Lewis Acid Catalyzed Highly Regio- and Stereocontrolled *Trans*-Hydrosilylation of Alkynes and Allenes

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Lewis acids such as $AlCl_3$ or $EtAlCl_2$ dramatically catalyzed the hydrosilylation of alkynes **1** with trialkylsilanes to produce the corresponding *cis*-vinylsilanes **2** in a regio- and *trans*-stereoselective manner. For example, the hydrosilylation of 1-dodecyne **1a** with triethylsilane in the presence of 0.2 equiv of $AlCl_3$ gave *cis*-1-(triethylsilyl)-1-dodecene in 93% yield. Other alkyl- and phenyl-substituted terminal and internal acetylenes also underwent *trans*-hydrosilylation very smoothly. In the case of alkoxy- or silyloxy-substituted acetylenes, the use of 1.2 equiv of $AlCl_3$ or $EtAlCl_2$ was essential to obtain the corresponding *trans*-hydrosilylation products in high yields. Moreover, $AlCl_3$ catalyzed the hydrosilylation of aromatic allenes **11**, producing the alkenylsilanes **12** with high regio- and stereoselectivities in moderate to high chemical yields. Not only the simple monosubstituted, but also the disubstituted and trisubstituted allenes, underwent the hydrosilylation reaction smoothly, serving as a useful tool for the synthesis of differently substituted vinylsilanes which are not easily available through the previously known methodologies. The mechanisms for these catalytic reactions of alkynes and allenes are proposed.

Introduction

The great versatility of vinylsilanes as building blocks has been increased in modern synthetic organic chemistry.[1] Hydrosilylation of alkynes[2] is one of the simplest and the most straightforward preparative methods to obtain vinylsilanes. It is well-known that hydrosilylation of alkynes is induced either by radical initiator[3] or by transition metal catalysts.[4] The radical-induced procedure often provides a mixture of *trans*- and *cis*-hydrosilylation products. Although the transition metal-catalyzed reaction proceeds with high stereoselectivity via a *cis*-hydrosilylation pathway, it usually produces a mixture of two regioisomers (terminal and internal products) in the reaction with terminal alkynes. Recently, we reported that the hydrosilylation of alkynes **1** with trialkylsilanes is catalyzed dramatically by Lewis acids such as $AlCl_3$ and $EtAlCl_2$, leading to *cis*-alkenylsilanes **2** with very high regio- and stereoselectivities in good to high yields (eq 1).[5,6] Although most hydrometalations of alkynes[7] proceed in a *cis*-manner, Lewis acid-catalyzed hydrosilylation proceeds in a *trans*-manner. Quite recently, our procedure was applied to the modification of the surface of porous silicon by Buriak and Allene.[8] They stated that Lewis acid catalysts are suitable for the hydrosilylation of porous silicon, because transition metal catalysts have the potential for activation of the weaker Si−Si bonds, instead of Si−H bonds, on the surface. In this paper, we detail the Lewis acid-catalyzed *trans*-hydrosilylation reactions of acetylenes together with the hydrosilylation of allenes.

Results and Discussion

Alkynes. The results of the Lewis acid-catalyzed hydrosilylation of alkynes are summarized in Table 1. First, we examined the hydrosilylation of 1-dodecyne (**1a**) using triethylsilane with several different kinds of Lewis acids. Lewis acid catalysts such as $ZrCl_4$ and $HfCl_4$ were not effective for the hydrosilylation of 1-dodecyne (entries 1 and 2). This is in marked contrast with the observation in the Lewis acid-catalyzed hydrostannation of **1a**, in

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

(3) (a) Selin, T. G.; West, R. *J. Am. Chem. Soc.* **1962**, *84,* 1860. (b) Benkeser, R. A.; Burrous, M. L.; Nelson, L. E.; Swisher, J. V. *J. Am. Chem. Soc.* **1961**, *83,* 4385.

(4) Transition metal complexes derived from Pt, Ir, Pd, Rh, Ru, Ni, Co, Fe, Re, and Mn metals have been used for hydrosilylation; see ref 2.

(5) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61,* 7654.

(6) Although $AlCl_3$-catalyzed hydrosilylation of alkynes had been reported by Voronkov's group, detailed information on regio- and stereoselectivities and generality of the reaction are not available: see (a) Voronkov, M. G.; Adamovich, S. N.; Pukhnarevich, V. B. *J. Gen. Chem. USSR (Engl. Transl.)* **1982**, *52,* 2058. (b) Voronkov, M. G.; Adamovich, S. N.; Sherstyannikova, L. V.; Pukhnarevich, V. B. *J. Gen. Chem. USSR (Engl. Transl.)* **1983**, *53,* 706. (c) Ulrich, F.; Hans, M. W. Ger. Pat. 2,804,204, 1979; *Chem. Abstr.* **1979**, *91,* 193413x. (d) Mackenzie, C. A.; Spialter, L.; Schoffman, M. Br. Pat. 684, 597, 1953; *Chem. Abstr.* **1954**, 2761d. (e) Hatcher, D. B. U.S. Pat. 2,555,589, 1971; *Chem. Abstr.* **1951**, 8814.

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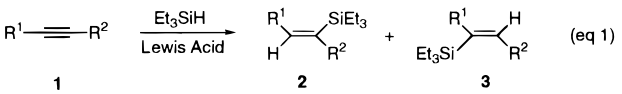
Table 1. Lewis Acid-Catalyzed Hydrosilylation of Alkynes with $HSiR_3$



1 2 3

1, 2, and 3 **a** ; $R^1 = CH_3(CH_2)_9$, $R^2 = H$ **g** ; $R^1 = (i\text{-}Pr)_3SiO(CH_2)_2$, $R^2 = H$
b ; $R^1 = PhCH_2$, $R^2 = H$ **h** ; $R^1 = (i\text{-}Pr)_3SiO(CH_2)_4$, $R^2 = H$
c ; $R^1 = t\text{-}C_4H_9$, $R^2 = H$ **i** ; $R^1 = PhCH_2O(CH_2)_2$, $R^2 = H$
d ; $R^1 = Me_3Si$, $R^2 = H$ **j** ; $R^1 = R^2 = CH_3(CH_2)_4$
e ; $R^1 =$, $R^2 = H$ **k** ; $R^1 = R^2 = Ph$
f ; $R^1 = Ph$, $R^2 = H$ **l** ; $R^1 = Ph$, $R^2 = CH_3$
m ; $R^1 = Ph$, $R^2 = C_2H_5$

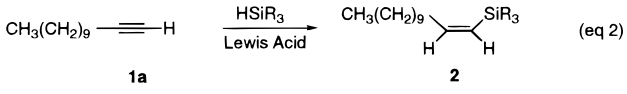
entry	Lewis acid (equiv)	1 R^1	1 R^2		yield (%)[a] 2	3
1	$ZrCl_4$ (0.2)	$CH_3(CH_2)_9$	H	**1a**	trace	0
2	$HfCl_4$ (0.2)	$CH_3(CH_2)_9$	H	**1a**	28	0
3	$AlCl_3$ (0.2)	$CH_3(CH_2)_9$	H	**1a**	93	0
4	$EtAlCl_2$ (0.2)	$CH_3(CH_2)_9$	H	**1a**	95	0
5[b]	Et_2AlCl (0.2)	$CH_3(CH_2)_9$	H	**1a**	0	0
6[c]	$AlCl_3$ (0.2)	$CH_3(CH_2)_9$	H	**1a**	90	0
7	$AlCl_3$ (0.2)	$PhCH_2$	H	**1b**	85	0
8	$AlCl_3$ (0.2)	$t\text{-}C_4H_9$	H	**1c**	82	0
9	$AlCl_3$ (0.2)	Me_3Si	H	**1d**	0	89
10	$EtAlCl_2$ (0.2)	1-cyclohexenyl	H	**1e**	75	0
11	$EtAlCl_2$ (0.2)	Ph	H	**1f**	77	0
12[d]	$EtAlCl_2$ (1.2)	$i\text{-}Pr_3SiO(CH_2)_2$	H	**1g**	86	0
13	$AlCl_3$ (1.2)	$i\text{-}Pr_3SiO(CH_2)_4$	H	**1h**	74	0
14	$EtAlCl_2$ (1.2)	$PhCH_2O(CH_2)_2$	H	**1i**	72	0
15	$AlCl_3$ (0.2)	$CH_3(CH_2)_4$	$CH_3(CH_2)_4$	**1j**	73	–
16	$AlCl_3$ (0.2)	Ph	Ph	**1k**	66	–
17	$AlCl_3$ (0.2)	Ph	CH_3	**1l**	76	10
18	$AlCl_3$ (0.2)	Ph	C_2H_5	**1m**	54	26

[a] Reactions were conducted in toluene at 0 °C under Ar unless otherwise noted. [b] The starting material **1a** was recovered quantitatively. [c] Reaction was carried out without any solvents. [d] Hexane was used as a solvent.

which the *trans*-hydrostannation proceeded very smoothly in the presence of $ZrCl_4$ or $HfCl_4$.[9] Fortunately, however, the reaction in the presence of 0.2 equiv of $AlCl_3$ afforded the *trans*-hydrosilylation product **2a** in 93% yield (entry 3). Neither a stereoisomer of **2a** (*cis*-addition product) nor a regioisomer (**3a**) was detected in the ^1H NMR spectra of the crude reaction pruduct. While $EtAlCl_2$ was also an efficient catalyst for the *trans*-hydrosilylation (entry 4), the starting material **1a** was recovered quantitatively in the Et_2AlCl-catalyzed reaction (entry 5). It seems that the reaction did not proceed due to lower Lewis acidity of Et_2AlCl, compared to $AlCl_3$ and $EtAlCl_2$. The use of nonpolar solvents such as toluene or hexane was essential for obtaining high stereoselectivity and chemical yield. Unlike $EtAlCl_2$, $AlCl_3$ is not soluble in such solvents, and thus the $AlCl_3$-catalyzed hydrosilylation proceeded in a heterogeneous system. The $AlCl_3$-catalyzed hydrosilylation of **1a** proceeded smoothly even without any solvents to give **2a** in 90% yield (entry 6). The $AlCl_3$- or $EtAlCl_2$-catalyzed hydrosilylation was examined with several other alkynes. The reactions of 3-phenyl-1-propyne **1b** and 3,3-dimethyl-1-butyne **1c** having a bulky *tert*-butyl group proceeded smoothly to produce **2b** and **2c**, respectively, in high yields (entries 7 and 8), whereas the hydrosilylation of (trimethylsilyl-)ethyne **1d** gave **3d** in 89% yield (entry 9). The regio-

(9) (a) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 2405. (b) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568.

Table 2. Lewis Acid-Catalyzed Hydrosilylation of 1-Dodecyne 1a with $HSiR_3$



1a 2

2n ; $R_3 = t\text{-}BuMe_2$ **q** ; $R_3 = Ph_2Me$
o ; $R_3 = (c\text{-}C_6H_{11})Me_2$ **r** ; $R_3 = PhMe_2$
p ; $R_3 = Ph_3$ **s** ; $R_3 = (EtO)_3$

entry	Lewis acid (equiv)	R_3SiH	product	yield (%)
1	$AlCl_3$ (0.2)	$t\text{-}BuMe_2SiH$	**2n**	78
2	$AlCl_3$ (0.2)	$(c\text{-}C_6H_{11})Me_2SiH$	**2o**	73
3	$EtAlCl_2$ (0.2)[a]	Ph_3SiH	**2p**	40
4	$EtAlCl_2$ (0.2)[a]	Ph_2MeSiH	**2q**	45
5	$EtAlCl_2$ (0.2)[a]	$PhMe_2SiH$	**2r**	60
6[b]	$AlCl_3$ (0.2)	$(EtO)_3SiH$	**2s**	0

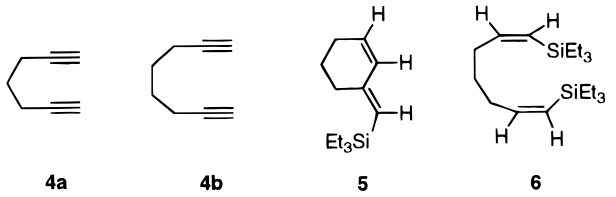
[a] If $AlCl_3$ was used in the hydrosilylation with the phenylsubstituted silanes, the silylating reagents were decomposed partially prior to adding to the acetylene **1a**. [b] The starting material **1a** was recovered quantitatively.

chemical difference in the hydrosilylation reaction of the alkyl (**1a**−**c**) and silyl (**1d**) substituted alkynes is very interesting and is discussed in the mechanistic section. The reactions of conjugated enynes, 1-ethynyl-1-cyclohexene **1e** and phenylacetylene **1f**, proceeded immediately to produce **2e** and **2f**, respectively, in moderate yields (entries 10 and 11). The hydrosilylation of alkynes bearing silyloxy and benzyloxy groups gave the corresponding *trans*-hydrosilylation products in good to high yields (entries 12−14). Here again, no regio- and stereoisomers were detected. Very interestingly, the use of 1.2 equiv of Lewis acids was essential for obtaining good chemical yields (entries 12−14). Most probably, 1.0 equiv of the Lewis acids would be needed to coordinate to an oxygen atom of a silyloxy or benzyloxy group, and the remaining 0.2 equiv of Lewis acid would act as a catalyst. The reactions of symmetrical internal acetylenes, such as 6-dodecyne **1j** and tolan **1k**, also proceeded smoothly (entries 15 and 16), whereas the reaction of unsymmetrical acetylenes, such as 1-phenyl-1-propyne **1l** and 1-phenyl-1-butyne **1m**, afforded a mixture of regioisomers, **2l** and **3l**, and **2m** and **3m**, respectively (entries 17 and 18). The regioisomeric ratio depended on steric bulk of the substituent R^2. The methyl substituent gave a ratio of 76:10, whereas the ethyl group afforded that of 54:26.

Next, we carried out the $AlCl_3$- or $EtAlCl_2$-catalyzed hydrosilylation of **1a** with various silanes, and the results are shown in Table 2. The reaction of *tert*-butyldimethylsilane and cyclohexyldimethylsilane proceeded smoothly to give the corresponding *trans*-hydrosilylation products **2n** and **2o**, respectively, in good yields (entries 1 and 2). The addition of phenyl-substituted silanes, such as triphenyl-, diphenylmethyl-, and phenyldimethylsilane, gave lower yields in comparison with that of alkyl-substituted silanes (entries 3−5 vs 1 and 2). The reaction of triethoxysilane did not proceed at all (entry 6). These results suggest that the silanes having an electron-donating substituent, such as alkyl groups, are more suitable to the Lewis acid-catalyzed hydrosilylation.

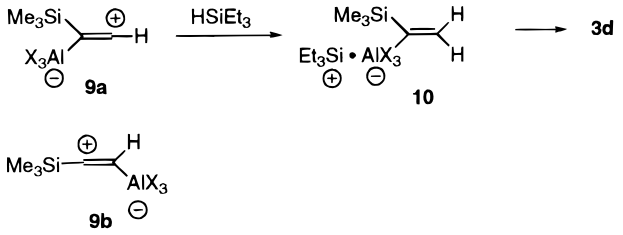
The Lewis acid-catalyzed hydrosilylation of diyne compounds was examined. Very interestingly, the $AlCl_3$ (0.2 equiv)-catalyzed hydrosilylation of 1,6-heptadiyne **4a** with 4 equiv of triethylsilane gave the six-membered cyclization product **5** in 60% yield, whereas that of 1,7-

octadiyne **4b** afforded bis-hydrosilylation product **6** in 47% yield. The assignment of the stereochemistry of **5** was made by NOE experiments (see Experimental Section).



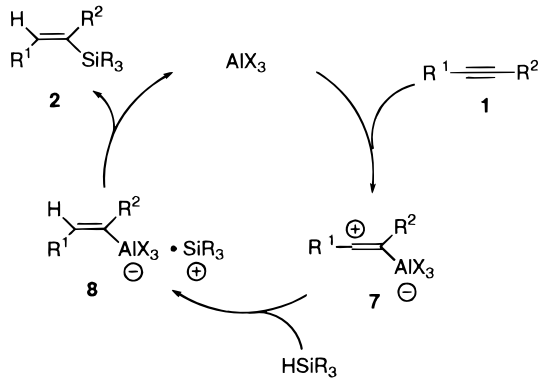
No cyclization product was obtained from **4b** under various reaction conditions: for example, the use of less than 4 equiv of triethylsilane gave a mixture of **6** and a mono-hydrosilylation product. The results are in marked contrast to the cyclization reaction of diyne compounds either by Ni-catalyzed-[10] or Rh-catalyzed hydrosilylation.[11]

Mechanism. A plausible mechanism for the $AlCl_3$- or $EtAlCl_2$-catalyzed *trans*-hydrosilylation is shown in Scheme 1. As we previously proposed for the Lewis acid-catalyzed hydro-[12] and allylstannation[13] of alkynes, and allylsilylation of alkynes,[14] $AlCl_3$ or $EtAlCl_2$ (AlX_3) would coordinate to the acetylenic bond of **1** to produce the zwitterionic intermediate **7** through a π-complex. A hydride from $HSiR_3$ would attack an electron deficient carbon from the side opposite to AlX_3 to produce an aluminum ate-complex **8**. The intermediate **8** would undergo coupling between trialkylsilyl cation and a vinyl group with retention of geometry to give **2** and AlX_3. This mechanism can explain the reverse regioselectivity in the hydrosilylation of (trimethylsilyl)acetylene **1d** mentioned above (Table 1, entry 9). The coordination of AlX_3 to **1d** would afford the zwitterionic intermediate **9a**, instead of another regioisomer **9b**, since the trialkylsilyl group stabilizes a β-cationic carbon significantly and destabilizes an α-cationic carbon.[1c] Subsequent reaction of **9a** with triethylsilane via a similar transformation pathway as shown in Scheme 1 would produce **3d** through **10**.



Allenes. The hydrosilylation of substituted allenes **11** was catalyzed dramatically by $AlCl_3$ to give the corresponding vinylsilanes **12** regio- and stereoselectively (eq 3). The results are summarized in Table 3. The $AlCl_3$-catalyzed (0.2 equiv) reaction of phenylallene **11a** (1 equiv) with dimethylethylsilane (2 equiv) gave the hydrosilylation product **12a** regioselectively in 76% yield

Scheme 1



(entry 1). No regioisomers of **12a** were detected by ^1H NMR and GC-MS analysis of the crude reaction mixture.[15] The reaction of *p*-tolylallene **11b** gave **12b** in 78% yield (entry 2), and the addition to *p*-fluorophenylallene **11c** afforded **12c** in 96% yield (entry 3). The latter result (entry 3) is in marked contrast with the case of $B(C_6F_5)_3$-catalyzed hydrostannation of **11c**,[12] in which only a trace amount of the hydrostannation product was obtained: the reason for this difference is not clear. On the other hand, the allene **11d**, bearing a strong electron-withdrawing trifluoromethyl group at the *para*-position of phenyl ring, underwent no hydrosilylation reaction. The reactions of the allenes **11a**−**c** with triethylsilane gave the corresponding hydrosilylation products in significantly lower yields, compared with those using ethyldimethylsilane. A sterically less demanding trialkylsilane is more suitable for the hydrosilylation of allenes. Actually, the hydrosilylation of 1,3-disubstituted allenes (**11e**−**g**) hardly proceeded even with ethyldimethylsilane, and therefore trimethylsilane was used in those cases (entries 5−9). The addition of trimethylsilane to the allenes **11e**−**g** occurred not only regio- but also stereoselectively to give the corresponding adducts (**12e**−**g**) in good to fair yields (entries 5−7). Very interestingly, in the case of **11e**, **11f**, and **11g**, the *E*-vinylsilanes (**12e**−**g**) were obtained stereoselectively (entries 5−7), and no stereoisomers were detected by the ^1H NMR and GC-MS analysis of the crude reaction mixture. Furthermore, even the trisubstituted allene **11h** underwent regioselective hydrosilylation with trimethylsilane to give the tetrasubstituted vinylsilane **12h** in 58% yield (entry 8). It should be noted that the tetrasubstituted vinylsilane **12h** cannot be obtained through the hydrosilylation of alkynes. 1,1-Disubstituted allene **11i** also reacted with trimethylsilane to give the vinylsilane **12i** in 46% yield (entry 9). All the allenes examined in Table 3 possess an aromatic substituent (see **11**), and a hydride from $HSiR_3$ always attacks the carbon attached to the aromatic ring. We also examined allenes substituted only with aliphatic groups. However, the hydrosilylation did not proceed at all with those aliphatic allenes.

Mechanism. The following mechanistic rationale can explain the regio- and stereoselective hydrosilylation of allenes (Scheme 2). $AlCl_3$ would coordinate to the double

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(11) Ojima, I.; Zhu, J.; Vidal, E. S.; Kass, D. F. *J. Am. Chem. Soc.* **1998**, *120*, 6690.

(12) Gevorgyan, V.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 2963.

(13) Asao, N.; Matsukawa, Y.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1513.

(14) (a) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4874. (b) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781.

(15) Possible regioisomers are shown below. These isomers were not detected.

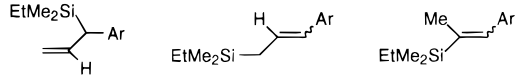
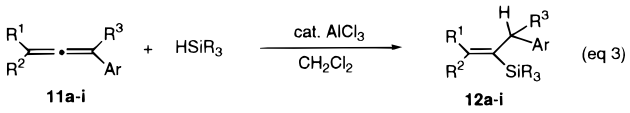


Table 3. Lewis Acid-Catalyzed Hydrosilylation of Allenes with $HSiR_3$

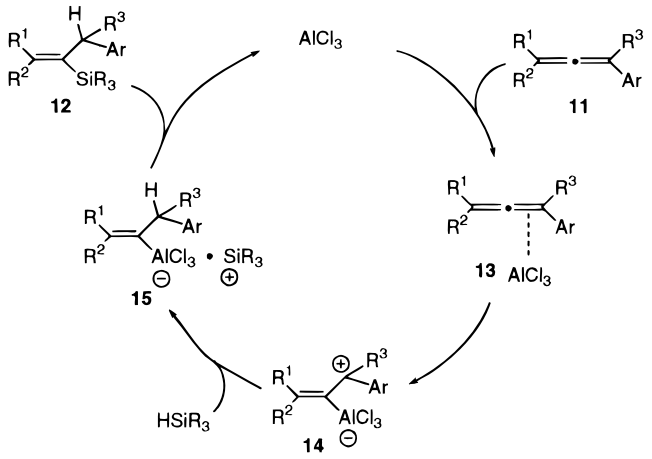


11a-i **12a-i**

	11							
entry	R^1	R^2	R^3	Ar		$HSiR_3$	product	yield (%)[a,b]
1	H	H	H	C_6H_5	**11a**	$HSiMe_2Et$	**12a**	76
2	H	H	H	*p*-Me-C_6H_4	**11b**	$HSiMe_2Et$	**12b**	78
3	H	H	H	*p*-F-C_6H_4	**11c**	$HSiMe_2Et$	**12c**	96
4[c]	H	H	H	*p*-CF_3-C_6H_4	**11d**	$HSiMe_2Et$	–	0
5	Me	H	H	*p*-Me-C_6H_4	**11e**	$HSiMe_3$	**12e**	60
6	Me	H	H	C_6H_5	**11f**	$HSiMe_3$	**12f**	66
7	Me	H	H	*p*-F-C_6H_4	**11g**	$HSiMe_3$	**12g**	72
8	Me	Me	H	*p*-F-C_6H_4	**11h**	$HSiMe_3$	**12h**	58
9	H	H	Me	*p*-F-C_6H_4	**11i**	$HSiMe_3$	**12i**	46

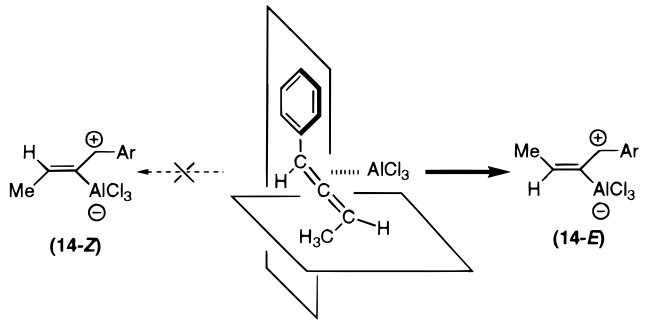
[a] The reactions were carried out in the Wheaton microreactors with 0.5 mmol of **11** and 1.0 mmol of $HSiR_3$ in CH_2Cl_2 (0.5 mL) at 0 °C in the presence of $AlCl_3$ (0.1 mmol). [b] Isolated yield. [c] The starting material **11d** was recovered.

Scheme 2



bond of an allene to produce the zwitterionic intermediate **14** through π-complex **13**. Hydride transfer from $HSiR_3$ to **14** would give the ate-complex **15**, which would undergo facile transmetalation to afford the vinylsilane **12** and $AlCl_3$. Aromatic groups such as *p*-CH_3-C_6H_4 and *p*-F-C_6H_4[16,17] stabilize significantly the benzyl cation of **14**, whereas *p*-CF_3-C_6H_4 destabilizes the carbocation due to the strong electron-withdrawing effect of CF_3-group. Accordingly, the reaction did not proceed at all in the case of **11d**. Probably, in the case of allenes substituted only with aliphatic groups, the stabilization of the carbocation derived from $AlCl_3$ coordination would be weak in comparison with that derived from aromatic allenes, and therefore the hydrosilylation did not occur with aliphatic allenes. The above mechanism also explains very nicely the regiochemistry of the hydrosilylation; Si always attaches at the central carbon of allenes, and hydride attaches at the carbon bearing the aromatic group. In the reaction of the 1,3-disubstituted allenes (**11e**–**g**), the *trans*-vinylsilanes (**12e**–**g**) were obtained stereoselectively, and this stereoselectivity can be explained by the geometry of allene double bond (Scheme 3). $AlCl_3$ would coordinate to the double bond of the allenes (**11e**–**g**) as shown in Scheme 3 in order to diminish the steric

Scheme 3



congestion between methyl group at C-3 and $AlCl_3$. The selective formation of the *trans*-vinylaluminate **14*E*** would give vinylsilanes **12e**–**g** stereoselectively.

In summary, we have succeeded in achieving the Lewis acid-catalyzed *trans*-hydrosilylation of alkynes and allenes with trialkylsilanes under mild conditions. Since this reaction proceeds in a highly regio- and stereocontrolled manner, we are now in a position to prepare a various type of vinylsilanes which are not easily available via the previously known methodologies.[1]

Experimental Section

General Information. All solvents were purified and dried before use according to the standard procedures. Reactions were performed under an argon atmosphere in oven-dried glassware. Trialkylsilanes, with exception of trimethylsilane, and the following alkynes were commercially available and dried whenever necessary: **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1j**, **1k**, **1l**, **1m**, **4a**, **4b**. Trimethylsilane was prepared according to the literature procedure.[18] The alkynes bearing silyloxy and benzyloxy groups were prepared according to the standard procedure from the corresponding alkynols.[19] The substituted allenes **11** were prepared according to the literature procedure.[20]

(*Z*)-1-(Triethylsilyl)-1-dodecene (2a). Preparation of **2a** from **1a** is representative. To a suspension of $AlCl_3$ (27 mg, 0.2 mmol) in toluene (1.0 mL) was added triethylsilane (0.19

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mL, 1.2 mmol) at 0 °C under an Ar atmosphere. The mixture was stirred for 5 min, and then **1a** (0.21 mL, 1.0 mmol) was added. The mixture was stirred for 1 h at 0 °C, and excess amounts of triethylamine (0.2 mL, 1.5 mmol) were added. After addition of aqueous $NaHCO_3$ solution, the usual workup gave a crude product, which was purified by silica gel column chromatography using hexane as an eluent to afford **2a** (263 mg, 0.93 mmol) in 93% yield. The addition order of reagent, substrate, and Lewis acid is important to obtain higher yields of the desired product. The order mentioned in the synthesis of **2a** is essential. If the acetylene **1a** was added to $AlCl_3$ prior to the addition of Et_3SiH, significant amounts of the trimerization product of **1a** (aromatic compounds) were obtained as a byproduct. Accordingly, it seems that coexistence of Et_3SiH is needed, when the coordination of $AlCl_3$ to the acetylene takes place, to instantaneously capture an activated triple bond. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.37 (dt, J = 7.3, 14.3 Hz, 1H), 5.38 (d, J = 14.3 Hz, 1H), 2.09 (dt, J = 7.3, 7.3 Hz, 2H), 1.27 (bs, 16H), 0.95 (t, J = 7.7 Hz, 9H), 0.90 (t, J = 6.6 Hz, 3H), 0.61 (q, J = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 150.4, 125.0, 34.1, 31.9, 29.8, 29.6, 29.5, 29.4, 22.7, 14.1, 7.5, 4.8 Hz. IR (neat) 2954, 2874, 1605, 1466 cm^{-1}. HRMS (EI) calcd for 282.2743 (M^+), found 282.2722 (M^+).

(*Z*)-3-Phenyl-1-(triethylsilyl)-1-propene (2b): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.17−7.32 (m, 5H), 6.50 (dt, J = 7.3, 14.3 Hz, 1H), 5.56 (dt, J = 1.5, 14.3 Hz, 1H), 3.47 (d, J = 7.3 Hz, 2H), 0.98 (t, J = 7.3 Hz, 9H), 0.69 (q, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 147.8, 140.5, 128.4, 126.6, 126.0, 40.0, 27.8, 7.5, 4.8 Hz. IR (neat) 2953, 2873, 1601, 1495, 1454 cm^{-1}. HRMS (EI) calcd for 203.1256 ($M^+ - C_2H_5$), found 203.1244 ($M^+ - C_2H_5$).

(*Z*)-3, 3-Dimethyl-1-(triethylsilyl)-1-butene (2c):[21] ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.45 (d, J = 16.0 Hz, 1H), 5.20 (d, J = 16.0 Hz, 1H), 1.05 (s, 1H), 0.95 (t, J = 7.0 Hz, 9H), 0.65 (q, J = 7.5 Hz, 6H).

1-(Triethylsilyl)-1-(trimethylsilyl)ethene (2d): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.39 (d, J = 5.1 Hz, 1H), 6.28 (d, J = 5.1 Hz, 1H), 0.91 (t, J = 8.0 Hz, 9H), 0.64 (q, J = 7.0 Hz, 6H), 0.09 (s, 9H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 151.1, 141.6, 7.4, 3.7, −0.2 Hz. IR (neat) 2955, 2875, 1460 cm^{-1}. HRMS (EI) calcd for 214.1573 (M^+), found 214.1579 (M^+).

(*Z*)-1-(Triethylsilyl)-3-cyclohexenylethene (2e): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.74 (dd, J = 1.1, 15.0 Hz, 1H), 5.65 (bs, 1H), 5.32 (d, J = 15.0 Hz, 1H), 2.00−2.10 (m, 4H), 1.55−1.67 (m, 4H), 0.93 (t, J = 8.1 Hz, 9H), 0.60 (q, J = 8.1 Hz. 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 150.8, 138.8, 125.7, 124.7, 27.8, 25.5, 22.7, 22.2, 7.6, 5.2 Hz. IR (neat) 2951, 2874, 1589, 1458 cm^{-1}. HRMS (EI) calcd for 222.1804 (M^+), found 222.1811 (M^+).

(*Z*)-β-Triethylsilylstyrene (2f):[21] ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.55 (d, J = 15.0 Hz, 1H), 7.25−7.28 (m, 5H), 5.76 (d, J = 15.0 Hz, 1H), 0.87 (t, J = 8.0 Hz, 9H), 0.56 (q, J = 7.0 Hz, 6H).

(*Z*)-4-(Triisopropylsiloxy)-1-(triethylsilyl)-1-butene (2g): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.43 (dt, J = 7.3, 14.3 Hz, 1H), 5.50 (d, J = 14.3 Hz, 1H), 3.73 (t, J = 7.0 Hz, 2H), 2.37 (dt, J = 7.0, 7.0 Hz, 2H), 1.07 (bs, 21H), 0.95 (t, J = 7.7 Hz, 9H), 0.62 (q, J = 6.9 Hz, 6H). IR (neat) 2954, 2868, 1607, 1464 cm^{-1}. Anal. Calcd for $C_{19}H_{42}OSi_2$: C, 66.58; H, 12.35. Found: C, 66.85; H, 12.62.

(*Z*)-6-(Triisopropylsiloxy)-1-(triethylsilyl)-1-hexene (2h): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.38 (dt, J = 7.0, 14.3 Hz, 1H), 5.40 (dt, J = 1.4, 14.3 Hz, 1H), 3.69 (t, J = 6.2 Hz, 2H), 2.14 (ddt, J = 1.4, 7.7, 7.7 Hz, 2H), 1.41−1.59 (m, 4H). IR (neat) 2945, 2868, 1605, 1462 cm^{-1}. Anal. Calcd for $C_{21}H_{46}OSi_2$: C, 68.03; H, 12.51. found: C, 67.75; H, 12.06.

(*Z*)-4-(Benzyloxy)-2-(triethylsilyl)-1-butene (2i): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.25−7.33 (m, 5H), 6.39 (dt, J = 7.3, 14.3 Hz, 1H), 5.52 (dt, J = 1.5, 14.3 Hz, 1H), 4.51 (s, 2H), 3.50 (ddt, J = 7.0 Hz, 2H), 2.44 (ddt, J = 1.5, 7.3, 7.3 Hz, 2H), 0.93 (t, J = 7.7 Hz, 9H), 0.61 (q, J = 7.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 145.6, 138.5, 128.3, 127.7, 127.6, 127.5, 72.9, 69.9, 34.4, 7.5, 4.6 Hz. IR (neat) 2952, 2874, 1607, 1454 cm^{-1}. HRMS (EI) calcd for 247.1518 ($M^+ - C_2H_5$), found 247.1521 ($M^+ - C_2H_5$)

(*Z*)-6-(Triethylsilyl)-6-dodecene (2j): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.98 (tt, J = 1.0, 7.2 Hz, 1H), 2.07 (dt, J = 7.0, 7.0 Hz, 2H), 1.98 (t, J = 7.2 Hz, 2H), 1.20−1.40 (m, 12H), 0.94 (t, J = 7.5 Hz, 9H), 0.89 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H), 0.64 (q, J = 7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$ 67.9 MHz) δ 144.0, 136.2, 38.4, 32.1, 31.8, 31.7, 30.8, 29.9, 22.7, 14.1, 14.0, 7.6, 4.3 Hz. IR (neat) 2956, 2873, 1608, 1460, cm^{-1}. HRMS (EI) calcd for 282.2743 (M^+), found 282.2750 (M^+).

(*Z*)-(Triethylsilyl)stilbene (2k): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.17−7.33 (m, 11H), 0.80 (t, J = 8.0 Hz, 9H), 0.41 (q, J = 8.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 147.6, 146.3, 145.2, 140.6, 128.3, 127.9, 127.8, 127.4, 127.2, 125.6, 7.5, 4.7 Hz. IR (neat) 2954, 2872, 1597, 1493, 1464 cm^{-1} . HRMS (EI) calcd for 294.1804 (M^+), found 294.1807 (M^+).

(*Z*)-1-Phenyl-2-(triethylsilyl)-1-propene (2l): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.17−7.25 (m, 6H), 1.95 (d, J = 1.8 Hz, 3H), 0.83 (t, J = 8.1 Hz, 9H), 0.43 (q, J = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 142.7, 140.7, 137.7, 128.4, 127.6, 126.6, 26.0, 7.5, 3.9 Hz. IR (neat) 2955, 2870, 1490, 1460 cm^{-1}. HRMS (EI) calcd for 232.1647 (M^+), found 232.1662 (M^+).

(*Z*)-1-Phenyl-1-(triethylsilyl)-1-propene (3l): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.98−7.28 (m, 5H), 6.22 (q, J = 7.0 Hz, 1H), 1.91 (d, J = 7.0 Hz, 3H,), 0.92 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 147.8, 147.7, 141.6, 127.6, 127.5, 125.1, 18.0, 7.4, 4.5 Hz. IR (neat) 2952, 2873, 1595, 1488 cm^{-1}.

(*Z*)-1-Phenyl-2-(triethylsilyl)-1-butene (2m): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.15−7.26 (m, 6H), 2.23 (dq, J = 1.5, 7.3 Hz, 2H), 1.10 (t, J = 7.3 Hz, 3H), 0.82 (t, J = 8.1 Hz, 9H), 0.43 (q, J = 8.0 Hz, 6H). IR (neat) 2956, 2873, 1490, 1458 cm^{-1}. Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 77.93; H, 10.12.

(*Z*)-1-Phenyl-1-(triethylsilyl)-1-butene (3m): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.99−7.25 (m, 5H), 6.09 (t, J = 7.3 Hz, 1H), 2.26 (dq, J = 7.3, 7.7 Hz, 2H), 1.05 (t, J = 7.7 Hz, 3H), 0.90 (t, J = 7.7 Hz, 9H), 0.64 (q, J = 7.7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 149.2, 147.7, 139.8, 127.6, 127.5, 125.1, 123.1, 25.6, 14.3, 7.5, 4.7 Hz. IR (neat) 2955, 2873, 1599, 1489 cm^{-1}. HRMS (EI) calcd for 246.1804 (M^+), found 246.1801 (M^+).

(*Z*)-1-(*tert*-Butyldimethylsilyl)-1-dodecene (2n): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.37 (dt, J = 7.3, 14.3 Hz, 1H), 5.46 (dt, J = 1.1, 14.3 Hz, 1H), 2.09 (dt, J = 7.3, 7.3 Hz, 2H), 1.27 (bs, 16H), 0.88 (bs, 12H) ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 150.3, 125.7, 33.7, 31.9, 29.8, 29.6, 29.4, 29.3, 26.4, 22.7, 16.8, 14.1, 1.9, −4.1 Hz. IR (neat) 2955, 2926, 1607, 1464 cm^{-1} HRMS(EI) calcd for 282.2743 (M^+), found 282.2720 (M^+).

(*Z*)-1-(Cyclohexyldimethylsilyl)-1-dodecene (2o): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.34 (dt, J = 7.3, 13.9 Hz, 1H), 5.42 (dt, J = 1.3, 13.9 Hz, 1H), 2.09 (dt, J = 7.0, 7.0 Hz, 2H), 1.65−1.75 (m, 6H), 1.00−1.40 (m, 20H), 0.89 (t, J = 7.0 Hz, 3H), 0.64 (tt, J = 2.8, 12.0 Hz, 1H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 149.9, 126.8, 126.7, 33.9, 32.0, 29.8, 29.7, 29.4, 28.2, 27.5, 27.1, 26.5, 24.2, 22.7, 14.1, −3.4 Hz. IR (neat) 2957, 2853, 1607, 1466 cm^{-1}. HRMS (EI) calcd for 308.2899 (M^+), found 308.2892 (M^+).

(*Z*)-1-(Triphenysilyl)-1-dodecene (2p): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.55−7.59 (m, 6H), 7.64−7.41 (m, 9H), 6.70 (dt, J = 7.3, 14.3 Hz, 1H), 6.02 (d, J = 14.3 Hz, 1H), 1.90 (dt, J = 7.3, 7.3 Hz, 2H), 0.94−1.30 (m, 16H), 0.88 (t, J = 8.6 Hz, 3H). IR (neat) 2954, 2853, 1603, 1485 cm^{-1}. Anal. Calcd for $C_{30}H_{38}Si$: C, 84.44; H, 8.98. found: C, 84.71; H, 9.25.

(*Z*)-1-(Methyldiphenylsilyl)-1-dodecene (2q): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.52−7.57 (m, 4H), 7.29−7.37 (m, 6H), 6.57 (dt, J = 7.3, 13.9 Hz, 1H), 5.80 (d, J = 13.9 Hz, 1H), 1.93 (dt, J = 7.3, 7.3 Hz, 2H), 1.09−1.26 (m, 16H), 0.88 (t, J = 6.6 Hz, 9H), 0.65 (s, 3H). IR (neat) 2957, 2853, 1603, 1466 cm^{-1}. Anal. Calcd for $C_{25}H_{36}Si$: C, 82.34; H, 9.95. Found: C, 82.61; H, 9.96.

(*Z*)-1-(Dimethylphenylsilyl)-1-dodecene (2r): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.53−7.58 (m, 2H), 7.33−7.37 (m, 3H), 6.44 (dt, J = 7.3, 13.9 Hz, 1H), 5.62 (dt, J = 1.5, 13.9 Hz, 1H), 2.04 (dt, J = 7.7, 7.7 Hz, 2H), 1.21−1.39 (m, 16H), 0.89 (t, J = 6.2 Hz, 3H), 0.38 (s, 6H). IR (neat) 2957,2855, 1605, 1466 cm$^{-1.}$ Anal. Calcd for $C_{20}H_{34}Si$: C, 79.31; H, 11.32. found: C, 79.64; H, 11.48.

(*E*)-1-(Triethylsilyl)-3-methylenecyclohexene (5): ^{1}H NMR ($CDCl_3$, 270 MHz) _ 6.11 (ddt, J = 0.7, 1.3, 9.6 Hz, 1H),

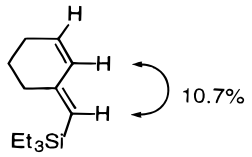

Figure 1. NOE experiments of **5**.

5.81 (dt, J = 4.4, 9.5 Hz, 1H), 5.20 (bs, 1H), 2.40 (m, 2H), 2.12 (m, 2H), 1.72 (tt, J = 6.1, 6.3 Hz, 2H), 0.94 (q, J = 7.6 Hz, 6H), 0.62 (t, J = 8.4 Hz, 9H). IR (neat) 2912, 2831, 1692, 1576, 1458 cm^{-1}. Anal. Calcd for $C_{13}H_{24}Si$: C, 74.91; H, 11.61. Found: C, 74.81; H, 11.96. NOE experiments were performed by irradiation of signals at 5.20 and 6.11 ppm. Signals showing NOE were indicated in Figure 1.

2-(Dimethylethylsilyl)-3-(4-methylphenyl)-1-propene (12a). Preparation of **12a** from **11a** is representative. To a suspension of $AlCl_3$ (13 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was added dimethyethylsilane (0.14 mL, 1.0 mmol) at 0 °C under Ar atmosphere. Very slow dropwise addition of allene **11a** (0.08 mL, 0.5 mmol) was carried out, and then the mixture was stirred for 1 h at room temperature. The reaction was monitored by GC-MS. Aqueous $NaHCO_3$ solution was added slowly at 0 °C, and then the usual workup gave crude product, which was purified by silica gel column chromatography using hexane as an eluent to afford **12a** (83 mg, 0.38 mmol) in 76% yield. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.02−7.10 (m, 4H), 5.48 (dt, J = 3.0, 1.5 Hz, 1H), 5.41 (dt, J = 3.0, 1.5 Hz, 1H), 3.41 (s, 2H), 2.32 (s, 3H), 0.87 (t, J = 8.1 Hz, 3H), 0.42 (q, J = 7.8 Hz, 2H), −0.03 (s, 6H); IR (neat) 3091, 2874, 1514, 1460 cm^{-1}. Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. Found: C, 76.76; H, 9.94.

2-(Dimethylethylsilyl)-3-phenyl-1-propene (12b): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.14−7.30 (m, 5H), 5.49 (dt, J = 3.0, 1.5 Hz, 1H), 5.42 (dt, J = 3.0, 1.5 Hz, 1H), 3.45 (s, 2H), 0.86 (t, J = 7.8 Hz, 3H), 0.46 (q, J = 7.8 Hz, 2H), −0.03 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 150.4, 149.1, 129.3, 128.1, 126.3, 125.9, 42.9, 7.28, 0.72, −3.84; IR (neat) 3084, 2835, 1495 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{20}Si$ 204.1334 (M^+), found 204.1353 (M^+).

2-(Dimethylethylsilyl)-3-(4-fluorophenyl)-1-propene (12c): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.93−7.12 (m, 4H), 5.48 (dt, J = 3.0, 1.5 Hz, 1H), 5.42 (dt, J = 3.0, 1.5 Hz, 1H), 3.42 (s, 2H), 0.86 (t, J = 7.8 Hz, 3H), 0.45 (q, J = 7.8 Hz, 2H), −0.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 161.4, 130.7, 130.6, 130.5, 126.5, 114.8, 42.1, 7.24, 6.72, −3.86; IR (neat) 3047, 2835, 1607, 1508, 1437 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{19}FSi$ 222.1240 (M^+), found 204.1353 (M^+).

(*E*)-2-(Trimethylsilyl)-1-(4-methylphenyl)-2-butene (12e): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.03−7.08 (m, 4H), 6.09 (tq, J = 5.4, 1.2 Hz, 1H), 3.51 (s, 2H), 2.31 (s, 2H), 1.76 (d, J = 5.4 Hz, 3H), −0.06 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 140.3, 137.6, 135.5, 134.9, 128.8, 128.3, 34.2, 21.0, 14.7, −1.26; IR (neat) 3047, 2870, 1616, 1510, 1454 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{22}Si$ 218.1491 (M^+), found 218.1477 (M^+).

(*E*)-2-(Trimethylsilyl)-1-phenyl-2-butene (12f): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.20−7.34 (m, 5H), 6.18 (tq, J = 5.4, 1.2 Hz, 1H), 3.62 (s, 2H), 1.84 (d, J = 5.4 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 142.5, 140.9, 140.2, 135.7, 128.5, 128.1, 34.7, 14.8, −1.30; IR (neat) 3084, 2853, 1614, 1495, 1452, 1248 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{20}Si$ 204.1333 (M^+), found 204.1371 (M^+).

(*E*)-2-(Trimethylsilyl)-1-(4-fluorophenyl)-2-butene (12g): ^{1}H NMR ($CDCl_3$, 270 MHz) δ m, 4H), 6.11 (tq, J = 5.4, 1.2 Hz, 1H), 3.52 (s, 2H), 1.76 (d, J = 5.4 Hz, 3H), −0.06 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.8 Hz) δ 160.8, 139.4, 136.0, 129.4, 129.3, 114.8, 114.2, 33.4, 14.3, −1.69; IR (neat) 3055, 2876, 1605, 1508 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{19}FSi$ 222.1239 (M^+), found 222.1233 (M^+).

1-(4-Fluorophenyl)-2-(trimethylsilyl)-3-methyl-2-butene (12h): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.92−7.06 (m, 4H), 3.48 (s, 2H), 1.96 (s, 3H), 1.75 (s, 3H), 0.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 161.1, 145.5, 136.9, 130.3, 129.3, 114.7, 36.7, 25.4, 21.4, 0.63; IR (neat) 3067, 2862, 1601, 1506, 1448 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{21}FSi$ 236.1395 (M^+), found 236.1390 (M^+).

2-(Trimethylsilyl)-3-(4-fluorophenyl)-1-butene (12i): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.93−7.26 (m, 4H), 5.70 (dd, J = 2.1, 0.9 Hz, 1H), 5.11 (dd, J = 2.1, 0.9 Hz, 1H) 3.64 (q, J = 6.9 Hz, 1H), 1.35 (d, J = 6.9 Hz, 3H), −0.07 (s, 9H); IR (neat) 3053, 2876, 1605, 1508, 1458, 1222 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{19}FSi$ 222.1239 (M^+), found 222.1195 (M^+).

Supporting Information Available: Full details of the 270 MHz ^{1}H NMR and ^{13}C NMR spectra of **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2k**, **2l**, **3l**, **2m**, **3m**, **2n**, **2o**, **2p**, **2q**, **2r**, **5**, **6**, **12a**, **12b**, **12c**, **12e**, **12f**, **12g**, **12h**, and **12i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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