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Facile preparation of organosilanes from benzylboronates and *gem*-diborylalkanes mediated by KO^tBu†

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Methods to efficiently synthesize organosilanes are valuable in the fields of synthetic chemistry and materials science. During the past decades, boron conversion has become a generic and powerful approach for constructing carbon–carbon and other carbon–heteroatom bonds, but its potential application in forming carbon–silicon remains unexplored. Herein, we describe an alkoxide base-promoted deborylative silylation of benzylic organoboronates, geminal bis(boronates) or alkyltriboronates, allowing for straightforward access to synthetically valuable organosilanes. This selective deborylative methodology exhibits operational simplicity, broad substrate scope, excellent functional group compatibility and convenient scalability, providing an effective and complementary platform for the generation of diversified benzyl silanes and silylboronates. Detailed experimental results and calculated studies revealed an unusual mechanistic feature of this C–Si bond formation.

Introduction

Organosilanes not only play pivotal roles in medicinal chemistry1 and material science,2 but they are also highly functionalized and versatile building blocks for further transformation in synthetic chemistry.3 In the past few decades, considerable attention has been placed on developing synthetic strategies to construct C(sp³)-Si bonds by cross-coupling reactions in the presence of transition metals, such as palladium, nickel, and copper salts, as catalysts (Fig. 1A).4 Highly reactive organometallic species, including Grignard reagents, organolithiums, organozincs or ganoaluminiums, are emerging as the most attractive substrates for the construction of organosilanes.^{5,6} Although these transformations are synthetically useful, these organometallic reagents exhibit a high basicity and strong nucleophilicity, making them incompatible with many functional groups. Organohalides are often used as precursors to organometallic reagents; therefore, substantial progress has been recently achieved to access silicon-containing molecules by cross-coupling from these abundant and structurally diverse feedstocks to replace preformed organometallic reagents.^{7,8} Despite these advances, a method to easily prepare

Interconversion of the main group elements has been a long-standing goal in organic chemistry. In this area, organoboron compounds have become valuable building blocks in organic synthesis because of their flexibility, as they can be synthesized from multiple different functional groups. Significant developments have been achieved for the interconversion of carbon-boron bonds to carbon-carbon and carbon-heteroatom (F, Cl, Br, I, O, N, S ...) bonds (Fig. 1B). In this context, the conversion of C-Si bonds into C-B bonds has been developed through the reaction with boron trihalides (BCl₃, BBr₃). At the

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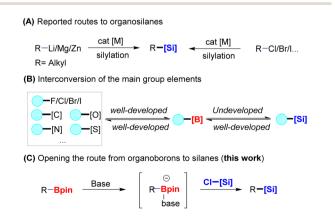


Fig. 1 Background and discovery. (A) Classic synthesis methods of organosilanes; (B) boron conversion; (C) deborylative silylation.

organosilanes without reactive coupling partners and metal catalysts is more attractive.

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Table 1 Effect of reaction parameters^a

Entry	Variation from standard conditions	Yield ^b (%)	
1	None	02 (049)	
1	1,0116	92 (84°)	
2	Without KO ^t Bu	0	
3	KOMe instead of KO ^t Bu	21	
4	NaO ^t Bu instead of KO ^t Bu	Trace	
5	LiO ^t Bu instead of KO ^t Bu	0	
6	KOH instead of KO ^t Bu	0	
7	K ₃ PO ₄ instead of KO ^t Bu	0	
8	Toluene as the solvent	69	
9	ⁿ Octane as the solvent	58	
10	MeCN as the solvent	0	
11	DMF as the solvent	Trace	
12	At 80 °C	64	

 $[^]a$ Reaction conditions: **1a** (0.4 mmol), **2a** (0.8 mmol), 2 equiv. of KO^fBu in THF (2 mL), 5 h, at 100 °C under Ar. b The yields were determined by GC-MS analysis using an internal standard. c Isolated yield.

Table 2 The scope of alkylborons^{abo}

	R ² R ³ + R ₃ SI-CI	Conditions A or B 100 °C, 12 h R ¹ SIR	Conditions A (Pr) ₃ SiCl (2a, 2 e KO'8u (2 equiv.) THF (0.2 M)	Conditions B R ₃ SiCl (2, 2 equiv.) KO'8u (2 equiv.) **octane (0.2 M)	
Benzyl substrates a Si(Pr) ₃ Me 3b, 87%	Si(Pr) ₃ 3c, 68%	Si(Pr) ₃	Si(Pr) ₃ Me 3e, 49%	MeO Si((Pr) ₃	CF ₃ O Si(Pr) ₃
Si(Pr)s 3h, 90% Multiborylated substrates ⁴	SI(Pr) ₃	Br Si(Pr) ₃ Me	3k, 79%	\$1(Pr) ₃ pph ₂ 31, 83%	3m, 85%
SiEt ₃ Bpin 3n, 74%	SiEt ₃ Me 30, 77%	Me SiEt ₃ Sp. 79%	Ph SiEt ₃ Spin 3q, 73%	SiEt _a Bpin 3r, 70%	SiEt ₀ Bpin 3e, 75%
8pin Sillt ₅ 3t, 78% (62%°)	SiEt ₃ Me Bpin 3u, 77%	MeO 3v, 42%	MeO Sepin 3w, 45%	SiEt ₃ Bpin 3x, 46%	SiEts Spin 3y, 87%
SiEt ₀ Bpin 3z, 75%	Br SEts Sepin 3aa, 80%	Me Me Bpin 3ab, 68%	SIEt ₃ Upin 3ac, 64%	3€t ₃ 8pin 3ad, 69%	SEt ₃ O bpin Jae, 58%
SiEt ₃ Bpin 3af, 67%	SiEt ₃ Opin Me 3ag, 49%	Sitts Spin 3ah, 52%	SÆL ₃ Bpin 3ai, 81%	SiEt ₃ Me Bpin 3aj. 62%	Me SiEts Upin 3ak, 65%
SiEt ₃ Bpin 3al, 80% Scope of chlorositanes *	Br SEts Spin Sam, 72%	Sets Spin Bpin San, 89%	SiEt ₃ Bpin Bpin 3ao, 83%	SEL ₃ Bpin Upin 3ap, 67%	SiEt ₃
Me Br Sar, 77%	Br Sas, 78%	Br 3at, 65%	Me Si Me Si Me Sau, 84%	Br Sav, 54%	Br Saw, 64%
Br Sax, 56%	Br Bpin Ph	Br SiMes Boin Me 3az, 76%	Br Jaas, 53%	Mo Be Bein 3aab, 73%	Br Sasc, 71%

^a Reaction conditions: 1 (0.4 mmol), 2a (0.8 mmol), 2 equiv. of KO $^{\prime}$ Bu in THF (2 mL), 5 h, at 100 $^{\circ}$ C under Ar. ^b Reaction conditions: 1 (0.4 mmol), 2b (0.8 mmol), 2 equiv. of KO $^{\prime}$ Bu in ⁿoctane (2 mL), 5 h, at 100 $^{\circ}$ C under Ar; yields given refer to isolated yields of product. ^c The reaction was carried out in THF; yields given refer to isolated yields of product.

outset of this project, no inverse approach from C–B bonds to C–Si bonds had been developed.

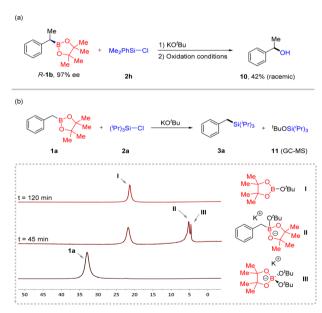
Because of the diagonal relationship between boron and silicon in the periodic table, the boryl and silyl groups exhibit related properties and reactivity for further functionalization, but the latter groups are more stable during storage and handling.¹⁴ Furthermore, silicon reagents exhibit significant differences in functionality in materials, which are important precursors to commercial polymers and copolymers.¹⁵ Thus, developing a method to prepare organosilanes from related boronates is an attractive goal because it fills the gap in boranesilane interconversion. Here, we develop the first deborylative silylation of benzylic boronate esters or multiboronates to organosilanes mediated by an alkoxide base under transition metal-free conditions (Fig. 1C). In this surprisingly simple approach, the *in situ* formation of boron–ate complexes can react with chlorosilanes through a concerted process to access valuable benzyl silanes and silylboronates.

Results and discussion

We commenced our studies using commercially available 2benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1a and chlorotriisopropylsilane 2a as model substrates. Based on a systematic examination of reaction conditions, we determined that the following settings were optimal: KO^tBu (2 equiv.) as a base in tetrahydrofuran (THF) at 100 °C. As a result, benzyltriisopropylsilane 3a was obtained in 84% isolated yield (Table 1, entry 1). KO^tBu was removed from standard conditions, and the target product could not be detected by GC-MS (Table 1, entry 2). While 3a was formed in 21% yield with KOMe (Table 1, entry 3), other commonly used bases, such as NaO^tBu, LiO^tBu, KOH and K₃PO₄, were ineffective for this cross-coupling reaction (Table 1, entries 4-7). These results demonstrated that potassium cations and alkoxide anions are indispensable for the high reactivity of this transformation. When the reaction was conducted in toluene or "octane with KO" Bu as a base, lower yields were obtained (Table 1, entries 8 and 9). However, other polar solvents, including MeCN and DMF, failed to generate silylated products (Table 1, entries 10-11). Lowering the temperature led to a lower yield with incomplete conversion of the benzyl boron esters, and byproduct tert-butoxytriisopropylsilanes (^tBuO-Si(^tPr)₃) were detected by GC-MS (Table 1, entry 12).

With the optimized conditions in hand, we then evaluated the generality of this method. First, we examined a scope of alkylborons using chlorotriisopropylsilanes or chlorotriethylsilane as coupling partners (Table 2). To our delight, benzyl boronates 1b-1m reacted smoothly with chlorosilanes 2a under standard conditions, affording benzyl silanes 3b-3m in 49-90% yields. For example, secondary boronates 1b and 1c participated in the reactions to obtain corresponding products 3b and 3c in 87% and 68% yields, respectively. Naphthalene substrate 1d was shown to exhibit high levels of reactivity. The products with OMe and OCF₃ groups were formed in acceptable yields (3e-3g). It should be mentioned that halo substituents, such as F, Cl, Br and I, on the substrates (1h-1k) did not influence the reaction, indicating their potential application in subsequent cross-coupling transformations. Furthermore, 11 and 1m bearing phosphine or ketone substituents on the phenyl group performed well, affording the corresponding products in 83% and 85% yields (31 and 3m, respectively). Remarkably, this strategy could be successfully applied to the

Scheme 1 Synthetic applications of the deboronative silylation.

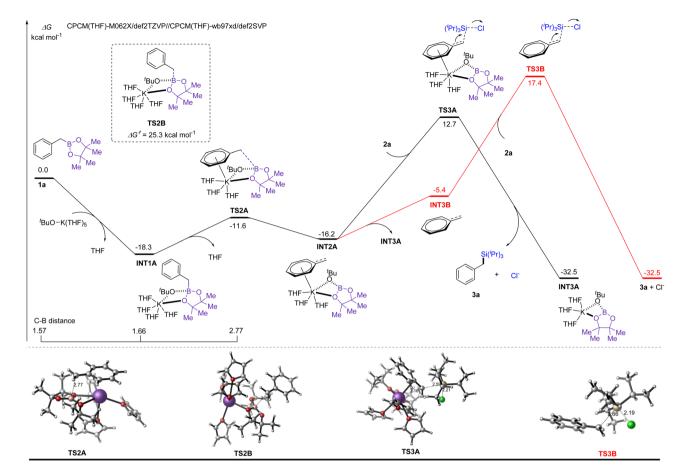


Scheme 2 Mechanistic experiments.

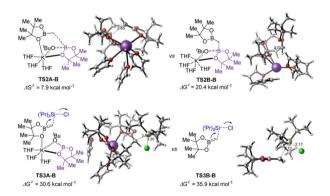
synthesis of geminal silylboronates, ¹⁶ which exhibit unique reactivity characteristics that allow them to participate in a variety of complexity-generating procedures. A range of carbon chain 1,1-bis(pinacolboronate) esters were tolerated under modified conditions, affording valuable silicated boronates in

70-79% yields (3n-3t). In addition, boronates 1u underwent cross-coupling with chlorotriethylsilane to form highly congested α-quaternary carbon centres 3u in 77% yield. Although oxygen-containing substrates participated in this reaction, their yields were low (42-46%; 3v-3x). Substrates possessing fluorine, chlorine, bromine, alkenyl and naphthyl groups were well tolerated in this system (3y-3ad). Delightedly, the common heterocyclic cores could favourably carry out these deboronative cross-coupling transformations (3ae-3ah). Selective functionalization of 1,2-bis(boronate esters) is a challenging topic in organic synthesis.17 Therefore, we tried the selective crosscoupling reaction with these bis(boronate esters) and chlorosilanes under standard conditions. We found that this crosscoupling exclusively occurs at the benzyl boron, providing 1,2silylboronates in moderate to good yields (3ai-3ak). Subsequently, 1,1,1-alkyltriboronates and 1,1,2-alkyltriboronates were selectively coupled with chlorosilanes to afford the corresponding products 3al-3ap in 67-89% yield. Most of these silylboronate compounds are difficult to synthesize by known methods. Primary alkylboronates were also examined, but only trace amounts of silanes 3aq were detected by GC-MS.

Next, we investigated the scope of chlorosilanes for cross-coupling with germinal boronates **1aa**. Substrates with different carbon chains were amenable to the cross-coupling reaction as well (**3ar–3au**). Notably, chlorosilane with a bulky substituent, such as a *tert*-butyl, showed lower yields (**3av**). The reaction of aryl chlorosilanes could afford target products **3aw**,



The calculated energy profiles for the alkoxide-promoted cross-coupling of 1a and 2a



The additional stabilization for substrate germinal boronates.

3ax and 3ay in satisfactory yields as well. Chlorodisilanes were also feasible substrates with good yields (3az). Additionally, the use of a chloro-containing example afforded product 3aaa in 53% yield. Finally, the presence of alkenyl substituents was tolerated (3aab and 3aac).

To showcase the synthetic applications of this robust deboronative platform, we performed late-stage modification of complex molecules and a series of sequential transformations (Scheme 1). Lithocholic acid derivative 1ar reacted with Et₃SiCl (2b) under optimized conditions, affording product 3aad in 62% yield. Oleic acid derivative **1as** bearing a *trans*-alkene group

provided silylboronate 3aae in 71% yield. Interestingly, by continuously treating 1at with chlorosilanes and KO^tBu, two deborylative silylations occurred, affording geminal disilanes 4 in 67% yield. When using 1,1,2-alkyltriboronate 1au with two reactive sites as a substrate, the selective process of silylation was observed give triethyl(1-phenyl-2,2-bis(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) silane 3aag, which can further undergo cross-coupling with alkyl bromide 5a under the condition of sodium alkoxide (NaO^tBu), 18 providing 1,2silylboronate 6 in 84% yield. Moreover, successive silylation and allylation led to the desired (1,2-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)pent-4-en-1-yl)triethylsilane 7 in 87% yield. These results demonstrate the excellent chemoselectivity of this method. A gram-scale reaction proceeded with 1y, affording a 76% isolated yield of silylated product 3y, which can then undergo oxidation or amination processes to afford hydroxyl- or amino-products (8, 9) in good yields, respectively.

To determine the reaction mechanism, we performed some experiments (Scheme 2). First, when R-1b (97% ee) was reacted with Me₂PhSi-Cl 2h under our conditions, racemic compound 10 was observed in 42% yield after oxidation treatment. GC-MS was used to detect the course of the reaction, and we found that byproduct 11 formed. Subsequently, in situ 11B NMR of the reaction process was performed using benzyl boron ester 1a and chlorosilane 2a as substrates, and three new resonances (I, II, and III) appeared at 45 minutes. The resonance at 5.1 ppm (II) is

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assigned to an "ate" complex. ¹⁹ Over time, this characteristic peak gradually disappeared. Based on these observations, we speculate that this transformation involves two processes. The first step was the generation of a carbanion through a deborylative pathway of an "ate" complex II. The second step was the nucleophilic reaction of the formed alkyl anion with chlorosilane to generate the final product.

The proposed mechanism was further supported by a detailed density functional theory (DFT) study, as shown in Fig. 2. Initially, the boron atom of 1a is coordinated with the oxygen of KO^tBu solvated by five tetrahydrofuran molecules, and then the oxygen of 1a replaces one molecule of THF at potassium to generate INT1A with an exothermic energy of 18.3 kcal mol⁻¹. In **INT1A**, the boron centre is more electronrich than that in 1a, and the C-B distance is elongated to 1.66 Å from 1.57 Å, decreasing the bond dissociation energy of the C-B bond. Subsequent C-B bond cleavage proceeds smoothly through transition state TS2A with an energy barrier of 6.7 kcal mol⁻¹, in which the potassium cation binds to the aromatic ring of 1a to stabilize the developing negative charge centre and simultaneously release one molecule of THF. The direct cleavage of the C-B bond via transition state TS2B without the assistance of potassium requires a higher activation free energy (25.3 kcal mol⁻¹). The negative charge centre in intermediate INT2A undergoes nucleophilic attack to chlorotriisopropylsilane 2a via transition state TS3A with an activation free energy of 28.9 kcal mol⁻¹, producing the desired alkyl silane 3a and byproduct INT3A. The calculational results indicate that the nucleophilic attack step is the rate-determining step, and the overall activation free energy for this transformation is 31.0 kcal mol⁻¹. The nucleophilic attack step for the alkyl anion released from INT2A must overcome an overall free energy of 35.7 kcal mol⁻¹ through transition state TS3B, which is 4.7 kcal mol⁻¹ higher than that of **TS3A**. This explains why the deborylative silvlation can be promoted by KOMe but failed with sodium alkoxide or lithium alkoxide (Table 1, entries 3-5). Therefore, both the alkoxide anion and potassium cation are indispensable in this transformation, as these entities participate in the formation of a more stable intermediate species, lowering the energy barrier of C-B bond cleavage and C-Si bond formation.

For substrate germinal boronates, the pathways for C–B bond cleavage through transition **TS2A-B** and the subsequent C–Si bond formation via **TS3A-B** have the lower energies (Fig. 3). Comparing the energy barrier of transition state **TS3A-B** in the rate-determining step, the stepwise S_N2 pathway through **TS3B-B** was found to be disfavoured kinetically and ruled out. Overall, DFT analysis further reveals that the transition states **TS2A-B** and **TS3A-B** are substantially stabilized by the coordination between the potassium cation and oxygen of the reserved boronate (see ESI† for details).

Conclusions

In summary, we have established a general and practical method for synthesizing alkyl silane derivatives from readily available benzylic boronates, geminal bis(boronates) or alkyltriboronates. This transition-metal-free transformation features excellent chemoselectivity, broad substrate scope, versatility, and scalability. These borylated silanes can readily be further functionalized by well-established organoboron chemistry to enhance the molecular complexity. In view of these features, this transformation should have high synthetic value in the field of materials and pharmaceuticals.

Data availability

The synthetic procedures, characterization, and spectral data supporting this article have been uploaded as part of the ESI.†

Author contributions

J. H. conceived the project and directed the research. S. J. and Z. S. supervised the mechanistic study. J. H. and Z. S. wrote the paper. M. T., W. Z., J. W. and H. S. performed the experiments. M. W. performed the DFT calculations.

Conflicts of interest

The authors declare no competing financial interest.

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