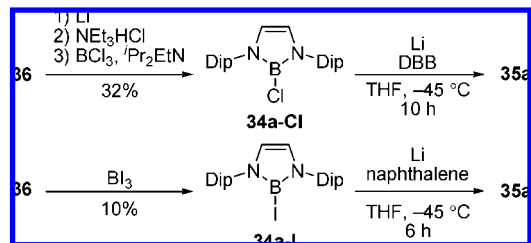
Scheme 6. Synthesis of Bromoborane **34a-Br** [Dip = 2,6-(*i*-Pr)₂C₆H₃]



for synthesis of **34a-Br** based on a report by DuMont and co-workers for the preparation of a phosphorus-containing heterocycle.³⁰ A dilithium diamide, derived from the same starting

- (20) (a) Schmidt, E. S.; Jockisch, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1999**, *121*, 9758–9759. (b) Baker, R. J.; Farley, R. D.; Jones, C.; Kloth, M.; Murphy, D. M. *J. Chem. Soc., Dalton Trans.* **2002**, 3844–3850.
- (21) Gallyl anions have been applied to coordination chemistry. See: (a) Jones, C.; Mills, D. P.; Rose, R. P.; Stasch, A. *Dalton Trans.* **2008**, 4395–4408. (b) Jones, C.; Rose, R. P.; Stasch, A. *Dalton Trans.* **2007**, 2997–2999. (c) Green, S. P.; Jones, C.; Mills, D. P.; Stasch, A. *Organometallics* **2007**, *26*, 3424–3430. (d) Arnold, P. L.; Liddle, S. T.; McMaster, J.; Jones, C.; Mills, D. P. *J. Am. Chem. Soc.* **2007**, *129*, 5360–5361. (e) Green, S. P.; Jones, C.; Lippert, K.-A.; Mills, D. P.; Stasch, A. *Inorg. Chem.* **2006**, *45*, 7242–7251. (f) Aldridge, S.; Baker, R. J.; Coombs, N. D.; Jones, C.; Rose, R. P.; Rossin, A.; Willock, D. J. *Dalton Trans.* **2006**, 3313–3320. (g) Jones, C.; Mills, D. P.; Rose, R. P. *J. Organomet. Chem.* **2006**, *691*, 3060–3064. (h) Jones, C.; Mills, D. P.; Platts, J. A.; Rose, R. P. *Inorg. Chem.* **2006**, *45*, 3146–3148. (i) Baker, R. J.; Jones, C.; Mills, D. P.; Murphy, D. M.; Hey-Hawkins, E.; Wolf, R. *Dalton Trans.* **2006**, 64–72. (j) Baker, R. J.; Jones, C.; Murphy, D. M. *Chem. Commun.* **2005**, 1339–1341. (k) Baker, R. J.; Jones, C.; Kloth, M. *Dalton Trans.* **2005**, 2106–2110. (l) Baker, R. J.; Jones, C.; Kloth, M.; Platts, J. A. *Organometallics* **2004**, *23*, 4811–4813. (m) Baker, R. J.; Jones, C.; Kloth, M.; Platts, J. A. *Angew. Chem., Int. Ed.* **2003**, *43*, 2660–2663. (n) Baker, R. J.; Jones, C.; Platts, J. A. *Dalton Trans.* **2003**, 3673–3674. (o) Baker, R. J.; Jones, C.; Platts, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 10534–10535. (p) Baker, R. B.; Jones, C. *Coord. Chem. Rev.* **2005**, *249*, 1857–1869.
- (22) (a) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715–2717. (b) Grigsby, W. J.; Power, P. P. *Chem. Commun.* **1996**, 2235–2236. (c) Grigsby, W. J.; Power, P. P. *Chem.—Eur. J.* **1997**, *3*, 368–375.

- (23) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463–3503.
- (24) Sundermann, A.; Reiher, M.; Schoeller, W. W. *Eur. J. Inorg. Chem.* **1998**, 305–310.
- (25) Metzler-Nolte, N. *New J. Chem.* **1998**, *22*, 793–795.
- (26) Brotherton, R. J.; McCloskey, A. L.; Petterson, L. L.; Steinberg, H. *J. Am. Chem. Soc.* **1960**, *82*, 6242–6245.
- (27) (a) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113–115. This work was highlighted in the following references. See: (b) Marder, T. B. *Science* **2006**, *314*, 64–70. (c) Braunschweig, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1946–1948.

Scheme 7. Synthesis of Boryllithium **35a**Scheme 8. Syntheses and Reduction of **34a-Cl** and **34a-I** To Form **35a** (DBB = 4,4'-Di-*tert*-butylbiphenyl)

N,N'-diaryldiimine **36** by reduction with elemental Li, was protonated by triethylammonium chloride to form aminoimine **37**. The reaction of the resulting aminoimine **37** with BBr_3 followed by addition of Pr_2EtN to trap generated HBr yielded **34a-Br** in a good yield. The preparation of boryllithium **35a** is illustrated in Scheme 7. The B–Br bond of **34a-Br** was reduced using an excess amount of lithium powder in the presence of a catalytic amount of naphthalene in THF or 1,2-dimethoxyethane (DME) at $-45\text{ }^{\circ}\text{C}$ for 6 h to form the corresponding boryllithium **35a**, showing a broad signal at δ_{B} 45.4 in the ^{11}B NMR spectrum with nearly quantitative conversion as judged by NMR spectroscopy (*vide infra*). Biphenyl or 4,4'-di-*tert*-butylbiphenyl can also be used as an electron mediator instead of naphthalene. Leaving the resulting THF solution of **35a** at room temperature for a day or adding water to the solution resulted in the formation of hydroborane **38a** in a quantitative yield, which was independently synthesized from a reaction of **34a-Br** with lithium aluminum hydride in 61% yield. The sensitivity of the THF solution of **35a** toward moisture indicates that the product seems to have an anionic boron moiety. The formation of deuterio-borane **38a-d₁** in 97% yield, using D_2O in place of water, shows that the adsorbed proton did not come from solvent THF or ligand backbone but from water.³¹ However, the THF solution of boryllithium **35a** could be stored at $-45\text{ }^{\circ}\text{C}$ for several months. Boryllithium **35a** could also be prepared with quantitative conversion from the other haloboranes, **34a-Cl** or **34a-I**, synthesized as shown in Scheme 8. Chloroborane **34a-Cl** is more attractive for large scale synthesis than **34a-Br** because of its stability against silica gel under an argon atmosphere. Although the reduction of **34a-Cl** with lithium naphthalenide requires several days to complete, using lithium 4,4'-di-*tert*-butylbiphenylide as a reducing agent reduces the reaction time to within 10 h.

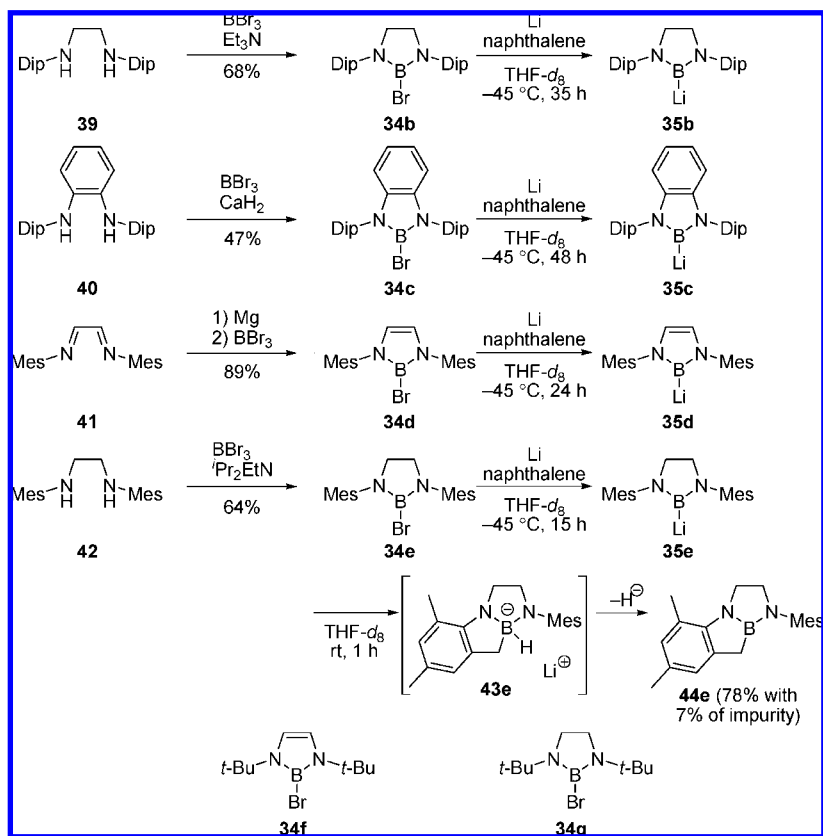
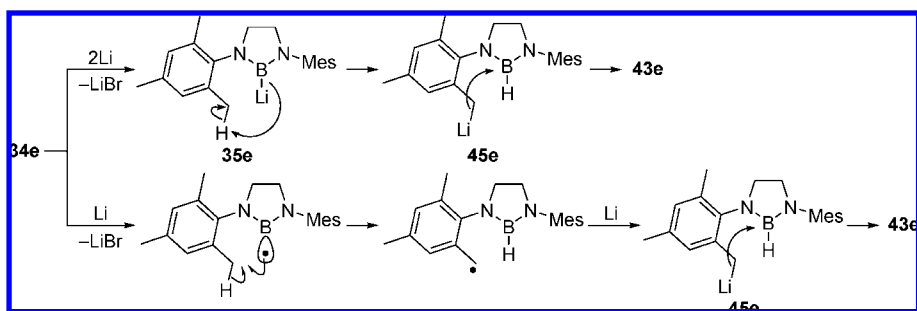
Modification of Bulky Substituents and Backbone. To find other applicable substituents and backbones to generate boryl-

lithiums, we examined modifications of the structure (Scheme 9).^{28b} We synthesized various bromoboranes having an unsaturated C=C bond, a saturated C–C bond, or a benzannulated C=C bond in the five-membered ring and Dip (2,6-diisopropylphenyl), Mes (2,4,6-trimethylphenyl), or *t*-Bu groups on each nitrogen atom as precursors for boryllithium. Reduction of these bromoboranes under the same conditions as the formation of the original boryllithium **35a** afforded the following results. Bromoboranes **34b**, **34c**, and **34d** could be reduced to the corresponding boryllithium **35b–d**, showing characteristic low-field signals (**35b**, δ_{B} 51.9; **35c**, δ_{B} 52.1; **35d**, δ_{B} 45.0) in ^{11}B NMR spectra of reaction mixtures at room temperature. In the reduction of **34e**, a low-field shifted signal of **35e** was observed as a minor product (δ_{B} 52.4, 18%, *vide infra*) at room temperature, accompanied by a major high-field signal of **43e** (δ_{B} 0.1, d, $^1J_{\text{BH}} = 64\text{ Hz}$, 82%). Hydroborate **43e** was characterized in solution by NMR spectroscopy and converted to the corresponding neutral borane **44e** (δ_{B} 39.6) during an isolation procedure through loss of hydride from the borate center. A low-temperature treatment of the reaction solution in the reduction of **34e** confirmed a quantitative formation of **35e** by low-temperature NMR spectroscopy. Two possible mechanisms for the formation of **43e** are illustrated in Scheme 10, where boryllithium **35e** adsorbed the benzylic proton to form the corresponding benzyllithium derivative **45e**. Then, the benzylic carbon of **45e** attacked the boron center having a hydrogen atom to form the corresponding hydroborate **43e**. One of these two mechanisms, a radical pathway, may have a minor or no contribution to the formation of hydroborate **43e** because of the quantitative formation of **35e** from **34e** at low temperature and clean conversion of **35e** to **43e**. The difference in the reactivities between C=C unsaturated **35d** and C–C saturated **35e** can be attributed to the difference in the flexibility of the five-membered heterocycle, because the saturated C–C bond in **35e** can rotate to make the benzylic protons of the mesityl group and the anionic boron center closer. On the other hand, no low-field shifted ^{11}B NMR signal above δ_{B} 40 was observed in the reduction of *tert*-butyl-substituted bromoboranes with an unsaturated C=C bond (**34f**) or a saturated C–C bond (**34g**), as Weber has observed the formation of diborane(4) or hydroborane in the reduction of **34e** with reducing agents such as Na/Hg,³² Na/K,⁸ or K-mirror.⁸

Crystallographic Study: Solid State Structures of Boryllithium. Crystallographic analysis of boryllithium revealed an ionic character of the boron–lithium bond in the solid state. Four structures of boryllithiums, (**35a**·DME)₂, **35a**·(THF)₂, **35b**(THF)₂, and **35c**(THF)₂, were observed in single crystals obtained at $-45\text{ }^{\circ}\text{C}$ from a hexane solution of the crude product in the reduction using DME or THF solvent (Figures 2–5). The selected structural parameters are summarized in Table 1 with reference compounds, calculated free boryl anions (**opt-46a–c**), and crystallographically analyzed hydroboranes (**38a–c**), which were independently synthesized from **34a-Br**, **34b,c** with LiAlH_4 , *N*-heterocyclic carbenes (**47**,³³ **49**,³⁴ **51**³⁵), and their

(28) (a) Yamashita, M.; Suzuki, Y.; Segawa, Y.; Nozaki, K. *Chem. Lett.* **2008**, *37*, 802–803. (b) Segawa, Y.; Yamashita, M.; Nozaki, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6710–6713.
 (29) Abrams, M. B.; Scott, B. L.; Baker, R. T. *Organometallics* **2000**, *19*, 4944–4956.
 (30) Burck, S.; Gudat, D.; Nieger, M.; Du Mont, W.-W. *J. Am. Chem. Soc.* **2006**, *128*, 3946–3955.
 (31) In a previous communication, we reported 82% yield. We have reexamined more carefully to prevent the decomposition of **35a** with water and moisture to get 97% yield. Detail for the experimental procedure is described in the Supporting Information.

(32) Weber, L.; Dobbert, E.; Stammer, H. G.; Neumann, B.; Boese, R.; Blaser, D. *Chem. Ber.* **1997**, *130*, 705–710.
 (33) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523–14534.
 (34) Arduengo, A. J.; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027–11028.
 (35) Korotkikh, N. I.; Raenko, G. F.; Pekhtereva, T. M.; Shvaika, O. P.; Cowley, A. H.; Jones, J. N. *Russ. J. Org. Chem.* **2006**, *42*, 1822–1833.

Scheme 9. Reduction of Various Bromoboranes (Dip = 2,6-(*i*-Pr)₂C₆H₃; Mes = 2,4,6-Me₃C₆H₂)**Scheme 10.** Two Possible Mechanisms for the Formation of Hydroborate **43e**

precursors, imidazolium salts (**48**,³³ **50**,³⁴ **52**³⁵). In (**35a**·DME)₂, boryllithium **35a** was crystallized with DME molecules, which chelated to the central lithium atom, and one of two oxygen atoms bridged two lithium atoms to form a dimeric structure with a four-coordinate lithium atom. Another structure of **35a**, **35a**·(THF)₂, contained two THF molecules coordinated to the central lithium atom to form a three-coordinate lithium atom. Other structures of boryllithiums, **35b**·(THF)₂ and **35c**·(THF)₂, which have a saturated C—C bond or a benzannulated C=C bond in the five-membered ring, have two THF molecules coordinated to the central lithium atom, as does **35a**·(THF)₂. The existence of a 2c-2e boron–lithium bond and sp² hybridization around the planar boron center in all crystal structures revealed that the products were boryllithiums, where the lithium atom directly bonded to the boryl group. The boron–lithium bond lengths [2.291(6) Å in (**35a**·DME)₂; 2.276(5) Å in **35a**·(THF)₂; 2.271(4) Å in **35b**·(THF)₂; 2.218(9) Å in **35c**·(THF)₂] were 8.5, 7.9, 7.6, and 5.1% longer than the sum of the covalent radii (2.11 Å),³ respectively. A similar elongation of the C—Li bond was reported in the crystal structure of 2,3,4,5-

C₆HF₄Li·(THF)₃.³⁶ The C—Li bond [2.136(5) Å] in 2,3,4,5-C₆HF₄Li·(THF)₃ was also longer than the sum of the covalent radii (2.00 Å). In the five-membered ring, the B—N bond lengths [1.465(4) and 1.467(4) Å in (**35a**·DME)₂; 1.474(3) and 1.480(4) Å in **35a**·(THF)₂; 1.4547(18) Å in **35b**·(THF)₂; 1.474(4) Å in **35c**·(THF)₂] and the N—B—N angles [99.2(2)° in (**35a**·DME)₂; 98.7(2)° in **35a**·(THF)₂; 101.89(16)° in **35b**·(THF)₂; 100.0(3)° in **35c**·(THF)₂] are closer to those in the calculated free boryl anions **opt-46a-c** than to those in the hydroboranes **38a-c**, indicating that these boryllithiums have a boryl anion character. The relationships between boryllithiums and hydroboranes are quite similar to those between *N*-heterocyclic carbenes (**47**,³³ **49**,³⁴ **51**³⁵) and imidazolium salts (**48**,³³ **50**,³⁴ **52**³⁵), which are protonated compounds of *N*-heterocyclic carbenes. In fact, in the structures of *N*-heterocyclic carbenes, the C—N bonds are longer and the N—C—N angle is smaller than those in the imidazolium salts.

(36) Kottke, T.; Sung, K. S.; Lagow, R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1517–1519.

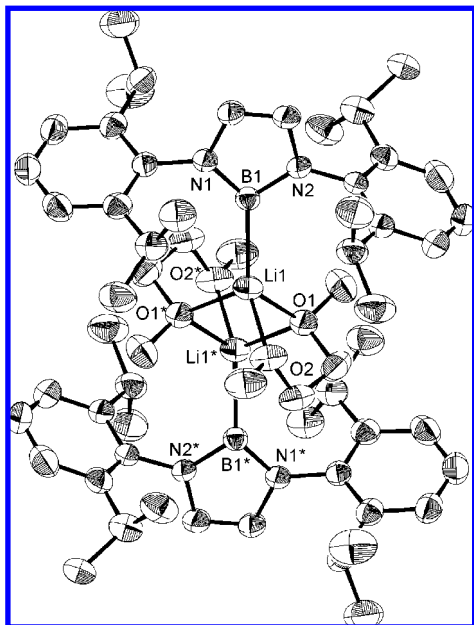


Figure 2. Crystal structure of $(35a \cdot DME)_2$ (50% thermal ellipsoids; hydrogen atoms and the minor part of the disordered moieties were omitted for clarity; half of the entire structure constitutes an asymmetric unit where the numbers with asterisks are in the second asymmetric unit).

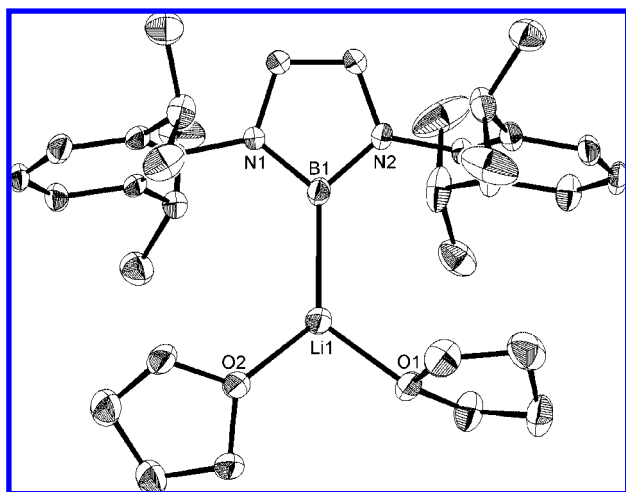


Figure 3. Crystal structure of $35a \cdot (THF)_2$ (50% thermal ellipsoids; hydrogen atoms are omitted for clarity).

NMR Spectroscopic Study: Structure of Boryllithium and the Bonding Properties of the B–Li Bond in Solution. To clarify the solution structure of boryllithium, several spectroscopic studies were performed. Dissolution of single crystals of $(35a \cdot DME)_2$ and $35a \cdot (THF)_2$ into THF- d_8 gave identical 1H , ^{13}C , and ^{11}B NMR spectra consisting of signals assignable to the N,N' -diaryldiazaborole moiety in **35a**. In the 1H NMR spectrum, two distinct methyl doublets were observed, reflecting inhibited rotation around the Ar–N bond likely due to steric repulsion. In contrast, the two 2,6-diisopropylphenyl rings are equivalent in the spectrum, indicating that there is one 2-fold rotation. The solvent molecules, which originally coordinated to the central lithium atom in the solid state, were found to dissociate from the lithium atom in solution [free DME (1 equiv) or THF (2 equiv) molecules were observed in 1H NMR spectroscopy], indicating that **35a** forms a structure ligated by some of the THF- d_8 molecules. In the ^{11}B NMR spectra, the

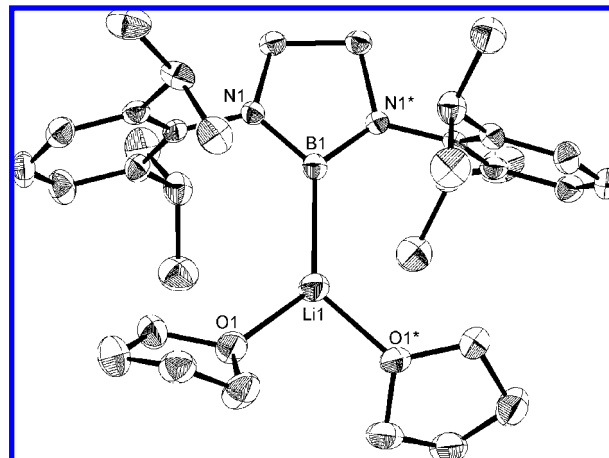


Figure 4. Crystal structure of $35b \cdot (THF)_2$ (50% thermal ellipsoids; hydrogen atoms are omitted for clarity; half of the entire structure constitutes an asymmetric unit where the numbers with asterisks are in the second asymmetric unit).

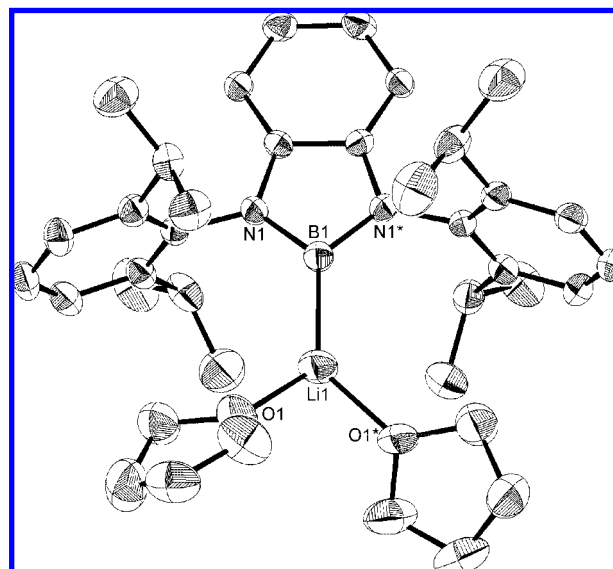


Figure 5. Crystal structure of $35c \cdot (THF)_2$ (50% thermal ellipsoids; hydrogen atoms are omitted for clarity; half of the entire structure constitutes an asymmetric unit where the numbers with asterisks are in the second asymmetric unit).

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 **38a** (22.9 ppm, half-width of $\nu_{1/2}$ = 379 Hz). It has been already reported that the ^{13}C NMR signal of N -heterocyclic carbene **53** (213.7 ppm in THF- d_8) shifts to a lower field than that of the protonated carbene (Figure 6), namely, imidazolium salt **54** (135.0 ppm in DMSO- d_6).³⁷ This low-field shift was also observed for carbene **47** (220.6 ppm in C_6D_6)³³ in comparison with imidazolium salt **48** (139.9 ppm in DMSO- d_6 , in this work), possessing the same aromatic substituent on the nitrogen atoms to boryllithium **35a** and hydroborane **38a**. Accordingly, boryllithium can be considered to have a similar electronic character to N -heterocyclic carbene; that is, the boron–lithium bond is ionic and the boron atom has a lone pair. In the other boryllithiums **35b–e**, a

(37) Arduengo, A. J.; Dixon, D. A.; Kumashiro, K. K.; Lee, C.; Power, W. P.; Zilm, K. W. *J. Am. Chem. Soc.* **1994**, *116*, 6361–6367.

Table 1. Structural Comparison between Boryllithiums and Related Compounds

opt-46a	(35a·DME) ₂	35a·(THF) ₂	38a		
B–Li (Å)	2.291(6)	2.276(5)			
B–N (Å)	1.496	1.465(4) 1.467(4)	1.474(3) 1.480(4)	1.418(3) 1.423(3)	
N–B–N (°)	97.79	99.2(2)	98.7(2)	105.25(16)	
opt-46b	35b·(THF) ₂	38b	opt-46c	35c·(THF) ₂	38c
B–Li (Å)	2.271(4)			2.218(9)	
B–N (Å)	1.473	1.4547(18) 1.457(4)	1.405(3) 1.407(3)	1.503	1.474(4) 1.420(3) 1.428(3)
N–B–N (°)	100.90	101.89(16)	109.11(17)	98.36	100.0(3) 106.64(19)
47	48	49	50	51	52
C–N (Å)	1.365(3) 1.369(3)	1.341(4) 1.339(4)	1.352(4) 1.346(6)	1.328(6) 1.312(6)	1.374(4) 1.372(4) 1.336(4) 1.322(4)
N–C–N (°)	101.4(2)	107.6(3)	104.7(3)	113.1(4)	103.8(2) 112.2(3)

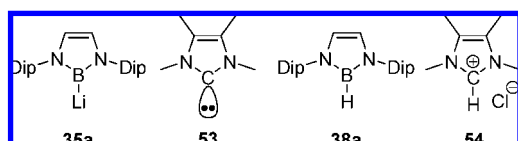


Figure 6. Boryllithium, carbene, and their protonated compounds.

similarly broadened and low-field shifted ^{11}B NMR signal was observed (δ_{B} 51.9 for **35b**, δ_{B} 52.1 for **35c**, δ_{B} 45.0 for **35d**, δ_{B} 52.4 for **35e**). Isolation of single crystals of boryllithium enabled us to remove cogenerated lithium bromide for the measurement of the ^7Li NMR spectra. In each ^7Li NMR spectrum of **35a**·(THF)₂, **35b**·(THF)₂, and **35c**·(THF)₂, a broad signal (δ_{Li} 0.46, $\nu_{1/2}$ = 36 Hz for **35a**·(THF)₂, δ_{Li} 0.68, $\nu_{1/2}$ = 35 Hz for **35b**·(THF)₂, δ_{Li} 0.44, $\nu_{1/2}$ = 50 Hz for **35c**·(THF)₂) was observed in contrast to that of the reference compound, LiCl in D₂O, which shows a very sharp signal (1.2 Hz). The large half-width may originate from the interaction of the lithium with the quadrupolar boron nucleus,³⁸ even in the THF-*d*₈ solvent. However, ^6Li enrichment of boryllithium **35a** did not lead to an appearance of spin–spin coupling between ^{11}B and ^6Li nuclei³⁹ in the ^{11}B NMR spectrum even in methylcyclohexane-*d*₁₄ solvent and even at -100 °C, probably due to the broadening of its ^{11}B NMR signal.

During low-temperature NMR measurement, the ^{11}B NMR signal of **35a** (δ_{B} 45.4 at 20 °C) in THF shifted to a higher

field (δ_{B} 38.5) at -100 °C (Figure 7). This chemical shift change was reversible between 20 and -100 °C. A similar temperature dependence on the ^{11}B NMR chemical shift was observed in methylcyclohexane-*d*₁₄. 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 ^1H NMR spectrum as broadened signals, which could be distinguished from those of free THF molecules (1.74 and 3.61 ppm). Although it is difficult to clarify the origin of the reversible chemical shift change, there are three possible reasons: the dissociation/association equilibrium of THF molecules to the lithium atom, changing aggregation of boryllithium as observed for the alkyllithium species, and changing strength of the B–Li bond, leading to a change of bond length. The direction of the σ_{22} component of the chemical shielding tensor on *N*-heterocyclic carbene **53** has been calculated to be along with the lone pair of the central carbon (Figure 8).³⁷ By analogy with carbene, boryllithium **35a** may have a similar σ_{22} component along the B–Li bond, which can be affected by a situation around the central boron atom.

DFT Study: Possible Solution Structures and the Lone Pair Character in the HOMO Orbital. To understand the characteristic B–Li bond, DFT calculation was performed. Using the crystal structure of **35a**·(THF)₂ as an initial structure, an optimized structure, **opt-35a**·(THF)₂, was obtained with no imaginary frequency in the vibrational analysis at the B3LYP/6-31+G* level.⁴⁰ The structural parameters, NPA charges of B, Li, and N atoms (B3LYP/6-31+G*), and calculated ^{11}B NMR chemical shifts⁴¹ of **opt-35a**·(THF)₂ (GAO/6-311++G**) were

(38) Rath, N. P.; Fehner, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 5345–5349.

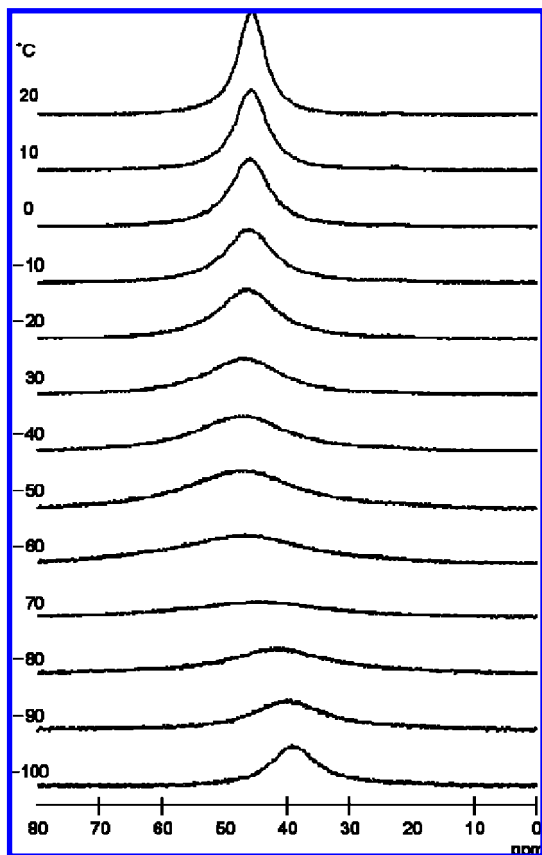


Figure 7. ^{11}B NMR spectra of single crystals of $35\text{a}\cdot(\text{THF})_2$ dissolved in THF solution from 20 to $-100\text{ }^\circ\text{C}$.

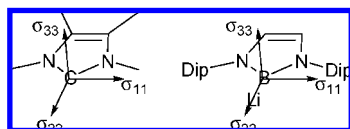


Figure 8. Shielding tensor primary component orientations in carbene **53** and boryllithium **35a**.

are summarized in Table 2 with some reference compounds such as free boryl anion **opt-46a**, nonsolvated boryllithium **opt-35a**, **opt-35a** $\cdot(\text{THF})_3$, and hydroborane **opt-38a**.⁴² The structural parameters of calculated **opt-35a** $\cdot(\text{THF})_2$ are close to the experimentally obtained values for **35a** $\cdot(\text{THF})_2$ by crystallographic study. Complexation of the free boryl anion **opt-46a** with lithium cation, giving **opt-35a**, made the B–N bond shorter and the N–B–N angle larger. Decrease of the positive charge on B and the negative charge on N were simultaneously observed by this B–Li complexation. Solvation by THF molecules to the lithium cation of **opt-35a**, giving **opt-35a** $\cdot(\text{THF})_2$ or **opt-35a** $\cdot(\text{THF})_3$, lengthened the B–Li bond,

Table 2. Structural Parameters (\AA and deg), NPA Charges of B, Li, and N Atoms, and Calculated ^{11}B NMR Chemical Shift (ppm) for Optimized Boryllithium and Related Compounds

	opt-46a	opt-35a	opt-35a $\cdot(\text{THF})_2$	opt-35a $\cdot(\text{THF})_3$	opt-38a
B–Li		2.159	2.268	2.363	
B–N	1.495	1.467	1.481	1.491	1.436
N–B–N	97.74	101.02	99.22	98.77	105.28
B	0.104	0.032	0.072	0.084	0.656
Li		0.769	0.755	0.768	
N	-0.770	-0.712	-0.728	-0.742	-0.663
δ_{B}	51.3	36.1	41.4	56.9	19.6

where the positive charge of the central boron atom increased. In all cases, nitrogen atoms directly connected to the boron atom accepted the negative charge of “boryl anion” to stabilize these boryllithiums and the free boryl anion, as Schleyer et al. indicated the stabilization effect of nitrogen atoms through their π -donor and σ -acceptor characters.⁴³ The calculated ^{11}B NMR chemical shifts for **opt-35a** $\cdot(\text{THF})_2$ (δ_{B} 41.4) and **opt-35a** (δ_{B} 36.1) were close to the two experimental values at $20\text{ }^\circ\text{C}$ (δ_{B} 45.4) and $-100\text{ }^\circ\text{C}$ (δ_{B} 38.5). The chemical shifts for the free anion **opt-46a** (δ_{B} 51.3) and **opt-35a** $\cdot(\text{THF})_3$ (δ_{B} 56.9) did not reproduce the experimental values. Since it is difficult to consider that the free boryllithium **opt-35a** can exist in the THF solution, boryllithium **35a** may exist as **35a** $\cdot(\text{THF})_2$ in THF solution. The HOMOs of the free phenyl anion (Ph^-), free boryl anion **opt-46a**, and **opt-35a** $\cdot(\text{THF})_2$ are shown in Figure 8. Two free anions, Ph^- and **opt-46a**, have similar shapes of HOMO, reflecting the lone-pair character of the central carbon and boron atom, respectively. Complexation of **opt-46a** with Li and solvation of two THF molecules to form **opt-35a** $\cdot(\text{THF})_2$ 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-38a** (Figure 9) 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 this orbital become the HOMO over the π -orbital of diazaborole, indicating a 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–Li⁴⁴ bonds by AIM analysis.^{45,46} Small $\rho(r)$ values (0.02889 e/a_0^3) and positive $\nabla^2\rho(r)$ values (0.08409 e/a_0^5) at the bond critical point of the B–Li bond in **opt-35a** $\cdot(\text{THF})_2$ as alkylolithiums were calculated to have a polar C–Li bond.⁴⁷ This result clearly indicates a similar bonding character of the B–Li bond in boryllithium **35a** to that of the C–Li bond in alkylolithium.

Reaction of Boryllithium with Electrophiles. In addition to our preliminary results for the reactivity of boryllithium, we performed a systematic study on the reactivity of boryllithium **35a** with general organic electrophiles (Scheme 11). Boryl-

(39) Del Bene, J. E.; Elguero, J. *Magn. Reson. Chem.* **2007**, *45*, 484–487.
 (40) A four-membered bridging structure consists of $-(\text{Li}-\text{B})_2-$, which corresponds to the $-(\text{Li}-\text{C})_2-$ structure observed for alkylolithium species, which is less probable because of the bulky substituents on the boron center.
 (41) The optimized B_2H_6 molecule at B3LYP/6-31+G* was used as a reference (δ_{B} 16.6) for the ^{11}B NMR chemical shift (GIAO/B3LYP/6-311++G**). The chemical shift for B_2H_6 in the gas phase was reported in the following reference: Onak, T. P.; Landesman, H.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533–1535.
 (42) A structure with one THF molecule, **opt-35a** $\cdot(\text{THF})_1$, could not be optimized to the minimum.

(43) Wagner, M.; van Eikema Hommes, N. J. R.; Nöth, H.; Schleyer, P. v. R. *Inorg. Chem.* **1995**, *34*, 607–614.
 (44) Lambert, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129–1140.
 (45) Bader, R. F. W. *Atoms In Molecules—A Quantum Theory*; Oxford University Press: New York, 1990.
 (46) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893–928.
 (47) This result is consistent with the fact that the previously reported AIM analyses on nonsolvated alkylolithiums have ionic C–Li bonds. See: (a) Bader, R. F. W.; Macdougall, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 6788–6795. (b) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909–5916.

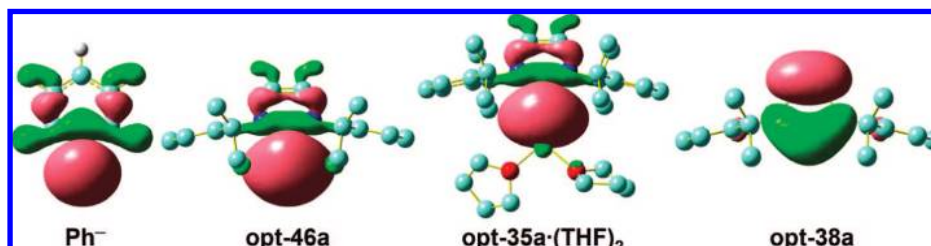
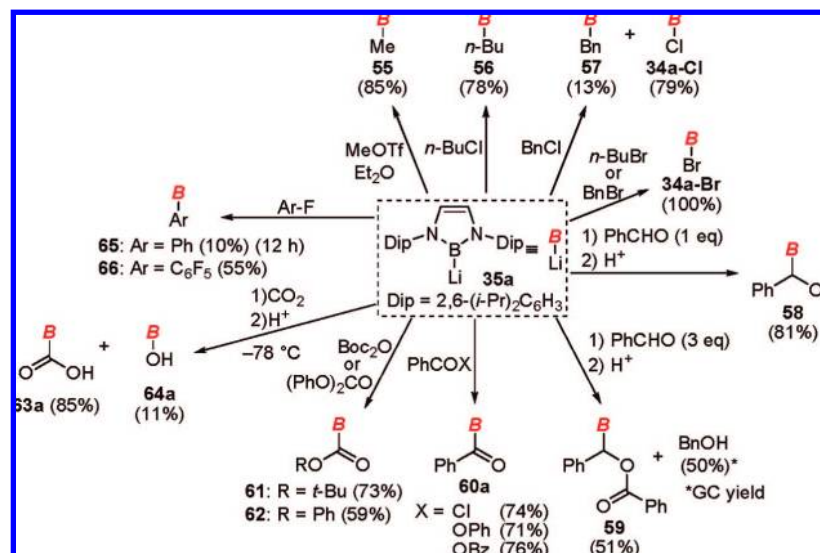


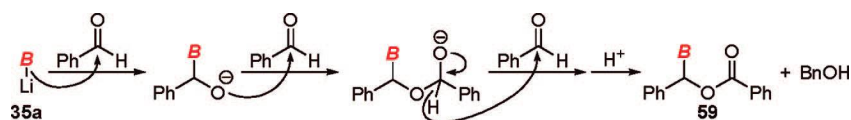
Figure 9. HOMOs of Free Phenyl Anion (Ph^-), **opt-46a**, **opt-35a**·(THF)₂, and **opt-38a**.

Scheme 11. Reactions of Boryllithium **35a** with Various Electrophiles^a



^a General conditions: THF, room temperature, 10 min, unless otherwise noted. All yields were determined by ¹H NMR compared with an internal standard.

Scheme 12. Plausible Mechanism for the Formation of α -Borylbenzyl Benzoate **59**



lithium reacted with methyl trifluoromethanesulfonate, 1-chlorobutane, or benzyl chloride to form corresponding alkylborane derivatives **55**, **56**, and **57**, but in the case of benzyl chloride, the chlorination product **34a-Cl** was also generated as a major compound, probably due to the halophilic attack or single electron transfer from **35a** to benzyl chloride including a radical chain reaction. Reaction with more reactive *n*-butyl bromide or benzyl bromide afforded the bromoborane **34a-Br** as the sole product. The reaction with carbonyl compounds gave the corresponding products in the same way that carbanions react. The reaction with 1 equiv of benzaldehyde followed by protonation formed α -borylbenzylalcohol **58** in 81% yield,^{48,49} while the reaction with 3 equiv of benzaldehyde afforded α -borylbenzyl benzoate **59** in 51% yield. The formation of **59** can be explained by the following two-step reaction: insertion of the second benzaldehyde molecule into the lithium–oxygen bond of α -borylbenzylalkoxide intermediate, followed by an intermolecular hydride transfer to the third benzaldehyde molecule to form lithium benzylalkoxide in the Oppenauer oxidation manner (Scheme 12).⁵⁰ The reaction with benzoyl

chloride, phenyl benzoate, and benzoic anhydride gave a substituted product benzoylborane **60a**⁵¹ in good yields. The X-ray crystallographic study of **58** and **60a** (Figures 10 and 11) revealed that an oxygen atom does not interact (intra- or intermolecularly) with the central boron atom to form three- or six-membered rings and that there is no intermolecular hydrogen bonding,⁵² probably due to the sterics of the two 2,6-diisopropylphenyl groups on nitrogen atoms. The reaction with anhydrous carbonates afforded the corresponding borylcarboxylate ester products, **61** and **62**, for both *t*-Bu and Ph groups. Reaction with carbon dioxide followed by protonation gave a borylcarboxylic acid, **63a**, in a high yield with a small amount of

(48) Several α -borylmethanol derivatives were synthesized by $\text{S}_{\text{N}}2$ reaction of halomethylborane with benzylaldehyde followed by deprotection. See: Singh, R. P.; Matteson, D. S. *J. Org. Chem.* **2000**, *65*, 6650–6653.

(49) Catalytic diboration of aldehyde to form α -boryl alcohol was also reported. See, refs 11b and 11d.

(50) Lithium alkoxides generated from *N,N*-dimethylformamide and carbonyl compounds were reported to transfer a hydride to benzaldehyde or benzophenone in Oppenauer oxidation fashion. See: (a) Screttas, C. G.; Steele, B. R. *J. Org. Chem.* **1988**, *53*, 5151–5153. The related Mg–Oppenauer oxidation reactions were also reported. See: (b) Meerwein, v. H.; Schmidt, R. *Liebigs Ann. Chem.* **1925**, *444*, 221–238. (c) Byrne, B.; Karras, M. *Tetrahedron Lett.* **1987**, *28*, 769–772. (d) Kloetzing, R. J.; Krasovskiy, A.; Knochel, P. *Chem.–Eur. J.* **2007**, *13*, 215–227.

(51) Yamashita, M.; Suzuki, Y.; Segawa, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 9570–9571.

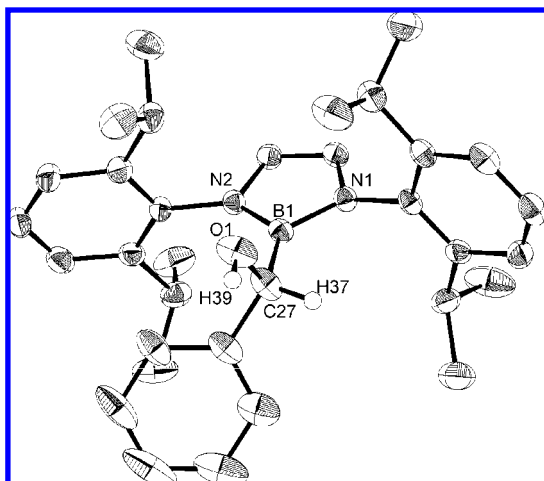


Figure 10. Crystal structure of **58** (50% thermal ellipsoids; all hydrogen atoms except OH and benzylic H and minor parts of the disordered moieties were omitted for clarity).

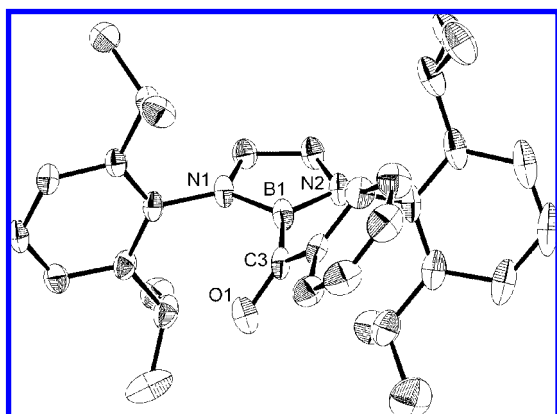


Figure 11. Crystal structure of **60a** (50% thermal ellipsoids; hydrogen atoms are omitted for clarity).

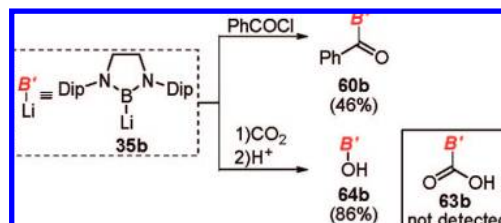
byproduct, hydroxyborane **64a** (*vide infra*). Boryllithium **35a** also reacted with fluoroarenes. The reaction with PhF yielded phenylborane **65** in a low yield because the reaction is slower than the decomposition of boryllithium. However, the reaction with C₆F₆ afforded a pentafluorophenylborane **66** in a moderate yield within a shorter reaction time.⁵³

Some reactions of saturated boryllithium **35b** with electrophiles were also examined (Scheme 13). The reaction with benzoyl chloride generated benzoylborane **60b** in a good yield. However, the reaction with CO₂ did not give any borylcarboxylic acid **63b**, and hydroxyborane **64b** was found as the sole product instead, which is in contrast to the reaction of **35a** with CO₂, giving hydroxyborane **64a** as a minor product. A plausible mechanism for the formation of these unexpected products, hydroxyboranes **64a** and **64b**, is shown in Scheme 14. The reaction of the boryl anion with CO₂ formed the corresponding borylcarboxylate anion **67**, the negatively charged carboxylate oxygen directly interacted with a vacant p-orbital of the boron

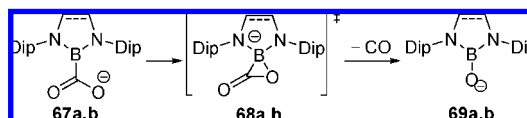
(52) Diaminoboryllithium [(H₂N)₂BLi] was calculated to react with formaldehyde to form a three-membered ring structure consisting of B, C, and O atoms. See ref 44. Acylborane [R₂BC(=O)R'] has been postulated to dimerize to form a six-membered ring structure consisting of B, C, and O atoms. See: (a) Schmid, G.; Nöth, H. *Chem. Ber.* **1968**, *101*, 2502–2505.

(53) Sun, H.; DiMaggio, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 2050–2051.

Scheme 13. Reactions of C–C Saturated Boryllithium **35b** with Carbonyl Compounds (NMR Yield)



Scheme 14. Plausible Mechanism (a, Unsaturated; b, Saturated) for the Formation of Hydroboranes **62a** and **62b**



atom to form the three-membered ring transition state **68**, and the following loss of carbon monoxide gave the boronate anion **69**, which can be protonated to afford the hydroxyboranes **64a** and **64b**. A similar reaction pathway was reported in the computational study^{11c} of Cu-catalyzed deoxygenation of carbon dioxide in the presence of a diborane(4) reagent.^{11a} The lower reactivity of borylcarboxylate **67a** in the rearrangement may be explained by a loss of aromaticity in the transition state **68a** that would destabilize the transition state more than the corresponding **68b**.

A series of borylcarbonyl compounds, **60a**, **60b**, **61**, **62**, and **63a**, are the first examples of fully characterized acylborane,⁵⁴ base-free borylcarboxylate ester, and base-free borylcarboxylic acid.⁵⁵ Table 3 shows the $\nu_{\text{C=O}}$ wavenumbers in the IR spectra and C=O bond lengths of the obtained borylcarbonyl compounds in the solid state along with those of the corresponding benzophenone,⁵⁶ benzoic acid,⁵⁷ and its phenyl⁵⁸ or *t*-butyl esters.^{56b} The $\nu_{\text{C=O}}$ wavenumbers of all the boryl derivatives are smaller, and the C=O lengths are longer than those of the corresponding phenyl derivatives, indicating weaker C=O bond strengths in borylcarbonyls. A similar tendency was also observed for silylcarbonyl derivatives (1618 cm⁻¹ for PhCO-SiMe₃, 1646 cm⁻¹ for HOCOSiMe₃).^{59,60} In CHCl₃ solution, borylcarboxylic acid **63a** showed two types of C=O vibration, which indicates that **63a** has an equilibrium between monomeric and dimeric structures in solution. Table 4 shows the ¹³C NMR chemical shift for carbonyl carbons of borylcarbonyl compounds

(54) Preparation of *n*-Bu₂BCOPh and *n*-Bu₂BCO₂Et has been proposed; however, there was no modern spectroscopic characterization. See ref 52.

(55) (a) Base-stabilized esters have been widely explored, mainly as a boron analogue of α -amino acid derivatives with hydroborate structure instead of α -carbon. See: Gabel, D.; El-Zaria, M. B. Product subclass 19: Carboxyboranes and Related Derivatives. In *Science of Synthesis*; Kaufmann, D. E., Matteson, D. S., Eds.; Georg Thieme Verlag: Stuttgart-New York, 2005; Vol. 6, pp 563–583.

(56) (a) The structure was deposited to Cambridge Crystallographic Data Centre (CCDC-245188) as a private communication (2004) by Coppens, P., and Moncol, J. (b) SDBSWeb: <http://www.aist.go.jp/RIODB/SDBS/> (National Institute of Advanced Industrial Science and Technology, 2007/03/06).

(57) Bruno, G.; Randaccio, L. *Acta Crystallogr., Sect. B* **1980**, *36*, 1711–1712.

(58) Adams, J. M.; Morsi, S. E. *Acta Crystallogr., Sect. B* **1976**, *32*, 1345–1347.

(59) Picard, J. P.; Calas, R.; Dunogues, J.; Duffaut, N.; Gervail, J.; Lapouyade, P. *J. Org. Chem.* **1979**, *44*, 420–424.

(60) Steward, O. W.; Dziedzic, J. E.; Johnson, J. S. *J. Org. Chem.* **1971**, *36*, 3475–3480.

Table 3. Carbonyl Vibrations (cm^{-1}) and the C=O Bond Distances (Å) of Borylcarbonyl Compounds Compared with Those of Reference Compounds

compd	KBr disk	CHCl_3 soln	C=O	compd	KBr disk	C=O
60a	1618	1628	1.241(2)	PhCOPh	1655	1.223(3)
60b	1638	1638	1.237(2)			
61	1690	1680	1.213(2)	PhCO_2^tBu	1713	
62	1719	1713	1.204(2)	PhCO_2Ph	1729	1.194(6)
63a	1666	1672, 1709		PhCO_2H	1689	1.252(2)

Table 4. ^{13}C NMR Chemical Shifts of the Borylcarbonyl Compounds with Those of Reference Compounds

compd	δ_c (C_6D_6)	compd	δ_c (C_6D_6)	compd	δ_c (C_6D_6)
60a	218.7	PhCOPh	195.2	PhCOCH_3	196.6
60b	221.0				
61	174.4	PhCO_2^tBu	165.0	PhCONMe_2	170.7
62	172.5	PhCO_2Ph	164.4	PhCOOMe	166.7
63a	181.6	PhCO_2H	172.7	PhCOF	157.4

with the same set of reference compounds and p-block element substituted benzoyl compounds.⁶¹ In the ^{13}C NMR spectra, carbonyl peaks of **60a**, **60b**, **61**, **62**, and **63a** appeared in a lower field than those of the corresponding benzophenone and benzoic acid derivatives. The carbonyl group of **60a** attached to a boron atom resonates in the lowest field among the p-block element-substituted benzoyl derivatives ($\text{B} > \text{C} > \text{N} > \text{O} > \text{F}$). Although the reason why **60a** has the lowest field signal is not clear, the boron atom may significantly affect the paramagnetic term to determine the carbonyl ^{13}C chemical shift. A low-field shift of the carbonyl signal has also been reported for benzoylsilane derivatives,^{59,62} in which the silicon atom has a lower electronegativity, similar to that of the boron atom, than that of the carbon atom (C, 2.50; B, 2.04; Si, 1.90).³

Conclusion

A series of lithium salts of boryl anion, boryllithiums, were synthesized and characterized by NMR spectroscopy and crystallographic analysis. Reduction of bromoborane **34a-Br** by lithium naphthalenide provided boryllithium **35a**. Both chloroborane (**34a-Cl**) and iodoborane (**34a-I**) were also usable as precursors. Structural modification of boryllithium, using saturated C–C and benzannulated C=C backbones in the five-membered ring and mesityl groups on the nitrogen atoms, also allowed generation of the corresponding boryllithium. The solid state structures of boryllithium showed that the boron–lithium

bond is polarized where the boron atom is anionic in all $(\mathbf{35a} \cdot \text{DME})_2$, $\mathbf{35a} \cdot (\text{THF})_2$, $\mathbf{35b} \cdot (\text{THF})_2$, and $\mathbf{35c} \cdot (\text{THF})_2$ when compared to the structures of hydroborane **38a–c** and optimized free boryl anion **opt-46a–c**. Dissolution of the isolated single crystals of $(\mathbf{35a} \cdot \text{DME})_2$, $\mathbf{35a} \cdot (\text{THF})_2$, $\mathbf{35b} \cdot (\text{THF})_2$, and $\mathbf{35c} \cdot (\text{THF})_2$ in THF- d_8 showed that the boron–lithium bond remained in solution and free DME or THF molecules were observed. Temperature-dependent ^{11}B NMR chemical shift changes of **35a** were observed in THF- d_8 or methylcyclohexane- d_{14} , suggesting a change of chemical shift anisotropy around the boron center. The HOMO of **opt-35a** $\cdot (\text{THF})_2$ had a lone pair character on the boron atom, as observed for phenyllithium, whereas the HOMO of hydroborane **38a** corresponds to the π -orbital of the boron-containing five-membered heterocycle. The polarity of the B–Li bond, estimated by AIM analysis, was similar to that of alkylolithium. Boryllithiums **35a** and **35b** behave as a base or a boron nucleophile in reaction with organic electrophiles via deprotonation, $\text{S}_{\text{N}}2$ -type substitution, halogen–metal exchange or electron-transfer, 1,2-addition to a carbonyl group, and $\text{S}_{\text{N}}\text{Ar}$ reaction. In the case of the reaction with CO_2 , intramolecular cyclization followed by CO elimination from borylcarboxylate anion took place to afford the corresponding boronate, which could be protonated to give hydroxyboranes **64a** and **64b**. The characters of a carbonyl group in the borylcarbonyl compounds **60a**, **60b**, **61**, **62**, and **63a**, which were obtained from the reaction of boryllithiums **35a** and **35b**, were investigated by X-ray crystallography, IR, and ^{13}C NMR spectroscopy to show that the boryl substituent weakened the C=O bond, when compared to their carbon substituted analogues.

Acknowledgment. The authors thank Professors Norihiro Tokitoh and Takahiro Sasamori for data processing of $(\mathbf{35a} \cdot \text{DME})_2$. This work was supported by KAKENHI (No. 17065005 for “Advanced Molecular Transformations of Carbon Resources”, No. 19027015 for “Synergy of Elements”, Nos. 18750027 and 20-9103) from MEXT, Japan, and by the Global COE Program for “Chemistry Innovation”. Computer resources for theoretical calculation were provided by the Research Center for Computational Science in the National Institutes of Natural Sciences. Y. Segawa acknowledges a JSPS fellowship for young scientists.

Supporting Information Available: Details for all experimental procedures, X-ray crystallography, and computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(61) The ^{13}C chemical shifts in C_6D_6 were measured with commercially available chemicals.

(62) Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Organometallics* **1982**, *1*, 994–998.