ORGANOMETALLICS
Communication
pubs.acs.org/Organometallics

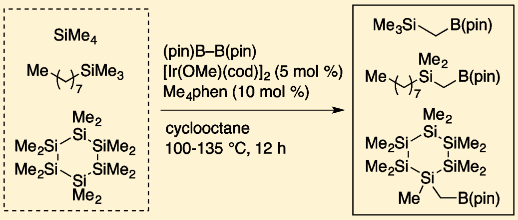
Functionalization of Tetraorganosilanes and Permethyloligosilanes at a Methyl Group on Silicon via Iridium-Catalyzed $C(sp^3)$−H Borylation

Toshimichi Ohmura,* Takeru Torigoe, and Michinori Suginome*

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

Ⓢ *Supporting Information*

ABSTRACT: In the presence of an iridium 3,4,7,8-tetramethyl-1,10-phenanthroline catalyst, a methyl group on the silicon atom of alkyltrimethylsilanes undergoes selective C−H borylation with bis(pinacolato)diboron in cyclooctane at 135 °C to give alkyl(borylmethyl)dimethylsilanes. The C−H borylation of tetramethylsilane takes place efficiently at 100 °C. Permethyloligosilanes can also undergo C−H borylation without cleavage of the Si−Si bonds.



With the rapid expansion of applications of organosilicon compounds in materials sciences and synthetic organic chemistry, increasing attention has been paid to the development of efficient methods for the synthesis of new classes of organosilicon compounds. Since the establishment of Kipping's method, i.e., alkylation of halosilanes with Grignard reagents,[1] conventional methods to prepare tetraorganosilanes have relied on Si−C bond-forming reactions.[2−6] In sharp contrast, a synthetic method via conversion of the C−H bond of the alkyl group in nonfunctionalized tetraalkylsilanes has been much less explored, except for deprotonation with *n*-BuLi to form (silylmethyl)lithiums[7] and radical chlorination with Cl_2 to afford (chloromethyl)silanes.[8] Recently, we have developed an iridium-catalyzed $C(sp^3)$−H borylation selectively at the methyl groups of methylchlorosilanes to give (borylmethyl)chlorosilanes.[9] This reaction provides a new synthetic strategy for functionalized organosilicon compounds via introduction of a functional group at methyl groups of a preformed organosilicon skeleton. We envisioned that if the C−H borylation was applicable to tetraalkylsilanes and fully alkylated oligosilanes, it would be highly valuable for the development of silicon-based functional organic molecules.

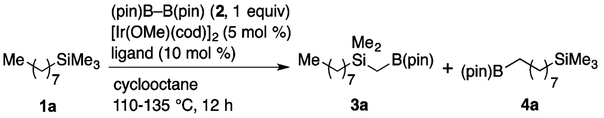
Since the first report by Hartwig and co-workers in 1999,[10] transition-metal-catalyzed borylation of $C(sp^3)$−H bonds has been recognized as a powerful method for the synthesis of alkylboron compounds.[11] Site selectivity of the reaction, as well as catalyst efficiency, is an important issue in the $C(sp^3)$−H borylation. The steric environment of the C−H bond is recognized as one of the major factors determining site selectivity.[12] Relatively reactive C−H bonds, which are located at allylic and benzylic positions or are on a cyclopropyl ring, can be preferentially borylated.[13] Directing-group-promoted $C(sp^3)$−H borylations have been reported recently, demonstrating remarkable rate acceleration and site selectivity in the $C(sp^3)$−H borylation.[14] In our previous work on the C−H borylation of methylchlorosilanes,[9] we found that the chlorine atom on the silicon atom promoted C−H borylation at the $C(sp^3)$−H bond located α to silicon, while the electronic effect of the silicon atom was left unclear. Herein, we describe an iridium-catalyzed $C(sp^3)$−H borylation of organosilanes, such as tetramethylsilane, alkyltrimethylsilanes, and permethyloligosilanes, which do not carry heteroatom functional groups on the silicon atom. We established a positive "α-effect" of silicon,[15,16] which allows us to convert otherwise unreactive methyl groups of unfunctionalized organosilanes to borylmethyl groups.

The reaction of trimethyl(octyl)silane (**1a**; 4 equiv) with bis(pinacolato)diboron (**2**) was examined to establish efficient $C(sp^3)$−H borylation conditions (Table 1). As we mentioned briefly in the previous paper,[9] **1a** underwent borylation sluggishly at 110 °C in the presence of $[Ir(OMe)(cod)]_2$ (2.5 mol %) and 3,4,7,8-tetramethylphenanthroline (Me_4phen, 5 mol %) (entry 1). We found that the C−H borylation of **1a** proceeded more efficiently at elevated reaction temperature (135 °C) with higher catalyst loading (10 mol % of Ir) (entry 2). The reaction gave a mixture of (borylmethyl)silane **3a** and (8-boryloctyl)silane **4a** in 78% yield in a ratio of 95:5, indicating that the sterically more demanding methyl group on the silicon atom reacted preferentially over the methyl group at the octyl terminus. The use of a phenanthroline-derived ligand is crucial for efficient C−H borylation: essentially no borylation took place in the absence of the diamine ligand (entry 3) or even in the presence of 4,4′-di-*tert*-butylbipyridine (dtbpy), which is known to be an effective ligand for $C(sp^2)$−H borylation of benzene derivatives (entry 4). The methyl-substituted phenanthrolines 4,7-Me_2phen and 2,9-Me_2phen showed moderate to good catalyst activities (entries 6 and 7), while the parent phenanthroline was much less effective (phen, entry 5). Use of excess silane (4 equiv) was essential for the

Received: September 7, 2013
Published: October 9, 2013

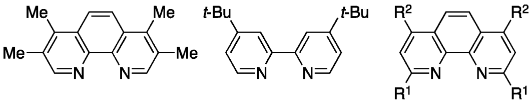
dx.doi.org/10.1021/om400900z | *Organometallics* 2013, 32, 6170−6173

Table 1. Iridium-Catalyzed C−H Borylation of 1a[a]



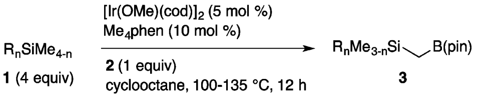
entry	ligand	1a/2	temp (°C)	yield (%)[b]	3a:4a[c]
1[d]	Me_4phen	4	110	10	>99:1
2	Me_4phen	4	135	81 (78)[e]	95:5
3	none	4	135	0	
4	dtbpy	4	135	2	
5	phen	4	135	12	92:8
6	4,7-Me_2phen	4	135	76	95:5
7	2,9-Me_2phen	4	135	41	88:12
8	Me_4phen	2	135	51	98:2
9	Me_4phen	1	135	41	95:5

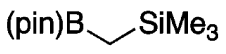
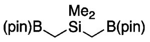
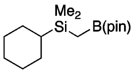
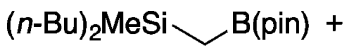
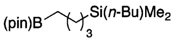
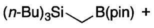
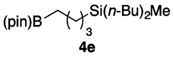
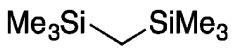
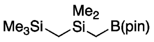
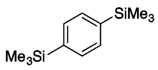
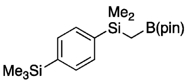
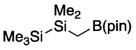
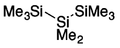
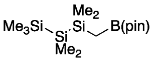
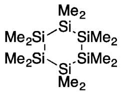
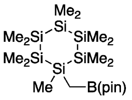
[a] Conditions: $[Ir(OMe)(cod)]_2$ (0.0075 mmol), ligand (0.015 mmol), **1a** (0.60 mmol), and **2** (0.15 mmol) were reacted in cyclooctane (0.3 mL) at the indicated temperature for 12 h. [b] GC yield based on **2**. [c] Determined by GC. [d] $[Ir(OMe)(cod)]_2$ (2.5 mol %) and Me_4phen (5 mol %) were used. [e] Isolated yield (**3a** + **4a**) based on **2**.



Me_4phen dtbpy phen ($R^1 = R^2 = H$)
4,7-Me_2phen ($R^1 = H$, $R^2 = Me$)
2,9-Me_2phen ($R^1 = Me$, $R^2 = H$)

Table 2. Synthesis of (Borylmethyl)silanes via Iridium-Catalyzed C−H Borylation[a]



entry	substrate	temp (°C)	product	% yield[b]
1[c]	$SiMe_4$ **1b**	100	 **3b**	82[d]
2	 **3b**	135	 **5**	49[e]
3	 **1c**	135	 **3c**	71
4	$n\text{-}Bu_2SiMe_2$ **1d**	135	 **3d**  **4d**	58 (72:28)
5	$n\text{-}Bu_3SiMe$ **1e**	135	 **3e**  **4e**	51 (29:71)
6	 **1f**	135	 **3f**	72
7	 **1g**	135	 **3g**	57[f]
8	$Me_3Si{-}SiMe_3$ **1h**	135	 **3h**	49
9	 **1i**	135	 **3i**	52
10	 **1j**	135	 **3j**	32[g]

[a] Conditions: $[Ir(OMe)(cod)]_2$ (0.015 mmol), Me_4phen (0.030 mmol), **1** (1.2 mmol, 4 equiv), and **2** (0.30 mmol) were reacted in cyclooctane (0.6 mL) at 100−135 °C for 12 h. [b] Isolated yield based on **2**. [c] Carried out with 10 equiv of **1b**. [d] The reaction gave a mixture with **5** (4%), which could be separated by column chromatography. [e] Unreacted **3b** (1.01 mmol, 3.37 equiv) could be recovered. [f] The reaction accompanied formation of **6** (29%, *o*:*m*:*p* = 0:62:38) and **7** (4%) (see text and ref 18). [g] Unreacted **1j** (1.04 mmol, 3.47 equiv) could be recovered.

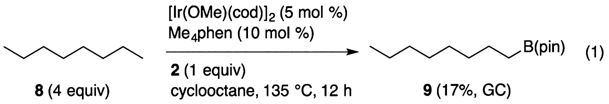
high-yield formation of the borylated products, while faster deactivation of the catalyst was observed with a decreased amount of **1a** (1−2 equiv) (entries 8 and 9). Use of pinacolborane instead of diboron **2** as a borylation reagent resulted in the formation of **3a** in 6% yield. This result indicated that only one of the two boron atoms of **2** is essentially utilized in spite of the formation of pinacolborane as a coproduct in the borylation.

The C−H borylation of alkylsilanes **1b**−**j**, including oligosilanes, could be achieved using the Ir/Me_4phen-catalyzed reaction with **2** in cyclooctane at 100−135 °C (Table 2). The C−H borylation of tetramethylsilane (**1b**; 10 equiv) took place efficiently at 100 °C to give (borylmethyl)trimethylsilane **3b** in 82% yield (entry 1). The reaction was accompanied by the formation of a small amount of double-borylated product bis(borylmethyl)dimethylsilane **5** (4%), which could be separated from **3b** by column chromatography. To the best of our knowledge, this is the first example of catalytic C−H functionalization of tetramethylsilane.[17] Diborylated **5** was synthesized selectively in moderate yield by borylation of **3b** at 135 °C (entry 2). Although an excess of **3b** (4 equiv) was used in the reaction, unreacted **3b** (3.37 equiv) could be recovered after purification by column chromatography. In the reaction of cyclohexyltrimethylsilane (**1c**), the methyl group on silicon was borylated selectively at 135 °C to give **3c** in good yield, in which the methylenes of the cyclohexyl ring were left untouched (entry 3). Selective borylation at the methyl group on silicon over the alkyl terminus was also observed in the borylation of dibutyldimethylsilane (**1d**) and tributylmethylsilane (**1e**) (entries 4 and 5). The borylation of **1d** gave a mixture of **3d** and **4d** in a ratio of 72:28, and that of **1e** resulted in **3e** and **4e** in a ratio of 29:71. Taking into account the number of C−H bonds of the methyl groups on silicon and at the butyl termini (6:6 for **1d** and 3:9 for **1e**), the site selectivity of the C−H borylation still relies mainly on the *α* effect of silicon, although the effect was partially offset by steric congestion around silicon by the butyl groups.

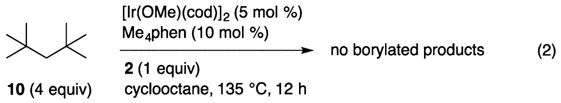
The C−H borylation of bis(trimethylsilyl)methane (**1f**) resulted in selective formation of **3f**, indicating that the monosilyl-substituted methyl was more reactive than the disilyl-substituted methylene (Table 2, entry 6). Interesting chemoselectivity was observed in the reaction of 1,4-bis(trimethylsilyl)benzene (**1g**) (entry 7). The borylation proceeded at the $C(sp^3)$−H bond of the methyl group over the $C(sp^2)$−H bond of the benzene ring to give **3g** in 57% yield. The reaction accompanied formation of (borylphenyl)trimethylsilane **6** (29%, *o*:*m*:*p* = 0:62:38) and (3,5-diborylphenyl)trimethylsilane **7** (4%), which were probably formed via unexpected protodesilylation to form phenyltrimethylsilane (**1k**) followed by the usual C(sp^2)−H borylation.[18]

The C−H borylation could be utilized in the conversion of permethyloligosilanes (Table 2, entries 8−10). Hexamethyldisilane (**1h**) reacted with **2** to give borylated **3h** in moderate yield without Si−Si bond cleavage (entry 8). Octamethyltrisilane (**1i**) underwent the C−H borylation selectively at the terminal trimethylsilyl moiety to afford **3i** (entry 9). Borylmethyl-substituted cyclic oligosilane **3j** was obtained in 32% yield via C−H borylation of dodecamethylcyclohexasilane (**1j**), in which unreacted **1j** (3.47 equiv) could be recovered after purification by column chromatography (entry 10). Although the yields of **3h−j** are moderate, these compounds are difficult to prepare by other methods.

To understand details of the *α* effect of silicon in the iridium-catalyzed C(sp^3)−H borylation, some control experiments were carried out (eqs 1−4). The reaction of *n*-octane (**8**) under conditions identical with the C−H borylation of **1a** resulted in inefficient formation of 1-boryloctane **9** (eq 1).[19] In addition, no borylation took place in the reaction of 2,2,4,4-tetramethylpentane (**10**), which is the carbon analogue of **1f** (eq 2). These results indicate that the C−H borylation of the methyl group is accelerated at the C(sp^3)−H bond located *α* to silicon.

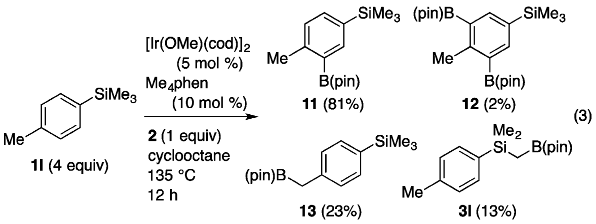


(1)



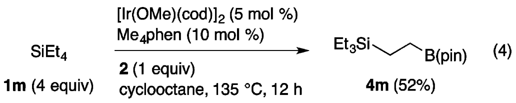
(2)

In sharp contrast to the selective C(sp^3)−H borylation of **1g** at the methyl group on silicon (entry 7, Table 2), 4-(trimethylsilyl)toluene (**1l**) underwent the C−H borylation mainly at the benzene ring to give **11** and **12**, in which the C−H bond ortho to the methyl group was borylated selectively (eq 3). Borylation of the C(sp^3)−H bonds of **1l** also took place to give **13** (23%) and **3l** (13%). These results indicate that (1) the reactivity of C−H bonds in the iridium-catalyzed borylation decreases in the order Ar−*H* > Ar−C*H*$_3$ > Si−C*H*$_3$ > alkyl−C*H*$_3$ and (2) no borylation takes place at the aromatic C(sp^2)−H bond located ortho to the sterically demanding trimethylsilyl group.[18]



(3)

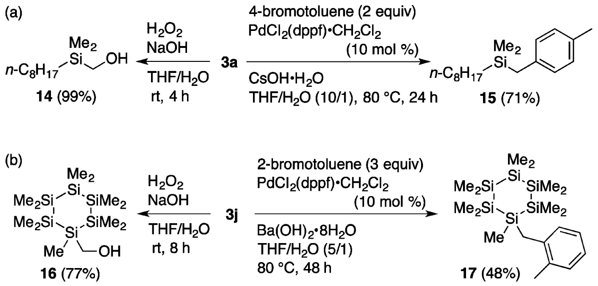
The C−H borylation of tetraethylsilane (**1m**) took place only at the ethyl terminus to give **4m** in 52% yield (eq 4). The lack of borylation at the methylene adjacent to the silicon atom indicates that the *α*-silyl effect in the iridium-catalyzed C−H borylation works effectively only on the methyl group on silicon.



(4)

The compounds obtained by the C−H borylation are expected to be useful synthetic intermediates via conversion of the boryl groups. Conversion of the C−B bond of **3a** to the C−O bond was achieved quantitatively under the conventional conditions using H_2O_2 and NaOH (Scheme 1a, left). The Suzuki−Miyaura cross-coupling of **3a** with 4-bromotoluene proceeded at 80 °C using $PdCl_2(dppf)\cdot CH_2Cl_2$ as a catalyst precursor and $CsOH\cdot H_2O$ as a base,[5i,20] giving **15** in 71% yield (Scheme 1a, right). These reactions were applied to the conversion of cyclohexasilane **3j**. Treatment of **3j** with H_2O_2/NaOH resulted in clean conversion to alcohol **16** (77%) without cleavage of the Si−Si bond (Scheme 1b, left). The arylmethyl-substituted **17** was synthesized via the Suzuki−Miyaura coupling of **3j** with 2-bromotoluene, in which $Ba(OH)_2\cdot 8H_2O$ was used as a base instead of $CsOH\cdot H_2O$,[21] although the yield of **17** was not high, probably because of slow transmetalation due to steric hindrance (Scheme 1b, right).[22]

Scheme 1. Conversion of Borylated Compounds



In conclusion, we have established an efficient functionalization of tetramethylsilane, alkyltrimethylsilanes, and permethyloligosilanes via iridium Me$_4$phen catalyzed C−H borylation. The borylation of alkyltrimethylsilanes took place selectively at the C(sp^3)−H bond located *α* to silicon, indicating that rate acceleration in the catalytic C−H borylation is achieved by the "*α*-effect" of silicon. Although details of the *α*-effect are not clear at this moment, the well-recognized *α*-effect for the stabilization of anionic charge *α* to silicon may play some role in the present *α*-effect. This catalytic method would be valuable for derivatization of organosilicon compounds for the development of new functional organosilicon materials and reagents. In this regard, application of this *α*-silyl effect to other direct C−H functionalizations is currently being pursued in this laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving experimental details and characterization data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for T.O.: ohmura@sbchem.kyoto-u.ac.jp.
*E-mail for M.S.: suginome@sbchem.kyoto-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Molecular Activation Directed Toward Straightforward Synthesis (No. 23105520)” from MEXT and ACT-C FS from JST.

■ REFERENCES

(1) (a) Kipping, F. S. *Proc. Chem. Soc* **1904**, *20*, 15. (b) Kipping, F. S. *Proc. R. Soc. Lond. A* **1937**, *159*, 139.

(2) Examples of tetraorganosilane synthesis via reaction of halosilane with organomagnesium or organolithium reagents: (a) Boeckman, R. K., Jr.; Blum, D. M.; Ganem, B.; Halvey, N. *Org. Synth.* **1978**, *58*, 152. (b) Trost, B. M.; Chan, D. M. T.; Manninga, T. N. *Org. Synth.* **1984**, *62*, 58. (c) Holmes, A. B.; Sporikou, C. N. *Org. Synth.* **1987**, *65*, 61. (d) Dondoni, A.; Merino, P. *Org. Synth.* **1995**, *72*, 21. (e) Smith, A. P.; Lamba, J. J. S.; Fraser, C. L. *Org. Synth.* **2002**, *78*, 82.

(3) Examples of triorganosilyl anion-based synthesis of tetraorganosilanes: (a) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. (b) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520. (c) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527. (d) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 3733. (e) Barret, A. G. M.; Flygare, J. A.; Hill, J. M.; Wallace, E. M. *Org. Synth.* **1996**, *73*, 50. (f) Lettan, R. B., II; Milgram, B. C.; Scheidt, K. A. *Org. Synth.* **2007**, *84*, 22.

(4) Examples of catalytic hydrosilylation of unsaturated hydrocarbons with trialkylsilanes: (a) Hill, J. E.; Nile, T. A. *J. Organomet. Chem.* **1977**, *137*, 293. (b) Doyle, M. P.; Devora, G. A.; Nefedov, A. O.; High, K. G. *Organometallics* **1992**, *11*, 549. (c) Takeuchi, R.; Tanouchi, N. *J. Chem. Soc., Chem. Commun.* **1993**, 1319. (d) Beresis, R. T.; Solomon, J. S.; Yang, M. G.; Jain, N. F.; Panek, J. S. *Org. Synth.* **1998**, *75*, 78. (e) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726. (f) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936.

(5) Examples of catalytic C−H silylation using triorganosilanes or hexaorganodisilanes: (a) Sakakura, T.; Tokunaga, Y.; Sodeyama, T.; Tanaka, M. *Chem. Lett.* **1987**, 2375. (b) Williams, N. A.; Uchimaru, Y.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1129. (c) Ezbiansky, K.; Djurovich, P. I.; LaForest, M.; Sinning, D. J.; Zayes, R.; Barry, D. H. *Organometallics* **1998**, *17*, 1455. (d) Kakiuchi, F.; Igi, K.; Matsumoto, M.; Chatani, N.; Murai, S. *Chem. Lett.* **2001**, *30*, 422. (e) Kakiuchi, F.; Tsuchiya, K.; Matsumoto, M.; Mizushima, E.; Chatani, N. *J. Am. Chem. Soc.* **2004**, *126*, 12792. (f) Tsukada, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5022. (g) Lu, B.; Falck, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 7508. (h) Ihara, H.; Suginome, M. *J. Am. Chem. Soc.* **2009**, *131*, 7502. (i) Ihara, H.; Ueda, A.; Suginome, M. *Chem. Lett.* **2011**, *40*, 916.

(6) (a) *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2. (b) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-Interscience: New York, 2000. (c) *Reagents for Silicon-Mediated Organic Synthesis*; Fuchs, P. L., Ed.; Wiley: New York, 2011.

(7) Peterson, D. J. *J. Organomet. Chem.* **1967**, *9*, 373.

(8) Krieble, R. H.; Elliott, J. R. *J. Am. Chem. Soc.* **1945**, *67*, 1810.

(9) Ohmura, T.; Torigoe, T.; Suginome, M. *J. Am. Chem. Soc.* **2012**, *134*, 17416.

(10) Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3391.

(11) (a) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890. (b) Ishiyama, T.; Miyaura, N. In *Boronic Acids*, 2nd ed.; Hall, D., Ed.; Wiley-VCH: Weinheim, Germany, 2011; Vol. *1*, p 135.

(12) For borylation of C(sp^3)−H bonds at the alkyl chain terminus, see: (a) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995. (b) Kondo, Y.; García-Cuadrado, D.; Hartwig, J. F.; Boaen, N. K.; Wagner, N. L.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1164. (c) Lawrence, J. D.; Takahashi, M.; Bae, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 15334. (d) Bae, C.; Hartwig, J. F.; Harris, N. K. B.; Long, R. O.; Anderson, K. S.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 767. (e) Bae, C.; Hartwig, J. F.; Chung, H.; Harris, N. K.; Switek, K. A.; Hillmyer, M. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6410. (f) Murphy, J. M.; Lawrence, J. D.; Kawamura, K.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 13684.

(13) For borylation of C(sp^3)−H bonds at the benzylic position of toluene derivatives, see: (a) Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2168. (b) Ishiyama, T.; Ishida, K.; Takagi, J.; Miyaura, N. *Chem. Lett.* **2001**, 1082. (c) Boebel, T. A.; Hartwig, J. F. *Organometallics* **2008**, *27*, 6013. For borylation of C(sp^3)−H bonds at the allylic position of cyclic alkenes, see: (d) Olsson, V. J.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6891. (e) Caballero, A.; Sabo-Etienne, S. *Organometallics* **2007**, *26*, 1191. (f) Olsson, V. J.; Szabó, K. J. *J. Org. Chem.* **2009**, *74*, 7715. For borylation of C(sp^3)−H bonds on cyclopropanes, see: (g) Liskey, C. W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 3375.

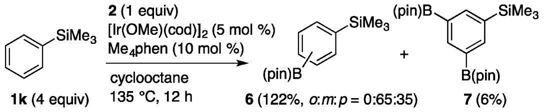
(14) (a) For borylation of the C(sp^3)−H bonds located β to the oxygen atom of aliphatic cyclic ethers, see: Liskey, C. W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 12422. For borylation of C(sp^3)−H bonds located α to the nitrogen atom of amides, ureas, and 2-aminopyridines, see: (b) Kawamorita, S.; Miyazaki, T.; Iwai, T.; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 12924. For borylation of C(sp^3)−H bonds located β to the pyridine ring of 2-alkylpiridines, see: (c) Kawamorita, S.; Murakami, R.; Iwai, T.; Sawamura, M. *J. Am. Chem. Soc.* **2013**, *135*, 2947. (d) Mita, T.; Ikeda, Y.; Michigami, K.; Sato, Y. *Chem. Commun.* **2013**, *49*, 5601. For borylation of C(sp^3)−H bonds at the benzylic methylenes of 2-(hydrodimethylsilyl)alkylbenzenes, see: (e) Cho, S. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 8157.

(15) A related α-effect of silicon has been observed in palladium-catalyzed intramolecular C(sp^3)−H arylation. See: Liang, Y.; Geng, W.; Wei, J.; Ouyang, K.; Xi, Z. *Org. Biomol. Chem.* **2012**, *10*, 1537.

(16) Following our first observation of a positive α-effect of silicon in iridium-catalyzed C(sp^3)−H borylation,[9] Sato and co-workers have reported C(sp^3)−H borylation of 2-(2-silylethyl)pyridine to give 2-(2-boryl-2-silylethyl)pyridine.[14d]

(17) Stoichiometric C−H activation of tetramethylsilane with tungsten and molybdenum complexes has been reported: (a) Tran, E.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 5071. (b) Wada, K.; Pamplin, C. B.; Legzdins, P.; Patrick, B. O.; Tsyba, I.; Bau, R. *J. Am. Chem. Soc.* **2003**, *125*, 7035.

(18) The reaction of **1k** under conditions identical with those described in Table 2 resulted in selective borylation at the C(sp^2)−H on the benzene ring to give **6** (122% based on **2**, *o*:*m*:*p* = 0:65:35) with a small amount of double-borylated **7** (see the equation shown below). The borylation of **1k** using Ir-dtbpy catalyst has been reported: Tajuddin, H.; Harrison, P.; Bitterlich, B.; Collings, J. C.; Sim, N.; Batsanov, A. S.; Cheung, M. S.; Kawamorita, S.; Maxwell, A. C.; Shukla, L.; Morris, J.; Lin, Z.; Marder, T. B.; Steel, P. G. *Chem. Sci* **2012**, *3*, 3505 .



(19) Hartwig and his co-worker have reported the Ir-Me$_4$phen-catalyzed borylation of *n*-octane at 120 °C under solvent-free conditions.[14a]

(20) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(21) Watanabe, T.; Miyaura, N.; Suzuki, A. *Synlett* **1992**, 207.

(22) The starting **3j** could be recovered in 48% yield by column chromatography.