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Silyl Group Transfer from Allylsilanes to Olefins Catalyzed by a Ruthenium(II) Complex

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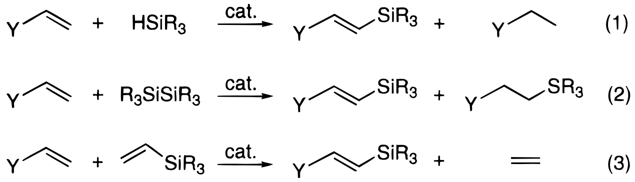
Summary: Dehydrogenative silylation of olefins, such as styrenes, methyl acrylate, and vinyl ether, using allyltriethoxysilane as the source of the silyl group can be catalyzed by $RuHCl(CO)(PPh_3)_3$ *to give the corresponding vinylsilanes in good to excellent yields. The ruthenium complex also catalyzed the self-dehydrogenative silylation of allylsilanes, yielding 1,3-bis(triorganosilyl)-propenes.*

Due to the fact that vinylsilanes are important synthetic intermediates in organic synthesis,[1] several synthetic methods have been reported.[2] Among these methods, hydrosilylation of acethylenes is the most popular. Recently, the direct synthesis of vinylsilanes from olefins, the so-called dehydrogenative silylation of olefins, has attracted a great deal of attention as a synthetic method of vinylsilanes, since olefins are usually inexpensive compared with acetylenes. This strategy offers considerable potential as a convenient, useful synthetic method. In this paper, we wish to describe a new approach to the dehydrogenative silylation reaction of olefins using allylsilanes as the source of the organosilyl group.[3]



Three methods have been reported for transition-metal-catalyzed dehydrogenative silylation reactions of olefins. In one case, a dehydrogenative silylation of olefins was carried out using hydrosilanes (eq 1).[4,5] In 1980, we reported the first example of the exclusive formation of vinylsilanes using triorganosilanes.[5a] Since then, a number of catalytic reactions of olefins with hydrosilanes giving rise to vinylsilanes as well as saturated addition products have been reported,[4] but those which give rise to vinylsilanes exclusively are still rare.[4e,5] In the second method, a disilane was employed as a silylating reagent in place of triorganosilanes (eq 2).[6] The only example of this reaction are those reported by Tanaka and co-workers. Finally, a vinylsilane can be used as a silylating reagent (eq 3).[5e,7,8] This type of

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(1) For reviews on the synthetic utility of vinylsilanes, see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Ager, D. J. *Chem. Soc. Rev.* **1982**, *11*, 493. Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 2, Chapter 9.1. Parnes, Z.; Bolestova, G. I. *Synthesis* **1984**, 991. Colvin, E. W. In *Silicon Reagents in Organic Synthesis*; Academic: London, 1988, Chapter 3. Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K.,1989; Chapter 14. Armitage, D. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 2, Chapter 1.

(2) For reviews on the synthesis of vinylsilanes, see: (a) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis via Metal Carbonyl*, 2nd ed.; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; p 673. (b) Lappert, M. F.; Nile, T. A.; Takahashi, S. *Adv. Organomet. Chem.* **1974**, *12*, 425. (c) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253. (d) Lukevics, E. *Russ. Chem. Rev.* (*Engl. Transl.*) **1977**, *46*, 264. (e) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Libr.* **1977**, *5*, 1. (f) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (g) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 25. (h) Corey, J. Y. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI Press: Greenwich, CT, 1991; pp 327−387.

(3) A part of the present paper has been reported; see: Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S. *Abstracts of Papers*, 74th Annual Meeting of Chemical Society of Japan, Tanabe, Kyoto; Chemical Society of Japan: Tokyo, 1997; Abstract 4D829.

(4) For examples of the dehydrogenative silylation of olefins using triorganosilanes, see: (a) Millan, A.; Towns, E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 673. (b) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101. (c) Millan, A.; Fernandez, M. J.; Bentz, P.; Maitlis, P. M. *J. Mol. Catal.* **1984**, *26*, 89. (d) Cornish, A. J.; Lappert, M. F. *J. Organomet. Chem.* **1984**, *271*, 153. (e) Ojima, I,; Fuchikami, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, *260*, 335. (f) Onopchenko, A.; Sbourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389. (g) Oro, L. A.; Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S. *J. Mol. Catal.* **1986**, *37*, 151. (h) Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S.; Oro, L. A. *Organometallics* **1986**, *5*, 1519. (i) Fernández, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreda, M.-C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1987**, *6*, 1751. (j) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. (k) Hori, Y.; Mitsudo, T.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3011. (l) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. (m) Kesti, M. R.; Abdulrahman, M.; Waymouth, R. M. *J. Organomet. Chem.* **1991**, *417*, C12. (n) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128. (o) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (p) Doyle, M. P.; Devora, G. A.; Nefedov, A. O.; High, K. G. *Organometallics* **1992**, *11*, 549. (q) Corey, J. Y.; Zhu, X.-H. *Organometallics* **1992**, *11*, 672. (r) Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095. (s) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1995**, *14*, 1082. (t) Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098. See also ref 4.

(5) (a) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 928. (b) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1193. (c) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, M. *J. Org. Chem.* **1986**, *51*, 3890. (d) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1987**, *52*, 4864. (e) Seki, Y.; Takeshita, K.; Kawamoto, K. *J. Organomet. Chem.* **1989**, *369*, 117. (f) Kakiuchi, F.; Tanaka, Y.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **1993**, *456*, 45. (g) Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748.

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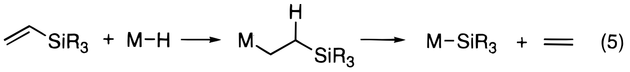
catalytic reaction has been studied by ourselves,[5e] as well as Wakatsuki's,[7] and Mercianic's groups.[8,9]

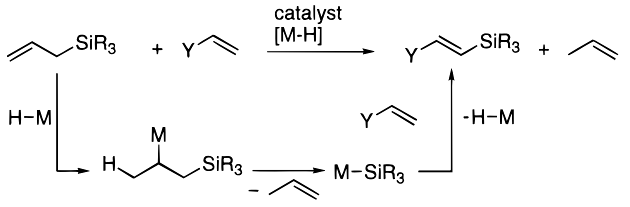
In the dehydrogenative silylation reaction, the generation of a silyl−metal species is a key step. In the cases of the reactions using hydrosilanes and disilanes as the silylating reagents, a silyl−metal species is generated via the oxidative addition of an Si−H or Si−Si bond to a metal center (eq 4).[4−6] When vinylsilanes were subjected to the dehydrogenative silylation reaction, the required silyl−metal species is formed through the addition of an M−H bond to the vinylsilane, followed by a β-silyl group elimination sequence (eq 5).[5e,7,8]

$$R_3Si{-}X + M \longrightarrow R_3Si{-}M{-}X \qquad (4)$$
$$X = H,\ SiR_3$$

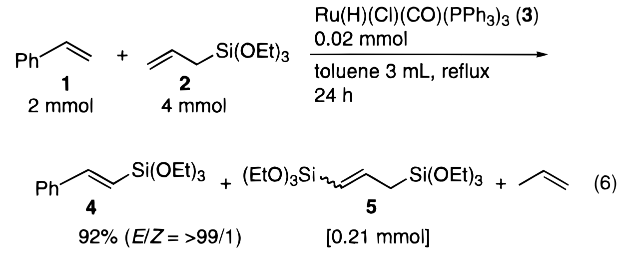


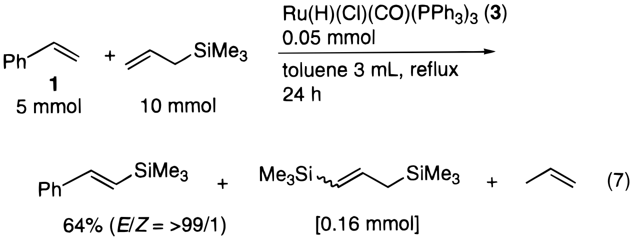
We expected that allylsilanes might also function as a silylating reagent, on the basis of our working hypothesis, which is shown in Scheme 1. Therefore, if the metal binds to an internal carbon of the allylsilane in the hydrometalation step,[10] the β-silyl group elimination can occur in the next step, leading to the desired silyl−metal species.

Scheme 1. Working Hypothesis of Dehydrogenative Silylation of Olefins Using Allyltriorganosilanes



To examine our working hypothesis, we examined the reaction of styrene (**1**) with allyltriethoxysilane (**2**) in the presence of RuHCl(CO)(PPh$_3$)$_3$ (**3**) as a catalyst under reaction conditions as shown in eq 6. The ruthenium complex is known to catalyze a silyl group transfer from vinylsilanes to olefins.[7] As anticipated, the silyl transfer from the allylsilane to styrene proceeded smoothly to give the corresponding vinylsilane (*E*)-β-(triethoxysilyl)styrene (**4**)[5c,11] in 92% yield along with a small amount of 1,3-bis(triethoxysilyl)propene[8i,j] (**5**; 0.21 mmol), which is a self-dehydrogenative silylation product of the allylsilane (vide infra). The bis(silyl)propene can be removed easily by silica gel column chromatography. The formation of the byproduct propene was confirmed by its trapping with bromine to give 1,2-dibromopropane. During the catalytic reaction, nitrogen gas was passed slowly into the refluxing reaction mixture and the gases introduced into a solution of Br$_2$ in CCl$_4$. The GC analysis of the reaction mixture showed that the vinylsilane **4** was obtained in 64% GC yield,[12] and the ^{1}H NMR spctrum of the CCl$_4$ solution indicated that 1,2-dibromopropane was formed in 54% NMR yield. Allyltrimethylsilane can also be substituted for **2** as the source of the silyl group. Allyltrimethylsilane was subject to the RuHCl(CO)(PPh$_3$)$_3$-catalyzed silylation reaction of styrene, resulting in a formation of the corresponding β-silylstyrene in 64% yield (eq 7).





The present catalytic reaction can be applied to several olefins, and some selected results are listed in Table 1. The reaction of 4′-chlorostyrene gave the corresponding silylated product in 97% yield with high stereoselectivity (E:Z = 99:1), even though a C−Cl bond is susceptible to cleavage by transition-metal complexes.[13] The reactions of styrenes having an electron-donating methyl or methoxy group also gave 1-(4-methylphenyl)-2-(triethoxysilyl)ethene (entry 2, 89% yield) and 1-(4-methoxyphenyl)-2-(triethoxysilyl)ethene[14] (entry 3, 64% yield), respectively. It is interesting to note that butyl vinyl ether, which is an ineffective olefin for the dehydrogenative silylation reaction with triorganosilanes, reacted with **2** to give the desired vinylsilane in 49% yield (entry 4). An electron-deficient olefin is also applicable to the present reaction. The reaction of

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(6) Hayashi, T.; Kawamoto, A. M.; Kobayashi, T.-A.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1990**, 563.

(7) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1995**, *500*, 349. Mise, T.; Takaguxhi, Y.; Umemiya, T.; Shimizu, S.; Wakatsuki, Y. *Chem. Commun.* **1998**, 699.

(8) (a) Marciniec, B.; Guliñski, J. *J. Organomet. Chem.* **1984**, *266*, C19. (b) Marciniec, B.; Maciejewski, H.; Guliñski, J.; Rzejak, L. *J. Organomet. Chem.* **1989**, *362*, 273. (c) Foltynowicz, Z.; Marciniec, B.; Pietraszuk, C. *J. Mol. Catal.* **1991**, *65*, 113. (d) Marciniec, B.; Pietraszuk, C. *J. Organomet. Chem.* **1991**, *412*, C1. (e) Marciniec, B.; Pietraszuk, C.; Pietraszuk, C. *J. Mol. Catal.* **1992**, *76*, 307. (f) Marciniec, B.; Pietraszuk, C. *J. Organomet. Chem.* **1993**, *447*, 163. (g) Foltynowicz, Z.; Pietraszuk, C.; Marciniec, B. *Appl. Organomet. Chem.* **1993**, *7*, 539. (h) Marciniec, B.; Pietraszuk, C.; Foltynowicz, Z. *J. Organomet. Chem.* **1994**, *474*, 83. (i) Marciniec, B.; Foltynowicz, Z.; Lewandowski, M. *J. Mol. Catal.* **1994**, *90*, 125. (j) Marciniec, B.; Foltynowicz, Z.; Pietraszuk, C.; Gulinski, J.; Maciejewski, H. *J. Mol. Catal.* **1994**, *90*, 213. (k) Marciniec, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003. (l) Marciniec, B.; Petraszuk, C. *Organometallics* **1997**, *16*, 4320.

(9) Marciniec and co-workers initially claimed that the dehydrogenative silylation of olefins proceeds through a transition-metal-catalyed cross olefin metathesis pathway.

(10) If the hydrometalation of olefin occurs in the opposite direction, i.e., the metal binds with the terminal carbon of the allylsilane, β-silyl elimination cannot take place. In this case, the starting allylsilane regenerates through β-hydride elimination.

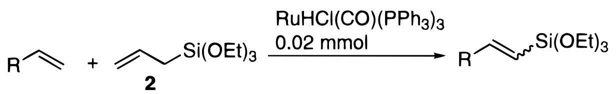
(11) Lewis, L. N.; Sy, K. G.; Bryant, G. L., Jr.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.

(12) The propene trapping experiment causes the slight decrease in the yield of the vinylsilane **4**.

(13) For examples, see the following reviews: Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047. de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379.

(14) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286.

Table 1. Dehydrogenative Silylation of Olefins with 2[a]

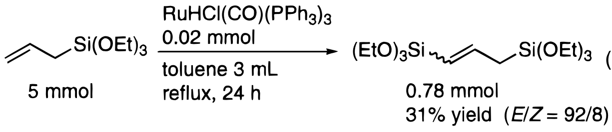


entry no.	R	time, h	yield, %[b,c]	yield of bis(silyl)propene, mmol[d]
1	4-ClC$_6$H$_4$	36	97 (99:1)	0.17
2	4-MeC$_6$H$_4$	36	89 (99:1)	0.19
3	4-MeOC$_6$H$_4$	48	64 (99:1)	0.09
4	BuO	48	49 (87:13)	0.06
5	MeOC=O	24	18 (93:7)	0.02

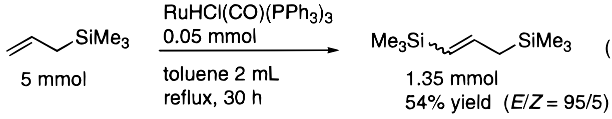
[a] Reaction conditions: olefin (2 mmol), **2** (4 mmol), toluene (3 mL), reflux. [b] GC yield. [c] Values in parentheses are *E*:*Z* ratios determined by GC. [d] 1,3-Bis(triethoxysilyl)propene.

methyl acrylate with **2** provided (*E*)-3-(triethoxysilyl)-2-propenoic acid methyl ester[5a,d] in 18% yield.

In all runs shown in Table 1, 1,3-bis(triethoxysilyl)propene was formed as the byproduct. This suggests that the allylsilanes function not only as silylating reagents but also as acceptors of the silyl group. On the basis of this observation, we carried out a self-dehydrogenative silylation of the allylsilanes. The expected silylated products, 1,3-bis(triorganosilyl)propenes, have unique structures for both the allylsilane and the vinylsilane moieties. Both of these moieties are useful in organic synthesis.[1,15] The self-dehydrogenative silylation of allyltriorganosilane took place under the reaction conditions shown in eqs 8 and 9. The reactions afforded the corresponding (*E*)- and (*Z*)-1,3-bis(triorganosilyl)propenes in good yields (31% (0.78 mmol) and 54% (1.35 mmol) yields, respectively).



(8)



(9)

In the reactions mentioned above, the key step is the generation of silyl−metal species via *β*-silyl group elimination. As a prototype of the present reaction, we have already demonstrated a silyl group exchange reaction of allyltrimethylsilane with diethylmethylsilane catalyzed by Co$_2$(CO)$_8$.[16] Recently, Brookhart and coworkers demonstrated the generation of a triphenylsilyl−palladium complex via the stoichiometic reaction of an allyltriphenylsilane with a triethylsilyl−palladium complex.[17] The result of this stoichiometric reaction indicates that the elimination of the *β*-silyl group from the allylsilane, to give the silyl−metal species, is an easy step.

In conclusion, this note reports a new route for the synthesis of vinylsilanes from olefins using allylsilanes. Allylsilanes function as a silylating reagent of olefins in the same manner as hydrosilanes and vinylsilanes. Both electron-rich and electron-deficient olefins can be used in the present reaction. The self-dehydrogenative silylation of allyltriorganosilanes affords 1,3-bis(triorganosilyl)propenes in moderate yields.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of nitrogen. Toluene was dried over CaH$_2$ and distilled under a nitrogen atmosphere. Allysilanes were dried over CaH$_2$ and distilled. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer operating at 270 and 67.5 MHz, respectively. The chemical shifts of the ^{1}H NMR and ^{13}C NMR signals are quoted relative to CHCl$_3$ (δ 7.26 and 77.0) or tetramethylsilane as internal standards. The ^{1}H NMR data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constants in Hz, relative intensity, and interpretation. ^{13}C NMR data are reported as follows: chemical shifts in ppm (δ). IR spectra were measured on a Hitachi 270-50 infrared spectrometer. GC-MS analyses were obtained using a Shimadzu GCMS-QP 5000 gas chromatograph−mass spectrometer.

Reaction of Allyltriethoxysilane with Styrene. General Procedure. The preparation of (*E*)-1-phenyl-2-(triethoxysilyl)ethene[5c,11] represents a typical example. A 10 mL two-necked flask equipped with a reflux condenser, a rubber septum cap, and a magnetic stirring bar was flame-dried three times by vacuum−nitrogen flow cycles, and nitrogen was then charged in the flask. RuHCl(CO)(PPh$_3$)$_3$ (0.02 mmol) was placed in the flask, and the solid was then dissolved in 3 mL of toluene. To this resulting solution were added allyltriethoxysilane (4 mmol), styrene (2 mmol), and hexadecane. The flask was evacuated until the solution just began to boil and then refilled to atmospheric pressure with nitrogen. This procedure was repeated three times. The solution was then refluxed for 24 h with stirring. Analysis of the reaction mixture by GC (hexadecane as a internal standard) showed the presence of (*E*)-1-phenyl-2-(triethoxysilyl)ethene (**4**) in 92% yield. The product was isolated by silica gel column chromatography (35 mm i.d. × 80 mm length; eluent 1/20 AcOEt/hexane) in 84% yield.

1-(4-Chlorophenyl)-2-(triethoxysilyl)ethene. The product was isolated by bulb-to-bulb distillation. ^{1}H NMR (CDCl$_3$): 1.26 (t, $J = 7.1$ Hz, 9 H), 3.87 (q, $J = 7.1$ Hz, 6 H), 6.14 (d, $J = 19.3$ Hz, 1 H), 7.15 (d, $J = 19.3$ Hz, 1 H), 7.31 (d, $J = 8.3$ Hz, 2 H), 7.40 (d, $J = 8.3$ Hz, 2 H). ^{13}C NMR (CDCl$_3$): 18.24, 58.62, 118.62, 127.94, 128.69, 134.39, 136.06, 147.60; IR (neat, cm^{-1}): 1076 (ν(C−O)). MS (EI, *m*/*z*): 300 (M$^+$, 12%). Anal. Calcd for C$_{14}$H$_{21}$ClO$_3$Si: C, 55.89; H, 7.04. Found: C, 55.95; H, 7.09.

1-(4-Methylphenyl)-2-(triethoxysilyl)ethene. The product was isolated by bulb-to-bulb distillation. ^{1}H NMR (CDCl$_3$): 1.27 (t, $J = 6.9$ Hz, 9 H), 2.35 (s, 3 H), 3.88 (q, $J = 6.9$ Hz, 6 H), 6.10 (d, $J = 19.1$ Hz, 1 H), 7.15 (d, $J = 7.9$ Hz, 2 H), 7.19 (d, $J = 19.1$ Hz, 1 H), 7.37 (d, $J = 7.9$ Hz, 2 H). ^{13}C NMR (CDCl$_3$): 18.24, 21.24, 58.55, 116.23, 126.70, 129.22, 134.93, 138.72, 149.06. IR (neat, cm^{-1}): 1076 (ν(C−O)). MS (EI, *m*/*z*): 280 (M$^+$, 10%). Anal. Calcd for C$_{15}$H$_{24}$O$_3$Si: C, 64.24; H, 8.64. Found: C, 64.24; H, 8.97.

Butyl (*E*)-2-(Triethoxysilyl)ethenyl Ether and Butyl (*Z*)-2-(Triethoxysilyl)ethenyl Ether. The product was isolated by bulb-to-bulb distillation as a mixture of *E* and *Z* isomers. ^{1}H NMR (CDCl$_3$; *E* isomer): 0.93 (t, $J = 7.3$ Hz, 3

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[15] Blumenkopf, T. A.; Overman, L. E. *Chem. Rev.* **1986**, *86*, 857. Colvin, E. W. In *Silicon Reagents in Organic Synthesis*; Academic: London, 1988, Chapter 5. Schinzer, D. *Synthesis* **1988**, 263. Sarkar, T. K. *Synthesis* **1990**, 1101. Sarkar, T. K. *Synthesis* **1990**, 969.

[16] Kodama, T.; Kajikawa, Y.; Murakami, H.; Ohe, K.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *Abstracts of Papers*, 36th Symposium on Organometallic Chemistry, Japan, Kinki Chemical Society: Osaka, Japan; 1989; Abstract PB119.

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H), 1.23 (t, $J = 7.1$ Hz, 9 H), 1.40 (qt, $J = 7.3$ Hz, 7.3 Hz, 2 H), 1.63 (tt, $J = 6.6$ Hz, 7.3 Hz, 2 H), 3.82 ($J = 7.3$ Hz, 6 H), 4.26 (d, $J = 15.7$ Hz, 1 H), 6.76 (d, $J = 15.7$ Hz, 1 H). ^{13}C NMR ($CDCl_3$; *E* isomer): 13.71, 18.51, 19.10, 30.95, 58.33, 67.93, 85.21, 161.00. ^{1}H NMR ($CDCl_3$; *Z* isomer): 0.93 (t, $J = 7.3$ Hz, 3 H), 1.23 (t $J = 7.1$ Hz, 9 H), 1.40 (qt, $J = 7.3$, 7.3 Hz, 2 H), 1.63 (tt, $J = 6.6$, 7.3 Hz, 2 H), 3.82 ($J = 7.3$ Hz, 6 H), 4.04 (d, $J = 8.64$ Hz, 1 H), 6.71 (d, $J = 8.64$ Hz, 1 H). ^{13}C NMR ($CDCl_3$; *Z* isomer): 13.71, 18.51, 18.83, 31.79, 58.19, 72.51, 89.49, 162.03. IR (neat, cm^{-1}): 1100, 1077 (ν(C−O)). MS (EI, *m*/*z*): 262 (M^+, 2%). Anal. Calcd for $C_{12}H_{26}O_4Si$ (mixture of *E* and *Z* isomers): C, 54.92; H, 9.99. Found: C, 54.94; H, 10.08.

(*E*)-3-(Triethoxysilyl)-2-propenoic acid Methyl Ester.[5a,d] ^{1}H NMR ($CDCl_3$): 1.24 (t, $J = 7.02$ Hz, 9 H, CH_3), 3.77 (s, 3 H, OCH_3), 3.84 (q, $J = 7.02$ Hz, 6 H, CH_2), 6.50 (d, $J = 18.9$ Hz, 1 H, SiCH═), 6.91 (d, $J = 18.9$ Hz, 1 H, CH═). ^{13}C NMR ($CDCl_3$): 18.15, 51.79, 58.78, 137.86, 138.06, 166.02. IR (neat, cm^{-1}): 1735 cm^{-1} (ν(C═O)). MS (EI, *m*/*z*): 233 ($M^+ - 15$, 22%), 203 ($M^+ - 45$, 100%).

Trapping of Propene with Br_2 in the Reaction of Allyltriethoxysilane with Styrene. A 30 mL three-necked flask equipped with a reflux condenser, a rubber septum cap, a nitrogen bubbling tube, and a magnetic stirring bar was flushed with nitrogen and then was flame-dried under a flow of nitrogen. The reflux condenser was connected to the second flask, containing a CCl_4 (10 mL) solution of Br_2 (0.2 mL, ca. 4 mmol). In the reaction flask was placed $RuHCl(CO)(PPh_3)_3$ (0.02 mmol), which was then dissolved in 3 mL of toluene. To the resulting solution were added allyltriethoxysilane (4 mmol), styrene (2 mmol), and hexadecane. Nitrogen gas was flowed slowly into the reaction mixture with stirring under toluene refluxing conditions. After the reaction mixture was refluxed for 24 h, GC analysis indicated that (*E*)-1-phenyl-2-(triethoxysilyl)ethene (**4**) was formed in 64% yield. To the CCl_4 solution was added 1,1,2,2-tetrachloroethane as an NMR internal integration standard. The ^{1}H NMR spectrum of the CCl_4 solution showed that 1,2-dibromopropane was formed in 54% yield (1.07 mmol), based on styrene.

Reaction of Allyltrimethylsilane with Styrene. A 10 mL two-necked flask equipped with a reflux condenser, a rubber septum cap, and a magnetic stirring bar was flame-dried three times by vacuum−nitrogen flow cycles, and nitrogen was then charged in the flask. $RuHCl(CO)(PPh_3)_3$ (0.05 mmol) was placed in the flask, and the solid was then dissolved in 3 mL of toluene. To this resulting solution was added allyltriethoxysilane (10 mmol), styrene (5 mmol), and tetradecane. The solution was then refluxed for 24 h with stirring. Analysis of the reaction mixture by GC (tetradecane as a internal standard) showed (*E*)-1-phenyl-2-(trimethylsilyl)ethene in 64% yield. A bulb-to-bulb distillation of the reaction mixture (80 °C/3 mmHg) afforded a pure sample.

Self-Dehydrogenative Silylation of Allyltriethoxysilane. A 10 mL two-necked flask equipped with a reflux condenser, a rubber septum cap, and a magnetic stirring bar was flame-dried three times by vacuum−nitrogen flow cycles, and nitrogen was then charged in the flask. $RuHCl(CO)(PPh_3)_3$ (0.02 mmol) was placed in the flask, and the solid was then dissolved in 3 mL of toluene. To this resulting solution was added allyltriethoxysilane (5 mmol) and hexadecane. The flask was evacuated until the solution just began to boil and was then refilled to atmospheric pressure with nitrogen. This procedure was repeated three times. The solution was refluxed for 24 h with stirring. Analysis of the reaction mixture by GC (hexadecane as a internal standard) showed the presence of 1,3-bis(triethoxysilyl)propene [8i,j] (*E*/*Z* = 92/8) in 31% GC yield (0.78 mmol). A bulb-to-bulb distillation of the reaction mixture (120 °C/10 mmHg) afforded a pure sample. ^{1}H NMR ($CDCl_3$; *E* isomer): 1.22 (t, $J = 7.08$ Hz, 18 H, CH_3), 1.83 (dd, $J = 7.96$, 1.22 Hz, 2 H, CH_2), 3.81 (q, $J = 7.08$ Hz, 12 H, OCH_2), 5.23 (dt, $J = 18.6$, 1.22 Hz, 1 H, SiCH═), 6.44 (dt, $J = 18.6$, 7.96 Hz, CH═). ^{13}C NMR ($CDCl_3$; *E* isomer): 18.21, 22.36, 55.33, 58.60, 119.25, 148.12. MS (EI, *m*/*z*): 163 ($Si(OEt)_3$, 100%). IR (neat, cm^{-1}): 1100, 1076 (ν(C−O)). Anal. Calcd for $C_{15}H_{34}Si_2O_6$ (mixture of *E* and *Z* isomers): C, 49.15; H, 9.35. Found: C, 48.96; H, 9.37.

Self-Dehydrogenative Silylation of Allyltrimethylsilane. A 10 mL two-necked flask equipped with a reflux condenser, a rubber septum cap, and a magnetic stirring bar was flame-dried three times by vacuum−nitrogen flow cycles, and nitrogen was then charged in the flask. $RuHCl(CO)(PPh_3)_3$ (0.05 mmol) was placed in the flask, and the solid was then dissolved in 2 mL of toluene. To this resulting solution was added allyltrimethylsilane (5 mmol) and tetradecane. The solution was refluxed for 30 h with stirring. Analysis of the reaction mixture by GC (hexadecane as a internal standard) showed the presence of 1,3-bis(trimethylsilyl)propene[18] (*E*/*Z* = 95/5) in 54% yield (1.35 mmol). ^{1}H NMR ($CDCl_3$): −0.01 (s, 9 H, $Si\mathit{Me}_3CH_2$), 0.03 (s, 9 H, $SiMe_3$), 1.62 (dd, $J = 7.83$, 1.08 Hz, 2 H, CH_2), 5.43 (dt, $J = 18.6$, 1.08 Hz, 1 H, $CH_2C\mathit{H}$═), 6.02 (dt, $J = 18.6$, 7.83 Hz, 1 H, CH═).

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