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Synthesis of (1-silyl)allylboronates by KO*t*Bu-catalyzed ring-opening *gem*-silylborylation of cyclopropenes†

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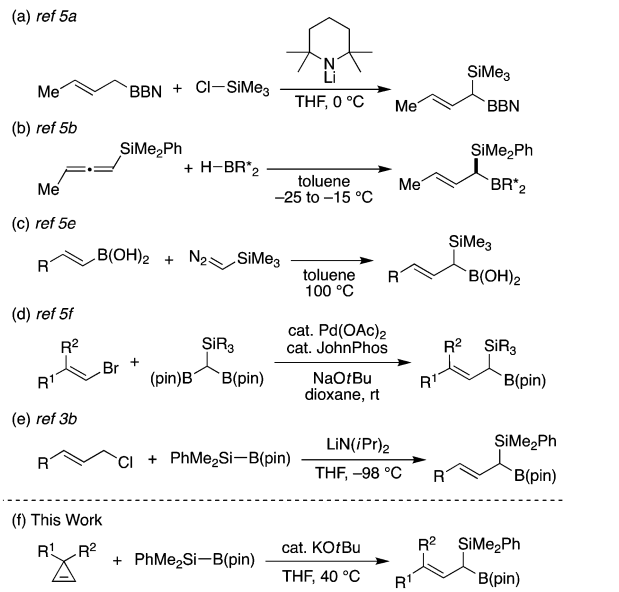
A KO*t*Bu-catalyzed ring-opening *gem*-silylborylation of cyclopropenes with silylboronates has been developed for the synthesis of (1-silyl)allylboronates, a useful class of compounds in organic synthesis. The reaction proceeds with high selectivity under mild conditions, and the reaction mechanism has been theoretically investigated using DFT calculations.

Allylic organometallic reagents are highly valued and play important roles in synthetic organic chemistry, particularly due to their broad and versatile reactivity.[1] Among them, allylsilanes and allylboranes are distinguished by their facile manipulation and exceptional selectivity in various transformations.[1e–i,2] In this regard, (1-silyl)allylboranes, a particular class of allylic *gem*-dimetalloids possessing both silicon and boron functionalities at the same allylic carbon, are anticipated to serve as useful building blocks for the synthesis of complex molecules.[3] The high potential of (1-silyl)allylboranes has been empirically evidenced by the broad scope of transformations through regio-, chemo-, and stereoselective C–C bond forming reactions.[3,4]

Despite the utility of these compounds, their efficient synthetic methods remain to be further developed. Most of the existing synthetic strategies rely on the use of preformed organosilicon and/or organoboron compounds as exemplified by silylation of allylboranes (Scheme 1a),[5a] hydroboration of allenylsilanes (Scheme 1b)[5b] or silylcyclopropenes,[5c] homologation of alkenylboronic acid derivatives with silylmethylene donors (Scheme 1c),[5d,e] and cross-coupling of bromoalkenes with diborylsilylmethanes (Scheme 1d).[5f] In contrast, direct introduction of both silicon and boron substituents into the allylic position has been essentially limited to *gem*-silylborylation of allylic carbenoids generated from allylic halides with lithium diisopropylamide at a very low temperature (−98 °C; Scheme 1e).[3b,5g] In this context, herein we describe the development of a new way of synthesizing (1-silyl)allylboronates *via* a ring-opening *gem*-silylborylation reaction of cyclopropenes with silylboronates[6] in the presence of a catalytic amount of KO*t*Bu (Scheme 1f), representing a rare example of concurrently introducing silicon and boron functional groups to the same allylic carbon under mild conditions.

Initially, we employed 3,3-diphenylcyclopropene (**1a**) as a model substrate and conducted the reaction with dimethyl (phenyl)silylboronate **2a** in THF at 40 °C (Table 1). No significant reaction took place in the absence of a catalyst (entry 1). We then focused on the use of base catalysts to activate **2a** as a silicon nucleophile,[7] and the reaction in the presence of 10 mol% of KO*t*Bu led to a clean formation of ring-opened



Scheme 1 (a)–(e) Reported examples of (1-silyl)allylboron synthesis and (f) ring-opening *gem*-silylborylation of cyclopropenes (this work).

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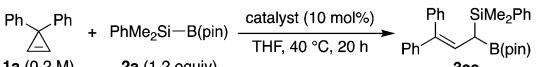
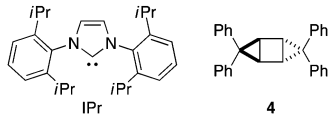
Table 1 Reaction of **1a** with **2a**: Catalyst screening



Entry	Catalyst	Conversion[a] (%)	Yield[a] (%)
1	None	8	0
2	**KO*t*Bu**	**100**	**79**
3	NaO*t*Bu	91	78
4	LiO*t*Bu	9	0
5	Cu(O*t*Bu)(IPr)	100	0[b]

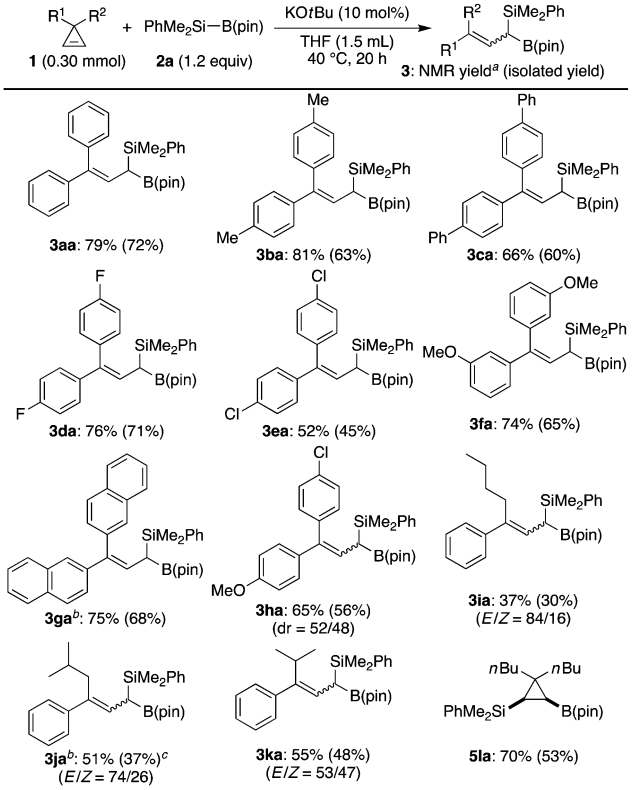
[a] Determined by ^{1}H NMR against internal standard (dimethyl terephthalate). [b] 3,3,6,6-Tetraphenyltricyclo[3.1.0.0^{2,4}]hexane (**4**) was obtained as the major product in 59% yield.



(1-(dimethyl(phenyl)silyl)-3,3-diphenylallyl)boronate **3aa** in 79% yield (entry 2). This ring-opening *gem*-silylborylation is in stark contrast to the simple 1,2-silylborylation of styrene derivatives reported by Ito and coworkers under similar reaction conditions.[7b] A high yield of **3aa** was also achieved by using NaO*t*Bu instead of KO*t*Bu (entry 3), but LiO*t*Bu was found to be ineffective presumably due to the lower basicity (entry 4). It is worth noting that the use of a transition-metal alkoxide catalyst such as Cu(O*t*Bu)(IPr)[8] led to the formation of a dimer of **1a** in the form of 3,3,6,6-tetraphenyltricyclo[3.1.0.0^{2,4}]hexane (**4**) with no formation of **3aa** (entry 5).[9]

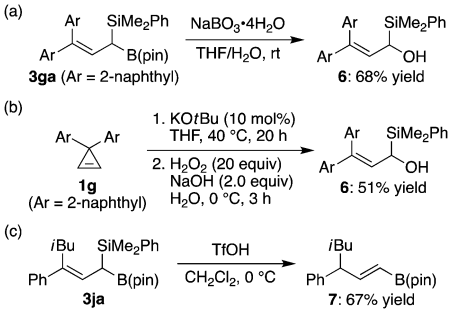
Under simple and mild conditions using KO*t*Bu as the catalyst, various 3,3-diarylcyclopropenes **1** could be transformed into the corresponding (1-silyl)allylboronates **3** by the reaction with silylboronate **2a** (Table 2). For example, in addition to unsubstituted phenyl group (**1a**), aryl groups having mildly electron-donating or electron-deficient substituents at the 4-positions (**1b–e**) were tolerated to give (1-silyl)allylboronates **3aa–ea** in moderate to good isolated yields (45–72% yield),[10] although highly electron-rich 3,3-di(4-methoxyphenyl)-cyclopropene and highly electron-deficient 3,3-di(4-trifluoromethylphenyl)cyclopropene were found to be unreactive (0% and 17% yield, respectively; data not shown in the table). On the other hand, 3-methoxyphenyl (**1f**) and 2-naphthyl (**1g**) groups were applicable as substituents on cyclopropenes and products **3fa** and **3ga** were obtained in 65–68% isolated yields. The structure of **3ga** was confirmed by X-ray crystallographic analysis.[11] Furthermore, the reaction proceeded well with substrate **1h** having one electron-donating 4-methoxyphenyl group and one electron-withdrawing 4-chlorophenyl group, and (1-silyl)allylboronate **3ha** was isolated in 56% yield as an almost 1 : 1 mixture of *E*/*Z* isomers. 3-Alkyl-3-phenylcyclopropenes **1i–k** could also be employed in the present ring-opening *gem*-silylborylation reaction to give products **3i–k** in moderate yields of 30–48%, and the selectivity toward *E* isomers was found to be higher with smaller alkyl groups (up to *E*/*Z* = 84/16). In contrast,

Table 2 Synthesis of (1-dimethyl(phenyl)silyl)allylboronates **3** from **1** and **2a**

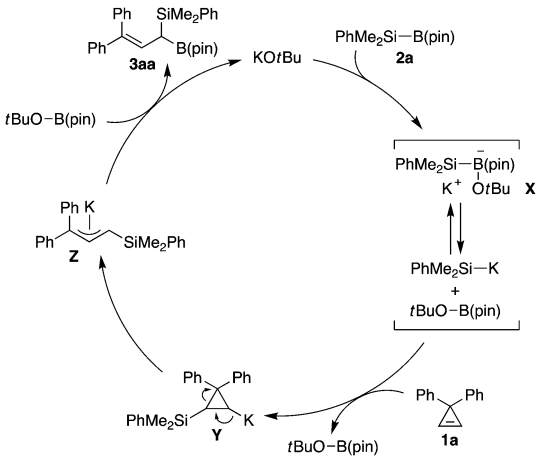


[a] Determined by ^{1}H NMR against internal standard (dimethyl terephthalate). [b] The reaction was conducted using 2.0 mmol of **1** in 10 mL of THF. [c] Isolated yield of (*E*)-**3ja**.

3,3-dialkylcyclopropene **1l** was found to give 1,2-silylborylation product **5la** without ring-opening. As shown for the reaction using 2.0 mmol of **1g** or **1j** as the substrate, the present reactions were readily conducted on a preparative scale as well. With regard to the silylboron reagents, trialkylsilylboronates such as **2b** and **2c** were also applicable for the reaction of cyclopropene **1a** to give corresponding (1-silyl)allylboronates **3ab** and **3ac** in high yields by raising the reaction temperature to 60 °C (eqn (1)).

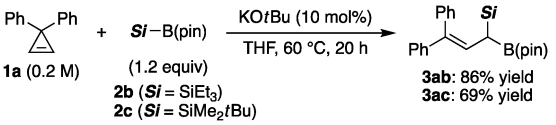


Scheme 2 Transformations of (1-silyl)allylboronates **3**.



Scheme 3 Proposed catalytic cycle for the synthesis of **3aa** from **1a** and **2a**.

As previously mentioned, (1-silyl)allylboronates are known to be transformed into various products with high selectivity.[3d] As a brief demonstration, we examined the selective conversion of either boron or silicon moiety of compounds **3**. For example, oxidation of the carbon–boron bond of **3ga** was achieved by the reaction with sodium peroxoborate to give allylic alcohol **6** in 68% yield with retaining the silyl group (Scheme 2a).[5c,12] A one-pot sequential process was also possible to prepare compound **6** from cyclopropene **1g** in a comparable overall yield (Scheme 2b). On the other hand, allylic desilylative protonation of **3ja** selectively took place under acidic conditions to give alkenylboronate **7** in 67% yield (Scheme 2c).[5c]

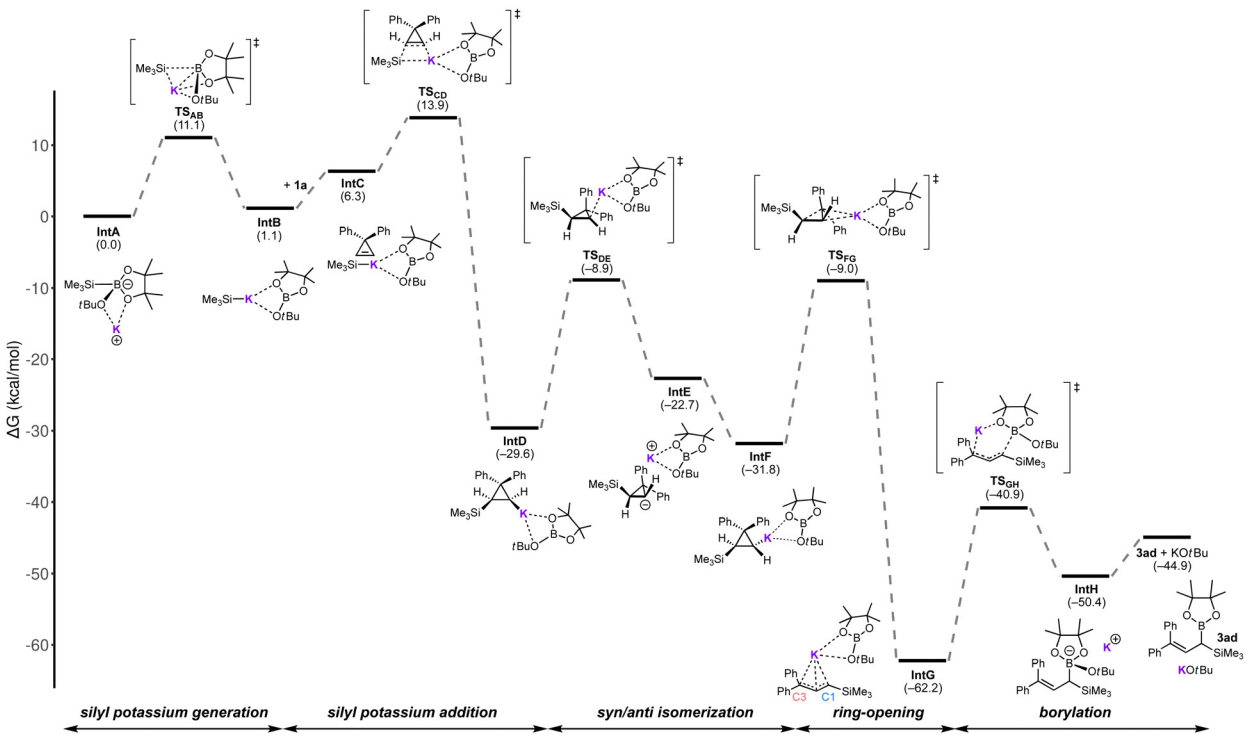


(1)

A proposed catalytic cycle for the reaction of cyclopropene **1a** with silylboronate **2a** is illustrated in Scheme 3. Initially, coordination of KO*t*Bu to silylboronate **2a** gives borate intermediate **X**,[7b] which is presumably in equilibrium with dissociated dimethyl(phenyl)silyl-potassium and *t*BuOB(pin).[7] Then, the silicon nucleophile attacks the alkene moiety of cyclopropene **1a**, resulting in the formation of silylated cyclopropylpotassium intermediate **Y**. Subsequent ring-opening of this intermediate takes place with the release of the ring-strain to give π-allylpotassium **Z**. Finally, borylation with *t*BuOB(pin) proceeds at the silicon-substituted allylic carbon of **Z**, leading to the formation of (1-silyl)allylboronate **3aa** along with regeneration of KO*t*Bu.[13]

To probe the feasibility of the above-mentioned catalytic cycle, a detailed reaction pathway was investigated by the DFT calculations for the reaction of **1a** with $Me_3SiB(pin)$ in the presence of KO*t*Bu at the M06/6-31+G(d) level of theory with solvation effect of THF (SMD) (see the ESI† for details). We assessed the Gibbs energy changes at standard conditions (298.15 K and 1 atm), and the resulting Gibbs energy profiles are depicted in Scheme 4.

At first, borate intermediate **IntA** formed by the coordination of KO*t*Bu to trimethylsilylboronate is converted to silylpotassium **IntB**



Scheme 4 Calculated energy diagram for the KO*t*Bu-catalyzed *gem*-silylborylation of **1a** with trimethylsilylboronic acid pinacol ester.

with a Gibbs free energy change $\left(\Delta G^{\circ}_{AB}\right)$ of 1.1 kcal mol^{-1} through **TS$_{AB}$** with activation energy $\left(\Delta G^{\circ\ddagger}_{AB}\right)$ of 11.1 kcal mol^{-1}.[7] Subsequently, the alkene of **1a** coordinates to **IntB** to give **IntC**, which undergoes addition of the silyl anion to form cyclopropylpotassium species **IntD** through four-membered *syn*-addition transition state **TS$_{CD}$** $\left(\Delta G^{\circ\ddagger}_{CD} = 7.6 \text{ kcal mol}^{-1};\ \Delta G^{\circ}_{CD} = -35.9 \text{ kcal mol}^{-1}\right)$. This exergonic step is likely driven by the substantial release of the strain energy of a cyclopropene ring (55.2 kcal mol^{-1} for cyclopropene *vs.* 27.5 kcal mol^{-1} for cyclopropane).[14]

The ring-opening of *syn*-isomer **IntD** was found to be energetically unfavorable ($\Delta G^{\circ\ddagger}_{\text{syn-opening}} = 27.8$ kcal mol^{-1}; see Fig. S2 in the ESI†), and the *syn*/*anti*-isomerization of **IntD** through **TS$_{DE}$** yields *anti*-isomer **IntE** $\left(\Delta G^{\circ\ddagger}_{DE} = 20.7 \text{ kcal mol}^{-1};\ \Delta G^{\circ}_{DE} = -6.9 \text{ kcal mol}^{-1}\right)$, which then relaxes to **IntF** $\left(\Delta G^{\circ}_{EF} = -9.1 \text{ kcal mol}^{-1}\right)$. **IntF** undergoes the ring-opening to give π-allylpotassium **IntG** *via* rate-determining **TS$_{FG}$** $\left(\Delta G^{\circ\ddagger}_{FG} = 22.8 \text{ kcal mol}^{-1};\ \Delta G^{\circ}_{FG} = -30.4 \text{ kcal mol}^{-1}\right)$, following the Woodward–Hoffmann rules in a conrotatory electrocyclic reaction of a 4-electron system.[15] Ring-opened **IntG** is calculated to be thermodynamically stable presumably due to the α-effect by the silyl group[16] and the resonance effect by the two aryl substituents. Allylpotassium species **IntG** then attacks the neighboring borate to form *gem*-silylborylated **IntH** *via* six-membered transition state **TS$_{GH}$** $\left(\Delta G^{\circ\ddagger}_{GH} = 21.3 \text{ kcal mol}^{-1}\right)$, which then regenerates the KO*t*Bu catalyst through the liberation of product **3ad** for the next cycle. The natural population analysis (NPA) of **IntG** revealed that the C1-position, bearing a $SiMe_3$ group, exhibits a higher negative charge compared to the C3-position (C1: −0.973 *vs.* C3: −0.324). This observation implies that the carbon–boron formation preferentially takes place at the C1-position.

In summary, we developed a KO*t*Bu-catalyzed ring-opening *gem*-silylborylation of cyclopropenes with silylboronates to give (1-silyl)allylboronates under simple and mild conditions. The utility of the resulting products was briefly examined, and the reaction mechanism was probed in detail using DFT calculations. Future studies will be directed toward further development of silylborylation using silylboronates under base catalysis.

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Conflicts of interest

There are no conflicts to declare.

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