Nucleophilic Boron

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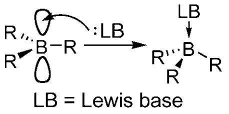
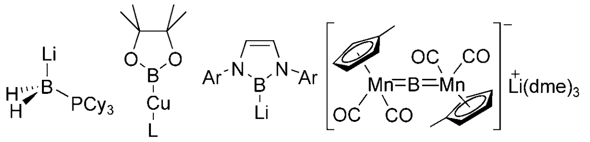
Nucleophilicity of a Base-Stabilized Borole Anion at the Boron Center

*Makoto Yamashita**

boron · carbenes · heterocycles · nucleophilicity · reduction

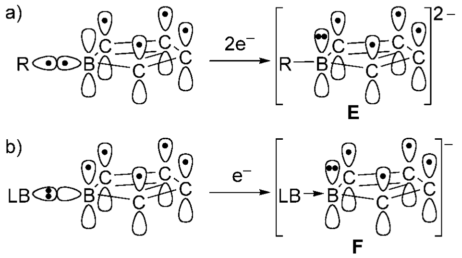




Scheme 1. Examples of nucleophilic boron reagents.

Neutral boron-containing compounds are widely used in organic and inorganic molecular chemistry. Most of these species have Lewis acidity because of a vacant p orbital that accepts a lone pair from a Lewis base. The highly acidic nature of the boron atom has limited synthetic methodologies to produce boron-containing materials. Therefore, development of nucleophilic boron reagents has been considered as one of the most important issues in boron chemistry. In this context, four types of nucleophilic boron reagents have been reported in the last two decades (Scheme 1). The first report of Lewis base stabilized dihydroboryl anion **A** described a number of reactions with various electrophiles to give the corresponding substituted products and adducts, although the reagent itself was not structurally characterized.[1] The discovery of borylcopper species **B**, prepared from copper salts and bis(pinacolato)diborane(4) by two independent groups, namely Ito and Hosomi[2] and Ishiyama and Miyaura,[3] resulted in a rapid expansion of the chemistry of nucleophilic borylcopper reagents to applications in a variety of organic syntheses.[4] A simple boryl anion, boryl lithium (**C**),[5] appeared on 2006 and showed its strong anionic nature, with nucleophilicity towards many electrophiles and transmetallation ability to form the corresponding boryl metal species. Recent research on transition metal borylene complexes[6] also gave a unique and anionic dimetalloborylene species (**D**)[7] having a nucleophilicity on the boron center to react with organic and inorganic electrophiles.

Boroles, which are isoelectronic to the cyclopentadienyl (Cp) cation and have 4π electrons that form an antiaromatic system, can generally accept two electrons into a vacant p orbital of the boron center to generate the corresponding stable 6π electron system **E** with two negative charges (Scheme 2a). This aromatic and dianionic nature have led to **E** being applied to organotransition metal chemistry as a dianion analogue of the Cp ligand.[8] It can be expected that the similar reduction of a neutral and Lewis base stabilized borole, which has one electron in its p orbital because of a coordination bond from the Lewis base to the sp^2 orbital of the boron center, may give the corresponding monoanionic Lewis base-stabilized borole derivative **F** (Scheme 2b). However, this type of compound has not been synthesized and isolated to date.



Scheme 2. Reduction of boron-substituted boroles and Lewis base stabilized boroles (substituents on carbon atoms are omitted for clarity). LB = Lewis base.

It has been shown that N-heterocyclic carbenes (NHC), which are singlet carbenes stabilized with adjacent nitrogen atom(s), were effective in stabilizing electron-deficient boron compounds, such as diborene,[9] the borenium cation,[10] and 9-boraanthracene[11] (Scheme 3). Based on the high donor ability of NHC, it can be expected that the above-mentioned Lewis base-stabilized borole anion could be synthesized by use of NHC.

Braunschweig et al. now report a synthesis of NHC-stabilized *B*-chloropentaphenylborole **1**[12] based on their previous report for a synthesis of Lewis base stabilized borole derivatives (Scheme 4).[13] Upon reduction of **1** with an excess amount of KC_8 in diethyl ether, they isolated the correspond-

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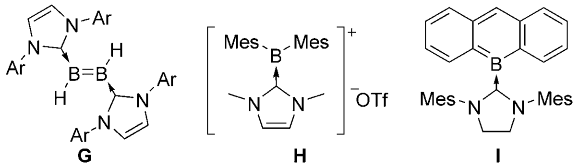
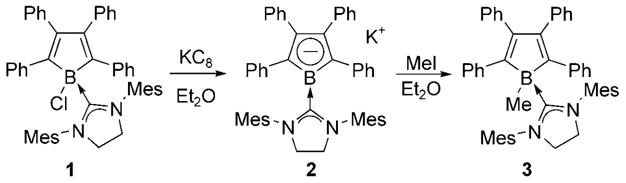
[*] Dr. M. Yamashita
Department of Chemistry and Biotechnology
Graduate School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, 113-8656 Tokyo (Japan)
Fax: (+81) 3-5841-7263
E-mail: makotoy@chembio.t.u-tokyo.ac.jp



Scheme 3. NHC-stabilized boron compounds. Ar = Dip (2,6-(iPr)$_2$C$_6$H$_3$), Mes (2,4,6-Me$_3$C$_6$H$_2$).



Scheme 4. Synthesis of NHC-stabilized borole anion **2** by reduction with KC$_8$ and its reaction with methyl iodide.

ing monoanionic compound **2**, which can be regarded as an isoelectronic species to the cyclopentadienyl anion. The ^{11}B NMR signal of **2** appeared at $\delta_B = 12$ ppm, which is shifted remarkably upfield compared to those of borata-alkenes or borole dianions.

The solid-state structure of **2** was unambiguously determined by X-ray crystallography. The potassium cation sit on the borole ring with simultaneous coordination from a phenyl ring of the second molecule to construct a dimer. A short B–C$_{carbene}$ bond (1.5406(15) Å), a small dihedral angle between boron and carbene planes (36.3°), and DFT calculations on a model compound indicated a significant π back-donation from an anionic boron center to the carbene carbon in **2**.

Surprisingly, the NHC-stabilized borole anion **2** reacts with methyl iodide at boron to form the substituted product **3** with an sp^3-hybridized boron atom; the product was isolated in 71% yield (Scheme 4). The highly nucleophilic nature of the anionic π orbital on the boron center is very unique, because the similar boron compounds, namely borabenzene, boratabenzene, and borataalkene, have a boron-containing conjugate π-system with no nucleophilicity at boron. The nucleophilicity is consistent with DFT calculations, which showed a contribution to the HOMO from the boron center.

This outstanding advance in molecular boron chemistry affords a new concept, with nucleophilicity on the π orbital of the boron center allowing the design of boron-containing functional materials. There is also a plenty of room for an application of the base-stabilized borole anion to transition metal chemistry as a designable alternative to the Cp ligand, because many NHCs are now available having a variety of steric and electronic effects, functional groups on their side chain, and chiral centers.[14]

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