Lewis Acid-Catalyzed Regio- and Stereoselective Hydrosilylation of Alkenes with Trialkylsilanes

Young-Sang Song,[†] Bok Ryul Yoo,[‡] Gyu-Hwan Lee,[†] and Il Nam Jung*[,‡]

Department of Chemistry, Han Nam University, Taejon 300-791, Korea, and Organometallic Chemistry Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Received March 29, 1999

The hydrosilylation of cyclic alkenes and linear alkenes with trialkylsilanes in the presence of Lewis acid catalysts under mild conditions gave the corresponding (trialkylsilyl)alkanes in fair to good yields. The reaction of 1-methylcyclohexene with triethylsilane at −20 °C gave *cis*-1-triethylsilyl-2-methylcyclohexane with regio- and stereoselectivity via a *trans* hydrosilylation pathway. Cycloalkenes having an alkyl group at the double-bonded carbon showed better reactivity than nonsubstituted compounds in the Lewis acid-catalyzed hydrosilylation. The catalytic reactivity of Lewis acids decreases in the following order: $AlBr_3$ > $AlCl_3$ > $HfCl_4$ > $EtAlCl_2$ > $ZrCl_4$ > $TiCl_4$. When triorganochlorosilane was used as an activator in the aluminum chloride-catalyzed reaction, the hydrosilylation rate drastically increased. The results are consistent with a stepwise mechanism proceeding via the formation of a trialkylsilylenium ion intermediate.

Introduction

Hydrosilylation[1] of unsaturated hydrocarbons such as alkenes and alkynes is one of the most effective and elegant methods for synthesizing organosilicon compounds. The addition of hydrosilanes to multiple bonds proceeds in the presence of catalysts such as radical initiators,[2] transition metal catalysts,[3] or Lewis acids.[4,5] Among the variety of catalytic hydrosilylations, the $AlCl_3$-catalyzed reaction[4,5] has received relatively little attention due to the strong catalytic activity of $AlCl_3$ for the polymerization of unsaturated hydrocarbons.[6,7] The hydrosilylations of alkenes and alkynes with chlorodialkylsilanes in the presence of $AlCl_3$ were first reported by Finke and Moretto[4a] in 1979 and later by Oertle and Wetter.[4b] In 1990, Yamamoto and Takemae studied the reaction of 1-methylcyclohexene with chlorodimethylsilane in the presence of $AlCl_3$ catalyst and found that the hydrosilylation proceeded stereoselectively in a *trans*-addition manner.[5] Voronkov and coworkers reported the hydrosilylation of alkynes and olefins with triethylsilane in the presence of a mixed catalytic system of H_2PtCl_6 and $AlCl_3$.[8] Although the $AlCl_3$-catalyzed hydrosilylation of alkynes[9] with triorganosilanes has been reported, to the best of our knowledge the hydrosilylation of alkenes with trialkylsilanes has not been previously examined.

Recently, we reported novel aluminum chloride-catalyzed addition reactions of allyltrimethylsilane with simple unactivated alkenes,[10] diallylsilanes,[11] conjugated dienes,[12] and alkynes.[13] In the allylsilylations of terminal alkenes and alkynes, the silyl group adds to the terminal carbon and the allyl group adds to the inner carbon of the multiple bond. Reaction with cyclic olefins gives allylsilylated products having the silyl and allyl groups in *trans* positions. Product yields were higher in the presence of Lewis acid catalysts in combination with chlorotrimethylsilane as an activator.[11,12,14,15] The continuous allylsilylation of alkenes did not give polyallylsilylation products but instead the silyl-rearranged allylsilylation products, indicating the formation of a silylenium ion during the allylsilylation. Our interest in the allylsilylation reaction and the formation of silylenium ion intermediates led us to examine the hydrosilylation of alkenes with trialkylsilanes in the presence of Lewis acid catalysts. We wish to report the first example of the regio- and stereoselective addition reaction of trialkylsilanes to cyclic and linear alkenes catalyzed by Lewis acids. We also provide a plausible mechanism for this hydrosilylation.

† Han Nam University.
‡ Korea Institute of Science and Technology.

(1) (a) Patai, S.; Rappoport, Z. In *The Chemistry of Organic Silicon Compounds*; John Wiley & Sons: New York, 1989; Part 2, p 1480. (b) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, 1992.
(2) Dohmaru, T.; Nagata, Y.; Tsurugi, J. *Chem. Lett.* **1973**, 1031.
(3) Transition metal complexes derived from Ni, Pd, Pt, Rh, Ru, Ir, Os, Co, Fe, Cr, and Mo metals have been used for hydrosilylation; see ref 1.
(4) (a) Finke, U.; Moretto, H. Ger. Pat. 2,804,204, 1979; *Chem. Abstr.* **1979**, *91*, 193413x. (b) Oertle, K.; Wetter, H. F. *Tetrahedron Lett.* **1985**, *26*, 5511.
(5) Yamamoto, K.; Takemae, M. *Synlett.* **1990**, 259.
(6) Olah, G. A. *Friedel−Crafts and Related Reactions*; John Wiley & Sons: New York, 1963; Vol. 2, pp 1301−1304.
(7) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley-Interscience: New York, 1982; pp 95−100.
(8) Voronkov, M. G.; Sushchinskaya, S. P.; Pukhnarevich, V. B. *Zh. Obshch. Khim.* **1981**, *51*, 242; *Chem. Abstr.* **1981**, *95*, 25190m.
(9) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654.
(10) Yeon, S. H.; Lee, B. W.; Yoo, B. R.; Suk, M.-Y.; Jung, I. N.*Organometallics* **1995**, *14*, 2361.
(11) Cho, B. K.; Choi, G. M.; Jin, J.-I.; Yoo, B. R.; Jung, I. N. *Organometallics* **1997**, *16*, 3576.
(12) Choi, G. M.; Yeon, S. H.; Jin, J.-I.; Yoo, B. R.; Jung, I. N. *Organometallics* **1997**, *16*, 5158.
(13) Yeon, S. H.; Han, J. S.; Hong, E.; Do, Y.; Jung, I. N. *J. Organomet. Chem.* **1995**, *499*, 159.
(14) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781.
(15) Jung, I. N.; Yoo, B. R. *Synlett* **1999**, 519.

10.1021/om990220p CCC: $18.00
Publication on Web 07/09/1999

Table 1. Hydrosilylation of Cycloalkenes with Et_3SiH

entry no.	cycloalkenes 2	reaction conditions $AlCl_3$ (equiv)	temp (°C)	time (h)	product 3	(%)[a]
1	**2a**	0.2	0	3.0	**3a**	74
2	**2b**	0.2	−20	1.0	**3b**	82
3	**2c**	0.2	0	1.5	**3c**	78
4	**2d**	0.2	0	4.0	**3d**	65
5[b]	**2e**	0.1	−20	1.0	**3e**	25

[a] Isolated yield. [b] The reaction of indene in the presence of 0.2 equiv of $AlCl_3$ at 0 °C gave mostly polymeric materials.

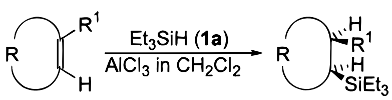
Table 2. Hydrosilylation of Linear Alkenes with Et_3SiH

entry no.	alkene 2	reaction conditions $AlCl_3$[a] temp (°C)	time (h)	product 3	(%)[b]
6[c]	**2f**	0	5.0	**3f**	66
7	**2g**	rt	4.0	**3g**	58
8	**2h**	rt	5.0	**3h**	57
9	**2i**	rt	5.0	**3i**	58
10	**2j**	−20	1.0	**3j**	57
11	**2k**	−20	1.5	**3k**	61
12[d]	**2l**	−20	1.5	**3l**	55
13	**2m**	−10	1.0	**3m**	70

[a] A 0.2 equiv amount of $AlCl_3$ was used as catalyst. [b] Isolated yield. [c] A 2.5:1 ratio of reactants **2f** and **1a** was used, and 23% of unreacted **1a** was recovered. [d] **3l** decomposed during this reaction to give benzene (0.01 g) and propyltriethylsilane (0.17 g).

Results and Discussion

Hydrosilylation of Cycloalkenes with Triethylsilane (1a). Five cycloalkenes, cyclohexene **2a**, 1-methylcyclohexene **2b**, cyclopentene **2c**, norbornene **2d**, and indene **2e**, were hydrosilylated with **1a** in the presence of aluminum chloride catalyst in methylene chloride at 0 °C to afford the corresponding hydrosilylated (triorganosilyl)cycloalkanes, in which a silyl group and a hydride were added to the carbon-carbon double bond in a *trans* manner (eq 1). The results obtained



(1)

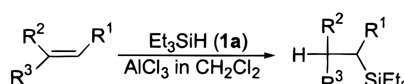
2 **3**

using optimum reaction conditions are summarized in Table 1.

The $AlCl_3$-catalyzed hydrosilylation of **2a** with **1a** at 0 °C for 3 h gave (triethylsilyl)cyclohexane (**3a**) in 74% yield as the major product along with methylcyclohexane (2%), methylbicyclohexyl (2%), cyclohexane (7%), dicyclohexylmethane (1%), and chlorotriethylsilane (12%). The formation of byproducts containing a methyl group could be explained by the reactions[16,17] of **2a** with CH_3Cl, formed through the hydrodechlorination of CH_2Cl_2 by the Si−H bond of **1a** in the presence of $AlCl_3$.[18,19] The hydrosilylation of **2b** at a lower temperature (−20 °C) for 1 h gave *cis*-1-(triethylsilyl)-2-methylcyclohexane (**3b**) in 82% yield and a trace amount of (cyclohexylmethyl)triethylsilane (**3b′**) obtained from the hydrosilylation of the isomerized methylenecyclohexane (**2b′**). No regio- and stereoisomers of **3b** were detected, indicating that the silyl group regio- and stereoselectively added to the less substituted carbon and the hydride added to the other carbon of the double bond in a *trans* manner. The results are consistent with the aluminum chloride-catalyzed *trans* allylsilylation of alkenes[10] and alkynes,[15] suggesting a stepwise hydrosilylation process and the involvement of a trialkylsilylenium ion. The higher reactivity of **2b** compared to **2a** may be attributed to the stability difference between the secondary and tertiary carbocations, generated by the addition of the silylenium ion to the carbon−carbon double bonds of **2a** and **2b**, respectively.

The reaction of cyclopentene (**2c**) with **1a** at 0 °C for 1.5 h afforded (triethylsilyl)cyclopentane (**3c**) in 78% yield. This reaction was more rapid than the reaction involving the six-membered ring **2a**, likely due to less steric hindrance for the incoming silyl cation to the carbon−carbon double bond of **2c** and higher ring strain relief in **2c** by the addition of the silylenium ion. The hydrosilylation of **2d** gave only *exo*-2-(triethylsilyl)-norbornane (**3d**)[20] in 65% yield without the formation of the *endo* isomer. This is due to the characteristic stability of the carbocation intermediate resulting from the silyl cation addition to **2d** as observed in other reactions.[21,22] In the case of **2e**, 0.1 equiv of $AlCl_3$ was used to prevent polymerization and the reaction was run at −20 °C. The yield of 2-(triethylsilyl)indane (**3e**) was only 25%, and a large amount of polymeric products was obtained. It is well known that **2e** is easily polymerized to high molecular weight materials due to its high reactivity in the presence of Lewis acid catalysts.[23,24]

Hydrosilylation of Linear Alkenes with 1a. The $AlCl_3$-catalyzed hydrosilylation with **1a** was extended to linear alkenes **2f**−**m** (eq 2). The results obtained are



(2)

2 **3**

f: $R^1 = R^2 = H, R^3 = Me$
g: $R^1 = R^2 = H, R^3 = {}^nBu$
h: $R^1 = R^2 = H$, R^3 = *n*-octyl
i: $R^1 = R^2 = H, R^3 = CH_2C_6F_5$
j: $R^1 = R^2 = H, R^3 = Ph$
k: $R^1 = R^2 = H$, R^3 = *p*-ClPh
l: $R^1 = H, R^2 = Me, R^3 = Ph$
m: $R^1 = R^2 = R^3 = Me$

summarized in Table 2.

As shown in Table 2, the product yields ranged from 55% to 70%, slightly lower than the yields from the cyclic alkenes. The reactivities of linear alkenes varied depending upon the size and delocalization ability of the substituents on the carbon−carbon double bond. The terminal alkenes **2g**−**i** required higher reaction temperatures and longer reaction times compared with the

(16) Olah, G. A.; Wang, Q. *Synthesis* **1992**, 1090.
(17) Olah, G. A.; Farooq, O.; Wang, Q.; Wu, A. H. *J. Org. Chem.* **1990**, *55*, 1224.
(18) Whitmore, F. C.; Pietrusza, E. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1947**, *69*, 2108.
(19) Doyle, M. P.; McOsker, C. C.; West, C. T. *J. Org. Chem.* **1976**, *41*, 1393.
(20) Kuivila, H. G.; Warner, C. R. *J. Org. Chem.* **1964**, *29*, 2845.
(21) Kwart, H.; Nyce, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 2601.
(22) Stille, J. K.; Sonnenberg, F. M.; Kinstle, T. H. *J. Am. Chem. Soc.* **1966**, *88*, 4922.
(23) Cheradame, H.; Sigwalt, P. *C. R. Acad. Sci.* **1965**, *260*, 159.
(24) Polton, A.; Sigwalt, P. *C. R. Acad. Sci.* **1969**, *268*, 1214.

Table 3. Results on the Hydrosilylation of 2a with R_3SiH

entry no.	$HSiR_3$ **1** (R_3)	$AlCl_3$ (equiv)	reaction time (h)	product[a] **3**	(%)
14	**1a** (Et_3)	0.2	3	**3a**	74
15	**1b** ($EtMe_2$)	0.2[b]	0.5	**3n**	66
		0.1	2	**3n**	87
16	**1c** ($^nC_6H_{11}Me_2$)	0.2	3	**3o**	81
17	**1d** ($PhMe_2$)	0.2	1.3	**3p**	21
18	**1e** ($Ph(CH_2)_2Me_2$)	0.2	3	**3q**	11
19	**1f** ($^tBuMe_2$)	0.2	3	**3r**	9

[a] Isolated yield. [b] (Trimethylsilyl)cyclohexane and (chloro(ethyl)methylsilyl)cyclohexane were obtained as byproducts.

Table 4. Lewis Acid-Catalyzed Hydrosilylation of 2a with 1a

entry no.	Lewis acid[a]	reaction conditions: solvent	temp (°C)	time (h)	**3a** (%)[b]
20	$AlCl_3$	CH_2Cl_2	0	3	74
21	$AlCl_3$	$CHCl_3$[c]	0	2	30
22	$AlCl_3$	hexane[d]	0 to rt	9	50
23	$AlCl_3$	neat	0 to rt	3	64
24	$EtAlCl_2$[e]	CH_2Cl_2	0 to rt	12	7
25	$AlBr_3$	CH_2Cl_2	0	1.5	61
26	$TiCl_4$	CH_2Cl_2	reflux	4	trace
27	$ZrCl_4$	CH_2Cl_2	reflux	7	33
28	$HfCl_4$	CH_2Cl_2	0	5	65

[a] A 0.2 equiv amount of Lewis acid was used as catalyst. [b] Isolated yield. [c] The exchange reaction between the Si−H bond of **1a** and the C−Cl bond of chloroform in the presence of aluminum chloride occurred predominantly to give chlorotriethylsilane (67%). [d] 12% of **2a** was also recovered. [e] 1.0 M solution in hexane.

branched alkene **2m** and the cyclic alkenes described above. The reactions of the styrene derivatives **2j**−**l** required lower temperatures (−20 °C) and shorter reaction times (1−1.5 h), compared with the aliphatic alkenes (**2f**−**i**), indicating that the phenyl group next to the double bond facilitates the hydrosilylation.

Substituent Effects on Silanes (1). The hydrosilylation of **2a** using various tertiary silanes was tested to examine the effects of substituents on the silicon atom. The results are shown in Table 3.

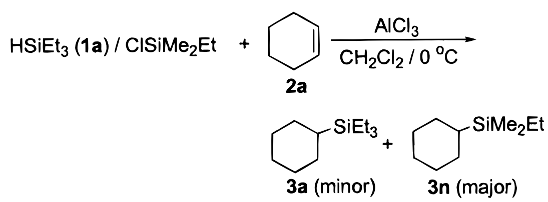
As shown in Table 3, the bulky *tert*-butyl or phenyl group-substituted silanes **1d**−**f** gave much lower yields (9 to 21%) compared with silanes **1a**−**c**. Protodesilylation[25] by acids and Friedel−Crafts alkylations[6] of the phenyl groups in the phenylsilanes were observed. These side reactions contributed to the low yields. The reaction of ethyldimethylsilane (**1b**) required less catalyst and proceeded faster than the reaction with **1a**, indicating again that bulky substituents decrease the reaction rate and yields. Silanes having two methyl groups and one simple alkyl group, **1b** and **1c**, afforded (ethyldimethylsilyl)cyclohexane (**3n**, 87%) and (*n*-hexyldimethylsilyl)cyclohexane (**3o**, 81%) in high yields.

Catalytic Activities of Lewis Acids. We also performed the hydrosilylation of **2a** with **1a** using various solvent systems and different Lewis acids as the catalyst. These results are summarized in Table 4.

As shown in Table 4, the reaction of **2a** with **1a** for 3 h at 0 °C in methylene chloride gave **3a** in 74% yield. The same reaction in *n*-hexane for 9 h gave only 50% yield of **3a** and a 3 h reaction without solvent at room temperature gave a 64% yield of product. When chloroform was used as the solvent, the reaction at 0 °C gave only a 30% yield of **3a**. The reduction of $CHCl_3$ to methylene chloride by **1a**[18] and the formation of chloro(triethyl)silane were also observed in this reaction. Methylene chloride was found to be the most effective solvent, consistent with previous observations in allylation reactions.[26−29]

Among the aluminum compounds, $EtAlCl_2$ was the least efficient catalyst and $AlBr_3$ catalyst required the shortest reaction time (1.5 h), likely due to its high solubility in organic solvents.[11] $ZrCl_4$ showed some activity but was certainly not comparable with aluminum chloride, while $TiCl_4$ showed no activity whatsoever. The reaction using $HfCl_4$ at 0 °C afforded **3a** in 65% yield, slightly lower than the yield from the $AlCl_3$-catalyzed reaction.

Effect of Chlorotrialkylsilane Activator. We have already shown that chlorotrimethylsilane is an activator for aluminum chloride catalyst in allylsilylation reactions.[11,12] To study the effects of trialkylchlorosilane addition to aluminum chloride for the hydrosilylation reactions, the reaction of **2a** with **1a** using chlorotriethylsilane as an activator was carried out. The reaction proceeded faster compared to the reaction without any activator. We explained the activation effect of chlorotrialkylsilanes in the allylsilylation of diallylsilanes[11] and conjugated dienes[12] by the formation of the complexes $R_3Si^+AlCl_4^-$ or $R_3Si^{\delta+}$-Cl→$^{\delta-}AlCl_3$ which promote the addition of trialkylsilyl cation to the carbon−carbon double bond. To check if a silylenium ion was generated from chloro(triorgano)silane and involved in the hydrosilylation, we performed the hydrosilylation of **2a** with **1a** using chloro(dimethyl)ethylsilane as an activator instead of chlorotriethylsilane (eq 3). The product



(3)

distributions were monitored by GLC from reaction times of 1 min to 60 min and the results are summarized in Table 5.

As shown in Table 5, the product **3n**, containing a dimethylethylsilyl group, was obtained in predominance at the beginning stages of the reaction, but the **3n**/**3a** ratio decreased as the reaction proceeded further. This suggests strongly that the dimethylethylsilyl cation might be generated as the aluminum chloride is mixed with dimethylethylsilyl chloride, and that the silyl cation could initiate the hydrosilylation reaction.

The conversion of triethylsilane to chlorotriethylsilane by hydrogen chloride has been reported.[30] In this

(25) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981.

(26) Fleming, I.; Dunogues, J.; Smithers, R. *Organic Reaction*; John Wiley & Sons: New York, 1989; Vol. 37, p57.
(27) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295.
(28) Seyferth, D.; Pornet, J.; Weinstein, R. M. *Organometallics* **1982**, *1*, 1651.
(29) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446.
(30) Sommer, L. H.; Citron, J. D. *J. Org. Chem.* **1967**, *32*, 2470.

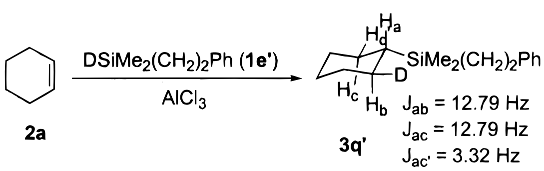
Table 5. Effect of Chlorotrialkylsilane in the Hydrosilylation of 2a[a]

reaction time (min)	**2a**[c]	products[b] **3a** + **3n**	**3n**/**3a**
1	96	3	6.3
2	86	6	5.7
4	83	10	5.5
8	72	17	5.1
16	51	32	5.0
32	17	58	4.5
60	0	70	3.9

[a] A 0.2 equiv amount of $AlCl_3$ was used as catalyst. [b] Yields were determined using decane as an internal standard. [c] Amount of **2a** remaining.

aluminum chloride-catalyzed reaction, a small amount of hydrogen chloride[31] resulting from the reaction of anhydrous aluminum chloride with adventitious water in the reaction mixture is responsible for the conversion. Since the hydrosilylation proceeds without the trialkylsilyl chloride activator, it is possible that the silylenium ion $R_3Si^+AlCl_4$- or polarized complex $R_3Si^{\delta+}$-Cl$\rightarrow^{\delta-}AlCl_3$ can be generated by the reaction of $AlCl_3$ with the chlorotriethylsilane converted from triethylsilane. The silylenium ion or polarized complex can then initiate the hydrosilylation.[11,12] Adding extra trialkylsilyl chloride activator to the reaction also leads to complexation.

Aluminum Chloride-Catalyzed *trans*-Hydrosilylation of 2a. To confirm the *trans*-hydrosilylation of cycloalkenes, **2a** was reacted with $DSiMe_2(CH_2)_2Ph$ (**1e′**). Product **3q′** was obtained in 12% yield (eq 4). NMR

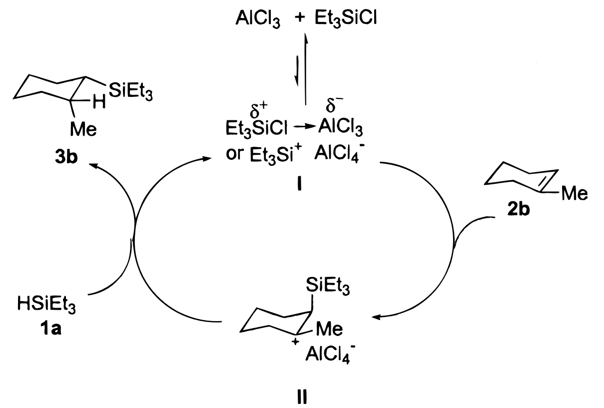


(4)

studies showed that the coupling constant between protons H_a and H_b in **3q′** was 12.79 Hz. Since *cis* coupling constants are generally smaller than *trans* coupling constants and are usually smaller than 6 Hz,[32] it can be concluded that the silyl group and deuterium are positioned in *trans* positions. The *trans* addition of hydridosilanes to cycloalkenes is consistent with a stepwise mechanism.

Reaction Mechanism. On the basis of our results and the analogy to the $AlCl_3$-catalyzed allylsilylation reactions,[10−13] we propose a possible mechanism for the $AlCl_3$-catalyzed hydrosilylation using **2b** as a representative alkene (Scheme 1). When the intermediate **I**, a silylenium ion ($Et_3Si^+AlCl_4^-$)[33] or polarized donor−acceptor complex ($Et_3Si^{\delta+}$-Cl$\rightarrow^{\delta-}AlCl_3$)[34] formed at the beginning stage of the reaction as explained above, interacts with **2b**, the triethylsilyl cation would be transferred to the carbon−carbon double bond of **2b** to generate the new intermediate **II**. The formation of the more stable tertiary carbocation in the intermediate **II**

Scheme 1. Catalytic Cycle for the Hydrosilylation of 2b with 1a

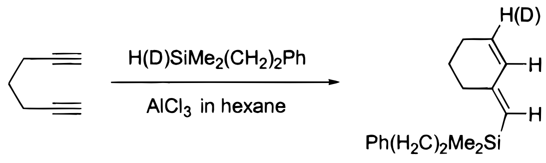


would be responsible for the regiochemistry of the products. When intermediate **II** interacts with **1a**, the hydride would be transferred from **1a** to **II** to give the hydrosilylated product **3b** and also regenerate the triethylsilyl cation. The stereochemistry of the hydrosilylation of **2b** could be explained by the approach of **1a** to the intermediate **II** from the other side of the triethylsilyl group, which would represent a less hindered approach. The regio- and stereoselective product *cis*-1-(triethylsilyl)-2-methylcyclohexane could best be explained by this *trans* hydrosilylation.

Yamamoto *et al.* proposed a different mechanism for the hydrosilylation of alkynes,[9] in which aluminum chloride coordinates to the acetylenic bond of alkyne and subsequently abstracts a hydride from **1a** to form the trialkylsilyl alkenylaluminate complex. This complex decomposes to the alkenylsilane and $AlCl_3$. One drawback of this mechanism is that it does not satisfactorily explain why the hydride from **1a** attacks the triple bond from the side opposite to $AlCl_3$ to produce the trialkylsilyl alkenylaluminate complex. The mechanism also does not outline the driving force for the decomposition of the trialkylsilyl alkenylaluminate complex to the hydrosilylated product and $AlCl_3$. Furthermore, they reported that 1,6-heptadiyne was hydrosilylated with **1a** to give the six-membered cyclization product, 3-((E)−(triethylsilyl)methylene)cyclohexene, in good yield. To possibly elucidate this mechanism further, we performed the hydrosilylation of 1,6-heptadiyne with **1e′** and found that in the product the deuterium was bonded to carbon number 3 of the ring (eq 5).[48]

(31) Thomas, C. A. *Anhydrous Aluminum Chloride in Organic Chemistry*; Reinhold Publishing Co.: New York, 1941.
(32) Pretsch, E.; Clerc, T.; Siebl, J.; Simon, W. *Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: New York, 1983; p H185.
(33) Olah, G. A.; Bach, T.; Prakash, G. K. S. *J. Org. Chem.* **1989**, *54*, 3770.
(34) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

(35) Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968; pp 42, 46.
(36) Barton, T. J.; Tully, C. R. *J. Org. Chem.* **1978**, *43*, 3649.
(37) Benkeser, R. A.; Mozdzen, E. C.; Muench, W. C.; Roche, R. T.; Siklosi, M. P. *J. Org. Chem.* **1979**, *44*, 1370.
(38) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1519.
(39) Sommer, L. H.; Marans, N. S. *J. Am. Chem. Soc.* **1951**, *73*, 5135.
(40) Dickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 308.
(41) Han, B. H.; Boudjouk, P. *Organometallics* **1983**, *2*, 769.
(42) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389.
(43) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101.
(44) Kakiuchi, F.; Tanaka, Y.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **1993**, *456*, 45.
(45) Skoda-Foldes, R.; Kollar, L.; Heil, B. *J. Organomet. Chem.* **1989**, *366*, 275.
(46) Seyferth, D.; Damrauer, R.; Turkel, R. M.; Todd, L. J. *J. Organomet. Chem.* **1969**, *17*, 367.
(47) Russell, G. A.; Nagpal, K. L. *Tetrahedron Lett.* **1961**, *13*, 421.



(5)

2n **(3s or 3s')**

This result strongly suggests that the intermediate has strong positive character and interacts intramolecularly with the other triple bond to form a cyclic ring which subsequently abstracts the deuteride from the silane. On the basis of this result, we feel that our proposed mechanism for aluminum chloride-catalyzed hydrosilylation provides a better explanation for the hydrosilylation of 1,6-heptadiyne than the mechanism proposed by Yamamoto *et al.*[9] According to our mechanism, the trialkylsilyl cation adds to the terminal carbon of the triple bond to form a carbocation beta to the silyl group and the carbocation interacts intramolecularly with the other triple bond to form a cyclic ring which subsequently abstracts the hydride from the silane to give the regio- and stereoselective *trans* hydrosilylation product.

Experimental Section

All reactions and manipulations were carried out under prepurified dinitrogen using Schlenk techniques. Glassware was flame-dried before use. Dried solvents were employed in all reactions. Lewis acids and alkenes were purchased from Aldrich Chemical Co. All alkenes and silanes were stored over molecular sieves (4 Å) and distilled before use. Silanes with Si−H bonds such as dimethylethylsilane, dimethyhexylsilane, dimethylphenylsilane, dimethyl(phenethyl)silane, *tert*-butyldimethylsilane, and deuterio(dimethyl)phenethylsilane were prepared using Grignard reagents,[35] alkyllithiums,[35,36] and lithium aluminum deuteride.[37] The reaction products were analyzed by GLC using a packed column (10% SE-30 or SE-54 on 80−100 mesh chromosorb W/AW, $^1/_8$ in. × 1.5 m) or a capillary column (SE-30, 30 m) with a Varian 3300 gas chromatograph, thermal conductivity detector, and Hitachi D-2500 integrator. Samples for characterization were purified by preparative GLC using a Donam system series DS 6200 gas chromatograph with a thermal conductivity detector and a 4-m × $^1/_8$ in. stainless steel column packed with 20% OV-101 on 80−100 mesh chromosorb P/AW. NMR spectra were recorded on a Varian Unity Plus 600 (FT, 600 MHz, ^{1}H), Bruker AMX 500 (FT, 500 MHz, ^{1}H; 125 MHz, ^{13}C), or a Varian Gem 300 (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C) spectrometer in $CDCl_3$ solvent. Mass spectra were obtained using a Hewlett-Packard 6890 GC/MS. HRMS (high-resolution mass (70 eV, EI) spectra) were performed by Korea Basic Science Institute, Seoul, Korea. Elemental analyses were performed by the chemical analysis laboratory of the Korea Institute of Science and Technology.

Typical Procedure for Reaction of 2a with 1a. To a suspension of $AlCl_3$ (0.2 g, 1.5 mmol) in methylene chloride (6.5 mL) under nitrogen atmosphere at 0 °C was added a mixture of **1a** (1.05 g, 9.0 mmol) and **2a** (0.62 g, 7.5 mmol). The reaction mixture was stirred for 3 h at 0 °C and then quenched with a water solution of sodium hydrogen carbonate. 15 mL of diethyl ether was added and the mixture was shaken. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent and low boilers were distilled off. The remaining reaction mixture was vacuum-distilled to give **3a**[8] (1.10 g, 74% yield based on **2a** consumed). Several other byproducts, cyclohexane (7%), methylcyclohexane (2%), methylbicyclohexyl (2%), dicyclohexylmethane (1%), and 0.06 g of unidentified high boilers, were also obtained along with unreacted **1a** (0.17 g, 16%). Data for **3a**: ^{1}H NMR (300 MHz) δ 0.47−0.55 (q, J = 7.0 Hz, 6H), 0.66−0.77 (tt, J = 12.4, 3.2 Hz, 1H), 0.92−0.97 (t, J = 8.1 Hz, 9H), 1.12−1.24 (m, 5H, ring-CHCH_2), 1.64−1.73 (m, 5H, ring-CHCH_2). ^{13}C NMR (75 MHz) δ 2.0, 7.72 (SiCH_2CH_3), 23.66, 27.17, 27.95, 28.40 (ring-carbons of cyclohexyl).

Reaction of 2b with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2b** (0.72 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave *cis*-**3b** (1.3 g, 82%, bp 34−36 °C/0.1 mmHg), methylcyclohexane (1%), *trans*-1,2-dimethylcyclohexane (4%), *cis*-1,2-dimethylcyclohexane (3%), and 0.07 g of unidentified high boiling compounds. Unreacted **1a** (0.14 g, 13%) was also recovered. Data for **3b**: ^{1}H NMR (600 MHz) δ 0.54−0.58 (q, J = 8.0 Hz, 6H), 0.94−0.97 (t, J = 8.1 Hz, 9H), 0.99−1.0 (d, J = 7.2 Hz, 3H), 1.16−1.24 (m, 1H), 1.42−1.53 (m, 6H), 1.68−1.72 (m, 2H), 1.99−2.03 (m, 1H). ^{13}C NMR (75 MHz) δ 3.15, 7.87 (SiCH_2CH_3), 16.53(CH_3), 21.17, 22.41, 28.17, 28.75, 29.22, 35.32 (ring-carbons of cyclohexyl). Anal. Calcd for $C_{13}H_{28}Si$: C, 73.50; H, 13.28. Found: C, 73.30; H, 13.40. The identification of **3b′** was performed by comparing with the authentic sample prepared by the hydrosilylation of **2b′** with **1a** in the presence of $AlCl_3$. Data for **3b′** (72% Yield): ^{1}H NMR (300 MHz) δ 0.47−0.49 (d, J = 6.63 Hz, 2H), 0.48−0.56 (q, J = 7.92 Hz, 6H), 0.90−0.96 (t, J = 7.83 Hz, 9H), 1.08−1.26 (m, 4H), 1.32−2.0 (m, 1H), 1.59−1.71 (m, 6H). ^{13}C NMR (75 MHz) δ 4.55, 7.93 (SiCH_2CH_3), 20.6 (CH_2), 26.68, 27.08, 34.56, 37.49 (ring-carbons of cyclohexyl). Anal. Calcd for $C_{13}H_{28}Si$: C, 73.5; H, 13.28. Found: C, 73.5; H, 13.40.

Reaction of 2c with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2c** (0.51 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave **3c** (1.07 g, 78%, bp 94−98 °C/13 mmHg), methylcyclopentane (2%), methylbicyclopentyl (4%), and 0.08 g of unidentified high boiling compounds. Unreacted **1a** (0.18 g, 17%) was also recovered. Data for **3c**: ^{1}H NMR (300 MHz) δ 0.49−0.57 (q, J = 7.9 Hz, 6H), 0.92−0.98 (t, J = 8.1 Hz, 9H), 1.27−1.79 (m, 9H). ^{13}C NMR (75 MHz) δ 2.78, 7.76 (SiCH_2CH_3), 23.31, 27.02, 28.31 (ring-carbons of cyclopentyl). Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12. Found: C, 71.59; H, 13.24.

Reaction of 2d with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2d** (0.71 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave *exo*-**3d**[38] (1.02 g, 65%), norbornane (2%), and 0.23 g of unidentified high boiling compounds. Unreacted **1a** (0.28 g, 27%) was also recovered. Data for **3d**: ^{1}H NMR (300 MHz) δ 0.47−0.56 (q, J = 7.0 Hz, 6H), 0.63−0.68 (t, J = 8.7 Hz, 1H), 0.92−0.97 (t, J = 8.0 Hz, 9H), 1.10−1.55 (m, 8H), 2.17−2.23 (d, J = 16.7 Hz, 2H). ^{13}C NMR (75 MHz) δ 2.8, 7.77 (SiCH_2CH_3), 26.23, 28.86, 32.87, 34.44, 36.84, 37.94, 38.17 (ring-carbons of norbornyl).

Reaction of 2e with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2e** (0.87 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave **3e**[39] (0.44 g, 25%), indane (2%), and 0.64 g of polymeric material. Unreacted **1a** (0.72 g, 69%) was also recovered. Data for **3e**: ^{1}H NMR (300 MHz) δ 0.59−0.67 (q, J = 7.0 Hz, 6H), 0.98−1.03 (t, J = 8.0 Hz, 9H), 1.67−1.81(quint, J = 9.5 Hz, 1H), 2.84−2.93 (q, J = 8.8 Hz, 2H), 2.99−3.07 (q, J = 8.2 Hz, 2H), 7.15(m, 2H), 7.22(m, 2H). ^{13}C NMR (75 MHz) δ 2.76, 7.72 (SiCH_2CH_3), 23.97 (ring-CH), 35.11 (ring-CH_2), 124.13, 125.89, 144.94 (phenyl-carbons).

Reaction of 2f with 1a. A 25-mL sealed stainless steel bomb in a dry ice/acetone bath was charged with aluminum chloride (0.2 g, 1.5 mmol), methylene chloride (6.5 mL), **1a** (1.05 g, 9.0 mmol), and **2f** (0.95 g, 22 mmol). The reaction mixture was stirred at 0 °C for 5 h, transferred to a 50 mL

(48) Data for **3s′**: ^{1}H NMR (300 MHz) δ 0.14 (s, 6H), 0.95−1.01 (t, J = 8.7 Hz, 2H), 1.71−1.75 (m, 2H), 2.1−2.13 (m, 2H), 2.41−2.45 (m, 2H), 2.63−2.67 (t, J = 8.7 Hz, 2H), 5.27 (s, 1H), 6.09 (s, 1H), 7.16−7.21 (m, 3H), 7.25−7.27(m, 2H).

two-neck round-bottom flask, and quenched with a water solution saturated with sodium hydrogen carbonate. A 15 mL amount of diethyl ether was added and the mixture was shaken. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent and low boilers were distilled off. The remaining crude product was vacuum-distilled to give propyltriethylsilane (**3f**;[40] 0.72 g, 66% yield based on **1a** consumed) and 0.11 g of self-dimeric products of **2f**. Unreacted **1a** (0.24 g, 23%) was also recovered.

Reaction of 2g with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2g** (0.63 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave hexyltriethylsilane (**3g**;[41] 0.84 g, 58%), hexane (21%), and 0.1 g of unidentified high boiling compounds. Unreacted 1-hexene (0.03 g, 5%) and **1a** (0.32 g, 31%) were also recovered.

Reaction of 2h with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2h** (1.05 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave decyltriethylsilane (**3h**;[42] 0.97 g, 57%), decane (24%), 2-methyldecane (1%), and 0.11 g of unidentified high boiling compounds. Unreacted 1-decene (0.11 g, 10%) and **1a** (0.34 g, 32%) were also recovered.

Reaction of 2i with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2i** (1.56 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave triethylpentafluorophenylpropylsilane (**3i**; 1.0 g, 58%, bp 50−52 °C/0.1 mmHg), propylpentafluorobenzene (23%), and 0.1 g of unidentified high boiling compounds. Unreacted **2i** (0.61 g, 39%) and **1a** (0.12 g, 14%) were also recovered. Data for **3i**: ^{1}H NMR (300 MHz) δ 0.47−0.60 (m, 8H), 0.89−0.97 (t, J = 8.0 Hz, 9H), 1.52−1.63 (m, 2H), 2.68−2.73 (t, J = 7.6 Hz, 2H). ^{13}C NMR (75 MHz) δ 3.29, 7.39 (SiCH_2CH_3), 11.37, 24.06, 26.28 (CH_2 of propyl), 115.33 (C, m), 137.40 (CF, d, J_{C-F} = 252 Hz), 139.40 (CF, d, J_{C-F} = 250 Hz), 145.05 (CF, d, J_{C-F} = 248 Hz). HRMS (m/e): calcd for $C_{15}H_{21}F_5Si$ ((M − Et)$^+$), 295.0941; found, 295.0940.

Reaction of 2j with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2j** (0.78 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave phenylethyltriethylsilane (**3j**;[43] 0.95 g, 57%), ethylbenzene (1%), and 0.36 g of polymeric material. Unreacted **1a** (0.44 g, 42%) was also recovered.

Reaction of 2k with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2k** (1.04 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave (p-chlorophenethyl)triethylsilane (**3k**;[44] 1.17 g, 61%) and 0.18 g of polymeric material. Unreacted **1a** (0.51 g, 48%) was also recovered.

Reaction of 2l with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2l** (0.89 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave triethyl(2-phenylpropyl)silane (**3l**;[45] 0.96 g, 55%) and 0.3 g of polymeric material. Unreacted **1a** (0.05 g, 5%) was also recovered.

Reaction of 2m with 1a. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2m** (0.53 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) gave 3-methyl-2-(triethylsilyl)butane (**3m**; 0.98 g, 70%, bp 82−84 °C/13 mmHg), 2,3-dimethylbutane (7%), 0.02 g of self-dimeric product of **2m**, and 0.1 g of unidentified high boiling compounds. Unreacted **1a** (0.15 g, 14%) was also recovered. Data for **3m**: ^{1}H NMR (300 MHz) δ 0.53−0.61 (q, J = 7.8 Hz, 6H), 0.74−0.83 (m, 1H), 0.85−0.98 (m, 18H), 1.82−1.93 (m, 1H). ^{13}C NMR (75 MHz) δ 3.24, 7.83 (SiCH_2CH_3), 9.43, 19.89, 23.24, 24.05, 28.57 (CH, CH$_3$). Anal. Calcd for $C_{11}H_{26}Si$: C, 70.88; H, 14.06. Found: C, 70.91; H, 14.30.

Reaction of 2a with 1b. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2a** (0.62 g, 7.5 mmol) with **1b** (0.79 g, 9.0 mmol) in the presence of $AlCl_3$ (0.1 g, 0.75 mmol) gave cyclohexyl(dimethyl)ethylsilane (**3n**; 1.1 g, 87%, bp 74−78 °C/13 mmHg), cyclohexane (2%), methylcyclohexane (1%), and 0.03 g of unidentified high boiling compound. Unreacted **1b** (0.13 g, 16%) was also recovered. Data for **3n**: ^{1}H NMR (300 MHz) δ 0.1 (s, 6H), 0.42−0.50 (q, J = 7.9 Hz, 2H), 0.55−0.65 (tt, J = 12.5, 2.9 Hz, 1H), 0.89−0.95 (t, J = 7.9 Hz, 3H), 1.06−1.23 (m, 5H), 1.63−1.72 (m, 5H). ^{13}C NMR (75 MHz) δ −5.83 (SiCH_3), 5.2, 7.48 (SiCH_2CH_3), 25.14, 27.09, 27.53, 28.21 (ring-carbons of cyclohexyl). Anal. Calcd for $C_{10}H_{22}Si$: C, 70.50; H, 13.02. Found: C, 70.81; H, 13.14.

Reaction of 2a with 1c. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2a** (0.62 g, 7.5 mmol) with **1c** (1.29 g, 9.0 mmol) gave cyclohexyl(dimethyl)hexylsilane (**3o**; 1.38 g, 81%, bp 38−42 °C/0.1 mmHg), cyclohexane (5%), methylcyclohexane (2%), dicyclohexyl (1%), dicyclohexylmethane (2%), methylbicyclohexyls (2%), and 0.04 g of unidentified high boiling compounds. Unreacted **1c** (0.22 g, 17%) was also recovered. Data for **3o**: ^{1}H NMR (300 MHz) δ 0.1 (s, 6H), 0.46−0.49 (m, 2H), 0.53−0.63 (tt, J = 12.1, 2.7 Hz, 1H), 0.87−0.91 (m, 3H), 1.02−1.28 (m, 13H), 1.64−1.73 (m, 5H). ^{13}C NMR (75 MHz) δ −5.3 (SiCH_3), 13.57, 14.17, 22.68, 23.94, 31.65, 33.55 (carbons of hexyl), 25.44, 27.09, 27.54, 28.22 (ring-carbons of cyclohexyl). Anal. Calcd for $C_{14}H_{30}Si$: C, 74.25; H, 13.35. Found: C, 74.46; H, 13.54.

Reaction of 2a with 1d. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2a** (0.62 g, 7.5 mmol) with **1d** (1.23 g, 9.0 mmol) gave cyclohexyl(dimethyl)phenylsilane (**3p**; 0.38 g, 21%, bp 50−54 °C/0.1 mmHg), diphenyldimethylsilane[46] (33%), dicyclohexyldimethylsilane[47] (13%), cyclohexyl(dimethyl)chlorosilane (17%), phenyl(dimethyl)chlorosilane (7%), cyclohexyldimethylsilane (7%), and 0.16 g of unidentified high boilers. Unreacted **1d** (0.12 g, 10%) was also recovered. Data for **3p**: ^{1}H NMR (300 MHz) δ 0.24 (s, 6H), 0.75−0.85 (tt, J = 12.2, 2.8 Hz, 1H), 1.02−1.23 (m, 5H), 1.66−1.70 (m, 5H), 7.34−7.36 (m, 3H), 7.48−7.51 (m, 2H). ^{13}C NMR (75 MHz) δ −5.12 (SiCH_3), 25.87, 26.96, 27.51, 28.13 (ring-carbons of cyclohexyl), 127.63, 128.73, 134.0, 138.72 (phenyl-carbons). Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. Found: C, 76.80; H, 10.40.

Reaction of 2a with 1e. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **2a** (0.62 g, 7.5 mmol) with **1e** (1.48 g, 9.0 mmol) in the presence of anhydrous $AlCl_3$ (0.2 g, 1.5 mmol) in methylene chloride solvent (6.5 mL) gave cyclohexyl(dimethyl)phenethylsilane (**3q**; 0.21 g, 11%, bp 78−82 °C/0.1 mmHg), cyclohexane (6%), chloro(cyclohexyl)-dimethylsilane (12%), chloro(phenethyl)dimethylsilane (32%), and 0.4 g of Friedel-Crafts polyalkylated compounds and unidentified high boiling compounds. Data for **3q**: ^{1}H NMR (300 MHz) δ 0.0 (s, 6H), 0.60−0.69 (tt, J = 12.2, 2.7 Hz, 1H), 0.85−0.91 (t, J = 8.8 Hz, 2H), 1.05−1.24 (m, 5H), 1.68−1.73 (m, 5H), 2.60−2.66 (t, J = 8.8 Hz, 2H), 7.15−7.21 (m, 3H), 7.23−7.32 (m, 2H). ^{13}C NMR (125 MHz) δ 0.0 (SiCH_3), 21.07 (SiCH_2), 30.73, 32.43, 32.91, 33.44 (ring-carbons of cyclohexyl), 35.51 (SiCH_2), 130.86, 133.15, 133.68, 150.89 (phenyl-carbons). Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 77.80, H, 10.80.

Reaction of 2a with 1f. Using the procedure described in the reaction of **2a** with **1a**, the reaction of **1a** (0.62 g, 7.5 mmol) with **1f** (1.05 g, 9.0 mmol) gave *tert*-butylcyclohexyl(dimethyl)-silane (**3r**; 0.11 g, 9%), cyclohexane (8%), dicyclohexyl (1%), dicyclohexylmethan (6%), methylbicyclohexyl (11%), and 0.2 g of unidentified high boiling compounds. Unreacted **1a** (0.13 g, 21%) and **1f** (0.24 g, 23%) were also recovered. Data for **3r**: ^{1}H NMR (300 MHz) δ 0.1 (s, 6H), 0.69−0.78 (t, J = 12 Hz, 1H), 0.9 (s, 9H), 1.07−1.24 (m, 5H), 1.71−1.74 (m, 5H). ^{13}C NMR (75 MHz) δ −7.5 (SiCH_3), 17.34, 24.08, 27.02, 27.39, 28.38, 28.76. Anal. Calcd. for $C_{12}H_{26}Si$: C, 72.64; H, 13.21. Found: C, 72.97; H, 13.44.

Reaction of 2a with 1a in the Presence of Chloro(dimethyl)ethylsilane Activator. The reaction of **2a** (0.62 g, 7.5 mmol) with **1a** (1.05 g, 9.0 mmol) in methylene chloride (6.5 mL) was carried out in the presence of aluminum chloride (0.2 g, 1.5 mmol) and chloro(dimethyl)ethylsilane (1.10 g, 9.0 mmol) under nitrogen atmosphere at 0 °C. The progress of the reaction was monitored by GLC at intervals of reaction times (1, 2, 4, 8, 16, 32, and 60 min) and calibrated with decane (0.12 g) as an internal standard.

Reaction of 2a with Deuteriophenethyldimethylsilane (1e′). Using the procedure described in the reaction of **2a** with **1e**, the reaction of **2a** (0.62 g, 7.5 mmol) with **1e′** (1.49 g, 9.0 mmol) gave *trans*-2-deuterio-1-(phenethyldimethylsilyl)cyclohexane (**3q′**; 0.22 g, 12%). Data for **3q′**: ^{1}H NMR (600 MHz) δ 0.0 (s, 6H), 0.63−0.68 (td, J = 12.8, 3.3 Hz, 1H), 0.89−0.92 (t, J = 9.0 Hz, 2H), 1.11−1.18 (m, 2H), 1.23−1.28 (m, 3H), 1.71−1.77 (m, 4H), 2.64−2.67 (t, J = 9.0 Hz, 2H), 7.19−7.25 (m, 3H), 7.30−7.33 (m, 2H). ^{13}C NMR (75 MHz) δ −5.36 (Si*C*H$_3$), 15.70 (Si*C*H$_2$), 25.25, 27.02, 27.14 (t, J_{C-D} = 19.3 Hz), 27.49, 28.18 (2*C*) (ring-carbons of cyclohexyl), 30.14 (Si*C*H$_2$), 125.48, 127.78, 128.29, 145.52 (phenyl-carbons).

Reaction of 1,6-Heptadiyne (2n) with 1e. Using the procedure described in the reaction of **2a** with **1e**, the reaction of **2n** (0.7 g, 7.5 mmol) with **1e** (1.48 g, 9.0 mmol) in the presence of anhydrous AlCl$_3$ (0.2 g, 1.5 mmol) in hexane solvent (6.5 mL) gave 3-((E)−(phenethyldimethylsilyl)methylene)cyclohexene (**3s**; 0.58 g, 30%). Data for **3s**: ^{1}H NMR (300 MHz) δ 0.10 (s, 6H), 0.96−1.01 (t, J = 8.7 Hz, 2H), 1.72−1.78 (m, 2H), 2.08−2.13 (m, 2H), 2.41−2.46 (m, 2H), 2.61−2.67 (t, J = 8.7 Hz, 2H), 5.27 (s, 1H), 5.78−5.90 (m, 1H), 6.08−6.12 (d, J = 9.9 Hz, 1H), 7.16−7.22 (m, 3H), 7.25−7.3 (m, 2H).

Acknowledgment. This research was supported financially by the Ministry of Science and Technology. We thank Prof. D. Son of Southern Methodist University, Dallas, Texas, for many valuable discussions during the preparation of this manuscript.

OM990220P