Synthesis of Mono-, Di-, and Trisilyl-Substituted Alkenes via the Hydrosilylation of Methylenecyclopropanes Catalyzed by Rh(I) Complexes

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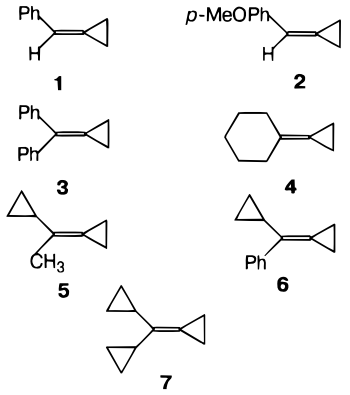
Introduction

Transition metal catalyzed hydrosilylation of alkenes and alkynes is an efficient and economical route to organosilanes.[1] In reality the hydrosilylation reaction is a rather complex process because in every case the results obtained depend on many factors such as catalyst, temperature, the nature of silane and substrate. Therefore, some types of organosilanes are almost inaccessible. In the present work we have focused our attention on the synthesis of mono-, di-, and trisilylated olefins, which are interesting as monomers and intermediates for organic synthesis. We suggested the use methylenecyclopropanes as a starting material, because the hydrosilylation of polyunsaturated compounds is known to proceed nonselectively with formation of complex mixtures of products.[1b,2] During the last decade methylenecyclopropanes have become available and found application in organic synthesis as versatile building blocks.[3]

Though numerous metal catalyzed reactions of methylenecyclopropanes are known,[4] only some of them are sufficiently selective to be used as synthetic methods. To our knowledge, hydrosilylation of methylenecyclopropanes has never been mentioned in the literature, with the only exception being the reaction of phenyl-substituted methylenecyclopropanes with triethylsilane catalyzed by the Wilkinson complex, which was published in our preliminary communication.[5]

Now we present the results of the hydrosilylation of methylenecyclopropanes **1**−**7** with various silanes.



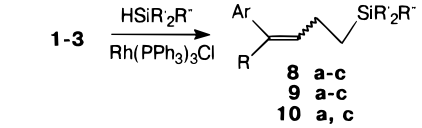
All selected hydrocarbons contain either tri- or tetrasubstituted double bonds. Though polysubstituted olefins are often reluctant to participate in the hydrosilylation reaction, these strained molecules readily underwent hydrosilylation. Hydrosilylation of methylenecyclopropanes **1**−**4** resulted in the cleavage of cyclopropane ring, leading to monosilylated olefins. The hydrosilylation reaction of methylenecyclopropanes **5**−**7** containing two reactive fragments, the methylenecyclopropane and vinylcyclopropane[6] moieties, lead to di- and trisilylated olefins.

Both H_2PtCl_6 (Speier catalyst) and Rh(I) complexes including tris(triphenylphosphine)rhodium chloride, bis(triphenylphosphine)carbonylrhodium chloride and di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium, which we have recently prepared,[8] were used as catalysts.

Results and Discussion

All olefins **1**−**7** were found to be unreactive toward silanes in the presence of the Speier catalyst, traditionally used for hydrosilylation of alkenes.

The reaction of methylenecyclopropanes **1**−**4** with various silanes catalyzed by the Wilkinson complex proceeds selectively with the cleavage of the C^1-C^2 bond of the cyclopropane ring to produce β-silyl-substituted alkenes in good yields.



8 R = H, Ar = Ph
9 R = H, Ar = *p*-MeOPh
10 R = Ar = Ph

a R' = R" = Et
b R' = Me, R" = Ph
c R' = R" = OEt

Monoaryl-substituted methylenecyclopropanes **1**, **2** react with triethylsilane at room temperature to give silylated styrenes **8a**, **9a** in quantitative yields (Table 1, entries 1, 4).

(1) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Oxford: University Press: New York, 1982, vol. 2, pp 117−120. (c) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *Organometallic Chemistry Reviews*. In Journal of Organometallic Chemistry Library; Seyferth, D., Davies, A. G., Fisher, E. O., Normant J. F., Reutov, O. A., Eds.; Elsevier: Amsterdam, 1977; vol. 5.

(2) (a) Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748−4750. (b) Green, M.; Spenses, J. L.; Stone, F. G. A.; Tsipis, K. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1519−1525.

(3) (a) Binger, P.; Buech, M. *Top. Curr. Chem.* **1987**, *135*, 77−151. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1−20. (c) De Meijere, A.; Wessjohann, L. *Synlett* **1990**, 20−32.

(4) (a) Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780−5781. (b) Noyori, R.; Kumagai, Y.; Umeda, I.; Takaya, H. *J. Am. Chem. Soc.* **1972**, *94*, 4018−4020. (c) Binger, P.; Cetinkaya, M.; Doyl, M. J.; Germer, A.; Shushard, U. In *Fundamental Research in Homogeneous Catalysis*; Plenum Press: New York, 1979, Vol. 3, pp 271−284. (d) Balme, G.; Fournet, G.; Gore, J. *Tetrahedron Lett.* **1986**, *27*, 3855−3858. (e) Fournet, G.; Balme, G.; Gore, J. *Tetrahedron Lett.* **1987**, *28*, 4533−4536. (f) Chiusoli, G. P.; Costa, M.; Schianchi, P.; Salerno, G. *J. Organomet. Chem.* **1986**, *315*, C45−C50. (g) Chiusoli, G. P.; Costa, M.; Pivetti, F. *J. Organomet. Chem.* **1989**, *373*, 377−384. (h) Stolle, A.; Salaun, J.; De Meijere, A. *Tetrahedron Lett.* **1990**, *31*, 4593−4596. (i) Lewis, R. T.; Motherwell, W. B.; Shipman, M. *J. Chem. Soc., Chem. Commun.* **1988**, 948−950. (j) Yamago, S.; Nakamura, E. *J. Chem. Soc., Chem. Commun.* **1988**, 1112−1113. (k) Motherwell, W. B.; Shipman, M. *Tetrahedron Lett.* **1991**, *32*, 1103−1106. (l) Lautens, M.; Reh, Y.; Delanghe, P. H. M. *J. Am. Chem. Soc.* **1994**, *116*, 8821−8823. (m) Chatani, N.; Takeyasu, T.; Hanafusa, T. *Tetrahedron Lett.* **1988**, *29*, 3979−3982.

(5) Bessmertnykh, A. G.; Grishin, Yu. K.; Donskaya, N. A.; Beletskaya, I. P. *Metalloorg. Khim.* **1993**, *6*, 30−35.

(6) Recently we have found that the hydrosilylation of vinylcyclopropane catalyzed by $Rh(PPh_3)_3Cl$ results in the addition to the cyclopropane ring to produce silylated olefins.[7]

(7) Bessmertnykh, A. G.; Blinov, K. A.; Grishin, Yu. K.; Donskaya, N. A.; Beletskaya, I. P. *Tetrahedron Lett.* **1995**, *36*, 7901−7905.

(8) (a) Donskaya, N. A.; Yur'eva, N. M.; Beletskaya, I. P. *Mendeleev Commun.* **1992**, 136−137. (b) Donskaya, N. A.; Yur'eva, N. M.; Voevodskaya, T. I.; Sigeev, A. S.; Beletskaya, I. P. *Zh. Org. Khim.* **1994**, *30*, 801−806.

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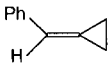
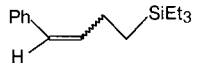
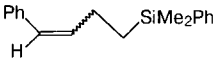
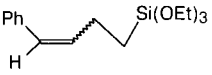
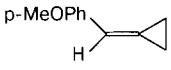
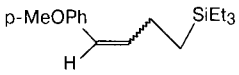
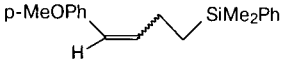
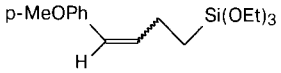
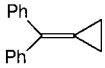
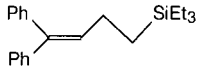
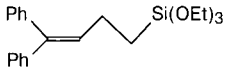
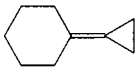
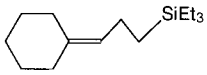
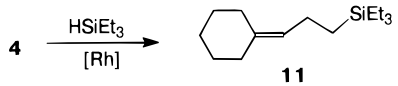
Table 1. Hydrosilylation of Methylenecyclopropanes 1−4

Entry	Substrate	Silane	Catalyst	Time and Temp.	Reactions products, [Yield[a],%] (Z-/E-)[b]
1	 **1**	$HSiEt_3$	$Rh(PPh_3)_3Cl$[c]	20°C, 20 h	 **8a** [95](1:3)
2	**1**	$HSiMe_2Ph$	$Rh(PPh_3)_3Cl$[c]	20°C, 20 h	 **8b** [83](1:2)
3	**1**	$HSi(OEt)_3$	$Rh(PPh_3)_3Cl$[c]	80°C, 10 h	 **8c** [41](1:2)
4	 **2**	$HSiEt_3$	$Rh(PPh_3)_3Cl$[c]	20°C, 20 h	 **9a** [96](3:1)
5	**2**	$HSiMe_2Ph$	$Rh(PPh_3)_3Cl$[c]	20°C, 10 h	 **9b** [88](2:3)
6	**2**	$HSi(OEt)_3$	$Rh(PPh_3)_3Cl$[c]	80°C, 50 h	 **9c** [65](1:5)
7	 **3**	$HSiEt_3$	$Rh(PPh_3)_3Cl$[c]	20°C, 65 h	 **10a** [84]
8	**3**	$HSiEt_3$	$Rh(PPh_3)_3Cl$[d]	20°, 48 h	**10a** [85]
9	**3**	$HSiEt_3$	$Rh(PPh_3)_3Cl$[c]	80°, 3 h	**10a** [70]
10	**3**	$HSiEt_3$	$Rh(CO)(PPh_3)_2Cl$[e]	20°, 10 d	**10a** [88]
11	**3**	$HSiEt_3$	$Rh(CO)(PPh_3)_2Cl$[e]	80°, 5 h	**10a** [96]
12	**3**	$HSi(OEt)_3$	$Rh_2Cl_2(C_4H_6)_4$[c]	20°, 10 h	 **10c** [60]
13	 **4**	$HSiEt_3$	$Rh(PPh_3)_3Cl$[c]	50°, 1 h	 **11** [82]
14	**4**	$HSiEt_3$	$Rh_2Cl_2(C_4H_6)_4$[c]	20°, 2 h	**11** [91]

[a] Isolated yield. [b] The ratio of Z-/E-isomers correspond to the time of full conversion of the starting compounds (GC). [c] 0.1 mol % of catalyst. [d] 1 mol % of catalyst. [e] 0.8 mol % of catalyst.

The increase of steric hindrance in methylenecyclopropane **3** due to the presence of two phenyl substituents at the double bond leads to a decrease in the hydrosilylation rate. The reaction of olefin **3** with triethylsilane was examined by varying the catalyst and temperature (Table 1, entries 7−11). The best yield of β-silylated olefin **10a** is achieved in the presence of $Rh(PPh_3)_3Cl$ or $Rh(CO)Cl(PPh_3)_2$ at 80 °C. The catalytic activity of $Rh(CO)Cl(PPh_3)_2$ was lower than that of the Wilkinson catalyst.

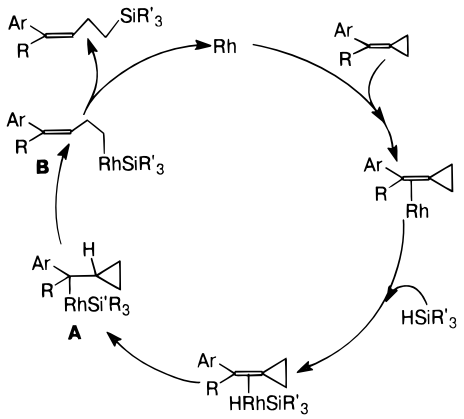
Cyclopropylidenecyclohexane **4**, lacking aryl substituents, is the least reactive of the methylenecyclopropanes examined. This compound fails to react with triethylsilane in the presence of the Wilkinson complex at room temperature, but reacts at 80 °C in 0.5 h to afford a mixture of three silylated olefins in the ratio of 1:1:1 (as measured by ^1H NMR). At lower temperature (50 °C) the hydrosilylation of **4** can be performed selectively with the formation of only **11**.



The use of di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium, which is more effective than the Wilkinson catalyst,[8] promotes the formation of **11** selectively in high yield even at room temperature (Table 1, entry 14).

It is noteworthy that the nature of the silane has no influence on the structure of hydrosilylation products formed from compounds **1**−**3**[9] though the reaction rates and product yields are sensitive to the structure of silane. The reactivity of silanes decreased in the order Et_3SiH

Scheme 1



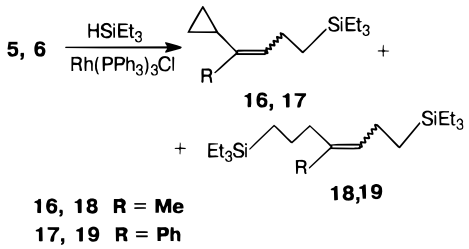
≥ $PhMe_2SiH$ > $(EtO)_3SiH$ ≫ Me_2ClSiH. For example, the hydrosilylation of methylenecyclopropanes **1-3** with Et_3SiH and $PhMe_2SiH$ proceeds at room temperature, but the reaction with less reactive triethoxysilane proceeds only at 80 °C in the presence of the Wilkinson complex (Table 1). Methyldichlorosilane and trichlorosilane fail to react with **1**−**3** even at 80−100 °C in the presence of any of the catalysts utilized.

Some conclusions on the mechanism may be derived from the analysis of the reaction products. For methylenecyclopropanes **1**−**4**, the classic catalytic cycle of Chalk−Harrod[10] can be considered as a background. The (cyclopropylmethyl)rhodium intermediate **A** (see Scheme 1) is formed by the migratory insertion of the C═C bond into the Rh−H bond. We propose, however, that in this case the cyclopropylmethyl−3-butenyl rearrangement of **A** to the open-chain intermediate **B** leads to the C^1-C^2 bond cleavage.

The hydrosilylation of **1**, **2** is not stereoselective because the isomerization of *Z*-isomer of **8a**−**c** and **9a**−**c** to a more stable *E*-isomer **8a**−**c** and **9a**−**c** is observed in the course of the reaction.

The hydrosilylation of compounds **1**−**3** is accompanied by a partial reduction to yield 1-phenyl-1-butene (**13**), 1-(*p*-methoxyphenyl)-1-butene (**14**), and 1,1-diphenyl-1-butene (**15**), correspondingly,[11] although yields do not exceed 5−7% in the case of triethyl- or dimethylphenylsilane. However, the hydrosilylation **3** with the less reactive triethoxysilane in the presence of the Wilkinson catalyst at 80 °C generates reduction product in 43% yield.

The hydrosilylation of cyclopropyl-substituted methylenecyclopropanes **5**−**7** containing several reactive sites is more complicated. The structure of reaction products was found to depend on the silane and catalyst.



Methylenecyclopropanes **5** and **6** react with an excess of triethylsilane in the presence of the Wilkinson complex to produce a mixture of mono- and disilylated alkenes **16**, **18** (in the ratio of 1:1) and **17**, **19** (in the ratio of 1:1), respectively (Table 2). Thus, while ring-opening in the methylenecyclopropane fragment is always observed, a cyclopropane ring may survive the reaction conditions.

We have developed methods for the selective formation of mono- and disilylated olefins. The ratio of mono- and disilylated products is almost independent on the reaction time or temperature,[12] but strongly depends on the nature of silane and ligand in Rh catalyst.

The use of triethylsilane and $Rh(CO)Cl(PPh_3)_2$ as a catalyst produces only disilylsubstituted compounds **18**, **19** in good yields (Scheme 2). Only a selective cleavage of the methylenecyclopropane fragment occurs in the hydrosilylation of compounds **5**, **6** with less reactive triethoxysilane. *β*-Silylated alkenes **20**, **21** were obtained in good yields. The reactions catalyzed by the Wilkinson catalyst and $Rh(CO)Cl(PPh_3)_2$ require elevated temperatures (Table 2). Complex $[(C_4H_6)_2RhCl]_2$ was found to be more efficient catalyst for this transformation and allows the reaction to be performed at room temperature (Table 2, entries 4, 8).

A quite unusual result was obtained in the reaction of (dicyclopropylmethylene)cyclopropane (**7**) with triethylsilane in the presence of the Wilkinson complex (Scheme 2). Two products are formed in this case in the ratio 2.3:1 (GC). They were isolated by distillation and characterized by NMR and elemental analyses data. The former is established to be disilylated olefin **24** (56% yield), in which the methylenecyclopropane moiety remained intact, in contrast to reactions of compounds **5**, **6** (Table 2, entry 9). The second product is trisilylated olefin **23**. The ratio of **24**:**23** is almost constant in the reaction course and independent of the conversion. The compound **24** was shown not to react with triethylsilane in the presence of Wilkinson complex at room temperature. It means that compound **23** did not form *via* **24**, and there are two independent paths of hydrosilylation of methylenecyclopropane **7**.

Conditions for selective hydrosilylation of **7** leading to either of mono- or trisilylated compounds have been established. The use of triethylsilane and $[(C_4H_6)_2RhCl]_2$ as catalyst provides preparation of only trisilylated olefin **23** in 73% yield (Table 2, entry 10). Hydrosilylation of **7** with less reactive triethoxysilane leads to monosilylated product **22** (Table 2, entry 11), analogous to reaction involving compounds **5**, **6**.

For compounds **5**−**7** the reaction seems to include the formation of complexes in which the methylenecyclopropane is coordinated to the rhodium atom at different sites within the molecule, e.g., the double bond, the vinylcyclopropane fragment, or the cyclopropane substituents (in **7**).

Conclusions. The hydrosilylation of methylenecyclopropanes catalyzed by Rh(I) complexes presents a useful preparative route to *β*-silylated olefins. The reaction of cyclopropyl-substituted methylenecyclopropanes may be accomplished selectively to give alkenes containing one, two, or even three silyl groups.

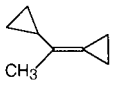
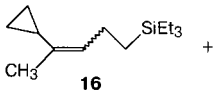
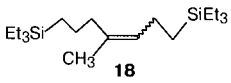
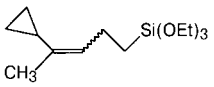
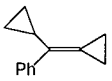
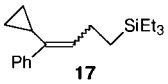
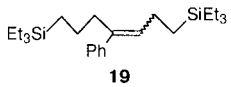
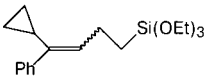
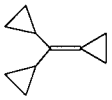
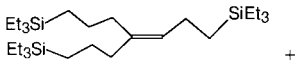
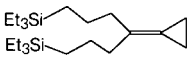
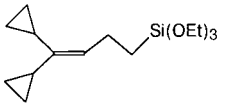
(9) In the hydrosilylation of vinylcyclopropanes the structure of the reaction products depends on the nature of silane.[7]

(10) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16−21.

(11) The structure of the compounds **13**−**15** was determined in comparison with authentic samples prepared by hydrogenation of the methylenecyclopropanes **1**−**3** in the presence of the Wilkinson catalyst.

(12) The amount of more stable isomers of mono- (**16**, **18**) and disilylated (**17**, **19**) olefins increased on prolonged contact with catalyst retained in the reaction mixture, as observed for hydrosilylation of compounds **1**, **2**. The isomerization of the double bond in the final products was also observed in the case of the methyl-substituted methylenecyclopropane **5**.

Table 2. Hydrosilylation of Methylenecyclopropanes 5−7

Entry	Substrate	Silane (Ratio of silane/olefine)	Catalyst	Time and Temp.	Reaction products [Yield[a],%](ratio[b], %)
1	 **5**	$HSiEt_3$ 2.2:1	$Rh(PPh_3)_3Cl$	20°, 3d	 **16** +  **18** [88](50/50)
2	**5**	$HSiEt_3$ 2.2:1	$Rh(PPh_3)_3Cl$	80°, 8h	**16** **18** [89](50/50)
3	**5**	$HSiEt_3$ 5:1	$Rh(CO)(PPh_3)_2Cl$	80°, 3h	**18**[86]
4	**5**	$HSi(OEt)_3$ 3:1	$Rh_2Cl_2(C_4H_6)_4$	20°, 2h	 **20**[78]
5	 **6**	$HSiEt_3$ 5:1	$Rh(PPh_3)_3Cl$	20°, 3d	 **17**  **19** [84](50/50)
6	**6**	$HSiEt_3$ 5:1	$Rh(CO)(PPh_3)_2Cl$	80°,3h	**19**[60]
7	**6**	$HSi(OEt)_3$ 3:1	$Rh(CO)(PPh_3)_2Cl$	80°,5h	 **21**[71]
8	**6**	$HSi(OEt)_3$ 3:1	$Rh_2Cl_2(C_4H_6)_4$	20°, 4d	**21**[81]
9	 **7**	$HSiEt_3$ 5:1	$Rh(PPh_3)_3Cl$	20°, 3d	 **23** +  **24** [80](30/70)
10	**7**	$HSiEt_3$ 5.4:1	$Rh_2Cl_2(C_4H_6)_4$	20°,2h	**23**[73]
11	**7**	$HSi(OEt)_3$ 3.5:1	$Rh_2Cl_2(C_4H_6)_4$	20°, 2h	 **22**[66]

[a] Isolated yield. [b] The ratio of the reaction products correspond to the time of full conversion of the starting compounds (GC).

Experimental Section

General Procedure. All manipulations were carried out under argon using syringe techniques. Solvents were freshly distilled under argon prior to use. Olefins were distilled over CaH_2 and degassed. All starting compounds were no less than 95% pure (by GC analysis). GC analyses were carried out on a Tsvet-530 gas chromatograph (thermoconductivity detector) equipped with packed silicone elastomer SE 30 on Chromaton N-AW column (2 mm × 3 m). Silica gel column chromatography was carried out with silica Silpearl 40/100.

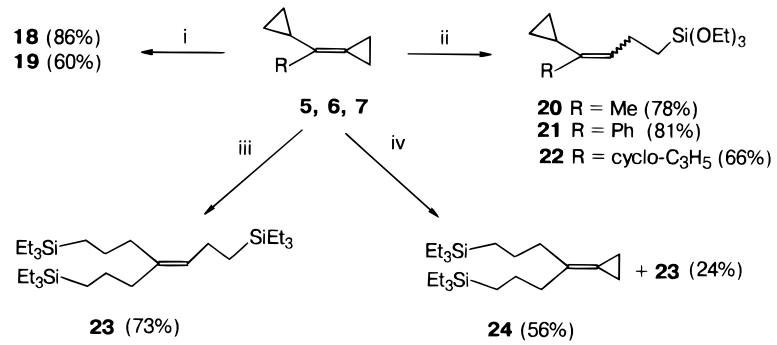
^1H and 13C NMR spectra were recorded on a Varian VXR-400 spectrometer in $CDCl_3$ (internal standard $CHCl_3$) unless otherwise indicated. IR spectra were recorded with a UR-20 infrared spectrometer. The Mass spectrum was recorded on a Finnigan MAT-112S.

Preparation of the Starting Compounds. (Phenylmethylene)cyclopropane (**1**),[13] [(*p*-methoxyphenyl)methylene]cyclopropane (**2**),[14] (diphenylmethylene)cyclopropane (**3**),[13] cyclopropylidenecyclohexane (**4**),[15] (1-methyl-1-cyclopropylmethylene)cyclopropane (**5**),[16] (1-phenyl-1-cyclopropylmethyl-

(13) Utimoto, K.; Tamura, M.; Sisido, K. *Tetrahedron* **1973**, *29*, 1169−1171.

(14) Salaun, J.; Hanack, M. *J. Org. Chem.* **1975**, *40*, 1994−1998.

Scheme 2



i $Rh(PPh_3)_2(CO)Cl$, 0.8 mol%, $HSiEt_3$, 80°C. ii $[(C_4H_6)_2RhCl]_2$, 0.1 mol%, $HSi(OEt)_3$, 20°C.
iii $[(C_4H_6)_2RhCl]_2$, 0.1 mol%, $HSiEt_3$, 20°C. iv $Rh(PPh_3)_3Cl$, 0.1 mol%, $HSiEt_3$, 20°C.

ene)cyclopropane (**6**),[17] and (dicyclopropylmethylene)cyclopropane (**7**)[16] were obtained by means of the reported procedures.

Tris(triphenylphosphine)rhodium chloride[18] and bis(triphenylphosphine)carbonylrhodium chloride[19] were synthesized by means of published standard procedures. Di-μ-chlorotetrakis(η^2-methylenecyclopropane)dirhodium was obtained as in ref 8b.

Hydrosilylation of the Compounds 1−4 Catalyzed by the Wilkinson Complex. (General Procedure). A Schlenk tube equipped with a magnetic stirring bar and a septum was charged with the Wilkinson complex (0.1 mol %) evacuated and filled with argon three times. Anhydrous toluene (10 mL) and silane (5.1 mmol) were added into the reactor via a syringe. The mixture was stirred for 5 min to produce a homogeneous solution. Methylenecyclopropane (5.0 mmol) was added via a syringe. The reaction mixture was stirred under the conditions shown in Table 1 until the starting compounds disappeared. The solvent was evaporated under reduced pressure, and the residue was passed through short column of SiO_2 (eluent hexane) to separate the catalyst. The reaction products were isolated by column chromatography (SiO_2) or distilled in vacuo.

4-(Triethylsilyl)-1-phenyl-1-butene (8a) (a mixture of *Z*-/*E*-isomers in the ratio of 1:3). 8a was prepared as a colorless oil from 0.65 g (5.0 mmol) of **1** and 0.59 g (5.1 mmol) of triethylsilane in 20 h at rt in the yield of 1.17 g (95%). The isomers were isolated by column chromatography (eluent pentane−ethyl acetate 10:1). (***Z*)-8a**: ^{1}H NMR δ 0.57 (6H, q, J = 8.0 Hz), 0.76 (2H, m), 0.98 (9H, t, J = 8.0 Hz), 2.37 (2H, m), 5.75 (1H, dt, J = 11.3 Hz, J = 7.3 Hz), 6.39 (1H, d, J = 11.3 Hz), 7.28 ($1H_p$, m), 7.30 ($2H_o$, m), 7.38 ($2H_m$, m). ^{13}C NMR δ 3.23 (3C), 7.30 (3C), 12.01, 22.77, 126.27, 127.30, 127.99 (2C), 128.60 (2C), 136.12, 137.72. (***E*)-8a**: ^{1}H NMR δ 0.60 (6H, q, J = 8.0 Hz), 0.76 (2H, m), 1.00 (9H, t, J = 8.0 Hz), 2.15 (2H, m), 6.31 (1H, dt, J = 15.7 Hz, J = 6.9 Hz), 6.41 (1H, d, J = 15.7 Hz), 7.21 ($1H_p$, m), 7.32 ($2H_m$, m), 7.39 ($2H_o$, m). ^{13}C NMR δ 3.44 (3C), 7.53 (3C), 11.20, 27.44, 125.98 (2C), 126.74, 128.31, 128.53 (2C), 134.01, 138.10. IR (neat): 740, 1240, 1500, 1600 cm^{-1}. Anal. Calcd for $C_{16}H_{26}Si$: C 77.97; H 10.63. Found: C 77.91; H 10.84.

4-(Dimethylphenylsilyl)-1-phenyl-1-butene (8b) (a mixture of *Z*-/*E*-isomers in the ratio of 1:2). 8b was prepared as a colorless liquid from 1.00 g (7.7 mmol) of **1** and 1.27 g (9.3 mmol) of dimethylphenylsilane in 20 h at rt in the yield of 1.69 g (83%) after distillation: bp 173 °C/2 mmHg. (***Z*)-8b**: ^{1}H NMR δ 0.54 (6H, s), 1.21 (2H, m), 2.51 (2H, m), 5.95 (1H, dt, J = 11.8 Hz, J = 7.4 Hz), 6.58 (1H, d, J = 11.8 Hz), 7.3−7.5 (5H, m), 7.55 (2H, m), 7.73 (3H, m). ^{13}C NMR δ −2.86 (2C), 16.38, 22.94, 126.44, 127.76, 127.83 (2C), 128.15 (2C), 128.75 (2C), 128.96, 133.61 (2C), 135.64, 137.67, 139.05. (***E*)-8b**: ^{1}H NMR δ 0.58 (6H, s), 1.21 (2H, m), 2.62 (2H, m), 6.47 (1H, m), 6.55 (1H, m), 7.3−7.5 (5H, m), 7.55 (2H, m), 7.78 (3H, m). ^{13}C NMR δ −2.95 (2C), 15.46, 27.42, 125.98 (2C), 126.77, 127.86 (2C), 128.50 (2C), 128.61, 128.96, 133.40, 133.65 (2C), 137.95, 139.14. IR (neat): 1250, 1605, 1660 cm^{-1}. Anal. Calcd for $C_{18}H_{22}Si$: C 81.13, H 8.32. Found: C 80.60; H 8.20.

4-(Triethoxysilyl)-1-phenyl-1-butene (8c) (a mixture of *Z*-/*E*-isomers in the ratio of 1:2). 8c was prepared as a colorless liquid from 1.00 g (7.7 mmol) of **1** and 1.38 g (8.4 mmol) of triethoxysilane at 80 °C for 10 h in the yield of 0.93 g (41%) after distillation: bp 95−100 °C/0.05 mmHg. (***Z*)-8c**: ^{1}H NMR δ 0.89 (2H, m), 1.34 (9H, t, J = 7.0 Hz), 2.55 (2H, m), 3.92 (6H, q, J = 7.0 Hz), 5.82 (1H, dt, J = 11.9 Hz, J = 7.2 Hz), 6.48 (1H, d, J = 11.9 Hz), 7.23 ($1H_p$, m), 7.36 ($2H_m$, m), 7.45 ($2H_o$, m). ^{13}C NMR δ 10.87, 18.20 (3C), 21.95, 58.22 (3C), 126.29 (2C), 127.80, 127.85, 127.94 (2C), 134.97, 137.05. (***E*)-8c**: ^{1}H NMR δ 0.92 (2H, m), 1.28 (9H, t, J = 7.0 Hz), 2.43 (2H, m), 3.93 (6H, q, J = 7.0 Hz), 6.38 (1H, dt, J = 15.9 Hz, J = 6.7 Hz), 6.61 (1H, d, J = 15.9 Hz), 7.24 ($1H_p$, m), 7.35 ($2H_m$, m), 7.41 ($2H_o$, m). ^{13}C NMR δ 10.20, 18.20 (3C), 26.21, 58.22 (3C), 125.82 (2C), 126.61, 128.29 (2C), 128.61, 132.71, 137.77. Anal. Calcd for $C_{16}H_{26}O_3Si$: C 65.26; H 8.90; Si 9.54. Found: C 64.85; H 8.60; Si 9.03.

4-(Triethylsilyl)-1-(*p*-methoxyphenyl)-1-butene (9a) (a mixture of *Z*-/*E*-isomers in the ratio of 3:1). 9a was prepared as a colorless oil from 0.80 g (5.0 mmol) of **2** and 0.59 g (5.1 mmol) of triethylsilane at rt for 20 h in the yield of 1.32 g (96%). The isomers were separated by column chromatography (eluent pentane−ethyl acetate 10:1). (***Z*)-9a**: ^{1}H NMR δ 0.57 (6H, q, J = 8.0 Hz), 0.75 (2H, m), 0.98 (9H, t, J = 8.0 Hz), 2.36 (2H, m), 3.85 (3H, s), 5.65 (1H, dt, J = 11.6 Hz, J = 7.2 Hz), 6.31 (1H, d, J = 11.6 Hz), 6.70 (2H, HA,HA′ of AA′BB′, J_{app} = 8.5 Hz), 7.38 (2H, HB,HB′ of AA′BB′, J_{app} = 8.5 Hz). ^{13}C NMR δ 3.32 (3C), 7.48 (3C), 12.14, 22.90, 55.22, 113.53 (2C), 126.81 (2C), 129.89, 130.47, 134.72, 158.11. (***E*)-9a**: ^{1}H NMR δ 0.57 (6H, q, J = 8.0 Hz), 0.65 (2H, m), 0.98 (9H, t, J = 8.0 Hz), 2.15 (2H, m), 3.75 (3H, s), 6.08 (1H, dt, J = 15.9 Hz, J = 6.9 Hz), 6.29 (1H, d, J = 15.9 Hz), 6.75 (2H, HA,HA′ of AA′BB′, J_{app} = 8.5 Hz), 7.20 (2H, HB,HB′ of AA′BB′, J_{app} = 8.5 Hz). ^{13}C NMR δ 3.32 (3C), 7.48 (3C), 11.21, 27.22, 55.24, 113.89 (2C), 126.92 (2C), 127.49, 130.85, 131.88, 158.46. IR (neat): 1250, 1610 1660 cm^{-1}. Anal. Calcd for $C_{17}H_{28}OSi$: C 73.85; H 10.21; Si 10.16. Found: C 74.36; H 10.41; Si 9.42.

4-(Dimethylphenylsilyl)-1-(*p*-methoxyphenyl)-1-butene (9b) (a mixture of *Z*-/*E*-isomers in the ratio of 2:3). 9b was prepared as a colorless oil from 0.40 g (2.5 mmol) of **2** and 0.40 g (3.0 mmol) of dimethylphenylsilane for 10 h at 20 °C in the yield of 0.70 g (88%). The isomers were separated by column chromatography (eluent pentane−ethyl acetate 10:1). (***Z*)-9b**: ^{1}H NMR δ 0.46 (6H, s), 1.19 (2H, m), 2.62 (2H, m), 3.85 (3H, s), 6.38 (1H, m), 6.55 (1H, m), 7.18 (2H, HA,HA′ of AA′BB′, J_{app} = 8.4 Hz), 7.45 (2H, HB,HB′ of AA′BB′, J_{app} = 8.4 Hz), 7.58 (3H, m), 7.68 (2H, m). ^{13}C NMR δ −2.96 (2C), 16.42, 22.91, 55.25, 113.56 (2C), 127.15 (2C), 127.63 (2C),

(15) Schweitzer, E. E.; Berninger, C. J.; Thompson, J. J. *J. Org. Chem.* **1968**, *33*, 336−339.
(16) Akhachinskaya, T. V.; Bakhbukh, M.; Grishin, Yu. K.; Donskaya, N. A.; Ustynyuk, Yu. A. *Zh. Org. Khim.* **1978**, *14*, 2317−2323.
(17) Dunkelblum, E. *Tetrahedron* **1974**, *30*, 3991−3996.
(18) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711−1732.

127.92, 128.84, 130.45, 130.55, 133.64 (2C), 139.16, 158.09. (***E***)-**9b**: ^{1}H NMR δ 0.49 (6H, s), 1.21 (2H, m), 2.44 (2H, m), 3.82 (3H, s), 5.85 (1H, dt, J = 15.9 Hz, J = 7.0 Hz), 6.57 (1H, d, J = 15.9 Hz), 6.95 (2H, HA,HA′ of AA′BB′, J_{app} = 8.4 Hz), 7.52 (2H, HB,HB′ of AA′BB′, J_{app} = 8.4 Hz), 7.58 (3H, m), 7.68 (2H, m). ^{13}C NMR δ −2.89 (2C), 15.58, 27.35, 55.25, 113.93 (2C), 127.02, 127.83, 128.92 (2C), 129.91 (2C), 130.77, 130.93, 133.64 (2C), 139.26, 158.63.

4-(Triethoxysilyl)-1-(*p*-methoxyphenyl)-1-butene (9c) (a mixture of *Z*-/*E*-isomers in the ratio of 1:5). **9c** was obtained as a colorless oil from 2.50 g (15.6 mmol) of **2** and 3.28 g (20.0 mmol) of triethoxysilane at 80 °C for 50 h in the yield of 3.29 g (65%) after distillation: bp 130−132 °C/0.05 mmHg. (***Z***)-**9c**: ^{1}H NMR δ 0.66 (2H, m), 1.20 (9H, t, J = 7.0 Hz), 2.43 (2H, m), 3.77 (3H, s), 3.80 (6H, q, J = 7.0 Hz), 5.61 (1H, dt, J = 12.0 Hz, J = 7.1 Hz), 6.28 (1H, d, J = 12.0 Hz), 6.82 (2H, HA,HA′ of AA′BB′, J_{app} = 8.4 Hz), 7.20 (2H, HB,HB′ of AA′BB′, J_{app} = 8.4 Hz). ^{13}C NMR δ 11.13, 18.34 (3C), 22.87, 55.32, 58.36 (3C), 113.54 (2C), 127.34, 129.25 (2C), 129.95, 133.30, 158.18. (***E***)-**9c**: ^{1}H NMR δ 0.81 (2H, m), 1.22 (9H, t, J = 7.0 Hz), 2.30 (2H, m), 3.81 (3H, s), 3.82 (6H, q, J = 7.0 Hz), 6.14 (1H, dt, J = 15.7 Hz, J = 6.6 Hz), 6.31 (1H, d, J = 15.7 Hz), 6.81 (2H, HA,HA′ of AA′BB′, J_{app} = 8.4 Hz), 7.25 (2H, HB,HB′ of AA′BB′, J_{app} = 8.4 Hz). ^{13}C NMR δ 10.45, 18.34 (3C), 26.26, 55.32, 58.36 (3C), 113.87 (2C), 127.00 (2C), 128.13, 129.35, 130.71, 158.69.

4-(Triethylsilyl)-1,1-diphenyl-1-butene (10a) was obtained from 0.50 g (2.4 mmol) of **3** and 0.29 g (2.5 mmol) triethylsilane at rt for 65 h in the yield of 0.65 g (84%) after the column chromatography (eluent pentane−ethyl acetate 10:1): ^{1}H NMR δ 0.47 (6H, q, J = 8.0 Hz), 0.69 (2H, m), 0.88 (9H, t, J = 8.0 Hz), 2.11 (2H, m), 5.85 (1H, t, J = 7.6 Hz), 7.21 (2H, m), 7.28 (4H, m), 7.39 (4H, m). ^{13}C NMR δ 3.37 (3C), 7.50 (3C), 12.09, 24.17, 126.75, 126.90, 127.27 (2C), 128.15 (2C), 128.18 (2C), 130.00 (2C), 133.07, 140.08, 140.28, 142.96. IR (neat): 730, 1240, 1610 cm^{-1}.

4-(Triethoxysilyl)-1,1-diphenyl-1-butene (10c) and 1,1-Diphenyl-1-butene (15) (a mixture 4:5). The reaction of 0.42 g (2.0 mmol) of **3** with 0.34 g (2.2 mmol) of triethoxysilane at 80 °C for 40 h leads to a mixture of **10c** and **15**. They were separated by column chromatography (eluent pentane) and distilled.

4-(Triethoxysilyl)-1,1-diphenyl-1-butene (10c). Yield of **10c** was 0.25 g (34%): bp 142−143 °C/0.01 mmHg. ^{1}H NMR δ 0.83 (2H, m), 1.23 (9H, t, J = 7.0 Hz), 2.27 (2H, m), 3.79 (6H, q, J = 7.0 Hz), 6.20 (1H, t, J = 7.5 Hz), 7.2−7.4 (10H, m). ^{13}C NMR δ 11.08, 18.35 (3C), 23.16, 58.40 (3C), 126.47, 126.82, 127.29 (2C), 128.12 (2C), 128.20 (2C), 130.00 (2C), 132.06, 140.17, 140.64, 142.83. IR (neat): 710, 770, 1090, 1115, 1600, 1665, 1715 cm^{-1}.

1,1-Diphenyl-1-butene (15). Yield of **15** was 0.18 g (43%): bp 132−133 °C/8 mmHg. The spectral characteristics coincided with the authentic sample.

[2-(Triethylsilyl)propylidene]cyclohexane (11). **11** was prepared from 0.60 g (4.9 mmol) of **4** and 0.58 g (5.0 mmol) of triethylsilane at 50 °C for 1 h in the yield of 0.97 g (82%) after distillation: bp 54−55 °C/3 mmHg. ^{1}H NMR δ 0.54 (6H, q, J = 8.0 Hz), 0.59 (2H, m), 0.96 (9H, t, J = 8.0 Hz), 1.54 (6H, m), 2.01 (2H, m), 2.07 (2H, m), 2.14 (2H, m), 5.13 (1H, t, J = 7.4 Hz). ^{13}C NMR δ 3.44 (3C), 7.46 (3C), 12.27, 21.27, 27.06, 27.84, 28.58, 28.63, 37.18, 124.80, 137.86.

At room temperature the starting compounds remain unchanged. The catalyst was transformed into an insoluble orange complex.

Three isomeric olefins (^{1}H NMR data) are formed at 80 °C for 0.5 h: bp 54−56 °C/3 mmHg. Identification of isomers was not carried out.

Hydrogenation of 1−3 Catalyzed by the Wilkinson Complex. (General Procedure). A Schlenk tube equipped with the septum was charged with the Wilkinson complex (2 mol %) evacuated and filled with hydrogen three times. Then anhydrous benzene (10 mL) was placed into the reactor via a syringe. The mixture was stirred to produce a homogeneous solution. Then methylenecyclopropane (5.0 mmol) was added. The reaction mixture was stirred at room temperature until the starting compound disappeared. The solvent was evaporated under reduced pressure, and the residue was passed through short column with SiO_2 to separate the catalyst. The reaction products were isolated by column chromatography (eluent pentane) or distillation in vacuo.

***(E)*-1-Phenyl-1-butene (13).**[5,20] **13** was prepared from 0.55 g (4.2 mmol) of **1** and isolated in 44% yield by column chromatography (eluent pentane) from a mixture with butylbenzene. ^{1}H NMR δ 1.11 (3H, t, J = 7.4 Hz), 2.25 (2H, m), 6.29 (1H, dt, J = 15.7 Hz, J = 6.6 Hz), 6.43 (1H, d, J = 15.7 Hz), 7.20 (1H, m), 7.33 (4H, m); ^{13}C NMR δ 13.66, 26.07, 125.88 (2C), 126.73, 128.45 (2C), 128.75, 132.64, 137.91.

1-(*p*-Methoxyphenyl)-1-butene (14)[5,21] **(a mixture of *Z*-/*E*-isomers in the ratio of 1:4).** **14** was prepared from 0.1 g (0.5 mmol) of **2** and isolated in 50% yield by column chromatography (eluent pentane−ethyl acetate 10:1) from a mixture with *p*-buthylanisole. (***Z***)-**14** ^{1}H NMR δ 1.08 (3H, t, J = 7.4 Hz), 2.36 (2H, m), 3.83 (3H, s), 5.59 (1H, dt, J = 11.6 Hz, J = 7.1 Hz), 6.34 (1H, d, J = 11.6 Hz), 6.85 (2H, HA,HA′ of AA′BB′, J_{app} = 8.4 Hz), 7.22 (2H, HB,HB′ of AA′BB′, J_{app} = 8.4 Hz). ^{13}C NMR δ 14.60, 22.02, 55.34, 113.56 (2C), 127.68, 129.95 (2C), 130.40, 133.20, 158.16. (***E***)-**14** ^{1}H NMR δ 1.10 (3H, t, J = 7.4 Hz), 2.23 (2H, m), 3.82 (3H, s), 6.17 (1H, dt, J = 15.9 Hz, J = 7.0 Hz), 6.34 (1H, d, J = 15.9 Hz), 6.83 (2H, HA,HA′ of AA′BB′, J_{app} = 8.5 Hz), 7.30 (2H, HB,HB′ of AA′BB′, J_{app} = 8.4 Hz). ^{13}C NMR δ 13.86, 26.10, 55.29, 113.93 (2C), 127.00 (2C), 128.14, 130.55, 130.81, 158.61.

1,1-Diphenyl-1-butene (15).[5,22] **15** was prepared from 0.50 g (2.4 mmol) of **3** for 20 h in quantitative yield: bp 110 °C/1 mmHg. ^{1}H NMR δ 1.02 (3H, t, J = 7.3 Hz), 2.11 (2H, m), 6.06 (1H, t, J = 7.0 Hz), 7.25 (10H, m). ^{13}C NMR δ 14.51, 23.18, 126.72, 126.82, 127.21 (2C), 128.04 (2C), 128.09 (2C), 129.89 (2C), 131.71, 140.24, 140.97, 142.82.

Hydrosilylation of 5−7 Catalyzed by the Wilkinson Complex. (General Procedure). A Schlenk tube equipped with magnetic stirrer and a septum was charged with the Wilkinson complex (0.8 mol %) and then evacuated and filled with argon three times.

Anhydrous toluene (10 mL) and silane (25.0 mmol) were introduced via syringe. The mixture was stirred for 5 min to produce a homogeneous solution. Then methylenecyclopropane (5.0 mmol) was added. The reaction mixture was stirred under the conditions shown in Table 2 until the starting compounds disappeared. The solvent was evaporated under reduced pressure, the residue was passed through short column of SiO_2 (eluent hexane) to remove the catalyst. The reaction products are isolated by column chromatography or distillation in vacuo.

5-(Triethylsilyl)-2-cyclopropyl-2-pentene (16) and 1,7-Bis(triethylsilyl)-4-methyl-3-heptene (18). **16** and **18** were obtained in the ratio 1:1 from 0.30 g (3.0 mmol) of **5** and 0.80 g (7.0 mmol) of triethylsilane for 3 d at rt in overall yield of 1.0 g (88%). The reaction mixture was distilled. The compounds **16** and **18** were additionally purified by column chromatography (eluent hexane).

5-(Triethylsilyl)-2-cyclopropyl-2-pentene (16) (a mixture of *Z*-/*E*-isomers in the ratio of 1:4). Bp 134 °C/14 mmHg. (***Z***)-**16** ^{1}H NMR δ 0.51 (4H, m), 0.52 (6H, q, J = 8.0 Hz), 0.63 (2H, m), 0.93 (9H, t, J = 8.0 Hz), 1.39 (3H, m), 1.64 (1H, m), 2.15 (2H, m), 5.26 (1H, t, J = 6.9 Hz). ^{13}C NMR δ 3.40 (3C), 3.83 (2C), 7.45 (3C), 11.95, 12.19, 18.77, 21.63, 129.36, 132.91. (***E***)-**16** ^{1}H NMR δ 0.42 (2H, m), 0.51 (2H, m), 0.52 (6H, q, J = 8.0 Hz), 0.58 (2H, m), 0.94 (9H, t, J = 8.0 Hz), 1.34 (1H, m), 1.49 (3H, m), 2.00 (2H, m), 5.23 (1H, t, J = 6.8 Hz). ^{13}C NMR δ 3.40 (3C), 4.09 (2C), 7.45 (3C), 11.79, 13.76, 18.68, 22.08, 126.57, 133.76.

1,7-Bis(triethylsilyl)-4-methyl-3-heptene (18) (a mixture of *Z*-/*E*-isomers in the ratio of 1:7). Bp 135 °C/2 mmHg. (***Z***)-**18** ^{1}H NMR δ 0.51 (6H, q, J = 8.0 Hz), 0.52 (4H,

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m), 0.52 (6H, q, J = 8.0 Hz), 0.93 (9H, t, J = 8.0 Hz), 0.94 (9H, t, J = 8.0 Hz), 1.35 (2H, m), 1.56 (3H, m), 2.00 (4H, m), 5.16 (1H, t, J = 6.9 Hz) ^{13}C NMR δ 3.48 (3C), 3.54 (3C), 7.58 (6C), 11.51, 12.35, 22.11, 22.51, 23.47, 35.96, 128.91, 133.75. (***E***)**-18** ^{1}H NMR δ 0.51 (6H, q, J = 8.0 Hz), 0.52 (2H, m), 0.52 (6H, q, J = 8.0 Hz), 0.58 (2H, m), 0.93 (9H, t, J = 8.0 Hz), 0.94 (9H, t, J = 8.0 Hz), 1.35 (2H, m), 1.65 (3H, m), 2.00 (4H, m), 5.19 (1H, t, J = 7.0 Hz). ^{13}C NMR δ 3.48 (3C), 3.54 (3C), 7.58 (6C), 11.09, 11.95, 15.78, 22.27, 29.87, 44.02, 128.11, 133.54.

Hydrosilylation of **5** at 80 °C for 8 h leads to the formation of a mixture (1:1) of **16 (a mixture of *Z*-/*E*-isomers in the ratio of 1:1)** and **18 (a mixture of *Z*-/*E*-isomers in the ratio of 1:9)** in 89% yield.

4-(Triethylsilyl)-1-cyclopropyl-1-phenyl-1-butene (17) and 1,7-Bis(triethylsilyl)-4-phenyl-3-heptene (19). A mixture of **17** and **19** in the ratio of 1:1 was prepared from 0.51 g (3.0 mmol) of **6** and 1.74 g (15.0 mmol) of triethylsilane for 3 d at rt in 84% overall yield. The reaction mixture was distilled.

4-(Triethylsilyl)-1-cyclopropyl-1-phenyl-1-butene (a mixture of *Z*-/*E*-isomers in the ratio of 1:1) (17). Yield of **17** was 0.32 g (37%): bp 109−110 °C/0.01 mmHg. (***Z***)**-17** ^{1}H NMR δ 0.42 (6H, q, J = 8.0 Hz), 0.55 (2H, m), 0.64 (4H, m), 0.85 (9H, t, J = 8.0 Hz), 1.57 (1H, m), 1.90 (2H, m), 5.48 (1H, t, J = 6.9 Hz), 7.18−7.35 (5H, m). ^{13}C NMR δ 3.27 (3C), 5.15 (2C), 7.36 (3C), 12.11, 18.31, 23.06, 126.44, 127.81 (2C), 128.74, 128.77 (2C), 140.08, 140.51. (***E***)**-17** ^{1}H NMR δ 0.30 (2H, m), 0.58 (6H, q, J = 8.0 Hz), 0.64 (2H, m), 0.72 (2H, m), 0.98 (9H, t, J = 8.0 Hz), 1.71 (1H, m), 2.39 (2H, m), 5.74 (1H, t, J = 6.8 Hz), 7.18−7.35 (5H, m). ^{13}C NMR δ 3.41 (3C), 6.56 (2C), 7.51 (3C), 11.33, 11.54, 22.69, 126.06, 127.22 (2C), 127.69 (2C), 135.02, 138.81, 142.75.

1,7-Bis(triethylsilyl)-4-phenyl-3-heptene (a mixture of *Z*-/*E*-isomers in the ratio of 1:2) (19). Yield of **19** was 0.57 g (47%): bp 168−170 °C/0.01 mmHg. (***Z***)**-19** ^{1}H NMR δ 0.44 (6H, q, J = 8.0 Hz), 0.47 (6H, q, J = 8.0 Hz), 0.52 (2H, m), 0.60 (2H, m), 0.87 (9H, t, J = 8.0 Hz), 0.89 (9H, t, J = 8.0 Hz), 1.32 (2H, m), 1.94 (2H, m), 2.35 (2H, t, J = 7.5 Hz), 5.48 (1H, t, J = 7.3 Hz), 7.14 (2H$_o$, m), 7.21 (1H$_p$, m), 7.36 (2H$_m$, m). ^{13}C NMR δ 3.29 (6C), 7.37 (3C), 7.45 (3C), 10.77, 12.27, 22.28, 23.08, 43.07, 126.20,127.86 (2C), 128.36 (2C), 130.58, 139.25, 141.42. (***E***)**-19** ^{1}H NMR δ 0.48 (6H, q, J = 8.0 Hz), 0.53 (4H, m), 0.58 (6H, q, J = 8.0 Hz), 0.89 (9H, t, J = 8.0 Hz), 0.99 (9H, t, J = 8.0 Hz), 1.70 (2H, m), 2.22 (2H, m), 2.52 (2H, t, J = 7.5 Hz), 5.72 (1H, t, J = 7.1 Hz), 7.14 (2H$_o$, m), 7.23 (1H$_p$, m), 7.33 (2H$_m$, m). ^{13}C NMR δ 3.32 (3C), 3.40 (3C), 7.42 (3C), 7.51 (3C), 11.39, 12.01, 22.90, 29.74, 33.79, 126.27 (3C), 128.10 (2C), 132.43, 138.39, 143.43. Anal. Calcd for $C_{25}H_{46}Si_2$: C 74.55, H 11.51. Found: C 73.78, H 11.80.

[Bis[3-(triethylsilyl)propyl]methylene]cyclopropane (24) and 4-[3-(triethylsilyl)propyl]-1,7-bis(triethylsilyl)-3-heptene (23). A mixture of **24** and **23** in the ratio of 2.3:1 was obtained from 1.15 g (8.6 mmol) of **7** and 4.86 (42.0 mmol) of triethylsilane for 3 d at rt in 80% overall yield. The reaction mixture was distilled.

[Bis[3-(triethylsilyl)propyl]methylene]cyclopropane (24). Yield was **24** was 1.75 g (56%): bp 139−140 °C/0.02 mmHg; ^{1}H NMR δ 0.51 (12H, q, J = 8.0 Hz), 0.61 (4H, m), 0.91 (18H, t, J = 8.0 Hz), 0.99 (4H, m), 1.52 (4H, m), 2.15 (4H, t, J = 7.6 Hz). ^{13}C NMR δ 1.97 (2C), 3.40 (6C), 7.49 (6C), 11.47 (2C), 22.28 (2C), 39.20 (2C), 114.97, 128.31; IR (neat): 1020, 1240, 1610, 1780 cm^{-1}. Anal. Calcd for $C_{22}H_{46}Si_2$: C 72.24, H 12.60, Si 15.29. Found: C 72.04, H 12.64, Si 15.31.

4-[3-(Triethylsilyl)propyl]-1,7-bis(triethylsilyl)-3-heptene (23). Yield of **23** was 0.99 g (24%): bp 180−182 °C/0.01 mmHg; ^{1}H NMR δ 0.50 (4H, m), 0.51 (12H, q, J = 8.0 Hz), 0.52 (6H, q, J = 8.0 Hz), 0.59 (2H, m), 0.93 (18H, t, J = 8.0 Hz), 0.94 (9H, t, J = 8.0 Hz), 1.37 (4H, m), 1.92 (2H, m), 2.02 (4H, m), 5.15 (1H, t, J = 6.9 Hz); 13C NMR δ 3.56 (3C), 3.60 (6C), 7.58 (9C), 11.40, 11.82, 12.45, 22.15, 22.83, 23.13, 34.48, 41.47, 128.60, 137.86. IR (neat): 1175, 1240, 1615, 1670 cm^{-1}. Anal. Calcd for $C_{28}H_{62}Si_3$: C 69.62, H 12.94, Si 17.44. Found: C 70.18, H 12.51, Si 16.94.

Hydrosilylation Catalyzed by Di-μ-chlorotetrakis[η^2-methylenecyclopropane]dirhodium. A Schlenk tube equipped with a magnetic stirrer and the septum was evacuated and filled with argon three times. Then anhydrous pentane (5 mL), the freshly prepared complex (0.1 mol %), and silane (5.0−20.0 mmol) were placed in the tube by means of a syringe. The mixture was stirred for 5 min to produce a homogeneous solution. Then methylenecyclopropane (5.0 mmol) was added. The reaction mixture was stirred at room temperature until the starting compounds disappeared. The solvent was evaporated under reduced pressure, and the residue was distilled in vacuo or passed through short column with SiO_2 (eluent hexane).

4-(Triethoxysilyl)-1,1-diphenyl-1-butene (10c). 10c was prepared from 0.40 g (2.0 mmol) of **3** and 0.33 g (2.0 mmol) of triethoxysilane for 10 h in the yield 0.44 g (60%).

[[2-(Triethylsilyl)propylidene]cyclohexane (11). 11 was prepared from 0.61 g (5.0 mmol) of **4** and 1.16 g (10.0 mmol) of triethylsilane for 2 h in the yield of **11** of 1.08 g (91%).

5-(Triethoxysilyl)-2-cyclopropyl-2-pentene (20) (a mixture of *Z*-/*E*-isomers in the ratio of 1:2). 20 was prepared from 1.54 g (14.0 mmol) of **5** and 7.05 g (43.0 mmol) of triethoxysilane for 2 h in the yield of 2.98 g (78%): bp 104−106 °C/1 mmHg. (***Z***)**-20** ^{1}H NMR δ 0.54 (2H, m), 0.61 (2H, m), 0.77 (2H, m), 1.26 (9H, t, J = 7.0 Hz), 1.42 (3H, m), 1.69 (1H, m), 2.28 (2H, m), 3.86 (6H, q, J = 7.0 Hz), 5.29 (1H, t, J = 6.9 Hz). ^{13}C NMR δ 3.62 (2C), 10.81, 11.98, 18.08 (3C), 18.60, 20.46, 58.02 (3C), 128.23, 133.16. (***E***)**-20** ^{1}H NMR δ 0.45 (2H, m), 0.56 (2H, m), 0.72 (2H, m), 1.26 (9H, t, J = 7.0 Hz), 1.37 (1H, m), 1.51 (3H, m), 2.15 (2H, m), 3.85 (6H, q, J = 7.0 Hz), 5.27 (1H, t, J = 6.9 Hz). ^{13}C NMR δ 3.88 (2C), 10.67, 13.54, 18.08 (3C), 18.49, 20.90, 58.02 (3C), 125.39, 134.06. IR (neat): 1090, 1120, 1660, 1720 cm^{-1}.

4-(Triethoxysilyl)-1-cyclopropyl-1-phenyl-1-butene (21) (a mixture of *Z*-/*E*-isomers in the ratio of 1:2). 21 was prepared from 0.40 g (2.3 mmol) of **6** and 1.15 g (7.0 mmol) of triethoxysilane for 4 d in the yield of 0.64 g (81%): bp 109−111 °C/0.05 mmHg. (***Z***)**-21** ^{1}H NMR δ 0.45 (2H, m), 0.63 (2H, m), 0.69 (2H, m), 1.20 (9H, t, J = 7.0 Hz), 1.60 (1H, m), 2.03 (2H, m), 3.75 (6H, q, J = 7.0 Hz), 5.54 (1H, t, J = 6.9 Hz), 7.18 (2H$_o$, m), 7.24 (1H$_p$, m), 7.35 (2H$_m$, m). ^{13}C NMR δ 5.06 (2C), 11.18, 18.24 (3C), 18.33, 22.10, 58.22 (3C), 126.45, 127.74 (2C), 127.83 (2C), 128.82, 140.26, 140.83. (***E***)**-21** ^{1}H NMR δ 0.34 (2H, m), 0.82 (2H, m), 0.86 (2H, m), 1.29 (9H, t, J = 7.0 Hz), 1.76 (1H, m), 2.56 (2H, m), 3.90 (6H, q, J = 7.0 Hz), 5.79 (1H, t, J = 6.9 Hz), 7.18 (2H$_o$, m), 7.27 (1H$_p$, m), 7.32 (2H$_m$, m). ^{13}C NMR δ 6.59 (2C), 10.61, 11.35, 18.34 (3C), 21.78, 58.37 (3C), 126.13, 127.21 (2C), 127.67 (2C), 134.00, 139.47, 142.46. IR (neat): 1080, 1115, 1230, 1600, 1620, 1640 cm^{-1}. Mass spectrum (EI, 70 eV) m/z: 334 (2%) (M$^+$), 163 (100%), 135 (29%), 131 (15%), 119 (60%), 115 (42%), 107 (18%), 91 (31%), 79 (66%).

4-(Triethoxysilyl)-1,1-dicyclopropyl-1-butene (22). 22 was prepared from 0.50 g (3.7 mmol) of **7** and 2.13 g (13.0 mmol) of triethoxysilane for 2 h in the yield of 0.74 g (66%): bp 91−93 °C/0.05 mmHg; ^{1}H NMR δ 0.23 (2H, m), 0.42 (2H, m), 0.56 (2H, m), 0.65 (2H, m), 0.66 (2H, m), 0.85 (1H, m), 1.17 (9H, t, J = 7.0 Hz), 1.58 (1H, m), 2.20 (2H, m), 3.78 (6H, q, J = 7.0 Hz), 5.10 (1H, t, J = 6.7 Hz); ^{13}C NMR δ 4.33 (2C), 4.66 (2C), 10.84, 12.33, 12.74, 18.23 (3C), 20.52, 59.23 (3C), 125.94, 138.25. IR (neat): 1090, 1130, 1600, 1660, 1730 cm^{-1}.

4-[3-(Triethylsilyl)propyl]-1,7-bis(triethylsilyl)-3-heptene (23). 23 was prepared from 0.50 g (3.7 mmol) of **7** and 2.32 g (20.0 mmol) of triethylsilane for 2 h in the yield of 1.31 g (73%).

Hydrosilylation of 5−7 Catalyzed by Rh(CO)(PPh$_3$)$_2$Cl. (General Procedure). A Schlenk tube equipped with a magnetic stirring bar and a septum was charged with the Rh(CO)(PPh$_3$)$_2$Cl (0.8 mol %), evacuated, and filled with argon three times. Then anhydrous toluene (10 mL) and silane (25.0 mmol) were added into the reactor via a syringe. The mixture was stirred for 5 min to produce a homogeneous solution. Methylenecyclopropane (5.0 mmol) was added via a syringe. The reaction mixture was stirred at 80 °C until the starting compounds disappeared. The solvent was evaporated under reduced pressure, and the residue was distilled in vacuo or passed through column with SiO_2.

4-(Triethylsilyl)-1,1-diphenyl-1-butene (10a). 10a was obtained from 0.31 g (1.5 mmol) of **3** and 1.16 g (3.7 mmol) triethylsilane at room temperature for 10 d in the yield of 0.42

g (88%). It was refined by column chromatography (eluent pentane−ethyl acetate 10:1).

4-(Triethylsilyl)-1,1-diphenyl-1-butene (10a). 10a was obtained from 0.10 g (0.05 mmol) of **3** and 0.15 g (1.25 mmol) of triethylsilane at 80 °C for 5 h in the yield of 0.15 g (96%).

1,7-Bis(triethylsilyl)-4-methylhept-3-ene (18) (a mixture of *Z*-/*E*-isomers in the ratio of 1:4). 18 was prepared from 0.78 g (7.2 mmol) of **5** and 5.77 mL (36.0 mmol) of triethylsilane at 80 °C for 3 h in the yield of 2.1 g (86%), 90% purity (GC), after passing through a short column with SiO_2 (eluent pentane).

1,7-Bis(triethylsilyl)-4-phenyl-3-heptene (19) (a mixture of *Z*-/*E*-isomers in the ratio of 1:1). 19 was prepared from 0.51 g (3.0 mmol) of **6** and 1.74 g (15.0 mmol) of triethylsilane for 3 h at 80 °C in the yield of 0.73 g (60%): bp 168−170 °C/0.01 mmHg.

4-(Triethoxysilyl)-1-cyclopropyl-1-phenyl-1-butene (21) (a mixture of *Z*-/*E*-isomers in the ratio of 1:1). 21 was prepared from 0.40 g (2.4 mmol) of **6** and 1.15 g (7.0 mmol) of triethoxysilane for 5 h at 80 °C in the yield of 0.56 g (71%): bp 121−122 °C/0.1 mmHg.

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Supporting Information Available: Tables and copies of ^{1}H NMR and ^{13}C spectra for compounds **8b**, **8c**, **9b**, **9c**, **10a**, **10c**, **11**, **16**, **17**, **18**, **20**-**22** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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