

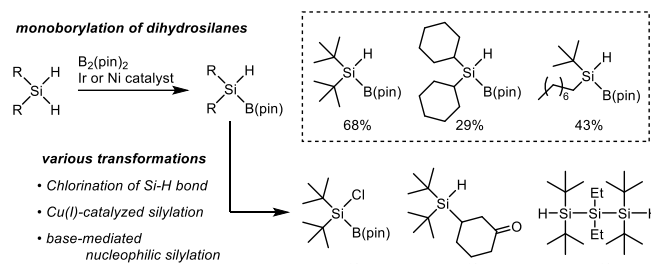
Synthesis of (hydrosilyl)boranes via Si–H monoborylation of dihydrosilanes

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Silylboranes can be easily activated by nucleophiles or transition-metal catalysts to construct carbon-silicon and carbon-boron bonds they thus have been used as useful synthetic reagents. The conventional synthetic method for accessing silylboranes involves a stoichiometric reaction between a silyl anion and a boron electrophile. Since silyl anion is produced by the reduction of chlorosilanes with alkali metals, the substituents on silicon atom are largely limited. Therefore, the alternative synthetic method is required. In 2008, the Hartwig group developed the pioneering Si–H borylation reaction catalyzed by an iridium complex¹⁾. This could be considered as one of the most direct synthetic method for silylboranes. Recently, we reported rhodium or platinum catalyst can be applied to much broader substrates²⁾. In particular, the functional-group-containing silylboranes can be obtained by platinum-catalyzed borylation. Thus, the discovery of new catalysts for Si–H borylation reactions would allow accessing to novel silylboranes.

During the research of our Si–H borylation reaction, we found that monoborylation of dihydrosilanes catalyzed by a nickel or an iridium complex to afford silylboranes, (hydrosilyl)boranes, bearing a hydrogen atom on silicon atom³⁾. In the case of *t*-Bu₂SiH₂, the corresponding (hydrosilyl)borane was obtained in high yield (68%). Although the steric bulkiness of substituents on silicon atom is essential for the stability of silylboranes, even less bulky (hydrosilyl)boranes are obtained in moderate yield. Additionally, they can be derived into various silicon compounds via subsequent transformations, including a chlorination of Si–H bond, a Cu(I)-catalyzed conjugated silylation, and a base-mediated nucleophilic silylation.



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