

## Synthesis of Novel Silylboron Compounds Using Trialkylsilylanions

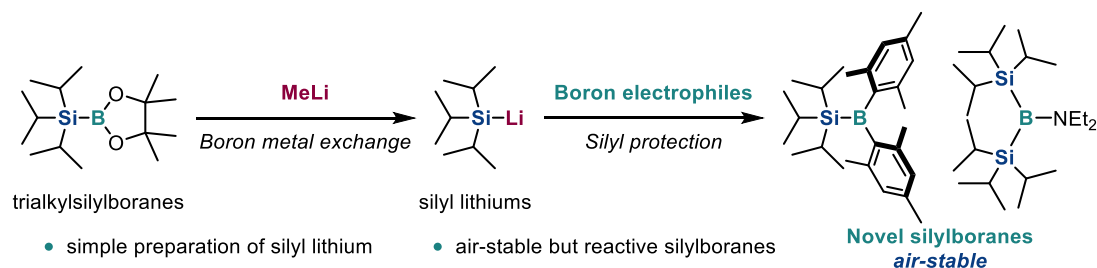
(<sup>1</sup>Graduate School of Chemical Science and Engineering, Hokkaido University, <sup>2</sup>Graduate School of Engineering, Hokkaido University, <sup>3</sup>WPI-ICReDD, Hokkaido University)

○Rikuro Takahashi,<sup>1</sup> Hajime Ito<sup>2,3</sup>

**Keywords:** Silylborane; Organosilicon Compounds; Organoboron Compounds; Silyl Anions; DFT Calculations

Silylboron compounds are a class of interelement compounds that contain an Si–B bond. The Si–B bond is generally inactive, but various reactivity was known using transition-metal catalysis which can activate the Si–B bond by the oxidative addition and transmetalation. In addition, the stoichiometric amount of base can coordinate to the boron. However, most silylboron compounds are unstable under air condition and decomposed by hydrolysis. Some stable silylboron compounds have been reported until today, but they require electronic stabilization or steric protection around boron atoms.<sup>1</sup>

We previously developed a general synthesis of sterically hindered trialkylsilylboranes by catalytic Si–H borylation reactions and realized that these reagents could be used as silyl anion equivalents via the boron metal exchange reactions.<sup>2</sup> We consider that these bulky silyl moieties can be utilized as protecting groups of the reactive boron center. Here, we found that the introduction of TIPS groups into silylborane compounds improves their stability, providing a new strategy for the design of stable silylborane compounds. The products, TIPS–BMes<sub>2</sub> and (TIPS)<sub>2</sub>B–NEt<sub>2</sub> are air stable and isolable by column chromatography. In addition, we studied the reactivity of TIPS–BMes<sub>2</sub> with carbon monoxide and obtained a spiro compound, accompanied by the cleavage of the carbon-oxygen triple bond and the dearomatization of the mesityl group. DFT studies were conducted to understand the reaction mechanism.



1) a) Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2002**, *124*, 8816. b) Noguchi, H.; Hojo, K.; Suginome, M. *J. Am. Chem. Soc.* **2007**, *129*, 758. c) Zhou, Z.; Wakamiya, A.; Kushida, T.; Yamaguchi, S. *J. Am. Chem. Soc.* **2012**, *134*, 4529.

2) Shishido, R.; Uesugi, M.; Takahashi, R.; Mita, T.; Ishiyama, T.; Kubota, K.; Ito, H. *J. Am. Chem. Soc.* **2020**, *142*, 14125.