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Rhodium-catalyzed transformation of propargyl alcohol derivatives to 2-silylmethyl-2-alkenals☆

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Abstract

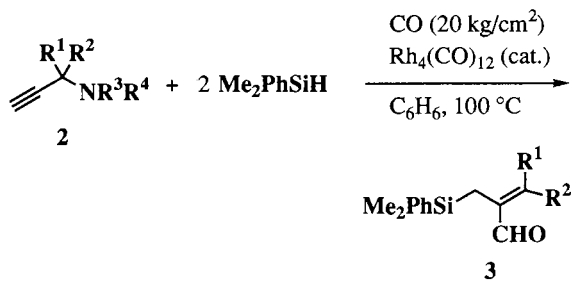
Propargyl-type alcohols (**6**) and the corresponding esters of carbonic acid (**4**) or acetic acid (**5**) react with two equivalents of Me_2PhSiH in the presence of catalytic amounts of $Rh_4(CO)_{12}$ under CO pressure at 100°C to give 2-(dimethylphenylsilylmethyl)-2-alkenals (**3**), whereas 2-substituted-3-(dimethylphenylsilyl)propenals (**7**, **8** and **9**) are also isolated with the concomitant formation of **3** when a similar reaction is operated with shortage of Me_2PhSiH or with lowering of reaction temperature. The isolated **9** is selectively converted to **3** by the $Rh_4(CO)_{12}$ catalyzed reaction with Me_2PhSiH under CO pressure. This fact suggests that the transformation of **4**, **5** or **6** to **3** is accomplished by either a one-pot procedure or a stepwise procedure relayed by **7**, **8** or **9**. Usefulness of this protocol is demonstrated by the synthesis of **18** in which ethisterone (**17**) is directly converted by a one-pot procedure.

Keywords: Silylformylation; CO incorporation; 2-Silylmethyl-2-alkenals

1. Introduction

2-(Trimethylsilylmethyl)-2-alkenal (**1**) is an intriguing building block wearing two functional groups that react independently with nucleophiles or electrophiles at the specific site. Some interesting examples have been demonstrated in the synthesis of 2-trimethylsilylmethyl-1,3-diene units via Peterson-type olefination [1] and in the construction of cyclopentane frameworks via Nazarov-type annulation [2] or via Trost-type annulation [3] (see Scheme 1).

Despite the promised synthetic potential of **1**, the conventional route to these type of compounds is accomplished by the oxidation of the corresponding alcohols derived from 2-methylpropen-1-ol [3] or carbonyl compounds [4] by a multistep transformation. In contrast to these cumbersome ways, the authors found a facile reaction to form 2-(dimethylphenylsilylmethyl)-2-alkenals (**3**) [5], during projects related to silylformylation of acetylenic compounds [6–9]. A mixture of a certain propargylamine (**2**) and two equivalents of Me_2PhSiH gives **3** in a one-pot procedure assisted by catalytic amounts of $Rh_4(CO)_{12}$ under CO pressure (20 kg cm^{-2}) (Eq. (1)).



2 **3** (1)

☆ Dedicated to the memory of the late Professor Rokuro Okawara

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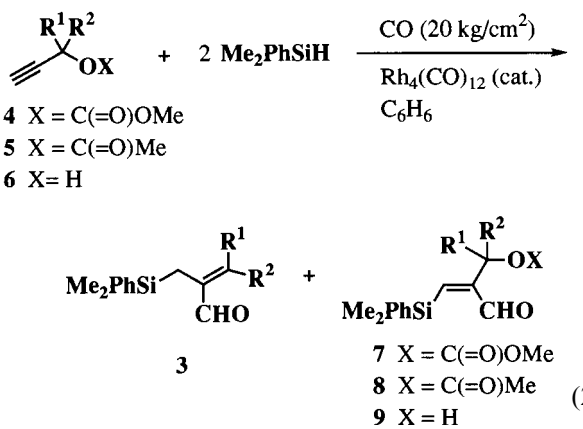
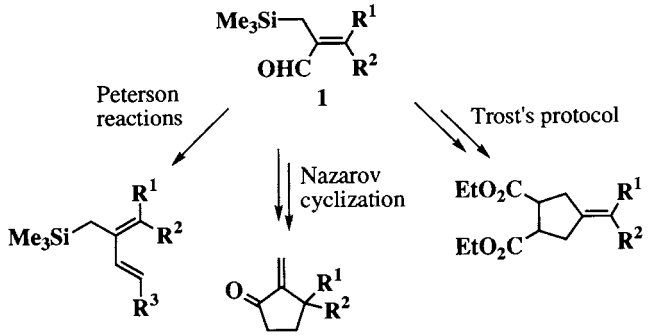
Although this protocol is applicable to a wide range of **2**, there is an appreciable bottleneck in applying this method to complex molecules. A multistep procedure is necessary for the access to substituted propargylamines. It is quite attractive to explore an alternative starting material to give **3** in an analogous procedure. Readily available propargyl-type alcohol (**6**) is the most desirable candidate because a novel type of carbonyl olefination of aldehydes and ketones would be accomplished by the intermediacy of **6** (Scheme 2). Reported herein is a novel one-pot transformation of propargyl-type alcohol derivatives (**4**, **5** and **6**) to **3** under silylformylation conditions.

2. Results and discussion

An amino group of **2** behaves as a leaving group in the transformation of **2** to **3**. On the basis of this intuitive analysis, the authors chose **4c** ($R^1 = H$, $R^2 = n$-Pent) as a model compound in order to discern the possibility of rhodium-catalyzed transformation of **4c** to **3c**, because it is well-documented that a methoxycarbonyloxy group is superior to either an acetoxy group or a hydroxy group in palladium-catalyzed substitution of some allylic derivatives [10]. Thus, **4c** was treated with two equivalents of Me_2PhSiH under typical silylformylation conditions [0.5 mol.% of $Rh_4(CO)_{12}$, CO (20 kg cm^{-2}), C_6H_6, 100°C, 3 h] [6g]. After chromatographic purification of the reaction mixture, **3c** was isolated as a single geometrical isomer ($Z > 98\%$) in 57% yield (entry 4 in Table 1) [11], regardless of the presence or absence of Et_3N. However, when four equivalents of Me_2PhSiH was charged as the starting substrate, **3c** was isolated as the sole carbonylated product even at r.t. (entry 8 in Table 1).

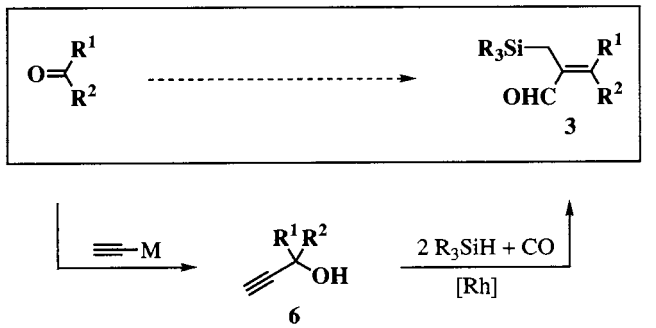


Similarly, **4b** was smoothly transformed to **3b**, whereas **4a** gave a mixture composed of almost equal amounts of **3a** and 2-methyl-3-dimethylphenylsilylpropenal in poor yield despite complete consumption of the starting **4a** under similar conditions (100°C, 3 h) (entry 1 in Table 1). Aldehyde **7a** formed by silylformylation of **4a** was concomitantly isolated in the reaction of **4a** at 25°C (entry 2 in Table 1).



Scheme 1. Synthetic application of **1**.

Since acetate **5** can be formed by acetylation of the corresponding propargylic alcohols regardless of the number of substituents on the propargyl carbon, it provides a simple measure for comparison of the steric effect of substituents in the formation of **3**. Monosubstituted acetates **5b** and **5c** were readily transformed to **3b** and **3c**, respectively, in good yields under standard conditions (entries 12 and 14). Silylformylation to give **8b** or **8c** became the predominant path at lower temperature, though net efficiency of CO incorporation into **5b** or **5c** was not affected by the reaction temperature (entries 13 and 15 in Table 1). In contrast to monosubstituted acetates **5b** or **5c**, the total yield of all carbonylated products was not acceptable in the reactions of other types of acetates, **5a**, **5d**, **5e** and **5g** (entries 10, 16, 17 and 18 in Table 1). These results may reflect the fact that silylformylation of these substrates brings about relatively insufficient yields of the corresponding aldehyde **8** under conventional conditions [12]. Anyway, the results of **5d**, **5e** and **5g** suggest that the transformation of **5** to **3** is appreciably affected by a steric environment around the propargyl carbon of **5**. An analogous decrease of yield dependent on the steric bulkiness was also observed in the transformation of the propargyl amine derivatives **2** to **3**. In particular, the following evidence obtained during the scrutinization of 1Eq. 1 is notable, that highly substituted **2** {R^1, $R^2 = -(CH_2)_5-$} bearing a benzylamino group is far more reactive than the corresponding one bearing dibenzylamino group [5].



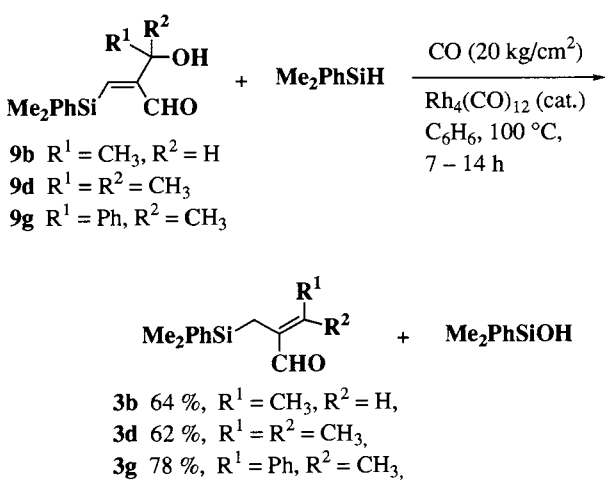
Scheme 2. Carbonyl olefination linking to **3**.

Table 1
Reactions of **4**, **5** and **6** with Me_2PhSiH under CO pressure

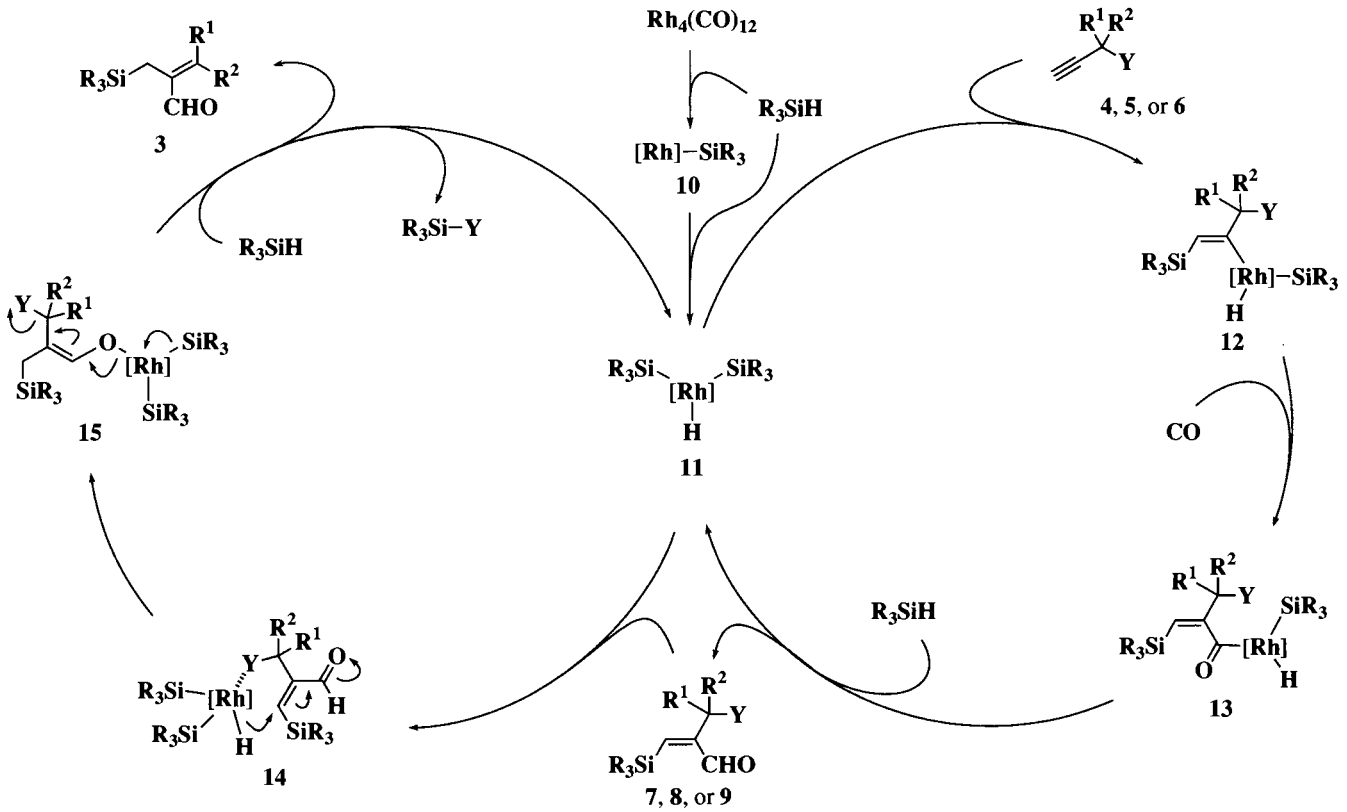
Entry	Acetylenic compounds				Ratio of acetylene	Conditions	Products	
		R^1	R^2	X	to Me_2PhSiH	(°C/h)	Yield (%)	
1	**4a**	H	H	C(=O)OMe	1:2	100/3	**3a** 36[a]	
2	**4a**	H	H	C(=O)OMe	1:2	25/24	**3a** 48[a]	**7a** 28
3	**4b**	Me	H	C(=O)OMe	1:2	100/3	**3b** 60[b]	
4	**4c**	*n*-Pent	H	C(=O)OMe	1:2	100/3	**3c** 57[b]	
5	**4c**	*n*-Pent	H	C(=O)OMe	1:2	25/24	**3c** 31[b]	**7c** 35
6	**4c**	*n*-Pent	H	C(=O)OMe	1:2	25/24[c]	**3c** 36	**7c** 33
7	**4c**	*n*-Pent	H	C(=O)OMe	1:1	25/24	**3c** 9	**7c** 57
8	**4c**	*n*-Pent	H	C(=O)OMe	1:4	25/24[c]	**3c** 61[b]	
9	**5a**	H	H	C(=O)Me	1:2	100/3	**3a** 31	
10	**5a**	H	H	C(=O)Me	1:2	25/24	**3a** 26	**8a** 32
11	**5b**	Me	H	C(=O)Me	1:3	100/3	**3b** 80[b,d]	
12	**5b**	Me	H	C(=O)Me	1:2	100/3	**3b** 72[b]	**8b** 5
13	**5b**	Me	H	C(=O)Me	1:2	50/47	**3b** 40[b]	**8b** 45
14	**5c**	*n*-Pent	H	C(=O)Me	1:2	100/3	**3c** 81[b]	
15	**5c**	*n*-Pent	H	C(=O)Me	1:2	25/24	**3c** 21[b]	**8c** 57
16	**5d**	Me	Me	C(=O)Me	1:2	100/3	**3d** 53	**8d** 6
17	**5e**	$-(CH_2)_5-$		C(=O)Me	1:2	100/13	**3e** 23	
18	**5g**	Ph	Me	C(=O)Me	1:2	100/3	Sluggish reaction	
19	**6b**	Me	H	H	1:2	100/13	**3b** 15	**9b** 70[e]
20	**6d**	Me	Me	H	1:2	100/5	**3d** 40[f]	**9d** 30
21	**6e**	$-(CH_2)_5-$		H	1:2	100/8	**3e** 81	
22	**6f**	$-(CH_2)_4-$		H	1:2	100/7	**3f** 72	
23	**6g**	Ph	Me	H	1:2	100/7	**3g** 83[g]	**9g** 5
24	**6h**	Ph	Ph	H	1:2	100/8	**3h** 56	**9h** 24

[a] Contaminated by 2-methyl-3-dimethylphenylsilylpropenal.
[b] Almost single geometry ($Z > 98\%$).
[c] In the presence of Et_3N.
[d] Slightly contaminated by 2-dimethylphenylsilylbutanal.
[e] $E:Z = 1:1$.
[f] Estimated from ^{1}H-NMR spectrum.
[g] $E:Z = 6.75:1$.

Mechanistic details aside, the above drawback prompted the exploitation of a new route in which **3** is directly derived from propargylic alcohols **6**. Thus, when **6e** was subjected to the carbonylation in the presence of two equivalents of Me_2PhSiH, **3e** was formed almost selectively although a relatively long reaction time (100°C, 8 h) was necessary for an acceptable conversion of **6e** (entry 21 in Table 1). Analogously, **6f** and **6g** gave **3f** and **3g**, respectively, in good yields under similar conditions (entries 22 and 23 in Table 1). It is notable that even less substituted **6b** gave **3b** in 15% yield with the concomitant formation of **9b** as a major component, although the hydroxy group contained in **6b** is far inferior to the tertiary one as a leaving group (entry 19 in Table 1). Since it is known that silylformylated product **9** is the sole product in the Rh-catalyzed carbonylation of **6** in the presence of one equivalent of Me_2PhSiH [6b], the fact that **3** was selectively formed in the reaction of **6** with two equivalents of Me_2PhSiH is intuitively elucidated by the idea that **9** formed at the first stage interacts subsequently with an extra mole of Me_2PhSiH. In fact, when the isolated **9g** was heated with one equivalent of Me_2PhSiH under CO pressure in the presence of a catalytic amount of $Rh_4(CO)_{12}$ for 7 h, **9g** was completely consumed to give **3g** (78%, $E:Z = 78:22$) and $Me_2PhSiOH$. In the present transformation, CO pressure (20 kg cm^{-2}) is crucial for the complete consumption of **9g**. Analogous transformation for **9b** and **9d** proceeded smoothly to give **3b** and **3d**, respectively, under CO pressure, as shown in Eq. (3).



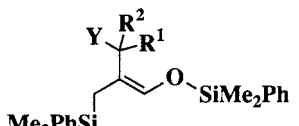
(3)



Scheme 3. Putative pathway for the formation of **3** (ligands on rhodium are eliminated for clarification).

Since silylformylation of **6** gives **9** in high yield regardless of the type of substitution on the propargyl carbon, these results suggest that the transformation of **6** to **3** is also attained through a two-step procedure relayed by **9**. Although there is no clear information relating to the intermediate at present, the transformation of **4**, **5** and **6** to **3** can be regarded as the result of the separate steps, the formation of **7**, **8** or **9** and the hydrosilylation of these compounds followed by the elimination of $Me_2PhSiOX$ {X = C(=O)OCH_3, C(=O)CH_3 or H}.

A persuasive possibility to elucidate the catalytic cycle is shown in Scheme 3. $Rh_4(CO)_{12}$ is readily converted to a mononuclear Rh–Si species **10** [6g] which has a sufficient capacity to form **11** as the result of oxidative addition of another R_3SiH. A similar type oxidative addition to form disilylrhodium species is demonstrated by Aizenberg et al. [13]. Silylformylation of **4**, **5** or **6** proceeds via the sequence of the following steps as shown in a previous report [6g], insertion of an acetylenic bond into Rh–Si bond to form **12** and the subsequent insertion of CO into the Rh–C bond to form **13**. The resultant enal, **7**, **8** or **9** again interacts with **11** to form **15**, which reacts with another mole of Me_2PhSiH to give **3** and R_3Si–Y and restores **11**. The final process of **15** to **3** is obscure at present. The following two steps may be plausible to recreate **11**: the formation of **16** as the result of the reductive elimination from **15** and the subsequent 1,4-elimination of R_3Si–Y from **16** to give **3**. However, any quantity of **16** was not detected in the reaction systems (see Scheme 3).



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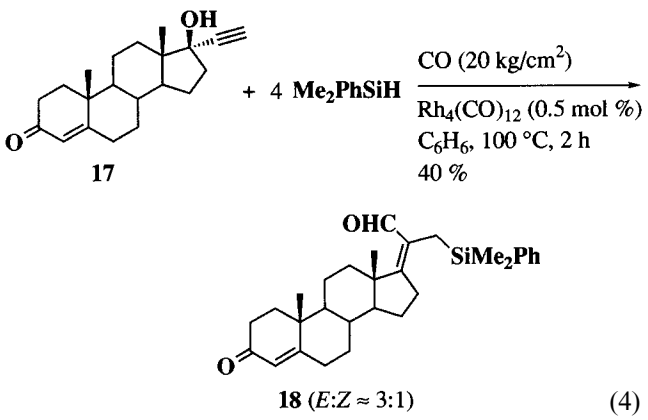
Apart from the mechanistic point of view, the present transformation of **4**, **5** and **6** to form **3** plays an important role for a virtual Wittig-type carbonyl olefination of aldehydes and ketones that is attained by the intervention of propargyl alcohol derivatives. The present transformation is also applicable to polyfunctionalized substrates, e.g. ethisterone (**17**) as shown in Eq. (4). It should be noted that the reaction can be conducted in single operation to give **18** (E:$Z \approx 3$:1) in a moderate yield without any protection of the carbonyl group of **17**. E-geometry of the isolated **18** was deduced by the observation of an NOE enhancement

(6%) between the formyl proton and the 18-methyl protons.



(4)

3. Conclusions

This paper reported a new route to form 2-(dimethylphenylsilylmethyl)-2-alkenals resulting either from $Rh_4(CO)_{12}$ catalyzed reaction of propargyl alcohol derivatives with more than two equivalents of Me_2PhSiH, or from $Rh_4(CO)_{12}$ catalyzed reaction of 2-(1-hydroxyalkyl)-3-dimethylphenylsilylpropenal with one equivalent of Me_2PhSiH under CO pressure. The authors have described the scope and limitations of this strategy and demonstrated the successful result for ethisterone. They have pointed out that their new transformation plays a key role in the substitution of the carbonyl oxygen to a 1-formyl-2-silylethylidene group.

4. Experimental

4.1. General

Anhydrous solvents were transferred via an oven-dried syringe. Benzene (thiophene-free) and all other solvents were utilized at their commercial level of purity. $Rh_4(CO)_{12}$ was prepared according to the literature procedures [14]. Propargyl-type alcohols **6**, **10** and Me_2PhSiH were obtained from Aldrich, Lancaster, Tokyo Kasei or Shin-etsu Chemicals. They were used as-received. Carbonates **4** and acetates **5** were prepared from the corresponding **6** according to a conventional method.

All reactions were monitored by thin layer chromatography carried out on 0.25 mm Merck silica gel plates (60 F-254) using UV light as a visualizing agent and 7% ethanolic phosphomolybdic acid and heat as developing agent. Merck silica gel (60, particle size 0.063–0.200 mm) was used for column chromatography.

Proton nuclear magnetic resonance (^{1}H-NMR) data were obtained in $CDCl_3$ at 200 MHz on a Varian GEM-200, at 300 MHz on a Varian Mercury 300, or at 500 MHz on a Varian INOVA-500 spectrometer. Chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for chloroform-d. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; and b, broad. Coupling constants are reported in Hz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were obtained at 50 MHz on a Varian GEM-200, at 75 MHz on a Varian Mercury 300, at 125.7 MHz on a Varian INOVA-500 and are reported in ppm with the center line of a triplet at 77.00 ppm for chloroform-d. Routine ^{13}C spectra were fully decoupled by broadband decoupling. IR data were recorded as a CCl_4 solution in 0.1 mm path length sodium chloride cavity cells on a JASCO FT/IR-230 spectrometer. Absorbance frequencies are reported in cm^{-1}. Melting points were obtained on a Büchi 510-K apparatus in sealed capillary tubes and are uncorrected. Boiling points are also uncorrected. Kügelrohr distillation was performed in a Büchi KR-3 oven. Elemental analyses were performed by the Microanalytical Center of Kyoto University.

4.2. Reactions of *4*, *5* or *6* with Me_2PhSiH under CO pressure

4.2.1. General procedure

A glass tube (28 mm o.d.) fitted with a stirring bar was charged with $Rh_4(CO)_{12}$ (0.4 mol.% of **4**, **5** or **6**) and benzene (7 ml) saturated by CO. The tube was put in a 100-ml stainless steel autoclave. The reactor was pressurized by CO to 20 kg cm^{-2}. The content was stirred for 5 min at ambient temperature and then the pressurized CO was purged in a hood. Into this tube, Me_2PhSiH (two equivalents of **4**, **5** or **6**) in C_6H_6 (2 ml), and **4**, **5** or **6** (ca. 3 mmol) in C_6H_6 (1 ml) were added consecutively through a syringe needle at ambient temperature. The reactor was pressurized again by CO to 20 kg cm^{-2}. The content was stirred for 2 h at 100°C and cooled to ambient temperature. After excess of CO was purged in a hood, the reaction mixture was concentrated under reduced pressure. The residual oily liquid was chromatographed on silica gel using a mixture of hexane:AcOEt (97:3) as an eluent to give the corresponding products.

The following compounds were isolated from the reaction of Me_2PhSiH with the corresponding propargyl alcohol derivatives.

*4.2.2. 2-(Dimethylphenylsilylmethyl)propenal (**3a**)*

A colorless liquid (b.p. 82°C/0.5 torr). IR: 1690 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (200 MHz) δ: 0.25 (s, 6H, Si(CH_3)$_2$), 1.98 (d, $J = 1.0$ Hz, 2H, SiCH_2), 5.80 (d, $J = 0.8$ Hz, 1H, =CH), 5.95 (q, $J = 1.0$ Hz, 1H, =CH), 7.35 (m, 3H, Ph), 7.50 (m, 2H, Ph), 9.45 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −3.56 (SiCH$_3$), 16.84 (SiCH$_2$), 127.88 (Ph *meta*), 129.31 (Ph *para*), 132.24 (=CH$_2$), 133.77 (Ph *ortho*), 138.00 (Ph *ipso*), 147.84 (=C q), 194.70 (CHO). Anal. Calc. for $C_{18}H_{20}N_4O_4Si$ {2,4-dinitrophenylhydrazone (red–brown leaflet from EtOH, m.p. 157.0–158.0°C)}: C, 56.23%; H, 5.24%; N, 14.57%. Found: C, 55.85%; H, 5.26%; N, 14.53%.

*4.2.3. (Z)-2-(Dimethylphenylsilylmethyl)-2-butenal (**3b**)*

A colorless liquid (b.p. 80°C/0.4 torr). IR: 1690 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (500 MHz) δ: 0.26 (s, 6H, Si(CH_3)$_2$), 1.66 (t of d, $J = 7.0$ and 0.7 Hz, 3H, CCH_3), 1.95 (broad s, 2H, SiCH_2), 6.41 (t of q, $J = 7.0$ and 0.8 Hz, 1H, =CH), 7.33–7.37 (m, 3H, Ph), 7.50–7.55 (m, 2H, Ph), 9.32 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −3.03 (SiCH$_3$), 13.77 (SiCH$_2$), 14.88 (CCH$_3$), 127.89 (Ph *meta*), 129.26 (Ph *para*), 133.72 (Ph *ortho*), 138.67 (Ph *ipso*), 142.64 (=C q), 147.13 (=CH), 195.14 (CHO). Anal. Calc. for $C_{19}H_{22}N_4O_4Si$ {2,4-dinitrophenylhydrazone of **3b** (red–orange leaflet from EtOH, m.p. 163.5–164.5°C}: C, 57.27%; H, 5.57%; N, 14.06%. Found: C, 56.97%; H, 5.57%; N, 13.94%.

*4.2.4. (Z)-2-(Dimethylphenylsilylmethyl)-2-octenal (**3c**)*

IR: 1680 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (500 MHz) δ: 0.26 (s, 6H, Si(CH_3)$_2$), 0.87 (t, $J = 7.3$ Hz, 3H, CH$_2$CH_3), 1.16–1.34 (m, 6H, 3 × CH_2), 1.94 (broad s, 2H, SiCH_2), 2.00 (t of d, $J = 7.3$ and 7.3 Hz, 2H, =CHCH_2CH$_2$), 6.28 (t, $J = 7.3$ Hz, 1H, =CH), 7.33–7.36 (m, 3H, Ph), 7.49–7.52 (m, 2H, Ph), 9.32 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −2.98 (SiCH$_3$), 13.77 (SiCH$_2$), 14.11 (CCH$_3$), 22.25 (CH$_2$CH$_3$), 28.03 (=CCH$_2$CH$_2$), 29.14 (CH$_2$CH$_2$CH$_3$), 31.40 (=CCH$_2$$CH_2$), 127.89 (Ph *meta*), 129.26 (Ph *para*), 133.76 (Ph *ortho*), 138.71 (Ph *ipso*), 141.28 (=C q), 152.97 (=CH), 195.41 (CHO). Anal. Calc. for $C_{23}H_{30}N_4O_4Si$ {2,4-dinitrophenylhydrazone of **3c** (red–orange leaflet from EtOH, m.p. 131.0–133.0°C}: C, 60.77%; H, 6.65%; N, 12.32%. Found: C, 60.70%; H, 6.64%; N, 12.17%.

*4.2.5. 2-(Dimethylphenylsilylmethyl)-3-methyl-2-butenal (**3d**)*

A colorless liquid (b.p. 80°C/0.2 torr). IR: 1665 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (300 MHz) δ: 0.24 (s, 6H, Si(CH_3)$_2$), 1.66 (s, 3H, =CCH_3), 1.97 (broad s, 2H, SiCH_2), 2.13 (s, 3H, =CCH_3), 7.34–7.39 (m, 3H, Ph), 7.50–7.56 (m, 2H, Ph), 10.12 (s, 1H, CHO). ^{13}C-NMR (75 MHz) δ: −2.57 (SiCH$_3$), 15.17 (SiCH$_2$), 19.11 (=CCH$_3$), 24.01 (=CCH$_3$), 127.62 (Ph *meta*), 128.90 (Ph *para*), 133.50 (Ph *ortho*), 134.31 (=C q), 139.04 (Ph *ipso*), 151.72 (=C q), 190.42 (CHO). Anal. Calc. for $C_{14}H_{20}OSi$: C, 72.36%; H, 8.67%. Found: C, 72.42%; H, 8.74%.

*4.2.6. 2-Cycohexylidene-3-(dimethylphenylsilyl)propanal (**3e**)*

A colorless liquid (b.p. 105°C/0.5 torr). IR: 1660 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (200 MHz) δ: 0.23 (s, 6H, Si(CH_3)$_2$, 1.4–1.7 (m, 6H, 3 × CH_2), 2.00 (s, 2H, SiCH_2), 2.10 (t, 2H, $J = 6.0$ Hz, CH_2), 2.69 (t, 2H, $J = 5.5$ Hz, CH_2), 7.35 (m, 3H, Ph), 7.50 (m, 2H, Ph), 10.16 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −2.58 (SiCH$_3$), 14.64 (SiCH$_2$), 26.36 (CH$_2$), 27.56 (CH$_2$), 28.69 (CH$_2$), 29.09 (CH$_2$), 33.61 (CH$_2$), 127.59 (Ph *meta*), 128.86 (Ph *para*), 131.68 (=C q), 133.63 (Ph *ortho*), 138.96 (Ph *ipso*), 159.40 (=C q), 189.95 (CHO). Anal. Calc. for $C_{17}H_{24}OSi$: C, 74.95%; H, 8.88%. Found: C, 74.86%; H, 8.95%.

*4.2.7. 2-Cycopentylidene-3-(dimethylphenylsilyl) propanal (**3f**)*

A pale yellow liquid. IR: 1669 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (200 MHz) δ: 0.26 (s, 6H, Si(CH_3)$_2$), 1.51 (ca. quint. $J = 7.0$ Hz, 2H, CH_2), 1.70 (ca. quint. $J = 7.0$ Hz, 2H, CH_2), 1.87 (broad s, 2H, SiCH_2), 2.10 (ca. t, $J = 6.4$ Hz, 2H, CH_2), 2.76 (ca. t, $J = 7.2$ Hz, 2H, CH_2), 7.30–7.36 (m, 3H, Ph), 7.45–7.53 (m, 2H, Ph), 9.95 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −2.69 (SiCH$_3$), 16.23 (SiCH$_2$), 24.58 (CH$_2$), 26.63 (CH$_2$), 29.54 (=CCH$_2$), 33.85 (=CCH$_2$), 127.74 (Ph *meta*), 129.06 (Ph *para*), 131.35 (=C q), 133.64 (Ph *ortho*), 139.27 (Ph *ipso*), 165.50 (=C q), 191.72 (CHO). Anal. Calcd. for $C_{22}H_{26}N_4O_4Si$ {2,4-dinitrophenylhydrazone of **3f** (orange needles from EtOH, m.p. 161.0–162.0°C)}: C, 60.25%; H, 5.98%; N, 12.78%. Found: C, 60.04%; H, 6.02%; N, 13.04%.

*4.2.8. 2-(Dimethylphenylsilylmethyl)-3-phenyl-2-butenal (**3g**)*

A pale yellow oily liquid (b.p. 140°C/0.2 torr). Anal. Calc. for $C_{25}H_{26}N_4O_4Si$ {2,4-dinitrophenylhydrazone of *E* and *Z* mixture of **3g** (orange needles from C_6H_6/EtOH/hexane, m.p. 195.0–196.0°C)}: C, 63.26%; H, 5.52%; N, 11.80%. Found C, 63.26%; H, 5.43%; N, 11.89%.

(*E*)-**3g**: IR: 1672 cm^{-1} ($\nu_{C=O}$), ^{1}H-NMR (200 MHz) δ: 0.36 (s, 6H, Si(CH_3)$_2$), 1.93 (broad s, 3H, CH_3), 2.13 (broad s, 2H, CH_2), 7.06–7.13 (m, 2H, Ph), 7.29–7.41 (m, 6H, Ph), 7.51–7.60 (m, 2H, Ph), 9.41 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −2.65 (SiCH$_3$), 15.74 (SiCH$_2$), 23.63 (=CCH$_3$), 127.92 (Ph *meta*), 128.06 (Ph *para*), 128.26 (Ph *meta*), 128.95 (Ph *ortho*), 129.27 (Ph *para*), 133.79 (Ph *ortho*), 136.81 (Ph *ipso*), 138.87 (Ph *ipso*), 140.84 (=C q), 155.01 (=C q), 193.69 (CHO).

(*Z*)-**3g**: IR: 1670 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (200 MHz) δ: 0.11 (s, 6H, SiCH_3), 1.94 (q, 2H, $J = 0.95$ Hz, CH_2),

2.40 (t, 3H, $J = 0.95$ Hz, CH_3), 6.96–7.02 (m, 3H, Ph), 7.21–7.37 (m, 7H, Ph), 10.30 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −2.43 (SiCH$_3$), 15.91 (CH$_2$), 19.70 (CH$_3$), 126.98 (Ph *meta*), 127.55 (Ph *para*), 127.66 (Ph *ortho*), 128.58 (Ph *meta*), 128.85 (Ph *para*), 133.72 (Ph *ortho*), 135.91 (Ph *ipso*), 139.19 (Ph *ipso*), 143.37 (=C q), 152.97 (=C q), 191.92 (CHO).

4.2.9. 2-(Dimethylphenylsilylmethyl)-3,3-diphenylpropenal (**3h**)

A yellow–orange oily liquid (b.p. 200°C/6 torr). IR: 1669 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (200 MHz) δ: 0.21 (s, 6H, Si(CH_3)$_2$), 2.24 (s, 2H, SiCH_2), 6.94–7.00 (m, 1H, Ph), 7.03–7.08 (m, 2H, Ph), 7.24–7.38 (m, 12H, Ph), 9.46 (s, 1H, CHO). ^{13}C-NMR (75 MHz) δ: −2.02 (SiCH$_3$), 17.59 (SiCH$_2$), 127.62 (Ph), 127.96 (Ph), 128.05 (Ph), 128.32 (Ph), 128.56 (Ph), 128.85 (Ph), 129.24 (Ph), 130.96 (Ph), 133.67 (Ph), 138.37 (Ph *ipso*), 138.63 (=C q), 139.48 (Ph *ipso*), 141.44 (Ph *ipso*), 159.90 (=C q), 194.07 (CHO). Anal. Calc. for $C_{24}H_{24}$OSi: C, 80.85%; H, 6.78%; Found C, 80.74%; H, 6.70%.

4.2.10. (Z)-2-(Methoxycarbonyloxymethyl)-3-dimethylphenylsilylpropenal (**7a**)

A colorless liquid (b.p. 120°C/0.15 torr). IR: 1753, 1682 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (300 MHz) δ: 0.54 (s, 6H, Si(CH_3)$_2$), 3.81 (s, 3H, OCH_3), 4.88 (d, $J = 1.5$ Hz, 2H, OCH_2), 7.20 (t, $J = 1.5$ Hz, 1H, =CH), 7.34–7.43 (m, 3H, Ph), 7.49–7.55 (m, 2H, Ph), 9.76 (s, 1H, CHO). ^{13}C-NMR (75 MHz) δ: −0.38 (SiCH$_3$), 55.03 (OCH$_3$), 65.56 (OCH$_2$), 128.17 (Ph *meta*), 129.64 (Ph *para*), 133.42 (Ph *ortho*), 136.80 (Ph *ipso*), 149.40 (=C q), 150.10 (=CH), 155.12 (OC(=O)), 191.13 (CHO). Anal. Calc. for $C_{14}H_{18}O_4Si$: C, 60.40%; H, 6.52%. Found: C, 60.34%; H, 6.54%.

4.2.11. (Z)-2-(1-Methoxycarbonyloxyhexyl)-3-dimethylphenylsilylpropenal (**7c**)

A pale yellow liquid (b.p. 130°C/0.2 torr). IR: 1748, 1683 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (300 MHz) δ: 0.52 (s, 3H, SiCH_3), 0.53 (s, 3H, SiCH_3), 0.87 (t, $J = 6.9$ Hz, 3H, CH$_2$CH_3), 1.20–1.38 (m, 6H, 3 × CH_2), 1.60–1.75 (m, 2H, CH_2), 3.77 (s, 3H, OCH_3), 5.52 (ddd, $J = 6.3$, 6.0 and 0.6 Hz, 1H, OCH), 7.14 (d, $J = 0.6$ Hz, 1H, =CH), 7.33–7.42 (m, 3H, Ph), 7.45–7.53 (m, 2H, Ph), 9.75 (s, 1H, CHO). ^{13}C-NMR (75 MHz) δ: −0.42 (SiCH$_3$), −0.34 (SiCH$_3$), 13.91 (CH$_2$$CH_3$), 22.41 ($CH_2$), 24.78 ($CH_2$), 31.34 ($CH_2$), 34.48 ($CH_2$), 54.79 (O$CH_3$), 75.15 (O$CH_2$), 128.25 (Ph *meta*), 129.66 (Ph *para*), 133.52 (Ph *ortho*), 137.26 (Ph *ipso*), 148.14 (=CH), 154.70 (=C q), 154.80 (OC(=O)), 191.21 (CHO). Anal. Calc. for $C_{19}H_{28}O_4Si$: C, 65.48%; H, 8.10%. Found: C, 65.30%; H, 8.16%.

4.2.12. (Z)-2-Acetoxymethyl-3-dimethylphenylsilylpropenal (**8a**)

A colorless liquid (b.p. 135°C/0.1 torr). ^{1}H-NMR (200 MHz) δ: 0.54 (s, 6H, Si(CH_3)$_2$), 2.11 (s, 3H, C(=O)CH_3), 4.82 (d, $J = 1.5$ Hz, 2H, OCH$_2$), 7.13 (d, $J = 1.5$ Hz, 1H, =CH), 7.35–7.41 (m, 3H, Ph), 7.49–7.55 (m, 2H, Ph), 9.77 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −0.69 (SiCH$_3$), −0.60 (SiCH$_3$), 20.70 (C(=O)CH$_3$), 62.35 (OCH$_2$), 128.43 (Ph *meta*), 129.89 (Ph *para*), 133.71 (Ph *ortho*), 137.23 (Ph *ipso*), 150.07 (=C q), 150.35 (=CH), 170.63 (OC(=O)), 191.89 (CHO). Anal. calc. for $C_{14}H_{18}O_3Si$: C, 64.09%; H, 6.91%. Found: C, 63.87%; H, 6.83%.

4.2.13. (Z)-2-(1-Acetoxyethyl)-3-dimethylphenylsilylpropenal (**8b**)

A colorless liquid (b.p. 150°C/0.2 torr). IR: 1748, 1687 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (200 MHz) δ: 0.52 (s, 6H, Si(CH_3)$_2$), 1.34 (d, $J = 6.5$ Hz, 3H, CHCH_3), 2.07 (s, 3H, C(=O)CH_3), 5.70 (dq, $J = 6.5$ and 1.0 Hz, 1H CHCH$_3$), 7.10 (d, $J = 1.0$ Hz, 1H, =CH), 7.33–7.41 (m, 3H, Ph), 7.46–7.55 (m, 2H, Ph), 9.76 (s, 1H, CHO). ^{13}C-NMR (50 MHz) δ: −0.65 (SiCH$_3$), −0.60 (SiCH$_3$), 20.22 (CH$_3$), 20.98 (C(=O)CH$_3$), 67.92 (OCH), 128.38 (Ph *meta*), 129.79 (Ph *para*), 133.66 (Ph *ortho*), 137.45 (Ph *ipso*), 147.41 (=CH), 156.10 (=C q), 169.91 (OC(=O)), 191.64 (CHO). Anal. Calc. for $C_{15}H_{20}O_3Si$: C, 65.18%; H, 7.29%. Found: C, 65.19%; H, 7.28%.

4.2.14. (Z)-2-(1-Methoxycarbonyloxyhexyl)-3-dimethylphenylsilylpropenal (**8c**)

A pale yellow oily liquid (b.p. 120°C/0.15 torr). IR: 1737, 1684 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (300 MHz) δ: 0.51 (s, 3H, SiCH_3), 0.52 (s. 3H, SiCH_3), 0.87 (t, $J = 6.6$ Hz, 3H, CH_3), 1.24–1.32 (m, 6H, 3 × CH_2), 1.59–1.67 (m, 2H, CH_2), 2.08 (s, 3H, C(=O)CH_3), 5.61 (ddd, $J = 6.9$, 4.8, and 0.9 Hz, 1H, OCH), 7.03 (d, $J = 0.9$ Hz, 1H, =CH), 7.35–7.41 (m, 3H, Ph), 7.46–7.52 (m, 2H, Ph), 9.75 (s, 1H, CHO). ^{13}C-NMR (75 MHz) δ: −0.25 (SiCH$_3$), −0.20 (SiCH$_3$), 14.03 (CCH$_3$), 21.18 (C(=O)CH$_3$), 22.52 (CH$_2$), 25.05 (CH$_2$), 31.43 (CH$_2$), 34.37 (CH$_2$), 71.61 (OCH), 128.12 (Ph *meta*), 129.50 (Ph *para*), 133.38 (Ph *ortho*), 137.24 (Ph *ipso*), 147.53 (=CH), 155.00 (=C q), 169.66 (OC(=O)), 191.12 (CHO). Anal. Calc. for $C_{19}H_{28}O_3Si$: C, 68.63%; H, 8.49%. Found: C, 68.34%; H, 8.53%.

4.2.15. (Z)-2-(1-Methoxycarbonyloxy-1-methylethyl)-3-dimethylphenylsilylpropenal (**8d**)

A colorless liquid (b.p. 100°C/0.2 torr). IR: 1729, 1688 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (300 MHz) δ: 0.50 (s, 6H, Si(CH_3)$_2$), 1.63 (s, 6H, 2 × CH_3), 2.00 (s, 3H, C(=O)CH_3), 6.90 (s, 1H, =CH), 7.35–7.40 (m, 3H, Ph), 7.50–7.56 (m, 2H, Ph), 9.76 (s, 1H, CHO). ^{13}C-NMR (75 MHz) δ: −0.34 (SiCH$_3$), 21.97 (C(=O)CH$_3$), 27.05

($OC(CH_3)_2$), 81.04 ($OC(CH_3)_2$), 127.99 (Ph *meta*), 129.26 (Ph *para*), 133.44 (Ph *ortho*), 137.74 (Ph *ipso*), 145.12 (=CH), 158.00 (=C q), 169.69 (OC(=O)), 191.07 (CHO). Anal. Calc. for $C_{16}H_{22}O_3Si$: C, 66.17%; H, 7.64%. Found: C, 66.15%; H, 7.80%.

4.2.16. (Z)-2-(1-Hydroxyethyl)-3-dimethylphenylsilylpropenal (**9b**)

See [6b].

4.2.17. (Z)-(1-Hydroxy-1-methylethyl)-3-dimethylphenylsilylpropenal (**9d**)

See [6b].

4.2.18. (Z)-2-(1-Hydroxy-1-phenylethyl)-3-dimethylphenylsilylpropenal (**9g**)

A yellow oily liquid (b.p. 150°C/5 torr). IR: 1682 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (500 MHz) δ: 0.57 (s, 6H, $SiCH_3$), 1.67 (s, 3H, CCH_3), 4.10 (s, 1H, OH), 7.30 (s, 1H, =CH), 7.21–7.24 (m, 2H, Ph), 7.29–7.41 (m, 6H, Ph), 7.53–7.56 (m, 2H, Ph), 9.71 (s, 1H, CHO). ^{13}C-NMR (125 MHz) δ: −0.34 ($SiCH_3$), 29.16 (CCH_3), 76.92 (OC), 124.59 (Ph), 127.00 (Ph), 128.24 (Ph), 128.29 (Ph), 129.70 (Ph), 133.50 (Ph), 137.22 (Ph *ipso*), 146.12 (Ph *ipso*), 148.96 (=C), 158.61 (=C q), 194.48 (CHO). Anal. Calc. for $C_{19}H_{22}O_2Si$: C, 73.51%, H, 7.14%. Found: C, 73.31%; H, 7.33%.

4.2.19. (Z)-2-(Hydroxydiphenylmehyl)-3-dimethylphenylsilylpropenal (**9h**)

A colorless needles from hexane (m.p. 104.5–105.5°C). IR: 1681 cm^{-1} (νC=O). ^{1}H-NMR (300 MHz) δ: 0.48 (s, 6H, $SiCH_3$), 4.79 (broad s, 1H, OH), 6.61 (s, 1H, =CH), 7.24–7.36 (m, 10H, Ph), 7.37–7.41 (m, SH, 5h), 9.85 (s, 1H, CHO). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: −0.39 ($SiCH_3$), 82.90 (OC), 127.31 (2 × Ph), 127.50 (2 × Ph), 128.08 (2 × Ph), 128.33 (Ph), 129.75 (Ph), 133.47 (Ph), 137.13 (Ph), 144.21 (2 × Ph *ipso*), 153.47 (=CH), 158.65 (=C q), 194.85 (CHO). Anal. Calc. for $C_{24}H_{24}O_2Si$: C, 77.38%; H, 6.49%. Found: C, 77.52%; H, 6.61%.

4.3. Reaction of **9b** with Me_2PhSiH under CO pressure

To a glass tube contained in a stainless steal pressure bottle, a benzene (7 ml) solution of $Rh_4(CO)_{12}$ (0.005 g, 0.0067 mmol) and a mixed solution of Me_2PhSiH (0.174 g 1.27 mmol) and **9b** (0.287 g, 1.22 mmol) in benzene (3 ml) were added successively. The reactor was pressurized to 20 kg cm^{-2} by CO gas and the content was stirred for 14 h at 100°C. The reactor was cooled to r.t. and then the excess CO gas was purged in a hood. The residue left by evaporation of volatiles was chromatographed on silica gel using a mixed solvent of hexane:ethyl acetate (97:3) as an eluent to give 0.171 g (64%) of **3b**.

4.4. Reaction of **9d** with Me_2PhSiH under CO pressure

To a glass tube contained in a stainless steal pressure bottle, a benzene (7 ml) solution of $Rh_4(CO)_{12}$ (0.012 g, 0.015 mmol) and a mixed solution of Me_2PhSiH (0.625 g 4.59 mmol) and **9d** (1.140 g, 4.59 mmol) in benzene (3 ml) were added successively. The reactor was pressurized to 20 kg cm^{-2} by CO gas and the content was stirred for 14 h at 100°C. The reactor was cooled to r.t. and then the excess CO gas was purged in a hood. The residue left by evaporation of volatiles was chromatographed on silica gel using a mixed solvent of hexane:ethyl acetate (97:3) as an eluent to give 0.662 g (62%) of **3d**.

4.5. Reaction of **9g** with Me_2PhSiH under CO pressure

To a glass tube contained in a stainless steal pressure bottle, a benzene (7 ml) solution of $Rh_4(CO)_{12}$ (0.005 g, 0.0067 mmol) and a mixed solution of Me_2PhSiH (0.127 g 0.93 mmol) and **9g** (0.281 g, 0.90 mmol) in benzene (3 ml) were added successively. The reactor was pressurized to 20 kg cm^{-2} by CO gas and the content was stirred for 7 h at 100°C. The reactor was cooled to r.t. and then the excess CO gas was purged in a hood. The residue left by evaporation of volatiles was chromatographed on silica gel using a mixed solvent of hexane:ethyl acetate (97:3) as an eluent to give 0.207 g (78%, $E:Z = 78:22$) of **3g**.

4.6. Reaction of ethisterone (**17**) with four equivalents of Me_2PhSiH under CO pressure

A glass tube (28 mm o.d.) fitted with a stirring bar was charged with $Rh_4(CO)_{12}$ (0.0068 g, 0.009 mmol) and benzene (7 ml) saturated by CO. The tube was put in a 100-ml stainless steel autoclave. The reactor was pressurized by CO to 20 kg cm^{-2}. The content was stirred for 5 min at ambient temperature and then the pressurized CO was purged in a hood. To this tube, Me_2PhSiH (0.698 g, 5.12 mmol) in C_6H_6 (2 ml) and **17** (0.352 g, 1.13 mmol) in C_6H_6 (1 ml) were added consecutively through a syringe needle at ambient temperature. The reactor was pressurized again by CO to 20 kg cm^{-2}. The content was stirred for 2 h at 100°C and cooled to ambient temperature. After excess of CO was purged in a hood, the reaction mixture was concentrated under reduced pressure. The residual oily liquid was chromatographed on silica gel using a mixture of hexane:AcOEt (95:5) as an eluent to give **18** (0.209 g, 40%, $E:Z \approx 3:1$) as a pale yellow resinous oil. This isomer mixture was recrystallized from EtOH to give *E*-**18** (0.127g) as colorless needles (m.p. 148.0–149.5°C). IR: 1680, 1665 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR (500 MHz) δ: 0.27 (s, 3H, $SiCH_3$), 0.29 (s, 3H, $SiCH_3$), 0.91–0.99 (m, 1H), 1.01 (s, 3H, CH_3), 1.02–1.22 (m,

2H), 1.19 (s, 3H, CH_3), 1.50–1.74 (m, 7H), 1.83 (s, 2H, SiCH_2), 1.82–1.88 (m, 1H), 2.00–2.09 (m, 2H), 2.18–2.47 (m, 6H), 5.74 (s, 1H, =CH), 7.30–7.36 (m, 3H, Ph), 7.46–7.50 (m, 2H, Ph), 10.17 (s, 1H, CHO). ^{13}C-NMR (125.7 MHz) δ: −2.22 (SiCH$_3$), 16.50 (SiCH$_2$), 17.29 (CH$_3$), 19.46 (CH$_3$), 21.57 (CH$_2$), 23.77 (CH$_2$), 31.68 (CH$_2$), 32.62 (CH$_2$), 32.93 (CH$_2$), 33.89 (CH$_2$), 34.97 (CH), 35.61 (CH$_2$), 38.42 (=C q), 40.05 (CH$_2$), 46.52 (=C q), 53.08 (CH), 55.51 (CH), 124.03 (=CH), 127.64 (Ph, *meta*), 128.96 (Ph *para*), 132.48 (=C q), 133.59 (Ph *ortho*), 139.09 (Ph *ipso*), 170.46 (=C q), 170.47 (=C q), 190.51 (CHO), 199.33 (C=O). Anal. Calc. for $C_{30}H_{40}O_2Si$: C, 78.21%; H, 8.75%. Found: C, 78.10%; H, 8.82%. {Additional signals for *Z*-**18**: ^{1}H-NMR δ: 0.26 (s, 3H, SiCH_3), 0.30 (s, 3H, SiCH_3), 5.74 (broad s, 1H, =CH), 9.98 (s, 1H, CHO).

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[11] *Z*-Geometries of **3b** and **3c** were deduced by the observation of a remarkable (12 and 16% enhancement, respectively) NOE effect between the vinyl proton and the formyl proton (Varian INOVA 500).

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