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A (Borylmethyl)silane Bearing Three Hydrolyzable Groups on Silicon: Synthesis via Iridium-Catalyzed C(sp^3)−H Borylation and Conversion to Functionalized Siloxanes

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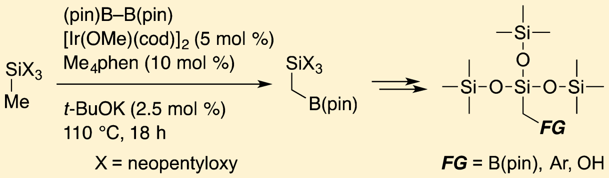
Supporting Information

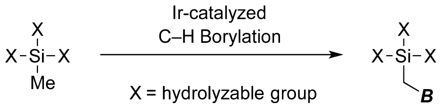
ABSTRACT: An iridium-catalyzed C(sp^3)−H borylation of X_3SiMe (X = hydrolyzable group) was established. A trialkoxy(methyl)silane bearing sterically demanding neopentyloxy groups (X = neopentyloxy) underwent C−H borylation at the methyl group on silicon, giving (borylmethyl)tris(neopentyloxy)silane in 70% isolated yield. The choice of the hydrolyzable group X was the key to efficient and chemoselective C−H borylation; trialkoxy(methyl)silanes bearing sterically less demanding alkoxy groups (X = ethoxy, *n*-butyloxy, and isobutyloxy) suffered from C−H activation at the alkoxy groups, and trichloro(methyl)silane (X = Cl) failed to react. A trimethylsiloxy group could substitute the neopentyloxy groups of the borylated product by the reaction of trimethylsilanol in the presence of tetrabutylammonium fluoride.



Monoorganosilanes bearing three hydrolyzable groups on the silicon atoms (X_3SiR: X = halogen or alkoxide; R = organic group) are important building blocks for the synthesis of branched polysiloxanes, including silsesquioxanes.[1] Another significant application of X_3SiR is their use as silane coupling agents, when the substituent R bears a functional group such as alkene and epoxide.[2] X_3SiR are synthesized by substitution of X_4Si with Grignard or organolithium reagents, but this method generally suffers from overreaction and therefore is not suitable for the selective introduction of a less hindered alkyl group.[3] Chlorodephenylation of Ph_3SiR with HCl in the presence of $AlCl_3$ limits the substrate scope because of the harsh conditions.[4] More general routes to X_3SiR are transition-metal-catalyzed reactions of X_3SiH, i.e., hydrosilylation of unsaturated substrates[5] and coupling with organohalides.[6] Considering the recent increasing attention to the development of siloxane-based materials, new entries of efficient methods for the preparation of X_3SiR are still highly desirable. We focused on a synthetic route starting from Cl_3SiMe, which is a less utilized feedstock despite its second most production in the Rochow−Müller direct process.[7] If the methyl group of Cl_3SiMe or its alkoxy derivatives can be converted to a functionalized organic group with retention of the hydrolyzable groups, it would be highly attractive for new access to X_3SiR.

We have pursued organosilicon compounds functionalized by a boryl group,[8] which is expected to serve as a handle for the introduction of organic functional groups via C−C bond forming reactions or via capture of guest molecules on the boron atoms. We established an iridium-catalyzed C−H borylation of methylsilanes, which enabled conversion of the C(sp^3)−H bond of the methyl group on silicon.[9,10] The C−H borylation is applicable to methylchlorosilanes, including Cl_2SiMe_2 and $ClSiMe_3$.[9a] However, the use of Cl_3SiMe in the C−H borylation protocol has met with difficulty. Herein we describe C−H borylation of methylsilanes bearing three hydrolyzable groups on the silicon atom (Scheme 1). We found a suitable hydrolyzable group X for efficient and chemoselective C−H borylation of the methyl group on silicon.

Scheme 1. Synthesis of Boryl-Functionalized Organosilicon Compounds Bearing Three Hydrolyzable Groups on the Silicon Atom



We began our study by synthesizing (borylmethyl)trichlorosilane **1** by C−H borylation of Cl_3SiMe according to the method established previously for C−H borylation of Cl_2SiMe_2 and $ClSiMe_3$.[9a] In the presence of $[Ir(OMe)(cod)]_2$ (5 mol %) and 3,4,7,8-tetramethylphenanthroline (Me_4phen, 10 mol %), Cl_3SiMe (4 equiv) was reacted with bis(pinacolato)diboron (1 equiv) in cyclohexane at 80 °C (Scheme 2A). However, no reaction took place after 18 h. Under almost identical conditions, Cl_2SiMe_2 underwent C−H borylation to give **2** in high yield (Scheme 2B).[9a] We separately observed that almost no reaction of Cl_2SiMe_2 took place in the presence of 20 mol % of Cl_3SiMe (Scheme 2B). These results

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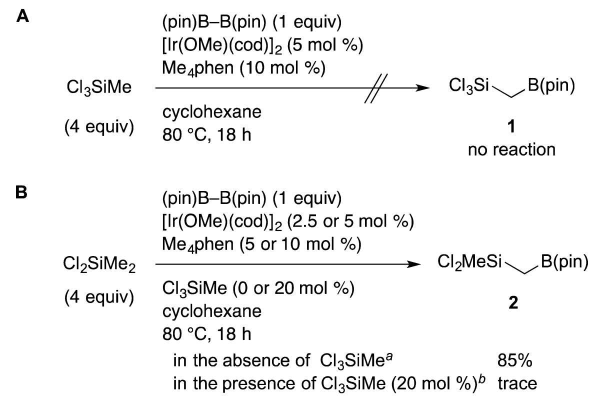
Scheme 2. Cl_3SiMe in C−H Borylation: (A) C−H Borylation of Cl_3SiMe; (B) C−H Borylation of Cl_2SiMe_2 in either the Absence or Presence of Cl_3SiMe

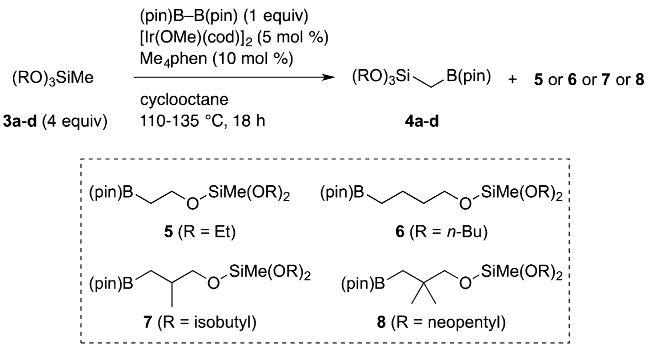


[a] $[Ir(OMe)(cod)]_2$ (2.5 mol %) and Me_4phen (5 mol %) were used. [b] $[Ir(OMe)(cod)]_2$ (5 mol %) and Me_4phen (10 mol %) were used.

indicate that Cl_3SiMe is a potential catalyst poison in the iridium-catalyzed C−H borylation.

We assumed that the highly Lewis acidic Cl_3SiMe might form a complex with Me_4phen, which caused deactivation of the iridium catalyst.[11] We turned our attention to the less Lewis acidic trialkoxy(methyl)silanes **3**, which could be prepared in a single step from Cl_3SiMe.[12] Triethoxy(methyl)silane (**3a**) reacted smoothly with bis(pinacolato)diboron in cyclooctane at 110 °C in the presence of the Ir-Me_4phen catalyst (10 mol %) (entry 1, Table 1). However, the reaction gave the undesired **5**, which was formed by borylation of the C−H bond at the terminus of the ethoxy group, as a major product with desired **4a** (**4a**:**5** = 21:79, entry 1). The formation of **5** is favorable because of the rather high reactivity of the C−H bond located β to the oxygen atom, as reported by Hartwig and coworkers.[13] The C−H borylation of methylsilanes **3b**,**c** bearing *n*-butyloxy and isobutyloxy groups, respectively,[12] proceeded at an elevated reaction temperature (135 °C) to give the borylated products with better chemoselectivity (**4b**:**6** = 67:33 and **4c**:**7** = 60:40) (entries 2 and 3). Finally, we found that the sterically more demanding methyltris(neopentyloxy)silane (**3d**)[12] underwent C−H borylation selectively at the methyl group on silicon to afford **4d** (**4d**:**8** > 99:1), albeit in low yield (20%, entry 4). In this case, the C−H borylation at the methyl groups on the neopentyl group was retarded significantly by the steric hindrance.

Table 1. Chemoselectivity in Iridium-Catalyzed C−H Borylation of Trialkoxy(methyl)silanes 3[a]

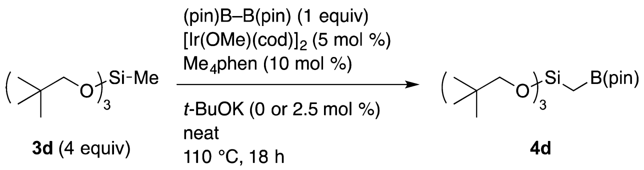


entry	R		temp (°C)	products	yield (%)[b] (ratio)[c]
1	Et	**3a**	110	**4a** + **5**	98 (21:79)
2	*n*-Bu	**3b**	135	**4b** + **6**	33 (67:33)
3	isobutyl	**3c**	135	**4c** + **7**	57 (60:40)
4	neopentyl	**3d**	135	**4d** + **8**	20 (>99:1)

[a] $[Ir(OMe)(cod)]_2$ (0.025 mmol), Me_4phen (0.052 mmol), **3** (2.0 mmol, 4 equiv), and (pin)B−B(pin) (0.50 mmol) were reacted in cyclooctane (0.5 mL) at 110−135 °C for 18 h. [b] Combined yield of the structural isomers after purification. [c] Determined by ^1H NMR.

We previously reported the effect of a catalytic amount of basic additives, e.g., *t*-BuOK, in acceleration of the iridium-catalyzed C−H borylation of aliphatic compounds.[14,15] To improve the yield of **4d**, the C−H borylation of **3d** was performed in the presence of an additive (Table 2). We found that the reaction of **3d** (4 equiv) with bis(pinacolato)diboron (1 equiv) took place efficiently at 110 °C in the presence of Ir-Me_4phen catalyst (10 mol %) and *t*-BuOK (2.5 mol %) without additional solvent, giving **4d** in good yield (entry 3), while **4d** was obtained only in 24% yield in the absence of *t*-BuOK under the same reaction conditions (entry 1). As observed in the previous study,[14] the Ir-*t*-BuOK system is sensitive to the amount of *t*-BuOK. Rate acceleration was observed with an Ir:*t*-BuOK ratio of 1:0.5−0.125 (entries 2−4), whereas no acceleration was observed with the ratio of 1:1.5−1 (entries 6 and 7). Other additives such as MeOK, Cs_2CO_3, and CsF were not effective for the C−H borylation of **3d** (entries 8−10). Finally, a multigram-scale reaction was carried out using the optimized ratio (Ir:*t*-BuOK = 1:0.25), by which 3.0 g of **4d** (70% yield) could be synthesized (entry 3).

Table 2. Improvement of C−H Borylation for Synthesis of 4d[a]



entry	additive (amt (mol %))	Ir:additive	yield (%)[b]
1	none	–	24
2	*t*-BuOK (1.25)	1:0.125	57
3	*t*-BuOK (2.5)	1:0.25	75 (70)[c]
4	*t*-BuOK (5.0)	1:0.5	36
5	*t*-BuOK (7.5)	1:0.75	26
6	*t*-BuOK (10)	1:1	18
7	*t*-BuOK (15)	1:1.5	3
8	MeOK (2.5)	1:0.25	34
9	Cs_2CO_3 (2.5)	1:0.25	37
10	CsF (2.5)	1:0.25	39

[a] $[Ir(OMe)(cod)]_2$ (0.025 mmol), Me_4phen (0.052 mmol), additive (0−15 mol %), **3d** (2.0 mmol, 4 equiv), and (pin)B−B(pin) (0.50 mmol) were reacted at 110 °C for 18 h. [b] Determined by ^1H NMR. [c] Isolated yield in multigram scale reaction. **4d** (3.0 g) was obtained.

Although the neopentyloxy group is an uncommon hydrolyzable group in the formation of a Si−O−Si linkage, **4d** could be converted to structurally defined oligosiloxanes by the reaction with an excess amount of trimethylsilanol in the presence of tetrabutylammonium fluoride (Scheme 3A).[16] The reaction took place at 50 °C with retention of the boryl group to give siloxane **9** in 71% yield.

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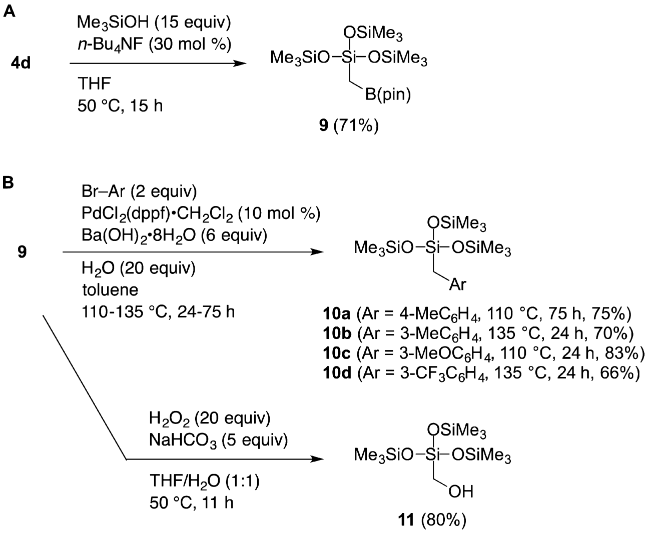
Scheme 3. **Synthesis of Functionalized Siloxanes: (A) Conversion of 4d to Siloxane 9 with Retention of the Boryl Group; (B) Conversion of 9 to Arylmethyl- and Hydroxymethyl-Substituted Siloxanes 10 and 11**[a]



[a] Isolated yields are given.

The boryl group in **9** could be utilized for further functionalization and bond formation (Scheme 3B). Suzuki–Miyaura coupling of **9** with aryl bromides was carried out in toluene at 110–135 °C using DPPF/Pd catalyst with $Ba(OH)_2$ as a base to give **10a–d** in good yields (Scheme 3B, top).[9b,17,18] Treatment of **9** with H_2O_2 under basic conditions allowed the formation of hydroxymethyl-substituted siloxane **11** in 80% yield (Scheme 3B, bottom).[19]

In conclusion, we have established a synthetic method for boryl-functionalized methylsilanes bearing three hydrolyzable groups on silicon. Methyltris(neopentyloxy)silane was found to be a suitable substrate for chemoselective iridium-catalyzed C–H borylation at the methyl group on silicon. The neopentyloxy group of the borylated product was used as a hydrolyzable group in the formation of the Si–O–Si linkage with retention of the boryl group. Further utilization of this new T unit for the synthesis of functionalized polysiloxanes is being undertaken in this laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00316.

Experimental details and characterization data of the products (PDF)

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Notes

The authors declare no competing financial interest.

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(18) The use of **4d** in Suzuki–Miyaura coupling was also examined. The reaction with 4-bromotoluene at 110 °C under the conditions shown in Scheme 3B gave the coupling product in 28% yield (see the Supporting Information).

(19) $NaHCO_3$ was a suitable base to obtain **11** in high yield. Use of NaOH instead of $NaHCO_3$ resulted in a low yield of **11**, probably due to redistribution of the Si–O–Si linkage.