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Potassium *tert*-butoxide-mediated regioselective silaboration of aromatic alkenes†

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The regio- and diastereoselective silaboration of aromatic alkenes with a silylboron compound proceeds in the presence of a catalytic amount of potassium *tert*-butoxide, providing a complementary method to the corresponding transition metal-catalyzed reactions.

Regio- and stereoselective silaborations of unsaturated compounds are synthetically useful because the silaboration products can be converted to multi-functionalized compounds through the stepwise derivatization of the Si–C and B–C bonds.[1,2] The silaboration requires an appropriate catalyst, and research efforts in this regard have focused almost exclusively on Si–B bond activation with transition-metal catalysts, including Pt,[3,4] Pd,[5–13] Ni,[14–16] Rh,[17–20] and Cu[21–26] metals. Consideration of the processing costs associated with heavy metals and the requirement for their effective removal from product streams can limit the use of the silaboration reaction on an industrial scale, and a transition-metal-free alternative would be desirable.

Recently, base-mediated activation of B–B and Si–B bonds has been focused as transition-metal-free procedures for silylation and borylation of unsaturated compounds (Fig. 1).[27–38] Heterolytic cleavage of Si–Si bonds with nucleophiles has been known for several decades and utilized in generation of silyl anions and other silylation reactions.[28,29] Diboron compounds were found to be activated by alkoxide bases, phosphines or *N*-heterocyclic carbenes (NHC) and underwent conjugate addition to cyclic and acyclic α,β-unsaturated carbonyls.[30–37] Fernández and co-workers recently reported a base-catalyzed diboration of alkenes and allenes.[32] Hoveyda and co-workers also reported an asymmetric boration of α,β-unsaturated compounds with diboron, which was promoted by a chiral NHC.[34] Other transition-metal-free procedures with diboron were also developed.[35–37] In contrast, base-mediated reaction of silylboron is still rare. Kawachi, Tamao and co-workers reported that silyl nucleophilic species could be generated through reactions between silylboron and a stoichiometric nucleophile, such as RLi, MeMgBr, and K(O-*t*-Bu).[28] Hoveyda and co-workers recently reported that a chiral NHC can also activate silylboron compounds, promoting enantioselective silylation of α,β-unsaturated compounds.[38] In this case, only the silyl group remained in the product and to the best of our knowledge, there have been no reported silaboration reaction conducted under transition-metal-free conditions where both the silyl and boryl groups are incorporated into the product. Herein, we report the first example of a transition-metal-free, base-mediated silaboration of aromatic alkenes.

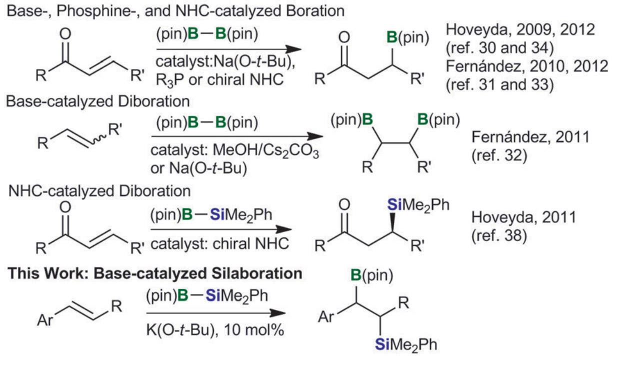

Fig. 1 Recent developments of nucleophile-mediated reactions of diboron and silyboron compounds.

Our initial efforts focused on the reaction of styrene (**1a**) with silylboron **2** under various reaction conditions (Table 1).[39] In the absence of a catalyst, no reaction occurred (entry 1). In contrast, the addition of a base catalyst in THF promoted the reaction. For example, the addition of 10 mol% of K(O-*t*-Bu) in THF at room temperature gave complete consumption of **1a** (0.3 mmol) and **2** (1.2 equiv., 0.36 mmol) within 1 h, affording the silaboration product **3a** in excellent yield (entry 2).

The reaction also proceeded in a highly regioselective manner, with only a single regioisomer being detected. A 10 mol% loading of the base catalyst gave the best results, with lower loadings (5 and 1 mol%) in lower yields with the remaining starting materials (entries 3 and 4, respectively). The use of a 50 mol% of catalyst gave a comparable yield to that of the 10 mol% loading (entry 5), whereas the use of a 100 mol% of the base catalyst resulted in a lower yield (entry 6). Furthermore, a reduction in the amount of **2** (1.0 equiv.), coupled with a 100 mol% loading of the base catalyst, led to a significant reduction in the yield (entry 7), likely because a reduction in the amount of the Lewis acidic **2** resulted in enhanced basicity, promoting decomposition of the product. Other alkoxy bases, such as KOMe and Li(O-*t*-Bu), gave

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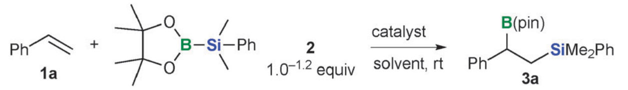
Table 1 Base-mediated silaboration of styrene **1a** with silylboron **2**[a]



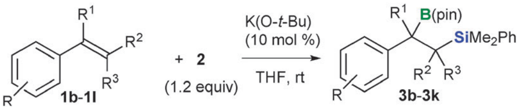
Entry	Base (mol%)	Solvent (mL)	Time (h)	Yield[b] (%)
1	None	THF	20	0
2	K(O-*t*-Bu), 10	THF	1	95 (91)
3	K(O-*t*-Bu), 5	THF	4	74
4	K(O-*t*-Bu), 1	THF	4	13
5	K(O-*t*-Bu), 50	THF	1	93
6	K(O-*t*-Bu), 100	THF	1	77
7[c]	K(O-*t*-Bu), 100	THF	4	22
8	KOMe, 10	THF	4	72
9	Li(O-*t*-Bu), 10	THF	4	14
10	LiOMe, 10	THF	4	0
11	Mg(OEt)$_2$, 10	THF	4	0
12[c]	TBAF, 10	THF	8	0
13[d]	Sm(O-*i*-Pr)$_3$, 10	THF	21	0
14	K(O-*t*-Bu), 10	DMF	4	0
15	K(O-*t*-Bu), 10	toluene	22	81
16	K(O-*t*-Bu), 10	1,4-dioxane	1	99

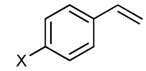
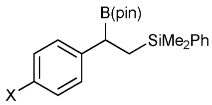
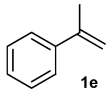
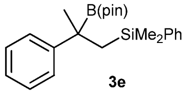
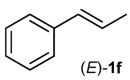
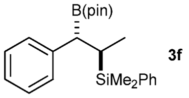
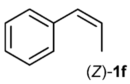
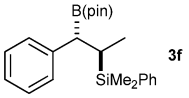
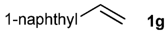
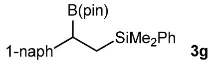
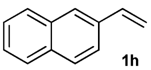
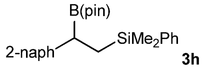
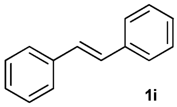
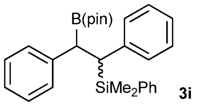
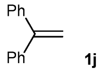
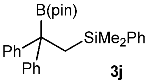
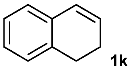
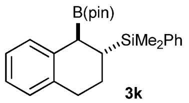
[a] Conditions: **1a** (0.3 mmol), **2** (0.36 mmol), K(O-*t*-Bu) (0.05 M, 0.6 mL, 0.03 mmol). [b] Yield was determined by GC analysis. Isolated yield is given in parentheses. [c] 1.0 equiv. (0.30 mmol) of **2** was used. The reaction was carried out at rt for 1 h then 50 °C for 7 h. [d] The reaction was carried out at 50 °C.

inferior results (entries 8 and 9, respectively). Li(O-*t*-Bu), Mg(OEt)$_2$, TBAF, and Sm(O-*i*-Pr)$_3$ did not afford the product (entries 10–13). DMF performed poorly as a solvent for the transformation and the reaction proceeded at a slower rate in toluene (entries 14 and 15, respectively). The use of 1,4-dioxane provided similar results to that of THF (entry 16).

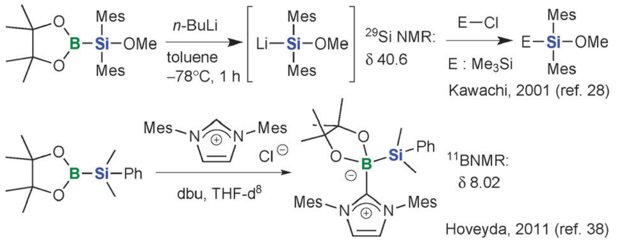
With the optimized reaction conditions in hand, we examined the scope of this novel catalysis with other aromatic alkenes (Table 2). The styrene type substrate with an electron donating methoxy substituent at the *para*-position (**1b**) underwent silaboration effectively (entry 1). 4-Chlorostyrene (**1c**) gave a low yield with formation of oligomeric side products (entry 2). 4-Trifluoromethylstyrene (**1d**) resulted in no reaction (entry 3). The reaction of 2-phenylpropene (**1e**) proceeded smoothly, affording the desired product **3e** in good yield (entry 4), with the boryl group being introduced at the sterically congested carbon alpha to the phenyl group. The (*E*)- and (*Z*)-isomers of **1f** were converted to the silaboration product **3f** with high levels of diastereoselectivity, with the major product having *anti* stereochemistry in both cases (entries 5 and 6, respectively).[40] Silaboration of the 1- and 2-vinylnaphthalenes also proceeded with moderate yields (entries 7 and 8, respectively). (*E*)-Stilbene (**1i**) reacted with **2** to afford the desired product **3i** in excellent yield (entry 9), although a low level of diastereoselectivity was observed (57 : 43 mixture). 1,1-Diphenylethene also performed well in the reaction, giving the corresponding silaboration product **3j** in good yield (entry 10). A good yield and stereoselectivity were observed in the reaction of 1,2-dihydronaphthalene (**1k**) (entry 11). In contrast, indene (**1l**) gave none of the desired products after quenching of the reaction mixture (entry 12). In all of the reactions shown in Table 2, only a single regioisomer was detected. It is worthy of note that non-aromatic alkenes, including 1-hexene and methyl acrylate, did not react under similar reaction conditions. Kawachi and co-workers reported that silyl anion species were generated through the reaction between silylboron compounds and *n*-BuLi. They carried out ^{29}Si NMR observations of the anionic species and trapping experiments with electrophiles (Scheme 1).[28] In contrast, as reported by O'Brien and Hoveyda, an NHC adduct of the silylboron compound is the key intermediate in the silylation reaction of α,β-unsaturated carbonyls.[38] Related diboron adducts with an alkoxide and NHC were also isolated by Marder and co-workers.[41,42]

Table 2 Potassium *tert*-butoxide-catalyzed silaboration of aromatic alkenes[a]

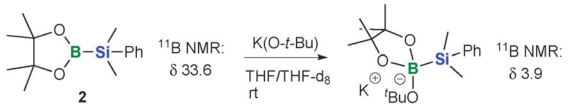


Entry	Substrate	Product	Time (h)	Yield[b] (%)
				
1	**1b** (X = OMe)	**3b**	4	87
2[c,d]	**1c** (X = Cl)	**3c**	1	67
3[e,f]	**1d** (X = CF$_3$)	**3d**	42	0
4[c,d]	 **1e**	 **3e**	1	66
5	 (*E*)-**1f**	 **3f**	17	85 (*anti*/*syn* 92 : 8)
6[e]	 (*Z*)-**1f**	 **3f**	14	82 (*anti*/*syn* 84 : 16)
7[c,f]	 **1g**	 **3g**	1	41
8[c,f]	 **1h**	 **3h**	1	55
9[d]	 **1i**	 **3i**	1	95 (57 : 43)
10	 **1j**	 **3j**	1	85
11[e,g]	 **1k**	 **3k**	1	72 (*trans*/*cis* 94 : 6)
12[e,f]	Indene **1l**	—	42	0

[a] Conditions: **1** (0.3 mmol), **2** (0.36 mmol), K(O-*t*-Bu) (1.0 M, 0.03 mL, 0.03 mmol), additional THF (0.57 mL). [b] Isolated yield. The stereochemical ratio was determined by ^{1}H NMR. [c] ^{1}H NMR yield determined after the crude samples were passed through a short silica gel column. [d] 1.1 equiv. of **2** was used. [e] The reaction was conducted at 50 °C. [f] 1.0 equiv. of **2** was used. [g] 15 mol% of K(O-*t*-Bu) was used.



Scheme 1 Observation of reaction products of silylboron compounds.



Scheme 2 *In situ* ^{11}B NMR observation of the K(O-*t*-Bu) adduct of **2**.

We carried out an *in situ* ^{11}B{^{1}H} NMR experiment to obtain a key intermediate of our reaction. Kawachi *et al.* did not provide spectroscopic results for the K(O-*t*-Bu)/Si–B case.[28] The NMR experiment revealed that an intermediate generated by the reaction between **2** and K(O-*t*-Bu) is the adduct product with a sp^3-B structure (Scheme 2). Treatment of **2** with an equimolar amount of K(O-*t*-Bu) in a THF/THF-d^8 (90 : 10) solution led to a new ^{11}B signal with a high-field shift (δ 3.9), resulting from the tetrahedral configuration of the B atom, whereas *t*-BuOB(pin) (δ 22.0) was not detected (ESI†).[42] These results are in contrast with Kawachi's report including heterolytic cleavage and generation of silyl anion species.[28] The high yield that was observed in a stoichiometric reaction (Table 1, entry 6) indicates that this species could be the key intermediate.

We at this stage cannot present a clear reaction mechanism that can explain all results we observed. We first envisaged that the free silyl anion nucleophile was generated and underwent nucleophilic attack to styrene substrates. However, the NMR experiment represents the complexation of the silylboron and the alkoxide rather than the free silyl anion generation. The low reactivity of substrates with an electron deficient substituent (4-CF$_3$, entry 3, Table 2), which is more electrophilic than parent styrene, does not match with that of the silyl nucleophile model. For related base-mediated diboration, Fernández proposed a novel concerted mechanism based on the DFT calculations.[32,33] This mechanism nicely explains the reactivity including the stereospecific diboration of *cis*- and *trans*- alkenes. However, this mechanism cannot be simply extrapolated to our silylboration reaction because Fernández's mechanism cannot account for the lack of stereospecificity we found in entries 5 and 6. Further detailed studies on the reaction mechanism are required.

We have reported the first example of the base-catalyzed silaboration of aromatic alkenes. The key intermediate for this catalysis would be the alkoxide adduct of silylboron reagents rather than silyl anion species, which we first postulated. This reaction performs well with sterically congested substrates with good diastereoselectivity under transition-metal-free conditions, providing a useful complementary method to transition-metal-catalyzed silaboration.

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