© 2009 The Chemical Society of Japan

Accounts

Silylboranes as New Tools in Organic Synthesis

Toshimichi Ohmura and Michinori Suginome*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510

Received August 5, 2008; E-mail: suginome@sbchem.kyoto-u.ac.jp

New reactivities of silylboranes are described with their applications to organic synthesis. The silylboranes add to unsaturated organic compounds such as alkynes, alkenes, 1,3-dienes, and allenes in the presence of nickel, palladium, and platinum catalysts. Reactions with isocyanide proceed in the absence of catalysts, giving 1,1-addition products. The silaborations proceed in highly regio- and stereoselective manners, leading to the formation of organic compounds bearing silyl and boryl groups. Silaborations accompanied by regioselective C–C bond cleavage in three-membered rings take place in the reactions of methylenecyclopropane and vinylcyclopropane derivatives. Unsaturated organic molecules, e.g., 1,3-diene and aldehyde, undergo silaborative C–C coupling reactions in the presence of transition-metal catalysts. Enantioselective silaboration of terminal allenes and silaborative C–C cleavage of *meso*-methylenecyclopropanes have been achieved. Silaborations in which the stereochemical course, i.e., cis and trans stereoselectivities, is governed by the ligand have been established in platinum-catalyzed intramolecular silaborations of alkenes. Synthetic applications of the silaboration products through Suzuki–Miyaura coupling, one-carbon homologation, oxidation, allylation, and Rh-catalyzed conjugate addition are also described. Synthesis of silylboranes, including those having heteroatom functional groups at the silicon atoms, is summarized.

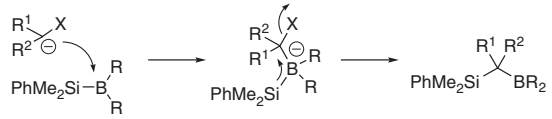
1. Introduction

Among the electropositive elements, silicon and boron are highly characteristic in that they form highly stable, covalent bonds to carbon. This characteristic nature allows organic chemists to design, synthesize, and store organosilicon and organoboron compounds just like ordinary organic compounds which consist of nonmetallic elements. The molecular nature of the organosilicon and organoboron compounds has attracted much interest in their application to organic synthesis and functional materials. Development of a variety of transformation reactions for organosilicon and organoboron compounds greatly enhances their utility in synthetic organic chemistry.[1] Further interests have focused on their direct application to functional materials[2] and drugs,[3] whose functions may arise from the unique nature of the electropositive elements.

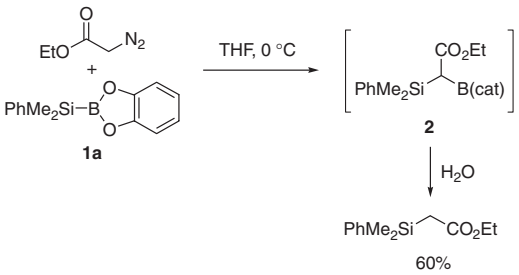
For the future "explosive" development of the chemistry of organoboron and organisilicon compounds, it is essential to explore new efficient methodologies for their synthesis. Although a number of preparative methods have been established, there still is much room to develop methods for highly efficient synthesis of organosilicon and organoboron compounds. Particular efforts are currently devoted to transition-metal-catalyzed reactions, which often lead to the synthesis of new derivatives that have been otherwise inaccessible, with remarkable control of chemo-, regio-, diastereo-, and even enantioselectivities. Although silicon and boron hydrides have been the most frequently used reagents for their catalytic synthesis through catalytic activation of hydride–silicon and –boron linkages, more recent studies have revealed that silicon- and boron-containing σ-bonds to non-hydrogen elements are also activated and undergo catalytic reactions. This was successfully demonstrated initially by a series of silicon reagents such as silicon–silicon, silicon–tin, and silicon–cyanide compounds, and then by boron compounds such as boron–sulfur and boron–boron compounds in more recent years.[4–6] From the viewpoint of organic synthesis, those catalytic reactions are quite attractive in that additional functional groups are introduced nearby the newly formed silicon–carbon and boron–carbon bonds in one step.

In the mid 90s, we were interested in developing the chemistry of silylboranes, which have relatively stable silicon–boron linkages, on the basis of our knowledge of bis-silylation reactions which proceed via activation of stable silicon–silicon linkages. In spite of the fact that compounds having silicon–boron bonds have been prepared and characterized since 1960,[7] their reactions, particularly those for organic synthesis, have not been explored well until recently. A report in 1987 demonstrated that triethylsilylborates (R_3SiBEt_3Li) reversibly added to carbon–carbon triple bonds in the presence of a copper or cobalt catalyst in methanol, leading to formation of formal hydrosilylation products via protodeboration, which shifted the

Published on the web January 14, 2009; doi:10.1246/bcsj.82.29



Scheme 1. Mechanism for reaction of silylborane with carbenoid.



Scheme 2. Reaction of silylborane **1a** with ethyl diazoacetate reported by Buynak and Geng.

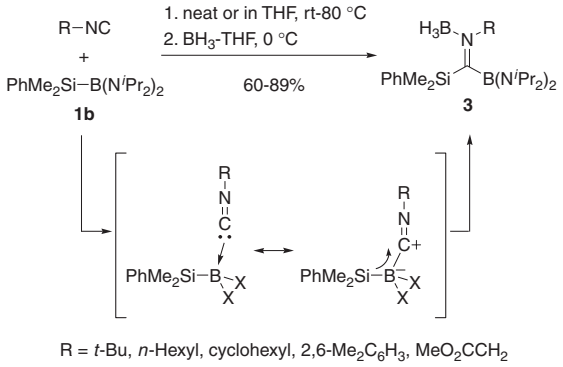
equilibrium to the adducts.[8] No other studies had appeared before 1996, prompting us to study reactivities of silylboronic acid derivatives [R_3Si–$B(OR)_2$] in the presence of transition-metal catalysts.

This account summarizes our studies on the transition-metal-catalyzed reactions of silylboronic acid derivatives with unsaturated organic compounds, which lead to the silaboration reaction, i.e., introduction of both silicon and boron compounds. Reactions are classified according to the relative positions of silicon and boron groups in the products. Starting from 1,1-addition, 1,2-, 1,3-, 1,4-, 1,5-, and 1,6-additions are shown below with selected synthetic applications of the silaboration products.[9]

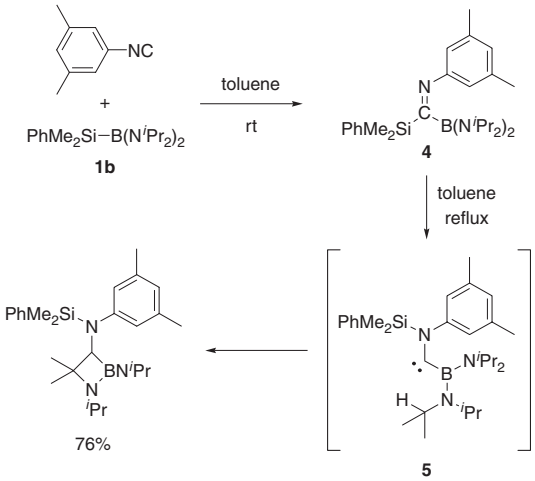
2. 1,1-Silaboration

2.1 Background. Nucleophilic attack of anionic species carrying leaving groups on the anionic atoms to tri-coordinated organoboron compounds leads to the 1,2-migration of the organic groups on the boron atoms through formation of a tetra-coordinated organoborate. This mechanism is generally operative in a variety of boron-based reactions, such as H_2O_2 oxidation of organoboron compounds and homologation of organoboron compounds. In a similar manner, silylboranes undergo nucleophilic attack of carbenes and carbenoids and subsequent 1,2-migration, leading to 1,1-silaboration of the divalent carbon atoms, to afford α-silylated organoboron compounds (Scheme 1). Buynak and Geng reported that reaction of (dimethylphenylsilyl)catecholborane (**1a**) with ethyl diazoacetate gives ethyl dimethylphenylsilylacetate that is formed via hydroxylation of α-boryl-α-silylester derivative **2** (Scheme 2).[10] More recently, related 1,1-silaboration of a variety of lithium carbenoids were reported.[11]

2.2 Silaboration of Isocyanide. We found that insertion of alkyl and aryl isocyanides, which have a carbene-like divalent carbon atom, to the B–Si bond of silylboranes proceeds thermally to give (boryl)(silyl)iminomethanes (Scheme 3).[12] The 1,1-silaboration of isocyanide may proceed through the initial coordination of the isocyanide to the boron atom of silylborane and subsequent migration of the silyl group from



Scheme 3. Reaction of silylborane **1b** with isocyanides.



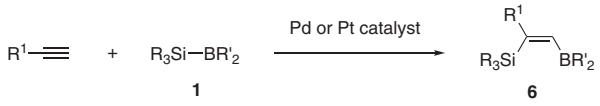
Scheme 4. Generation of α-boryl-α-aminocarbene **5** from (boryl)(silyl)iminomethane **4**.

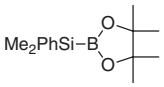
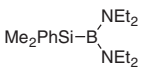
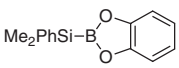
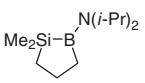
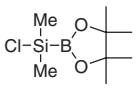
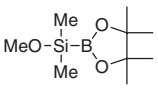
the boron to the isocyano carbon. The reaction rate was much influenced by the substituent on the boron atom: silylborane having dialkylamino groups showed much higher reactivity than the corresponding pinacol ester. The products, (boryl)(silyl)iminomethanes, are moisture sensitive, suffering from decomposition on silica gel. The imines could be stabilized by conversion into the corresponding imine–borane complexes **3**, being isolated through silica gel column chromatography. The (boryl)(silyl)iminomethane **4** underwent unusual four-membered ring formation at higher temperature through probable generation of α-boryl-α-aminocarbene **5** by thermal 1,2-shift of the silyl group (Scheme 4).[13]

3. 1,2-Silaboration

3.1 Silaboration of Alkyne. 3.1.1 Cis Silaboration: In contrast to the reaction with isocyanide, no insertion of alkynes to the Si–B bond of silylborane took place in the absence of transition-metal catalysts. Although Cu-catalyzed addition of the silicon–boron bond of $Me_2PhSiBEt_3Li$ to alkynes has been reported, the addition process, which was in equilibrium with starting materials, required in situ protodeboration to shift the equilibrium to the product side.[8] For the "productive" silaboration of alkynes, group 10 transition-metal complexes were found to be effective (Tables 1 and 2). It was initially found that a palladium complex generated in situ from

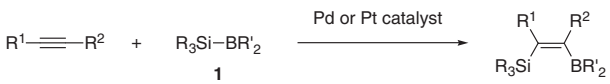
Table 1. Silaboration of Terminal Alkynes

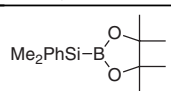
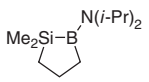


Entry	R^1	Silylborane		Catalyst	Conditions	Yield/%	Ratio[a)]
1	n-C_6H_{13}		**1c**	$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, 110 °C, 1 h	92	>99:1
2	n-C_6H_{13}	**1c**		$Pd_2(dba)_3$/$P(OEt)_3$ (Pd/L = 1/2)	toluene, 110 °C, 4 h	99	>99:1
3	n-C_6H_{13}	**1c**		$PdCl_2(PPh_3)_3$	toluene, 110 °C, 2 h	89	>99:1
4	n-C_6H_{13}	**1c**		$Pt(PPh_3)_4$	toluene, 110 °C, 1 h	80	90:10
5	$Cl(CH_2)_3$	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	87	>99:1
6	$NC(CH_2)_3$	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	77	>99:1
7	$TBDMSOCH_2$	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	83	>99:1
8	$THPO(CH_2)_2$	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	88	>99:1
9	$MEMO(CH_2)_3$	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	85	>99:1
10	$HO(CH_2)_2$	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	77	>99:1
11	Ph	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	82	>99:1
12	cyclohexen-1-yl	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	94	>99:1
13	EtO_2C	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	77	>99:1
14	acetyl	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	88	>99:1
15	Me_3Si	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	76	>99:1
16	H	**1c**		$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	91	—[b)]
17	n-C_6H_{13}		**1d**	$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, 110 °C, 2 h	94	>99:1
18	n-C_6H_{13}		**1a**	$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, 110 °C, 2 h	78	>99:1
19	n-C_6H_{13}		**1e**	$Pd(acac)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/4)	toluene, rt, 6 h	84	>99:1
20	n-C_6H_{13}		**1f**	$CpPd(\eta$-$C_3H_5)$/PPh_3 (Pd/L = 1/1.2)	toluene, rt, 0.2 h	99	>99:1
21	n-C_6H_{13}		**1g**	$CpPd(\eta$-$C_3H_5)$/PPh_3 (Pd/L = 1/1.2)	toluene, rt, 4 h	80	>99:1

a) Regioisomeric ratio. b) Z:E = 90:10. c) 2,4-Dihexyl-1,1-dimethylsilole was formed as major product.

Table 2. Silaboration of Internal Alkynes



Entry	R^1	R^2	Silylborane	Catalyst	Conditions	Yield/%	Ratio[a)]
1	Ph	Ph	 **1c**	$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	74	—
2	Ph	Me	**1c**	$Pd(OAc)_2$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	toluene, reflux	85	93:7
3	Ph	Me	**1c**	$Pt(PPh_3)_4$	toluene, reflux	75	82:18
4	Ph	Me	 **1e**	$CpPd(\eta$-$C_3H_5)$/t-$BuCH_2CMe_2NC$ (Pd/L = 1/2)	toluene, rt, 3 h	77	>99:1
5	n-Bu	n-Bu	**1c**	$Pt(PPh_3)_4$	toluene, reflux	72	—

a) Regioisomeric ratio.

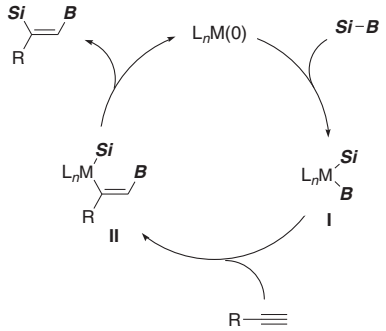
$Pd(OAc)_2$ with *t*-$BuCH_2CMe_2NC$ (Pd/L = 1/15), which were developed for the activation of Si–Si bonds,[14] catalyzed the addition of (dimethylphenylsilyl)pinacolborane (**1c**) to both terminal and internal alkynes in the temperature ranges of 50–110 °C (Tables 1 and 2).[15] Tanaka's research group also found that combination of $Pd_2(dba)_3$ (dba = dibenzylideneacetone) and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (etpo) (Pd/L = 1/2) was effective for silaboration of alkynes.[16] We later established that palladium complexes bearing tertiary phosphite or phosphine, such as $Pd_2(dba)_3/P(OEt)_3$ (Pd/L = 1/2) and $PdCl_2(PPh_3)_2$, also showed high activity for the silaboration of alkynes (Entries 2 and 3 in Table 1).[17] It should be noted that the palladium-catalyzed silaboration of terminal alkynes proceeded with nearly complete regio- and stereoselectivities to give (*Z*)-1-boryl-2-silyl-1-alkenes **6**. A platinum complex, $Pt(PPh_3)_4$, also served as an active catalyst for the silaboration, although the regioisomer, (*E*)-2-boryl-1-silyl-1-alkene, was formed as a minor product (Entry 4 in Table 1).

Silaboration of aliphatic alkynes bearing various functional groups and conjugated alkynes gave the corresponding adducts in high yields with high regio- and stereoselectivities (Entries 5–14 in Table 1). Silaboration of trimethylsilylethyne proceeded with the same regiochemical preference but a small amount of the stereoisomer was formed (Z:E = 96:4, Entry 15 in Table 1). Gaseous acetylene reacted with the silylborane under atmospheric pressure gave a 9:1 mixture of (*Z*)- and (*E*)-1-silyl-2-borylethene in 91% yield (Entry 16 in Table 1). The formation of the minor E isomer can be attributed to palladium-catalyzed isomerization of the Z isomer under the reaction conditions. Both $Pd(OAc)_2/t$-$BuCH_2CMe_2NC$ and $Pt(PPh_3)_4$ catalysts were effective for silaboration of internal alkynes such as diphenylethyne and 5-decyne (Table 2). Silaboration of 1-phenyl-1-propyne gave a cis adduct in which the silyl group was α to the phenyl group in high yield with good regioselectivity (Entries 2–4 in Table 2).

In addition to the pinacol ester of (triorganosilyl)boronic acid, silylboranes bearing bis(dialkylamino) and catecholato groups on the boron atoms reacted with terminal alkynes (Entries 17 and 18 in Table 1). (Triorganosilyl)dimesitylboranes were also applied to alkyne silaboration by another group.[18] Five-membered cyclic silylborane reacted with 1-octyne and 1-phenyl-1-propyne at room temperature in the presence of Pd/*t*-$BuCH_2CMe_2NC$ (Pd/RNC = 1/2–1/4) catalyst (Entry 19 in Table 1 and Entry 4 in Table 2).[19]

A reaction mechanism for palladium- and platinum-catalyzed silaboration of alkynes is proposed as follows (Scheme 5): (a) oxidative addition of the Si–B bond to M^0 (M = Pd and Pt) gives (boryl)(silyl)M^{II} **I**, (b) insertion of alkyne into M–B bond of **I** affords (2-boryl-1-alkenyl)(silyl)M^{II} **II**, and (c) product formation via reductive elimination from **II**. Ozawa's group observed all the elementary processes in stoichiometric reaction of silylborane with a platinum complex, followed by reaction with phenylacetylene.[20]

3.1.2 Silaboration of Si-Functionalized Silylboranes: We have recently found that hetero-substituents on the silicon atoms of silylpinacolboranes have remarkable effect on the reaction rate of silaboration reaction.[21] Large rate-accerelation was observed in the silaboration of 1-octyne with (chlorodimethylsilyl)pinacolborane (**1f**) in the presence of a catalyst



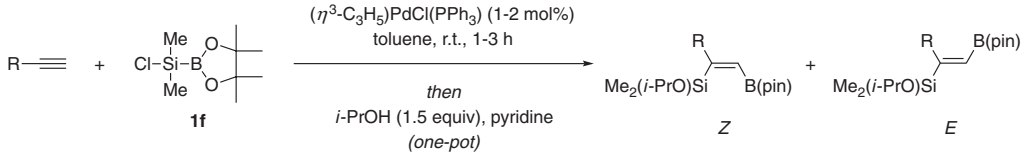
Scheme 5. Proposed mechanism for palladium- and platinum-catalyzed cis silaboration of alkynes.

generated in situ from $CpPd(\eta^3\text{-}C_3H_5)$ with PPh_3 (Pd/L = 1/1.2) (Entry 20 in Table 1). The reaction was complete within 15 min at room temperature using 1.0 mol % of the catalyst, in contrast to the reaction of (dimethylphenylsilyl)pinacolborane (**1c**), which took 70 h under the same reaction conditions. Methoxy-substituted silylpinacolborane **1g** showed moderate rate-acceleration (Entry 21 in Table 1). When a dialkylamino group was on the silicon atom, no silaboration but silole formation became a major reaction pathway. The silole formation is discussed below.

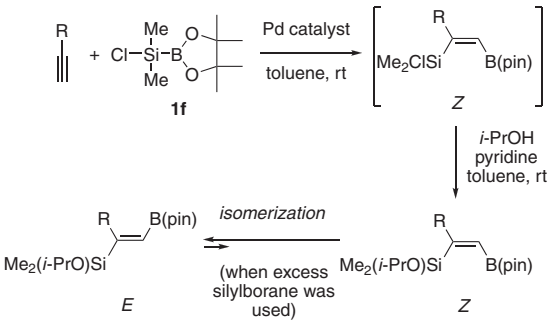
3.1.3 Trans Silaboration: We found reversal of stereochemistry in the silaboration of terminal alkynes with (chlorodimethylsilyl)pinacolborane (**1f**) (Table 3).[22] E isomer was obtained selectively when silaboration using a slightly excess amount of silylborane (silylborane:alkyne = 1.2:1.0) and conversion of the chloro group on the silicon atom to an isopropoxy group were carried out in a single flask. This stereochemical outcome was in sharp contrast to the formation of Z isomer in the corresponding palladium-catalyzed reaction using excess 1-octyne (silylborane:alkyne = 1.0:1.2) under otherwise identical reaction conditions. This stereoselective formation of the E isomer is ascribed to Z-to-E isomerization of initially formed Z isomer in the second step (Scheme 6).

As mentioned above, dramatic change of the reaction course was found in the reaction of terminal alkynes with silylpinacolboranes bearing dialkylamino groups on the silicon atoms.[21] The silylborane reacted with two equivalents of terminal alkynes to give 2,4- and 3,4-disubstituted siloles in high yields, in which no simple silaboration product formed at all (Table 4). This results indicate that (aminosilyl)boranes served as silylene equivalents under the palladium-catalyzed reaction conditions. The regioselectivity of the reaction was affected by the phosphine ligand of the palladium catalyst. Bulky, electron-donating phosphines such as P(*t*-Bu)$_2$(biphenyl-2-yl) and P(*t*-Bu)$_2$[(2′-methylbiphenyl)-2-yl] were ligand of choice for the reaction of aliphatic alkynes, achieving high regioselectivities with reasonable reaction rates (Entries 1–4). On the other hand, for aryl alkynes, palladium complex bearing PPh_3 gave 2,4-disubstituted siloles with high regioselectivities (Entries 5–11). The reaction is applicable to a variety of alkynes having functional groups such as silyloxy and chloro groups (Entries 3 and 4), both electron-rich and electron-deficient aryl groups (Entries 5–8), and bulky aryl groups such as 2,4,6-trimethylphenyl and 1-naphthyl groups (Entries 9–11). It should be noted that the reaction offers a selective synthetic route to 2,4-

Table 3. Silaboration of Terminal Alkynes with Silylborane **1f**



Entry	Alkyne	Excess alkyne (alkyne:silylborane = 1.2:1.0)		Excess silylborane (alkyne:silylborane = 1.0:1.2)	
		Yield/%	Z:E	Yield/%	Z:E
1	*n*-$C_4H_9C{\equiv}CH$	93	>99:1	87	8:92
2	*n*-$C_6H_{13}C{\equiv}CH$	93	>99:1	92	11:89
3	*n*-$C_8H_{17}C{\equiv}CH$	91	>99:1	91	8:92
4	$TBDMSO(CH)_2C{\equiv}CH$	90	>99:1	82	9:91
5	$TBDMSO(CH)_3C{\equiv}CH$	81	>99:1	82	7:93
6	$Cl(CH)_3C{\equiv}CH$	94	>99:1	84	11:89
7	$NC(CH)_3C{\equiv}CH$	87	>99:1	81	7:93
8	$PhC{\equiv}CH$	87	>99:1	80	62:38
9	*cyclo*-$C_6H_{11}C{\equiv}CH$	90	>99:1	91	67:33
10	*t*-$BuC{\equiv}CH$	87	>99:1	76	90:10



Scheme 6. Reaction pathway of trans silaboration affording E isomer.

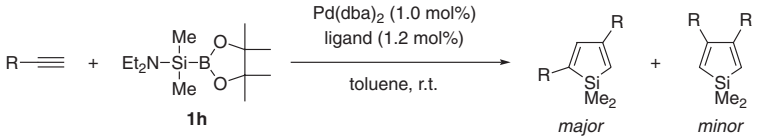
disubstituted siloles, which has been difficult to prepare by other methods.[23]

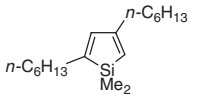
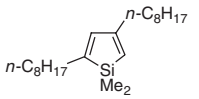
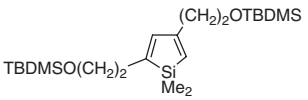
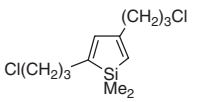
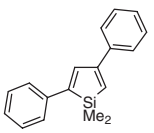
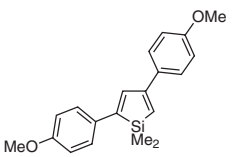
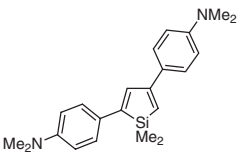
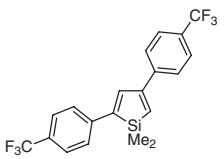
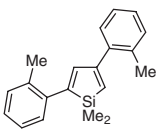
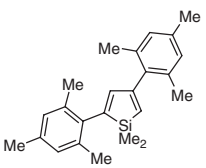
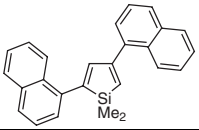
3.2 Silaboration of Alkene. 3.2.1 Intermolecular Silaboration: Silaboration of 1-octene with (dimethylphenylsilyl)pinacolborane (**1c**) took place under reflux in dioxane in the presence of platinum catalysts such as $Pt(PPh_3)_4$ and $Pt(CH_2{=}CH_2)(PPh_3)_2$ (Scheme 7).[24] The reaction gave 2-boryl-1-silyloctane **7** in moderate yield with formation of a 1,1-addition product, i.e., 1-boryl-1-silyloctane **8**. The 1,1-adducts was formed as minor isomers in the reaction of aliphatic, terminal alkenes, whereas styrene and its derivatives afforded **7** with high selectivity. Gaseous ethylene reacted with silylborane under the pressure of 60 atm in toluene to give 2-boryl-1-silylethane in 73% yield. The formation of the minor 1,1-isomer in the reaction of aliphatic alkenes may involve β-hydride elimination in the catalytic cycle.

3.2.2 Intramolecular Silaboration: Intramolecular version of alkene silaboration has recently been achieved with high stereoselectivity as well as high regioselectivity (Table 5).[25] A platinum catalyst was found effective for cyclization of silylboranes **1i** bearing 3-alkenyloxy groups on the silicon atoms, giving five-membered cyclic silyl ethers in high yields through intramolecular silaboration. Stereochemistry of the reaction of secondary homoallylic substrates was highly dependent on the phosphorus ligands on the platinum catalysts. Trans cyclic products were selectively formed in the presence of $Pt(dba)_2$–$PCyPh_2$ (Pt/L = 1/2) catalyst. The trans:cis ratio was affected by the substituent on the carbon atom adjacent to the oxygen atom: substrates bearing Me and *n*-alkyl groups gave the products with trans:cis ratio of 81:19 to 84:16, whereas high stereoselectivities (trans:cis = 87:13 to 92:8) were observed in the reaction of the substrates having sterically hindered Ph, *i*-Pr, and *t*-Bu groups. On the other hand, a $Pt(dba)_2$–$P[O(2,4\text{-}t\text{-}Bu_2C_6H_3)]_3$ catalyst gave cis products with high stereoselectivities. In contrast to the trans cyclization, the stereoselectivity of the cyclization was not sensitive to the substituents of the homoallylic positions (trans:cis = 8:92 to 6:94).

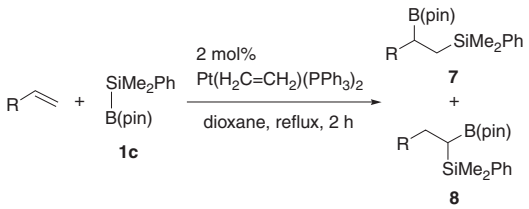
3.3 Silaboration of Allene. 3.3.1 Background and Initial Stage: Palladium-catalyzed silaboration of allenes was reported in 1999 independently by our group and Tanaka's group, which used $Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)[26] and $Pd_2(dba)_3$/etpo (Pd/L = 1/2)[27] as catalyst. The silaboration of allene proceeded with introduction of the boryl group to the central carbon atom of the allene to give β-borylallylsilanes (Table 6). In the palladium–isocyanide-catalyzed reaction, regioselectivity of the silaboration depended on the electronic nature of the substituents on the allenes. In the reaction of terminal allenes having electron-donating substituents such as alkyl, 4-methoxyphenyl, and methoxy groups, silylborane added to the internal C–C double bond to give 2-boryl-3-silyl-1-alkenes **9** (Entries 1–5 and 9). In contrast, the silylborane preferably added to the terminal C–C double bond to afford 2-boryl-1-silyl-2-alkene **10** in the silaboration of allenes bearing electron-withdrawing groups such as 4-trifluoromethylphenyl and perfluoroalkyl groups (Entries 7 and 8). Silaboration of phenylpropadiene gave a mixture of **9** and **10** under the initial conditions using the palladium/ligand ratio of 1/2–1/4 (Entry 5), which was later improved by using a catalyst with a palladium/PR_3 ratio of 1/1 (Entry 6).[28] The modified catalyst system, e.g., $Pd(dba)_2$/PPh_3 (Pd/L = 1/1.2), worked effectively even below room temperature in silaboration of terminal allenes.

Table 4. Reaction of Terminal Alkynes with Silylborane **1h**



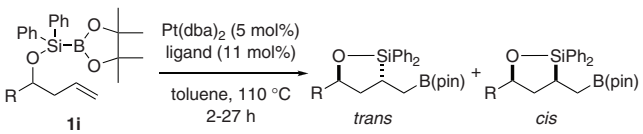
Entry	Alkyne	Ligand	Product	Yield/%	Ratio
1	*n*-$C_6H_{13}C{\equiv}CH$	P(*t*-Bu)$_2$		74	90:10
2	*n*-$C_8H_{17}C{\equiv}CH$	P(*t*-Bu)$_2$		71	96:4
3	$TBDMSO(CH_2)_2C{\equiv}CH$	P(*t*-Bu)$_2$		83	93:7
4	$Cl(CH_2)_3C{\equiv}CH$	P(*t*-Bu)$_2$, Me		78	91:9
5	$PhC{\equiv}CH$	PPh_3		92	95:5
6	4-$MeOC_6H_4C{\equiv}CH$	PPh_3		96	96:4
7	4-$Me_2NC_6H_4C{\equiv}CH$	PPh_3		80	88:12
8	4-$CF_3C_6H_4C{\equiv}CH$	PPh_3		73	94:6
9	2-$MeC_6H_4C{\equiv}CH$	PPh_3		78	95:5
10	2,4,6-$Me_3C_6H_2C{\equiv}CH$	PPh_3		80	97:3
11	1-naphthyl	PPh_3		75	99:1

Reaction mechanism for the silaboration of allene is proposed as follows (Scheme 8).[26b] Oxidative addition of the Si–B bond in silylborane to Pd^0 followed by coordination of allene gives (boryl)(silyl)Pd^{II} complex **I**. Regioselective insertion of the terminal C–C double bond of allene to the Pd–B bond affords σ-allyl palladium intermediate **II**. Isomerization of σ-allyl to π-allyl complex takes place to give complex **III**, from which β-borylallylsilane is formed via reductive elimination with regeneration of Pd^0. All steps described above are rationalized by theoretical calculation.[29]



Scheme 7. Platinum-catalyzed intermolecular silaboration of alkenes.

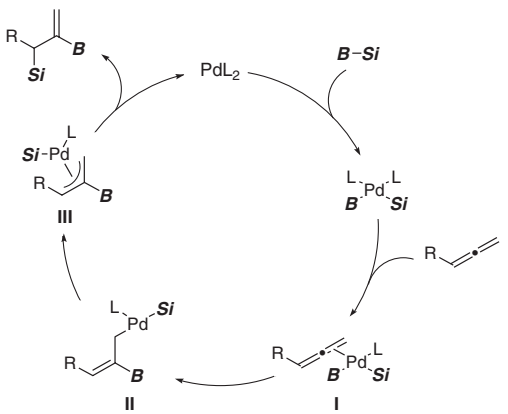
Table 5. Platinum-Catalyzed Intramolecular Silaboration of Alkenes



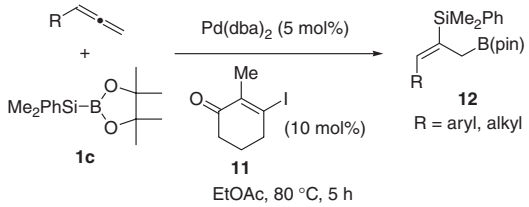
Entry	R	$PCyPh_2$		$P(O\text{-}C_6H_3\text{-}^tBu\text{-}2)_3$	
		Yield/%	trans:cis	Yield/%	trans:cis
1	Me	71	81:19	87	7:93
2	*i*-Bu	79	82:18	92	6:94
3	$Ph(CH_2)_2$	76	84:16	91	8:92
4	*i*-Pr	88	87:13	90	7:93
5	Ph	80	88:12	82	7:93
6	*t*-Bu	96	92:8	76	6:94

An interesting change of regioselectivity was observed by Cheng's research group when the reaction was carried out with organic iodide **11**, leading to the formation of β-silylallylboranes **12** (Scheme 9).[30] A reaction mechanism which does not involve oxidative addition of the Si–B bond was proposed.

3.3.2 Asymmetric Silaboration with Chiral Silylboranes: Using optically active silylboranes, enantioface selection was induced to silaboration of allenes.[31] In the presence of $CpPd(\eta^3\text{-}C_3H_5)/PPh_3$ (Pd/L = 1/1.2) catalyst, a silylborane (−)-**1j** derived from (−)-pinanediol added to 5-phenyl-1,2-pentadiene in toluene at room temperature, giving a β-borylallylsilane **9a** with the diastereomer ratio of 81:19 (Entry 1 in Table 7). Silylboranes **1k–1n** bearing other chiral auxiliaries such as (*R*,*R*)-2,3-butanedioxy and (*S*,*S*)-1,2-diphen-

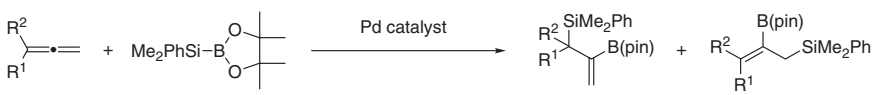


Scheme 8. Proposed reaction mechanism for palladium-catalyzed silaboration of allenes.



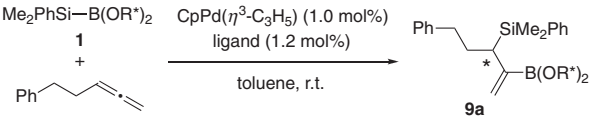
Scheme 9. Silaboration of allenes under Cheng's conditions.

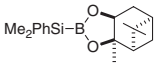
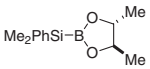
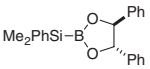
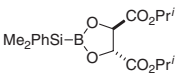
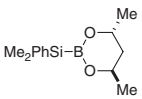
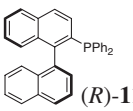
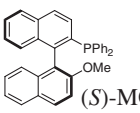
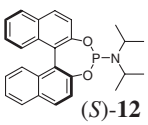
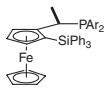
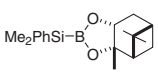
Table 6. Silaboration of Terminal Allenes with **1c**



Entry	R^1	R^2	Catalyst	Conditions	Yield/%	**9**:**10**
1	$Ph(CH_2)_2$	H	$Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)	octane, 120 °C, 2 h	99	100:0
2	*cyclo*-C_6H_{11}	H	$Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)	octane, 120 °C, 2 h	76	100:0
3	*t*-Bu	H	$Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)	octane, 120 °C, 2 h	88	94:6
4	4-$MeOC_6H_4$	H	$Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)	octane, 120 °C, 2 h	76	94:6
5	Ph	H	$Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)	octane, 120 °C, 2 h	95	86:16
6	Ph	H	$Pd(dba)_2/PPh_3$ (Pd/L = 1/1.2)	toluene, rt, 4 h	99	94:6
7	4-$CF_3C_6H_4$	H	$Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)	octane, 120 °C, 2 h	81	36:64
8	*n*-C_6F_{13}	H	$Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)	octane, 120 °C, 2 h	94	0:100
9	MeO	H	$Pd(acac)_2$/2,6-$Me_2C_6H_3NC$ (Pd/L = 1/4)	octane, 120 °C, 2 h	92	100:0
10	H	H	$Pd(acac)_2$/*t*-$BuCH_2CMe_2NC$ (Pd/L = 1/4)	octane, 80 °C, 2 h	93	—
11	Me	Me	$PdCl_2(PPh_3)_2$	octane, 120 °C, 2 h	88	100:0

Table 7. Enantioface-Selective Silaboration of 5-Phenyl-1,2-pentadiene with Chiral Silylboronic Esters



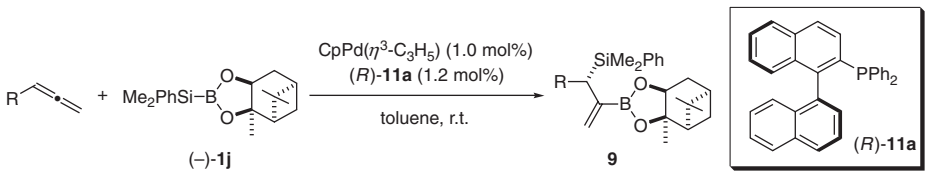
Entry	Silylborane	Ligand	Yield /%	Diastereomeric ratio
1	 (−)-**1j**	PPh_3	96	81:19
2	 **1k**	PPh_3	86	51:49
3	 **1l**	PPh_3	94	52:48
4	 **1m**	PPh_3	90	68:32
5	 **1n**	PPh_3	85	58:42
6	(−)-**1j**	 (*R*)-**11a**	99	94:6
7	(−)-**1j**	 (*S*)-MOP	88	83:17
8	(−)-**1j**	 (*S*)-**12**	95	71:29
9	(−)-**1j**	 **13** [Ar = 3,5-$(CF_3)_2C_6H_3$]	95	90:10
10	 (+)-**1j**	(*R*)-**11a**	96	63:37

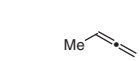
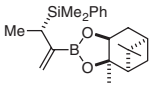
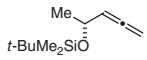
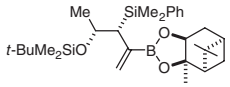
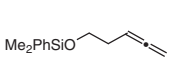
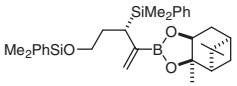
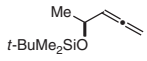
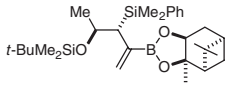
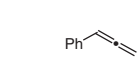
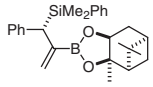
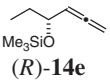
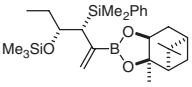
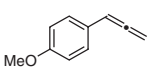
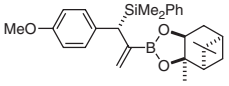
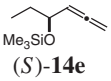
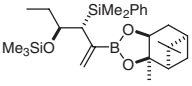
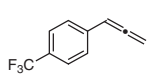
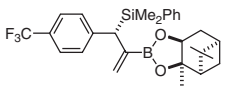
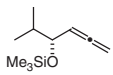
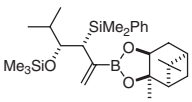
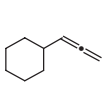
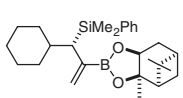
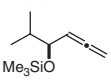
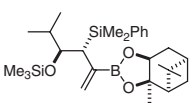
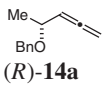
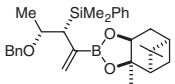
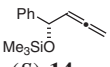
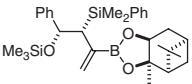
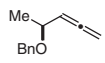
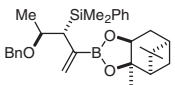
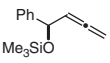
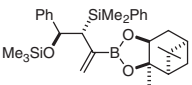
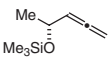
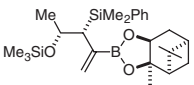
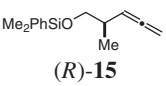
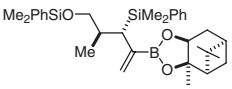
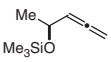
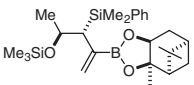
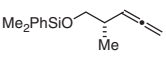
yl-1,2-ethanedioxy groups were much less effective for the enantioface selection of the allene (Entries 2–5). Enantioface selectivity was much improved by carrying out the reaction with a chiral palladium catalyst. Silylborane (−)-**1j** and a palladium catalyst bearing chiral monodentate phosphine (*R*)-**11a** was the best combination for enantioface-selective silaboration of the allene, resulting in formation of **9a** with the diastereomer ratio of 94:6 (Entry 6). Palladium catalysts bearing other chiral phosphines such as (*S*)-MOP, (*S*)-**12**, and **13** resulted in inferior enantioface selection (Entries 7–9). Silylborane (+)-**1j** with Pd/(*R*)-**11a** catalyst gave the product with a diastereomer ratio of 63:37 (Entry 10), indicating (−)-**1j** with Pd/(*R*)-**11a** catalyst (or (+)-**1j** with Pd/(*S*)-**11a** catalyst) is a matched combination for the enantioface-selective silaboration. Using (*R*)-**11a** as a chiral ligand, addition of both (−)-**1j** and (+)-**1j** took place from the same enantioface of the allene C–C double bond, indicating that the enantioface selection is mainly governed by the chiral ligand. The double asymmetric induction conditions using (−)-**1j** with Pd/(*R*)-**11a** catalyst could be applicable to various terminal allenes, affording optically active β-borylallylsilanes **9** with the diastereomer ratio of up to 98:2 (Table 8). The diastereomer ratio depended on the bulkiness of the substituent R of allenes. No marked electronic effect of para substituents of the arylallenes on the diastereomer ratio was observed (Entries 4 and 5).

The double asymmetric induction system, using both a chiral silylborane and a chiral palladium catalyst, is effective for enantioface-selective silaboration of terminal allenes having stereogenic carbon centers α to the double bonds (Entries 7–22 in Table 8).[32] In the presence of a Pd/(*R*)-**11a** catalyst, (−)-**1j** added to α-alkoxyallenes **14** (Entries 7–20) and α-(alkoxymethyl)allene **15** (Entries 21 and 22) with efficient control of the stereochemistry of the new stereogenic carbon centers formed in the products. The diastereomer ratio was in the range of 99:1 to 96:4 for matched combination (Entries 7, 9, 11, 13, 15, 17, 19, and 21), whereas even the mismatched combinations gave 95:5 to 92:8 ratios (Entries 8, 10, 12, 14, 16, 18, 20, and 22). These results demonstrate that the system is a nearly ideal reagent-controlled asymmetric reaction, which allows access to any desirable diastereomers of the β-borylallylsilanes in nearly enantiomerically pure forms.

3.3.3 Asymmetric Silaboration with Achiral Silylboranes: Under the double asymmetric induction conditions, the enantioface selection of allene relies mainly on the chiral ligand as described above, though the use of a pinanedioxy group as chiral auxiliary was crucial in obtaining high diastereomeric ratio. To explore catalytic asymmetric silaboration of allene that does not rely on the stoichiometric use of a chiral auxiliary, silaboration of terminal allenes with achiral silylboranes was examined in the presence of chiral palladium catalysts (Scheme 10).[33] In the silaboration of cyclohexylpropadiene with (dimethylphenylsilyl)pinacolborane (**1c**) at room temperature, palladium catalyst bearing (*R*)-**11a** gave the product with 74% ee, whereas (+)-NMDPP, (*S*)-MONOPHOS, (*R*,*R*)-**16**, (*S*)-QUINAP, and (*S*)-MOP afforded lower enantiomeric excesses. Optimization of the ligand structure revealed that binaphthyl-based phosphine (*R*)-**11g**, 2-[bis(3,5-dimethylphenyl)phosphino]-1,1′-binaphthyl, gave the product with 84% ee at room temperature. Structure of the silylborane also affected the enantioselectivity (Scheme 11): pinacolboryl groups gave higher selectivity than catechol and ethylene glycol derivatives, and methyldiphenylsilyl was better than dimethylphenylsilyl and triphenylsilyl groups. The highest selectivity was attained in the reaction with (methyldiphenylsilyl)pinacolborane (**1p**) (89% ee at room temperature). Under the optimized conditions using the Pd/(*R*)-**11g** catalyst with silylborane **1p**, silaboration of various terminal allenes proceeded at 0 °C with high enantioselectivity (up to 93% ee) (Table 9). The enantioselectivity depended on the bulkiness of substituents of allenes: the enantiomeric excesses of the products ranged between 91 and 93% ee for bulky alkyl groups

Table 8. Enantioface-Selective Silaboration of Terminal Allenes via Double Asymmetric Induction



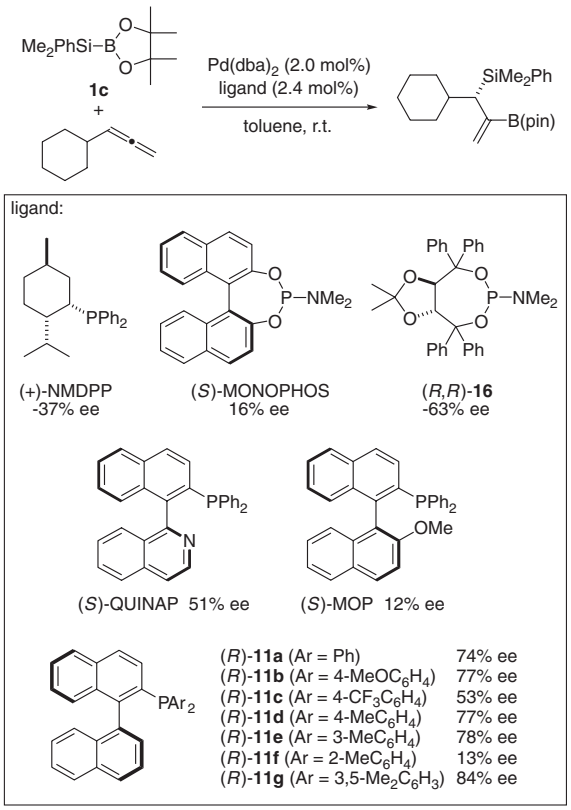
Entry	Allene	Product	Yield/%	Ratio[a]	Entry	Allene	Product	Yield/%	Ratio[a]
1			92	93:7	13	 (*R*)-**14d**		90[d]	99:1
2			91	94:6	14	 (*S*)-**14d**		90[d]	92:8
3			95	96:4	15	 (*R*)-**14e**		98[e]	98:2
4			96	95:5	16	 (*S*)-**14e**		98[e]	93:7
5			92	96:4	17	 (*R*)-**14f**		94[f]	97:3
6			95	98:2	18	 (*S*)-**14f**		94[f]	93:7
7	 (*R*)-**14a**		94[b]	97:3	19	 (*S*)-**14g**		84[g]	97:3
8	 (*S*)-**14a**		94[b]	95:5	20	 (*R*)-**14g**		84[g]	92:8
9	 (*R*)-**14b**		87[c]	98:2	21	 (*R*)-**15**		88	96:4
10	 (*S*)-**14b**		87[c]	93:7	22	 (*S*)-**15**		81	94:6
11	(*R*)-**14c**		98	98:2					
12	(*S*)-**14c**		98	94:6					

a) Diastereomeric ratio. b) Total yield of Entries 7 and 8. c) Total yield of Entries 9 and 10. d) Total yield of Entries 13 and 14. e) Total yield of Entries 15 and 16. f) Total yield of Entries 17 and 18. g) Total yield of Entries 19 and 20.

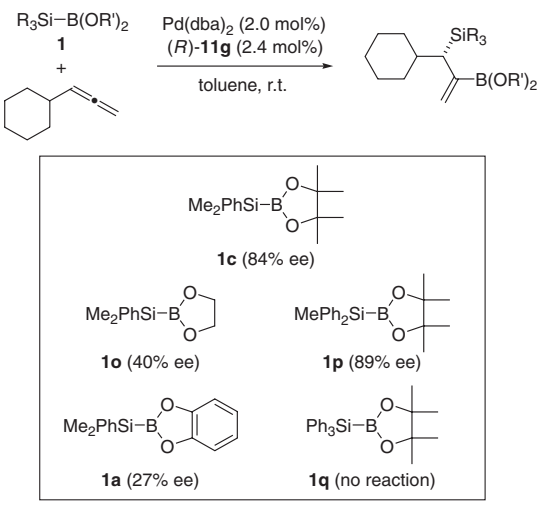
(Entries 1–3), 88–90% ee for arylallenes (Entries 4–7), and 80–82% ee for less sterically demanding allenes (Entries 8 and 9). Silaboration of allenes having silyloxy, acetoxy, and formyl groups also proceeded in high yield (Entries 2, 3, and 10), affording functionalized β-borylallylsilanes with high enantiomeric excesses.

4. 1,3-Silaboration

4.1 Silaborative C–C Cleavage of Methylenecyclopropanes. Silaboration of methylenecyclopropanes proceeds in the presence of palladium and platinum catalysts via cleavage of the C–C bond in the cyclopropane ring, giving 1,3-silaboration compounds.[34,35] In the reaction of certain methylenecyclopropanes, selective formations of different isomers were achieved by choice of the catalysts. *E*- and *Z*-Alkenylboron products **18a** were selectively formed with $Pd(OAc)_2$/*t*-$BuCH_2CMe_2NC$ (Pd/L = 1/7.5) (E:Z = 83:17) and $Pt(C_2H_4)(PPh_3)_2$ (E:Z = 17:83), respectively, via cleavage of a proximal C–C bond in reactions of benzylidenecyclopropane (**17a**) with (dimethylphenylsilyl)pinacolborane (**1c**) (Scheme 12). In the reaction of cyclohexylidenecyclopropane (**17b**), proximal C–C bond cleavage took place selectively with



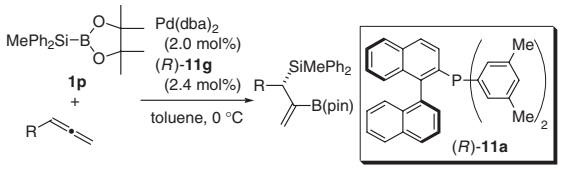
Scheme 10. Optimization of ligand in enantioselective silaboration of cyclohexylpropadiene.

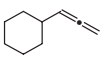
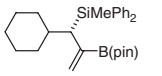
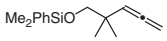
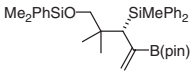
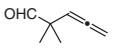
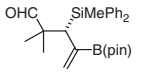
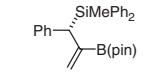
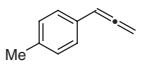
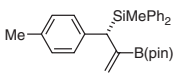
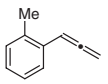
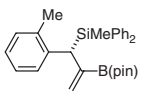
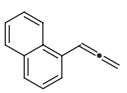
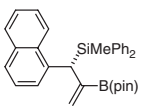
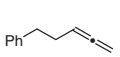
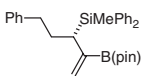
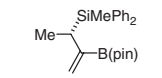
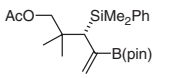


Scheme 11. Optimization of silylborane in enantioselective silaboration of cyclohexylpropadiene.

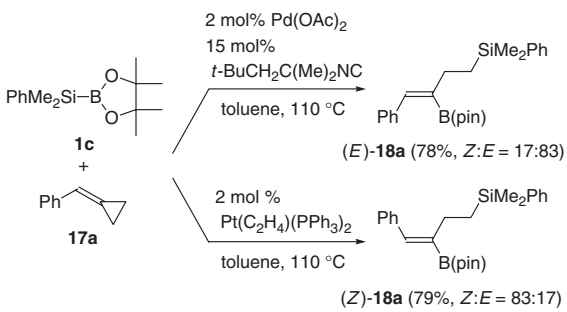
a platinum catalyst to afford alkenylborane **18b′**, whereas a palladium catalyst promoted distal C–C bond cleavage, resulting in selective formation of allylborane **18b** (Scheme 13). Selective 1,3-introduction of the boryl and the silyl groups was observed in the reaction of cyclohexane-fused methylenecyclopropanes **17c** in the presence of a palladium catalyst. In sharp contrast, a $Pt(C_2H_4)(PPh_3)_2$ catalyst resulted in 1,4-introduction of the two groups to give **18c′** selectively (Scheme 14).

Table 9. Enantioselective Silaboration of Terminal Allenes with **1p**



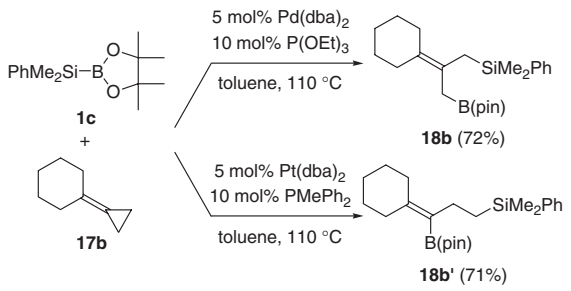
Entry	Allene	Product	Yield/%	% ee
1			90	91
2			97	92
3			95	93
4			93	88
5			94	89
6			93	90
7			86	90
8			96	82
9			91	80
10[a)]			91	90

a) Reaction with Me_2PhSi–B(pin) (**1c**) at −10 °C in the presence of 4.0 mol % of catalyst.

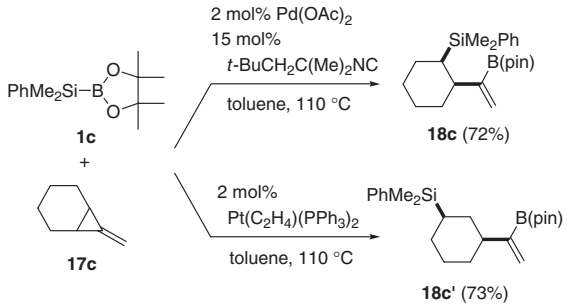


Scheme 12. Silaborative C–C cleavage of methylenecyclopropane **17a**.

4.2 Asymmetric Silaboration of Methylenecyclopropanes. It was found that use of palladium–phosphine catalysts with a Pd/P ratio of 1/1, which exhibited high catalyst activity in the silaboration of allenes, was also effective for the reaction of methylenecyclopropane.[36] In the presence of $Pd(dba)_2/PPh_3$ (Pd/L = 1/1.2) catalyst, reaction of cyclohex-



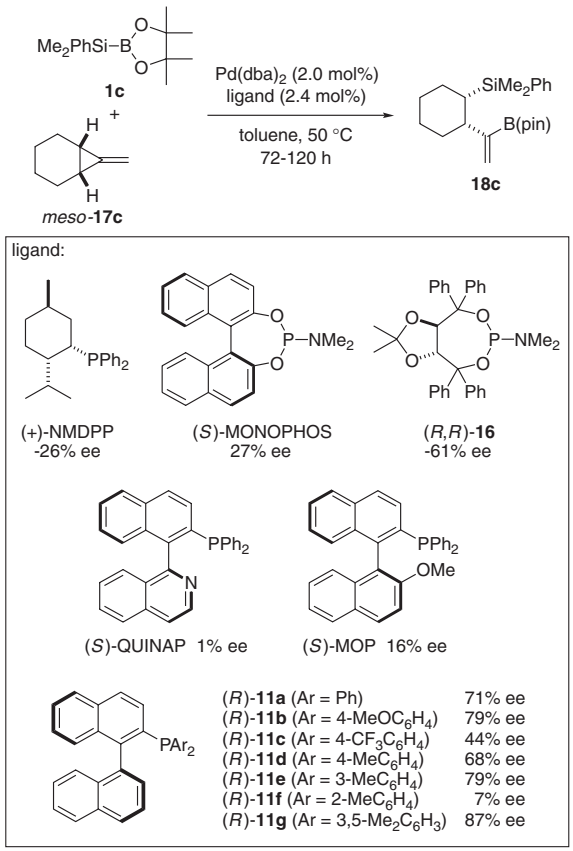
Scheme 13. Silaborative C–C cleavage of methylenecyclopropane **17b**.



Scheme 14. Silaborative C–C cleavage of methylenecyclopropane **17c**.

ane-fused methylenecyclopropane **17c** with (dimethylphenylsilyl)pinacolborane (**1c**) proceeded at 50 °C, whereas the original catalyst system required 110 °C. Based on this catalyst system, enantioselective silaborative C–C cleavage of *meso*-methylenecyclopropanes was examined with palladium catalysts bearing chiral monodentate phosphorus ligands (Scheme 15). The phosphine (*R*)-**11a** having a binaphthyl group was again found effective for differentiation of enantiotopic C–C bonds in **17c**, giving a 2-boryl-4-silyl-1-butene derivative **18c** with 71% ee. Other monodentate chiral phosphines such as (+)-NMDPP, (*S*)-MONOPHOS, (*R*,*R*)-**16**, (*S*)-QUINAP, and (*S*)-MOP afforded lower enantioselectivities. Optimization of the reaction conditions using derivatives of (*R*)-**11a** having substituted aryl groups on the phosphorus atom revealed that (*R*)-**11g** was the ligand of choice for the reaction (87% ee). Further improvement of enantioselectivity was achieved by using (methyldiphenylsilyl)pinacolborane (**1p**), resulting in 90% ee for the formation of **18c**. Under the optimized reaction conditions using **1p** with Pd/(*R*)-**11g** catalyst, silaborative C–C cleavage of various *meso*-methylenecyclopropanes **17** afforded the corresponding products **18** in high yields with high ees (Table 10). The reactions of bicyclic methylenecyclopropanes **17c**–**17f** and **17h** that have fused five- to eight-membered rings gave the corresponding products with 89–91% ee (Entries 1–4 and 6), whereas a little lower ee was observed in the reaction of non-fused *meso*-methylenecyclopropane **17g** (81% ee, Entry 5).

We proposed a mechanism involving C–C double bond insertion and subsequent β-carbon elimination for the palladium-catalyzed enantioselective silaborative C–C cleavage of *meso*-methylenecyclopropane (Scheme 16). The C–C double bond in methylenecyclopropane coordinates to the B–Pd–Si complex on a less sterically congested π-face opposite to the



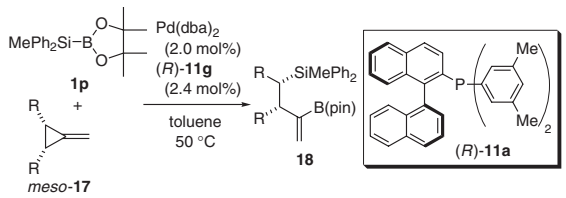
Scheme 15. Optimization of ligand in enantioselective silaborative C–C cleavage of *meso*-**17c**.

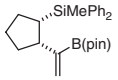
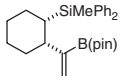
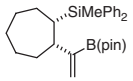
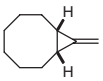
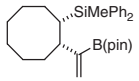
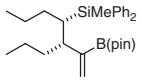
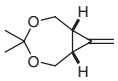
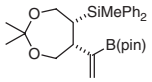
substituents on the cyclopropane ring. After insertion of the C–C bond into the B–Pd bond, β-carbon elimination takes place at one of the two enantiotopic proximal C–C bonds in the three-menbered ring. Absolute configuration of the product indicates that the bond ***a*** in the intermediate **A** is cleaved selectively. The mechanism of enantio-discrimination in the silaboration of methylenecyclopropanes may follow that of allene silaboration as suggested by the common use of silylborane **1p** with Pd/(*R*)-**11g** as the best set of reagents. In silaboration of allene, terminal C–C double bond insertion into the Pd–B bond takes place from the π-face opposite to the substituent on allene, affording σ-allyl complex **B** (Scheme 17). Isomerization of **B** to π-allylpalladium intermediate then proceeds with discrimination of enantioface of the double bond, in which the β-face is favorably selected under the conditions using silylborane **1p** with Pd/(*R*)-**11g**. The enantioface-discriminating step for the allene silaboration may correspond to the enantiobond-discriminating step in the methylenecyclopropane silaboration.

5. 1,4-Silaboration

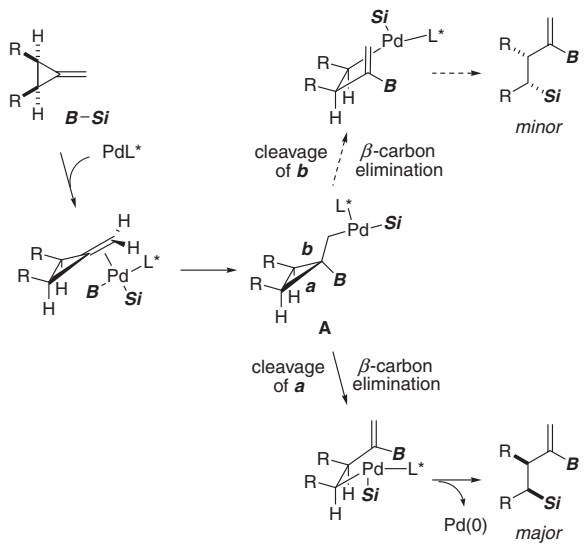
5.1 Silaborative Dimerization of Alkyne. In sharp contrast to palladium- and platinum-catalysts, a phosphine-free nickel catalyst promoted double insertion of alkyne into the silicon–boron bond of (dimethylphenylsilyl)pinacolborane (**1c**). In the presence of a nickel(0) catalyst generated in situ by the reaction of $Ni(acac)_2$ with diisobutylaluminum hydride (DIBAH), **1c** reacted with two equivalents of 1-hexyne in

Table 10. Asymmetric Silaborative C–C Cleavage of *meso*-Methylenecyclopropanes

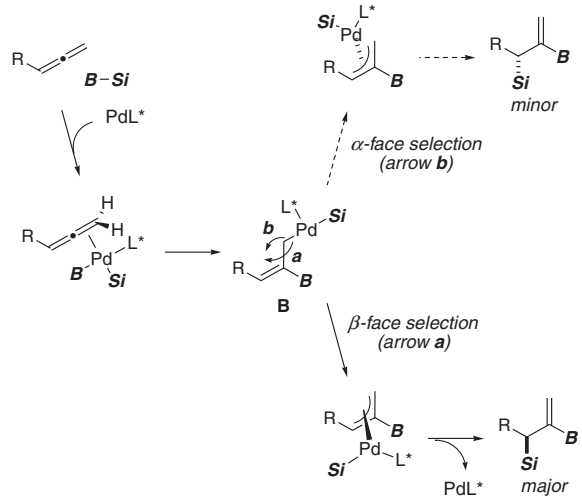


Entry	MCP	Product	Yield/%	% ee
1[a)]	 **17d**	 **18d**	72	90
2	 **17c**	 **18c**	87	90
3	 **17e**	 **18e**	95	91
4	 **17f**	 **18f**	85	90
5[a)]	 **17g**	 **18g**	72	81
6[b)]	 **17h**	 **18h**	50	89

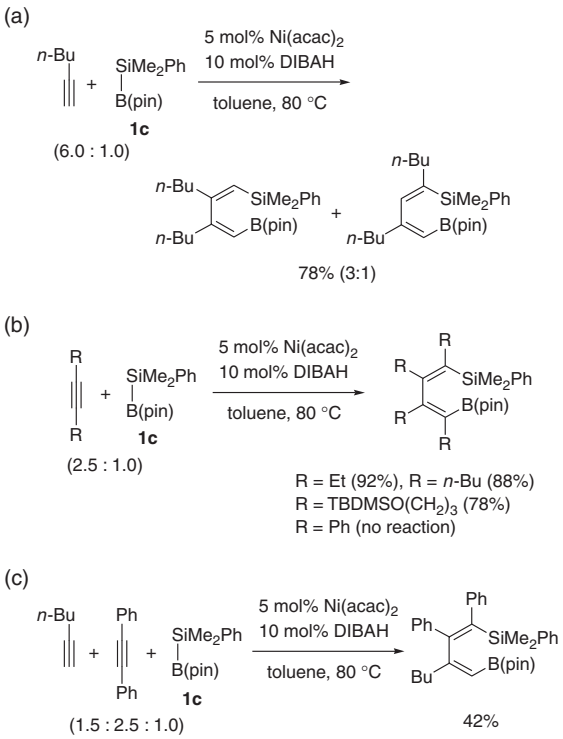
a) $Pd(dba)_2$ (3.0 mol %) and (*R*)-**11g** (3.6 mol %) were used. b) $Pd(dba)_2$ (4.0 mol %) and (*R*)-**11g** (4.8 mol %) were used.



Scheme 16. Proposed mechanism for enantioselective silaborative C–C cleavage of methylenecyclopropane.



Scheme 17. Proposed mechanism for enantioselective silaboration of allene.



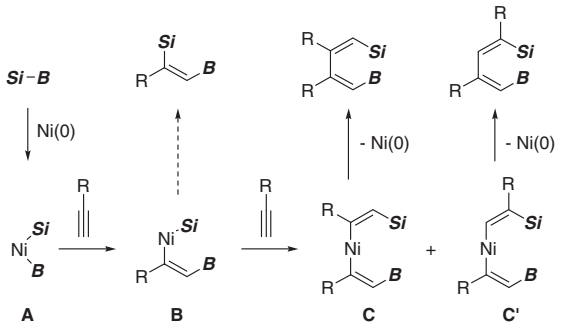
Scheme 18. Nickel-catalyzed silaborative dimerization of alkynes.

toluene at 80 °C (Scheme 18a).[37] The reaction gave head-to-head and head-to-tail dimers (3:1) in good total yield with almost no formation of a single insertion product (<5%). The silaborative dimerization is applicable to internal aliphatic alkynes such as 3-hexyne (Scheme 18b). Cross-dimerization of diphenylacetylene with 1-hexyne was demonstrated on the basis of the assumption that diphenylacetylene reacted only in the second insertion step (Scheme 18c).

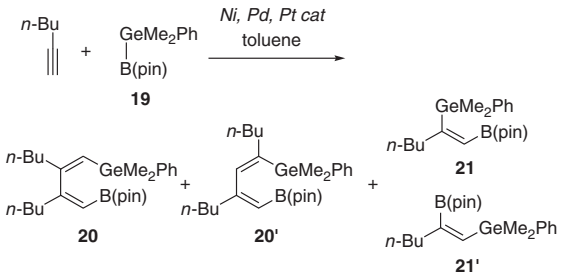
The nickel-catalyzed silaborative dimerization may proceed as follows (Scheme 19): (a) oxidative addition of the Si–B bond to Ni^0 gives (silyl)(boryl)Ni^{II} intermediate **A**, (b) insertion of terminal alkyne into the Ni–B bond of **A** affords

(silyl)(2-boryl-1-alkenyl)Ni^{II} **B** with high regioselectivity, (c) insertion of the second alkyne into the Ni–Si bond of **B** yields **C** and **C′** with moderate regioselectivity, (d) the diene products are formed by reductive elimination from **C** and **C′** with regeneration of Ni^0. The preference for the double insertion over single insertion is due to relatively slow reductive elimination from **B** and fast insertion of the second alkyne into Ni–Si bonds.

Related reaction of (dimethylphenylgermyl)pinacolborane (**19**) with 1-hexyne demonstrated that the ratio of monoinsertion products and double insertion products depended on the central metal of the catalyst (Scheme 20). With Ni^0 catalyst, the reaction gave 1:2 coupling product **20** (74% yield) with a trace amount of 1:1 coupling product **21**. On the other hand, no formation of **20** was observed when the reaction was carried out with $Pt(CH_2{=}CH_2)(PPh_3)_2$ catalyst, which gave **21** in 87% yield. A $Pd(acac)_2$/*t*-$BuCH_2CMe_2NC$ catalyst gave almost 1:1 mixture of **20** and **21**. These results suggest that the order of the ease of the second insertion into the Pd–Ge bond relative to



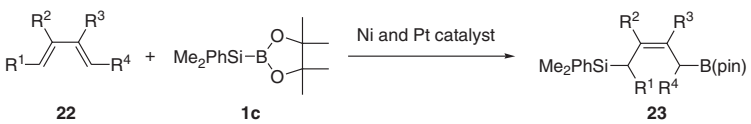
Scheme 19. Possible mechanism for Ni-catalyzed silaborative dimerization of alkynes.



catalyst	**20**+**20'** (**20**:**20'**)	**21**+**21'** (**21**:**21'**)
$Ni(acac)_2$/DIBAH	74% (74:26)	trace
$Pd(acac)_2$/*t*-$BuCH_2CMe_2NC$	39% (96:4)	46% (>99:1)
$Pt(CH_2{=}CH_2)(PPh_3)_2$	0%	87% (91:9)

Scheme 20. Group 10 transition-meal-catalyzed reaction of germylborane **19** with 1-hexyne.

Table 11. 1,4-Silaboration of 1,3-Dienes with **1c**

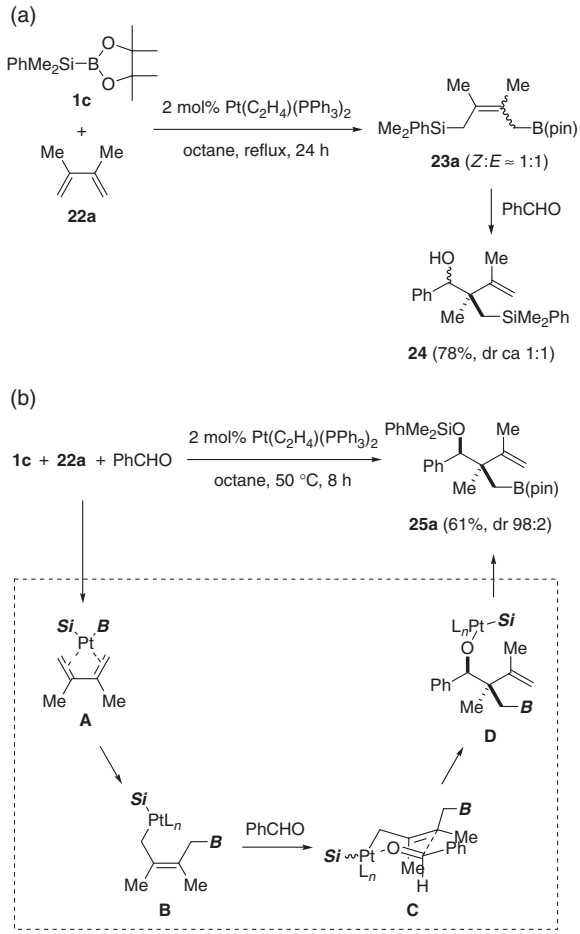


Entry	Diene	Catalyst	Product	Yield/%
1	**22a**	$Pd(OAc)_2$/*t*-$BuCH_2CMe_2NC$ (Pd/L = 1/15)	—	0
2	**22a**	$Pt(CH_2{=}CH_2)(PPh_3)_2$	**(*Z*)-23a** + **(*E*)-23a** (48 : 52)	95
3	**22a**	$Ni(acac)_2$/DIBAH	**(*Z*)-23a**	90
4	**22b**	$Ni(acac)_2$/DIBAH	**23b**	90
5	**22c**	$Ni(acac)_2$/DIBAH	**23c** + **23c'** (72 : 28)	92
6	**22d**	$Ni(acac)_2$/DIBAH	**23d** + **23d'** (67 : 33)	84
7	**22e**	$Ni(acac)_2$/$PCyPh_2$/DIBAH (Ni/L = 1/2)	**23e**	99
8	**22f**	$Ni(acac)_2$/$PCyPh_2$/DIBAH (Ni/L = 1/2)	**23f**	93

the reductive elimination of the monoinsertion products is Ni > Pd > Pt.

5.2 Silaboration of 1,3-Diene. Silaboration of 2,3-dimethylbutadiene (**22a**) with (dimethylphenylsilyl)pinacolborane (**1c**) did not take place in the presence of $Pd(OAc)_2$/*t*-$BuCH_2CMe_2NC$ catalyst, despite the fact that the catalyst effectively promotes silaboration of alkynes and allenes (Entry 1 in Table 11). The silaboration of **22a** proceeded in high yield with a $Pt(CH_2{=}CH_2)(PPh_3)_2$ catalyst at 110 °C in octane, although a mixture of stereoisomers (Z:E = ca. 1:1) was obtained (Entry 2).[38] We finally found that nickel catalyst promoted stereoselective 1,4-silaboration of **22a**.[39] In the presence of a nickel catalyst generated in situ from $Ni(acac)_2$ with DIBAH, the reaction proceeded at 80 °C, giving (*Z*)-1-boryl-2,3-dimethyl-4-silyl-2-butene **23a** in high yield with complete Z selectivity (Entry 3). The reaction of isoprene (**22c**) and 2-methyl-1,3-pentadiene (**22d**) afforded the corresponding 1,4-adducts as a mixture of regioisomers (Entries 5 and 6). For silaboration of 1,3-cyclohexadiene (**22e**), use of a phosphine ligand was crucial. The nickel catalyst with $PCyPh_2$ gave 1-boryl-4-silyl-2-cyclohexene **23e** in quantitative yield with high cis selectivity (cis:trans = >99:1, Entry 7), whereas no reaction proceeded in the absence of phosphine ligands. Seven-membered diene **22f** also gave the corresponding 1,4-adduct **23f** in 93% yield using the nickel–phosphine catalyst (Entry 8). Enantioselective silaboration of **22e** was achieved by Moberg's group in 70% ee using a platinum catalyst bearing a chiral phosphoramidite ligand.[40] They also reported that related nickel-catalyzed reaction of (dimethylphenylsilyl)pinacolborane (**1c**) with acyclic 1,4-disubstituted butadiene resulted in the formation of dienylboranes and allylic silanes as major products.[41] Platinum-catalyzed 1,4-silaboration of conjugated enynes having bulky substituents at the alkynyl carbons was also reported by Moberg's group.[42]

5.3 Three-Compornent Coupling of Silylborane, 1,3-Diene, and Aldehyde. As described above, platinum-catalyzed silaboration of 2,3-dimethylbutadiene (**22a**) gave a 1:1 mixture of *Z*- and *E*-allylic boronate **23a**, which subsequently reacted with benzaldehyde to give homoallylic alcohol **24** as a 1:1 mixture of syn/anti diastereomers (Scheme 21a). Remarkable change of reaction course was observed when the silaboration of **22a** was carried out in the presence of benzaldehyde under otherwise the same reaction conditions (Scheme 21b).[38] The reaction gave silyl ethers of homoallylic alcohols **25a**, which have a borylmethyl group at the allylic position, in good yield with high diastereoselectivity (dr 98:2). Stereoselective formation of **25a** is rationalized by the following mechanism. Oxidative addition of the Si–B bond to Pt^0 and coordination of **22a** gives complex **A**, which undergoes insertion of the diene into the Pt–B bond in a 1,4-fashion. Resultant σ-allyl platinum complex **B** reacts with aldehyde via six-membered cyclic intermediate **C**, resulting in C–C bond formation at the position γ to the platinum atom to give (alkoxy)(silyl)platinum **D**, which undergoes reductive elimination of the product with regeneration of Pt^0. The allylplatination of aldehyde proceeds through chair-like intermediate **C**, in which the substituent on the aldehyde occupies the equatorial position leading to the observed high syn/anti selectivity.



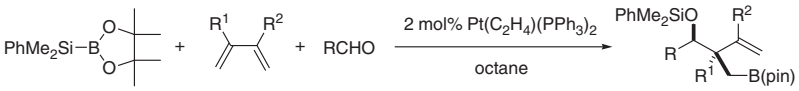
Scheme 21. Platinum-catalyzed reaction of silylborane **1c** with diene **22a** in the absence or presence of benzaldehyde.

The platinum-catalyzed three-component coupling was applicable to various 1,3-dienes **22g**–**22h** and aldehydes (both electron-rich and electron-deficient aromatic aldehydes and aliphatic aldehydes) with (dimethylsilyl)pinacolborane (**1c**) (Table 12). In the reaction of unsymmetrical **22g**, the C–C bond formations took place selectively at the less substituted C–C double bond (Entries 1–6).

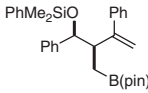
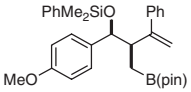
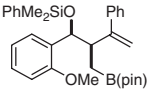
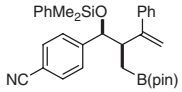
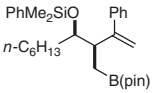
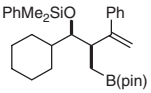
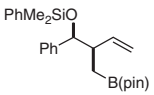
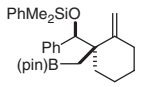
6. 1,5- and 1,6-Silaboration

Nickel-catalyzed reaction of vinylcyclopropanes **26** with a silylborane proceeded with cleavage of the cyclopropane ring to afford formal 1,5-silaboration products **27**.[43] In the presence of Ni^0–PCy_3 catalyst generated in situ by the reaction of $Ni(acac)_2/PCy_3$ with DIBAH, (1-phenylethenyl)cyclopropane reacted with (dimethylphenylsilyl)pinacolborane (**1c**) in toluene at 90 °C, giving (*E*)-5-boryl-2-phenyl-1-silyl-2-pentene in high yield (Scheme 22). In the reaction, one of the two proximal C–C bonds of the cyclopropane ring was cleaved with formation of a C–B bond with C–Si bond formation at the terminal vinyl carbon. Use of nickel complex and PCy_3 in a ratio of 1:1 was crucial to secure high activity of the catalyst. The silaborative C–C cleavage was applicable to various vinylcyclopropanes having a substituent at the internal and terminal vinyl carbons, providing the corresponding allylsi-

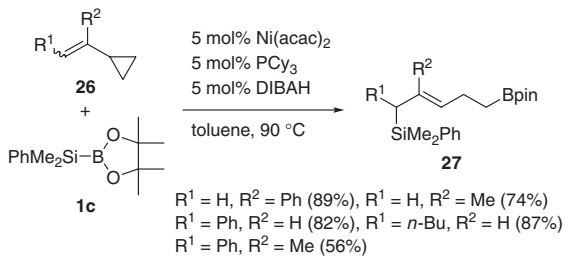
Table 12. Silaborative Coupling of 1,3-Dienes and Aldehydes with **1c**



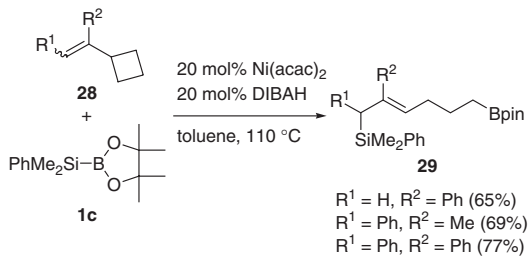
1c 22 25

Entry	Diene	Aldehyde	Temp/°C	Product	Yield/%	Ratio[a)]
1	 **22g**	PhCHO	120		79	99:1
2	**22g**	4-$MeOC_6H_4CHO$	120		77	99:1
3	**22g**	2-$MeOC_6H_4CHO$	120		83	99:1
4	**22g**	4-NCC_6H_4CHO	120		80	99:1
5	**22g**	heptanal	120		71	93:7
6	**22g**	*cyclo*-$C_6H_{10}CHO$	120		60	96:4
7	 **22b**	PhCHO	50		63	95:5
8	 **22h**	PhCHO	80		60	99:1

a) Diastereomeric ratio.



Scheme 22. Nickel-catalyzed silaborative C–C cleavage of vinylcyclopropanes.



Scheme 23. Nickel-catalyzed silaborative C–C cleavage of vinylcyclobutanes.

lanes **27** in good yields with high regio- and stereoselectivity. The reaction may proceed through the formation of (π-allyl)(silyl)nickel(II) intermediate via cleavage of the proximal C–C bond of the cyclopropane ring with formation of the C–B bond.

Vinylcyclobutanes **28** also reacted with (dimethylphenylsilyl)pinacolborane (**1c**) with cleavage of the cyclobutane ring in the presence of a nickel catalyst (Scheme 23).[43] The reaction took place at 110 °C with a phosphine-free nickel catalyst to afford formal 1,6-silaboration products **29** with regioselective introduction of the boron atom via cleavage of the proximal C–C bond in the cyclobutane ring.

7. Synthetic Application of Silaboration Products

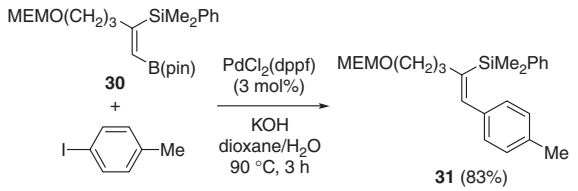
Compounds prepared by the catalytic silaboration of unsaturated hydrocarbons can be useful synthetic intermediates in organic synthesis on the basis of selective functionalization at the carbon–boron and the carbon–silicon bonds. In this section, examples of synthetic application of the silaboration products are shown.

Catalytic silaborations of alkynes, allenes, and methylenecyclopropanes provided new alkenylboron derivatives bearing silyl groups in the molecules. They can generally be good synthetic intermediates for the synthesis of organosilicon

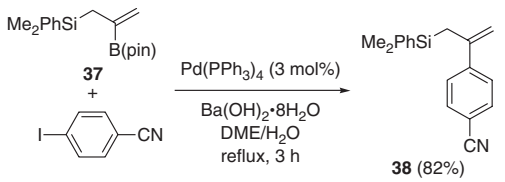
compounds via Suzuki–Miyaura coupling. For example, compound **30**, obtained by silaboration of 5-methoxyethoxy-1-pentyne, reacted under standard coupling conditions to give stereo-defined trisubstituted alkenylsilane **31** in high yield (Scheme 24).[15] Through stereocomplementary silaborations of 1-octyne, stereoselective synthesis of four isomers of 1,2-diaryloct-1-ene **34** and **36** was achieved with (*Z*)- and (*E*)-1-boryl-2-silyl-1-octene **32** via Suzuki–Miyaura coupling followed by Hiyama coupling (Scheme 25).[22] A functionalized allylsilane **38** was obtained via Suzuki–Miyaura coupling of β-borylallylsilane **37**, a product of allene silaboration, with 4-cyanoiodobenzene (Scheme 26).[26]

The alkenylboron compounds are also converted into functionalized organic compounds via reactions other than Suzuki–Miyaura coupling. Rhodium-catalyzed 1,4-addition of **39** to methyl vinyl ketone afforded δ-silyl-γ,δ-unsaturaterd ketone **40** in 78% yield (Scheme 27a).[17] Oxidation of **18a** gave β-silylketone **41** without epimerization (Scheme 27b).[36] Diastereoselective conversion of alkenylborane **18**, produced by silaborative C–C cleavage of methylenecyclopropanes, was achieved via a homologation–allylboration sequence (Table 13).[36] Reaction of **18** with $ClCH_2Li$ afforded allylborane derivatives **42**, which further reacted with aldehydes to give homoallylic alcohol **43** in good yield with high diastereomeric ratios (93:7–97:3).

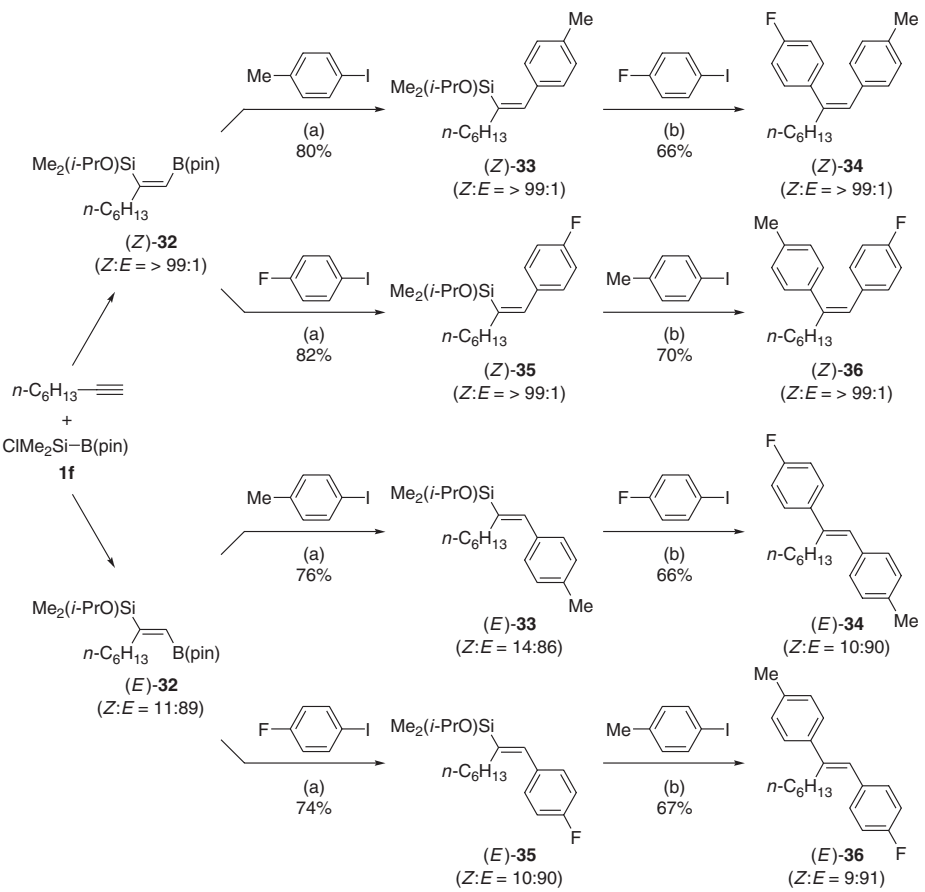
Allylsilane moieties in the β-borylallylsilanes could react with various electrophiles with retention of the boryl group (Table 14). Reaction of β-borylallylsilane **46** with benzaldehyde dimethyl acetal proceeded in the presence of $TiCl_4$ to give boryl-substituted homoallylic ether **47** as a single stereoisomer (Entry 2).[44] Cyclization/allylation of aldehyde with β-borylallylsilanes **48** and **50** bearing siloxy groups was promoted by Me_3SiOTf to give boron-substituted cyclic unsaturated ethers **49** and **51** in good yields (Entries 3 and 4).[44] Related reactions



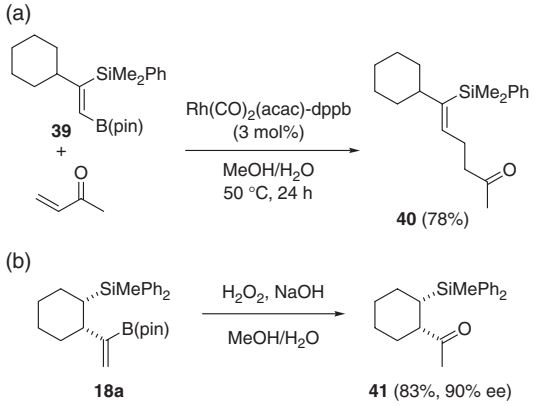
Scheme 24. Conversion of **30** to alkenylsilane **31** via Suzuki–Miyaura coupling.



Scheme 26. Synthesis of allylsilane **38** via Suzuki–Miyaura coupling of **37**.

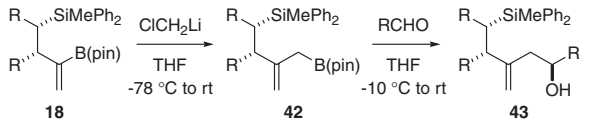


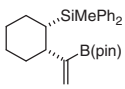
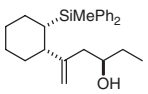
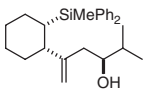
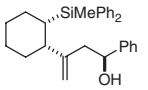
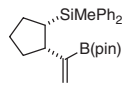
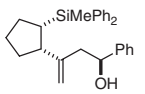
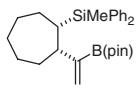
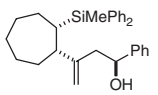
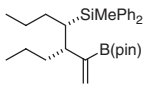
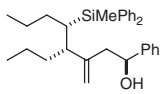
Scheme 25. Stereo-complementary synthesis of 1,2-diaryl-1-octenes via Suzuki–Miyaura coupling and Hiyama coupling of **32**. (a) $Pd(OAc)_2$ (2.0 mol %), S-PHOS (2.4 mol %), K_3PO_4 (2.0 equiv), H_2O (7.0 equiv), toluene, 100 °C, 5 h. (b) $Pd(dba)_2$ (5.0 mol %), Bu_4NF (1.5 equiv), THF, 50 °C, 3 h.



Scheme 27. Synthesis of functionalized organosilanes via selective conversion of boryl group.

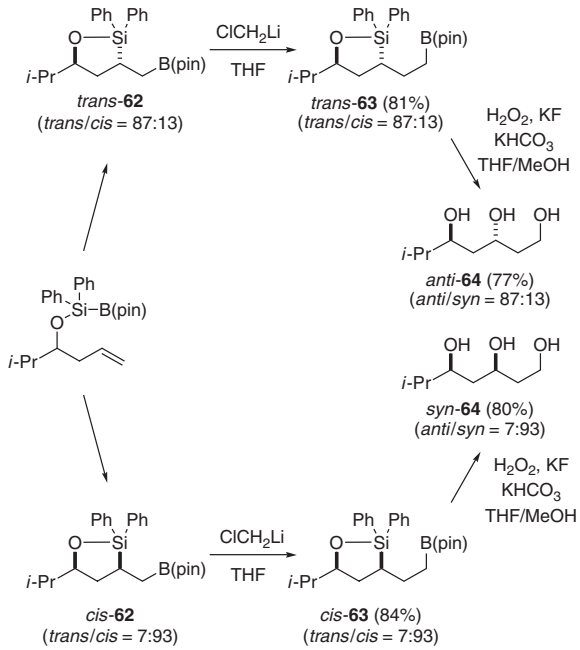
Table 13. Diastereoselective Conversion of **18** via Homologation Followed by Allylboration



Entry	Substrate	Aldehyde	Product	Yield /%	Ratio[a)]
1	 **18c**	EtCHO		78	94:6
2	**18c**	*i*-PrCHO		80	94:6
3	**18c**	PhCHO		70	97:3
4	 **18d**	PhCHO		63	93:7
5	 **18e**	PhCHO		69	97:3
6	 **18g**	PhCHO		71	93:7

a) Diastereomeric ratio.

of enantioenriched β-borylallylsilanes **52**, **52′**, **54**, and **56** proceeded with highly efficient chirality transfer from the stereogenic centers α to the silyl group (Entries 5–8) with no strong influence of the other stereogenic center (Entries 5 and 6).[32,33] 2-Boryl-5-phenyl-3-silyl-1-pentene **58** reacted with two equivalents of aldehyde in the presence of Me_3SiOTf, resulting in formation of tricyclic compounds **59** and **60** (Entries 9 and 10).[45] The reaction may proceed sequentially through allylation of the aldehyde with **58** and acetal formation with the second



Scheme 28. Stereo-complementary synthesis of 1,3,5-triols via homologation/oxidation of **62**.

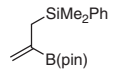
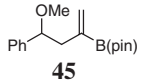
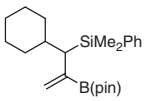
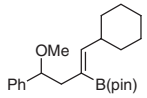
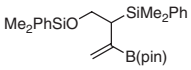
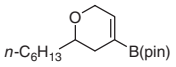
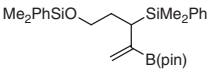
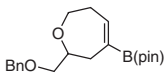
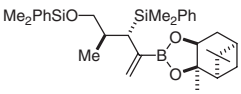
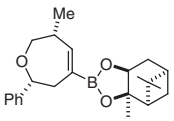
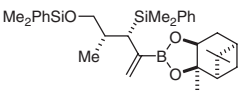
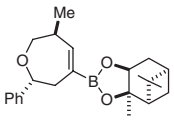
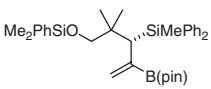
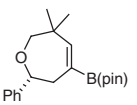
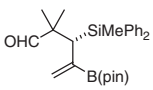
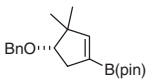
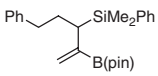
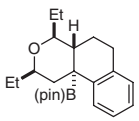
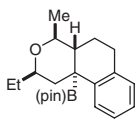
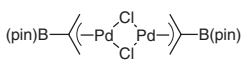
equivalent of the aldehyde, followed by Prins-type oxonium ion–alkene cyclization, ending up with intramolecular Friedel–Crafts reaction. π-Allyl palladium complex **61** bearing boryl groups at the central carbon atoms of π-allyl ligands was synthesized by the reaction of **44** with $PdCl_2(CH_3CN)_2$ (Entry 11).[26]

Reaction of *trans*-**62**, a product of intramolecular silaboration, with $ClCH_2Li$ led to the formation of one-carbon homologation product **63** in 81% yield (Scheme 28).[25] Under Tamao oxidation conditions, both the C–B and C–Si bonds of **63** were oxidized to afford *anti*-1,3,5-triol **64** in 77% yield. Application of the same homologation/oxidation conditions to *cis*-**62** afforded *syn*-**64** in high yield. By this strategy, either diastereomer of 1,3,5-triols is now accessible from the same starting compound simply by choosing the appropriate ligand in the intramolecular silaboration.[46]

8. Preparation of Silylboranes

Silylboranes used for catalytic silaboration are accessible on the basis of the reaction of (organosilyl)lithium with boron electrophiles. Reaction of (dimethylphenylsilyl)lithium (**65**) with chlorobis(diethylamino)borane gave bis(diethylamino)-(dimethylphenylsilyl)borane (**1r**) (Scheme 29). Silylborane **1r** was converted into silylboranes **1t** bearing various dialkoxy groups on the boron atom by treatment with acetyl chloride followed by reaction with diols.[10] Practical synthesis of (triorganosilyl)pinacolboranes, e.g., (dimethylphenylsilyl)pinacolborane (**1c**), was achieved by the reaction of triorganosilyllithium with two equivalents of pinacolborane (**66**) or isopropoxypinacolborane (**67**) (Scheme 30).[47] This method was applicable to preparation of [(diethylamino)diphenylsilyl]-pinacolborane (**1u**), in which [(diethylamino)diphenylsilyl]-lithium (**68**) was used as a silicon reagent (Scheme 31).[48] The diethylamino group on **1u** could be converted to a chloro group

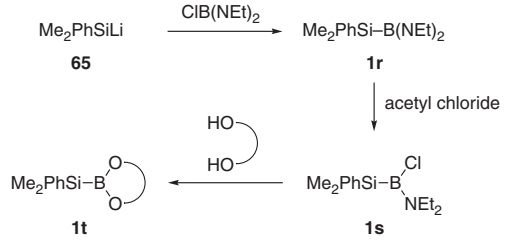
Table 14. Conversion of β-Borylallylsilanes to Give Functionalized Organoboron Compounds

Entry	β-Borylallylsilane	Electrophile	Conditions	Product	Yield/%
1	 **44**	$PhCH(OMe)_2$	$TiCl_4$, CH_2Cl_2, −78 °C	 **45**	99
2	 **46**	$PhCH(OMe)_2$	$TiCl_4$, CH_2Cl_2, −78 °C	 **47**	95
3	 **48**	heptanal	Me_3SiOTf, CH_2Cl_2, −78 °C	 **49**	89
4	 **50**	$BnOCH_2CHO$	Me_3SiOTf, CH_2Cl_2, −78 °C	 **51**	83
5	 **52** (dr 96 : 4)	PhCHO	Me_3SiOTf, CH_2Cl_2, −78 °C	 **53** (dr 96 : 4)	89
6	 **52'** (dr 94 : 6)	PhCHO	Me_3SiOTf, CH_2Cl_2, −78 °C	 **53'** (dr 94 : 6)	77
7	 **54** (92% ee)	PhCHO	Me_3SiOTf, CH_2Cl_2, −78 °C	 **55** (92% ee)	71[a]
8	 **56** (93% ee)	—	$BnOSiMe_3$, Me_3SiOTf, CH_2Cl_2, −78 °C	 **57** (93% ee)	58[a]
9	 **58**	EtCHO (2 equiv)	Me_3SiOTf, CH_2Cl_2, −78 to 0 °C	 **59**	92
10	**58**	1. EtCHO 2. MeCHO	$TiCl_4$, CH_2Cl_2, −78 to 0 °C	 **60**	81
11	**44**	$PdCl_2(CH_3CN)_2$	MeOH, rt	 **61**	quant

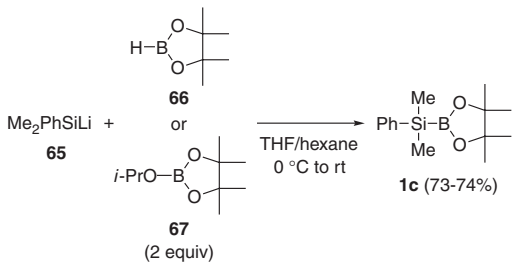
a) Yield after Suzuki–Miyaura coupling with ethyl 4-bromobenzoate.

via reaction with hydrogen chloride to give (chlorodiphenylsilyl)pinacolborane (**1v**), which allowed reactions with various alcohols in the presence of pyridine to afford (alkoxydiphenylsilyl)pinacolboranes **1i**.

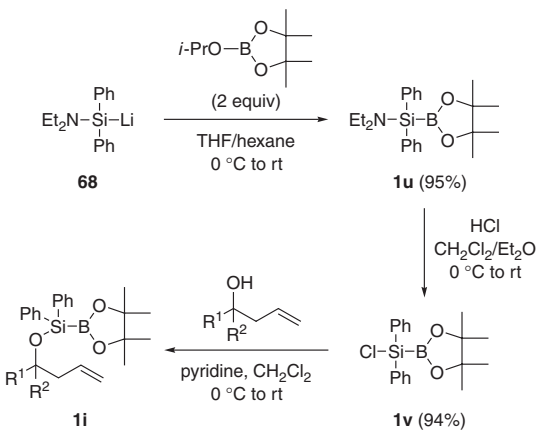
One of the limitations of the method via silyllithium is the need for at least one aryl group on the silicon atom. To prepare silylboranes that do not have any aryl groups on silicon, conversion of (dimethylphenylsilyl)pinacolborane (**1c**) was



Scheme 29. Synthetic route of silylboranes.



Scheme 30. Practical synthesis of silylborane **1c**.

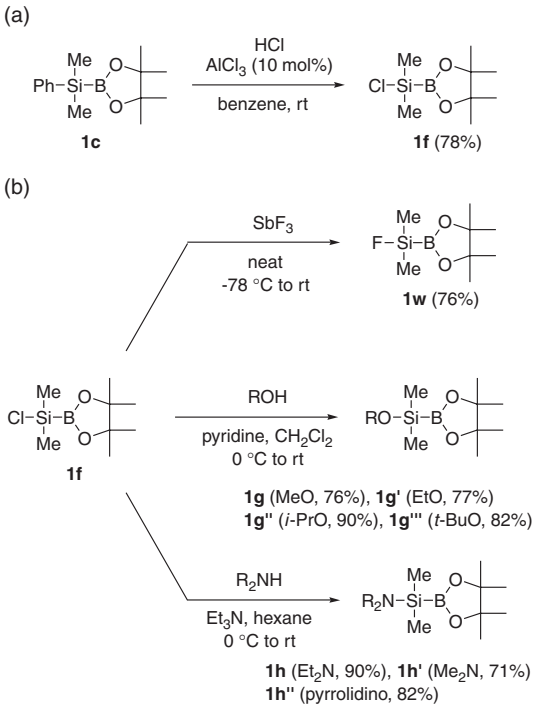


Scheme 31. Synthesis of XPh_2Si–B(pin).

examined.[48] It was found that hydrogen chloride reacted with **1c** in the presence of catalytic aluminum chloride to give (chlorodimethylsilyl)pinacolborane (**1f**) in 78% yield (Scheme 32a).[49] It should be noted that the chlorodephenylation on silicon proceeded smoothly without cleavage of the Si–B bond. The silylborane **1f** is suitable for introduction of functional groups on the silicon atoms (Scheme 32b). Fluorination of **1f** was successfully achieved with SbF_3 under solvent-free conditions to afford (fluorodimethylsilyl)pinacolborane (**1w**) in 76% yield. Introduction of alkoxy and dialkylamino groups was achieved by the reaction with alcohols and dialkylamines, respectively, in the presence of appropriate bases (pyridine for alcohol and triethylamine for dialkylamine).

9. Conclusion

We have developed catalytic silaborations of alkynes, alkenes, allenes, and 1,3-dienes, in which silicon and boron substituents added to the unsaturated carbon–carbon bond in either 1,2- or 1,4-fashion. Silaboration which is accompanied by the cleavage of small-ring C–C bonds have also been



Scheme 32. Synthesis of XMe_2Si–B(pin).

developed with use of methylenecyclopropanes and small-ring vinylcycloalkanes. In the reactions of former derivatives, the reaction courses can be switched by the choice of catalysts. Silaborative C–C bond forming reactions were also established: silaborative alkyne dimerization was catalyzed by nickel catalysts and silaborative aldehyde-1,3-diene coupling proceeded with high stereoselectivity in the presence of platinum catalysts. The substituents of silylboranes have strong impact on their reactivity and even the course of the catalytic reaction. A particular example is demonstrated by the silole formation in the reaction of alkynes with a silylborane bearing an amino group on the silicon atom. Mechanism and application of the generation of silylene-related species with the particular silylborane is an active research project in our group. The functionalization at the silicon atom of silylborane also allowed the development of intramolecular silaboration of alkenes, which showed interesting complementary stereoselectivities.

Throughout the studies, it has been really important to use proper transition-metal catalysts for individual reactions. Although we have so far found that nickel, palladium, and platinum catalysts are able to activate silicon–boron bonds, the outcome of the reaction is highly dependent upon the central metal, ligand, and even the metal/ligand ratio. A critical case was found in the reaction of alkynes, in which use of nickel catalyst afforded silaboration dimerization product, while palladium catalysts gave simple 1,2-silaboration products. The metal/ligand ratio is critically influential in the enantioselective silaboration reactions. A catalyst with metal/ligand ratio of 1/1 allows the reaction proceed below room temperature with high enantioselectivity, whereas a catalyst with metal/ligand ratio of $<1/2$ resulted in the need for raising temperature above 100 °C to bring the reaction to completion. By establishing a highly active catalyst, the development

of asymmetric silaboration of allenes and methylenecyclopropanes has been made possible. Silylborane-based enantioselective catalytic reactions are developed also by other research groups, leading to enantioselective 1,4-silaboration of 1,3-cyclohexadiene[40] and Rh-catalyzed silylation of α,β-unsaturated carbonyl compounds.[50]

Electropositive elements with high carbon affinity may play key roles in future organic chemistry. They are stable, storable, reactive, and interactive with other molecules by virtue of semimetallic nature of the elements. Much effort needs to be devoted to the development of new reagents and reactions for the synthesis of organoboron and organosilicon compounds.

References

1 a) N. Miyaura, Y. Yamamoto, in *Comprehensive Organometallic Chemistry III*, ed. by R. H. Crabtree, D. M. P. Mingos, Elsevier, Oxford, **2007**, Vol. 9, p. 145. b) A. Hosomi, K. Miura, in *Comprehensive Organometallic Chemistry III*, ed. by R. H. Crabtree, D. M. P. Mingos, Elsevier, Oxford, **2007**, Vol. 9, p. 297.

2 a) S. Yamaguchi, C. Xu, T. Okamoto, *Pure Appl. Chem.* **2006**, *78*, 721. b) S. Yamaguchi, A. Wakamiya, *Pure Appl. Chem.* **2006**, *78*, 1413. c) *Macromolecules Containing Metal and Metal-Like Elements (Boron-Containing Polymers)*, ed. by A. S. Abd-El-Aziz, C. E. Carraher, Jr., C. U. Pittman, Jr., M. Zeldin, Wiley-Interscience, **2007**, Vol. 8.

3 Bortezomib (Velcade®): a) W. Yang, X. Gao, B. Wang, in *Boronic Acid*, ed. by D. Hall, Wiley, Weinheim, **2005**, p. 481. Silanediol protease inhibitors: b) S. M. Sieburth, C.-A. Chen, *Eur. J. Org. Chem.* **2006**, 311.

4 a) I. Beletskaya, C. Moberg, *Chem. Rev.* **1999**, *99*, 3435. b) L.-B. Han, M. Tanaka, *Chem. Commun.* **1999**, 395. c) S. Onozawa, M. Tanaka, *J. Synth. Org. Chem., Jpn.* **2002**, *60*, 826. d) Y. Ito, *J. Organomet. Chem.* **1999**, *576*, 300. e) M. Suginome, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221. f) I. Beletskaya, C. Moberg, *Chem. Rev.* **2006**, *106*, 2320. g) M. Suginome, T. Matsuda, T. Ohmura, A. Seki, M. Murakami, in *Comprehensive Organometallic Chemistry III*, ed. by R. H. Crabtree, D. M. P. Mingos, Elsevier, Oxford, **2007**, Vol. 10, p. 725. h) H. E. Burks, J. P. Morken, *Chem. Commun.* **2007**, 4717. i) M. Suginome, *J. Synth. Org. Chem., Jpn.* **2007**, *65*, 1048.

5 a) M. Ishikawa, A. Naka, *Synlett* **1995**, 794. b) M. Murakami, M. Suginome, Y. Ito, *J. Synth. Org. Chem., Jpn.* **1995**, *53*, 509. c) M. Suginome, Y. Ito, *J. Synth. Org. Chem., Jpn.* **1997**, *55*, 1040. d) M. Suginome, Y. Ito, *J. Chem. Soc., Dalton Trans.* **1998**, 1925. e) M. Suginome, Y. Ito, in *Activation of Unreactive Bonds and Organic Synthesis (Top. Organomet. Chem. Vol. 3)*, ed. by S. Murai, Springer, **1999**, p. 3. f) M. Suginome, Y. Ito, in *Transition-Metal Catalyzed Reactions*, ed. by S.-i. Murahashi, S. G. Davies, Blackwell, London, **1999**, p. 419.

6 a) T. B. Marder, N. C. Norman, *Top. Catal.* **1998**, *5*, 63. b) T. Ishiyama, N. Miyaura, *J. Synth. Org. Chem., Jpn.* **1999**, *57*, 503. c) T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2000**, *611*, 392. d) T. Ishiyama, *J. Synth. Org. Chem., Jpn.* **2003**, *61*, 1176. e) V. M. Dembitsky, H. Abu Ali, M. Srebnik, *Adv. Organomet. Chem.* **2003**, *17*, 327. f) V. M. Dembitsky, H. Abu Ali, M. Srebnik, *Adv. Organomet. Chem.* **2004**, *51*, 193. g) T. Ishiyama, N. Miyaura, *Chem. Rec.* **2004**, *3*, 271.

7 a) D. Seyferth, H. P. Kögler, *J. Inorg. Nucl. Chem.* **1960**, *15*, 99. b) A. H. Cowley, H. H. Sisler, G. E. Ryschkewitsch, *J. Am. Chem. Soc.* **1960**, *82*, 501.

8 K. Nozaki, K. Wakamatsu, T. Nonaka, W. Tückmantel, K. Oshima, K. Utimoto, *Tetrahedron Lett.* **1986**, *27*, 2007.

9 Related reviews, see: a) Y. Ito, *J. Organomet. Chem.* **1999**, *576*, 300. b) M. Suginome, Y. Ito, *J. Organomet. Chem.* **2003**, *680*, 43. See also Ref. 4.

10 J. D. Buynak, B. Geng, *Organometallics* **1995**, *14*, 3112.

11 a) T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu, T. Hiyama, *Angew. Chem., Int. Ed.* **2001**, *40*, 790. b) M. Shimizu, H. Kitagawa, T. Kurahashi, T. Hiyama, *Angew. Chem., Int. Ed.* **2001**, *40*, 4283. c) T. Kurahashi, T. Hata, H. Masai, H. Kitagawa, M. Shimizu, T. Hiyama, *Tetrahedron* **2002**, *58*, 6381. d) M. Shimizu, T. Kurahashi, H. Kitagawa, T. Hiyama, *Org. Lett.* **2003**, *5*, 225. e) M. Shimizu, T. Kurahashi, H. Kitagawa, K. Shimono, T. Hiyama, *J. Organomet. Chem.* **2003**, *686*, 286. f) M. Murakami, I. Usui, M. Hasegawa, T. Matsuda, *J. Am. Chem. Soc.* **2005**, *127*, 1366.

12 M. Suginome, T. Fukuda, Y. Ito, *Organometallics* **2000**, *19*, 719.

13 M. Suginome, T. Fukuda, Y. Ito, *J. Organomet. Chem.* **2002**, *643–644*, 508.

14 Y. Ito, M. Suginome, M. Murakami, *J. Org. Chem.* **1991**, *56*, 1948.

15 M. Suginome, H. Nakamura, Y. Ito, *Chem. Commun.* **1996**, 2777.

16 S. Onozawa, Y. Hatanaka, M. Tanaka, *Chem. Commun.* **1997**, 1229.

17 M. Suginome, T. Matsuda, H. Nakamura, Y. Ito, *Tetrahedron* **1999**, *55*, 8787.

18 J. C. A. Da Silva, M. Birot, J.-P. Pillot, M. Pétraud, *J. Organomet. Chem.* **2002**, *646*, 179.

19 M. Suginome, H. Noguchi, T. Hasui, M. Murakami, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 323.

20 T. Sagawa, Y. Asano, F. Ozawa, *Organometallics* **2002**, *21*, 5879.

21 T. Ohmura, K. Masuda, M. Suginome, *J. Am. Chem. Soc.* **2008**, *130*, 1526.

22 T. Ohmura, K. Oshima, M. Suginome, *Chem. Commun.* **2008**, 1416.

23 a) A. Schäfer, M. Weidenbruch, S. Pohl, *J. Organomet. Chem.* **1985**, *282*, 305. b) J. Belzner, H. Ihmels, *Tetrahedron Lett.* **1993**, *34*, 6541. c) B. Wrackmeyer, G. Kehr, J. Süß, *Chem. Ber.* **1993**, *126*, 2221.

24 M. Suginome, H. Nakamura, Y. Ito, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516.

25 T. Ohmura, H. Furukawa, M. Suginome, *J. Am. Chem. Soc.* **2006**, *128*, 13366.

26 a) M. Suginome, Y. Ohmori, Y. Ito, *Synlett* **1999**, 1567. b) M. Suginome, Y. Ohmori, Y. Ito, *J. Organomet. Chem.* **2000**, *611*, 403.

27 S. Onozawa, Y. Hatanaka, M. Tanaka, *Chem. Commun.* **1999**, 1863.

28 T. Ohmura, H. Taniguchi, M. Suginome, unpublished results. The palladium catalyst system (Pd/L = 1/1) was applied to asymmetric silaboration of allenes, giving high regioselectivities. See Refs. 31–33.

29 Y. Abe, K. Kuramoto, M. Ehara, H. Nakatsuji, M. Suginome, M. Murakami, Y. Ito, *Organometallics* **2008**, *27*, 1736.

30 K.-J. Chang, D.-K. Rayabarapu, F.-Y. Yang, C.-H. Cheng, *J. Am. Chem. Soc.* **2005**, *127*, 126.

31 M. Suginome, T. Ohmura, Y. Miyake, S. Mitani, Y. Ito, M. Murakami, *J. Am. Chem. Soc.* **2003**, *125*, 11174.

32 T. Ohmura, M. Suginome, *Org. Lett.* **2006**, *8*, 2503.

33 T. Ohmura, H. Taniguchi, M. Suginome, *J. Am. Chem. Soc.* **2006**, *128*, 13682.
34 M. Suginome, T. Matsuda, Y. Ito, *J. Am. Chem. Soc.* **2000**, *122*, 11015.
35 T. Pohlmann, A. de Meijere, *Org. Lett.* **2000**, *2*, 3877.
36 T. Ohmura, H. Taniguchi, Y. Kondo, M. Suginome, *J. Am. Chem. Soc.* **2007**, *129*, 3518.
37 M. Suginome, T. Matsuda, Y. Ito, *Organometallics* **1998**, *17*, 5233.
38 M. Suginome, H. Nakamura, T. Matsuda, Y. Ito, *J. Am. Chem. Soc.* **1998**, *120*, 4248.
39 M. Suginome, T. Matsuda, T. Yoshimoto, Y. Ito, *Org. Lett.* **1999**, *1*, 1567.
40 M. Gerdin, C. Moberg, *Adv. Synth. Catal.* **2005**, *347*, 749.
41 M. Gerdin, C. Moberg, *Org. Lett.* **2006**, *8*, 2929.
42 C. Lüken, C. Moberg, *Org. Lett.* **2008**, *10*, 2505.
43 M. Suginome, T. Matsuda, T. Yoshimoto, Y. Ito, *Organometallics* **2002**, *21*, 1537.
44 M. Suginome, Y. Ohmori, Y. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 4601.
45 M. Suginome, Y. Ohmori, Y. Ito, *Chem. Commun.* **2001**, 1090.
46 For reviews on stereoselective synthesis of 1,3-polyols, see: a) T. Oishi, T. Nakata, *Synthesis* **1990**, 635. b) S. E. Bode, M. Wolberg, M. Müller, *Synthesis* **2006**, 557.
47 M. Suginome, T. Matsuda, Y. Ito, *Organometallics* **2000**, *19*, 4647.
48 T. Ohmura, K. Masuda, H. Furukawa, M. Suginome, *Organometallics* **2007**, *26*, 1291.
49 For conversion of Si–Ph bond to Si–Cl bond, see: K. Tamao, M. Kumada, *J. Organomet. Chem.* **1971**, *30*, 339.
50 a) C. Walter, G. Auer, M. Oestreich, *Angew. Chem., Int. Ed.* **2006**, *45*, 5675. b) C. Walter, M. Oestreich, *Angew. Chem., Int. Ed.* **2008**, *47*, 3818.

Toshimichi Ohmura was born in Hyogo, Japan, in 1973. He received his B.S. and Ph.D. from Hokkaido University in 1996 and 2001, respectively, under the guidance of Prof. Norio Miyaura. He spent one year as postdoctoral fellow with Prof. John F. Hartwig at Yale University from 2001 to 2002. After a JST postdoctoral fellow at Kyoto University, he became an assistant professor at Kyoto University in 2004. His current research interests are development of new transition-metal-catalyzed reactions for efficient synthesis of functional organic and organometallic materials.

Michinori Suginome was born in 1966. He graduated from Kyoto University in 1988, where he received his Ph.D. under the supervision of Professor Yoshihiko Ito in 1993. In that year he joined the faculty at Kyoto University as an assistant professor. He was promoted to an associate professor in 2002, and has been a full professor since 2004. In the meantime, he pursued his academic career also at Massachusetts Institute of Technology during 1998–1999, where he joined the research group of Professor Gregory C. Fu. He has received the Japan Chemical Society Award for Young Chemist (1999), the Society of Silicon Chemistry Japan Award for Young Chemist (2001), Nagoya Silver Medal (2005), and Mukaiyama Award (2005).