

Report for Interdisciplinary research startup

1. **Name of project leader:** Hajime Ito

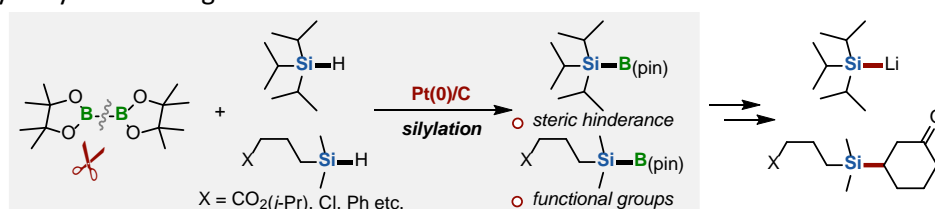
2. **Project title:** 金属-金属結合を切断する新規触媒系の開発融合研究 / Development of a new catalyst system that promotes the cleavage of a weak metal-metal bond

3. **Report**

The catalytic cleavage of the boron-boron (B-B) bond and its functionalization is important subject in organic chemistry because the resulting boron-containing molecules can be further manipulated by several ways. So far, late transition-metal-catalysts (Group 8 - 11 elements) have been used for this purpose. In order to validate the tendency of the cleavage of B-B bond by computational analysis, $B_2(eg)_2$ was set as a model diboron compound. The AFIR calculation was conducted using Pt(0), MePd(II)OAc, Pt(0), Cu(I)F, Cu(I)Ot-Bu, Cu(I)OMe, Ag(I)OMe, and Au(I)OMe in combination with PH_3 , a model phosphine ligand. Additional calculation was performed using Cu(I)OMe, Ag(I)OMe, and Au(I)OMe with NHC ligand. As a result, all calculated metal complexes except Pd(0)- PH_3 and Au(I)OMe-NHC smoothly promoted the cleavage of B-B bond (the calculated activation energy is less than 100 kJ/mol). Subsequently, an early transition-metal complex such as Zr(IV) Cp_2Cl_2 was used in calculation. However, in this case, the activation energy was very high (155.8 kJ/mol), which suggested the B-B bond cleavage was difficult.

Next, we designed a chemical reaction using Pt(0) and $B_2(pin)_2$ without a ligand (the calculated activation energy is 1.2 kJ/mol: almost barrierless!), which is a relatively rare combination for the catalytic transformation of diboron compounds. To develop a new functionalization method, we turned our attention to silylation of diborons. Iridium-catalyzed silylation of diborons with a silylhydride to prepare silylboranes was actively studied by Hartwig (*Organometallics* **2008**, 27, 6013–6019). However, synthesizable silylboranes are limited. In particular, the synthesis of trialkylsilylboranes bearing steric hindrance or functional groups has not been reported. Therefore, if a general synthetic method of trialkylsilylboranes is developed, such a method would be effective due to its novelty and good performance. Furthermore, silylboranes thus obtained are useful precursors for C-Si and Si-Si bond formation reactions, serving as silyl anion equivalents in the presence of a transition-metal catalyst or an appropriate base like MeLi.

We thus began the chemical experiment using a catalytic amount of Pt(0)/C in the presence of $B_2(pin)_2$ and R_3Si-H . Fortunately, various types of trialkylsilylboranes were successfully obtained in synthetically useful yields. Moreover, we conducted the AFIR study to reveal each step of the catalytic cycle, proposing a reasonable Pt(0)-mediated catalytic cycle under ligand-free conditions.



This research was done by a collaborative way with experimental chemists (Ito's group) and computational chemists (Maeda's group). The interdisciplinary research money was mainly used for the setup of the mixed lab to enhance the mutual collaboration between experimental and computational chemists. Highly costed experimental devices including a high vacuum manifold (300,000 yen), a crushed ice maker (450,000 yen), and a diaphragm pump (350,000 yen) were purchased in order to accelerate the chemical experiments.

4. **Research achievements**

- 1) Ryosuke Shishido, Minami Uesugi, Rikuro Takahashi, Tsuyoshi Mita, Tatsuo Ishiyama, Koji Kubota*, and Hajime Ito* "General Synthesis of Trialkyl- and Dialkylarylsilylboranes: Versatile Silicon Nucleophiles in Organic Synthesis" *submitted for publication*.
- 2) Ryosuke Shishido, Minami Uesugi, Koji Kubota, and Hajime Ito "Development of General Synthetic Method for Trialkylsilylboranes" The 46th Symposium on Main Group Element Chemistry, O-07 (oral presentation), Carrefour hall, Matsuyama University, Matsuyama, Japan, December 5th, 2019 **【Excellent Lecture Award】**.
- 3) Ryosuke Shishido, Minami Uesugi, Koji Kubota, and Hajime Ito "Development of Novel Synthetic Method for Trialkylsilylboranes" The 100th CSJ Annual Meeting, 1H8-42 (oral presentation), Noda Campus, Tokyo University of Science, Chiba, Japan, March 22th, 2020.