Platinum-Catalyzed Stereospecific Synthesis of Silicon-Stereogenic Optically Active Silylboranes and Their Application

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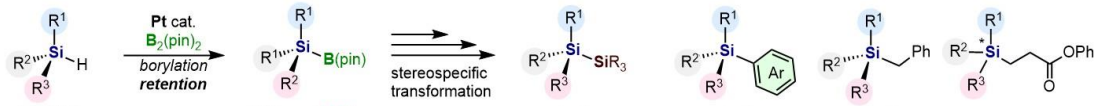
Since its first synthesis by Suginome and Ito in 1996, silylborane has shown attractive features in synthetic organic chemistry, especially as a powerful silyl transfer reagent.[1] Although silicon-stereogenic optically active silylborane has a strong potential to allow the introduction of silicon-stereogenic silyl groups into various molecules, the synthesis of such silicon-stereogenic silylboranes is so far unprecedented. Very recently, we reported a platinum- or rhodium-catalyzed borylation of hydrosilanes following the pioneering study of an iridium-catalyzed Si–H borylation reported by Hartwig,[2] which provides access to trialkylsilylboranes with bulky alkyl groups and dialkylarylsilylboranes.[3] Based on this study, we envisioned that the synthesis of chiral silylboranes could be achieved via the stereospecific transition-metal-catalyzed Si–H borylation of the corresponding chiral hydrosilanes.

Silicon-stereogenic optically active silylboranes were successfully obtained via a stereospecific $Pt(PPh_3)_4$-catalyzed Si–H borylation of silicon-stereogenic hydrosilanes in high yield and perfect enantiospecificity (up to 99% *ee*, >99% *es*) with retention of the configuration. Furthermore, the usefulness of silicon-stereogenic silylborane is proven to keep perfect stereospecificity in the generation of the unprecedented chiral silyl nucleophile, silicon–silicon bond-forming reactions, transition-metal-catalyzed carbon–silicon bond-forming cross-coupling reactions, and a conjugate addition reaction (>99% *es*).



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