

## 論文の内容の要旨

論文題目     Synthesis and Property of Low-Oxidation State Boron Compounds  
                    (低酸化数ホウ素化合物の合成と性質)

氏     名     荒巻     吉孝

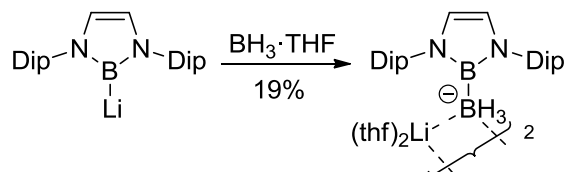
### 1. General Introduction

Since boron is group 13 element and it has three valence electrons, the oxidation state of most boron compounds is three. Boron(III) compounds are known as useful reagents in synthetic organic chemistry, for instance, hydroboranes for hydroboration and boronic acids for Suzuki-Miyaura cross-coupling reaction. Synthetically, boron compounds work as an electrophile due to a vacant p-orbital to accept electrons and their low electronegativity to induce a polarized bond where the boron atom is positively charged. On the other hand, much less has been known about boron nucleophile and boron-centered radical, and thus the methodology to introduce boryl substituents into organic compounds and transition metals is still limited. This is contrastive to the rich chemistries of carbon, which show variety of faces, such as carbocation, carbanion, carbon-centered radical, and carbene. If it becomes easy to handle boron analogue of these species, such as boryl cation, boryl anion, boryl radical, and borylene, the synthetic methods for boron compounds would be further developed explosively. Recently, boron compounds possessing low oxidation state, such as boron(I) and boron(II) were synthesized and isolated. Nozaki *et al.* reported the synthesis of boryllithium as the first isolating species of boryl anion equivalent and revealed that it worked as a nucleophile to alkyl halides, carbonyl compounds, and metal halides. This report also showed the reductive cleavage of a boron-halogen bond is a powerful tool to obtain low oxidation-state boron compounds. This method is also applied to the synthesis of the compounds having B=B bond and B  $\equiv$  B bond. Following to these examples, the author addressed the synthesis of new low oxidation-states boron compounds. In his PhD study, the author worked on the following four topics; New reactivity of the boryl anion as a nucleophile and evaluation of its strong electron donating ability (Chapter 2), New reactivity of the boryl anion as a base with molecular dihydrogen (Chapter 3), Synthesis and reactivity of a *B*-heterocyclic radical (Chapter 4), and Synthetic studies on base-stabilized borylene (Chapter 5).

## 2. Boryltrihydroborate: Synthesis, Structure, and Reactivity

Since the discovery of the boryllithium, the first isolated boryl anion, nucleophilic reaction of the boryllithium with organic compounds and transition-metals has been well studied. In contrast, nucleophilic attack of the boryl anion to main group element's center or small molecules was rather less studied. In this chapter, the reaction of nucleophilic boryl anion with borane was studied. The reaction of boryllithium with borane-THF complex afforded the first boryl-substituted borohydride, lithium boryltrihydroborate in 19% isolated yield (Scheme 1). This compound was fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallographic study. The result of NMR study indicated the hydride and  $sp^3$  boron center of borylborate were more negatively charged due to the strong electron-donating ability of boryl ligand. Therefore, the boryl ligand is considered to be much stronger  $\sigma$ -donor compared to *N*-heterocyclic carbene, which is known as strong  $\sigma$ -electron donor in organometallic chemistry. X-ray analysis revealed this borylborate formed a dimeric structure bridged by two lithium atoms with four THF molecules. Reactions of the borylborate with alkyl iodides showed that the compound underwent an ionic reduction, organometallic reduction with palladium catalyst, and radical reduction with AIBN. This reaction scope was evaluated by Curran's group at University of Pittsburgh as shown in the bottom side of Scheme 1. This result was published on *Journal of American Chemistry* in August 2nd, 2010.

**Scheme 1.** Synthetic scheme of boryl borate.



## 3. Reactions of Boryl Anions as a Nucleophile toward Molecular Dihydrogen

The splitting of molecular dihydrogen by transition-metals has been well studied as oxidative addition. Recently it has been reported the reactions of heavier main group element having low-oxidation number with dihydrogen. This means boryl anion species may react with dihydrogen molecules because they also have low-oxidation number. The reactions of boryl anion species with dihydrogen were performed and their reactivity and reaction mechanism were discussed in this chapter with the comparison to those of the other heavier main group elements, alkyllithium, and carbene.

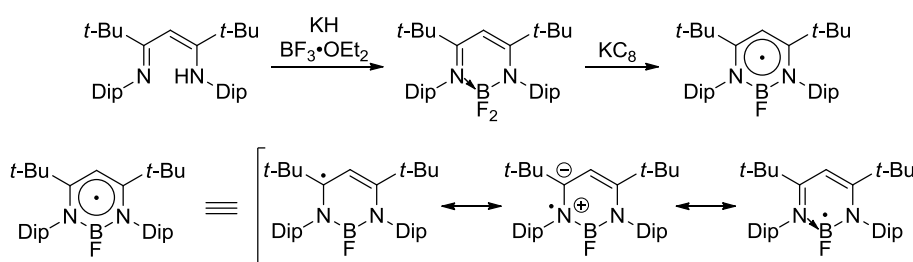
## 4. A *B*-heterocyclic Radical: Synthesis, Structure, and Reactivity

There are only few reports on the synthesis of boron-centered radical. A neutral boryl radical has only five electrons and the electron deficient boron center is unstable. This is contrastive to the other second low element-centered radical, such as carbon-, oxygen- and nitrogen-centered radical, has seven electrons. Until now, two methods are known to isolate boron centered radicals. The first one is the reduction of neutral boron compounds to form anionic boryl radical. The second one is the

coordination of a Lewis base to form base-stabilized boryl radical. Including these species, there are few examples of the isolation of boron-centered radical. This situation motivated the author to synthesize a new type of base-stabilized boryl radical.

As a precursor of a radical, aminodifluoroborane stabilized by monoanionic  $\beta$ -diiminate ligand was synthesized. The reduction of the precursor by  $\text{KC}_8$  gave an NMR silent compound and its ESR spectrum implied the product was an organic radical ( $g = 2.002$ ). The X-ray structural analysis revealed a planar structure of six-membered ring consisted by nitrogen, carbon, and  $\text{sp}^2$  hybridized boron center. The calculated spin density showed that the spin density was mainly localized on the carbon atoms and the spin density on the boron was calculated to be close to zero, however, a small contribution of boron-centered radical was observed in ESR spectroscopy. Therefore, this radical is considered to be an intermediate described by the resonance structures of allylic radical, ylidic nitrogen-centered radical and base-stabilized boryl radical. This *B*-heterocyclic radical reacted with oxygen containing compounds to give products with strong B-O bond formation. This result was published on *Journal of American Chemical Society* in December 3rd, 2012.

**Scheme 2.** Synthetic scheme of a *B*-heterocyclic radical and its resonance structures



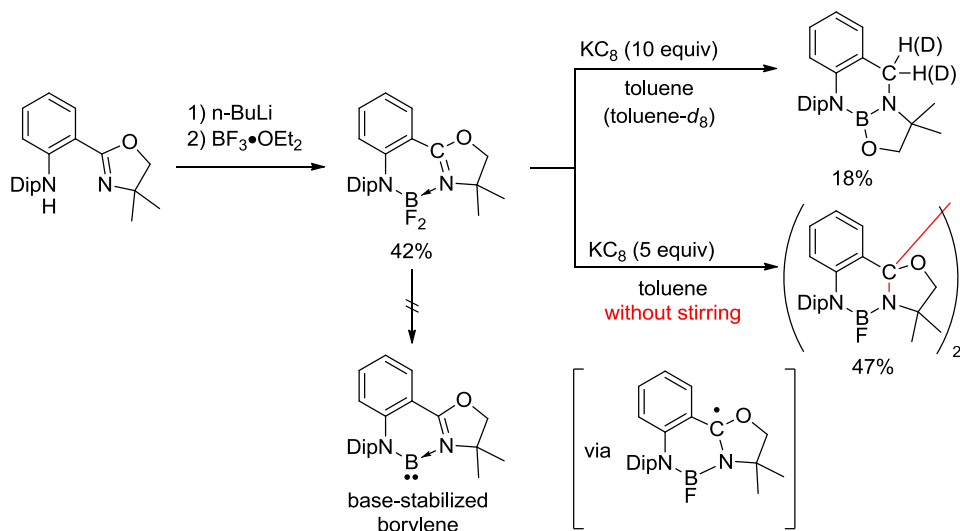
## 5. Synthetic Studies on Two-Coordinate Base-Stabilized Borylene

Borylene, which has one covalent bond and two non-bonding electrons, is a neutral boron analogue of carbene. Borylene has been known as reactive intermediate and observed by IR spectroscopy under matrix-isolation condition at low temperature. The coordination of Lewis-base could stabilize borylene to form “base-stabilized borylene”. The only example of the isolation of borylene was reported by Bertrand as the form stabilized by two CAAC ligands and it worked as a Brønsted base in the reaction with proton, but did not react with Lewis acid other than proton because the borylene center was hindered by bulky carbenes. Therefore, considering the application of base-stabilized borylene as a neutral ligand to transition-metal center, less-hindered base-stabilized borylene with one neutral ligand may be more promising. Although some transition-metal complexes possessing a base-stabilized borylene ligand, the synthetic scheme was limited and there is no report to isolate mono-base-stabilized borylene itself.

Oxazoline-coordinated aminodifluoroborane was synthesized as a precursor. The reduction with 10 equiv. of  $\text{KC}_8$  did not give the desired product and resulted in a formation of the rearrangement product. The condition using 5 equiv. of  $\text{KC}_8$  without stirring gave the dimerized compounds

(Scheme 3). Considering the reaction mechanism, the benzylic radical could be generated. To prevent the generation of benzylic radical, a new diamine ligand was synthesized. Following the previous schemes, trialkylamine-coordinated difluoroboranes were synthesized. In this case, the reduction with lithium DTBB led to a contraction of six-membered ring through a cleavage of C-N bond (Scheme 4). These results were published on *New Journal of Chemistry* in July 9th, 2010.

**Scheme 3.** Synthesis and reduction of oxazoline-coordinated difluoroborane



**Scheme 4.** Reduction of trialkylamine-coordinated difluoroborane

