Crystal Structure of Boryllithium with Two THF Molecules and DFT Analysis of Its Property as a Boryl Anion

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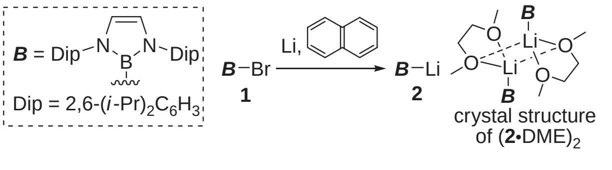
The second crystal structure of boryllithium **2** with two coordinating THF solvent molecules was obtained. The ^{11}B NMR chemical shift of a THF solution, made by dissolving single crystals of **2**•$(THF)_2$ in THF-d_8, significantly and reversibly changed depending on temperature (from 20 to −100 °C). The calculated ^{11}B chemical shift by GIAO method was close to two experimental values. The character of the sp^2 lone pair on the boron center in **opt-2**•$(THF)_2$ was shown to be similar to those in the calculated free phenyl anion and boryl anion. AIM analyses for **opt-2**•$(THF)_2$ suggested that the B–Li bond of boryllithium is polarized, similar to the C–Li bond of alkyllithium.

Aggregation of alkyllithium molecules in solution, in solid state, or in gas phase have been widely investigated by experimental and theoretical studies.[1] In general, alkyllithiums form aggregates in solution and solid state,[2] while a THF solution of bulky alkyllithiums, such as *tert*- or *sec*-butyllithium, contains monomeric species as a major component.[3] In the case of phenyllithium, a similar monomeric species is known as a minor component at low concentration in THF.[3,4]

On the other hand, we recently have succeeded to prepare boryllithium, a boron analogue of alkyllithium, by reduction[5] of an appropriate bromoborane precursor **1** (Scheme 1).[6,7] In that report, the solid-state structure of (**2**•DME)$_2$ contains four-coordinate Li atom with bridging DME to form a dimeric structure. Dissolution of crystalline (**2**•DME)$_2$ into THF-d_8 led to the appearance of free DME signals in its ^{1}H NMR spectrum. This result indicated that THF-d_8 molecules replaced coordinating DME molecules at the lithium center. However, there was no detailed information of THF-coordinated structure of boryllithium in contrast to the structure of alkyllithiums which have been widely investigated with THF coordination. Herein, we report a monomeric crystal structure of boryllithium coordinated by THF, temperature-dependent ^{11}B NMR chemical shift of boryllithium, and similarity between boryllithium and phenyllithium.

A new crystal structure of boryllithium, namely, **2**•$(THF)_2$, was obtained as its monomeric form. A residue from a reaction mixture in the reduction of **1** with lithium naphthalenide in THF was dissolved in hexane and cooled down to −45 °C to afford colorless single crystals of **2**. X-ray analysis of the crystals revealed three-coordinate lithium atom with two THF molecules (Figure 1).[8,9] The selected bond lengths and angles of **2**•$(THF)_2$ are summarized in Table 1 with reference compounds.[6] The boron–lithium bond in **2**•$(THF)_2$ is longer than the sum of covalent radii (2.11 Å)[10] as was observed for (**2**•DME)$_2$.[6] Similar elongation of a C–Li bond was reported in the crystal structure of 2,3,4,5-C_6HF_4Li•$(THF)_3$.[11] Standard deviation for B–Li bonds in both **2**•$(THF)_2$ and (**2**•DME)$_2$ showed no significant difference in these bond distances. The B–O bonds in **2**•$(THF)_2$ were apparently shorter than those in (**2**•DME)$_2$ reflecting that decreasing the number of oxygen atoms coordinating to the central lithium atom made the lithium atom more positive.[12] The B–N bond lengths and N–B–N bond angles in **2**•$(THF)_2$ were close to free boryl anion **4** rather than those in (**2**•DME)$_2$. Thus, the boron atom in **2**•$(THF)_2$ is also negatively charged as (**2**•DME)$_2$.

Dissolution of **2**•$(THF)_2$ into THF-d_8 afforded identical ^{1}H, ^{11}B, and ^{13}C NMR spectra to those of a THF-d_8 solution of



Scheme 1. Synthesis of boryllithium **2** and its crystal structure with coordinated DME molecules.

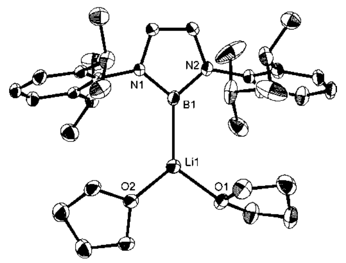
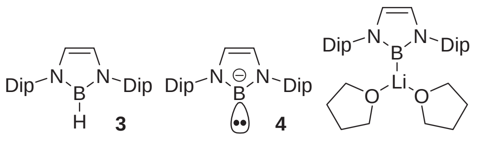


Figure 1. Crystal structure of **2**•$(THF)_2$ (50% thermal ellipsoids, hydrogen atoms are omitted for clarity).

Table 1. Structural comparison of boryllithiums and reference compounds (**4** and **opt-2**•$(THF)_2$ were optimized at B3LYP/6-31+G(d) level).



3 4

opt-2•(THF)$_2$

	2•(THF)$_2$ (X-ray)	(**2**•DME)$_2$ (X-ray)	**3** (X-ray)	**4**	**opt-2**•(THF)$_2$
B–Li/Å	2.276(5)	2.291(6)			2.270
B–N/Å	1.474(3)	1.465(4)	1.418(3)	1.496	1.480
	1.480(4)	1.467(4)	1.423(3)	1.496	1.481
B–O/Å	1.913(5)	2.002(6)			1.968
	1.973(5)	2.090(6)			1.990
		2.104(6)			
N–B–N/°	98.7(2)	99.2(2)	105.25(16)	97.8	99.3

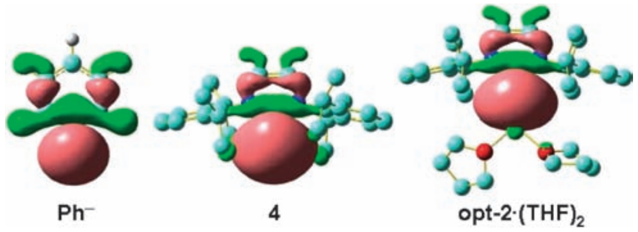


Figure 2. HOMOs of free phenyl anion (Ph^-), free boryl anion **4**, and **opt-2**·$(THF)_2$.

(**2**·DME)$_2$.[6] Cooling the solution of **2**·$(THF)_2$ down to −100 °C induced a higher-field shift of ^{11}B NMR signal to δ_B 39.3 compared to that at 20 °C (δ_B 45.4) and the shift was reversible (See Supporting Information).[20] This phenomena was also observed in its methylcyclohexane-d_{14} solution (δ_B 35.7 at −100 °C and δ_B 44.0 at 20 °C).[13] Although currently we do not have any experimental evidence to explain the temperature dependence of ^{11}B NMR chemical shift, several reasons, such as changes in solvation to the lithium atom and in B–Li bond length, may be expected.[14]

An optimized structure, **opt-2**·$(THF)_2$, was obtained by theoretical calculation.[15] Structural parameters of **opt-2**·$(THF)_2$ are similar to the corresponding experimental values in **2**·$(THF)_2$ (Table 1). The calculated ^{11}B NMR chemical shift for **opt-2**·$(THF)_2$ (δ_B 41.4) by GIAO calculation[16] was close to two experimental values. A theoretical comparison between carbanion and boryl anion provided a similarity of these two species. The HOMOs of free phenyl anion (Ph^-), free boryl anion **4**, and **opt-2**·$(THF)_2$ are shown in Figure 2. Two free anions, Ph^- and **4**, has a similar shape of HOMO reflecting lone-pair character on the central carbon and boron atom, respectively. Complexation of **4** with Li and solvation of two THF molecules did not affect the lone-pair character. This result also suggested a polar character of B–Li bond. This similarity prompted us to compare the ionic nature of B–Li and C–Li[17] bonds by using AIM analysis.[18] 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 B–Li bond as alkyllithiums were calculated to have polar C–Li bond.[19] This result clearly indicates similar bonding character of the B–Li bond in boryllithium **2** and the C–Li bond in alkyllithium.

In summary, we have obtained the second crystal structure of boryllithium **2** with two coordinating THF solvent molecules. The ^{11}B NMR chemical shift of a THF solution, made by dissolving single crystals of **2**·$(THF)_2$ in THF-d_8, significantly and reversibly changed depending on temperature (from 20 to −100 °C). The calculated ^{11}B chemical shift by GIAO method was close to two experimental values. The character of the sp^2 lone pair on the boron center in **opt-2**·$(THF)_2$ was shown to be similar to those in the calculated free phenyl anion and boryl anion. AIM analyses for **opt-2**·$(THF)_2$ suggested that the B–Li bond of boryllithium is polarized, similar to the C–Li bond of alkyllithium.

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8 CCDC-661722 contains the supplementary crystallographic data for **2**·$(THF)_2$. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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11 The C–Li bond (2.136(5) Å) in 2,3,4,5-C_6HF_4Li·$(THF)_3$ was also longer than the sum of covalent radii (2.00 Å).[10] See: T. Kottke, K. Sung, R. J. Lagow, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1517.

12 The O–Li bond (av 1.957(4) Å) in 2,3,4,5-C_6HF_4Li·$(THF)_3$ were close to those in **2**·$(THF)_2$.

13 It is noteworthy that no ^{11}B–^{6}Li coupling was observed in ^{11}B NMR spectrum when single crystals of ^{6}Li-labeled **2**·$(THF)_2$ were dissolved into methylcyclohexane-d_{14} at −100 °C probably due to the broadness of the ^{11}B NMR signal. A theoretical study about ^{11}B–^{7}Li coupling constant has been reported. See: J. E. Del Bene, J. Elguero, *Magn. Reson. Chem.* **2007**, *45*, 484.

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15 A four-membered bridging structure consists of $-(Li-B)_2-$, which corresponds to $-(Li-C)_2-$ structure observed for alkyllithium species is less probable because of the bulkyl substituents on the boron center.

16 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**). Chemical shift for B_2H_6 in gas phase was reported in the following reference. See: T. P. Onak, H. Landesman, R. E. Williams, I. Shapiro, *J. Phys. Chem.* **1959**, *63*, 1533.

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20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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