

TITLE: General synthesis of silylboranes and their application in the synthesis of a diverse range of organosilicon compounds

Abstract

Organosilicon chemistry has a long history of success, but in terms of structural diversity, it falls far short of its homolog, carbon-based molecules. A search on Reaxys reveals 32 million compounds with sp^3 carbons, while sp^3 silicon has been synthesized in only 1/30 of that number, 1.2 million. One of the reasons for the lack of synthesis of diverse organosilicon compounds may be the difficulty in generating silicon nucleophilic reagents. Because silicon is a more positive element than carbon, it is more difficult than carbon to put electrons into the silicon center. For example, when chlorosilane is reduced with Li to form a silyl anion, an aromatic substituent is needed on the silicon atom to stabilize the silyl anion. One good way to make a carbon-carbon bond is the reaction of a carbon nucleophile with a carbon electrophile, but due to the difficulty of making silicon nucleophiles, silicon-silicon bond formation is not as flexible as carbon-carbon bond formation.

Tamao and Kawachi reported that silyl nucleophile or silyl anion species could be formed when silylboranes were subjected to Lewis bases in 2001 (*Chem. Lett.* **2001**, 1216). However, the existing silylboranes require silyl nucleophiles generated by the reaction of chlorosilane with lithium, etc.; thus, this can not be a new method for generating silyl nucleophiles.

We have recently focused on the development of a new synthetic method for silylboranes via transition metal-catalyzed borylation of hydrosilanes. Although an Ir catalysis was reported by Hartwig for this reaction in 2008 (*Organometallics*, **2008**, 6013), only a limited number of the silylboranes were synthesized. We then have improved the catalytic activity and reaction scope by using Pt and Rh catalysts (*JACS* **2020**, 14125). The improvement of this reaction has made it possible to synthesize a variety of silylboranes and to generate novel silyl anion species that could not be generated by the known methods. In addition, the iterative and modular synthesis of differently substituted oligosilanes using the newly synthesized silylboranes has been developed.

Professor Hajime Ito is a Distinguished Professor at Hokkaido University. He was born in Osaka, Japan, in 1968. He completed his PhD in 1996 under the direction of the late Professor Yoshihiko Ito. He then worked as an Assistant Professor at Tsukuba University in collaboration with Professor Akira Hosomi and moved to Institute for Molecular Science. He also joined Professor Kim D. Janda's research group at the Scripps Research Institute as a research associate in 2001. In 2002 he was appointed as an Associate Professor at Hokkaido University, working with Professor Masaya Sawamura. He was promoted to a Full Professor at the same university in 2010. He was also appointed as the vice director and PI of the Institute for Chemical Reaction Design and Discovery (WPI-ICReDD) in 2018.

