Rh(I)-Catalyzed Dehydrogenative Silylation of Divinylsilanes with Dimethylphenylsilane

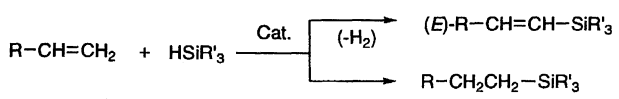
Yukio Kawanami and Keiji Yamamoto*

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152

(Received December 11, 1995)

Rh(I)-catalyzed dehydrogenative silylation was selectively carried out by using divinylsilanes and half an equimolar amount of trialkylsilanes under ambient conditions to give 1,2-disilylethene and ethylvinylsilane derivatives in equimolar amounts. The mechanistic aspects for the dehydrogenative silylation were discussed in terms of the consecutive migratory insertions of the alkene moiety into both Rh–Si and Rh–H bonds which are formed by an oxidative addition of the hydrosilane to the Rh(I) catalyst precursor.

The electrophilic substitution of alkenylsilanes, such as the aliphatic Friedel–Crafts reactions, is one of the most versatile methods for the stereoselective synthesis of functionally substituted alkenes.[1,2] The preparative method for the requisite alkenylsilanes includes homogeneous hydrosilylation of alkynes, which gives rise preferably to *E*-stereochemistry. However, the common Pt-catalyzed hydrosilylation of terminal alkynes sometimes encounters difficulty in controlling the regio- and stereoselectivity in the alkenylsilane.[3] Recently, complete control of the selectivity has been achieved by cationic rhodium complex-catalyzed hydrosilylation of 1-alkyne with triethylsilane.[4] On the other hand, dehydrogenative silylation of 1-alkenes would be an attractive means to obtain certain 1-alkenylsilanes, provided that the rigorous control be possible not contaminated by the conventional hydrosilylation of the alkene employed (Eq. 1). Therefore, much effort has been paid for the conditions in terms of the suitable combination of a hydrosilane, an alkene substrate, and a catalyst, for the highly selective dehydrogenative silylation of alkenes to take place. Murai and his co-workers have found that the catalyst precursors such as $Ru_3(CO)_{12}$[5] or $Fe_3(CO)_{12}$[6] and $Co_2(CO)_8$[7] are particularly effective for the dehydrogenative silylation of styrenes and acrylates, respectively. Despite ample examples of less selective dehydrogenative silylation reported by using simple Rh(I) or Ir(I) complexes, the reaction of 1,5-dienes with diethylmethylsilane catalyzed by $RhCl(PPh_3)_3$ was found to give exclusively the dehydrogenative silylation product instead of the usual hydrosilylation product.[8,9] However, the mechanistic divide into either dehydrogenative silylation or hydrosilylation as indicated in Eq. 1 appears to be controversial and to require further study.



(1)

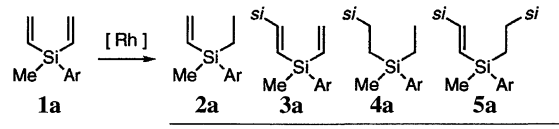
During a course of our study on an attempted desymmetrization of divinylsilanes by way of Rh(I)-catalyzed hydrosilylation using dimethylphenylsilane, we have observed an exclusive formation of 1,2-disilylethene derivative, a product of the dehydrogenative silylation. Although the choice of divinylsilanes as substrates is fortuitous, it appears necessary for elucidating the mechanistic aspects of Rh(I)-catalyzed dehydrogenative silylation. Here we wish to report a clean control to the dehydrogenative silylation of divinylsilanes and related allylvinylsilanes catalyzed by Rh(I) complexes, the crucial conditions for the control being the molar ratio of the substrate to the hydrosilane more than two.[10]

Results and Discussion

We have observed selective dehydrogenative silylation when a solution of methyl(*o*-tolyl)divinylsilane (**1a**), a half equimolar amount of Me_2PhSiH, and $[Rh(dppb)(cod)]ClO_4$# (0.2 mol% based on **1a**) in CH_2Cl_2 was allowed to react at r.t. for 1 h, the result being tabulated in Table 1, Entry 1. When an equimolar amount of Me_2PhSiH to the substrate **1a** was added under otherwise the same conditions, both dehydrogenative silylation products and hydrosilylation products were formed (Table 1, Entry 2). All major products (**2a**, **3a**, **4a**, and **5a**) were isolated by preparative GLC and identified as indicated unambiguously by their respective spectral data (see Experimental Section). There were found two minor products, (*E*)-1-(dimethylphenylsilyl)-2-[ethylmethyl(*o*-tolyl)silyl]ethene (**6a**) and [2-(dimethylphenylsilyl)ethyl]methyl(*o*-tolyl)vinylsilane (**7a**). Then, by employing excess (twice or three times) amounts of Me_2PhSiH, we have obtained essentially the same results that indicate the formation of **4a** and **5a**, in addition to a little **6a** and the double hydrosilylation product from **1a**, bis[2-(dimethylphenylsilyl)eth-

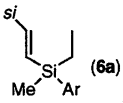
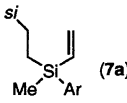
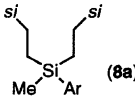
#dppb: 1,4-Bis(diphenylphosphino)butane, cod: 1,5-Cyclooctadiene.

Table 1. Effect of Relative Amount of Me_2PhSiH on the Dehydrogenative Silylation of **1a**[a)]



1a **2a** **3a** **4a** **5a**

Entry	Me_2PhSiH/equiv	Composition/%[b)]				
		2a	**3a**	**4a**	**5a**	Others
1	0.5	49	49	2	Trace	—
2	1.1	30	15	15	19	**6a**,[c)] 8: **7a**,[d)] 4
3	2.0	—	Trace	45	40	**8a**,[e)] 9
4	3.0	—	Trace	44	38	**8a**, 12

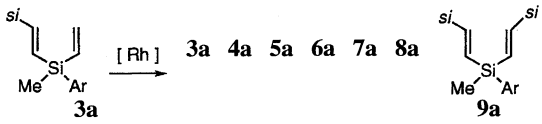
a) Conditions: **1a** (1 mmol), Me_2PhSiH, and [Rh(dppb)(cod)]ClO_4 (0.2 mol% based on **1a**) in CH_2Cl_2 (0.25 mL) at r. t. (Ar=*o*-Tolyl; *si*=Me_2PhSi). Reaction time 12 h except for Entry 1 (1 h). b) GLC peak areas. Well correspond to the relative integration in ^1H NMR of methyl signals of *o*-tolyl group in the product mixture. c)  (**6a**)  (**7a**)  (**8a**)

yl]methyl(*o*-tolyl)silane (**8a**), in a significant yield (Table 1, Entries 3 and 4).

It is worthy of mentioning that dihydrogen arising from, at best formally, the formation of **3a** was exclusively taken up with **1a** to give **2a** in an equimolar amount and that no hydrogen transfer to **3a** in an *intramolecular* mode took place at all. This is also the case in the selective dehydrogenative silylation of 1,5-hexadiene.[8)] It appears evident that the stoichiometry between divinylsilane **1a** and Me_2PhSiH requires exactly 2 : 1 for the selective dehydrogenative silylation, and that the second half an equimolar Me_2PhSiH to **1a** reacts quite differently to give rise to hydrosilylation products, **4a** from **2a**, **5a** from **3a**, and **7a** from **1a**, respectively (see Entry 2). Such consecutive hydrosilylations became even clear by using excess Me_2PhSiH, giving **4a**, **5a**, and **8a** with complete consumption of **2a** and **3a** (and **1a**), respectively (Entries 3 and 4). All these results strongly suggest that the observed Rh(I)-catalyzed hydrosilylation of any alkene substrate that concerns must proceed slower than the Rh(I)-catalyzed dehydrogenative silylation of **1a**, except for the formation of **8a**. In fact, the reaction given in Entry 1 was found to complete in 1 h, whereas other entries seemed to require ca. 12 h for completion of hydrosilylation.

In order to look at any insight into the mechanistic aspects discussed above, a similar Rh(I)-catalyzed reaction of **3a** with Me_2PhSiH was carried out. In Table 2 are summarized composition of products detected. As is seen from Table 2, Entry 1, in which a deficient amount of Me_2PhSiH was used, the extent of hydrosilylation of **3a** to form **5a** apparently surpassed that of dehydrogenative silylation to form **9a** (and **6a**). However, it is emphasized that the detection of **9a** is indicative of the rapid dehydrogenative silylation to take place, despite the use of sterically more hindered **3a** than **1a** as a substrate. The dehydrogenative silylation of **3a** was indeed favored when excess 1-hexene (5 equiv) was added to the reaction mixture with slow addition of one equivalent Me_2PhSiH (Table 2, Entry 2). Product **9a** became principal with concomitant formation of **6a** and hexane at the

Table 2. Effect of Relative Amount of Me_2PhSiH on the Dehydrogenative Silylation of **3a**[a)]



3a **3a** **4a** **5a** **6a** **7a** **8a** **9a**

Entry	Me_2PhSiH/equiv	Composition/%[b)]						
		3a	**4a**	**5a**	**6a**	**7a**	**8a**	**9a**
1	0.5	30	1	37	14	4	4	10
2[c)]	1.0	2	1	20	27	4	—	45

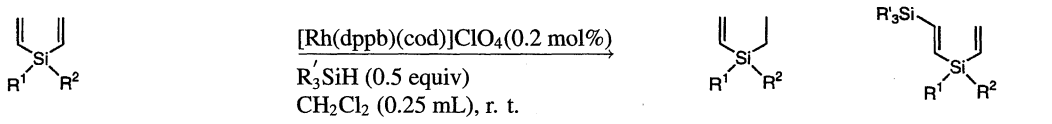
a) Conditions: See Table 1, footnote a. Reaction time 12 h. (Ar=*o*-Tolyl; *si*=Me_2PhSi). b) GLC peak areas. c) Additive 1-hexene (5 equiv) and slow addition of Me_2PhSiH.

expense of decreasing **5a**. No significant amount of hexylsilane derivative was detected in this particular case. Thus, all results described here may be rationalized by considering the fact that the Rh(I)-catalyzed dehydrogenative silylation of either divinylsilane **3a** or **1a** precedes the closely related Rh(I)-catalyzed hydrosilylation of these substrates (vide infra).

The Rh(I)-catalyzed, selective dehydrogenative silylation of **1a** could be carried out by using half an equimolar hydrosilane other than Me_2PhSiH, such as Et_3SiH, *t*-$BuMe_2SiH$, and $(EtO)_3SiH$. All reactions were found to proceed more or less slowly, giving the corresponding 1,2-disilylethene derivatives (**3a′**—**3a‴**) in moderate yields. Particularly, the sluggish reaction of **1a** with *t*-$BuMe_2SiH$ required heating at 60 °C. The results are given in Table 3. The selective dehydrogenative silylation of dimethyldivinylsilane (**1b**) and diphenyldivinylsilane (**1c**) as well as **1a** was readily carried out to give 1,2-disilylethene derivatives **3b** and **3c**, respectively, in good isolated yield under the standard conditions that is given in Table 1, Entry 1. The reaction of **1c** required a prolonged reaction time, presumably because of the steric reason. The results are also summarized in Table 3.

Divinylsilanes were not necessarily of choice for the present Rh(I)-catalyzed dehydrogenative silylation. Thus, allyldimethylvinylsilane (**10**) underwent, under the standard

Table 3. Rh(I)-Catalyzed Dehydrogenative Silylation of Divinylsilanes (**1**) with Me_2PhSiH

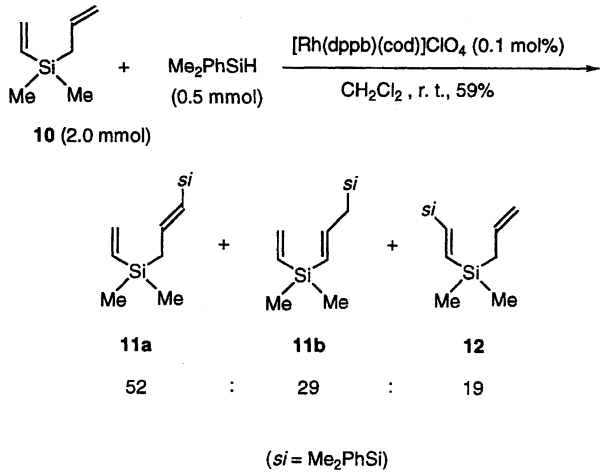


1a-c **2a-c** **3a-c**

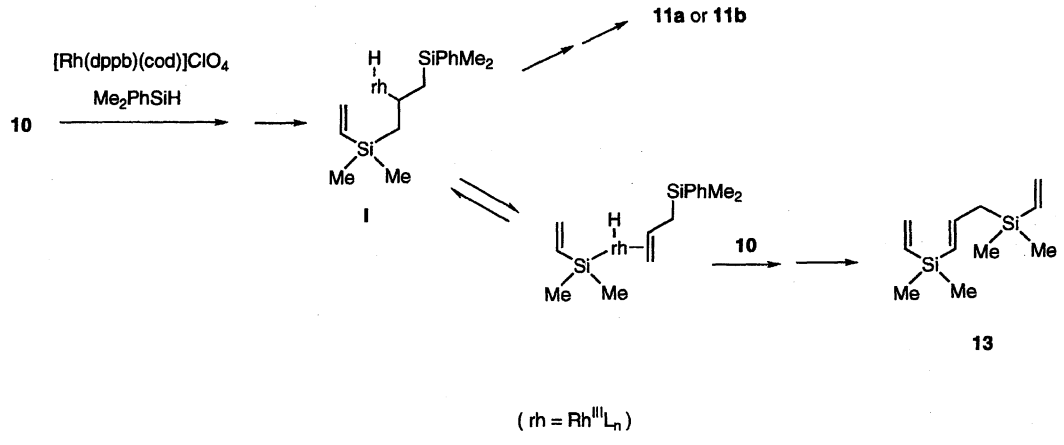
Divinylsilane R^1, R^2	Hydrosilane R'_3SiH	Reaction time/h	**3**, Yield/%[a]
R^1=Me, R^2=*o*-Tolyl (**1a**)	Me_2PhSiH	1	**3a**, 89
	Et_3SiH	18	**3a′**, 60 (85)[c]
	t-$BuMe_2SiH$	70[b]	**3a″**, 11 (64)[c]
	$(EtO)_3SiH$	3	**3a‴**, 47 (87)[c]
R^1=R^2=Me (**1b**)	Me_2PhSiH	1	**3b**, 76
R^1=R^2=Ph (**1c**)	Me_2PhSiH	42	**3c**, 81

a) Substrate (**1**) 1 mmol; Isolated yield. b) Heated at 60 °C. c) Conversion determined by GLC.

conditions, dehydrogenative silylation preferentially at the allyl group rather than at the vinyl group to give **11a** and **11b**, and **12**, respectively, in a ratio 81 : 19 and in 59% combined yield as shown in Scheme 1. Competitive formation of **11b** with **11a** (in a ratio 29 : 52) would be a token of the intermediacy of 1,3-disila-2-propylrhodium species **I** (see, Scheme 2) that arises from the migratory insertion of the allyl group of **10** into the Si–Rh bond. Among others, consisting mostly of hydrogenation products from **10**, were obtained 1,3-bis(dimethylvinylsilyl)propene (**13**) in 9% isolated yield. The formation of **13** must arise from the Rh(I)-catalyzed dehydrogenative silylation of **10** with transiently formed dimethylvinylsilane, implicating an intervention of the crossover reaction where possible silylrhodation–desilylrhodation sequence is postulated as depicted in Scheme 2. In fact, there are precedents to show the possibility of the reversible alkene insertion into the metal–silicon bond in competition with the metal–hydrogen bond.[11,12] We were unable to detect allyldimethylphenylsilane that should be replaced with **10** in order to form eventually **13** after the crucial crossover took place. However, it should be mentioned at this point that both diallyldimethylsilane and allyltrimethylsilane could not undergo the dehydrogenative silylation under the standard conditions, but afforded simple hydrosilylation products in good yield.[13] Therefore, from the standpoint of 1,ω-diene structures that are required apparently for the present dehydrogenative silylation, 3-sila-1,4-pentadienes (**1a—c**) and 3-sila-1,5-hexadiene (**10**) are suitable substrates, whereas 4-sila-1,6-heptadiene can not be used. According to Murai and

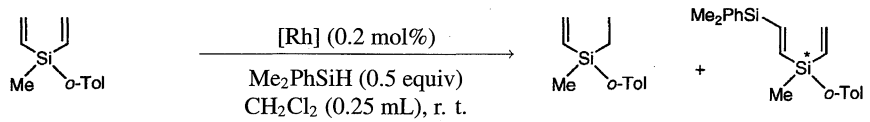


Scheme 1. Dehydrogenative silylation of allyldimethylvinylsilane (**10**).



Scheme 2. Crossover reaction of **10** to **13**.

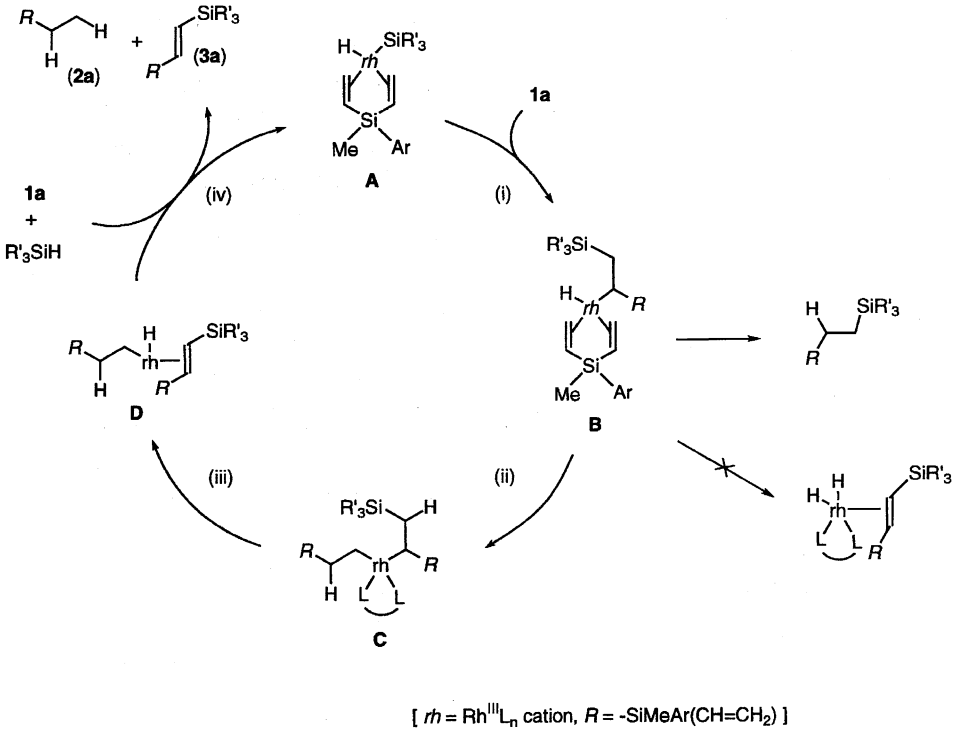
Table 4. Effect of Rh(I) Catalyst on the Dehydrogenative Silylation of **1a**



1a **2a** **3a**

Rh catalyst	(L*/Rh)/equiv	Time/h	Convn/%	% ee[a]
$[Rh(dppb)(cod)]ClO_4$		1	100	—
$RhCl(PPh_3)_3$		1	100	—
$1/2[RhCl(cod)]_2$		1	100	—
$Rh(CO)_2(acac)$		2	100	—
$RhCl_3 \cdot 3H_2O$		15	N. R.	
$[Rh(L^*)(cod)]ClO_4$				
L*=(*S*)-BINAP[b]	(1)	3	79[c]	5
(*S*,*S*)-DIOP[d]	(1)	16	100[e]	5
	(2)	17	100[e]	15

a) Determined by HPLC using a chiral column (CHIRALCEL OD). b) 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl. c) Determined by GLC using an internal standard (decene). d) 2,2-Dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane. e) Racemic **2a** was obtained in every case.



Scheme 3. Proposed mechanism of dehydrogenative silylation.

co-workers,[8] the reaction of 1,4-pentadiene with Et_2MeSiH using $RhCl(PPh_3)_3$ as a catalyst gave mainly hydrosilylation products with a little 1-silyl-1,4-pentadiene while that of 1,5-hexadiene gave selectively 1-silyl-1,5-hexadiene, and also 1,6-heptadiene afforded dehydrogenative silylation products which contain isomerized 1-silylheptadienes. Thus, it is evident that the general trends of 1,ω-dienes used in the present study for undergoing dehydrogenative silylation are quite different from the reported ones, presumably because there must be marked difference in the respective binding ability of 1,ω-dienes to the Rh(I) catalyst.

Finally, a few Rh(I) complexes were examined as a catalyst precursor for the dehydrogenative silylation of **1a** with Me_2PhSiH (Table 4). As is seen from Table 4, every Rh(I) complex employed was equally effective for achieving 100% conversion of **1a** in 1—2 h to give **2a** and **3a**, the latter becoming potentially chiral at the silicon atom. Therefore, the reaction in terms of desymmetrization of **1a** using a chiral Rh(I) catalyst that contains either (*S*)-BINAP or (*S*,*S*)-DIOP was carried out. The results are also given in Table 4. Although the extent of desymmetrization of **1a** was found to be only 5% when a discrete chiral Rh(I) cationic complex was used, the presence of excess DIOP did enhance the new type of asymmetric induction at the silicon atom up to 15%.

With regard to the formation of alkenylsilanes rather than hydrosilylation product in the Rh(I)-catalyzed reaction of alkenes with trialkylsilanes (R'_3SiH), it has been proposed that the key steps of the mechanism are the insertion of the alkene into the Rh–SiR'_3 bond rather than into the Rh–H bond, followed by β-hydride elimination.[10,14] As a result, dihydrogen, each of which must be originated from both the alkene and the hydrosilane, is used for the quantitative hydrogenation of another alkene molecule to give an alkane in an equimolar amount to the alkenylsilane. One of the salient features of the present dehydrogenative coupling of **1a** with Me_2PhSiH, however, is the complete absence of an *intramolecular* hydrogen transfer to **3a** to form **6a**. The formation of **6a** is most conceivable based on the mechanism mentioned above, because the primary product **3a** that is in proximity to the catalyst would be more susceptible to hydrogenation than **1a** to form **2a**. In the Rh(I)-catalyzed reaction of 1,5-hexadiene with Et_2MeSiH, it was expected that the hydrogen transfer would take place in an intramolecular fashion to give 1-silyl-1-hexene, but this was not the case and the products were 1-silyl-1,5-hexadiene and 1-hexene.[8] In order to accommodate such an observation and all results presented here, the following catalytic cycle may be considered. Thus, **1a** for example, R'_3SiH, and the Rh(I) catalyst precursor bind together, to form **A** that enters into the catalytic loop as shown in Scheme 3. The plausible steps involved in the loop are; (i) migratory insertion of the alkene moiety of **1a** into the Rh–Si bond in the presence of excess **1a** to give **B**; (ii) *consecutive* migratory insertion of another **1a** into the Rh–H bond would follow to form **C** prior to β-hydride elimination of **B** that is usually postulated; (iii) β-hydride elimination of **C** that takes place preferentially at an α-position to the silicon, presumably due to both steric and electronic reason, to form **D**, where 1,2-disilylethene holds an *E*-geometry; and (iv) reductive elimination from **D** affords **2a** and **3a** in equimolar amounts when Me_2PhSiH is used and regenerates **A**, thus completing the catalytic cycle. Although there have been a number of detailed discussion about the consecutive migratory insertion in the Rh(I)-catalyzed dehydrogenative silylation of alkenes, typically of styrene,[10,11,15] we are not in a position to distinguish whether the step (i) in Scheme 3 precedes the step (ii) or vice versa.[16] However, it is suggested that any dihydridorhodium(III) species may not participate in the hydrogenation of styrene in the concomitant formation of (*E*)-β-silylstyrene using R'_3SiD.[16] The fact may reinforce little β-hydride elimination of **B** in Scheme 3 to take place, directing to the consecutive insertion as exemplified in step (ii).

A homolog of intermediate **B**, that is given in Scheme 2 could undergo β-silyl group elimination in terms of the reversibility of step (i),[11] which may well account for the observed crossover reaction to give **13** starting from **10**. As is seen from Table 1, in the presence of excess Me_2PhSiH as for the dehydrogenative silylation of **1a**, an enhanced rate of hydrosilylation by way of **B** would become significant. This is particularly the case for **3a** as a starting material (see Table 2). However, it should be mentioned that our data of the formation of **8a** may not preclude the Chalk–Harrod mechanism to be operative, which is most commonly suggested for the conventional transition metal-catalyzed hydrosilylation of alkenes.[17]

In conclusion, we have found the clean control to the dehydrogenative silylation of divinylsilanes (**1a—c**) and allylvinylsilane (**10**) and discussed briefly the plausible mechanism with respect to the controlling factors, in terms of the consecutive migratory insertion of the alkene substrates into the Rh–Si bond and into the Rh–H bond, respectively.

Experimental

General. ^1H, ^{13}C, and ^{29}Si NMR spectra were measured with JEOL Model FX-90Q (^1H: 90 MHz; ^{13}C: 22.5 MHz), EX-270 (^1H: 270 MHz; ^{13}C: 67.8 MHz; ^{29}Si: 53.5 MHz) or GSX-500 (^1H: 500 MHz; ^{13}C: 125 MHz) spectrometers in $CDCl_3$. Chemical shifts are reported in ppm relative to Me_4Si (^1H: as an internal standard; ^{29}Si: an external standard), $CHCl_3$ (^1H: 7.26 ppm as an internal standard) or $CDCl_3$ (^{13}C: 77.0 ppm as internal standard). Splitting patterns are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). IR spectra were recorded on JASCO Model IR-700 spectrometer. Data are given in cm^{-1} with only significant diagnostic bands. Analytical thin layer chromatography (TLC) was performed by using Merck precoated TLC plate (silica gel 60 F_{254}) with indicator. Visualization of the spots was performed by UV light and by *p*-anisaldehyde–H_2SO_4/EtOH solution, phosphomolybdic acid/EtOH solution, aqueous $KMnO_4/K_2CO_3$/NaOH or iodine. Analytical gas–liquid chromatography (GLC) was performed on a Shimadzu Model GC-4CPT, GC-8A or GC-6A instrument equipped with a Silicone DC-550 or Silicone SE-30 (3 mm×3 m) column, or an OV-1 or DAICEL Chirasil (0.25 mm×25 m) capillary column, using He or N_2 gas as a carrier gas. Preparative GLC was performed on a Varian Model 920 instrument equipped with a Silicone SE-30 (3/8″×3 m) column, using He as a carrier gas.

Starting Materials. Preparation of methyl(*o*-tolyl)divinylsilane (**1a**) was carried out according to a standard method using dichloromethyl(*o*-tolyl)silane[18] and a THF solution of vinylmagnesium bromide. After usual workup, **1a** was obtained by distillation, bp 123—125 °C/22 Torr (60% yield) (1 Torr=133.322 Pa). Dimethyldivinylsilane (**1b**),[19] diphenydivinylsilane (**1c**)[20] and allyldimethylvinylsilane (**10**)[21] were similarly prepared by reported procedures.

1a: ^1H NMR (270 MHz) δ=0.46 (s, 3H), 2.41 (s, 3H), 5.77 (dd, *J*=3.7, 19.9 Hz, 2H), 6.09 (dd, *J*=3.7, 14.8 Hz, 2H), 6.36 (dd, *J*=19.9, 14.8 Hz, 2H), 7.1—7.6 (m, 4H); ^{13}C NMR (67.8 MHz) δ=−3.8, 23.2, 125.0, 129.7, 129.8, 133.8, 134.8, 135.6, 136.5, 144.2; ^{29}Si NMR (53.5 MHz, using an INEPT pulse sequence: Δ=21.9 ms) δ=−17.7; IR (neat) 3040, 1584, 1246, 1006, 952 cm^{-1}. Found: C, 76.58; H, 8.54%. Calcd for $C_{12}H_{16}Si$: C, 76.52; H, 8.56%.

1b: ^1H NMR (270 MHz) δ=0.15 (s, 6H), 5.71 (dd, *J*=4.3, 19.9 Hz, 2H), 5.98 (dd, *J*=4.3, 14.5 Hz, 2H), 6.16 (dd, *J*=19.9, 14.5 Hz, 2H).

1c: ^1H NMR (270 MHz) δ=5.78 (dd, *J*=18.5, 5.6 Hz, 2H), 6.23 (dd, *J*=14.5, 5.6 Hz, 2H), 6.53 (dd, *J*=18.5, 14.5 Hz, 2H), 7.6—7.3 (m, 10H).

10: ^1H NMR (270 MHz) δ=0.08 (s, 6H), 1.58 (dt, *J*=8.0, 1.1 Hz, 2H), 4.8—4.9 (m, 2H), 5.69 (dd, *J*=4.2, 19.7 Hz, 1H), 5.78 (ddt, *J*=16.4, 10.2, 8.0 Hz, 1H), 5.97 (dd, *J*=4.2, 14.5 Hz, 1H), 6.14 (dd, *J*=14.5, 19.7 Hz, 1H).

Me_2PhSiH[22] was prepared by a reported procedure, and Et_3SiH, *t*-$BuMe_2SiH$, and $(EtO)_3SiH$ were purchased and purified by distillation before use.

$[Rh(dppb)(cod)]ClO_4$,[23] $[Rh[(S)$- binap$](cod)]ClO_4$,[24] $[Rh[(S,S)$- diop$](cod)]ClO_4$,[23] $RhCl(PPh_3)_3$,[25] $[RhCl(cod)]_2$,[26] and $Rh(CO)_2(acac)$[27] were prepared by reported procedures.

General Procedure for the Dehydrogenative Silylation (Table 3, Entry 1). To a solution of divinylsilane **1a** (0.21 mL, 1.0 mmol), $[Rh(dppb)(cod)]ClO_4$ (0.80 mg, 2×10^{-3} mmol) and CH_2Cl_2 (0.25 mL) was added Me_2PhSiH (0.080 mL, 0.50 mmol) at room temperature under ambient atmosphere. After being stirred for 1h, the reaction mixture was filtered through a Florisil plug (eluent: hexane) and the filtrate was concentrated in vacuo (silylated product (**3a**) : hydrogenated product (**2a**)=1 : 1 by ^1H NMR analysis). Bulb-to-bulb distillation of the residue afforded the hydrogenated product (74 mg, 79% yield based on the hydrosilane) and the silylated product (143 mg, 89% yield).

Dehydrogenative Silylation of Divinylsilane 1a in Various Molar Ratios of 1a to Me_2PhSiH. To a solution of divinylsilane **1a** (0.21 mL, 1.0 mmol), $[Rh(dppb)(cod)]ClO_4$ (0.80 mg, 0.0020 mmol), and *n*-decane as an internal standard in CH_2Cl_2 (0.25 mL) was added Me_2PhSiH (appropriate amount given in Table 1) at room temperature under an ambient atmosphere. Reaction time was given in Table 1. The reaction mixture was analyzed by GLC to obtain the composition of the products. All products were isolated by preparative GLC, and spectral data and analytical data of each compound were measured.

Ethylmethyl(*o*-tolyl)vinylsilane (2a): ^1H NMR (270 MHz) δ=0.38 (s, 3H), 0.8—1.0 (m, 5H), 2.43 (s, 3H), 5.74 (dd, J=3.8, 19.9 Hz, 1H), 6.06 (dd, J=3.8, 14.4 Hz, 1H), 6.33 (dd, J=14.4, 19.9 Hz, 1H), 7.1—7.5 (m, 4H); ^{13}C NMR (67.8 MHz) δ=−4.5, 6.1, 7.4, 23.1, 124.8, 129.3, 129.7, 132.8, 135.1, 135.6, 137.4, 143.9; ^{29}Si NMR (53.5 MHz, using an INEPT pulse sequence: Δ=19.8 ms) δ=−8.6; IR (neat) 3044, 1586, 1250, 1006, 950 cm^{-1}. Found: C, 75.77; H, 9.70%. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53%.

[2-(Dimethylphenylsilyl)ethenyl]methyl(*o*-tolyl)vinylsilane (3a): ^1H NMR (270 MHz) δ=0.34 (s, 6H), 0.46 (s, 3H), 2.38 (s, 3H), 5.74 (dd, J=3.9, 20.1 Hz, 1H), 6.09 (dd, J=3.9, 14.5 Hz, 1H), 6.37 (dd, J=14.5, 20.1 Hz, 1H), 6.82 (AB, J=22.2 Hz, 1H), 6.89 (AB, J=22.2 Hz, 1H), 7.1—7.6 (m, 9H); ^{13}C NMR (67.8 MHz) δ=−3.9, −2.9, 23.2, 124.9, 127.7, 128.9, 129.5, 129.7, 133.7, 133.8, 134.9, 135.5, 136.5, 138.4, 144.2, 148.8, 151.5; ^{29}Si NMR (53.5 MHz, using an INEPT pulse sequence: Δ=29.0 ms) δ=−17.5, −10.4; IR (neat) 3044, 1578, 1247, 1010, 954 cm^{-1}. Found: C, 74.48; H, 8.36%. Calcd for $C_{20}H_{26}Si_2$: C, 74.46; H, 8.12%.

[2-(Dimethylphenylsilyl)ethyl]ethylmethyl(*o*-tolyl)silane (4a): ^1H NMR (270 MHz) δ=0.24 (s, 6H), 0.27 (s, 3H), 0.6—1.0 (m, 9H), 2.36 (s, 3H), 7.1—7.5 (m, 9H); ^{13}C NMR (67.8 MHz) δ=−4.7, −3.66, −3.62, 5.8, 6.2, 7.5, 7.9, 22.9, 124.7, 127.6, 128.7, 129.0, 129.7, 133.6, 135.1, 136.2; IR (neat) 3044, 1244 cm^{-1}.

[2-(Dimethylphenylsilyl)ethenyl][2-(dimethylphenylsilyl)ethyl]methyl(*o*-tolyl)silane (5a): ^1H NMR (270 MHz) δ=0.24 (s, 6H), 0.33 (s, 6H), 0.35 (m, 3H), 0.5—0.9 (m, 4H), 2.32 (s, 3H), 6.76 (AB, J=22.6 Hz, 1H), 6.82 (AB, J=22.6 Hz, 1H), 7.1—7.5 (m, 14H); IR (neat) 3062, 1245, 1011 cm^{-1}.

[2-(Dimethylphenylsilyl)ethenyl]ethylmethyl(*o*-tolyl)silane (6a): ^1H NMR (270 MHz) δ=0.33 (s, 6H), 0.36 (s, 3H), 0.8—1.0 (m, 5H), 2.39 (s, 3H), 6.80 (AB, J=22.4 Hz, 1H), 6.85 (AB, J=22.4 Hz, 1H), 7.1—8.6 (m, 9H); IR (neat) 3060, 3046, 1587, 1247, 1011 cm^{-1}.

[2-(Dimethylphenylsilyl)ethyl]methyl(*o*-tolyl)vinylsilane (7a): ^1H NMR (270 MHz) δ=0.25 (s, 6H), 0.36 (s, 3H), 0.60—0.75 (m, 2H), 0.75—0.90 (m, 2H), 2.36 (s, 3H), 5.70 (dd, J=3.9, 20.1 Hz, 1H), 6.04 (dd, J=3.9, 14.5 Hz, 1H), 6.30 (dd, J=14.5, 20.1 Hz, 1H), 7.1—7.5 (m, 9H); IR (neat) 3040, 1246, 1006, 948 cm^{-1}.

Bis[2-(dimethylphenylsilyl)ethyl]methyl(*o*-tolyl)silane (8a): ^1H NMR (270 MHz) δ=0.24 (s, 12H), 0.27 (s, 3H), 0.5—0.9 (m, 8H), 2.31 (s, 3H), 7.1—7.5 (m, 14H); ^{13}C NMR (67.8 MHz) δ=−3.8, −2.7, −2.6, 7.0, 8.8, 23.8, 125.6, 128.6, 129.7, 129.9, 130.6, 134.5, 136.1, 137.0, 140.2, 144.6; ^{29}Si NMR (53.5 Hz, using an INEPT sequence Δ=17.0, 19.8 ms) δ=−1.3, 2.0; IR (neat) 3060, 1244 cm^{-1}. Found: C, 73.60; H, 9.33%. Calcd for $C_{28}H_{40}Si_3$: C, 72.96; H, 8.74%.

Bis[2-(dimethylphenylsilyl)ethenyl]methyl(*o*-tolyl)silane (9a): ^1H NMR (270 MHz) δ=0.34 (s, 12H), 0.46 (s, 3H), 2.36 (s, 3H), 6.81 (AB, J=22.2 Hz, 2H), 6.88 (AB, J=22.2 Hz, 2H), 7.1—7.6 (m, 14H); IR ($CHCl_3$) 1246, 1010 cm^{-1}.

Preparative Scale Dehydrogenative Silylation (Preparation of Disilylethene 3a). The general procedure as described above was performed. A mixture of divinylsilane **1a** (1.9 g, 10 mmol), $[Rh(dppb)(cod)]ClO_4$ (14 mg, 0.02 mmol), CH_2Cl_2 (2.5 mL), and $PhMe_2SiH$ (0.81 mL, 5.0 mmol) was stirred for 1 h. After workup, bulb-to-bulb distillation (5 Torr) of the crude product afforded the hydrogenated product **2a** (0.81 g, 85% yield) and the silylated product **3a** (1.37 g, 85% yield).

Reaction of 3a with Me_2PhSiH Catalyzed by $[Rh(dppb)(cod)]ClO_4$. To a mixture of **3a** (0.32 g, 1.0 mmol), $[Rh(dppb)(cod)]ClO_4$ (0.80 mg, 2×10^{-3} mmol) and *n*-decane as an internal standard in CH_2Cl_2 (0.20 mL) was added Me_2PhSiH (80 μL, 0.50 mmol) at room temperature. After being stirred for 12 h at the same temperature, the product composition was analyzed by GLC.

Reaction of 3a with Me_2PhSiH Catalyzed by $[Rh(dppb)(cod)]ClO_4$ in the Presence of 1-Hexene. To a mixture of **3a** (0.64 g, 2.0 mmol), 1-hexene (1.2 mL, 10 mmol), $[Rh(dppb)(cod)]ClO_4$ (16 mg, 0.04 mmol), and *n*-decane as an internal standard in CH_2Cl_2 (0.15 mL) was added portionwise Me_2PhSiH (0.24 mL, 2.0 mmol) in CH_2Cl_2 (0.30 mL) over 3 h at room temperature. After 12 h of reaction time, the product composition was determined by GLC analysis (Table 2).

Dehydrogenative Silylation of Divinylsilanes for Table 3. Same procedure was performed to obtain the following products: **3a′**, **3a″**, **3a‴**, **3b**, and **3c**.

[2-(Triethylsilyl)ethenyl]methyl(*o*-tolyl)vinylsilane (3a′): General procedure as described for **1a** was performed except using Et_3SiH (80 μL, 0.5 mmol) instead of Me_2PhSiH. Bulb-to-bulb distillation (6 Torr) of the crude product gave **3a′** (91 mg, 60% yield).

3a′: ^1H NMR (270 MHz) δ=0.45 (s, 3H), 0.58 (q, J=7.5 Hz, 6H), 0.93 (t, J=7.5 Hz, 9H), 2.40 (s, 3H), 5.74 (dd, J=3.9, 20.1 Hz, 1H), 6.09 (dd, J=3.9, 14.5 Hz, 1H), 6.37 (dd, J=14.5, 20.1 Hz, 1H), 6.66 (AB, J=22.7 Hz, 1H), 6.80 (AB, J=22.7 Hz, 1H), 7.1—7.6 (m, 4H); ^{13}C NMR (67.8 MHz) δ=−3.8, 3.1, 7.3, 23.1, 124.8, 129.5, 129.7, 133.5, 135.2, 135.5, 136.8, 144.2, 148.3, 150.7; IR (neat) 3044, 1584, 1246, 1010, 952, 806, 788, 742 cm^{-1}. Found: C, 71.38; H, 10.00%. Calcd for $C_{18}H_{30}Si_2$: C, 71.44; H, 9.99%.

[2-(*t*-Butyldimethylsilyl)ethenyl]methyl(*o*-tolyl)vinylsilane (3a″): *t*-$BuMe_2SiH$ (82 μL, 0.50 mmol) was used as a silane. Bulb-to-bulb distillation (5 Torr) gave **3a″** (13 mg, 11% yield).

3a″: ^1H NMR (270 MHz) δ=0.03 (s, 6H), 0.45 (s, 3H), 0.86 (s, 9H), 2.40 (s, 3H), 5.74 (dd, J=3.9, 20.1 Hz, 1H), 6.09 (dd, J=3.9, 14.8 Hz, 1H), 6.37 (dd, J=14.8, 20.1 Hz, 1H), 6.73 (AB, J=22.6 Hz, 1H), 6.79 (AB, J=22.6 Hz, 1H), 7.1—7.5 (m, 4H); ^{13}C NMR (67.8 MHz) δ=−6.5, −3.8, 16.6, 23.1, 26.4, 124.8, 129.5, 129.7,

133.5, 135.1, 135.5, 136.7, 144.2, 148.2, 151.5; IR (neat) 1246, 1008 cm^{-1}.

[2-(Triethoxysilyl)ethenyl]methyl(*o*-tolyl)vinylsilane (3a‴): $(EtO)_3SiH$ (92 μL, 0.5 mmol) was used as a silane. Bulb-to-bulb distillation (0.3 Torr) gave **3a‴** (83 mg, 47% yield).

3a‴: ^1H NMR (270 MHz) δ=0.48 (s, 3H), 1.23 (t, J=6.9 Hz, 9H), 2.41 (s, 3H), 3.83 (q, J=6.9 Hz, 6H), 5.77 (dd, J=3.9, 20.1 Hz, 1H), 6.11 (dd, J=3.9, 14.6 Hz, 1H), 6.37 (dd, J=14.6, 20.1 Hz, 1H), 6.44 (d, J=22.7 Hz, 1H), 7.18 (d, J=22.7 Hz, 1H), 7.1—7.6 (m, 4H); ^{13}C NMR (67.8 MHz) δ=−4.0, 18.2, 23.2, 58.5, 124.9, 129.6, 129.7, 134.0, 134.4, 135.5, 136.0, 142.0, 144.1, 153.8; IR (neat) 3044, 1584, 1246, 1100, 1014, 954, 786, 744 cm^{-1}. Found: C, 61.36; H, 8.72%. Calcd for $C_{18}H_{30}O_3Si_2$: C, 61.66; H, 8.62%.

[2-(Dimethylphenylsilyl)ethenyl]dimethylvinylsilane (3b): Dimethyldivinylsilane (**1b**) (0.15 mL, 0.11 g, 1.0 mmol) was used as an olefin. Bulb-to-bulb distillation (6 Torr) gave **3b** (93 mg, 76% yield).

3b: ^1H NMR (270 MHz) δ=0.15 (s, 6H), 0.34 (s, 6H), 5.69 (dd, J=4.2, 19.7 Hz, 2H), 5.97 (dd, J=4.2, 19.7 Hz, 2H), 6.16 (dd, J=14.6, 19.7 Hz, 2H), 6.67 (AB, J=22.3 Hz, 1H), 6.75 (AB, J=22.3 Hz, 1H), 7.3—7.6 (m, 5H); ^{13}C NMR (67.8 MHz) δ=−3.3, −2.9, 127.7, 128.9, 132.2, 133.8, 138.2, 138.6, 149.7, 150.5; IR (neat) 3040, 1244, 1008, 950, 726, 696 cm^{-1}. LRMS (GC/MS, EI, 70 eV) m/z (rel intensity) 246 (3) [M^+], 231 (15) [$M-CH_3^+$], 218 (6), 161 (10), 135 (100) [$PhMe_2Si^+$]. HRMS (GC/MS, EI, 70 eV). Found: m/z 246.1232. Calcd for $C_{14}H_{22}Si_2$: [M^+], 246.1260.

[2-(Dimethylphenylsilyl)ethenyl]diphenylvinylsilane (3c): Diphenyldivinylsilane (**1c**) (0.24 g, 1.0 mmol) was used as an olefin. Bulb-to-bulb distillation (2 Torr) gave **3c** (0.15 g, 81% yield).

3c: ^1H NMR (270 MHz) δ=0.37 (s, 6H), 5.75 (dd, J=3.9, 20.1 Hz, 1H), 6.25 (dd, J=3.9, 14.5 Hz, 1H), 6.49 (dd, J=14.5, 20.1 Hz, 1H), 6.92 (AB, J=22.4 Hz, 1H), 6.99 (AB, J=22.4 Hz, 1H), 7.3—7.5 (m, 15H); ^{13}C NMR (67.8 MHz) δ=−2.9, 127.8, 128.9, 129.4, 133.8, 134.3, 135.5, 136.5, 145.8, 154.7; IR (neat) 3060, 3040, 1584, 1244, 1008, 958, 728, 698 cm^{-1}.

Dehydrogenative Silylation of Allyldimethylvinylsilane (10). To a solution of **10** (0.34 mL, 2.0 mmol), $[Rh(dppb)(cod)]ClO_4$ (0.80 mg, 2×10^{-3} mmol) and CH_2Cl_2 (0.50 mL) was added $PhMe_2SiH$ (0.08 mL, 0.5 mmol) at room temperature. After being stirred for 1 h, the reaction mixture was filtered through a Florisil plug (eluent: hexane) and the filtrate was concentrated to give a crude product. Purification of the residue by bulb-to-bulb distillation and GPC afforded a mixture of two silylpropenylvinylsilanes **11a**, **11b**, and (silylethenyl)allylsilane **12** (39 mg, 59% combined yield) in a ratio 52 : 29 : 19 and lower boiling point product **13** (10 mg, 9% yield, see Schemes 1 and 2).

Dimethyl[3-(dimethylphenylsilyl)-2-propenyl]vinylsilane (11a): ^1H NMR (270 MHz) (detected as a mixture of the three components) δ=1.87 (dd, J=7.8, 1.1 Hz, 2H), 5.42 (dt, J=18.1, 1.1 Hz, 1H), 6.03 (dt, J=18.1, 7.8 Hz, 1H), 5.6—6.2 (m, 3H), 7.3—7.6 (m, 5H); IR (neat) 3060, 3040, 1598, 1244, 1006, 986, 948, 760, 728, 696 cm^{-1}. LRMS (GC/MS, EI, 12 eV) m/z (rel intensity) 260 (2) [M^+], 245 (22) [$M-CH_3^+$], 135 (100) [$PhMe_2Si^+$].

Dimethyl[3-(dimethylphenylsilyl)-1-propenyl]vinylsilane (11b): ^1H NMR (270 MHz) (detected as a mixture of the three components) δ=1.74 (dd, J=7.9, 1 Hz, 2H), 5.57 (dt, J=18.4, 1 Hz, 1H), 6.09 (dt, J=18.4, 7.9 Hz, 1H), 5.6—6.2 (m, 3H), 7.3—7.6 (m, 5H); LRMS (GC/MS, EI, 12 eV) m/z (rel intensity) 260 (2) [M^+], 245 (13) [$M-CH_3^+$], 135 (100) [$PhMe_2Si^+$].

Allyl[2-(dimethylphenylsilyl)ethenyl]dimethylsilane (12): ^1H NMR (270 MHz) (detected as a mixture of the three components) δ=1.58 (dt, J=8.2, 1 Hz, 2H), 4.8—4.9 (m, 2H), 5.7—5.8 (m, 1H), 6.66 (AB, J=23 Hz, 1H), 6.72 (AB, J=23 Hz, 1H), 7.3—7.6 (m, 5H); LRMS (GC/MS, EI, 12 eV) m/z (rel intensity) 260 (6), 245 (26) [$M-CH_3^+$], 219 (89), 182 (38), 135 (100) [$PhMe_2Si^+$].

1,3-Bis(dimethylvinylsilyl)propene (13): ^1H NMR (270 MHz) δ=0.06 (s, 6H), 0.10 (s, 6H), 1.71 (dd, J=1.3, 7.5 Hz, 2H), 5.43 (dt, J=18.4, 1 Hz, 1H), 5.6—6.2 (m, 7H); IR (neat) 3040, 1598, 1246, 1006, 950 cm^{-1}. LRMS (GC/MS, EI, 70 eV) m/z (rel intensity) 210 (11) [M^+], 195 (39) [$M-CH_3^+$], 182 (37).

Determination of Enantiomeric Excess of 3a. A mixture of disilylethene **3a** (0.11 g, 0.35 mmol) and $Hg(OAc)_2$ (0.22 g, 0.70 mmol) in THF/H_2O (1.4 mL, 50/50 vol%) at 0 °C for 10 h. To the resulting suspension was added aqueous NaOH (0.4 mL, 3 M, M=mol dm^{-3}) and $NaBH_4$ (26 mg, 0.70 mmol) in aqueous NaOH (0.5 mL, 3 M) successively at 0 °C. After being stirred for 1 h at this temperature, the mixture was filtered through a celite pad. The filtrate was extracted with Et_2O, dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue by column chromatography on silica gel (eluent: Et_2O/hexane=1/10) gave [2-(dimethylphenylsilyl)ethenyl](2-hydroxyethyl)methyl(*o*-tolyl)silane (33 mg, 29% yield).

To a mixture of the alcohol obtained above (33 mg, 0.10 mmol) and pyridine (0.05 mL) was added *p*-bromobenzoyl chloride (22 mg, 0.10 mmol) at 0 °C. After being stirred for 3 h, the reaction mixture was diluted with Et_2O and poured into saturated NH_4Cl. The aqueous layer was extracted with Et_2O and combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue by column chromatography on silica gel (eluent: Et_2O/hexane=1/100) gave [2-(*p*-bromobenzoyloxy)ethyl][2-(dimethylphenylsilyl)ethenyl]methyl(*o*-tolyl)silane as a colorless oil (16 mg, 30% yield). The enantiomeric excess of the product was determined by HPLC (equipped with a DAICEL CHIRALCEL OD capillary column, eluent: 0.15% IPA in hexane) analysis.

[2-(Dimethylphenylsilyl)ethenyl](2-hydroxyethyl)methyl(*o*-tolyl)silane: ^1H NMR (270 MHz) δ=0.34 (s, 6H), 0.42 (s, 3H), 1.2—1.5 (m, 2H), 2.39 (s, 3H), 3.7—3.8 (m, 2H), 6.84 (s, 2H), 7.1—7.5 (s, 9H); IR (neat) 3332, 3044, 1584, 1246, 808, 740, 698 cm^{-1}.

[2-(Dimethylphenylsilyl)ethenyl][2-(*p*-bromobenzoyloxy)ethyl]methyl(*o*-tolyl)silane: ^1H NMR (270 MHz) δ=0.33 (s, 6H), 0.47 (s, 3H), 1.5—1.6 (m, 2H), 2.41 (s, 3H), 4.3—4.5 (m, 2H), 6.86 (s, 2H), 7.1—7.8 (m, 13H); ^{13}C NMR (67.8 MHz) δ=−3.7, −3.0, 15.2, 23.1, 63.2, 125.1, 127.7, 129.0, 129.3, 129.7, 129.9, 131.0, 131.5, 133.8, 134.4, 135.0, 138.1, 143.9, 148.5, 151.6, 165.8; IR (neat) 3062, 3002, 1715, 1588, 1268 cm^{-1}.

This work was supported by a Grant-in-Aid for Scientific Research No. 04440318 from the Ministry of Education, Science and Culture to which the authors thanks are due.

References

1) I. Fleming, J. Dunogues, and S. H. Smithers, *Org. React.*, **37**, 57 (1989).

2) For typical examples of our own, see: K. Yamamoto, O. Nunokawa, and J. Tsuji, *Synthesis*, **1977**, 721; K. Yamamoto, J. Yoshitake, N. T. Qui, and J. Tsuji, *Chem. Lett.*, **1978**, 859; K. Yamamoto, M. Ohta, and J. Tsuji, *Chem. Lett.*, **1979**, 713.

3) L. N. Lewis, K. G. Sy, G. L. Brayant, and P. E. Donahue, *Organometallics*, **10**, 3750 (1991). Cf. K. Tamao, J. Yoshida, H. Yamamoto, T. Kakui, H. Matsumoto, M. Takahashi, A. Kurita, M. Murata, and M. Kumada, *Organometallics*, **1**, 855 (1982).

4) R. Takeuchi, S. Nitta, and D. Watanabe, *J. Org. Chem.*, **60**, 3045 (1995).

5) Y. Seki, K. Takashita, K. Kawamoto, S. Murai, and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, **19**, 928 (1980); Y. Seki, K. Takeshita, K. Kawamoto, S. Murai, and N. Sonoda, *J. Org. Chem.*, **51**, 3890 (1986).

6) F. Kakiuchi, Y. Tanaka, N. Chatani, and S. Murai, *J. Organomet. Chem.*, **456**, 45 (1993).

7) K. Takeshita, Y. Seki, K. Kawamoto, S. Murai, and N. Sonoda, *J. Chem. Soc., Chem. Commun.*, **1983**, 1193; K. Takeshita, Y. Saki, K. Kawamoto, S. Murai, and N. Sonoda, *J. Org. Chem.*, **52**, 4864 (1987).

8) F. Kakiuchi, K. Nogami, N. Chatani, Y. Seki, and S. Murai, *Organometallics*, **12**, 4748 (1993), and references cited therein.

9) For a review, see: J. Y. Corey, in "Advances in Silicon Chemistry," ed by G. L. Larson, JAI Press, London (1991), Vol. 1, pp. 327—387.

10) In general, excess alkene substrate is known to favor the formation of, if not selective, dehydrogenative silylation: A. Millan, E. Towns, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, **1981**, 673; A. Millan, M.-J. Fernandez, P. Bentz, and P. M. Maitlis, *J. Mol. Catal.*, **26**, 88 (1984); See also Ref. 4.

11) For an Fe complex, see: C. L. Randolph and M. S. Wrighton, *J. Am. Chem. Soc.*, **108**, 3366 (1986); For a Ru complex: Y. Seki, K. Takeshita, and K. Kawamoto, *J. Organomet. Chem.*, **369**, 117 (1989); Y. Wakatsuki, H. Yamazaki, M. Nakano, and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, **1991**, 703; B. Marciniec and C. Pietraszuk, *J. Chem. Soc., Chem. Commun.*, **1995**, 2003; For a Rh complex: S. B. Dukett and R. N. Perutz, *Organometallics*, **11**, 90 (1992).

12) For pertinent reviews, see: I. Ojima, in "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappuport, Wiley, New York (1989), Chap. 25; T. Don Tilley, in "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Pappoport, Wiley, New York (1989), Chap. 24.

13) Rh(I)-catalyzed hydrosilylation products of diallyldimethylsilane and allyltrimethylsilane using Me_2PhSiH were obtained in 65% and 97% yield, respectively, under the standard conditions given in the Table 1.

14) A. Onopchenko, E. T. Sabourin, and D. L. Beach, *J. Org. Chem.*, **48**, 5101 (1983); R. Takeuchi, H. Yasue, and I. Ebata, "42rd Symposium on Organometallic Chemistry," Hiroshima, 1995, Abstr., No. PB 225, *Organometallics*, in press.

15) J. M. Brown and G. L. Lloyd-Jones, *J. Am. Chem. Soc.*, **116**, 866 (1994); See also: I. Ojima, T. Fuchikami, and M. Yatabe, *J. Organomet. Chem.*, **260**, 335 (1984).

16) Y. Kimae, K. Tamao, Y. Nakagawa, H. Seshimo, and Y. Ito, "Xth International Symposium on Organosilicon Chemistry," Poznán, 1993, Abstr., No. P-65. We thank Professor Tamao for a personal communication in this respect.

17) J. L. Speier, *Adv. Org. Chem.*, **17**, 407 (1979); A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).

18) B. Resibois and C. Hode, *Ann. Chim.*, **4**, 203 (1969); *Chem. Abstr.*, **71**, 61463r (1969).

19) J. A. Sonderquist and A. Hassner, *J. Organomet. Chem.*, **156**, 227 (1978). For ^1H NMR in CCl_4 and GCMS data, see: R. I. Damja, C. Eaborn, and W. C. Shaw, *J. Organomet. Chem.*, **291**, 25 (1985); T. J. Barton and W. D. Wulff, *J. Organomet. Chem.*, **168**, 23 (1979).

20) G. Fritz and P. Schober, *Z. Anorg. Allg. Chem.*, **372**, 21 (1970).

21) V. I. Zhun, A. L. Tsvetkov, V. D. Sheldyakov, I. A. Lavygin, O. V. Leitan, N. V. Chalbysheva, V. N. Bochkarev, and T. F. Slyusarenko, *Z. Obshch. Khim.*, **58**, 1599 (1988).

22) G. Schott and D. Gutschick, *Z. Anorg. Allg. Chem.*, **325**, 175 (1963); P. Reich and H. Kriegsmann, *Z. Anorg. Allg. Chem.*, **334**, 272 (1965).

23) D. Sinou and H. B. Kagan, *J. Organomet. Chem.*, **114**, 325 (1976).

24) K. Tani, T. Yamagata, S. Otsuka, H. Kumobayashi, and S. Akutagawa, *Org. Synth.*, **67**, 33 (1989).

25) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, **1966**, 1711; J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, **10**, 67 (1967).

26) G. Giordano and R. H. Crabtree, *Inorg. Synth.*, **19**, 218 (1979).

27) Yu. S. Varsharskii and T. G. Cherkasova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **12**, 899 (1967); F. Bonatti and G. Wilkinson, *J. Chem. Soc.*, **1964**, 3156.