Stereospecific Synthesis of Silicon-Stereogenic Optically Active Silylboranes and their Application to Synthesis of Chiral Organosilanes

Xihong Wang,[†] Chi Feng,[‡] Koji Kubota*[,†,‡] and Hajime Ito*[,†,‡]

[†]Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 001-0021, Japan

[‡]Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

ABSTRACT: Silylboranes have widespread applications in organic synthesis as versatile silylation reagents, which has inspired interest in studying methods for their synthesis. Silicon-stereogenic optically active silylboranes would allow the introduction of silicon-stereogenic silyl groups into various molecules. However, the synthesis of such silicon-stereogenic silylboranes remains unknown to date. Here, we report the first synthesis of silicon-stereogenic optically active silylboranes via stereospecific $Pt(PPh_3)_4$-catalyzed Si–H borylation of silicon-stereogenic hydrosilanes in high yield and perfect enantiospecificity (>99% *es*) with retention of the configuration. Furthermore, the first characterization of silicon-stereogenic silylboranes by single crystal X-ray diffraction analysis was reported. This protocol is suitable for the stereospecific synthesis of silicon-stereogenic trialkyl-, dialkylbenzyl-, dialkylaryl-, and diarylalkyl-substituted silylboranes with excellent enantiomeric purity. The utility of the silicon-stereogenic silylboranes is demonstrated in silicon–silicon cross-coupling, transition-metal-catalyzed carbon–silicon bond-forming cross-coupling, and conjugate addition reactions with perfect enantiospecificity (>99% *es*). The absolute configurations of the chiral silicon products were successfully confirmed by single-crystal X-ray diffraction analysis. The established synthetic strategy can be expected to expand the chemical space of silicon-stereogenic optically active organosilicon compounds with potentially interesting properties.

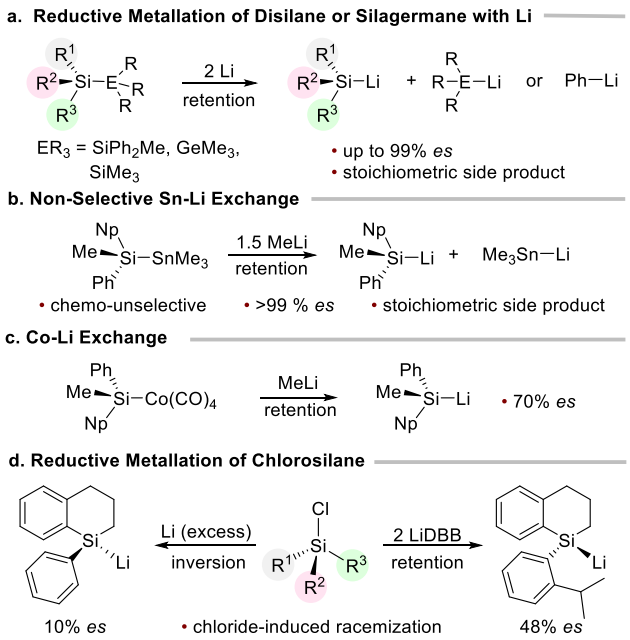
INTRODUCTION

The asymmetric synthesis of optically active compounds with carbon stereogenic centers is a major topic in organic synthesis and has developed significantly over the last several decades.[1] Compared to the synthesis of chiral carbon compounds, synthetic methods for chiral compounds with a stereogenic silicon, which is a cognate of carbon, are much less studied.[2-7] Recently, chiral organosilicon compounds bearing silicon stereocenters have shown attractive and widespread application prospects in organic synthesis[2], materials science[3], medicinal chemistry[4] and polymer chemistry[5] due to their unique electronic and physical properties. The development of new synthetic methods for such silicon-stereogenic optically active compounds has been an important research subject.[6] Transition-metal-catalyzed desymmetrization of prochiral silicon-containing molecules is an efficient approach for the synthesis of silicon-stereogenic chiral molecules.[7] Although significant progress has been made, the scope of synthesizable silicon-stereogenic compounds is still limited.[7]

The introduction of silicon stereocenters into molecules via silicon-stereogenic optically active nucleophiles is a fundamental approach. Silyllithiums are general and useful synthetic intermediates for obtaining various organosilicon compounds.[8] Enantiomerically pure silyllithiums that show configurational stability can be used as useful silicon-stereogenic silyl group transfer reagents.[9-15] However, their synthesis is extremely limited, and only a few successful examples have been reported so far. Sommer[9], Kawakami[10] and Strohman[11] have made great contributions in this direction, showing that the reaction of chiral disilanes with lithium metal generates chiral silyllithiums with retained configuration via the reduction of Si–Si or Si–Ph bonds (Scheme 1a). Similarly, lithium metal selectively cleaves the Si–Ge bond in optically active silylgermane to yield enantiomerically pure silyllithium without racemization (Scheme 1a).[12] Kawakami[10,13] also obtained silyllithium in a stereo-retentive manner via tin–lithium exchange of enantiomerically pure silylstannane derivatives (Scheme 1b). However, these three methods generate stoichiometric amounts of undesired side products, such as achiral silyl lithium, phenyllithium, trimethylgermyl and trimethylstannyl lithium, respectively, which compete in the nucleophilic reaction of the chiral silyllithium. In 1976 Corriu[14] developed a cobalt–lithium exchange system in which chiral silyllithium was partially racemized (Scheme 1c). In addition, enantiomerically pure chlorosilane undergoes significant racemization with lithium metal or di-*tert*-butylbiphenylide (LiDBB) due to chloride-induced racemization, as reported by Oestreich (Scheme 1d).[10,15] It should be noted that all these known methods require a silicon center containing at least one aryl group, which significantly limits their application. Therefore, the development of practical and widely applicable methods that allow the synthesis of various silicon-stereogenic nucleophiles is highly desired,

as they have great significance for the construction of novel chiral organosilicon molecules.

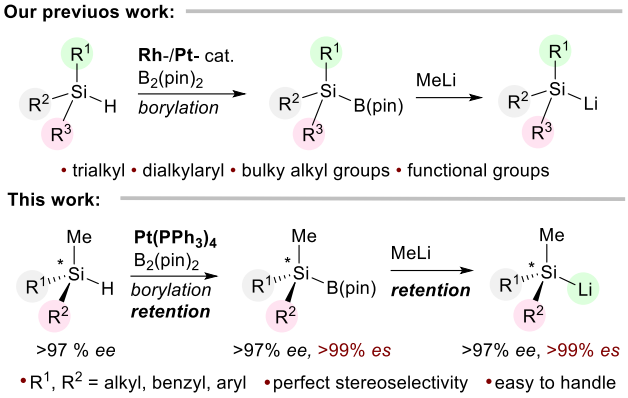
Scheme 1. Reported Methods for the Synthesis of Silicon-Stererogenic Optically Active Silyllithium



Silylboranes have become indispensable reagents for introducing silicon and boron groups into various substrates.[16] For example, they have been used in base-mediated nucleophilic substitution reactions,[17] transition-metal- and *N*-heterocyclic-carbene (NHC)-catalyzed additions of unsaturated compounds,[18] and transition-metal-catalyzed silylative cross-coupling and substitution reactions.[19,20] Despite the widespread use of silylboranes in synthesis, silicon-stereogenic optically active silylboranes have not yet been synthesized.[21] Following the pioneering study of an iridium-catalyzed Si–H borylation reported by Hartwig, our group developed a platinum- or rhodium-catalyzed borylation of hydrosilanes, which provides access to trialkylsilylboranes with bulky alkyl groups and dialkylarylsilylboranes.[22] Moreover, we demonstrated that the preparation of trialkylsilyllithium species from the corresponding trialkylsilylboranes is feasible. Thus, based on our previous research, we envisioned that the synthesis of chiral silylboranes could be realized via the stereospecific transition-metal-catalyzed Si–H borylation of the corresponding chiral hydrosilanes.

Herein, we report the first example of the synthesis of silicon-stereogenic optically active silylboranes via the stereospecific $Pt(PPh_3)_4$-catalyzed borylation of chiral hydrosilanes in high yield and perfect stereoselectivity with retention of their configuration (Scheme 2). The first single-crystal X-ray diffraction analyses of the chiral silylboranes are also presented. The newly synthesized silicon-stereogenic silylboranes are easy to handle and can be used as silicon-stereogenic silyl group transfer reagents with high enantiomeric purity, exhibiting complete enantiospecificity in silicon–silicon cross-coupling, palladium(0)-catalyzed carbon–silicon bond forming cross-coupling and copper(I)-catalyzed silyl conjugate addition reactions.

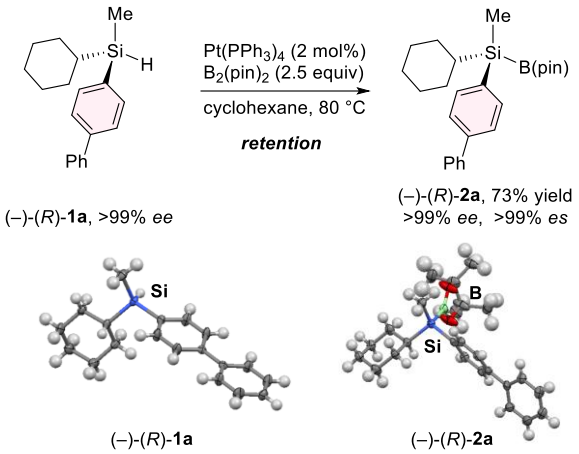
Scheme 2. Synthesis of Chiral Silylboranes and Generation of Silyl Nucleophile



RESULTS AND DISCUSSION

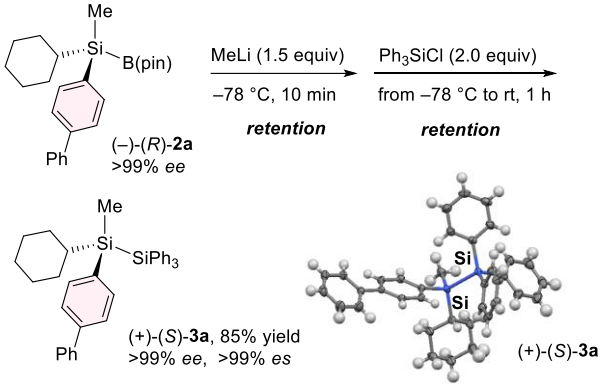
We started the investigation of the synthesis of silicon-stereogenic optically active silylboranes based on our previous research.[22] In order to avoid ambiguity in the stereochemistry and selectivity of the starting hydrosilane and desired silylborane, we screened a number of hydrosilanes and then searched for a crystalline hydrosilane and corresponding silylborane derivative that could be analyzed using single crystal X-ray diffraction analysis. For this purpose, a chiral silane, (–)-(*R*)-[(1,1′-biphenyl)-4-yl](cyclohexyl)methylsilane [(–)-(*R*)-**1a**] with >99% *ee* was prepared by resolution of the corresponding racemic hydrosilane using a preparative HPLC equipped with chiral columns (Scheme 3, see Supporting Information for details). The absolute configuration of (–)-(*R*)-**1a** was clearly determined via single-crystal X-ray diffraction analysis (see Supporting Information for details). After screening of the catalyst for the borylation of (–)-(*R*)-**1a** (see Supporting Information for details), we found that $Pt(PPh_3)_4$ is suitable for the borylation reaction of (–)-(*R*)-**1a** with bis(pinacolato)diboron for the synthesis of(–)-(*R*)-[(1,1′-biphenyl)-4-yl](cyclohexyl)methyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane [(–)-(*R*)-**2a**] in 73% yield with perfect enantiospecificity (>99% *ee* and >99% *es*).[22] Single crystal X-ray analysis of the product unambiguously proved the reaction proceeded with retention of the configuration of the silicon stereogenic center (Scheme 3, see Supporting Information for details).

Scheme 3. Stereospecific Borylation of Chiral Hydrosilane (–)-(*R*)-1a



We then investigated the reaction of the chiral silylborane (–)-(*R*)-**2a** with chlorotriphenylsilane in the presence of methyllithium as a nucleophilic activator of the silylborane to observe whether the newly synthesized chiral silylborane could act as a silicon-stereogenic silyl group transfer reagent (Scheme 4). Gratifyingly, when (–)-(*R*)-**2a** (>99% *ee*) was reacted with methyllithium in THF at –78 °C for 10 min, it then reacted with chlorotriphenylsilane to give (+)-(*S*)-1-[(1,1′-biphenyl)-4-yl]-1-cyclohexyl-1-methyl-2,2,2-triphenyldisilane [(+)-(*S*)-**3a**] in 85% yield with perfect enantiospecificity (>99% *ee*, >99% *es*). Through single-crystal X-ray diffraction analysis, we confirmed the absolute configuration to be (+)-(*S*)-**3a**; the nucleophilic reaction therefore proceeds with retention of the configuration (Scheme 4, see Supporting Information for details).

Scheme 4. Stereospecific Silylation of Silicon-Stererogenic Optically Active Silylborane (–)-(*R*)-2a

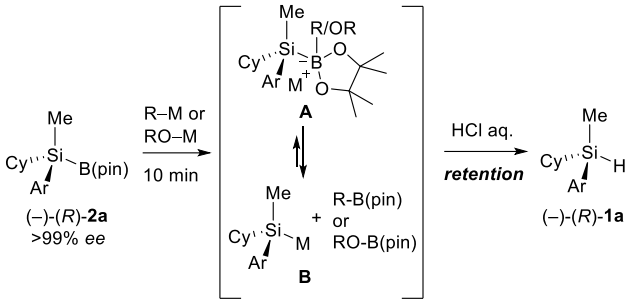


Subsequently, we performed *in situ* $^{11}B\{^1H\}$ NMR and $^{29}Si\{^1H\}$ NMR experiments to explore key intermediates in the reaction of (±)-**2a** with methyl lithium (see Supporting Information for details). Kawachi and Tamao reported the formation of Ph_3SiLi (^{29}Si: δ –9.1) via a boron–lithium exchange reaction between triphenylsilylborane and methyl lithium.[23] Previous work by our group showed that *i*-Pr_3SiLi (^{29}Si: δ 14.7) was the major product in the reaction of *i*-Pr_3Si–B(pin) with MeLi, and that the *i*-Pr_3Si–B(pin)/MeLi ate complex (^{11}B: δ 8.2) was generated as a minor product.[22] Similarly, two new ^{11}B signals appeared when (±)-**2a** was treated with 1.5 equiv of MeLi in THF-d_8 at –78 °C. However, in contrast to our previous results, the small signal was consistent with Me–B(pin) (δ 33.5), and the large signal was assumed to correspond to the (±)-**2a**/MeLi ate complex (δ 8.5). The ^{29}Si NMR spectrum showed only one peak (δ –15.5), which most likely corresponded to (±)-{[(1,1′-biphenyl)-4-yl](cyclohexyl)(methyl)silyl}lithium. The ^{29}Si signal of the (±)-**2a**/MeLi ate complex was not observed, probably due to dynamic processes in equilibrium and the adjacent quadrupolar boron atom.[24] We then carried out $^{29}Si\{^1H\}$ NMR analysis at –95 °C, and a broad peak was detected (δ –17.1), which was assumed to correspond to (±)-{[(1,1′-biphenyl)-4-yl](cyclohexyl)(methyl)silyl}lithium, although no Si–Li coupling was observed. These results indicate that there is an equilibrium between (±)-{[(1,1′-biphenyl)-4-yl](cyclohexyl)(methyl)silyl}lithium and the (±)-**2a**/MeLi ate complex.

We then decided to investigate the stereospecificity and configurational stability of the silicon-stereogenic optically active silyl nucleophiles generated from the chiral silylboranes. As shown in Table 1, the chiral silyl nucleophile was first formed as an equilibrium between ate complex **A** and silyllithium intermediate **B** from (–)-(*R*)-**2a** (>99% *ee*) via treatment with methyllithium in THF at –78 °C. The nucleophile was then quenched with 1 M aqueous HCl to give the corresponding chiral hydrosilanes (–)-(*R*)-**1a** in 83% yield with >99% *ee* (entry 1).[10] The absolute configuration of (–)-(*R*)-**1a** was unchanged, demonstrating that all processes proceeded with retention of the configuration with perfect stereoselectivity (>99% *ee*).[10,11b,15]Even when the reaction temperature was increased to –40 °C, (–)-(*R*)-**1a** was obtained with >99% *ee*, although the yield decreased to 68% (entry 2), and 26% of (–)-(*R*)-**2a** was recovered (see Supporting Information for details). Further increasing the reaction temperature to room temperature resulted in a decreased yield of 21%, but high enantiomeric purity was still observed (entry 3, >99% *ee*). Only 17% of (–)-(*R*)-**2a** was recovered, and other unidentified side products were observed (see Supporting Information for details). Next, we examined the nucleophilic activators for the activation of silylboranes. When we used *n*-butyllithium instead of methyllithium, 54% yield was obtained with >99% *ee* (entry 4). With the more reactive and basic *sec*-butyllithium, the yield was further reduced to only 20%, but the stereospecificity of the protonation was unchanged (>99% *ee*) (entry 5). When lithium *tert*-butoxide was used as the nucleophile, the reaction did not proceed, even though *tert*-butoxide has been reported to be a good activator for other silyl boranes such as Me_2PhSi–B(pin)(entry 6).[25] With potassium *tert*-butoxide, only 8% product yield was obtained, but no erosion of enantiomeric purity (>99% *ee*) was observed (entry 7). When the reaction was carried out with methylmagnesium bromide, the enantiomeric excess of (–)-(*R*)-**1a** was reduced to 95% *ee* and the yield was very low (6%, entry 8). When toluene was used as the solvent, the yield of (–)-(*R*)-**1a** was 32% with >99% *ee* (entry 9), whereas the use of *n*-hexane as the solvent resulted in 43% yield with >99% *ee*, suggesting that a less-polar solvent affects the yield but not the stereoselectivity (entry 10). In addition, when (–)-(*R*)-**2a** was reacted with methyllithium in THF at –78 °C for a longer reaction time of 2 h, (–)-(*R*)-**1a** was obtained in 87% yield with >99% *ee* after quenching

with 1 M aqueous HCl (entry 11). These results demonstrate the high stability of the chiral ate complex and the silyllithium with regards to stereochemistry.

Table 1. Configurational Stability of Silicon-Stereogenic Optically Active Silyl Nucleophile under Various Conditions

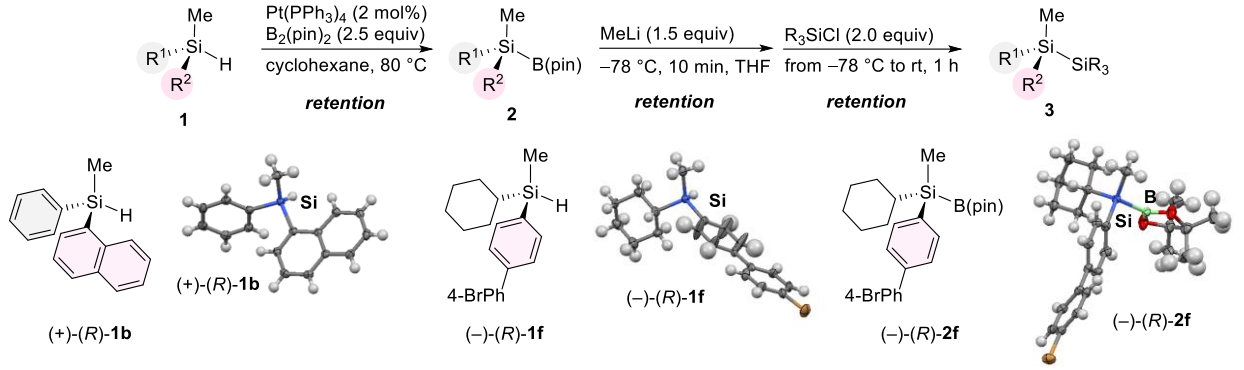


entry	activator	temp. (°C)	solvent	yield (%)	*ee* (%)
1	MeLi	–78	THF	83	>99
2	MeLi	–40	THF	68	>99
3	MeLi	rt	THF	21	>99
4	*n*-BuLi	–78	THF	54	>99
5	*s*-BuLi	–78	THF	20	>99
6	*t*-BuOLi	–78	THF	N.R.	-
7	*t*-BuOK	–78	THF	8	>99
8	MeMgBr	–78	THF	6	95
9	MeLi	–78	Toluene	32	>99
10	MeLi	–78	Hexane	43	>99
11[b]	MeLi	–78	THF	87	>99

[a]Conditions: (–)-(*R*)-**2a** (0.1 mmol), activator (0.15 mmol), and HCl aq. (1 M, 200 μL) in 0.5 mL solvent. The yields are isolated yields. The *ee* values were determined by HPLC with a chiral stationary phase. [b](–)-(*R*)-**2a** with methyllithium in THF at –78 °C for 2 h.

We also applied the stereospecific borylation and silylation for other silicon-stereogenic optically active hydrosilanes (Table 2). Notably, (+)-(*R*)-methyl(naphthalen-1-yl)phenylsilane [(+)-(*R*)-**1b**] (>99% *ee*) bearing two aryl groups and one alkyl group also reacted well in the borylation reaction,[26] producing (+)-(*R*)-methyl(naphthalen-1-yl)phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane[(+)(*R*)-**2b**] in 72% yield (entry 2, >99% *ee*).[27] The stereoretentive silicon–silicon coupling reaction of (+)-(*R*)-**2b** with benzylchlorodimethylsilane then proceeded smoothly to afford (–)-(*S*)-1-benzyl-1,1,2-trimethyl-2-(naphthalen-1-yl)-2-phenyldisilane [(–)-(*R*)-**3b**] in a moderate yield (51%) without loss of enantiomeric purity (>99% *ee*) (entry 1). The absolute configuration of (+)-(*R*)-**1b** was unambiguously confirmed by single-crystal X-ray diffraction analysis after crystallization (see Supporting Information for details), but the absolute configurations of (+)-(*R*)-**2b** and (–)-(*R*)-**3b** were deduced from the results for (–)-(*R*)-**1b.** (+)-(*S*)-*tert*-butyl(methyl)phenylsilane [(+)-(*S*)-**1c**], a chiral monoaryldialkylsilane, was prepared by the conventional optical resolution method reported by Oestreich.[28,29] (+)-(*S*)-**1c** can easily be converted into (+)-(*S*)-*tert*-butyl(methyl)phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane [(+)-(*S*)-**2c**] and (+)-(*R*)-1-(*tert*-butyl)-1-methyl-1,2,2,2-tetraphenyldisilane [(+)-(*S*)-**3c**] in high yield with perfect stereoselectivity [(+)-(*S*)-**2c**: 72% yield, >99% *ee*; (+)-(*S*)-**3c**: 80% yield, >99% *ee*] (entry 2).[30] The trialkyl-substituted hydrosilane (–)-[3-(benzyloxy)propyl](cyclohexyl)methylsilane [(–)-**1d**] underwent the borylation reaction to afford the desired (+)-[3-(benzyloxy)propyl](cyclohexyl)methyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane [(+)-**2d**] in 67% yield with >99% *ee* (entry 3). (+)-**2d** was then used in the silylation reaction with chlorotriphenylsilane to give (–)-1-[3-(benzyloxy)propyl]-1-cyclohexyl-1-methyl-2,2,2-triphenyldisilane [(–)-**3d**] in 86% yield with >99% *ee*, showing the perfect stereoselectivity of the reaction steps (entry 4). Moreover, borylation of (+)-benzyl(cyclohexyl)methylsilane [(+)-**1e**] provided (+)-benzyl(cyclohexyl)methyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane [(–)-**2e**] in 71% yield with excellent enantioselectivity (>99% *ee*) (entry 4). (–)-**2e** was then reacted with chlorotriphenylsilane and benzylchlorodimethylsilane, respectively, to obtain (–)-1-benzyl-1-cyclohexyl-1-methyl-2,2,2-triphenyldisilane [(–)-**3e**] (entry 4, 78% yield, >99% *ee*) and (–)-1,2-dibenzyl-1-cyclohexyl-1,2,2-trimethyldisilane [(–)-**3e′**] (entry 5, 90% yield, >99% *ee*).[31] Additionally, (–)-(*R*)-[4′-bromo-(1,1′-biphenyl)-4-yl](cyclohexyl)methylsilane [(–)-(*R*)-**1f**] also efficiently underwent the $Pt(PPh_3)_4$-catalyzed borylation reaction to afford (–)-(*R*)-[4′-bromo-(1,1′-biphenyl)-4-yl](cyclohexyl)methyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane [(–)-(*R*)-**2f**] in 72% yield with >99% *ee*. However, since the bromine substituent also reacted with methyl lithium to generate the aryl lithium species, the silicon–silicon coupling reaction of (–)-(*R*)-**2f** resulted in a complex mixture (entry 6). The absolute configurations of (–)-(*R*)-**1f** and (–)-(*R*)-**2f** were unambiguously confirmed by single-crystal X-ray diffraction analysis. These results clearly show that the $Pt(PPh_3)_4$-catalyzed borylation of various optically active hydrosilanes proceeded stereospecifically with retention of configuration, followed by the stereospecific generation of silyl nucleophiles and their reaction with silicon electrophiles, all of which occurred in a stereoretentive manner.

Table 2. Synthesis of Silicon-Stereogenic Optically Active Silylboranes and Disilanes[a]



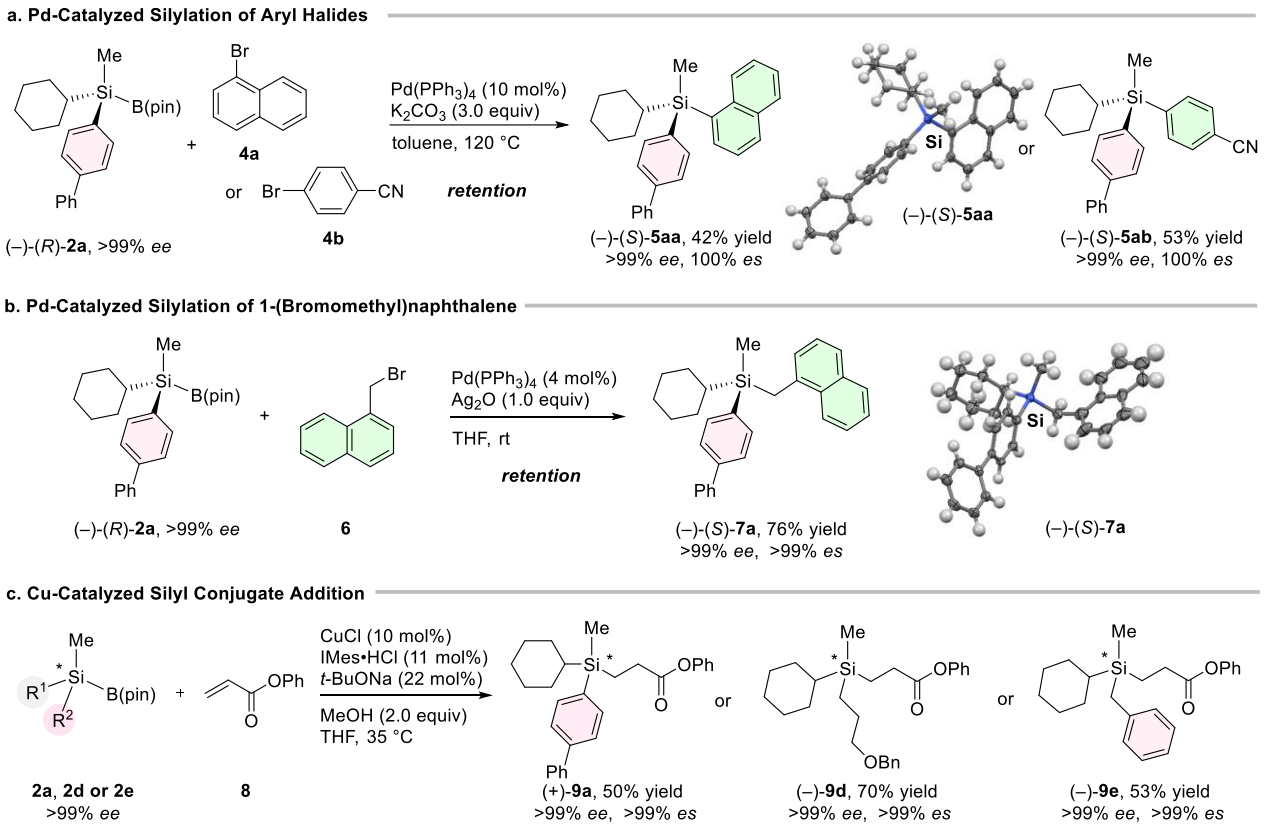
entry	1	R^1	R^2	*ee* of **1** (%)[b]	yield of **2** (%)[c]	*ee* of **2** (%)[b]	R_3SiCl	yield of **3** (%)[c]	*ee* of **3** (%)[b]
1	(+)-(*R*)-**1b**	Ph	1-Naphthyl	>99	(+)-(*R*)-**2b**, 72	(>99)[d]	$Me_2BnSiCl$	(–)-(*S*)-**3b**, 51[e]	>99
2	(+)-(*S*)-**1c**	Ph	*t*-Bu	97	(+)-(*S*)-**2c**, 72	97	Ph_3SiCl	(+)-(*R*)-**3c**, 80	97
3	(–)-**1d**	Cy	$BnO(CH_2)_3$	>99	(+)-**2d**, 67	(>99)[d]	Ph_3SiCl	(–)-**3d**, 72	>99
4	(+)-**1e**	Cy	Bn	>99	(–)-**2e**, 71	>99	Ph_3SiCl	(–)-**3e**, 78	>99
5	(+)-**1e**	Cy	Bn	>99	-	>99	$Me_2BnSiCl$	(–)-**3e′**, 90	>99
6	(–)-(*R*)-**1f**	Cy	4-Br-bi-phenyl	>99	(–)-(*R*)-**2f**, 72	>99	Ph_3SiCl	complex mix-ture	-

[a]Conditions for borylation reaction system: **1** (0.3 mmol), $Pt(PPh_3)_4$ (2 mol%), $B_2(pin)_2$ (0.75 mmol) in cyclohexane (0.3 mL) at 80 °C; conditions for the Si–Si coupling reaction system: **2** (0.1 mmol), MeLi (1.2 M in Et_2O, 0.15 mmol), chlorosilane (0.2 mmol) in THF (0.5 mL). [b] The *ee* values were determined by chiral HPLC. [c] The yields are isolated yields. [d]This is the presumed *ee* value. [e](–)-(*R*)-**2b** with methyllithium in THF at –78 °C for 30 min.

Subsequently, we investigated transition-metal-catalyzed silylation reactions with the silicon-stereogenic optically active silylboranes (Scheme 5). The He group reported the palladium-catalyzed reaction of silylboranes with aryl bromides in 2015.[32] By modifying the reaction conditions, the more sterically hindered (–)-(*R*)-**2a** was compatible with this reaction with no erosion of the enantiomeric excess, albeit affording moderate yields (Scheme 5a). We conducted the reaction of (–)-(*R*)-**2a** with 1-bromonaphthalene to afford the corresponding (–)-(*S*)-(1,1′-biphenyl)-4-yl(cyclohexyl)methyl(naphthalen-1-yl)silane [(–)-(*S*)-**5aa**] in 42% yield with outstanding enantiospecificity (>99% *ee*, >99% *es*). The absolute configuration of (–)-(*S*)-**5aa** was confirmed by single-crystal X-ray diffraction analysis, showing retention of the stereochemistry (Scheme 4a, see Supporting Information for details). The reaction of (–)-(*R*)-**2a** with 4-bromobenzonitrile proceeded well to furnish (–)-(*S*)-4-[(1,1′-biphenyl)-4-yl(cyclohexyl)(methyl)silyl]benzonitrile [(–)-(*S*)-**5ab**] (53% yield, >99% *ee*, >99% *es*). The absolute configuration of (–)-(*S*)-**5ab** was deduced from (–)-(*R*)-**2a**.

We further investigated transition metal-catalyzed reactions for the introduction of a chiral silicon group. We performed a palladium-catalyzed silylation reaction of primary alkyl halides and silylboranes, which was reported by the Xu group in 2016.[33] The reaction proceeded effectively between (–)-(*R*)-**2a** and 1-(bromomethyl)naphthalene to afford the desired (–)-(*S*)-(1,1′-biphenyl)-4-yl(cyclohexyl)methyl(naphthalen-1-ylmethyl)silane [(–)-(*S*)-**7a**] in 76% yield in a completely stereoretentive manner (>99% *ee*, >99% *es*) (Scheme 4b). The absolute configuration of (–)-(*S*)-**7a** was also unambiguously confirmed by single-crystal X-ray diffraction analysis (Scheme 5b, see Supporting Information for details).

Scheme 5. Applications of Silicon-Stereogenic Optically Active Silylboranes



We next examined the utility of silicon-stereogenic optically active silylboranes in the copper(I)-catalyzed conjugate addition of a silicon-stereogenic optically active silyl group to phenyl acrylate (Scheme 5c). In 2010, the Hoveyda group reported the first example of enantioselective conjugate silyl additions to unsaturated carbonyls catalyzed by a copper(I)/NHC-catalyzed system.[34] Under the modified reaction conditions, (–)-(*R*)-**2a** was successfully applied in this reaction, and (+)-phenyl {3-[(1,1′-biphenyl)-4-yl](cyclohexyl)(methyl)silyl}propanoate [(+)-**9a**] was obtained in 50% yield without loss of enantioselectivity (>99% *ee*, >99% *es*). The reaction of the less sterically hindered silane [(+)-**2d**] produced (–)-phenyl {3-[3-(benzyloxy)propyl](cyclohexyl)(methyl)silyl}propanoate [(–)-**9d**] in 70% yield with perfect enantiospecificity (>99% *ee*, >99% *es*). In addition, the reaction of (–)-**2e** with phenyl acrylate also proceeded well to give (–)-phenyl [3-benzyl(cyclohexyl)(methyl)silyl]propanoate [(–)-**9e**] (53% yield, >99% *ee*, >99% *es*). It should be noted that all the copper(I)-catalyzed reactions proceeded in a stereospecific manner, although it was not possible to determine the stereochemistry in all cases due to the lack of crystallinity of the products.

CONCLUSIONS

Silicon-stereogenic optically active silylboranes were first synthesized by $Pt(PPh_3)_4$-catalyzed stereospecific borylation of the chiral hydrosilanes. The corresponding chiral silyl nucleophiles generated from the chiral silylboranes are configurationally stable even at room temperature, and reacted with chlorosilanes to yield the corresponding disilanes in a stereoretentive manner (>99% stereospecificity). It is worth noting that the newly synthesized chiral silylboranes can be used as silicon-stereogenic optically active silyl transfer reagents in various transition-metal-catalyzed silylation reactions. The present study opens novel chemistry of chiral silylboranes, providing exciting opportunities to develop new silicon-stereogenic optically active bioactive molecules, polymers, and optoelectronic materials.

ASSOCIATED CONTENT

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AUTHOR INFORMATION

Corresponding Author

*kbt@eng.hokudai.ac.jp
*hajito@eng.hokudai.ac.jp

Notes

The authors declare no competing financial interest.

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(30) Similarly to those of (+)-(*R*)-**2b** and (–)-(*R*)-**3b**, the absolute configurations of (+)-(*S*)-**2c** and (+)-(*S*)-**3c** were deduced from the above results.

(31) It was not possible to determine the absolute configurations of [(–)-**1d**], [(+)-**2d**], [(–)-**3d**], [(+)-**1e**], [(–)-**2e**], [(–)-**3e**], [(–)-**3e′**], and [(–)-**3e′**] because we could not obtain their crystals for single crystal XRD analysis.

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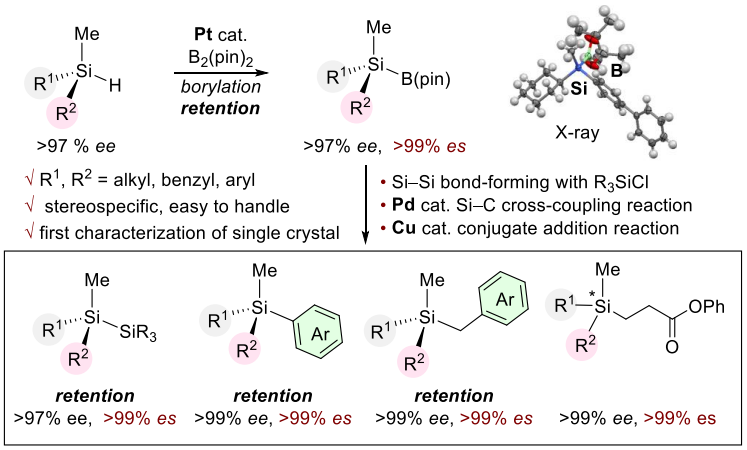
Me
Si
H
R1
R2
Pt cat.
B2(pin)2
borylation
retention
B(pin)
>97 % ee
>97% ee, >99% es
X-ray
B
Si
√ R1, R2 = alkyl, benzyl, aryl
√ stereospecific, easy to handle
√ first characterization of single crystal
• Si–Si bond-forming with R3SiCl
• Pd cat. Si–C cross-coupling reaction
• Cu cat. conjugate addition reaction
SiR3
Ar
OPh
O
retention
>97% ee, >99% es
>99% ee, >99% es
>99% ee, >99% es
>99% ee, >99% es