Highly Efficient $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Olefins†

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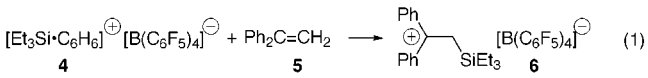
Received November 12, 2001

A convenient and highly efficient method for the Lewis acid-catalyzed trans-selective hydrosilylation of alkenes has been developed. The mechanism of this novel protocol operates via direct addition of silylium type species across C═C bond followed by trapping of the resultant carbenium ion with boron-bound hydride. A number of diversely substituted silanes possessing both aryl and alkyl groups at silicon atom were efficiently prepared using this hydrosilylation methodology. The possibility to employ aryl-containing hydrosilanes in this reaction opens broad capabilities for the synthesis of alcohols via a trans-selective hydrosilylation/Tamao−Fleming oxidation sequence, complementary to the existing cis-selective hydroboration/oxidation protocol.

Introduction

Hydrosilylation of alkenes and alkynes is a very practical and straightforward approach to organosilicon compounds. A number of transition-metal complexes effectively catalyze this reaction, providing cis stereochemistry of addition.[1] Recently, Lewis acid-assisted methodologies, providing alternative trans stereochemistry of addition, have been developed.[2,3,4] The first approach, introduced by Oertle and Wetter,[2a] proceeds via formation of a hydroalane species from $AlCl_3$ and hydrosilane, hydroalumination of the alkene, followed by transmetalation of the resulting alane with hydrosilane[2] (Scheme 1A). The second approach, developed by Yamamoto,[3] presumes reversible addition of Lewis acid to a C−C multiple bond (alkyne or allene), trapping of the formed carbenium ion of the zwitterionic intermediate with silicon-bound hydride, followed by a transmetalation step (Scheme 1B).[5] The former protocol[2] requires the use of chloro-containing hydrosilanes, which are not easily handled, whereas the later[3,4] is limited to trialkylsilanes only. Neither protocol allows the use of aryl-containing silanes, which is unfortunate since the corresponding hydrosilylation products have broad synthetic applications as precursors of alcohols via the Tamao−Fleming oxidation protocol.[6]

It was reported by Lambert[7] that the stoichiometric reaction between ate-complex **4** and alkene **5** results in formation of carbenium borate complex **6** (eq 1), which proceeds via addition of a silylium species across a double bond. Shortly thereafter, he showed that species **6** could



(1)

be obtained in situ in the presence of a catalytic amount of $Ph_3C^+[B(C_6F_5)_4]^-$ (**7**) and a stoichiometric amount of Et_3SiH. Addition of the silylium species to an alkene with formation of **6** was followed by trapping of the resulting carbocation with hydride delivered by Et_3SiH, to accomplish the catalytic cycle (Scheme 2).[8] The main purpose of Lambert's experiment was to investigate the formation of β-silyl cationic species **6**, rather than to develop the hydrosilylation methodology.[8] Accordingly, the single experiment on hydrosilylation of olefin **5** which was performed (in an NMR tube) and described in the paper[8] does not permit generalization of this approach. Furthermore, the reaction described proceeds in two-phase conditions (liquid−oil), which complicates isolation of the products. Thus, motivated by the importance of development of novel hydrosilylation methodologies[1] and intrigued by Lambert's findings,[7,8] we decided to (a) explore the possibility to replace **7** with another catalyst which would allow for performing the reaction under more convenient homogenious conditions, (b) clarify the stereochemistry of addition, and (c) investigate the scope of this reaction targeting the use of aryl-containing hydrosilanes. Herein we wish to report a hydrosilylation protocol, which operates via direct addition of a silylium

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† Dedicated to Prof. Yoshinori Yamamoto on the occasion of his 60th Birthday.

(1) (a) Ojima I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 1479. (b) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, 1992. (c) Hiyama, T.; Kusumoto, T. In *Compehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 763.

(2) (a) Oertle, K.; Wetter, H. *Tetrahedron Lett.* **1985**, *26*, 5511. (b) Yamamoto, K.; Takemae, M. *Synlett* **1990**, 259. (c) Kubota, T.; Endo, M.; Hirahara, T. Jpn. Pat. 09316087, **1997**.

(3) (a) Asao N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem*. **1996**, *61*, 7654. (b) Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem*. **1999**, *64*, 2494.

(4) Song, Y.-S.; Yoo, B. R.; Lee, G.-H.; Jung, I. N. *Organometallics* **1999**, *18*, 3109.

(5) K. Yamamoto (ref 2b) questioned Oertle−Wetter's (ref 2a) mechanism for $AlCl_3$-catalyzed hydrosilylation of alkenes, whereas Jung (ref 4) confronted Y. Yamamoto's mechanism (ref 3) for hydrosilylation of alkynes. Both proposed alternative mechanisms presume the addition of silylium species across a C−C multiple bond followed by trapping of the resulting β-silyl cation with silicon-bound hydride. However, these mechanisms are highly unlikely since, as is generally accepted, the employment of a weekly coordinating counteranion is necessary for the generation of silylium type species. For a review on R_3Si^+, see: Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325.

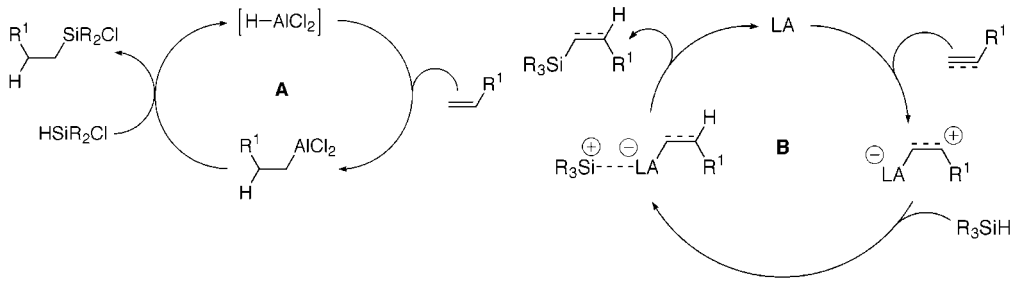
(6) For a review, see: Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599.

(7) Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7867.

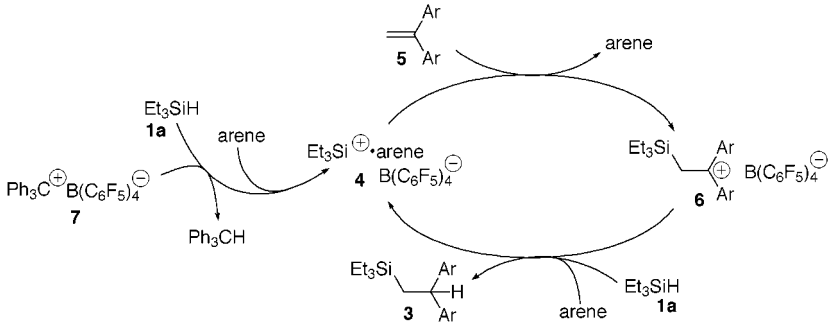
(8) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem*. **1999**, *64*, 2729.

10.1021/jo016279z CCC: $22.00
Published on Web 02/26/2002

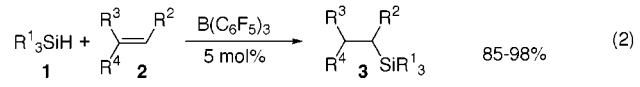
Scheme 1. Mechanisms for Hydrosilylation in the Presence of Traditional Lewis Acids



Scheme 2. Lambert's Mechanism for the $Ph_3C^+[B(C_6F_5)_4]^-$-Catalyzed Hydrosilylation[8]



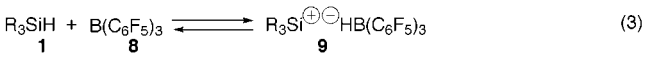
species across the double bond followed by trapping of the formed carbenium ion with boron-bound hydride. This novel methodology is highly efficient, convenient, *truly catalytic* in Lewis acid and completely compatible with both alkyl and arylsilanes (eq 2).



R^1 = Alkyl, Ph; R^2, R^3 = H, Alkyl; R^4 = Alkyl, Ar

Results and Discussion

Since reversible formation of organic solvent-soluble ate-complex **9** from hydrosilane **1** and borane **8** was documented by Piers[9] (eq 3),[10] we decided to test if the silylium cation from complex **9**, analogous to that from complex **4**, would undergo addition across the C−C double bond, and the resulting carbenium ion would be trapped with hydride. Given that both steps proceed, it would allow for the development of a novel preparatively convenient catalytic hydrosilylation protocol.



We found, indeed, that styrene (**2a**) underwent smooth hydrosilylation with 1.2 equiv of Et_3SiH (**1a**) in the presence of 5 mol % of $B(C_6F_5)_3$ to give the corresponding tetraalkylsilane (**3a**) in 96% yield (eq 1, Table 1, entry 1). *No side polymerization processes, typical for the traditional Lewis acid-catalyzed hydrosilylation methodologies,*[4] *were observed!* Trialkylsilanes **1b,c** were similarly effective, affording the corresponding hydrosilylation products **3b,c** in excellent yields. As expected, TIPS-H (**1d**) did not undergo hydrosilylation at all.[11] Remarkably, aryl-containing hydrosilanes (**1e**−**h**) were equally effective, leading to (**3e**−**h**) in excellent yields (Table 1, entries 5−9). To the best of our knowledge, *this is the first example of arylsilanes efficiently employed in Lewis acid-catalyzed hydrosilylation.* Inspired by the successful results in the hydrosilylation of styrene, we tested this method for other types of alkene substrates. The results are summarized in Table 2. Diversely substituted styrene derivatives (**2b**−**g**) underwent hydrosilylation smoothly to produce the corresponding silanes in very high yields. Amazingly, even extremely polymerizable under cationic conditions, indene (**2g**) gave high yield of silane **3o**. Aliphatic alkenes **2h**−**l** efficiently reacted with various silanes, providing **3p**−**u** in excellent yields (Table 2, entries 7−12). Hydrosilylation of the double bond in cyclohexenes showed little sensitivity toward substitution pattern. Thus, 10 mol % of catalyst was needed to complete formation of **3t** (Table 2, entry 11). Although trace amounts of double silylation products were observed employing silicon dihydride **1h** (Table 1, entry 8, and Table 2, entry 12), the corresponding monosilylation products, synthetically useful[1] hydrosi-

Table 1. $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Styrene 2a

	silane		product 3		yield,[a] %
1	Et_3SiH	**1a**	$PhCH_2CH_2SiEt_3$	**3a**	96[b]
2	$EtMe_2SiH$	**1b**	$PhCH_2CH_2SiMe_2Et$	**3b**	95
3	Et_2MeSiH	**1c**	$PhCH_2CH_2SiMeEt_2$	**3c**	95
4	*i*-Pr_3SiH	**1d**	$PhCH_2CH2Si(Pr-i)_3$	**3d**	NR
5	$PhMe_2SiH$	**1e**	$PhCH_2CH_2SiMe_2Ph$	**3e**	96
6	Ph_2MeSiH	**1f**	$PhCH_2CH_2SiMePh_2$	**3f**	93
7	Ph_3SiH	**1g**	$PhCH_2CH_2SiPh_3$	**3g**	92
8	Ph_2SiH2	**1h**	$PhCH_2CH_2SiPh_2H$	**3h**	85[c]

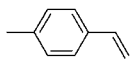
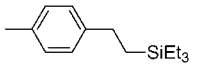
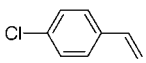
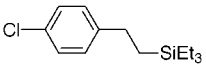
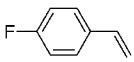
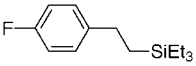
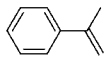
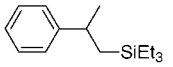
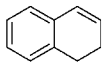
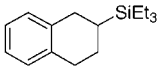
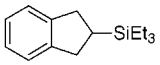
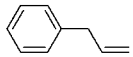
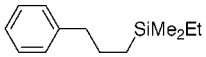
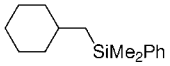
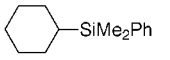
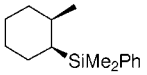
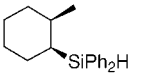
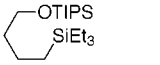
[a] Isolated yields. [b] 57% yield was obtained under conditions of $AlCl_3$-catalyzed reaction.[4] [c] Traces of double-silylation product (**3i**) were detected by GC/MS analysis of the crude reaction mixture.

(9) (a) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887. (b) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.

(10) For involvement of **8** in reduction of alcohols, ethers, and carboxylic acids, see: (a) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919. (b) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179. (c) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 1672.

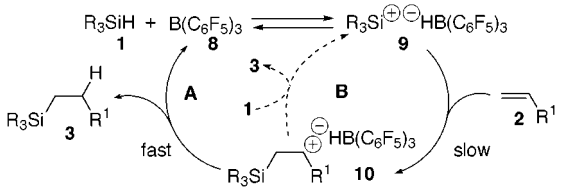
(11) It was shown that **1d** does not form ate-complex **8**; see ref 9b.

Table 2. Hydrosilylation of Differently Substituted Alkenes

	Substrate		Silane	Product		Yield,% [a,b]	
1		**2b**	**1a**		**3j**	94	
2		**2c**	**1a**		**3k**	95	(61)
3		**2d**	**1a**		**3l**	96	
4		**2e**	**1a**		**3m**	97	(55)
5		**2f**	**1a**		**3n**	85	
6		**2g**	**1a**		**3o**	88	(25)
7	*n*-$C_6H_{13}CH{=}CH_2$	**2h**	**1d**	*n*-$C_8H_{17}SiMe_2Ph$	**3p**	92	
8		**2i**	**1b**		**3q**	92	
9		**2j**	**1d**		**3r**	95	
10		**2k**	**1d**		**3s**	98	(21)
11		**2l**	**1d**		**3t**	92[c]	
12	"	**2l**	**1h**		**3u**	86[d]	
13		**2m**	**1a**		**3v**	87	

[a] Isolated yields. [b] Yields obtained under conditions of $AlCl_3$-catalyzed hydrosilylation[4] are shown in parentheses. [c] Reaction was performed on a 5 mmol scale with 10 mol % of $B(C_6F_5)_3$. Ratio cis/trans = 96:4. [d] Traces of double-silylation product were detected by GC/MS analysis of crude reaction mixture; formation of the isomeric *trans*-**3u** was not detected by GC/MS analysis of the crude reaction mixtures.

Scheme 3. $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Alkenes



lanes **3h**,**u**, were obtained in very good yields. Initial experiments demonstrated that properly protected oxygen-containing olefins (e.g., **2m**) can be successfully employed in the $B(C_6F_5)_3$-catalyzed hydrosilylation reaction (Table 2, entry 13). Notably, due to relatively low oxophilicity of $B(C_6F_5)_3$, we were able to complete hydrosilylation of **2m** using 5 mol % of this Lewis acid only.[12] Comparison of yields obtained using novel $B(C_6F_5)_3$-catalyzed and traditional $AlCl_3$-mediated hydrosilylation methodologies (yields in parentheses) clearly demonstrates the superiority of this new protocol.

As discussed above, this hydrosilylation reaction operates via fast equilibration of **1** and **8** forming complex **9** (eq 3, Scheme 3),[9] slow addition of silylium cation[13] of **9** across the double bond of alkene **2** affording the β-silylcarbenium complex **10**, and fast trapping of **10** with boron-bound hydride to produce the hydrosilylation product **3** and regenerate the catalyst (Scheme 3). This mechanism is supported by the following experiments. The observed absence of an isotope effect ($k_H/k_D = 0.96 \pm 0.05$) presumes formation of **10** in a rate-determining step,[14] which then is quickly quenched by boron-carried hydride (Scheme 3, path A). An alternative pathway for hydride delivery, similar to the last step in Lambert's mechanism (Scheme 2),[8] involving delivery of hydride to **10** by hydrosilane (Scheme 3, path B) was ruled out based on the results of the following experiments. Hydrosilylation of styrene **2a** with a (1:1) mixture of Ph_3SiD/*i*-Pr_3SiH gave $PhCHDCH_2SiPh_3$ (**3g**-d_1) exclusively. Since it is well-known that *i*-Pr_3SiH (**1d**) is a superior hydride donor compared to Ph_3SiH (**1g**)[15] and neither formation

(12) It was reported that switching from fully hydrocarbon to oxygen-containing substrates in the traditional Lewis acid-mediated hydrosilylation of alkynes required an increase of the amount of $AlCl_3$ used from 0.2 to 1.2 equiv. See ref 3b.

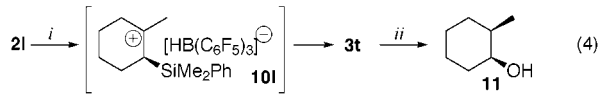
(13) Here and below formation or involvement of *free* silylium cation is not presumed.

(14) Transformation **9** to **10** is the only step which does not involve formation/breakage of any of element-H(D) bonds.

(15) Mayr, H.; Basso, N.; Hagen, G. *J. Am. Chem. Soc.* **1992**, *114*, 3060.

of complex **9** from **1d** nor deuterium scrambling between **1d** and **1g**-d_1 is possible,[9b] it becomes apparent that hydride is delivered by boron and not by silicon.[16]

Like traditional Lewis acid-assisted methodologies,[2−4] this proposed $B(C_6F_5)_3$-catalyzed hydrosilylation protocol operates via trans stereochemistry of addition, which was confirmed by hydrosilylation of **2l** (Table 2, entries 11, 12, eq 4). "Bulky hydride" prefers to attack carbocation **10l** from the less sterically hindered face, affording cis products **3t,u**. Alcohol **11** with stereochemistry opposite to one provided by hydroboration/oxidation sequence, could be easily obtained from arylsilane **3t** by Tamao−Fleming oxidation (eq 4).



(4)

i. $PhMe_2SiH$ (1.2 equiv.), $B(C_6F_5)_3$ (10 mol%), CH_2Cl_2, rt
ii. KBr/CH_3COOOH in CH_3COOH, yield 86%

In conclusion, an efficient protocol for the Lewis acid-catalyzed hydrosilylation of alkenes was developed. A mechanism, involving addition of silylium cation across the C=C bond followed by trapping of the formed carbenium cation with boron-bound hydride was confirmed. Tolerance of this novel Lewis acid-catalyzed methodology toward aryl-containing hydrosilanes allows for its broad application for the synthesis of alcohols via trans-selective hydrosilylation/Tamao−Fleming oxidation sequence, complementary to the existing cis-selective hydroboration/oxidation protocol.

Experimental Section

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) and DPX-400 (400 MHz) instruments. IR spectra were recorded on a Genesis II FT-IR Mattson spectrometer. GC/MS analysis was performed on a Hewlett-Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Merck silica gel (Kieselgel 60, 63−200 μm). Elemental analysis was performed by Midwest Microlab, LLC (Indianapolis, IN).

All manipulations were conducted under argon atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous dichloromethane was purchased from Aldrich and stored over calcium hydride. $B(C_6F_5)_3$ is commercially available, but for our purpose it was prepared according to the known procedure.[17] Deuterated silanes Et_3SiD and Ph_3SiD were prepared by reduction of the corresponding commercially available (Aldrich, Acros Organics) chlorosilanes with $LiAlD_4$ in anhydrous ether.[18] All other chemicals and solvents were purchased from Aldrich, Acros Organics and used without additional purification.

Products **3a**,[19] **3c**,[20] **3e**,[21] **3f**,[22] **3i**,[23] **3p**,**s**,[24] and **11**[25] are known compounds, and their analytical data were in agreement with the literature data. Spectral data for new compounds **3l**,**n**,**r**,**t**−**v** are provided below, as well as for known compounds **3b**,[26] **3g**,[27] **3h**,[28] **3j**,**k**,[29] **3o**,[4] **3m**,[30] and **3q**,[31] for which spectral data presented in the literature is incomplete. (+) and (−) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiment.

General Procedure for Hydrosilylation of Alkenes. The preparation of **3a** is representative. To a stirred solution of $B(C_6F_5)_3$ (26 mg, 5 mol %) in anhydrous CH_2Cl_2 (1 mL) was added Et_3SiH (**1a**) (1.2 mmol, 140 mg, 193 μL), followed by addition of styrene (**2a**) (1 mmol, 104 mg, 114 μL). The reaction mixture was stirred at room temperature and the reaction course was monitored by GC/MS analysis. After the reaction was complete (10−12 h for **3a**), the mixture was filtered through a short column (silica gel, CH_2Cl_2 as an eluent) and concentrated. Purification by column chromatography (silica gel, hexane as an eluent) gave 212 mg of **3a** (96%).

3b: ^1H NMR ($CDCl_3$, 500.13 MHz) δ 7.39 (t, 2H), 7.32 (d, 2H), 7.28 (t, 1H), 2.74 (m, 2H), 1.07 (t, J = 7.9 Hz, 3H), 1.01 (m, 2H), 0.64 (q, J = 7.9 Hz, 2H), 0.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 145.9, 128.77 (+), 128.26 (+), 125.96 (+), 30.54 (−), 17.42 (−), 7.85 (+), 7.33 (−), −3.47 (+); FT-IR (film, cm^{-1}) 3060, 3025, 2951, 2909, 2879, 1493, 1453, 1414, 1249, 1008, 958, 896, 834, 772, 697; GC/MS *m*/*z* 192 (M^+, <1), 177 (M − Me, 5), 163 (M − Et, 90), 59 (100).

3g: ^1H NMR ($CDCl_3$, 500.13 MHz) δ 7.61 (m, 6H), 7.84−7.41 (m, 9H), 7.30 (m, 2H), 7.24−7.21 (m, 3H), 2.83 (m, 2H), 1.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 145.4, 136.1 (+), 135.3, 130.0 (+), 128.8 (+), 128.4 (+), 128.2 (+), 126.1 (+), 30.4 (−), 15.9 (−); GC/MS *m*/*z* 286 ($M^+ - C_6H_6$, 30), 259 (Ph_3Si^+, 100).

3h: ^1H NMR ($CDCl_3$, 400.13 MHz) δ 7.66 (m, 4H), 7.46 (m, 6H), 7.33 (t, 2H), 7.27 (m, 3H), 5.00 (t, J = 3.7 Hz, 1H), 2.86 (m, 2H), 1.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 144.9, 135.7 (+), 134.6, 130.2 (+), 128.9 (+), 128.6 (+), 128.4 (+), 126.3 (+), 31.0 (−), 14.8 (−); FT-IR (film, cm^{-1}) 3066, 3049, 3023, 2923, 2121, 1495, 1453, 1428, 1117, 803, 733, 698; GC/MS *m*/*z* 259 (<1), 210 ($M^+ - C_6H_6$, 55), 183 (Ph_2HSi^+, 95), 132 ($M^+ - 2C_6H_6$, 100).

3j: ^1H NMR ($CDCl_3$, 500.13 MHz) δ 7.15 (m, 4H), 2.63 (m, 2H), 2.37 (s, 3H), 1.01 (t, J = 8.0 Hz, 9H), 0.95 (m, 2H), 0.62 (q, J = 8.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 143.1, 135.3, 129.4 (+), 128.0 (+), 30.0 (−), 21.4 (+), 14.3 (−), 7.9 (+), 3.7 (−); FT-IR (film, cm^{-1}) 3011, 2950, 2909, 2877, 1512, 1457, 1414, 1236, 1171, 1010, 967, 802, 766, 732; GC/MS *m*/*z* 234 (M^+, <1), 205 (M − Et, 90), 87 (100).

3k: ^1H NMR ($CDCl_3$, 500.13 MHz) δ 7.27 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 2.62 (m, 2H), 1.00 (t, J = 7.9 Hz, 9H), 0.89 (m, 2H), 0.59 (q, J = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 144.4, 131.5, 129.5 (+), 128.8 (+), 29.9 (−), 14.0 (−), 7.9 (+), 3.7 (−); FT-IR (film, cm^{-1}) 3028, 2951, 2907, 2877, 1489, 1459, 1412, 1235, 1174, 1092, 1010, 799, 756, 728; GC/MS *m*/*z* 254 (M^+, <1), 225 (M − Et, 50), 87 (100).

3l: ^1H NMR ($CDCl_3$, 500.13 MHz) δ 7.18 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HF}$ = 5.6 Hz, 2H), 6.99 (ps.-t, $^3J_{HH} \approx {}^3J_{HF}$ = 8.7 Hz, 2H),

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2.63 (m, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.90 (m, 2H), 0.59 (q, J = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 161.5 (d, $^1J_{CF}$ = 242.7 Hz), 141.5, 129.4 (d, $^3J_{CF}$ = 19.2 Hz) (+), 115.4 (d, $^2J_{CF}$ = 24.5 Hz) (+), 29.7 (−), 14.2 (−), 7.9 (+), 3.7 (−); ^{19}F NMR ($CDCl_3$, 470.59 MHz) δ −120.0; FT-IR (film, cm^{-1}) 3037, 2952, 2908, 2878, 1601, 1508, 1459, 1414, 1226, 1155, 1010, 967, 821, 775, 737; GC/MS m/z 209 (M − Et, 60), 87 (100). Anal. Calcd for $C_{14}H_{23}FSi$: C, 70.53; H, 9.72. Found: C, 70.51; H, 9.76.

3m: ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.33 (t, 2H), 7.28 (d, 2H), 7.22 (t, 1H), 2.93 (sextet, J = 7.1 Hz, 1H), 1.34 (d, J = 6.9 Hz, 3H), 1.05 (dd, J = 14.8, 7.5 Hz, 1H), 0.97 (dd, J = 14.8, 7.3 Hz, 1H), 0.94 (t, J = 7.9 Hz, 9H), 0.54−0.42 (m, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 150.6, 128.7 (+), 127.0 (+), 126.2 (+), 36.6 (+), 26.9 (+), 22.0 (−), 7.9 (+), 4.1 (−); FT-IR (film, cm^{-1}) 3060, 3025, 2953, 2906, 2874, 1601, 1491, 1453, 1412, 1374, 1237, 1011, 794, 758, 739, 698; GC/MS m/z 205 (M − Et, 60), 163 (100).

3n: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.09 (m, 4H), 2.87−2.70 (m, 4H), 1.99 (m, J = 12.8 Hz, 1H), 1.58 (qd, J = 12.6, 5.7 Hz, 1H), 1.16 (tdd, J = 12.3, 5.8 Hz, 2.5 Hz, 1H), 1.01 (t, J = 7.9 Hz, 9H), 0.64 (q, J = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 137.9, 137.3, 129.3 (+), 128.8 (+), 125.4 (×2) (+), 30.7 (−), 30.5 (−), 24.6 (−), 19.5 (+), 7.7 (+), 2.0 (−); GC/MS m/z 246 (M$^+$, 2), 217 (M − Et, 40), 129 (100).

3o: ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.30 (m, 2H), 7.21 (m, 2H), 3.10 (dd, J = 15.2, 9.0 Hz, 2H), 2.96 (dd, J = 15.2, 11.1 Hz, 2H), 1.81 (tt, J = 11.1, 9.0 Hz, 1H), 1.08 (t, J = 7.9 Hz, 9H), 0.70 (q, J = 8.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 145.4, 126.3 (+), 124.6 (+), 35.5 (−), 23.8 (+), 8.2 (+), 3.2 (−); FT-IR (film, cm^{-1}) 3071, 3026, 2953, 2909, 2875, 1459, 1415, 1328, 1239, 1016, 833, 743; GC/MS m/z 232 (M$^+$, 5), 203 (M − Et, 20), 116 (100).

3q: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.34 (t, 2H), 7.25 (m, 3H), 2.69 (t, J = 7.6 Hz, 2H), 1.67 (m, 2H), 0.98 (t, J = 7.9 Hz, 3H), 0.62 (m, 2H), 0.54 (q, J = 7.9 Hz, 2H), 0.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 142.8, 128.5 (+), 128.3 (+), 125.7 (+), 40.1 (−), 26.2 (−), 14.8 (−), 7.4 (+), 6.9 (−), −3.9 (+); FT-IR (film, cm^{-1}) 3085, 3063, 3031, 2952, 2924, 1604, 1496, 1456, 1415, 1245, 1170, 1012, 959, 834, 792, 745, 698; GC/MS m/z 191 (M − Me, 10), 177 (M − Et, 100).

3r: ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.59 (m, 2H), 7.42 (m, 3H), 1.75−1.65 (m, 5H), 1.49 (m, 1H), 1.28−1.16 (m, 3H), 1.00 (m, 2H), 0.83 (d, J = 6.8 Hz, 2H), 0.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 140.8, 133.9 (+), 129.1 (+), 128.1 (+), 37.4 (−), 34.8 (+), 27.0 (−), 26.7 (−), 25.1 (−), −1.4 (+); FT-IR (film, cm^{-1}) 3068, 2921, 2851, 1447, 1427, 1249, 1112, 830, 725, 705; GC/MS m/z 217 (M − Me, 2), 154 (M$^+$ − C_6H_6, 30), 135 (PhMe$_2$Si$^+$, 100). Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.68; H, 10.43.

3t: ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.56 (m, 2H), 7.39 (m, 3H), 2.04 (m, 1H), 1.74 (m, 1H), 1.57−1.47 (m, 6H), 1.24 (m, 1H), 1.13 (m, 1H), 0.98 (d, J = 7.2 Hz, 3H), 0.33 (s, 3H), 0.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 140.0, 134.3 (+), 129.0 (+), 128.0 (+), 35.6 (−), 30.7 (+), 29.7 (+), 28.8 (−), 22.4 (−), 21.6 (−), 16.7 (+), −3.1 (+); FT-IR (film, cm^{-1}) 3064, 3012, 2956, 2918, 2830, 1449, 1436, 1250, 1110, 868, 819, 767, 731, 700; GC/MS m/z 232 (M$^+$, 1), 217 (M − Me, <1), 135 (PhMe$_2$Si$^+$, 100). Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.68; H, 10.44.

3u: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.66 (m, 4H), 7.39 (m, 6H), 4.86 (d, J = 4.4 Hz, 1H), 2.10 (m, 1H), 1.73−1.46 (m, 8H), 1.31 (m, 1H), 1.02 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 135.9 (+), 135.7 (+), 135.2, 135.1, 129.8 (+), 129.7 (+), 128.40 (+), 128.35 (+), 35.0 (−), 30.4 (+), 28.5 (+), 28.2 (−), 23.8 (−), 22.1 (−), 17.0 (+); FT-IR (film, cm^{-1}) 3067, 3049, 2921, 2850, 2120, 1428, 1114, 894, 946, 819, 806, 733, 634; GC/MS m/z 280 (M$^+$, 2), 202 (M$^+$ − C_6H_6, 20), 183 (Ph$_2$HSi$^+$, 100). Anal. Calcd for $C_{19}H_{24}Si$: C, 81.36; H, 8.62. Found: C, 81.29; H, 8.59.

3v: ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 3.71 (t, J = 6.5 Hz, 2H), 1.59 (ps-quint. J = 7.0 Hz, 2H), 1.40 (m, 2H), 1.10−1.07 (m, 21H), 0.95 (t, J = 7.9 Hz, 9H), 0.53 (q, J = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 63.4 (−), 37.5 (−), 20.5 (−), 18.4 (+), 12.4 (+), 11.5 (−), 7.9 (+), 3.7 (−); FT-IR (film, cm^{-1}) 2941, 2868, 1463, 1110, 1014, 891, 721, 681; GC/MS m/z 301 (M$^+$ − i-Pr, 10), 115 (Et$_3$Si$^+$, 100). Anal. Calcd for $C_{19}H_{44}OSi_2$: C, 66.20; H, 12.87. Found: C, 66.52; H, 12.71.

Experiments on H/D Isotope Effect Measurement. Styrene **2a** was subjected to the reaction with a 5-fold excess of Et$_3$SiH/Et$_3$SiD mixture (1:1) under standard reaction conditions. The mixture of hydrosilylation products **3a**/**3a**-d_1 was separated from Et$_3$SiOSiEt$_3$ by column chromatography on silica gel (eluent hexane) and deuterium purity was determined by integration of signals at δ 2.67 vs 0.95 in the ^{1}H NMR spectra ($CDCl_3$, 500.13 MHz). Determined H/D product isotope effect: 0.96 ± 0.05.

Tamao−Fleming oxidation of 2l. The reaction was performed according to the modified Fleming procedure.[32] Peracetic acid (Aldrich, 32% solution in acetic acid, 5 mL) was added dropwise at 0 °C to a stirred mixture of silane **2l** (3 mmol), potassium bromide (500 mg), and anhydrous sodium acetate (1.2 g) in glacial acetic acid (15 mL). The mixture was allowed to warm to room temperature and stirred for an additional 18 h. Then the reaction mixture was diluted (ether) and carefully neutralized ($NaHCO_3$ solution). The Etheral layer was washed (Na_2SO_3, and brine) and dried ($MgSO_4$). Ether was removed at ambient pressure, and the residue was purified by preparative column chromatography (eluent hexane, then hexanes−ether 5:1) to obtain *cis*-2-methylcyclohexanol (**11**) as a colorless oil: yield 294 mg (86%).

Acknowledgment. The support of the Petroleum Research Fund (AC1-36370), administered by the American Chemical Society, is gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR charts for **3n**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016279Z

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