JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Catalytic Functionalization of Methyl Group on Silicon: Iridium-Catalyzed $C(sp^3)$−H Borylation of Methylchlorosilanes

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

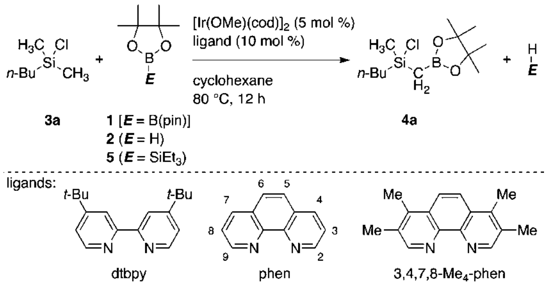
ABSTRACT: A methyl group of methylchlorosilanes undergoes C−H borylation in an iridium-catalyzed reaction with bis(pinacolato)diboron in cyclohexane at 80 °C, giving (borylmethyl)chlorosilanes selectively.

Since the establishment of Rochow's direct method in the 1940s,[1] methylchlorosilanes (Me_nSiCl_{4-n}, $n = 1-3$) have been important feedstocks in the industrial production of silicon-based materials including silicone resins, elastomers, and oils. In addition to these oligomers and polymers, a number of organosilicon compounds have been synthesized from methylchlorosilanes and utilized in organic and inorganic synthesis.[2] In these applications, the conversion of methylchlorosilanes is based on reactions at their Si−Cl bonds, which are efficiently converted into Si−O, Si−N, and Si−C bonds. In contrast, the methyl groups of methylchlorosilanes are always left intact in these conversions, except when radical chlorination gives (chloromethyl)chlorosilanes.[3] It would be highly desirable to explore reactions at their methyl groups through catalytic $C(sp^3)$−H bond functionalization. Although such an innovative transformation has never been shown to date, recent rapid progress in transition-metal-catalyzed C−H bond functionalization may help our exploitation.[4,5]

In sharp contrast to the catalytic borylation of the $C(sp^2)$−H bond of aromatic and heteroaromatic compounds using bis(pinacolato)diboron (**1**) or pinacolborane (**2**),[6] much less progress has been made in the catalytic borylation of the $C(sp^3)$−H bond.[7] Indeed, the terminal methyl groups of aliphatic hydrocarbons,[8−10] benzylic methyl groups,[11−13] and allylic methylenes of cycloalkenes[14] have been reported as limited $C(sp^3)$−H bonds that can undergo catalytic borylation with high efficiency. Quite recently, borylations of the $C(sp^3)$−H bonds located β to the oxygen atom of aliphatic cyclic ethers[15] and α to the nitrogen atom of amides, ureas, and 2-aminopyridines[16] have been reported. Herein, we describe an iridium-catalyzed $C(sp^3)$−H borylation at the methyl groups of methylchlorosilanes to give (borylmethyl)chlorosilanes. The reaction achieves direct catalytic functionalization of methyl groups on silicon,[5] in which the chlorine acts as a directing group. It is noted that the reaction achieves direct catalytic functionalization of methylchlorosilanes, keeping the chlorine atom at the silicon atom left untouched.

In the course of our attempted reactions of chlorosilanes with boron reagents, we found that a $C(sp^3)$−H bond of a methyl group on silicon underwent borylation in the presence of a transition metal catalyst. For instance, butylchlorodimethylsilane (**3a**, 4 equiv) was reacted with **1** in cyclohexane at 80 °C in the presence of $[Ir(OMe)(cod)]_2$ (5 mol %, 10 mol % Ir) and a ligand (10 mol %) (Table 1). An iridium catalyst bearing 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy), the most effective catalyst for $C(sp^2)$−H borylation,[6c,d] afforded (borylmethyl)chlorosilane **4a** (18% based on **1**) selectively with **2** after 12 h (entry 1). It is also noted that the borylation took place selectively at the methyl group with no borylation of the butyl group. This result indicates that the methyl group of **3a** underwent C−H borylation under rather mild conditions, even though the methyl group is sterically hindered by the α-branch at the silicon atom. To improve the

Table 1. Screening of Reaction Conditions in C−H Borylation of 3a[a]



entry	boron reagent	ligand	yield (%)[b]
1	(pin)B−B(pin) (**1**)	dtbpy	18
2	**1**	phen	17
3	**1**	5,6-Me_2-phen	15
4	**1**	4,7-Me_2-phen	67
5	**1**	2,9-Me_2-phen	1
6	**1**	4,7-$(OMe)_2$-phen	45
7	**1**	3,4,7,8-Me_4-phen	74
8	H−B(pin) (**2**)	3,4,7,8-Me_4-phen	15
9	Et_3Si−B(pin) (**5**)	3,4,7,8-Me_4-phen	36
10[c]	**1**	3,4,7,8-Me_4-phen	84

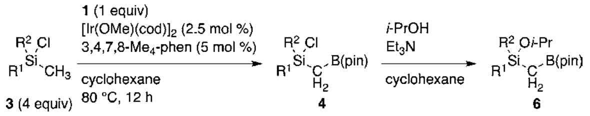
[a] **3a** (0.60 mmol), a boron reagent (0.15 mmol), $[Ir(OMe)(cod)]_2$ (0.0075 mmol), and ligand (0.015 mmol) were stirred in cyclohexane (0.6 mL) at 80 °C for 12 h unless otherwise noted. [b] ^1H NMR yield based on the boron reagent. [c] Modified procedure: **1** (0.15 mmol), $[Ir(OMe)(cod)]_2$ (0.0038 mmol), and 3,4,7,8-Me_4-phen (0.0075 mmol) were stirred in cyclohexane (0.6 mL) at 80 °C for 3 min. **3a** (0.60 mmol) was added to the solution, and the resulting mixture was stirred at 80 °C for 12 h.

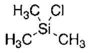
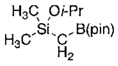
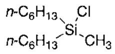
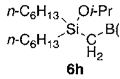
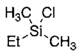
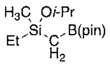
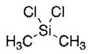
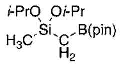
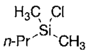
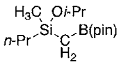
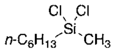
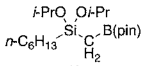
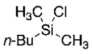
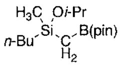
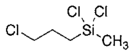
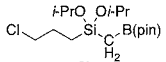
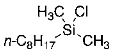
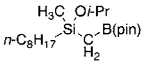
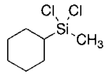
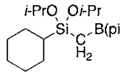
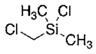
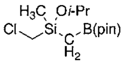
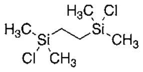
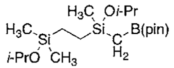
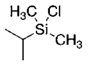
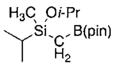
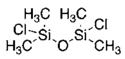
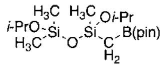
Received: August 9, 2012
Published: October 8, 2012

ACS Publications © 2012 American Chemical Society

dx.doi.org/10.1021/ja307956w | *J. Am. Chem. Soc.* 2012, 134, 17416−17419

Table 2. Iridium-Catalyzed C−H Borylation of Methylchlorosilanes[a]



entry	silane	product	yield (%)[b]	entry	silane	product	yield (%)[b]
1	 **3b**	 **6b**	55 (93)[c]	8[d]	 **3h**	 **6h**	48
2	 **3c**	 **6c**	38 (55)[c]	9	 **3i**	 **6i**	58 (77)[c]
3	 **3d**	 **6d**	80	10	 **3j**	 **6j**	71
4	 **3a**	 **6a**	82	11	 **3k**	 **6k**	70
5	 **3e**	 **6e**	83	12	 **3l**	 **6l**	72
6	 **3f**	 **6f**	60	13	 **3m**	 **6m**	81
7[d]	 **3g**	 **6g**	51	14	 **3n**	 **6n**	67

[a] **1** (0.30 mmol), $[Ir(OMe)(cod)]_2$ (0.0075 mmol), and 3,4,7,8-Me_4-phen (0.015 mmol) were stirred in cyclohexane (1.2 mL) at 80 °C for 3 min. **3** (1.2 mmol) was added to the solution, and the resulting mixture was stirred at 80 °C for 12 h. The product **4** was treated with *i*-PrOH and Et_3N to convert to the isopropoxysilane **6**. [b] Isolated yield based on **1**. [c] ^1H NMR yield before isolation. [d] 10 mol % of Ir-3,4,7,8-Me_4-phen catalyst was used.

yield of **4a**, iridium catalysts bearing various 1,10-phenanthroline ligands were examined (entries 2−7). The yield was improved to 67% with a 4,7-dimethyl derivative (4,7-Me_2-phen, entry 4), while the parent 1,10-phenanthroline (phen) and 5,6-dimethyl derivative (5,6-Me_2-phen) gave **4a** in low yields (entries 2 and 3). 2,9-Dimethyl-1,10-phenanthroline (2,9-Me_2-phen) completely suppresses the borylation (entry 5). Product **4a** was obtained in moderate yield in the presence of 4,7-dimethoxy-1,10-phenanthroline (entry 6). We finally found that an iridium catalyst bearing 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-Me_4-phen) was most effective for the borylation of **3a** with **1**, giving **4a** in 74% yield (entry 7).[17] Other boron reagents were checked in the reaction of **3a** using the Ir-3,4,7,8-Me_4-phen catalyst (entries 8 and 9). Hydroborane **2** also participated in the borylation, although the yield of **4a** was low (entry 8). This result indicates that diboron **1** can afford both of the boron atoms for borylation, although incorporation of the second boron atom from **2** is not efficient. We also found that Et_3Si−B(pin) (**5**)[13] served as a boron source to give **4a** in moderate yield (entry 9). An optimized experimental procedure using **1** and the Ir-3,4,7,8-Me_4-phen catalyst was finally established as follows: A cyclohexane solution of $[Ir(OMe)(cod)]_2$, 3,4,7,8-Me_4-phen, and **1** was prepared and stirred at 80 °C for 3 min. **3a** was then added to the solution, and the resulting mixture was stirred at 80 °C. This modified procedure improved the yield of **4a** to 84% even with a reduced catalyst loading (5 mol % Ir) (entry 10).

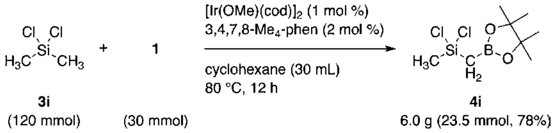
A variety of chlorosilanes **3** were subjected to borylation using **1** in the presence of the Ir-3,4,7,8-Me_4-phen catalyst (Table 2). To avoid handling of the moisture-sensitive chlorosilanes, the borylated products **4** were converted to the corresponding isopropoxysilanes **6** via reaction with *i*-PrOH in the presence of Et_3N. Chlorotrimethylsilane (**3b**) was borylated efficiently to give **6b** in high yield, although the isolated yield dropped because of the instability of **6b** against silica gel column chromatography (entry 1). Borylation of *n*-alkylchlorodimethylsilanes afforded the corresponding products in high yields, except for the reaction of ethyl-substituted **3c**, which gave **4c** in moderate yield (entries 2−5). The reaction was applicable to **3f** bearing a chloromethyl group (entry 6). Probably because of steric hindrance around the methyl group, borylations of isopropyl-substituted **3g** and dihexyl-substituted **3h** were sluggish, giving borylated **6g** and **6h** in moderate yields by using 10 mol % of the catalyst (entries 7 and 8).[18]

Dichloromethylsilane derivatives also underwent borylation (entries 9−12). The reaction of dichlorodimethylsilane (**3i**) gave the borylated product **6i** in good yield after conversion to diisopropoxysilane (entry 9). Dichloromethylsilanes **3j**, **3k**, and **3l** bearing hexyl, 3-chloropropyl, and cyclohexyl groups were effectively borylated to give the corresponding (borylmethyl)-silanes **6j**, **6k**, and **6l** in 70−72% yields (entries 10−12).[18]

Substrates including two chlorodimethylsilyl groups were also borylated. Selective monoborylation of 1,2-bis(chlorodimethylsilyl)ethane **3m** took place to give **6m** in high yield (entry 13). The borylation was applicable to 1,3-dichloro-1,1,3,3-tetramethyldisiloxane **3n** to give **6n** in good yield (entry 14).[18]

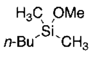
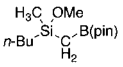
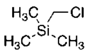
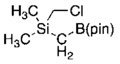
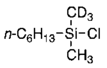
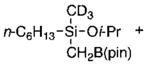
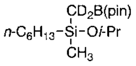
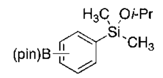
Borylation of **3i** could be carried out on a multigram scale using a reduced amount of the catalyst (Scheme 1). The borylation took place efficiently using 2 mol % of the Ir-3,4,7,8-Me_4-phen catalyst to give 6.0 g of **4i** (78%) after distillation.

Scheme 1. Multigram Scale Synthesis of 4i Using Lower Catalyst Loading



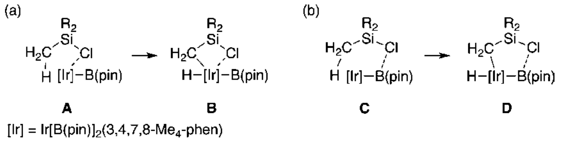
To understand details of the C−H borylation, some substrates were subjected to the borylation conditions using **1** with the Ir-3,4,7,8-Me_4-phen catalyst (Table 3). The reaction of *t*-BuCl (**7**), a carbon analogue of chlorotrimethlsilane (**3b**), did not give the desired borylation product at all, indicating that a silicon atom is essential for the C−H borylation (entry 1). As Et_3SiCl (**8**) resulted in no reaction (entry 2), the C−H borylation takes place selectively at the methyl group on the silicon atom. No reaction took place with trimethyloctylsilane (**9**) at 80 °C (entry 3),[19] while the reaction of butyl(methoxy)dimethylsilane (**10**) gave the corresponding borylation product albeit in low (<5%) yield (entry 4). It is also noted that the reaction of (chloromethyl)-trimethylsilane (**12**) gave the borylated product **13**, although the yield was low (20%, entry 5).[20] On the basis of these observations, we propose that the chlorine atom acts as a directing group in the C−H bond activation step in the catalytic cycle.[21] Indeed, borylation of deuterium-labeled **3o** gave a mixture of **6o-H** and **6o-D** in the ratio 73:27 (k_H/k_D = 2.7), indicating that cleavage of the C−H bond in the catalytic cycle is involved in the rate-determining step (entry 6). Two possible directing modes can be proposed (Scheme 2): one is coordination of chlorine to the iridium center (**A** to **B**), and the other is its coordination to the boron atom bound to the iridium center (**C** to **D**). Because the active catalytic species is assumed to be $Ir[B(pin)]_3(3,4,7,8\text{-}Me_4\text{-}phen)$,[22] the former may be ruled out in the present C−H borylation due to the vacant coordination site. On the other hand, the latter may be reasonably rationalized on the basis of recent reports on the *ortho*-selective borylation of *N*-(*tert*-butoxycarbonyl)anilines[23] and the *β*-selective borylation of cyclic ethers.[15] In the reaction of chlorodimethyl(phenyl)silane (**3p**), the borylation took place preferentially at the $C(sp^2)$−H on the phenyl group, leaving the $C(sp^3)$−H of the methyl group untouched (entry 7, Table 3). This result indicates that the directing effect of the chlorine is rather weak.

Table 3. Reaction of Various Substrates under C−H Borylation Conditions[a]

entry	substrate	results[b]
1	*t*-BuCl (**7**)	no desired product
2	Et_3SiCl (**8**)	no reaction
3	$n\text{-}C_8H_{17}SiMe_3$ (**9**)	no reaction
4	 **10**	 **11** (< 5%)
5[c]	 **12**	 **13** (20%)
6[d]	 $n\text{-}C_6H_{13}\text{-}\overset{CD_3}{\underset{CH_3}{Si}}\text{-}Cl$ **3o** (4 equiv)	 $n\text{-}C_6H_{13}\text{-}\overset{CD_3}{\underset{CH_2B(pin)}{Si}}\text{-}Oi\text{-}Pr$ +  $n\text{-}C_6H_{13}\text{-}\overset{CD_2B(pin)}{\underset{CH_3}{Si}}\text{-}Oi\text{-}Pr$ **6o-H** **6o-D** 72% (**6o-H**:**6o-D** = 73:27)
7	 **3p**	 **14** (105%, *o*:*m*:*p* = 0:67:33)

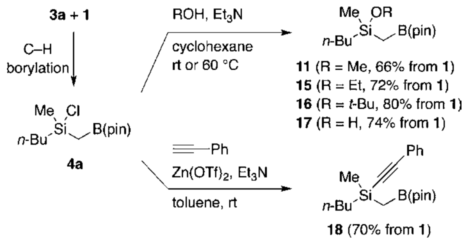
[a]Reactions were carried out at 80 °C according to the procedure described in footnote *a* in Table 2. [b]Yield based on **1** and isomer ratio were determined by ^1H NMR. [c]10 mol % of Ir-3,4,7,8-Me_4-phen catalyst was used. [d]Isolated yield.

Scheme 2. Possible Models for Chlorine Atom Directed $C(sp^3)$−H Activation

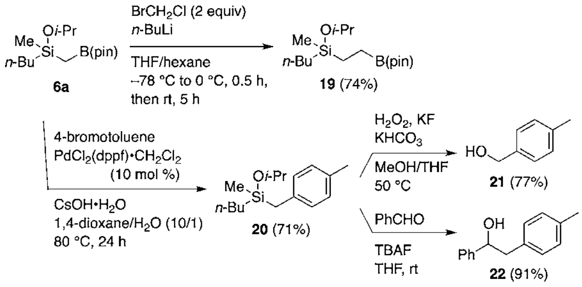


Synthetic applications of (borylmethyl)chlorosilanes were demonstrated (Schemes 3 and 4). In addition to the conversion to the isopropoxy derivative **6a** as shown in Table 2, MeOH, EtOH, *t*-BuOH, and H_2O reacted with **4a** in the presence of triethylamine to give the corresponding (borylmethyl)-alkoxysilanes **11**, **15**, and **16** and silanol **17** in high yields (Scheme 3, top). Reactions of **4a** with carbon nucleophiles, such as MeMgI and PhMgBr, resulted in low-yield formation of the desired tetraorganosilanes, probably because attack of the nucleophiles to the boron center took place competitively. We found that successful ethynylation of **4a** was achieved by the reaction with ethynylbenzene in the presence of $Zn(OTf)_2$ and Et_3N (Scheme 3, bottom).[24] Conversion of the boryl and silyl groups was then examined using **6a** as a model substrate (Scheme 4). One-carbon homologation of **6a** with $ClCH_2Li$, which was generated by the reaction of $ClCH_2Br$ with *n*-BuLi, gave (borylethyl)silane **19** in 74% yield (Scheme 4, top).[25] A benzylic silane **20** was synthesized in good yield via Suzuki−Miyaura coupling of **6a** with 4-bromotoluene using

Scheme 3. Conversion of the Chlorine on 4a



Scheme 4. Conversion of the Boryl and Silyl Groups on 6a



$PdCl_2(dppf)\cdot CH_2Cl_2$ as a catalyst and $CsOH\cdot H_2O$ as a base (Scheme 4, bottom).[4g] The silyl group of **20** could be utilized for C−O and C−C bond formations,[26,27] leading to synthesis of alcohols **21** and **22**.

In conclusion, we have established an efficient functionalization of the methyl groups of methylchlorosilanes via iridium-catalyzed C−H borylation. The reaction is promoted by the directing effect of the chlorine atom on the silicon atom. This catalytic reaction provides a new opportunity to supply organosilicon feedstocks on the basis of conversion of the C−H bond of a methyl group in methylchlorosilanes. In this regard, application of related C−H activation chemistry is currently being pursued in this laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

ohmura@sbchem.kyoto-u.ac.jp; suginome@sbchem.kyoto-u.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by a Grant-in-Aid for Young Scientists (A) (No. 22685010) from JSPS.

■ REFERENCES

(1) (a) Rochow, E. G. *J. Am. Chem. Soc.* **1945**, *67*, 963. (b) Rochow, E. G. *Silicon and Silicones*; Springer-Verlag: 1987.

(2) (a) Rappoport, Z., Apeloig, Y., Eds. *The Chemistry of Organosilicon Compounds*, Vol. 2; Wiley: 1998. (b) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-Interscience: 2000. (c) Beckmann, J. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, M. P., Eds.; Elsevier: 2007; Vol. 3, p 409. (d) Fuchs, P. L., Ed. *Reagents for Silicon-Mediated Organic Synthesis*; Wiley: 2011.

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

(4) A recent review on transition-metal-catalyzed C(sp^3)−H functionalization: (a) Jazzar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem.—Eur. J.* **2010**, *16*, 2654. Recent examples of transition-metal-catalyzed C(sp^3)−H functionalization: (b) Stowers, K. J.; Fortner, K. C.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 6541. (c) He, G.; Chen, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 5192. (d) Hasegawa, N.; Charra, V.; Inoue, S.; Fukumoto, Y.; Chatani, N. *J. Am. Chem. Soc.* **2011**, *133*, 8070. (e) Young, A. J.; White, M. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 6824. (f) Ano, Y.; Tobisu, M.; Chatani, N. *J. Am. Chem. Soc.* **2011**, *133*, 12984. (g) Ihara, H.; Ueda, A.; Suginome, M. *Chem. Lett.* **2011**, *40*, 916. (h) Novák, P.; Correa, A.; Gallardo-Donaire, J.; Martin, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 12236. (i) Wasa, M.; Engle, K. M.; Lin, D. W.; Yoo, E. J.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 19598. (j) Tsukano, C.; Okuno, M.; Takemoto, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 2763. (k) Simmons, E. M.; Hartwig, J. F. *Nature* **2012**, *483*, 70. (l) Zhang, S.-Y.; He, G.; Zhao, Y.; Wright, K.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2012**, *134*, 7313. (m) Xie, P.; Xie, Y.; Qian, B.; Zhou, H.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 9902.

(5) Examples of transition-metal-catalyzed C−H functionalization of the methyl groups on silicon: (a) Manabe, T.; Yanagi, S.; Ohe, K.; Uemura, S. *Organometallics* **1998**, *17*, 2942. (b) Liang, Y.; Geng, W.; Wei, J.; Ouyang, K.; Xi, Z. *Org. Biomol. Chem.* **2012**, *10*, 1537.

(6) Selected seminal contributions, see: (a) Iverson, C. N.; Smith, M. R., III *J. Am. Chem. Soc.* **1999**, *121*, 7696. (b) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III *Science* **2002**, *295*, 305. (c) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (d) Ishiyama, T; Takagi, J.; Hartwig, J. F.; Miyaura, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 3056.

(7) (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: 2011; Vol. *1*, p 135.

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

(9) (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.

(10) Murphy, J. M.; Lawrence, J. D.; Kawamura, K.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 13684.

(11) Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2168.

(12) Ishiyama, T.; Ishida, K.; Takagi, J.; Miyaura, N. *Chem. Lett.* **2001**, *30*, 1082.

(13) Boebel, T. A.; Hartwig, J. F. *Organometallics* **2008**, *27*, 6013.

(14) (a) Olsson, V. J.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6891. (b) Caballero, A.; Sabo-Etienne, S. *Organometallics* **2007**, *26*, 1191. (c) Olsson, V. J.; Szabó, K. J. *J. Org. Chem.* **2009**, *74*, 7715.

(15) Liskey, C. W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 12422.

(16) Kawamorita, S.; Miyazaki, T.; Iwai, T; Ohmiya, H.; Sawamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 12924.

(17) The efficiency of an Ir-3,4,7,8-Me_4-phen catalyst has also been demonstrated recently in C(sp^3)−H silylation and borylation. See refs 4k and 15.

(18) Double borylated products were not observed at all under the conditions using an excess amount of **3** (4 equiv). When the borylation of **3b** was carried out with 2.2 equiv of **1** in cyclooctane at 110 °C for 12 h, the double borylated Me(*i*-PrO)Si[CH_2B(pin)]$_2$ (28%) was obtained with **6b** (35%) after treatment with *i*-PrOH/Et_3N.

(19) We found that the reaction of **9** at elevated temperature (110 °C) resulted in formation of a C−H borylated product, (n-C_8H_{17})Me_2SiCH_2B(pin) (10%). This result indicates that reactivity of the C(sp^3)−H bond located α to silicon is increased also by an electronic effect of the silicon atom. See also ref 5b.

(20) No C−H borylation took place with Me_3SiBr and Me_3SiI, while Me_3SiOH resulted in selective *O*-borylation at the hydroxyl group to form Me_3SiOB(pin) (170% yield based on **1**).

(21) The directing effect of a chlorine atom has been observed in the *ortho*-selective C−H borylation of chlorobenzenes using a silica-supported phosphine-iridium catalyst. Kawamorita, S.; Ohmiya, H.; Hara, K.; Fukuoka, A.; Sawamura, M. *J. Am. Chem. Soc.* **2009**, *131*, 5058.

(22) (a) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2003**, *125*, 16114. (b) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 14263.

(23) Roosen, P. C.; Kallepalli, V. A.; Chattopadhyay, B.; Singleton, D. A.; Maleczka, R. E., Jr.; Smith, M. R., III. *J. Am. Chem. Soc.* **2012**, *134*, 11350.

(24) Jiang, H.; Zhu, S. *Tetrahedron Lett.* **2005**, *46*, 517.

(25) Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687.

(26) Tamao, K.; Nakagawa, Y.; Ito, Y. *Org. Synth.* **1996**, *73*, 94.

(27) Bennetau, B.; Dunogues, J. *Tetrahedron Lett.* **1983**, *24*, 4217.