Rhodium-Catalyzed Silylformylation of Acetylenic Bonds: Its Scope and Mechanistic Considerations

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"Silylformylation" of alkynes, which means the simultaneous introduction of a trialkylsilyl group and a formyl group into a carbon−carbon triple bond to give 3-silyl-2-alkenal, is attained selectively by the interaction of an alkyne with a monohydrosilane in the presence of Rh catalyst under CO pressure (over 10 kg/cm^2). The presence of Rh catalyst is crucial for the attainment of this coupling, regardless of the types of precursors: $Rh_4(CO)_{12}$, $RhH(CO)(PPh_3)_3$, $[Rh(COD)Cl]_2$, $[Rh(COD)(PPh_3)_2]PF_6$, or $[Rh(COD)(DPPB)]PF_6$. This silylformylation is applicable to both terminal and internal alkynes. In the terminal ones, the terminal sp carbon is selectively silylated. The sp carbon bearing the bulkier substituent is formylated preferentially in internal alkynes, except for those containing a strong electron-withdrawing group. When a 1 mol excess of 1-alkynes is used under silylformylation conditions, the formation of 2-cyclopentenone derivatives is confirmed in addition to the usual silylformylation. All of these cyclopentenones are composed of two molecules of 1-alkyne and one molecule each of hydrosilane and CO. A catalyst precursor of these reactions, $Rh_4(CO)_{12}$, reacts almost quantitatively with hydrosilane and phenylacetylene to form $Rh(CO)_4SiR_3$ and $Rh_2(CO)_7$(phenylacetylene), respectively, under CO pressure in the stoichiometric reaction. Both of these species catalyze silylformylation with a similar efficiency to $Rh_4(CO)_{12}$. Furthermore, $Rh(CO)_4SiR_3$ readily reacts with phenylacetylene under a CO atmosphere to give 1,5-disilyl-2,4-diphenyl-1(*Z*),4(*Z*)-pentadien-3-one and $Rh_4(CO)_{12}$. On the basis of these results, a plausible pathway for silylformylation is elucidated by the sequence of the insertion of alkyne into the Rh−Si bond to form Rh−vinyl species and the subsequent insertion of CO. The insertion of another 1 mol of alkyne into Rh−vinyl species prior to CO insertion results in cyclopentenone annulations.

Introduction

Catalytic incorporation of carbon monoxide is one of the most elegant and economical synthetic tools for the direct introduction of a carbonyl group into organic molecules.[1] Various carbonylation reactions catalyzed by transition-metal complexes have been explored since the discovery of Roelen's reaction.[2] That of acetylenic compounds has been particularly interesting, since it provides a facile means for the synthesis of α,β-unsaturated ketones,[3,4] esters,[5] lactones,[6] amides,[7] and lactams.[7c] Although hydroformylation of acetylenic bonds could be an attractive method for the preparation of α,β-unsaturated aldehydes,[2f,8] a serious drawback is that the presence of excess hydrogen in the reaction vessel causes consecutive hydrogenation of carbon−carbon and/or carbon−oxygen double bonds of the resulting unsaturated aldehydes. In addition, there is no reliable

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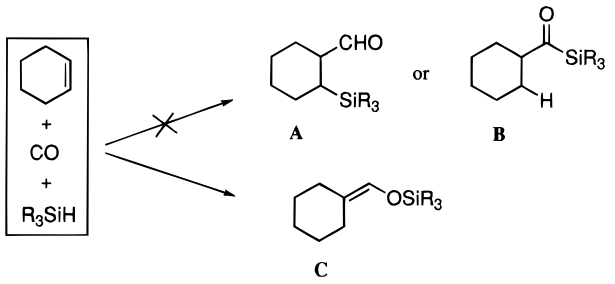
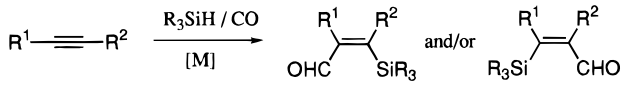
Scheme 1. Patterns Incorporating CO in the Presence of R_3SiH



Scheme 2. Silylformylation of Alkynes



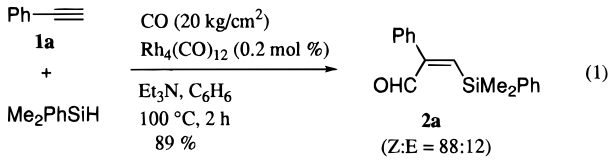
means to control the regiochemistry in the introduction of a hydrogen atom and a formyl group except for the hydroformylation of acetylenic bonds bearing a triorganosilyl group on one side of two sp carbons.[9] Hydrosilanes have been widely used in recent organic synthesis as a synthetic equivalent of molecular hydrogen. Carbonylation in the presence of hydrosilanes, which is conceptually comparable to the carbonylation under hydrogen pressure, has been explored by Murai and coworkers.[10] Their pioneering work established a method using $Co_2(CO)_8$ as a catalyst to introduce CO and hydrosilanes into alkenes,[11] aldehydes,[12] and cyclic ethers.[13] However, the most characteristic point in the Murai reaction of alkenes is that the isolated product is neither β-silyl aldehyde (**A**) nor acylsilane (**B**), which would be expected from the formal analogy with Roelen's reaction, but an enol silyl ether (**C**) (Scheme 1).

In 1989 we discovered the first examples of "silylformylation" of alkynes,[14] in which simultaneous incorporation of a triorganosilyl group and a formyl group into an acetylenic bond is attained by rhodium-catalyzed coupling of an alkyne, a hydrosilane, and CO as shown in Scheme 2. This finding triggered burgeoning interest in the incorporation of CO into alkynes,[15−18] enamines,[19] aldehydes,[20] epoxides,[21] and *N*,*N*-acetals[22] using R_3SiH/CO/transition-metal systems. The tacit assumption in explaining these reactions is that starting substrates insert into the transition-metal−silicon bond first formed; however, no definitive evidence supporting this assumption has yet been obtained. For organic synthesis the present rhodium-catalyzed silylformylation of alkynes is an ideal vehicle for the construction of many building blocks because of its high regio- and chemoselectivity, in sharp contrast to the results of hydroformylation. It provides a convenient access to β-silyl enals, which have been prepared by an indirect and relatively tedious procedure[23] and which have attracted the attention of many synthetic organic chemists as precursors of silyl-substituted dienes,[24] dienones,[25] and α,β-unsaturated ketones.[26]

In this paper, we report on the following three topics concerning rhodium-catalyzed silylformylation of alkynes: (i) full details of alkyne silylformylation focused on the regio- and stereoselectivity of the reactions, (ii) a novel type of cyclopentenone annulation which results from the coupling of two molecules of an alkyne and one molecule each of a hydrosilane and CO, and (iii) stoichiometric reactions of $Rh_4(CO)_{12}$ with hydrosilanes under CO pressure that provide informative suggestions on the reaction mechanism.

Results and Discussion

Preparation of β-Silyl Alkenals by Silylformylation of Acetylenic Compounds. As described in our previous paper,[14] β-silyl alkenals are generally synthesized by carbonylation of alkynes in the presence of trialkylhydrosilanes and catalytic amounts of $Rh_4(CO)_{12}$. Typically, a benzene[27] solution of phenylacetylene (**1a**), Me_2PhSiH (1 equiv based on **1a**), and $Rh_4(CO)_{12}$ (0.1−1 mol % based on **1a**) was stirred under CO pressure (20 kg/cm^2) to give the β-silylalkenal **2a** in 70−90% yield (eq 1). Addition of Et_3N to the reaction mixture was



not crucial for the silylformylation, but both the reaction

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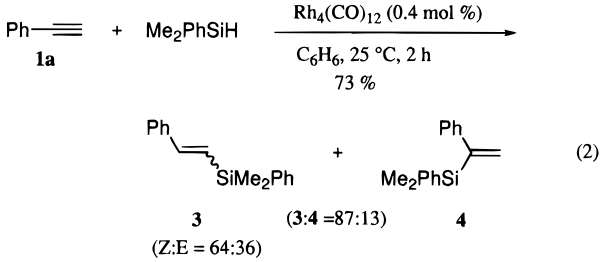
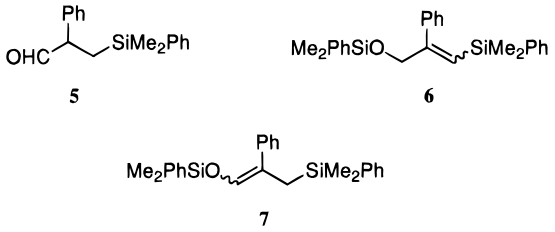
rate and the yield of the product were somewhat improved in its presence. It is well-known that rhodium complexes behave as an efficient catalyst for the hydrosilylation of alkynes. In fact, $Rh_4(CO)_{12}$ catalyzed the hydrosilylation of **1a** under an inert-gas atmosphere (*vide infra*). Though hydrosilylation is almost completely suppressed under CO pressure, it becomes an appreciable competing process in the silylformylation. Two practical procedures were devised to exclude the hydrosilylation; all of the reactants, solvents, and the catalyst were mixed at low temperature (−70 °C), where hydrosilylation does not occur, and then the reaction vessel was pressurized by CO. Alternatively, a solution of the catalyst was saturated with CO (20 kg/cm^2; 5 min) prior to the addition of reactants. In either procedure, the product yields remained unaltered when the CO pressure was reduced to 7−10 kg/cm^2, whereas appreciable amounts of hydrosilylation products were concomitantly formed as byproducts under less than 5 kg/cm^2 of CO pressure. When 10−20 kg/cm^2 of CO pressure and 0.1−0.2 mol % of the catalyst were applied, the reaction was complete within 2 h at 100 °C. Although the reaction became slower (600−700 turnover frequency at room temperature after 17 h), the silylformylation proceeded smoothly even at room temperature.

There are two possible regiochemistries with respect to the addition of the formyl group and the silyl group; however, it was confirmed that **2a** was the sole regioisomer in the silylformylation of **1a** with Me_2PhSiH. Of the two possible stereoisomers of **2a** (*Z* and *E*), the *Z* isomer was found to be a kinetic product, which was slowly isomerized to the thermodynamically more stable *E* isomer under the carbonylation conditions.[28−30] Typically, the *Z*:*E* ratio of **2a** was 88:12 in the reaction at 100 °C for 2 h, and the ratio of *E* form increased when a longer reaction time was applied. In other words, stereoselective preparation of the kinetic product (*Z* form of **2a**) is possible with careful selection of the reaction conditions; in fact, the *Z* to *E* ratio was 98:2 at 20 °C for 17 h. The extreme result (absence of detectable *E* isomer) was observed in the reaction containing a relatively large amount of catalyst (mole ratio of **1a** to $Rh_4(CO)_{12}$ ~320), in which the silylformylation was completed within 20 min at 25 °C. Such high regio- and stereoselectivities observed in the silylformylation are in notable contrast to the hydrosilylation, which resulted in rather sluggish selectivities. Treatment of **1a** and Me_2PhSiH with a catalytic amount of $Rh_4(CO)_{12}$ at room temperature under an N_2 atmosphere gave a mixture of the two regioisomers **3** and **4** in a ratio of 87:13 as shown in eq 2. The *Z* to *E* ratio of **3** was also low (64:36).



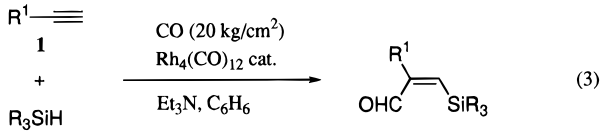
(2)

The use of a 1:1 mixture of **1a** and Me_2PhSiH is also critical to the formation of **2a** in high yields; alteration of the ratio caused the concomitant formation of several types of byproducts. As described later in detail, cyclopentenones resulting from the participation of two molecules of **1a** were obtained as a minor product when an excess amount of **1a** (**1a**:Me_2PhSiH = 2:1) was used in the carbonylation. In contrast to the above result, the subsequent hydrosilylation of **2a** took place in the presence of excess Me_2PhSiH. For example, in the silylformylation using a 1:2 mixture of **1a** and Me_2PhSiH at 95 °C for 13 h, appreciable amounts of **5**, **6**, and **7** in addition to **2a** were detected in the NMR



spectrum of the reaction mixture. Compounds **6** and **7** were derived from the subsequent hydrosilylation of **2a**, whereas **5** was formed by protodesilylation of the enol silyl ether part of **7**.

Some other hydrosilanes in addition to Me_2PhSiH were applicable to the silylformylation of **1a**, in which most of them were completely consumed after stirring a mixed solution at 100 °C for 2 h or at 25 °C for 15 h. Although the rough profiles of the reactions were identical in most silanes, details of the rate of reaction and the yield of the product were remarkably affected by the substituents contained in hydrosilanes, as shown in Table 1.



(3)

2 $SiR_3 = SiMe_2Ph$
8 $SiR_3 = SiMePh_2$
9 $SiR_3 = SiEt_3$
10 $SiR_3 = SiEt_2Me$
11 $SiR_3 = Si^tBuMe_2$
12 $SiR_3 = SiMe_2(OEt)$
13 $SiR_3 = Si(OMe)_3$

For example, it was found that silylformylation of **1a**

(27) Benzene is not the solvent of choice in silylformylation. All of the following solvents gave similar results under similar conditions: toluene, hexane, $CHCl_3$, CH_2Cl_2, CH_3CN, and THF.

(28) The stereoisomers of *β*-silylalkenals were easily diagnosed by ^{1}H NMR spectra using the NOE technique. In a typical example using both isomers of **2e**, which were completely separated by silica gel column chromatography, 12% enhancement of signals was observed in the NOE experiment between the formyl proton and the vinyl one in the *E* form, whereas it was not seen in the *Z* form. Similar experiments on all of the *β*-silylalkenals described in this paper revealed that the formyl proton contained in the *Z* form generally appeared at 0.3−0.5 ppm lower field than the *E* form. This observation is consistent with a previous report.[29]

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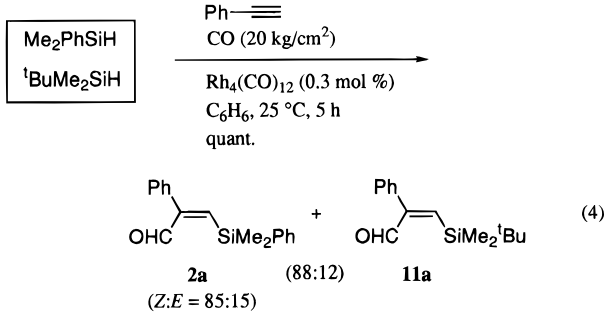
(30) 3-Silylalkenals **2a**, **2c**, **2d**, **2e**, **2j**, **2k**, **9e**, and **10e**, isolated as a mixture of *Z* and *E* forms, were exclusively converted to the corresponding *E* form by stirring a benzene solution of the respective sample in the presence of a catalytic amount of HI for 14 h at 25 °C. Although the process from *E* form to *Z* form exists in a particular case such as **2m**, in which separate $CDCl_3$ solutions of the isolated *E* and *Z* isomers settled down into an identical mixture (*Z*:*E* = 19:81) even in the absence of HI, all these results consistently suggest that the *E* form of the silylformylation product is generally more thermodynamically stable than the *Z* form.

Table 1. Silylformylation of Phenylacetylene (1a)[a]

entry no.	hydrosilane	conditions[b]	products	yield (%)[c]	*Z*:*E*[d]
1	Me_2PhSiH	A	**2a**	89	88:12
2	Me_2PhSiH	B	**2a**	90	98:2
3	$MePh_2SiH$	A	**8**	94	83:17
4	$MePh_2SiH$	B	**8**	84	97:3
5	Et_3SiH	A	**9a**	92	91:9
6	Et_3SiH	B	**9a**	85	98:2
7	Et_2MeSiH	A	**10a**	75	79:21
8	Et_2MeSiH	B	**10a**	78	98:2
9	$^tBuMe_2SiH$	A	**11a**	22[f]	92:8
10	$^tBuMe_2SiH$	B[e]	**11a**	82	98:2
11	$Me_2(EtO)SiH$	B	**12**	70[g]	50:50
12	$(MeO)_3SiH$	B	**13**	47[h]	14:86
13	$^iPr_3SiH$	A		0	
14	Ph_2SiH_2	A		0	

[a] All reactions were conducted on a scale of 3−9 mmol in a benzene solution containing 0.2 mol % of $Rh_4(CO)_{12}$ and equimolar amounts of **1a**, hydrosilane, and Et_3N under CO pressure (20 kg/cm^2). [b] Legend: (A) reaction was carried out for 2 h at 100 °C; (B) reaction was carried out for 15 h at 25 °C. [c] Isolated yield. [d] Determined from the ^1H NMR spectra. [e] Reaction time was increased to 65 h. [f] The reaction was not completed. [g] The product was obtained as a mixture of **12** and hemiacetal **14** (**12**:**14** = 2:1) by direct distillation of the reaction mixture. [h] The product was obtained as a mixture of **13** and hemiacetal **15** (**13**:**15** = 6:1) by direct distillation of the reaction mixture.

with hydrosilanes bearing a phenyl group proceeds approximately 10 times faster than that with trialkylsilanes. The rate was roughly estimated from the turnover frequencies of $Rh_4(CO)_{12}$, 570, 460, and 60, which were obtained in the silylformylation at 25 °C for 3.5 h using Me_2PhSiH, $MePh_2SiH$, and Et_2MeSiH as the hydrosilane, respectively. It takes 65 h to complete silylformylation of **1a** with $^tBuMe_2SiH$ at 25 °C (entry 10 in Table 1); this is approximately 4 times as long as that with Et_2MeSiH.[31] The operation at 100 °C in order to accelerate reaction rate did not improve the yield of **11a** (entry 9 in Table 1) but resulted in the formation of significant amounts of byproducts derived from the participation of 2 mol of **1a** and the corresponding silane (*vide infra*). The high reactivity of Me_2PhSiH is also reflected in the result that **2a** was formed predominantly (**2a**/**11a** > 7) in the competitive reaction starting from 1 equiv each of **1a**, Me_2PhSiH, and $^tBuMe_2SiH$ (eq 4). Despite the presence of an excess of hydrosilanes, any side reaction product was detected at all because the reaction was carried out at 25 °C.



In an extreme case, as exemplified in the reaction of $^iPr_3SiH$, incorporation of CO was completely suppressed because of the steric hindrance. The alkoxysilanes

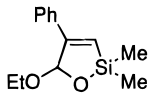
(31) Poor reactivity of $^tBuMe_2SiH$ was in some cases complemented by the use of acetonitrile as a solvent instead of benzene (see entries 7, 8, and 11 in Table 2).

Table 2. Silylformylation of 1-Alkyne with Hydrosilanes[a]

entry no.	alkyne **1**	R^1	hydrosilane	products	yield (%)[b]	*Z*:*E*[c]
1	**1b**	H	Me_2PhSiH	**2b**	73	0:100
2	**1c**	Me	Me_2PhSiH	**2c**	99	80:20
3	**1d**	Et	Me_2PhSiH	**2d**	91	94:6
4	**1e**	$^nC_3H_7$	Me_2PhSiH	**2e**	93	95:5
5	**1e**	$^nC_3H_7$	Me_2PhSiH	**2e**	62[d]	90:10
6	**1e**	$^nC_3H_7$	Et_3SiH	**9e**	91	97:3
7	**1e**	$^nC_3H_7$	$^tBuMe_2SiH$	**11e**	13[e]	99:1
8	**1e**	$^nC_3H_7$	$^tBuMe_2SiH$	**11e**	91[d,f]	100:0
9	**1f**	$^nC_4H_9$	Me_2PhSiH	**2f**	86[d]	85:15
10	**1f**	$^nC_4H_9$	Et_2MeSiH	**10f**	81[d]	89:11
11	**1f**	$^nC_4H_9$	$^tBuMe_2SiH$	**11f**	71[d,f]	100:0
12	**1g**	$^nC_5H_{11}$	Me_2PhSiH	**2g**	71	87:13
13	**1g**	$^nC_5H_{11}$	Et_3SiH	**9g**	82[d]	95:5
14	**1h**	$^nC_6H_{13}$	Et_3SiH	**9h**	86[d]	96:4
15	**1i**	$^cC_6H_{11}$	Me_2PhSiH	**2i**	96	100:0
16	**1j**	$CH_2{=}CHCH_2$	Me_2PhSiH	**2j**	90	73:27
17	**1k**	Me_3SiCH_2	Me_2PhSiH	**2k**	94	91:9
18	**1l**	Me_3Si	Me_2PhSiH	**2l**	55	100:0
19	**1m**	$HOCH_2$	Me_2PhSiH	**2m**	83	37:63
20	**1m**	$HOCH_2$	Me_2PhSiH	**2m**	78[d]	77:23
21	**1n**	$MeOCH_2$	Me_2PhSiH	**2n**	32[g]	88:12
22	**1o**	$Cl(CH_2)_3$	Me_2PhSiH	**2o**	78	88:12

[a] Reactions were conducted on a scale of 2−10 mmol in a benzene solution containing 0.3 mol % of $Rh_4(CO)_{12}$ and equimolar amounts of **1**, hydrosilane, and Et_3N under CO pressure (10−30 kg/cm^2) for 2 h at 100 °C unless stated otherwise. [b] Isolated yield. [c] Determined from the ^1H NMR spectra. [d] The reaction was carried out in the absence of Et_3N. [e] Reaction time was increased to 17 h. [f] The reaction was carried out in an acetonitrile solution for 17 h at 90 °C. [g] The reaction was carried out for 15 h at 25 °C.

$Me_2(EtO)SiH$ and $(MeO)_3SiH$ reacted readily with **1a** to incorporate CO; however, the obtained product was a mixture of the corresponding *β*-silylalkenal (**12a** or **13a**) and hemiacetal (**14** or **15**). These products did not



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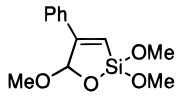

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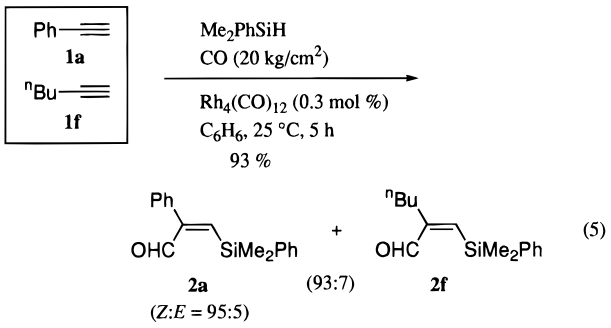
allow further purification except by bulb-to-bulb distillation, due to a facile hydrolysis of Si−O bonds. They changed to resinous intractable materials during storage in a sealed tube even at room temperature. In sharp contrast to monohydrosilane, the dihydrosilane Ph_2SiH_2 did not cause silylformylation at all; hydrosilylation was the sole reaction pattern observed.

Other alkynes as well as **1a** were also active to the silylformylation. The reactions of 1-alkynes generally gave the corresponding 2-substituted 3-silylpropenals in high yields as summarized in Table 2, in which no regioisomer was detected. As reported earlier,[15a] some of the homopropargyl alcohols reacted with hydrosilanes and CO to give α-(silylmethylene)-*γ*-lactones accompanied by the elimination of an H_2 molecule. This evidence makes us expect that the intermediate involved in the catalytic cycle of silylformylation is susceptible to the free hydroxy group contained as alcohols or water. However, the reaction of **1m** afforded the corresponding alkenal as the sole product in high yield. Analogously, silylformylation of **1** was not affected by the presence of more than 1 equiv of either H_2O or methanol. Functional groups contained in the alkyne molecules, such as olefinic, Me_3Si, hydroxy, methoxy, and chloro groups, remained intact as shown

in entries 16−22. It should also be pointed out that **2j** was isolated as the sole product in the silylformylation of **1j**, though the structure of **2j** is in the same category as 4-pentenal derivatives which are readily converted to cyclopentanone rings by Rh-catalyzed operations.[32,33] There is an interesting report[3] that an ethylene molecule is incorporated together with CO and H_2 into terminal alkynes to form α,β-unsaturated ketones with the assistance of $Rh_4(CO)_{12}$. Similar participation of ethylene is also expected in our silylformylation because of the analogy of starting materials; however, **2e** was the sole product (95%) in the reaction of **1e** with Me_2-PhSiH in the presence of CO (25 kg/cm^2) and ethylene (15 kg/cm^2).

It is of interest that the rate of silylformylation strongly depends on the substituents linked to an sp carbon of the acetylenic part. A competitive reaction using Me_2PhSiH as a hydrosilane revealed that phenylacetylene reacts much faster than 1-hexyne to give **2a** predominantly, as shown in eq 5. (Trimethylsilyl)-



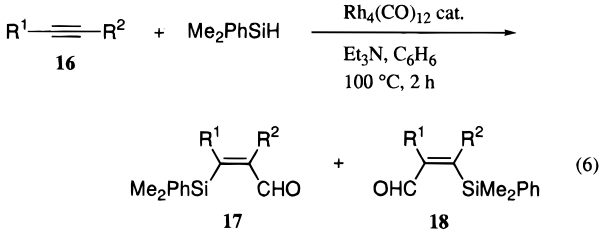
acetylene was susceptible to silylformylation despite the apparent retardation of the rate because of a bulky substituent, whereas 3,3-dimethyl-1-butyne did not give any coupling product under similar conditions. The results of experiments varying the pair of an alkyne and a silane suggest that all the substituents contained in alkynes and hydrosilanes actually affect the reaction rate. The reactivity of alkynes decreased in the order phenylacetylene > 1-hexyne > (trimethylsilyl)acetylene ≫ 3,3-dimethyl-1-butyne, whereas that of hydrosilane was Me_2PhSiH, $MePh_2SiH$ > Et_2MeSiH, Et_3SiH > $^tBuMe_2SiH$ ≫ $^iPr_3SiH$. Thus, the rate of silylformylation largely depends on the combination of alkynes and hydrosilanes. The following order of the rate is deduced from the yield: a pair of phenylacetylenes and Me_2-PhSiH > that of 1-hexyne and Me_2PhSiH ≫ a pair of phenylacetylenes and $^tBuMe_2SiH$ > a pair of 1-hexynes and $^tBuMe_2SiH$ ≈ a pair of (trimethylsilyl)acetylenes and Me_2PhSiH.

The silylformylation of internal acetylenes also proceeded smoothly. As shown in Table 3, 2-butyne (**16a**), 2-hexyne (**16b**), 1-phenylpropyne (**16c**), and diphenylacetylene (**16d**) gave the corresponding β-silylalkenals in good yields. Two regioisomers were formed in the reaction of unsymmetrically substituted alkynes **16b** and **16c**. The regioselectivity seems to be governed by the steric bulkiness of the substituents; the formyl group was always introduced at the sp carbon bearing the bulkier substituent. Derivatives of propiolates, **16e** and **16f**, were different from the dialkyl- or alkylarylacetylenes due to the fact that the electronic effect was a major factor determining the regiochemistry; α-silyl β-formyl α,β-unsaturated esters **18e** and **18f** were obtained as single isomers. Hydrosilylation was a serious competitive reaction in the silylformylation of **16e** and **16f**. (Trimethylsilyl)acetylenes **16g** and **16h** did not give any carbonylated products; this could be attributable to steric hindrance arising from the bulkiness of the Me_3Si group.

Table 3. Silylformylation of Internal Alkynes (16) with Me_2PhSiH[a]

	alkyne **16**			yield (%) of product[b]			
				17		**18**	
entry no.		R^1	R^2				
1	**a**	Me	Me	**a**	94[c]		
2	**b**	Me	$^nC_3H_7$	**b**	60	**b**	26
3	**c**	Me	Ph	**c**	74	**c**	8
4	**d**	Ph	Ph	**d**	90[d]		
5	**e**	Me	CO_2Me	**e**	0	**e**	67
6	**f**	Ph	CO_2Et	**f**	0	**f**	43
7	**g**	Me	$SiMe_3$	**g**	0	**g**	0
8	**h**	Ph	$SiMe_3$	**h**	0	**h**	0

[a] Reactions were conducted on a scale of 2−10 mmol in benzene solution containing 1 mol % of $Rh_4(CO)_{12}$ and equimolar amounts of **16**, Me_2PhSiH, and Et_3N under CO pressure (10−30 kg/cm^2) for 2 h at 100 °C. [b] Isolated yield. [c] *Z*:*E* = 100:0. [d] *Z*:*E* = 95:5.



In the above experiments, $Rh_4(CO)_{12}$ acted as an efficient catalyst for the silylformylation. In an extreme case, turnover frequency exceeded 12 000. Although the efficiency as the catalyst was lower than for $Rh_4(CO)_{12}$, it was discovered that the rhodium complexes $RhH(CO)(PPh_3)_3$, $Rh(acac)(CO)_2$, $[Rh(COD)Cl]_2$, $[Rh(COD)(PPh_3)_2]PF_6$, $[Rh(COD)(DPPB)]PF_6$, and $[RhCp^*Cl_2]_2$ (acac = 2,4-pentanedionato, COD = 1,5-cyclooctadiene, and DPPB = 1,4-bis(diphenylphosphino)butane; Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) had sufficient ability to accomplish the silylformylation. The extent of regio- and stereoselectivity in the reactions catalyzed by these complexes was similar to the result observed in the $Rh_4(CO)_{12}$-catalyzed one. We should stress that no carbonylation took place when $Co_2(CO)_8$, $Ru_3(CO)_{12}$, or $[Ir(COD)(PPh_3)_2]PF_6$ was used as a catalyst. The role of the rhodium catalyst in the silylformylation is an interesting problem, as described in the section that follows on Mechanistic Considerations.

Cyclopentenone Annulation. Silylformylation of alkynes provides a clear and selective formation of a β-silyl alkenals as long as starting substrates, alkynes and hydrosilanes, are mixed in a nearly equal mole ratio. Though sometimes the presence of small amounts of side reaction products has been detected by TLC analyses of the reaction mixtures, their quantities were usually too small to warrant concentrating our effort on their isolation. However, appreciable amounts of

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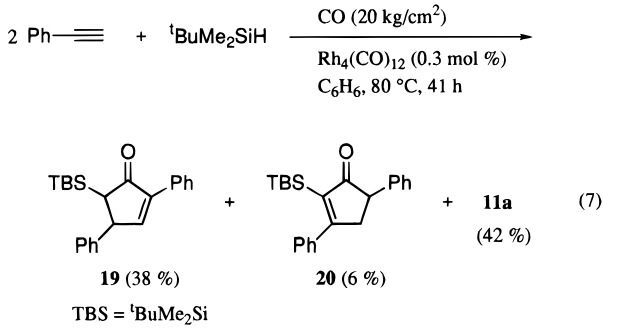
(33) Eilbrachat, P.; Acker, M.; Haedrich, I. *Chem. Ber.* **1988**, *121*, 519.

side reaction products were detected in some combinations of an alkyne and a hydrosilane. For example, no product other than **11a** was observed in the reaction of **1a** with ^{t}BuMe$_2$SiH at room temperature despite a prolonged period (65 h) for the completion of the reaction, whereas interesting byproducts were obtained in the same reaction at 100 °C. When all of **1a** was consumed after 16 h, the silylformylation product **11a** was obtained as a major component (49% yield) (*vide supra*). Unexpectedly, cyclopentenone derivatives **19**[34] and **20**[35] were also isolated in 23 and 3% yields, respectively, in addition to **11a**. It is apparent that the formation of **19** and **20** was achieved by the coupling of two molecules of **1a** and one molecule each of ^{t}BuMe$_2$SiH and CO. In fact, the reaction mixture containing 2 mol equiv of **1a** and 1 mol equiv of Me$_2$PhSiH at 100 °C raised the yields of **19** and **20** to 38% and 6%, respectively (eq 7). This reaction pattern resembles the

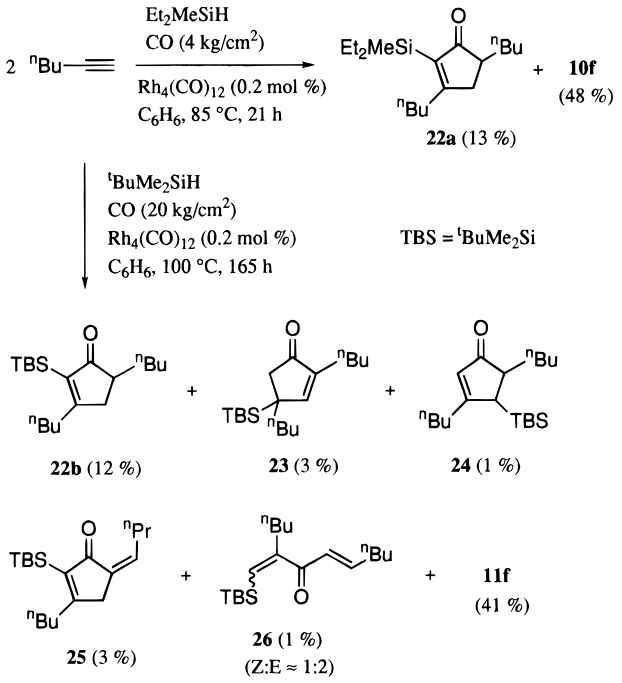


(7)

Pauson−Khand type cyclopentenone annulation, which is attained by the combination of an alkene, an alkyne, and Co$_2$(CO)$_8$ or Ti complex in most instances.[36]

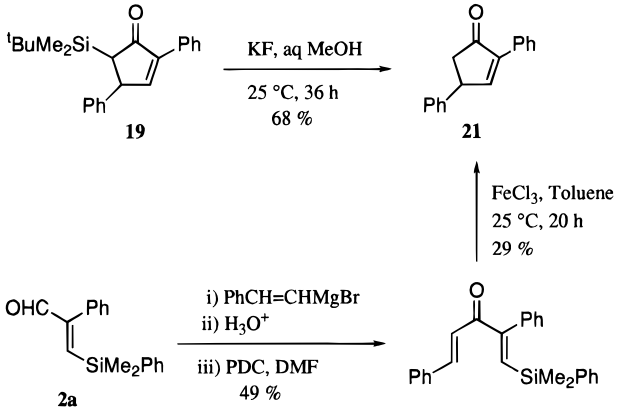
The cyclopentenone annulation was a common side reaction in the silylformylation when excess amounts of alkynes were present in the reaction mixture. For example, the silylformylation of **1a** with either Me$_2$PhSiH or Et$_2$MeSiH (**1a**:silane > 2:1) gave congeners of **19**, which was detected in the ^{1}H NMR spectra of their reaction mixture. Their purification through a silica gel column gave a small amount of 2,4-diphenylcyclopent-2-enone **21**[34] (a few percent based on the charged **1a**). Similar reactions using 1-hexyne (**1f**) gave homologues of **20** as the major cyclocarbonylation products. The reaction of **1f** with Et$_2$MeSiH (**1f**:Et$_2$MeSiH = 3:1) gave **10f** and **22a** in 48% and 13% yields, respectively. In the silylformylation of **1f** with ^{t}BuMe$_2$SiH, **22b** was isolated as a major byproduct in addition to **11f**, though other byproducts, **23**−**26**, were also isolated as minor products. These results are summarized in Scheme 3.

Scheme 3. Rh$_4$(CO)$_{12}$-Catalyzed Carbonylation in the Presence of an Excess of 1-Hexyne

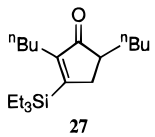


Reactions of Rh$_4$(CO)$_{12}$ with Hydrosilanes or Alkynes. No visible change was detected by mixing Rh$_4$(CO)$_{12}$ and Me$_2$PhSiH under nitrogen or a CO atmosphere as described in the following section, whereas a similar mixture prepared by stirring for more than 8 h under CO pressure (20 kg/cm^2) changed from wine red to straw yellow. At the same time the appearance of a characteristic singlet (δ 0.81) assignable to a Me$_2$PhSi group was observed with a consumption of the corresponding amount of Me$_2$PhSiH in the ^{1}H NMR spectrum of this mixture. This fact implies strongly that a new species is formed as the sole product bearing a Me$_2$PhSi group in the mixture. Both starting substrates were completely consumed, and the species showing a singlet peak at δ 0.81 was formed as the sole product in the reaction of Rh$_4$(CO)$_{12}$ with 4 molar equiv of Me$_2$PhSiH under CO pressure (20 kg/cm^2). Unfor-

(34) It is difficult to determine the precise positions of substituents of **19** from NMR spectra. We carried out protodesilylation of **19** by KF in aqueous MeOH at 25 °C for 36 h to give **21** as a single product. Assignment of **21** was unequivocally performed by the comparison of spectral data with those of an authentic sample prepared according to the sequence shown:



(35) The structures of **20** and **22** were determined by spectroscopic analogy with **19**. It is worthwhile to point out that Ojima and co-workers proposed the structure **27** for the cyclopentenone derivative isolated as a side reaction product in the silylformylation of 1-hexyne catalyzed by some Co−Rh bimetallic clusters:[16b]



(36) (a) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977. (b) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855. (c) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (d) Schore, N. E. *Org. React.* **1991**, *40*, 1. (e) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, p 1037. (f) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688.

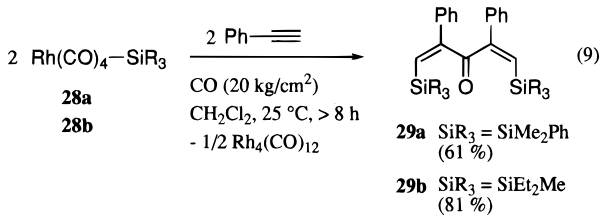
tunately, this species was not isolated as a specific form because removal of the solvent caused decomposition of the compound even under this atmosphere. Since the new compound was stable as long as it was stored in the original solution under a CO atmosphere (preferably more than 5 kg/cm^2 of CO pressure) regardless of the solvent, CH_2Cl_2, $CHCl_3$, $CDCl_3$, C_6H_6, and hexane, a freshly prepared solution of the new compound was used for a spectroscopic study. No ^{1}H NMR resonance was detected in the Rh−H region, and the sole singlet peak assigned to Si−CH_3 protons appeared at δ 0.81. The chemical shift of the latter peak is at lower field than those of Me_2PhSiH (δ 0.34) and is comparable to those of $Me_2PhSiCl$ (δ 0.68); this suggests that the Me_2PhSi group is bonded to electron-withdrawing species. Ortho protons of the phenyl group were significantly deshielded (δ 7.58−7.65). A ^{13}C NMR resonance assigned to the CO coordinated to Rh was observed at δ 189.37, which splits into a doublet (J = 66 Hz) due to a coupling with a single ^{105}Rh nuclei. Only terminal CO absorptions were observed in the IR spectrum ($\nu_{C=O}$ 2102, 2049, 2017, and 1982 cm^{-1}). Thus, the plausible structure of a new product is a mononuclear silylrhodium carbonyl complex, $Rh(CO)_4SiMe_2Ph$ (**28a**). Similar rhodium−

$$Rh_4(CO)_{12} \xrightarrow[\text{Solvent}\\ 25\ ^\circ\text{C},\ >8\ \text{h}]{4\ R_3SiH\\ CO\ (20\ kg/cm^2)} 4\ Rh(CO)_4{-}SiR_3 + 2\ H_2 \quad (8)$$

28a $SiR_3 = SiMe_2Ph$
28b $SiR_3 = SiEt_2Me$
28c $SiR_3 = Si^tBuMe_2$

silyl compounds were isolated from the reaction of Et_2MeSiH or ^{t}BuMe$_2$SiH with $Rh_4(CO)_{12}$ under CO pressure. Cobalt homologues of these complexes, $Co(CO)_4SiMe_3$ ($\nu_{C=O}$ 2090, 2026, 1995 cm^{-1}) and $Co(CO)_4SiEt_3$ ($\nu_{C=O}$ 2089, 2026, and 1995 cm^{-1}), were actually prepared and subjected to a spectroscopic study.[37] These spectral features are comparable to our data for $Rh(CO)_4SiMe_2Ph$. To our knowledge, the rhodium carbonyl complex **28** is the first example of a nonbridging rhodium(I)−silyl complex derived from the reaction of $Rh_4(CO)_{12}$ with R_3SiH, though a series of complexes, $Rh(PR^1_3)_3SiR_3$, has been isolated and characterized structurally by X-ray analyses.[38] This type of declusterization of carbonyl clusters has been established and used widely as a preparative route for $M(CO)_nSiR_3$ under an inert-gas atmosphere using other metals.[39−42]

It is noteworthy that the isolated $Rh(CO)_4SiR_3$ reacted readily with phenylacetylene at room temperature even under an atmosphere of CO. The product isolated was divinyl ketones; **29a** and **29b** were derived from the corresponding Rh−Si species **28a** and **28b**, respectively (eq 9). Insertion of phenylacetylene into the Rh−Si



(9)

bond in **28** must be involved at the first stage in the conversion of **28** to **29**. The resulting vinyl−rhodium species could react with CO to form an acyl−rhodium intermediate, coupling of which with another molecule of the vinyl−rhodium species would afford the vinyl ketones **29**. Possibility of the insertion of unsaturated molecules into a transition-metal−silyl bond has been pointed out in the catalytic reactions related to hydrosilylation[42g,43b,44] or silylformylation.[10,16a] However, there has been little direct evidence supporting the insertion of unsaturated molecules into a metal−silyl bond in organometallic complexes.[38,45] Thus, the fact that **29** was readily derived from **28** and **1a** provides not only positive evidence of this but also deep insight into the mechanism of silylformylation.

Another remarkable feature of a rhodium−silyl species is that the triorganosilyl group is exchangeable between **28** and a free hydrosilane under CO pressure (20 kg/cm^2). The presence of this exchanging step was revealed by measurement of the ^{1}H NMR spectrum of an equimolar mixture of **28c** and Me_2PhSiH in which **28a** and ^{t}BuMe$_2$SiH appeared increasingly with a concomitant decrease of **28c** and Me_2PhSiH. The reverse behavior, appearance of **28c** and Me_2PhSiH with a concomitant decrease of **28a** and ^{t}BuMe$_2$SiH, was observed in the ^{1}H NMR spectrum of a mixture of **28a** and ^{t}BuMe$_2$SiH, though the extent of the exchange is less than that derived from a mixture of **28c** and Me_2-

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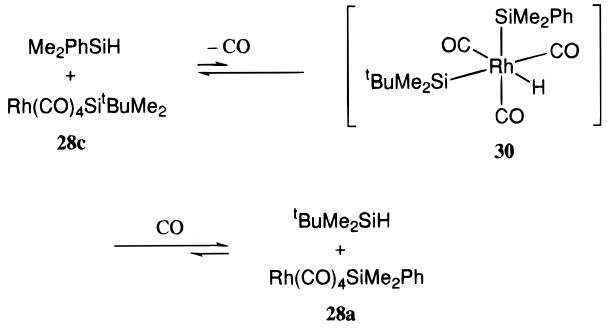
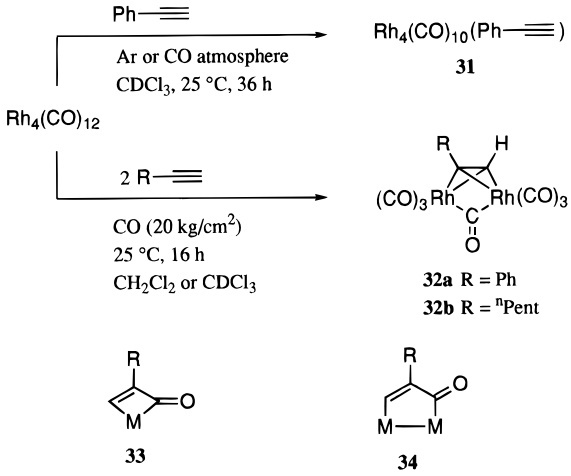
Scheme 4. Reversible Exchange of a Triorganosilyl Group



PhSiH in the same reaction time. The results obtained from both experiments suggest that exchange of a triorganosilyl group between **28** and a hydrosilane is a reversible process, the equilibrium point of which depends on a combination of two triorganosilyl groups. In the combination of **28c** and Me_2PhSiH, an equilibrium lies predominantly to the side of **28a** (**28a**:**28c** ≈ 88:12).[46] The process of this equilibration is elucidated by the intervention of disilylrhodium(III) species **30** (Scheme 4). This type of silyl group exchange has been well-documented in cobalt complexes under thermal[42e,47] and photochemical[37b,43g] conditions.

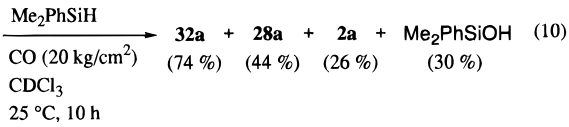
The reaction of phenylacetylene with a stoichiometric amount of $Rh_4(CO)_{12}$ afforded multimetallic rhodium carbonyls coordinated to phenylacetylene, presumably $Rh_4(CO)_{10}$(phenylacetylene) (**31**), under either an Ar or a CO atmosphere, the structure of which was deduced from the known[48,49] $Rh_4(CO)_{10}$(diphenylacetylene): ^1H NMR δ 7.00−7.30 (m, Ph), 9.16 (quint, CH). Complex **31** reacted with Me_2PhSiH to form (*E*)-**3** as the sole organic product, and no type of silylformylation occurred under a CO atmosphere. When 20 kg/cm^2 of CO pressure was applied to a solution of the tetranuclear complex **31**, the cluster was decomposed to a rhodium carbonyl having a bridging CO ligand and coordinated phenylacetylene. In fact, complex **32a** was isolated as the sole product (yellow-brown blocks from CH_2Cl_2/hexane) in the reaction of **1a** with $Rh_4(CO)_{12}$ under CO pressure (20 kg/cm^2), irrespective of the quantity of **1a** used. The structure of **32a** was elucidated on the basis of IR and ^1H and ^{13}C NMR spectroscopy and elemental analysis. It is slightly different from cobalt dinuclear complexes.[16a,50] Moreover, no specific indication of CO insertion was observed at this stage, while there are some precedents reporting the formation of such complexes as **33**[51] and **34**[52,53] in the reaction of metal carbonyls with alkynes. The coordination of alkynes to rhodium metal in **32** is relatively stable, and the

Scheme 5. Reactions of $Rh_4(CO)_{12}$ with 1a under CO Pressure



coordinated alkyne was not replaced by a free one in solution. The stability of **32** in a $CDCl_3$ solution was confirmed by the comparison of ^1H NMR spectra of **32a** and **32b** containing 1 mol equiv of **1g** and **1a**, respectively.

The reaction of this dinuclear species, **32a**, with Me_2PhSiH under CO pressure gave rise to the formation of some amount of silylformylation product **2a** (26%), but the rate was substantially slower than that of the reaction of $Rh(CO)_4SiMe_2Ph$ with phenylacetylene under CO pressure (eq 10). The silylrhodium complex **28a**



was formed concomitantly in 44% yield. Although it cannot be completely excluded that there is an unknown pathway leading from **32a** to **2a**, the poor stoichiometry for this formation and the concomitant formation of $Rh(CO)_4SiMe_2Ph$ suggest that the reaction of **32** with Me_2PhSiH under CO pressure gives $Rh(CO)_4SiMe_2Ph$ (**28a**) and free phenylacetylene. As a result, the **1a** liberated is silylformylated under the reaction conditions catalyzed by **28a**.

Mechanistic Considerations of Silylformylation. It is conceivable that the mechanism for silylformylation of alkynes is closely related to that for hydrosilylation.[43] However, the greatest discrepancy between these reactions is that the former reaction of 1-alkynes is extremely regioselective as well as stereoselective, whereas the latter gives a mixture of regio- and stereoisomers (eq 2). It is interesting to reveal the role of rhodium metal in the catalytic cycle of silylformylation. First of all, a couple of deuterium labeling reactions using deuteriophenylacetylene (**1a-D**) and Me_2PhSiD as a reactant were designed to confirm the origin of the formyl proton. Alkenal **2a-D**$_{(formyl)}$ (*Z*:*E* = 87:13) deuterated (>98%) at the formyl carbon was selectively given in 73% yield from the reaction of **1a** with Me_2-

(46) The time required for the equilibrium in these controlled experiments was far longer than the silylformylation. Phenylacetylene may act as a catalyst for the exchange between silyl groups.

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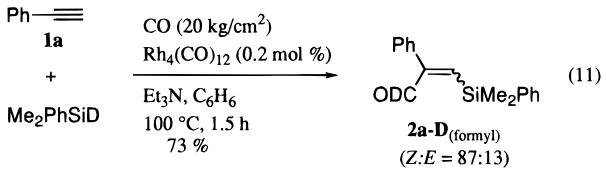
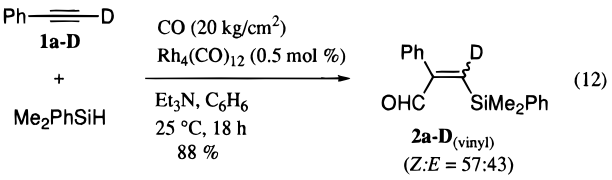
PhSiD under conventional silylformylation conditions (eq 11). Alkenal **2a-D**$_{(vinyl)}$ (*Z*:*E* = 57:43) deuterated



(>94%) at the vinyl carbon was selectively isolated from the reaction of **1a-D** with Me_2PhSiH under similar conditions (eq 12).[54] This observation shows clearly that

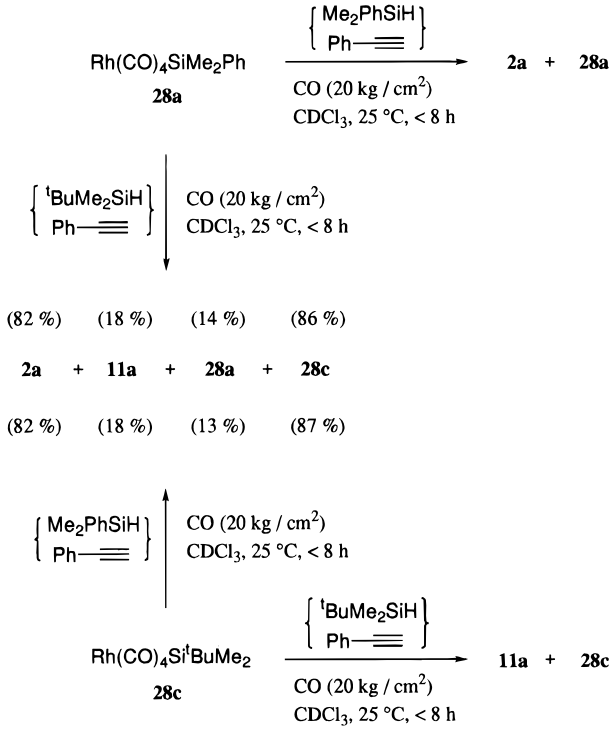


the hydrogen atom of the formyl group is derived from the hydrosilane used and that there is minimal scrambling of hydrogen atoms between a hydrosilane and a terminal acetylene in Rh-catalyzed silylformylation.

Second, the course of silylformylation was monitored using a spectroscopic method. As noted previously, hydrosilylation of alkynes becomes a serious competitive reaction in silylformylations unless the reaction is carried out under CO pressure. An interesting observation was obtained in the experiments using $Rh_4(CO)_{12}$, **1a**, and Me_2PhSiH in a ratio of 1:4:4, that is, stoichiometric amounts of **1a** and the silane based on one Rh atom. Silylformylation of **1a** proceeded to give **2a** selectively with recovery of $Rh_4(CO)_{12}$ in the reaction under CO pressure (20 kg/cm^2). When both substrates were mixed at once in a $CDCl_3$ solution of $Rh_4(CO)_{12}$ under a CO atmosphere, smooth progress of the silylformylation of **1a** was observed by monitoring the ^{1}H NMR spectra of the mixture; this clearly showed that **2a** was formed as a major product with concomitant formation of small amounts of hydrosilylation products and $Me_2PhSiOH$. A similar result was obtained when **1a** was added into the solution provided by mixing Me_2PhSiH and $Rh_4(CO)_{12}$ under a CO atmosphere for 30 min prior to use. In sharp contrast to these results, when Me_2PhSiH was treated with the solution prepared from $Rh_4(CO)_{12}$ and **1a** under a CO atmosphere, the sole reaction observed was not silylformylation but hydrosilylation. These results unequivocally suggest that the prior interaction among a silane, a rhodium complex, and CO is important in silylformylation.

Disappearance of the spin−spin coupling between the $SiCH_3$ and SiH protons was observed in the ^{1}H NMR spectrum of a solution containing Me_2PhSiH and $Rh_4(CO)_{12}$ in the ratio 4:1 under an Ar atmosphere. This finding indicates that rhodium species interact reversibly with the Si−H bond, whereas the inherent signals assigned to Me_2PhSiH itself did not change at all in a similar sample as long as the solution was stored under CO atmosphere. This fact is elucidated by an assumption either that interaction between Me_2PhSiH and

Scheme 6. Silylformylation Induced by 28



rhodium species does not exist at all or that the rate of the interaction is too rapid to be detected on the time scale of ^{1}H NMR under a CO atmosphere. Despite no clear indication of the presence of intermediate detectable in the ^{1}H NMR spectrum of a mixture resulting in the silylformylation, the fact that silylformylation proceeds smoothly suggests that each step of the catalytic cycle of silylformylation occurs more rapidly than the time scale of ^{1}H NMR.

In contrast to the results described above, **28** was selectively formed in the reaction of $Rh_4(CO)_{12}$ with 4 mol equiv of R_3SiH under CO pressure (20 kg/cm^2). The solution containing **28** resulted in silylformylation regardless of a stoichiometric or catalytic reaction to give the corresponding product in the presence of equal amounts of **1** and a hydrosilane under CO pressure. An interesting behavior of **28** was also observed when **28** and a hydrosilane have different types of triorganosilyl groups. For example, the two silylformylation products **2a** and **11a**, and the two silyl−rhodium species **28a** and **28c**, were obtained from two stoichiometric reactions under CO pressure (20 kg/cm^2), that of ^{t}BuMe$_2$SiH with $Rh(CO)_4SiMe_2Ph$ (**28a**) and that of Me_2PhSiH with $Rh(CO)_4Si^tBuMe_2$ (**28c**) in the presence of an equimolar amount of **1a** as shown in Scheme 6. It is interesting that the relative ratios of these products were almost identical in these two independent experiments. This result suggests that exchange of silyl groups between R_3SiH and $Rh(CO)_4SiR'_3$ occurs prior to the insertion of phenylacetylene into the Rh−Si bond. In particular, the fact that the ratios of **2a** to **11a** are identical in the two separate reactions seems to reflect that the relative quantities of **28a** and **28c** in both reaction systems are controlled by a certain equilibrium triggered by the presence of free Me_2PhSiH or ^{t}BuMe$_2$PhSiH. Thus, the results shown in Scheme 4 suggest the presence of a preequilibrium between the hydrosilane and the rhodium−silyl complex. The resulting mixture of **28a** and **28c** reacts with phenylacetylene and CO, resulting in

(54) The deuterium content of these compounds was determined by ^{1}H NMR integration of the residual proton signals at the site of labeling relative to the intensity of another signal assigned to one proton at an unlabeled position.

Scheme 7. Silylformylation Induced by Rhodium Species

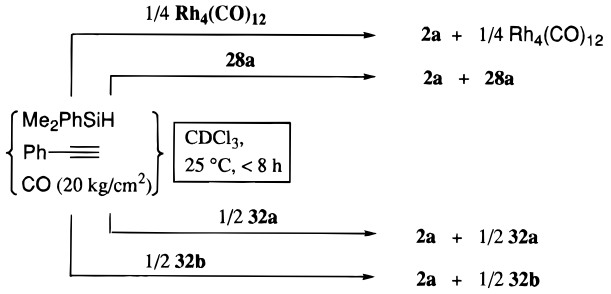


Table 4. Relative Efficiency of Catalyst Precursors in Silylformylation of 1a[a]

entry no.	catalyst	substrate/ Rh	yield of **2a** (%)[b]	turnovers/ min
1	$Rh_4(CO)_{12}$	84	82	3.4
2	**28a**	86	88	3.8
3	**28c**	82	70	2.9
4	**32a**	83	65	2.7
5	$RhH(CO)(PPh_3)_3$	83	16[c]	0.2

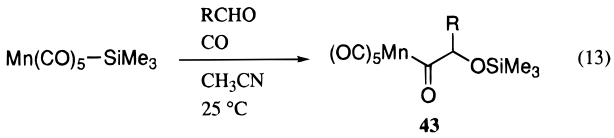
[a] Reactions were conducted in a benzene (7 mL) solution containing the fixed mole ratio **1a**:Me_2PhSiH:[Rh] = 83:83:1 at 25 °C for 20 min under CO pressure (20 kg/cm^2). [b] Isolated yield. [c] Reaction time was increased to 1 h because of the low conversion within the prescribed time.

the predominant formation of **2a**. Since a mixture of free silanes (Me_2PhSiH:^{t}$BuMe_2SiH$ ≈ 12:88) might be present in the reaction mixture at that stage, these hydrosilanes contribute to the generation of **28a** and **28c** in a ratio of close to 13:87 in the final step of the reactions.

Both of the well-characterized complexes **28** and **32** readily interacted with a mixture containing an equimolar amount of **1a** and Me_2PhSiH under CO pressure to give **2a** as selectively as did $Rh_4(CO)_{12}$ itself. All complexes used as starting substrates were recovered intact after the completion of silylformylation, as shown in Scheme 7. This suggests that complexes **28** and **32** are uniformly effective as catalysts for silylformylation. However, the result of **32b** suggests strongly that the alkyne molecules contained in **32** are not incorporated directly as a component of silylformylation. This point is also supported by the finding that the major product is **2f** (**2f**:**2a** ≈ 3:1) in the reaction of **32a** with a stoichiometric mixture of Me_2PhSiH and **1f**, despite the overwhelming priority of **1a** in the catalytic competitive silylformylation (eq 5). All these species showed catalytic ability comparable to that of $Rh_4(CO)_{12}$ for silylformylation at 25 °C despite the apparent difference in behavior between **28** and **32** in the stoichiometric reactions (Table 4). In contrast to these precursors derived from $Rh_4(CO)_{12}$, a stable mononuclear complex, $RhH(CO)(PPh_3)_3$ showed far inferior catalytic efficiency at 25 °C, though the efficiency improved in the reactions under practical operation at 100 °C.

From these results, we conclude that the most plausible catalytic cycle involves a mononuclear $Rh(CO)_4SiR_3$ as an intermediate at the present stage. The catalytic cycle is similar to the Murai reaction, the cobalt-catalyzed silylformylation of alkenes,[10] and is comparable to well-known cobalt- or rhodium-catalyzed hydroformylation of alkenes and alkynes. Ojima and coworkers reported that similar silylformylation of alkynes was catalyzed by a mixed-metal cluster, $Co_2Rh_2(CO)_{12}$. They pointed out that the heteronuclear cluster framework plays an important role in the smooth proceeding of reactions.[16a] However, we confirmed that several monometallic rhodium complexes, $RhH(CO)(PPh_3)_3$, $[Rh(COD)(DPPB)]PF_6$, and $Rh(acac)(CO)_2$, also catalyzed the silylformylation, though the reaction rate was substantially lower than that with $Rh_4(CO)_{12}$ as described above. We conclude that the presence of Rh metal, regardless of the nuclearity, is essential in order to catalyze the silylformylation of alkynes. The idea that $Rh_4(CO)_{12}$ generates mononuclear metal carbonyl species such as $Rh(CO)_4SiR_3$ is rather more reasonable than the notion that $RhH(CO)(PPh_3)_3$ produces multinuclear metal carbonyl species, since metal carbonyl clusters have generally been known to decompose to metal carbonyl complexes with lower nuclearity under CO pressure. In spite of the claim[55] that the cluster framework of $Rh_4(CO)_{12}$ is retained in the hydroformylation, it is difficult to assume that the nuclearity of $Rh_4(CO)_{12}$ remains intact during the silylformylation of alkynes on the basis of our observations on stoichiometric reactions of $Rh_4(CO)_{12}$ with R_3SiH or phenylacetylene under CO pressure.

Thus, the catalytic cycles A and B for silylformylation are proposed as one persuasive possibility (Scheme 8). In cycle A, $Rh(CO)_4SiR_3$ (**28**), which is initially formed by the reaction of R_3SiH with $Rh_4(CO)_{12}$ and equilibrates with **40** in the reaction system, is allowed to react with acetylene to form the vinyl−rhodium species **37**. Insertion of CO between the carbon−rhodium bond of **37** affords the acyl−rhodium intermediate **38**. Oxidative addition of a Si−H bond to the rhodium metal is followed by reductive elimination of the silylformylation product and regeneration of $Rh(CO)_4SiR_3$ in the presence of R_3SiH. When hydrosilane is absent, **38** reacts with another molecule of **37** to afford divinyl ketones as described previously (eq 9). Recent demonstration of alkene insertion into a Rh−Si bond[38] makes it possible to propose the process from **35** to **37**. Moreover, the pathway to form **38** from **35** through continuous insertion of alkyne and CO is supported by the evidence of eq 9 and the reported result that manganese acyl complexes (**43**) are obtained from the reaction of $Mn(CO)_5SiMe_3$ with aldehydes as shown in eq 13.[56] The



(13)

final stage of forming **2**, **8**, **9**, **10**, **11**, **12**, or **13** from **38** is also supported by the evidence that the cobalt−acyl complex liberates aldehyde in the interaction with hydrosilane.[57]

An alternative cycle, shown in cycle B of Scheme 8, can be proposed. Complex **40** derived from **35** by the oxidative addition of R_3SiH interacts directly with an alkyne to form **42** via **41**. The insertion of CO into the rhodium−carbon(vinyl) bond of **42** leads to **39**. The rest of the cycle is shared with cycle A. It is difficult at present to conclude unequivocally which of these cycles

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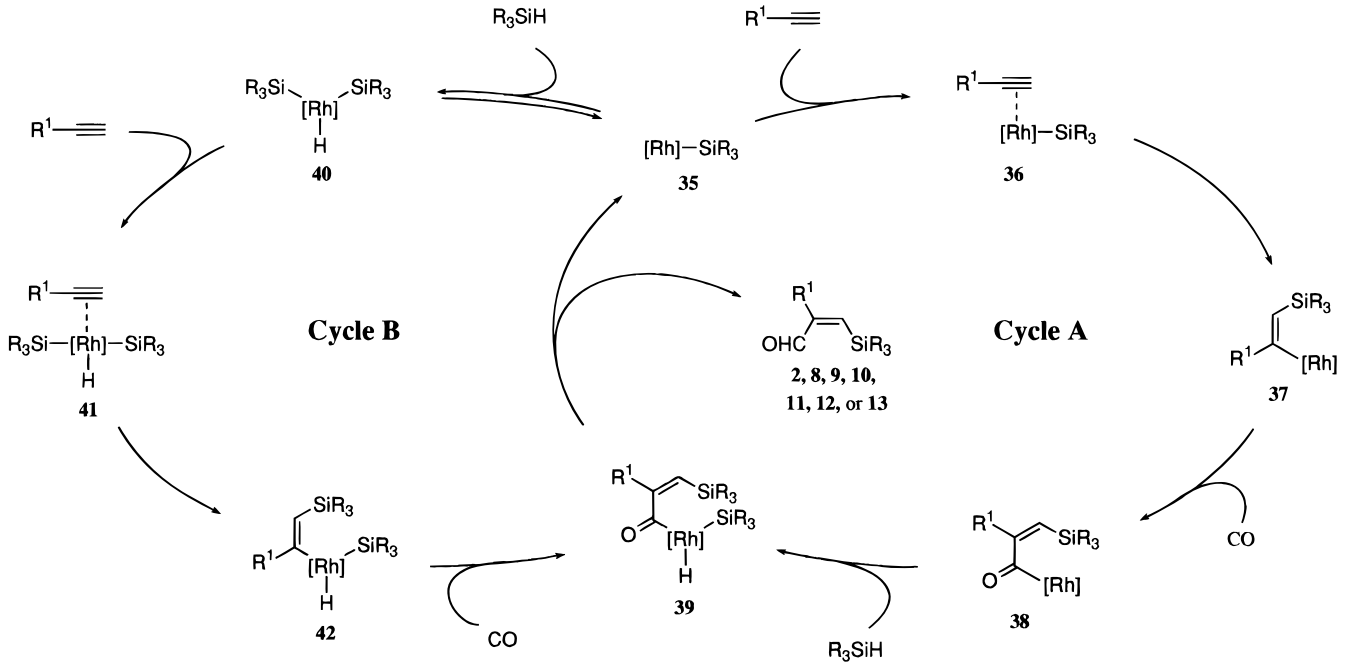
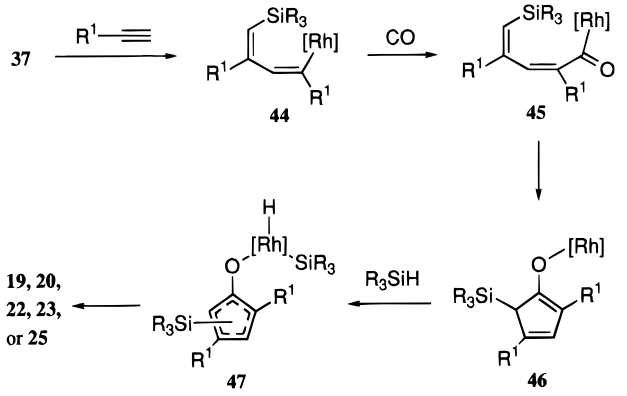
(56) Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.
(57) Wegman, R. W. *Organometallics* **1986**, *5*, 707.

Scheme 8. Catalytic Cycle for Silylformylation[a]

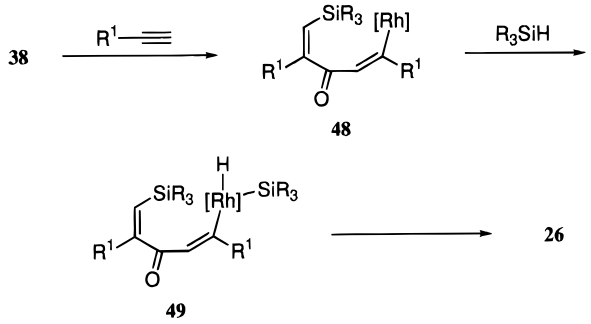


[a] Ligands on rhodium are eliminated for clarification.

Scheme 9. Plausible Pathway To Form Cyclopentenone Derivatives



Scheme 10. Plausible Pathway To Form 26



dominates silylformylation because the observable steps such as the formation of **28** and silyl exchange in Scheme 4 require far longer time than that sufficient for silylformylation.

In whichever cycle silylformylation may take place, the findings obtained so far are consistent with both of those shown in Scheme 8. Furthermore, the postulated key intermediates **37** or **42** and **38** or **39** are connectable to the sequence for the formation of the products contained in eq 7 and Scheme 3. The pathways branching from **37** and **38** are illustrated in Schemes 9 and 10, respectively. Analogous elucidation from **42** and **39** leads to the same products. The second vinyl complex of Rh, **44**, is formed by the immediate insertion of the second molecule of alkyne into the Rh−C bond of **37**. The subsequent insertion of CO into the resultant Rh−C bond of **44** gives **45**, which cyclizes to form **46**. The final products **19**, **20**, **22**, **23**, **24**, and **25** are derived from **47**, which represents some isomers generated by proto- or silatropy from **46** and subsequent oxidative addition of R_3SiH to Rh metal (Scheme 9). The formation of divinyl ketone **26** is also described by a similar sequence starting from **38**, as shown in Scheme 10. Analogous elucidation from **42** and **39** leads to the same products.

Conclusion

Detailed studies of "silylformylation" of alkynes attained by the interaction of hydrosilane and CO have been presented in which triorganosilyl groups are introduced into an acetylenic triple bond in a substantially (*Z*)-selective mode. The presence of a catalytic amount of rhodium complex is crucial for smooth incorporation of CO regardless of the forms of the precursors over a considerably wide range of complexes. The reactions proceed selectively to form the sole regioisomer formylated on the internal sp carbon of 1-alkynes in a controlled mole ratio (1:1) of alkyne to hydrosilane. When an excess of alkyne is present in this reaction, a new type of cyclopentenone annulation is realized, despite a relatively poor yield. These two types of carbonylations are elucidated consistently by postulation of the insertion of an alkyne into a Rh−Si bond as a key catalytic step. Mechanistic aspects aside, however, the present novel reaction composed of an alkyne, hydrosilane, and CO should prove to be a simple and efficient approach to form **2**. The structure of **2** is of interest as a versatile building block for the synthesis of complex molecules via a Peterson olefination,[24a,26] a

Nazarov type cyclopentenone annulation,[58] or a Trost type cyclopentane annulation.[59]

Experimental Section

General Considerations. All carbonylation reactions were carried out in a glass tube held in a 100 mL stainless steel autoclave under carbon monoxide unless otherwise indicated. Anhydrous solvents were transferred via an oven-dried syringe. The following solvents and reagents were distilled prior to use: tetrahydrofuran (THF) from sodium benzophenone ketyl and *N*,*N*-dimethylformamide (DMF) from calcium hydride. Benzene (thiophene free) and all other solvents were utilized at their commercial level of purity. The following preparations were based on standard literature procedures: $Rh_4(CO)_{12}$,[60] $RhCl(PPh_3)_3$,[61] $RhH(CO)(PPh_3)_3$,[62] $Rh(acac)(CO)_2$,[63] $[Rh(COD)Cl]_2$,[64] $[Rh(COD)(PPh_3)_2]PF_6$,[65] [Rh(COD)(DPPB)]PF_6,[66] $[RhCp^*Cl_2]_2$,[67] $Ru_3(CO)_{12}$,[68] $[Ir(COD)(PPh_3)_2]PF_6$,[69] and **1j**.[70] Dicobalt octacarbonyl ($Co_2(CO)_8$) was purchased from Strem. Acetylenes except for **1j** and silanes were obtained from Aldrich, Lancaster, Tokyo Kasei, Shin-etsu Chemicals, or Petrarch. These were used as received.

All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60 F-254) using UV light as the visualizing agent and 7% ethanolic phosphomolybdic acid and heat as the developing agent. E. Merck silica gel (60, particle size 0.063−0.200 mm) was used for column chromatography. Medium-pressure preparative liquid chromatography was performed on a YFLC-600 system equipped with a silica gel (particle size 0.025−0.040 mm) column. Preparative thin-layer chromatography (PTLC) separations were carried out on 2 mm E. Merck silica gel plates (60F-254).

Proton nuclear magnetic resonance (^{1}H NMR) data were obtained at 200 MHz on a Varian GEM-200 or at 500 MHz on a Varian VXR-500 spectrometer. Chemical shifts are reported in δ units, in parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-*d*. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; m, multiplet; b, broad. Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were obtained at 50 MHz on a Varian GEM-200 or at 125.7 MHz on a Varian VXR-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 broad-band decoupling. Infrared data were recorded in 0.2 mm path length sodium chloride cavity cells on a JASCO IR-810 spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectra were recorded on a JEOL JMS-AX505H gas chromatograph−mass spectrometer using 2-methylpropane gas for chemical ionization (CI) or electron impact (EI) at 70 eV. 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.

Carbonylations. All carbonylation reactions were carried out in glass tubes held in a 100 mL stainless steel autoclave. The procedure for the synthesis of **2a** is described as a typical example.

$Rh_4(CO)_{12}$-Catalyzed Silylformylation of 1a with Me_2PhSiH (Procedure 1). A glass tube (28 mm o.d.) fitted with a stirring bar was charged with $Rh_4(CO)_{12}$ (0.012 g, 0.016 mmol) and benzene (8 mL) saturated by CO. The tube was placed in a 100 mL stainless steel autoclave. The reactor was pressurized by CO to 20 kg/cm^2. The contents were stirred for 5 min at ambient temperature, and then the pressurized CO was purged under a hood. Into this tube were added subsequently Me_2PhSiH (1.210 g, 8.89 mmol) in C_6H_6 (3 mL), **1a** (0.937 g, 9.17 mmol) in C_6H_6 (3 mL), and Et_3N (0.831 g, 8.21 mmol) through a syringe needle at ambient temperature. The reactor was pressurized again by CO to 20 kg/cm^2. The contents were stirred for 2 h at 100 °C and cooled to ambient temperature. After excess CO was purged under a hood, the reaction mixture was concentrated under reduced pressure. The residual oily liquid was chromatographed on silica gel using hexane/AcOEt (98/2) as an eluent to give an oily liquid. The subsequent bulb-to-bulb distillation of this oil gave pure 3-(dimethylphenylsilyl)-2-phenylpropenal (**2a**; 2.115 g, 89%, *Z*:*E* = 88:12, bp 165 °C/0.1 Torr) as a pale yellow oil. Both *Z* and *E* stereoisomers were isolated by iterative column chromatography on silica gel. (*Z*)-**2a**: IR (CCl_4) 2730 (CHO), 1693 (C=O), 1580 (C=C), 1560 (C=C), and 1250 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.61 (s, 6H, Si(C**H**$_3$)$_2$), 7.29 (s, 1H, =C**H**), 7.38−7.45 (m, 8H, Ph), 7.58−7.65 (m, 2H, Ph), and 10.08 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.74 (Si**C**H$_3$), 128.17 (Ph), 128.33 (Ph), 128.39 (Ph), 128.61 (Ph), 129.69 (Ph), 133.78 (Ph), 137.47 (Ph, ipso), 137.92 (Ph, ipso), 152.00 (=**C**H), 154.54 (=**C**, q), and 192.46 (**C**HO). Anal. Calcd for $C_{17}H_{18}OSi$: C, 76.64; H, 6.81. Found: C, 76.85; H, 7.01. (*E*)-**2a**: IR (CCl_4) 2730 (CHO), 1693 (C=O), 1600 (C=C), 1582 (C=C), and 1252 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.19 (s, 6H, Si(C**H**$_3$)$_2$), 7.05−7.13 (m, 3H, Ph), 7.13 (s, 1H, =C**H**), 7.35−7.40 (m, 6H, Ph), 7.40−7.50 (m, 2H, Ph), and 9.71 (s, 1H, C**H**O); ^{13}C NMR (50 MHz. $CDCl_3$) δ −2.48 (Si**C**H$_3$), 128.08 (Ph), 128.15 (Ph), 128.45 (Ph), 129.33 (Ph), 129.56 (Ph), 133.79 (Ph), 135.31 (Ph, ipso), 137.48 (Ph, ipso), 154.11 (=**C**H), 157.14 (=**C**, q), and 194.52 (**C**HO).

Silylformylations of **1a** catalyzed by other complexes were carried out on a 1 mmol scale in a manner similar to procedure 1 in the presence of Me_2PhSiH. Results are summarized in the sequence of solvent, yield of **2a**, and *Z*:*E* as follows: $Co_2(CO)_8$ (C_6H_6, 0%, −), $Ru_3(CO)_{12}$ (C_6H_6, 0%, −), $[Ir(COD)(PPh_3)_2]PF_6$ (CH_2Cl_2, 0%, −), $RhCl(PPh_3)_3$ (C_6H_6, 4%, 80:20), $RhH(CO)(PPh_3)_3$ (C_6H_6, 87%, 90:10), $Rh(acac)(CO)_2$ (C_6H_6, 87%, 90:10), [Rh(COD)(DPPB)]PF_6 (CH_2Cl_2, 73%, 88:12), and $[Rh(COD)Cl]_2$ (C_6H_6, 85%, 92:8), $[RhCp^*Cl_2]_2$ (CH_2Cl_2, 41%, 88:12).

$Rh_4(CO)_{12}$-Catalyzed Hydrosilylation of 1a with Me_2PhSiH under an Ar Atmosphere. Into a hexane (5 mL) solution of $Rh_4(CO)_{12}$ (0.0096 g, 0.0128 mmol) in a 30 mL round flask fitted with a stirrer bar, a reflux condenser, and a dropping funnel was added dropwise a hexane (3 mL) solution of **1a** (0.333 g, 3.26 mmol) and Me_2PhSiH (0.448 g, 3.29 mmol) at 25 °C. Since a slightly exothermic reaction started immediately after the addition of the first few drops, the rest of the solution was added at a rate that maintained the temperature of the contents below 50 °C. After the complete addition of substrates, the mixture was stirred for a further 2 h at 25 °C. Volatiles were evaporated under reduced pressure, and the residue was distilled to give 0.567 g (73%) of a mixture of **3** and **4** ((*E*)-**3**:(*Z*)-**3**:**4** = 31:56:13) as a colorless liquid (bp 110 °C/0.2 Torr).[45c,71]

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Silylformylation of 1a in the Presence of an Excess of Me_2PhSiH. A C_6H_6 (12 mL) solution containing $Rh_4(CO)_{12}$ (0.0073 g, 0.009 76 mmol), Me_2PhSiH (0.740 g, 5.43 mmol), **1a** (0.260 g, 2.54 mmol), and Et_3N (0.214 g, 2.11 mmol) prepared in a way similar to procedure 1 was stirred for 13 h at 95 °C under CO pressure (20 kg/cm^2) and cooled to ambient temperature. The residue obtained by evaporation of volatiles from the reaction mixture was chromatographed on a silica gel column to give a viscous mixture (0.711 g) containing **2a** as a pale yellow oily liquid. Further purification of this sample was not carried out. Its ^{1}H NMR spectrum allowed us to deduce that the mixture contains **2a**, **5**, and, **6** as major products. **5** (prepared from catalytic hydrogenation (Pd/C, H_2, AcOEt) of **2a**): bp 110 °C/0.1 Torr (colorless oil); IR (CCl_4) 2700 (CHO), 1723 (C═O), 1600 (aromatic C═C), and 1248 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.11 (s, 3H, SiC**H**$_3$), 0.12 (s, 3H, SiC**H**$_3$), 1.24 (dd, J = 14.8 and 9.5 Hz, 1H, C**H**$_2$), 1.56 (dd, J = 14.8 and 5.6 Hz, 1H, C**H**$_2$), 3.50 (ddd, J = 9.5, 5.6, and 1.9 Hz, 1H, C**H**), 7.09−7.15 (m, 2H, Ph), 7.26−7.5 (m, 7H, Ph), and 9.58 (d, J = 1.9 Hz, 1H, C**H**O). **6**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.23 (s, 6H, Si(C**H**$_3$)$_2$), 0.40 (s, 6H, Si(C**H**$_3$)$_2$), 4.46 (s, 2H, C**H**$_2$), 6.11 (s, 1H, ═C**H**), and 7.1−7.5 (m, 15H, 3 × Ph).

3-(Methyldiphenylsilyl)-2-phenylpropenal (8). With $Rh_4(CO)_{12}$ (0.0053 g, 0.007 09 mmol), $MePh_2SiH$ (0.595 g, 3.00 mmol), and **1a** (0.306 g, 3.00 mmol) as starting materials, **8** (0.926 g, 94%, Z:E = 83:17, bp 195 °C/0.15 Torr) was obtained analogously to **2a** as an orange-yellow viscous oil. (*Z*)-**8**: IR (CCl_4) 2740 (CHO), 1698 (C═O), 1582 (C═C), 1567 (C═C), and 1253 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (s, 6H, SiC**H**$_3$), 7.32−7.49 (m, 12H, Ph and ═C**H**), 7.54−7.64 (m, 4H, Ph), and 9.99 (s, 1H, C**H**O) (additional signals for (*E*)-**8:** δ 0.24 (s, 6H, SiC**H**$_3$) and 9.77 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.61 (Si**C**H$_3$), 128.30 (Ph), 128.43 (Ph), 128.80 (Ph), 129.98 (Ph), 134.69 (Ph), 136.01 (Ph, ipso), 137.34 (Ph, ipso), 149.79 (═**C**H), 155.56 (═**C**, q), and 192.48 (**C**HO). Anal. Calcd for $C_{22}H_{20}OSi$: C, 80.44; H, 6.14. Found: C, 80.27; H, 6.22.

3-(Triethylsilyl)-2-phenylpropenal (9a). With $Rh_4(CO)_{12}$ (0.0046 g, 0.006 15 mmol), Et_3SiH (0.349 g, 3.00 mmol), **1a** (0.307 g, 3.01 mmol), and Et_3N (0.315 g, 3.11 mmol) as starting materials, **9a** (0.680 g, 92%, Z:E = 91:9, bp 125 °C/0.15 Torr) was obtained analogously to **2a** as a pale yellow viscous oil. (*Z*)-**9a**: IR (CCl_4) 2730 (CHO), 1695 (C═O), 1580 (C═C), and, 1563 (C═C) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.80 (m closed to q, 6H, Si(C**H**$_2$CH$_3$)$_3$), 1.02 (m closed to t, 9H, Si(CH$_2$C**H**$_3$)$_3$), 7.14 (s, 1H, ═C**H**), 7.37 (approximately s, 5H, Ph), and 10.03 (s, 1H, C**H**O) (additional signals for (*E*)-**9a**: δ 6.97 (s, 1H, ═C**H**) and 9.69 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ 5.05 (Si**C**H$_2$), 7.29 (SiCH$_2$**C**H$_3$), 128.26 (Ph), 128.33 (Ph), 128.46 (Ph), 137.68 (Ph, ipso), 152.77 (═**C**H), 155.64 (═**C**, q), and 192.81 (**C**HO). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 72.93; H, 9.04.

3-(Diethylmethylsilyl)-2-phenylpropenal (10a). With $Rh_4(CO)_{12}$ (0.0059 g, 0.007 89 mmol), Et_2MeSiH (0.409 g, 4.00 mmol), **1a** (0.408 g, 3.99 mmol), and Et_3N (0.387 g, 3.82 mmol) as starting materials, **10a** (0.696 g, 75%, Z:E = 79:21, bp 125 °C/0.15 Torr) was obtained analogously to **2a** as a pale yellow oily liquid. (*Z*)-**10a**: IR (CCl_4) 2740 (CHO), 1697 (C═O), 1582 (C═C), 1567 (C═C), and 1253 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.28 (s, 3H, SiC**H**$_3$), 0.78 (m closed to q, 4H, Si(C**H**$_2$)$_2$), 1.02 (m closed to t, 6H, Si(CH$_2$C**H**$_3$)$_2$), 7.14 (s, 1H, ═C**H**), 7.37 (centered m, 5H, Ph), and 10.07 (s, 1H, C**H**O) (additional signals for (*E*)-**10a**: δ −0.14 (s, 3H, SiC**H**$_3$), 0.46 (q, J = 7.6 Hz, 4H, Si(C**H**$_2$CH$_3$)$_2$), 0.86 (t, J = 7.6 Hz, 6H, Si-(CH$_2$C**H**$_3$)$_2$), 6.98 (s, 1H, ═C**H**), 7.11−7.18 (m, 2H, Ph), 7.32−7.40 (m, 3H, Ph), and 9.68 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.80 (Si**C**H$_3$), 6.76 (Si**C**H$_2$), 7.23 (SiCH$_2$**C**H$_3$), 128.23 (Ph), 128.35 (Ph), 128.48 (Ph), 137.67 (Ph, ipso), 153.57 (═**C**H), 155.14 (═**C**, q), and 192.70 (**C**HO). Anal. Calcd for $C_{14}H_{20}$-OSi: C, 72.35; H, 8.67. Found: C, 72.15; H, 8.85.

3-(*tert*-Butyldimethylsilyl)-2-phenylpropenal (11a). A C_6H_6 (12 mL) solution containing $Rh_4(CO)_{12}$ (0.0079 g, 0.0106 mmol), ^{t}BuMe$_2$SiH (0.480 g, 4.12 mmol), **1a** (0.436 g, 4.27 mmol), and Et_3N (0.412 g, 4.07 mmol) prepared in a way similar to procedure 1 was stirred for 65 h at 25 °C under CO pressure (20 kg/cm^2). The residue obtained by evaporation of volatiles from the reaction mixture was purified by chromatographic separation and bulb-to-bulb distillation to give **11a** (0.830 g, 82%, bp 145 °C/0.3 Torr, Z:E = 98:2) as a pale yellow liquid. (*Z*)-**11a**: IR (CCl_4) 2740 (CHO), 1695 (C═O), 1582 (C═C), 1565 (C═C), and 1253 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.30 (s, 6H, Si(C**H**$_3$)$_2$), 0.99 (s, 9H, ^{t}Bu), 7.19 (s, 1H, ═C**H**), 7.37 (s, 5H, Ph), and 10.09 (s, 1H, C**H**O) (additional signals for (*E*)-**11a**: δ −0.19 (s, 6H, Si(C**H**$_3$)$_2$), 0.93 (s, 9H, ^{t}Bu), 7.05 (s, 1H, ═C**H**), 7.37 (s, 5H, Ph), and 9.68 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.61 (Si**C**H$_3$), 17.00 (^{t}Bu, q), 26.22 (^{t}Bu), 128.30 (Ph), 128.47 (Ph), 137.81 (Ph, ipso), 153.11 (═**C**H), 155.55 (═**C**, q), and 192.83 (**C**HO). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 73.06; H, 9.13.

3-(Dimethylethoxysilyl)-2-phenylpropenal (12). With $Rh_4(CO)_{12}$ (0.0285 g, 0.0381 mmol), (EtO)Me_2SiH (0.647 g, 6.21 mmol), **1a** (0.616 g, 6.03 mmol), and Et_3N (0.665 g, 6.57 mmol) as starting materials, a mixture of **12** and **14** (0.983 g, 70%, bp 140 °C/0.2 Torr, (*Z*)-**12**:(*E*)-**12**:**14** = 1:1:1) was obtained as a pale yellow liquid after immediate distillation of the mixture. IR (CCl_4): 2735 (CHO), 1698 (C═O), 1592 (C═C), 1565 (C═C), and 1253 ($SiCH_3$) cm^{-1}. (*Z*)-**12**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.40 (s, 6H, Si(C**H**$_3$)$_2$), 1.24 (t, J = 7.1 Hz, 3H, C**H**$_3$), 3.76 (q, J = 7.1 Hz, 2H, C**H**$_2$), 6.97 (s, 1H, ═C**H**), 7.2−7.4 (m, 5H, Ph), and 10.20 (s, 1H, C**H**O). (*E*)-**12**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.03 (s, 6H, Si(C**H**$_3$)$_2$), 1.14 (t, J = 7.1 Hz, 3H, C**H**$_3$), 3.60 (q, J = 7.1 Hz, 2H, C**H**$_2$), 6.91 (s, 1H, ═C**H**), 7.3−7.6 (m, 5H, Ph), and 9.70 (s, 1H, C**H**O). **14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.32 (s, 3H, SiC**H**$_3$), 0.37 (s, 3H, SiC**H**$_3$), 1.23 (t, J = 7.1 Hz, 3H, C**H**$_3$), 3.68 (dq, J = 9.3 (d) and 7.1 (q) Hz, 1H, OC**H**$_2$), 3.79 (dq, J = 9.3 (d) and 7.1 (q) Hz, 1H, OC**H**$_2$), 6.06 (s, 1H, OC**H**), 6.59 (s, 1H, ═C**H**), and 7.3−7.45 (m, 5H, Ph).

3-(Trimethoxysilyl)-2-phenylpropenal (13). With $Rh_4(CO)_{12}$ (0.0266 g, 0.0356 mmol), $(MeO)_3SiH$ (0.719 g, 5.88 mmol), **1a** (0.592 g, 5.79 mmol), and Et_3N (0.395 g, 3.90 mmol) as starting materials, a mixture of **13** and **15** (0.683 g, 47%, bp 140 °C/0.3 Torr, (*Z*)-**13**:(*E*)-**13**:**15** = 5:1:1) was obtained as a pale yellow oily liquid after immediate distillation of the mixture. IR (CCl_4): 2695 (CHO), 1703 (C═O), 1605 (C═C), and 1587 (C═C) cm^{-1}. (*Z*)-**13**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.38 (s, 9H, Si(OC**H**$_3$)$_3$), 6.62 (s, 1H, ═C**H**), 7.26−7.43 (m, 5H, Ph), and 9.73 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ 50.16 (O**C**H$_3$), 126.45 (Ph), 127.84 (Ph), 129.04 (Ph), 134.57 (Ph, ipso), 141.75 (═**C**H), 158.25 (═**C**, q), and 194.13 (**C**HO). (*E*)-**13:** ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.66 (s, 9H, Si(OC**H**$_3$)$_3$), 6.79 (s, 1H, ═C**H**), 7.26−7.43 (m, 5H, Ph), and 10.22 (s, 1H, C**H**O). **15**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.36 (s, 3H, SiOC**H**$_3$), 3.58 (s, 3H, SiOC**H**$_3$), 3.61 (s, 3H, OC**H**$_3$), 5.82 (d, J = 0.8 Hz, 1H, OC**H**), 6.29 (d, J = 0.8 Hz, 1H, ═C**H**), and 7.26−7.43 (m, 5H, Ph).

Competition between Me_2PhSiH and ^{t}BuMe$_2$SiH in the Silylformylation of 1a. A C_6H_6 (10 mL) solution containing $Rh_4(CO)_{12}$ (0.0022 g, 0.002 94 mmol), Me_2PhSiH (0.136 g, 1.00 mmol), ^{t}BuMe$_2$SiH (0.116 g, 1.00 mmol), and **1a** (0.102 g, 1.00 mmol) prepared in a way similar to procedure 1 was stirred for 5 h at 25 °C under CO pressure (20 kg/cm^2). The residue obtained by evaporation of volatiles from the reaction mixture was passed through a short pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was distilled to give 0.248 g (quantitative, bp 145 °C/0.3 Torr) of a mixture of **2a** (Z:E = 85:15) and **11a** as a yellow oily liquid. The ratio of both products (**2a**:**11a** = 88:12) was determined by the ^{1}H NMR spectrum of the distilled sample.

3-(Dimethylphenylsilyl)propenal (2b) (Procedure 2). A glass tube fitted with a stirring bar was charged with $Rh_4(CO)_{12}$ (0.0012 g, 0.016 mmol) and benzene (10 mL) saturated with CO. The tube was put in a 100 mL stainless steel autoclave. The reactor was cooled to an external temperature of −78 °C with an acetone−dry ice bath under an atmosphere

of CO. Into this tube were added subsequently Me_2PhSiH (0.218 g, 1.60 mmol) in C_6H_6 (2 mL) and Et_3N (0.190 g, 1.88 mmol) in C_6H_6 (2 mL) through a syringe needle at the same temperature. The reactor was pressurized by acetylene (**1b**) to 2.5 kg/cm^2 and then CO to 20 kg/cm^2. The contents were stirred for 2 h at 100 °C and cooled to ambient temperature. After excess CO was purged under a hood, the reaction mixture was concentrated under reduced pressure. The residual oily liquid was chromatographed on silica gel using hexane/AcOEt (97/3) as an eluent to give 0.017 g (7%) of dimethylphenylvinylsilane and 0.222 g (73%) of (*E*)-**2b** as a colorless liquid, respectively. (*E*)-**2b**: bp 126 °C/0.3 Torr; IR (CCl_4) 2700 (CHO), 1694 (C═O), 1590 (C═C), and 1253 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.47 (s, 6H, Si(C**H**$_3$)$_2$), 6.55 (dd, J = 18.7 and 7.6 Hz, 1H, ═C**H**), 7.29 (d, J = 18.7 Hz, 1H, ═C**H**), 7.35−7.45 (m, 3H, Ph), 7.50−7.55 (m, 2H, Ph), and 9.54 (d, J = 7.6 Hz, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.66 (Si**C**H$_3$), 128.24 (Ph), 129.87 (Ph), 133.91 (Ph), 135.83 (Ph, ipso), 145.24 (═**C**H), 156.66 (═**C**H), and 194.83 (**C**HO). Anal. Calcd for $C_{11}H_{14}OSi$: C, 69.42; H, 7.41. Found: C, 69.17; H, 7.26.

3-(Dimethylphenylsilyl)-2-methylpropenal (2c). With $Rh_4(CO)_{12}$ (0.0040 g, 0.005 35 mmol), Me_2PhSiH (0.367 g, 2.69 mmol), **1c** (0.5 mL, ca. 0.35 g, 8.73 mmol), and Et_3N (0.206 g, 2.04 mmol) as starting materials, **2c** (0.542 g, 99%, *Z*:*E* = 80:20, bp 118 °C/0.14 Torr) was obtained analogously to **2b** as a colorless oily liquid. (*Z*)-**2c**: IR (CCl_4) 2730 (CHO), 1695 (C═O), 1595 (C═C), and 1253 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.50 (s, 6H, Si(C**H**$_3$)$_2$), 1.93 (d, J = 1.1 Hz, 3H, C**H**$_3$), 6.97 (q, J = 1.1 Hz, 1H, ═C**H**), 7.35−7.41 (m, 3H, Ph), 7.48−7.58 (m, 2H, Ph), and 9.77 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.41 (Si**C**H$_3$), 18.61 (**C**H$_3$), 128.30 (Ph), 129.63 (Ph), 133.68 (Ph), 138.02 (Ph, ipso), 150.46 (═**C**H), 152.85 (═**C**, q), and 193.68 (**C**HO). Anal. Calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89. Found: C, 70.32; H, 7.96. (*E*)-**2c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.50 (s, 6H, Si(C**H**$_3$)$_2$), 1.81 (d, J = 0.8 Hz, 3H, C**H**$_3$), 6.84 (q, J = 0.8 Hz, 1H, ═C**H**), 7.35−7.41 (m, 3H, Ph), 7.50−7.55 (m, 2H, Ph), and 9.46 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.20 (Si**C**H$_3$), 13.38 (C**H**$_3$), 128.25 (Ph), 129.68 (Ph), 133.83 (Ph), 137.13 (Ph, ipso), 151.21 (═**C**H), 153.57 (═**C**H), and 196.10 (**C**HO).

2-Ethyl-3-(dimethylphenylsilyl)propenal (2d). With $Rh_4(CO)_{12}$ (0.0104 g, 0.0139 mmol), Me_2PhSiH (0.680 g, 4.99 mmol), **1d** (2 mL, ca. 1.4 g, 25.9 mmol), and Et_3N (0.513 g, 5.06 mmol) as starting materials, **2d** (0.989 g, 91%, *Z*:*E* = 94:6, bp 120 °C/0.07 Torr) was obtained analogously to **2a** as a pale yellow liquid. (*Z*)-**2d**: IR (CCl_4) 2720 (CHO), 1688 (C═O), 1593 (C═C), and 1251 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.52 (s, 6H, Si(C**H**$_3$)$_2$), 1.06 (t, J = 7.5 Hz, 3H, C**H**$_3$), 2.34 (q, J = 7.5 Hz, 2H, C**H**$_2$), 6.93 (b s, 1H, ═C**H**), 7.35−7.41 (m, 3H, Ph), 7.48−7.58 (m, 2H, Ph), and 9.81 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.32 (Si**C**H$_3$), 12.22 (**C**H$_3$), 24.41 (**C**H$_2$), 128.31 (Ph), 129.61 (Ph), 133.70 (Ph), 138.18 (Ph, ipso), 147.98 (═**C**H), 158.65 (═**C**, q), and 193.63 (**C**HO). Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.54; H, 8.38. (*E*)-**2d**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.51 (s, 6H, Si(C**H**$_3$)$_2$), 0.89 (t, J = 7.5 Hz, 3H, C**H**$_3$), 2.28 (q, J = 7.5 Hz, 2H, C**H**$_2$), 6.76 (s, 1H, ═C**H**), 7.36−7.42 (m, 3H, Ph), 7.51−7.58 (m, 2H, Ph), and 9.43 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.97 (Si**C**H$_3$), 13.51 (**C**H$_3$), 21.59 (**C**H$_2$), 128.22 (Ph), 129.68 (Ph), 133.85 (Ph), 137.29 (Ph, ipso), 150.92 (═**C**H), 159.56 (═**C**, q), and 195.99 (**C**HO).

3-(Dimethylphenylsilyl)-2-propylpropenal (2e). With $Rh_4(CO)_{12}$ (0.0071 g, 0.0095 mmol), Me_2PhSiH (0.694 g, 5.09 mmol), **1e** (0.375 g, 5.50 mmol), and Et_3N (0.498 g, 4.92 mmol) as starting materials, **2e** (1.100 g, 93%, *Z*:*E* = 95:5, bp 136 °C/0.07 Torr) was obtained analogously to **2a** as a pale yellow oil. (*Z*)-**2e**: IR (CCl_4) 2740 (CHO), 1692 (C═O), 1592 (C═C), and 1255 ($SiCH_3$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.52 (s, 6H, Si(C**H**$_3$)$_2$), 0.92 (t, J = 7.3 Hz, 3H, C**H**$_3$), 1.48 (sext, J = 7.3 Hz, 2H, $CH_2C\mathbf{H}_2CH_3$), 2.30 (t, J = 7.3 Hz, 2H, $C\mathbf{H}_2CH_2CH_3$), 6.94 (s, 1H, ═C**H**), 7.35−7.42 (m, 3H, Ph), 7.50−7.60 (m, 2H, Ph), and 9.79 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.35 (Si**C**H$_3$), 13.51 (**C**H$_3$), 21.37 ($\mathbf{C}H_2CH_3$), 33.68 (═C**C**H$_2$), 128.28 (Ph), 129.66 (Ph), 133.66 (Ph), 138.16 (Ph, ipso), 149.42 (═**C**H), 157.11 (═**C**, q), and 193.63 (**C**HO). Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.47; H, 8.96. (*E*)-**2d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.51 (s, 6H, Si(C**H**$_3$)$_2$), 0.80 (t, J = 7.2 Hz, 3H, C**H**$_3$), 1.29 (sext, J = 7.2 Hz, 2H, $CH_2C\mathbf{H}_2CH_3$), 2.26 (t, J = 7.2 Hz, 2H, $C\mathbf{H}_2CH_2CH_3$), 6.78 (s, 1H, ═C**H**), 7.35−7.42 (m, 3H, Ph), 7.50−7.60 (m, 2H, Ph), and 9.43 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.01 (Si**C**H$_3$), 13.97 (**C**H$_3$), 22.58 ($\mathbf{C}H_2CH_3$), 30.23 (═CC**H**$_2$), 128.19 (Ph), 129.58 (Ph), 133.84 (Ph), 137.25 (Ph, ipso), 151.38 (═**C**H), 158.14 (═**C**, q), and 196.10 (**C**HO).

3-(Triethylsilyl)-2-propylpropenal (9e). With $Rh_4(CO)_{12}$ (0.0063 g, 0.008 43 mmol), Et_3SiH (0.576 g, 4.95 mmol), **1e** (0.347 g, 5.09 mmol), and Et_3N (0.474 g, 4.68 mmol) as starting materials, **9e** (0.957 g, 91%, *Z*:*E* = 97:3, bp 136 °C/0.07 Torr) was obtained analogously to **2a** as a pale yellow oil. (*Z*)-**9e**: IR (CCl_4) 2730 (CHO), 1686 (C═O), and 1588 (C═C) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.65−0.77 (m, 6H, Si(C**H**$_2$CH$_3$)$_3$), 0.85−1.03 (m, 12H, Si($CH_2C\mathbf{H}_3$)$_3$ and C**H**$_3$), 1.45 (sext, J = 7.5 Hz, 2H, $CH_2C\mathbf{H}_2CH_3$), 2.28 (dt, J = 7.3 (t) and 1.1 (d) Hz, 2H, $C\mathbf{H}_2CH_2CH_3$), 6.74 (t, J = 1.1 Hz, 1H, ═C**H**), and 9.75 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ 5.52 (Si**C**H$_2$), 7.47 ($SiCH_2\mathbf{C}H_3$), 13.70 (**C**H$_3$), 21.82 ($\mathbf{C}H_2CH_3$), 33.96 (═C**C**H$_2$), 148.95 (═**C**H), 157.52 (═**C**, q), and 193.62 (**C**HO). Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.85; H, 11.39. Found: C, 67.62; H, 11.46. (*E*)-**9e**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.42−0.63 (m, 6H, Si(C**H**$_2$CH$_3$)$_3$, 0.85−1.03 (m, 12H, Si($CH_2C\mathbf{H}_3$)$_3$ and C**H**$_3$), 1.43 (sext, J = 7.4 Hz, 2H, $C\mathbf{H}_2CH_3$), 2.30 (t, J = 7.2 Hz, 2H, ═CC**H**$_2$), 6.61 (s, 1H, ═C**H**), and 9.41 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ 4.09 (Si**C**H$_2$), 7.40 ($SiCH_2\mathbf{C}H_3$), 14.41 (**C**H$_3$), 22.92 ($\mathbf{C}H_2CH_3$), 31.10 (═C**C**H$_2$), 150.90 (═**C**H), 158.17 (═**C**, q), and 195.63 (**C**HO).

3-(*tert*-Butyldimethylsilyl)-2-propylpropenal (11e). With $Rh_4(CO)_{12}$ (0.0060 g, 0.008 02 mmol), ^{t}BuMe$_2$SiH (0.568 g, 4.88 mmol), and **1e** (0.338 g, 4.96 mmol) in acetonitrile as starting materials, **11e** (0.944 g, 91%, *Z*:*E* = 98:2, bp 116 °C/0.09 Torr) was obtained as a colorless liquid after reaction for 17 h at 90 °C. (*Z*)-**11e**: IR (CCl_4) 2730 (CHO), 1688 (C═O), 1590 (C═C), and 1253 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.22 (s, 6H, Si(C**H**$_3$)$_2$), 0.89 (t, J = 7.2 Hz, 3H, $CH_2C\mathbf{H}_3$), 0.93 (s, 9H, ^{t}Bu), 1.44 (sext, J = 7.2 Hz, 2H, $CH_2C\mathbf{H}_2CH_3$), 2.27 (dt, J = 7.2 (t) and 0.9 (d) Hz, 2H, ═CC**H**$_2$), 6.81 (t, J = 0.9 Hz, 1H, ═C**H**), and 9.81 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.34 (Si**C**H$_3$), 13.49 ($CH_2\mathbf{C}H_3$), 16.76 (^{t}Bu, q), 21.54 ($\mathbf{C}H_2CH_3$), 26.14 (^{t}Bu), 33.87 ═C**C**H$_2$), 149.78 (═**C**H), 157.45 (═**C**, q), and 194.11 (**C**HO). Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.58; H, 11.63.

2-Butyl-3-(dimethylphenylsilyl)propenal (2f). With $Rh_4(CO)_{12}$ (0.0114 g, 0.0152 mmol), Me_2PhSiH (1.596 g, 11.71 mmol), and **1f** (0.956 g, 11.63 mmol) as starting materials, **2f** (2.465 g, 86%, *Z*:*E* = 85:15, bp 120 °C/0.04 Torr) was obtained analogously to **2a** as a pale yellow oil. (*Z*)-**2f**: IR (CCl_4) 2730 (CHO), 1688 (C═O), 1590 (C═C), and 1252 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.50 (s, 6H, Si(C**H**$_3$)$_2$), 0.90 (t, J = 7.0 Hz, 3H, C**H**$_3$), 1.22−1.44 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2CH_3$), 2.30 (dt, J = 7.2 (t) and 1.2 (d) Hz, 2H, ═CC**H**$_2$), 6.93 (t, J = 1.2 Hz, 1H, ═C**H**), 7.35−7.40 (m, 3H, Ph), 7.48−7.55 (m, 2H, Ph), and 9.77 (s, 1H, C**H**O) (additional signals for (*E*)-**2f**: δ 0.50 (s, 6H, Si(C**H**$_3$)$_2$), 6.75 (s, 1H, ═C**H**), and 9.42 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.32 (Si**C**H$_3$), 13.70 (**C**H$_3$) 22.26 (**C**H$_2$), 30.42 (**C**H$_2$), 31.39 (**C**H$_2$), 128.30 (Ph), 129.60 (Ph), 133.68 (Ph), 137.18 (Ph, ipso), 149.25 (═**C**H), 157.42 (═**C**, q), and 193.70 (**C**HO). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 72.81; H, 9.19.

2-Butyl-3-(diethylmethylsilyl)propenal (10f). With $Rh_4(CO)_{12}$ (0.0050 g, 0.006 69 mmol), Et_2MeSiH (0.502 g, 4.91 mmol), and **1f** (0.402 g, 4.89 mmol), **10f** (0.839 g, 81%, *Z*:*E* = 89:11, bp 100 °C/0.08 Torr) was obtained analogously to **2a** as a colorless liquid. (*Z*)-**10f**: IR (CCl_4) 2730 (CHO), 1687 (C═O), 1590 (C═C), and 1255 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz,

$CDCl_3$) δ 0.19 (s, 3H, SiC**H**$_3$), 0.62−0.74 (m, 4H, Si(C**H**$_2$CH$_3$)$_2$), 0.82−1.00 (m, 9H, Si(CH$_2$C**H**$_3$)$_2$ and C**H**$_3$), 1.20−1.45 (m, 4H, C**H**$_2$C**H**$_2$CH$_3$), 2.28 (dt, J = 7.8 (t) and 1.1 (d) Hz, 2H, =CC**H**$_2$), 6.76 (t, J = 1.1 Hz, 1H, =C**H**), and 9.78 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.56 (Si**C**H$_3$), 6.95 (Si**C**H$_2$), 7.13 (SiCH$_2$**C**H$_3$), 13.69 (**C**H$_3$), 22.22 (**C**H$_2$CH$_3$), 30.54 (**C**H$_2$), 31.38 (**C**H$_2$), 150.25 (=**C**H), 157.58 (=**C**, q), and 193.98 (**C**HO). Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.85; H, 11.39. Found: C, 67.73; H, 11.52. (*E*)-**10f**: IR (CCl_4) 2685 (CHO), 1685 (C=O), 1590 (C=C), and 1247 (SiCH$_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.18 (s, 3H, SiC**H**$_3$), 0.62−0.75 (m, 4H, Si(C**H**$_2$CH$_3$)$_2$), 0.90 (t, J = 6.5 Hz, 3H, C**H**$_3$), 0.92−1.02 (m, 6H, Si(CH$_2$C**H**$_3$)$_2$), 1.25−1.42 (m, 4H, C**H**$_2$C**H**$_2$CH$_3$), 2.29 (t, J = 7.2 Hz, 2H, =CC**H**$_2$), 6.61 (s, 1H, =C**H**), and 9.40 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −5.25 (Si**C**H$_3$), 5.60 (Si**C**H$_2$), 7.12 (SiCH$_2$**C**H$_3$), 13.69 (**C**H$_3$), 22.95 (**C**H$_2$CH$_3$), 28.41 (=C**C**H$_2$), 31.73 (=CCH$_2$**C**H$_2$), 151.85 (=**C**H), 158.25 (=**C**, q), and 196.17 (**C**HO).

2-Butyl-3-(*tert*-butyldimethylsilyl)propenal (11f). With $Rh_4(CO)_{12}$ (0.0053 g, 0.007 09 mmol), ^{t}BuMe$_2$SiH (0.575 g, 4.94 mmol), and **1f** (0.481 g, 5.85 mmol) as starting materials, (*Z*)-**11f** (0.792 g, 71%, bp 95 °C/0.3 Torr) was obtained analogously to **2a** as a pale yellow liquid after reaction in acetonitrile for 17 h at 90 °C. (*Z*)-**11f**: IR (CCl_4) 2735 (CHO), 1687 (C=O), 1588 (C=C), and 1252 (SiCH$_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.22 (s, 6H, Si(C**H**$_3$)$_2$), 0.90 (t, J = 7.3 Hz, 3H, CH$_2$C**H**$_3$), 0.93 (s, 9H, ^{t}Bu), 1.14−1.48 (m, 4H, C**H**$_2$C**H**$_2$CH$_3$), 2.30 (dt, J = 7.4 (t) and 1.1 (d) Hz, 2H, =CC**H**$_2$), 6.81 (t, J = 1.1 Hz, 1H, =C**H**), and 9.81 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.36 (Si**C**H$_3$), 13.67 (CH$_2$**C**H$_3$), 16.74 (^{t}Bu, q), 22.20 (**C**H$_2$CH$_3$), 26.12 (^{t}Bu), 30.58 (=C**C**H$_2$), 31.55 (=CCH$_2$**C**H$_2$), 149.44 (=**C**H), 157.74 (=**C**, q), and 194.03 (**C**HO). Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.75; H, 11.80.

3-(Dimethylphenylsilyl)-2-pentylpropenal (2g). With $Rh_4(CO)_{12}$ (0.0046 g, 0.006 15 mmol), Me$_2$PhSiH (0.545 g, 4.00 mmol), and **1g** (0.384 g, 3.99 mmol) as starting materials, **2g** (0.737 g, 71%, *Z*:*E* = 87:13, bp 130 °C/0.14 Torr) was obtained analogously to **2a** as a pale yellow oil. (*Z*)-**2g**: IR (CCl_4) 2750 (CHO), 1687 (C=O), 1588 (C=C), and 1252 (SiCH$_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.51 (s, 6H, Si(C**H**$_3$)$_2$), 0.88 (t, J = 6.6 Hz, 3H, C**H**$_3$), 1.20−1.51 (m, 6H, C**H**$_2$C**H**$_2$C**H**$_2$CH$_3$), 2.30 (dt, J = 7.5 (t) and 1.2 (d) Hz, 2H, =CC**H**$_2$), 6.93 (t, J = 1.2 Hz, 1H, =C**H**), 7.35−7.40 (m, 3H, Ph), 7.48−7.55 (m, 2H, Ph), and 9.78 (s, 1H, C**H**O) (additional signals for (*E*)-**2g**: δ 0.50 (s, 6H, Si(C**H**$_3$)$_2$), 6.75 (s, 1H, =C**H**), and 9.42 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.31 (Si**C**H$_3$), 13.82 (**C**H$_3$), 22.27 (**C**H$_2$), 27.93 (**C**H$_2$), 31.39 (**C**H$_2$), 31.65 (**C**H$_2$), 128.30 (Ph), 129.61 (Ph), 133.70 (Ph), 138.20 (Ph, ipso), 149.21 (=**C**H), 157.47 (=**C**, q), and 193.69 (**C**HO). Anal. Calcd for $C_{16}H_{24}$-OSi: C, 73.78; H, 9.29. Found: C, 73.84; H, 9.35.

3-(Triethylsilyl)-2-pentylpropenal (9g). With $Rh_4(CO)_{12}$ (0.0041 g, 0.005 48 mmol), Et$_3$SiH (0.465 g, 4.00 mmol), and **1g** (0.384 g, 3.99 mmol) as starting materials, **9g** (0.790 g, 82%, *Z*:*E* = 95:5, bp 125 °C/0.15 Torr) was obtained analogously to **2a** as a pale yellow liquid. (*Z*)-**9g**: IR (CCl_4) 2730 (CHO), 1687 (C=O), and 1588 (C=C) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.55−0.78 (m, 6H, Si(C**H**$_2$CH$_3$)$_3$), 0.83−1.01 (m, 9H, Si-(CH$_2$C**H**$_3$)$_3$), 0.96 (t, J = 7.5 Hz, 3H, C**H**$_3$), 1.15−1.47 (m, 6H, C**H**$_2$C**H**$_2$C**H**$_2$CH$_3$), 2.29 (dt, J = 7.5 (t) and 1.1 (d) Hz, 2H, =CC**H**$_2$), 6.74 (t, J = 1.1 Hz, 1H, =C**H**), and 9.74 (s, 1H, C**H**O) (additional signals for (*E*)-**9g**: δ 6.61 (s, 1H, =C**H**), and 9.41 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ 5.21 (Si**C**H$_2$), 7.21 (SiCH$_2$**C**H$_3$), 13.82 (**C**H$_3$), 22.28 (**C**H$_2$CH$_3$), 28.10 (**C**H$_2$), 31.33 (**C**H$_2$), 31.68 (=C**C**H$_2$), 149.14 (=**C**H), 158.04 (=**C**, q), and 194.12 (**C**HO). Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.78; H, 11.93.

3-(Triethylsilyl)-2-hexylpropenal (9h). With $Rh_4(CO)_{12}$ (0.0022 g, 0.002 94 mmol), Et$_3$SiH (0.465 g, 4.00 mmol), and **1h** (0.441 g, 3.99 mmol) as starting materials, **9h** (0.871 g, 86%, *Z*:*E* = 96:4, bp 130 °C/0.14 Torr) was obtained analogously to **2a** as a pale yellow liquid. (*Z*)-**9h**: IR (CCl_4) 2728 (CHO), 1685 (C=O), and 1588 (C=C) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.65−0.78 (m, 6H, Si(C**H**$_2$CH$_3$)$_3$), 0.83−1.01 (m, 9H, Si(CH$_2$C**H**$_3$)$_3$), 0.88 (t, 3H, J = 6.6 Hz, C**H**$_3$), 1.20−1.48 (m, 8H, C**H**$_2$C**H**$_2$C**H**$_2$C**H**$_2$CH$_3$), 2.29 (dt, J = 7.0 (t) and 1.1 (d) Hz, 2H, =CC**H**$_2$), 6.74 (t, J = 1.1 Hz, 1H, =C**H**), and 9.75 (s, 1H, C**H**O) (additional signals for (*E*)-**9h**: δ 6.61 (s, 1H, =C**H**) and 9.41 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ 5.21 (Si**C**H$_2$), 7.21 (SiCH$_2$**C**H$_3$), 13.84 (**C**H$_3$), 22.41 (**C**H$_2$CH$_3$), 28.38 (**C**H$_2$), 28.76 (**C**H$_2$), 31.47 (**C**H$_2$), 31.71 (**C**H$_2$), 149.14 (=**C**H), 158.03 (=**C**, q), and 194.12 (**C**HO). Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.79; H, 11.88. Found: C, 70.62; H, 11.92.

2-Cyclohexyl-3-(dimethylphenylsilyl)propenal (2i). With $Rh_4(CO)_{12}$ (0.0099 g, 0.0132 mmol), Me$_2$PhSiH (0.152 g, 1.11 mmol), **1i** (0.113 g, 1.04 mmol), and Et$_3$N (0.116 g, 1.14 mmol) as starting materials, **2i** (0.290 g, 96%, *Z* form only, bp 135 °C/0.05 Torr) was obtained analogously to **2a** as a pale yellow oil. (*Z*)-**2i**: IR (CCl_4) 2730 (CHO), 1689 (C=O), 1588 (C=C), and 1255 (SiCH$_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.51 (s, 6H, Si(C**H**$_3$)$_2$), 1.04−1.50 (m, 5H, cyclohexyl), 1.61−1.90 (m, 5H, cyclohexyl), 2.54−2.72 (tt, J = 11.5 and 2.8 Hz, 1H, =CC**H**), 6.90 (s, 1H, =C**H**), 7.35−7.45 (m, 3H, Ph), 7.49−7.61 (m, 2H, Ph), and 9.79 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.29 (Si**C**H$_3$), 25.98 (**C**H$_2$), 26.35 (2 × **C**H$_2$), 32.30 (2 × **C**H$_2$), 37.93 (**C**H), 128.23 (Ph), 129.50 (Ph), 133.63 (Ph), 138.32 (Ph, ipso), 146.53 (=**C**H), 162.51 (=**C**, q), and 193.55 (**C**HO). Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88. Found: C, 75.19; H, 9.12.

3-(Dimethylphenylsilyl)-2-(2-propenyl)propenal (2j). With $Rh_4(CO)_{12}$ (0.0051 g, 0.006 82 mmol), Me$_2$PhSiH (0.548 g, 4.02 mmol), **1j** (0.364 g, 5.51 mmol), and Et$_3$N (0.418 g, 4.13 mmol) as starting materials, **2j** (0.834 g, 90%, *Z*:*E* = 73:27, bp 124 °C/0.09 Torr) was obtained analogously to **2a** as a pale yellow liquid. (*Z*)-**2j**: IR (CCl_4) 2740 (CHO), 2720 (CHO), 1687 (C=O), 1640 (C=C), 1594 (C=C), and 1253 (SiCH$_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.52 (s, 6H, Si(C**H**$_3$)$_2$), 3.08 (dddd, J = 6.2, 1.4, 1.4, and 0.9 Hz, 2H, =CC**H**$_2$), 5.09 (ddt, J = 18.2 (d), 1.7 (d), and 1.4 (t) Hz, 1H, =C**H**$_2$), 5.12 (ddt, J = 9.3 (d), 1.7 (d), and 1.4 (t) Hz, 1H, =C**H**$_2$), 5.82 (ddt, J = 18.2 (d), 9.3 (d), and 6.2 (t) Hz, 1H, =C**H**), 6.98 (t, J = 0.9 Hz, 1H, =C**H**), 7.35−7.45 (m, 3H, Ph), 7.49−7.60 (m, 2H, Ph), and 9.81 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.43 (Si**C**H$_3$), 35.51 (**C**H$_2$), 117.40 (=**C**H$_2$), 128.32 (Ph), 129.66 (Ph), 133.68 (Ph), 134.96 (=**C**H), 137.92 (Ph, ipso), 150.24 (=**C**H), 154.91 (=**C**, q), and 193.02 (**C**HO). Anal. Calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.88. Found: C, 73.04; H, 8.00. (*E*)-**2j**: IR (CCl_4) 2705 (CHO), 1695 (C=O), 1640 (C=C), 1595 (C=C), and 1255 (SiCH$_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.51 (s, 6H, Si-(C**H**$_3$)$_2$), 3.02 (ddd, J = 6.1, 1.7, and 1.7 Hz, 2H, =CC**H**$_2$), 4.85, (ddt, J = 17.2 (d), 1.7 (t), and 1.7 (t) Hz, 1H, =C**H**$_2$), 4.94 (ddt, J = 10.4 (d), 1.7 (d), and 1.7 (t) Hz, 1H, =C**H**$_2$), 5.70 (ddt, J = 17.2 (d), 10.4 (d), and 6.0 (t) Hz, 1H, =C**H**), 6.90 (s, 1H, =C**H**), 7.32−7.45 (m, 3H, Ph), 7.48−7.60 (m, 2H, Ph), and 9.45 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.03 (Si**C**H$_3$), 31.93 (**C**H$_2$), 116.09 (=**C**H$_2$), 128.26 (Ph), 129.77 (Ph), 133.92 (Ph), 134.90 (=**C**H), 137.02 (Ph, ipso), 152.54 (=**C**H), 155.08 (=**C**, q), and 195.46 (**C**HO).

3-(Dimethylphenylsilyl)-2-((trimethylsilyl)methyl)propenal (2k). With $Rh_4(CO)_{12}$ (0.0035 g, 0.004 68 mmol), Me$_2$-PhSiH (1.362 g, 10.00 mmol), **1k** (1.733 g, 15.45 mmol), and Et$_3$N (1.031 g, 10.18 mmol) as starting materials, **2k** (2.585 g, 94%, *Z*:*E* = 91:9, bp 140 °C/0.59 Torr) was obtained analogously to **2a** (reaction time was increased to 14 h) as a pale yellow liquid. (*Z*)-**2k**: IR (CCl_4) 2740 (CHO), 1685 (C=O), 1578 (C=C), and 1252 (SiCH$_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.00 (s, 9H, Si(C**H**$_3$)$_3$), 0.51 (s, 6H, Si(C**H**$_3$)$_2$), 1.91 (bs, 2H, =CC**H**$_2$), 6.75 (bs, 1H, =C**H**), 7.35−7.42 (m, 3H, Ph), 7.52−7.58 (m, 2H, Ph), and 9.73 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.94 (Si**C**H$_3$), −0.10 (Si**C**H$_3$), 22.70 (**C**H$_2$), 128.25 (Ph), 129.51 (Ph), 133.63 (Ph), 138.58 (Ph, ipso), 146.32 (=**C**H), 155.47 (=**C**, q), and 193.12 (**C**HO). Anal. Calcd for $C_{15}H_{24}$-OSi_2: C, 65.15; H, 8.75. Found: C, 65.24; H, 8.79. (*E*)-**2k**: ^{1}H NMR (200 MHz, $CDCl_3$) δ −0.07 (s, 9H, Si(C**H**$_3$)$_3$), 0.50 (s, 6H, Si(C**H**$_3$)$_2$), 1.84 (s, 2H, =CC**H**$_2$), 6.57 (s, 1H, =C**H**), 7.35−7.42 (m, 3H, Ph), 7.50−7.59 (m, 2H, Ph), and 9.41 (s, 1H,

C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.77 (Si**C**H_3), −1.01 (Si**C**H_3), 19.15 (**C**H_2), 128.20 (Ph), 129.61 (Ph), 133.97 (Ph), 137.54 (Ph, ipso), 146.57 (=**C**H), 156.64 (=**C**, q), and 196.29 (**C**HO).

3-(Dimethylphenylsilyl)-2-(trimethylsilyl)propenal (2l). With $Rh_4(CO)_{12}$ (0.0041 g, 0.005 48 mmol), Me_2PhSiH (0.138 g, 1.01 mmol), **1l** (0.193 g, 1.96 mmol), and Et_3N (0.115 g, 1.14 mmol) as starting materials, (*Z*)-**2l** (0.416 g, 55%, bp 128 °C/0.8 Torr) was obtained analogously to **2a** as a pale yellow liquid with the concomitant formation of 3-(dimethylphenylsilyl)-propanal (0.017 g, 17%). (*Z*)-**2l**: IR (CCl_4) 2710 (CHO), 1675 (C=O), 1590 (C=C), and 1250 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.18 (s, 9H, Si(C**H**$_3$)$_3$), 0.53 (s, 6H, Si(C**H**$_3$)$_2$), 7.35−7.42 (m, 3H, Ph), 7.50−7.59 (m, 2H, Ph), 7.57 (s, 1H, =C**H**), and 10.02 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.74 (Si**C**H_3), −0.39 (Si**C**H_3), 128.32 (Ph), 129.62 (Ph), 133.70 (Ph), 137.88 (Ph, ipso), 164.89 (=**C**H), 167.57 (=**C**, q), and 197.19 (**C**HO). Anal. Calcd for $C_{14}H_{22}OSi_2$: C, 64.06; H, 8.45. Found: C, 63.79; H, 8.67. **3-(Dimethylphenylsilyl)propanal**: IR (CCl_4) 2715 (CHO), 1732 (C=O), and 1255 ($SiCH_3$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.30 (s, 6H, Si(C**H**$_3$)$_2$), 0.99−1.03 (m, 2H, C**H**$_2$), 2.36−2.40 (m, 2H, C**H**$_2$), 7.35−7.39 (m, 3H, Ph), 7.48−7.51 (m, 2H, Ph), and 9.72 (t, J = 1.6 Hz, 1H, C**H**O); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −3.29 (Si**C**H_3), 7.40 (**C**H_2), 38.38 (**C**H_2), 127.91 (Ph), 129.21 (Ph), 133.51 (Ph), 137.92 (Ph, ipso), and 202.87 (**C**HO).

2-(Hydroxymethyl)-3-(dimethylphenylsilyl)propenal (2m). With $Rh_4(CO)_{12}$ (0.0040 g, 0.005 35 mmol), Me_2PhSiH (0.685 g, 5.02 mmol), and **1m** (0.309 g, 5.51 mmol) as starting materials, **2m** (0.862 g, 78%, *Z*:*E* = 77:23, bp 128 °C/0.8 Torr) was obtained analogously to **2a** as a pale yellow liquid. (*Z*)-**2m**: IR (CCl_4) 3630 (OH), 2730 (CHO), 1680 (C=O), 1600 (C=C), and 1252 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.54 (s, 6H, Si(C**H**$_3$)$_2$), 2.13 (bs, 1H, O**H**), 4.36 (d, J = 1.4 Hz, 2H, C**H**$_2$OH), 7.20 (t, J = 1.4 Hz, 1H, =C**H**), 7.32−7.46 (m, 3H, Ph), 7.48−7.61 (m, 2H, Ph), and 9.80 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.67 (Si**C**H_3), 62.56 (O**C**H_2), 128.39 (Ph), 129.83 (Ph), 133.72 (Ph), 137.42 (Ph, ipso), 149.24 (=**C**H), 154.42 (=**C**, q), and 193.61 (**C**HO). Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32. Found: C, 65.30; H, 7.35. (*E*)-**2m**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.53 (s, 6H, Si(C**H**$_3$)$_2$), 2.12 (bs, 1H, O**H**), 4.29 (s, 2H, C**H**$_2$OH), 6.99 (s, 1H, =C**H**), 7.35−7.45 (m, 3H, Ph), 7.52−7.58 (m, 2H, Ph), and 9.48 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.93 (Si**C**H_3), 59.04 (O**C**H_2), 128.38 (Ph), 129.88 (Ph), 133.76 (Ph), 136.89 (Ph, ipso), 154.37 (=**C**H), 155.01 (=**C**, q), and 196.43 (**C**HO).

Isomerization of (*Z*)-2 to (*E*)-2. Isomerization of **2e** is described as a typical example. Into a C_6H_6 (10 mL) solution of **2e** (*Z*:*E* = 92:8, 0.118 g, 0.508 mmol) was mixed 0.05 mL of aqueous HI (57 wt %) at 25 °C. The mixture was stirred for 5 h at 25 °C and then diluted with Et_2O (50 mL). The resulting solution was subsequently washed with aqueous sodium thiosulfate (10%, 10 mL), aqueous $NaHCO_3$ (saturated, 10 mL), and water (15 mL), dried (anhydrous $MgSO_4$), filtered, and evaporated. The residual oil was distilled to give isomerized **2e** (*Z*:*E* = 9:91, 0.103 g, 87%). Pure (*E*)-**2e** was obtained by TLC separation with hexane/AcOEt (94:6) as eluent.

3-(Dimethylphenylsilyl)-2-(methoxymethyl)propenal (2n). With $Rh_4(CO)_{12}$ (0.0125 g, 0.0167 mmol), Me_2PhSiH (0.682 g, 5.01 mmol), **1n** (0.353 g, 5.04 mmol), and Et_3N (0.506 g, 5.00 mmol) as starting materials, **2n** (0.377 g, 32%, *Z*:*E* = 88:12, bp 125 °C/0.2 Torr) was obtained analogously to **2a** as a pale yellow liquid. (*Z*)-**2n**: IR (CCl_4) 2720 (CHO), 1686 (C=O), 1601 (C=C), and 1251 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.54 (s, 6H, Si(C**H**$_3$)$_2$), 3.41 (s, 3H, OC**H**$_3$), 4.15 (d, J = 1.7 Hz, 2H, OC**H**$_2$), 7.23 (t, J = 1.7 Hz, 1H, =C**H**), 7.35−7.42 (m, 3H, Ph), 7.51−7.57 (m, 2H, Ph), and 9.79 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.61 (Si**C**H_3), 58.69 (O**C**H_3), 70.25 (O**C**H_2), 128.34 (Ph), 129.73 (Ph), 133.74 (Ph), 137.69 (Ph, ipso), 148.82 (=**C**H), 152.30 (=**C**, q), and 192.70 (**C**HO). Anal. Calcd for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74. Found: C, 66.50; H, 7.73. (*E*)-**2n**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.51 (s, 6H, Si(C**H**$_3$)$_2$), 3.17 (s, 3H, OC**H**$_3$), 4.05 (s, 2H, OC**H**$_2$), 7.04 (s, 1H, =C**H**), 7.35−7.42 (m, 3H, Ph), 7.51−7.57 (m, 2H, Ph), and 9.48 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.99 (Si**C**H_3), 58.10 (O**C**H_3), 66.63 (O**C**H_2), 128.09 (Ph), 129.46 (Ph), 133.74 (Ph), 137.69 (Ph, ipso), 153.43 (=**C**H), 155.83 (=**C**, q), and 194.65 (**C**HO).

2-(3-Chloropropyl)-3-(dimethylphenylsilyl)propenal (2o). With $Rh_4(CO)_{12}$ (0.0086 g, 0.0115 mmol), Me_2PhSiH (0.708 g, 5.20 mmol), **1o** (0.532 g, 5.19 mmol), and Et_3N (0.469 g, 4.64 mmol) as starting materials, **2o** (1.083 g, 78%, *Z*:*E* = 88:12, bp 210 °C/0.2 Torr) was obtained analogously to **2a** as a pale yellow liquid. (*Z*)-**2o**: IR (CCl_4) 2700 (CHO), 1692 (C=O), 1597 (C=C), and 1252 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.52 (s, 6H, Si(C**H**$_3$)$_2$), 1.85−1.99 (m, 2H, C**H**$_2$), 2.47 (dt, J = 7.6 (t) and 1.1 (d) Hz, 2H, C**H**$_2$), 3.52 (t, J = 6.5 Hz, 2H, C**H**$_2$Cl), 7.02 (t, J = 1.1 Hz, 1H, =C**H**), 7.34−7.42 (m, 3H, Ph), 7.48−7.56 (m, 2H, Ph), and 9.77 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.43 (Si**C**H_3), 29.35 (**C**H_2), 30.94 (**C**H_2), 44.19 (**C**H_2), 128.37 (Ph), 129.73 (Ph), 133.65 (Ph), 137.78 (Ph, ipso), 150.95 (=**C**H), 155.34 (=**C**, q), and 193.25 (**C**HO) (additional signals for (*E*)-**2o**: ^{1}H NMR δ 0.53 (s, 6H, Si(C**H**$_3$)$_2$), 3.36 (t, J = 6.5 Hz, 2H, C**H**$_2$Cl), 6.86 (t, J = 1.1 Hz, 1H, =C**H**), and 9.43 (s, 1H, C**H**O); ^{13}C NMR δ −2.15 (Si**C**H_3), 26.01 (**C**H_2), 31.62 (**C**H_2), 44.62 (**C**H_2), 128.30 (Ph), 129.73 (Ph), 133.87 (Ph), and 193.25 (**C**HO)). Anal. Calcd for $C_{14}H_{19}ClOSi$: C, 63.02; H, 7.18. Found: C, 63.12; H, 7.32.

Competition between 1a and 1f in Silylformylation. A C_6H_6 (10 mL) solution containing $Rh_4(CO)_{12}$ (0.0022 g, 0.002 94 mmol), Me_2PhSiH (0.136 g, 1.00 mmol), **1a** (0.102 g, 0.999 mmol), and **1f** (0.082 g, 0.999 mmol) prepared in a way similar to procedure 1 was stirred for 5 h at 25 °C under CO pressure (20 kg/cm^2). The residue obtained by evaporation of volatiles from the reaction mixture was passed through a short pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was distilled to give 0.246 g (93%, bp 145 °C/0.3 Torr) of a mixture of **2a** (*Z*:*E* = 95:5) and **2f** as a pale yellow oily liquid. The ratio of both products (**2a**:**2f** = 93:7) was determined by the ^{1}H NMR spectrum of the distilled sample.

3-(Dimethylphenylsilyl)-2-methylbut-2-enal (17a). With $Rh_4(CO)_{12}$ (0.0077 g, 0.0103 mmol), Me_2PhSiH (0.682 g, 5.00 mmol), and **16a** (0.415 g, 7.66 mmol) as starting materials, **17a** (1.022 g, 94%, *Z* form only, bp 131 °C/0.2 Torr) was obtained analogously to **2a** as a pale yellow liquid. (*Z*)-**17a**: IR (CCl_4) 2740 (CHO), 1680 (C=O), 1585 (C=C), and 1257 ($SiCH_3$) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.52 (s, 6H, Si(C**H**$_3$)$_2$), 1.86 (q, J = 1.0 Hz, 3H, C**H**$_3$), 2.06 (q, J = 1.0 Hz, 3H, C**H**$_3$), 7.32−7.40 (m, 3H, Ph), 7.43−7.55 (m, 2H, Ph), and 9.80 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.20 (Si**C**H_3), 11.24 (**C**H_3), 21.04 (C**H**$_3$), 128.27 (Ph), 129.48 (Ph), 133.55 (Ph), 138.38 (Ph, ipso), 148.24 (=**C**, q), 161.15 (=**C**, q), and 193.51 (**C**HO). Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.51; H, 8.54.

3-(Dimethylphenylsilyl)-2-propylbut-2-enal (17b) and 3-(Dimethylphenylsilyl)-2-methylhex-2-enal (18b). With $Rh_4(CO)_{12}$ (0.0114 g, 0.0152 mmol), Me_2PhSiH (0.543 g, 3.99 mmol), **16b** (0.380 g, 4.63 mmol), and Et_3N (0.417 g, 4.12 mmol) as starting materials, a mixture of **17a** and **18b** (0.832 g, 85%, **17b**:**18b** = 70:30, bp 123 °C/0.07 Torr) was obtained analogously to **2a** as a colorless liquid. The following data were obtained from a mixture of both isomers. IR (CCl_4): 2730 (CHO), 1677 (C=O), 1578 (C=C), and 1250 ($SiCH_3$) cm^{-1}. **17b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.53 (s, 6H, Si(C**H**$_3$)$_2$), 0.93 (t, J = 7.5 Hz, 3H, C**H**$_3$), 1.38 (sext, J = 7.5 Hz, 2H, CH_2C**H**$_2$-CH_3), 2.10 (s, 3H, C**H**$_3$), 2.39 (t, J = 7.5 Hz, 2H, C**H**$_2$$CH_2CH_3$), 7.31−7.42 (m, 3H, Ph), 7.44−7.55 (m, 2H, Ph), and 9.79 (s, 1H, C**H**O) (additional signals for **18b**: δ 0.53 (s, 6H, Si(C**H**$_3$)$_2$), 0.96 (t, J = 7.5 Hz, 3H, C**H**$_3$), 1.40 (sext, J = 7.5 Hz, 2H, CH_2C**H**$_2CH_3$), 1.88 (s, 3H, C**H**$_3$), 2.46 (t, J = 7.5 Hz, 2H, C**H**$_2$-CH_2CH_3), 7.31−7.42 (m, 3H, Ph), 7.44−7.55 (m, 2H, Ph), and 9.82 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.09 (Si**C**H_3), 13.96 (CH_2**C**H_3), 20.75 (=C**C**H_3), 21.68 (**C**H_2CH_3), 27.51

(=C**C**H_2), 128.28 (Ph), 129.46 (Ph), 133.49 (Ph), 138.54 (Ph, ipso), 152.67 (=**C**, q), 160.87 (=**C**, q), and 193.59 (**C**HO) (additional signals for **18b**: δ 0.13 (Si**C**H_3), 10.97 (CH_2**C**H_3), 14.21 (=C**C**H_3), 21.91 (**C**H_2CH_3), 36.28 (=**C**CH_2), 128.24 (Ph), 129.35 (Ph), 133.60 (Ph), 138.93 (Ph, ipso), 147.66 (=**C**, q), 164.83 (=**C**, q), and 194.08 (**C**HO)). Anal. Calcd for $C_{15}H_{22}$OSi: C, 73.11; H, 9.00. Found: C, 73.21; H, 9.30.

3-(Dimethylphenylsilyl)-2-phenylbut-2-enal (17c) and 3-(Dimethylphenylsilyl)-2-methyl-2-phenylhex-2-enal (18c). With $Rh_4(CO)_{12}$ (0.0068 g, 0.009 09 mmol), Me_2PhSiH (0.553 g, 4.06 mmol), **16c** (0.461 g, 3.97 mmol), and Et_3N (0.425 g, 4.19 mmol) as starting materials, a mixture of **17c** and **18c** (0.908 g, 82%, **17c**:**18c** = 90:10, bp 160 °C/0.12 Torr) was obtained analogously to **2a** as a pale yellow oil. **17c**: IR (CCl_4) 2735 (CHO), 1682 (C=O), 1560 (C=C), and 1255 (SiCH_3) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.61 (s, 6H, Si(C**H**$_3$)$_2$), 1.97 (s, 3H, C**H**$_3$), 7.05−7.09 (m, 3H, Ph), 7.26−7.41 (m, 5H, Ph), 7.43−7.56 (m, 2H, Ph), and 9.97 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.40 (Si**C**H_3), 22.92 (=C**C**H_3), 127.66 (Ph), 128.36 (Ph), 129.46 (Ph), 129.68 (Ph), 133.61 (Ph), 135.96 (Ph, ipso), 138.09 (Ph, ipso), 152.90 (=**C**, q), 163.02 (=**C**, q), and 192.57 (**C**HO). Anal. Calcd for $C_{18}H_{20}$OSi: C, 77.09; H, 7.19. Found: C, 76.93; H, 7.25. **18c**: IR (CCl_4) 2740 (CHO), 1683 (C=O), 1600 (C=C), 1578 (C=C), and 1255 (SiCH_3) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.32 (s, 6H, Si(C**H**$_3$)$_2$), 1.63 (s, 3H, C**H**$_3$), 6.79−7.00 (m, 3H, Ph), 7.13−7.63 (m, 7H, Ph), and 9.99 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.04 (Si**C**H_3), 13.35 (=C**C**H_3), 125.68 (Ph), 126.42 (Ph), 128.42 (Ph), 128.63 (Ph), 129.62 (Ph), 133.66 (Ph), 138.48 (Ph, ipso), 143.18 (Ph, ipso), 148.23 (=**C**, q), 165.04 (=**C**, q), and 194.35 (**C**HO).

3-(Dimethylphenylsilyl)-2,3-diphenylprop-2-enal (17d). With $Rh_4(CO)_{12}$ (0.0090 g, 0.0120 mmol), Me_2PhSiH (0.768 g, 5.64 mmol), **16d** (1.004 g, 5.63 mmol), and Et_3N (0.590 g, 5.82 mmol) as starting materials, **17d** (1.734 g, 90%, *Z*:*E* = 95:5, bp 210 °C/0.05 Torr) was obtained analogously to **2a** as a pale yellow oil. **17d**: IR (CCl_4) 2730 (CHO), 1687 (C=O), 1595 (C=C), and 1253 (SiCH_3) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.41 (s, 6H, Si(C**H**$_3$)$_2$), 6.74−6.91 (m, 4H, Ph), 6.98−7.15 (m, 6H, Ph), 7.35−7.45 (m, 3H, Ph), 7.58−7.67 (m, 2H, Ph), and 10.15 (s, 1H, C**H**O) (additional signals for (*E*)-**17d**: δ −0.03 (s, 6H, Si(C**H**$_3$)$_2$) and 9.57 (s, 1H, C**H**O)); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.15 (Si**C**H_3), 126.19 (Ph), 126.88 (Ph), 127.18 (Ph), 127.59 (Ph), 127.92 (Ph), 128.48 (Ph), 129.70 (Ph), 129.99 (Ph), 133.69 (Ph), 135.31 (Ph, ipso), 138.30 (Ph, ipso), 142.38 (Ph, ipso), 151.86 (=**C**, q), 166.01 (=**C**, q), and 193.13 (**C**HO). Anal. Calcd for $C_{23}H_{22}$OSi: C, 80.65; H, 6.48. Found: C, 80.41; H, 6.62.

3-(Methoxycarbonyl)-3-(dimethylphenylsilyl)-2-methylprop-2-enal (18e). With $Rh_4(CO)_{12}$ (0.0028 g, 0.0037 mmol), Me_2PhSiH (0.283 g, 2.08 mmol), **16e** (0.194 g, 1.98 mmol), and Et_3N (0.199 g, 1.97 mmol) as starting materials, **18e** (0.345 g, 67%, bp 126 °C/0.27 Torr) was obtained analogously to **2a** as a pale yellow oil accompanied by 0.028 g (6%) of hydrosilylation product. **18e**: IR (CCl_4) 2730 (CHO), 1724 (C=O), 1693 (C=O), 1655 (C=C), 1588 (C=C), and 1252 (SiCH_3) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.54 (s, 6H, Si(C**H**$_3$)$_2$), 1.84 (s, 3H, C**H**$_3$), 3.73 (s, 3H, OC**H**$_3$), 7.35−7.41 (m, 3H, Ph), 7.52−7.58 (m, 2H, Ph), and 9.75 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.10 (Si**C**H_3), 13.82 (=C**C**H_3), 51.65 (O**C**H_3), 128.37 (Ph), 130.03 (Ph), 133.72 (Ph), 136.60 (Ph, ipso), 147.64 (=**C**, q), 154.08 (=**C**, q), 171.55 (**C**O_2CH_3), and 192.81 (**C**HO). Anal. Calcd for $C_{14}H_{18}O_3$Si: C, 64.09; H, 6.91. Found: C, 64.22; H, 7.15.

3-(Ethoxycarbonyl)-3-(dimethylphenylsilyl)-2-phenylprop-2-enal (18f). With $Rh_4(CO)_{12}$ (0.0050 g, 0.006 69 mmol), Me_2PhSiH (0.425 g, 3.12 mmol), **16f** (0.530 g, 3.04 mmol), and Et_3N (0.313 g, 3.08 mmol) as starting materials, a mixture of **18f** (0.463 g, 45%) and the hydrosilylation product ethyl 2-(dimethylphenylsilyl)-3-phenylpropenoate (0.404 g, 43%) were obtained analogously to **2a** as a pale yellow oil. **18f** (slightly contaminated by its protodesilylation product): pale yellow oil, bp 180 °C/0.2 Torr; IR (CCl_4) 2720 (CHO), 1707 (C=O), 1695 (C=O), 1620 (C=C), and 1253 (SiCH_3) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.62 (s, 6H, Si(C**H**$_3$)$_2$), 0.95 (t, *J* = 7.2 Hz, 3H, CH_2C**H**$_3$), 3.92 (q, *J* = 7.2 Hz, 2H, C**H**$_2$$CH_3$), 7.18−7.25 (m, 3H, Ph), 7.30−7.43 (m, 5H, Ph), 7.60−7.70 (m, 2H, Ph), and 9.92 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.25 (Si**C**H_3), 13.63 (CH_2**C**H_3), 60.77 (O**C**H_2), 128.13 (Ph), 128.35 (Ph), 128.59 (Ph), 128.83 (Ph), 130.01 (Ph), 133.88 (Ph), 134.69 (Ph, ipso), 136.67 (Ph, ipso), 150.02 (=**C**, q), 155.39 (=**C**, q), 170.51 (**C**O_2CH_2), and 192.17 (**C**HO). **3-(Ethoxycarbonyl)-2-phenylprop-2-enal**: yellow oil, bp 145 °C/0.27 Torr; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12 (t, *J* = 7.1 Hz, 3H, CH_2C**H**$_3$), 4.13 (q, *J* = 7.1 Hz, 2H, C**H**$_2$$CH_3$), 6.71 (s, 1H, =C**H**), 7.19−7.30 (m, 2H, Ph), 7.35−7.43 (m, 3H, Ph), and 9.76 (s, 1H, C**H**O); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.54 (CH_2**C**H_3), 61.17 (O**C**H_2), 128.07 (Ph), 129.01 (Ph), 129.15 (Ph), 131.33 (Ph, ipso), 136.28 (=**C**H), 149.62 (=**C**, q), 165.27 (**C**O_2CH_2), and 193.11 (**C**HO). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.85; H, 6.22.

$Rh_4(CO)_{12}$-Catalyzed Cyclocarbonylation of 1a in the Presence of ^{t}BuMe$_2$SiH. A C_6H_6 (12 mL) solution of $Rh_4(CO)_{12}$ (0.0071 g, 0.009 44 mmol), ^{t}BuMe$_2$SiH (0.418 g, 3.60 mmol), and **1a** (0.804 g, 7.87 mmol) prepared in a way similar to procedure 1 was stirred for 41 h at 80 °C under CO pressure (10 kg/cm^2). Oily materials left after evaporation of volatiles from the reaction mixture were separated by medium-pressure liquid chromatography on silica gel using hexane/AcOEt (95/5) as an eluent to give **19** (0.479 g, 38%) and **20** (0.082 g, 6%) as well as **11a** (0.371 g, 42%). **19**: yellow viscous oil, bp 190 °C/0.3 Torr (solidifies on storage); IR (CCl_4) 1693 (C=O), 1600 (C=C), 1253 (SiCH_3) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.13 (s, 3H, SiC**H**$_3$), 0.15 (s, 3H, SiC**H**$_3$), 0.94 (s, 9H, ^{t}Bu), 2.57 (d, *J* = 1.1 Hz, 1H, C**H**Si), 4.14 (dd, *J* = 3.2 and 1.1 Hz, 1H, C**H**Ph), 7.17−7.42 (m, 8H, Ph), 7.64 (d, *J* = 3.2 Hz, 1H, =C**H**), 7.73−7.76 (m, 2H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ −6.81 (SiCH_3), −6.75 (SiCH_3), 17.86 (^{t}Bu, q), 26.87 (^{t}Bu), 47.96 (**C**HPh), 50.83 (**C**HSi), 127.20 (Ph), 127.46 (Ph), 128.55 (Ph), 129.10 (Ph), 131.74 (Ph, ipso), 142.04 (Ph, ipso or =**C**, q), 142.85 (=**C**, q or Ph, ipso), 158.53 (=**C**H), 208.84 (**C**=O). Anal. Calcd for $C_{23}H_{28}$OSi: C, 79.26; H, 8.10. Found: C,79.35; H, 8.09. **20**: brownish yellow viscous oil, bp 190 °C/0.3 Torr; IR (CCl_4) 1703 (C=O), 1605 (C=C), 1573 (C=C), 1248 (SiCH_3) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.17 (s, 3H, SiC**H**$_3$), −0.12 (s, 3H, SiC**H**$_3$), 0.90 (s, 9H, ^{t}Bu), 3.05 (dd, *J* = 19.1 and 3.1 Hz, 1H, C**H**$_2$), 3.42 (dd, *J* = 19.1 and 7.5 Hz, 1H, C**H**$_2$), 3.70 (dd, *J* = 7.5 and 3.1 Hz, 1H, C**H**Ph), 7.18−7.43 (m, 10H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ −4.78 (Si**C**H_3), −4.73 (Si**C**H_3), 17.38 (^{t}Bu, q), 27.35 (^{t}Bu), 45.97 (**C**H_2), 52.67 (**C**HPh), 126.60 (Ph), 126.90 (Ph), 127.55 (Ph), 128.21 (Ph), 128.81 (Ph), 128.95 (Ph), 139.69, 139.76, 140.21 (Ph ipso, Ph ipso, and =**C**Si), 186.07 (=**C**Ph), 212.64 (**C**=O). Anal. Calcd for $C_{23}H_{28}$OSi: C, 79.26; H, 8.10. Found: C, 79.18; H, 8.19.

Protodesilylation of 19. To a methanol (10 mL) solution of **19** (0.058 g, 0.165 mmol) were added KF (0.096 g, 1.65 mmol) and water (0.1 mL). The mixture was stirred for 36 h at 25 °C. The residue resulting from the evaporation of methanol was diluted with 70 mL of AcOEt. The solution was washed with 10 mL of water and dried over $MgSO_4$. Volatiles were evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel to give **21** (0.0261 g, 68%).

Authentic Preparation of 21. 1-(Dimethylphenylsilyl)-2,5-diphenylpenta-1,4-dien-3-one (0.957 g, 49%) was obtained as a pale yellow oily liquid by the following three steps: addition of (2-phenylethenyl)magnesium bromide (4.2 mmol) to **2a** (0.787 g, 2.95 mmol) in THF (25 mL) to give 1-(dimethylphenylsilyl)-2,5-diphenylpenta-1,4-dien-3-ol, subsequent PDC oxidation of this crude alcohol in DMF (15 mL), and column chromatography on silica gel. Into a 50 mL flask containing this divinyl ketone (0.957 g, 2.59 mmol) was added $FeCl_3$ (0.442 g, 2.72 mmol). The resulting solution was stirred for 20 h at 25 °C and worked up according to the literature[58] to give **21** (0.126 g, 22%) as a pale yellow oily liquid. **21**: bp 160 °C/0.14 Torr; IR (CCl_4) 1715 (C=O) and 1605 (C=C) cm^{-1}; ^{1}H NMR

(500 MHz, $CDCl_3$) 2.58 (dd, J = 19.0 and 2.9 Hz, 1H, C**H**$_2$), 3.18 (dd, J = 19.0 and 6.8 Hz, 1H, C**H**$_2$), 4.18 (ddd, J = 6.8, 2.9, and 2.4 Hz, 1H, C**H**Ph), 7.21−7.43 (m, 8H, Ph) 7.75−7.78 (m, 2H, Ph), and 7.80 (d, J = 2.4 Hz, 1H, =C**H**); ^{13}C NMR (50 MHz, $CDCl_3$) δ 43.67 (**C**H), 45.59 (**C**H$_2$), 127.39 (Ph), 128.66 (Ph), 128.85 (Ph), 129.17 (Ph), 131.28 (Ph ipso), 142.08 (Ph, ipso), 143.05 (=**C**Ph), 160.82 (=**C**H), 207.54 (**C**=O).

$Rh_4(CO)_{12}$-Catalyzed Cyclocarbonylation of 1f in the Presence of Et_2MeSiH. A C_6H_6 (12 mL) solution of $Rh_4(CO)_{12}$ (0.0052 g, 0.006 95 mmol), Et_2MeSiH (0.339 g, 3.31 mmol), and **1f** (0.804 g, 9.78 mmol) prepared in a way similar to procedure 1 was stirred for 21 h at 85 °C under CO pressure (4 kg/cm^2). Oily materials left after evaporation of volatiles from the reaction mixture were directly distilled to remove **10f** (120 °C/0.1 Torr, 0.340 g, 48%). Then, the residue was purified by medium-pressure liquid chromatography on silica gel using hexane/AcOEt (96/4) as an eluent to give **22a** (0.131 g, 13%) after bulb-to-bulb distillation as a pale yellow oily liquid: bp 140 °C/0.1 Torr; IR (CCl_4) 1692 (C=O), 1587 (C=C), 1245 (Si-C) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.18 (s, 3H, SiC**H**$_3$), 0.72 (m, 4H, Si(C**H**$_2$CH$_3$)$_2$), 0.88 (t, J = 7.8 Hz, 9H, Si-(CH$_2$C**H**$_3$)$_2$ and CH$_2$C**H**$_3$), 0.94 (t, J = 7.3 Hz, 3H, CH$_2$C**H**$_3$), 1.22−1.33 (m, 5H, 2 × C**H**$_2$ and CHC**H**$_2$), 1.38 (sext, J = 7.3 Hz, 2H, C**H**$_2$), 1.50 (quint, J = 7.8 Hz, 2H, C**H**$_2$), 1.72−1.79 (m, 1H, CHC**H**$_2$), 2.25 (dd, J = 18.6 and 2.9 Hz, 2H, ring C**H**$_2$), 2.25−2.31 (m, 1H, ring C**H**), 2.48 (t, J = 8.0 Hz, 2H, C**H**$_2$), 2.75 (dd, J = 18.6 and 7.3 Hz, 1H, ring C**H**$_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −5.11 (Si**C**H$_3$), −5.09 (Si**C**H$_3$), 5.54 (Si**C**H$_2$), 5.58 (Si**C**H$_2$), 7.43 (SiCH$_2$**C**H$_3$), 13.95 (**C**H$_3$), 13.97 (**C**H$_3$), 22.70 (CH$_2$**C**H$_2$CH$_3$), 22.97 (CH$_2$**C**H$_2$CH$_3$), 29.58 (**C**H$_2$), 30.83 (**C**H$_2$), 31.35 (**C**H$_2$), 33.91 (**C**H$_2$), 39.63 (ring **C**H$_2$), 46.52 (ring **C**H), 136.92 (=**C**Si), 189.04 (=**C**CH$_2$), 216.42 (**C**=O). Anal. Calcd for $C_{18}H_{34}OSi$: C, 73.39; H, 11.64. Found: C,73.20; H, 11.64.

$Rh_4(CO)_{12}$-Catalyzed Cyclocarbonylation of 1f in the Presence of ^{t}BuMe$_2$SiH. A C_6H_6 (12 mL) solution of $Rh_4(CO)_{12}$ (0.0078 g, 0.0104 mmol), ^{t}BuMe$_2$SiH (0.528 g, 4.54 mmol), and **1f** (0.752 g, 9.15 mmol) prepared in a way similar to procedure 1 was stirred for 165 h at 100 °C under CO pressure (20 kg/cm^2). Oily materials obtained by evaporation of volatiles from the reaction mixture were directly distilled to remove **11f** (120 °C/0.1 Torr, 0.232 g, 23%). Then, the residue was separated by medium-pressure liquid chromatography on silica gel and subsequent preparative TLC using hexane/AcOEt (93/7) as an eluent to give **22b** (0.169 g, 12%), **23** (0.042 g, 3%), **24** (0.019 g, 1%), **25** (0.041 g, 3%), **26** (0.015 g, 1%), and **11f** (0.189 g, 18%) in addition to some inseparable products. **22b**: bp 160 °C/0.2 Torr, pale yellow oil; IR (CCl_4) 1690 (C=O), 1580 (C=C), 1247 (SiCH$_3$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.21 (s, 3H, Si**C**H$_3$), 0.23 (s, 3H, SiC**H**$_3$), 0.86 (s, 9H, ^{t}Bu), 0.89 (t, J = 7.1 Hz, 3H, C**H**$_3$), 0.95 (t, J = 7. 3 Hz, 3H, C**H**$_3$), 1.22−1.34 (m, 5H, 2 × C**H**$_2$ and CHC**H**$_2$), 1.38 (sext, 2H, C**H**$_2$), 1.47−1.55 (m, 2H, C**H**$_2$), 1.73−1.81 (m, 1H, CHC**H**$_2$), 2.26 (dd, J = 18.8 and 2.9 Hz, 1H, ring C**H**$_2$), 2.25−2.31 (m, 1H, ring C**H**), 2.50 (dd, J = 7.8 and 7.8 Hz, 2H, =CC**H**$_2$), 2.76 (dd, J = 18.8 and 7.1 Hz, 1H, ring C**H**$_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ −4.43 (Si**C**H$_3$), −4.24 (Si**C**H$_3$), 13.78 (2 × **C**H$_3$), 17.41 (^{t}Bu, q), 22.53 (**C**H$_2$), 22.95 (**C**H$_2$), 26.67 (^{t}-Bu), 29.45 (**C**H$_2$), 30.38 (**C**H$_2$), 31.23 (**C**H$_2$), 34.38 (**C**H$_2$), 39.32 (ring **C**H$_2$), 46.46 (ring **C**H), 136.80 (=**C**Si), 189.77 (=**C**CH$_2$), and 216.64 (**C**=O). Anal. Calcd for $C_{19}H_{36}OSi$: C, 73.95; H, 11.76. Found: C, 73.90; H, 11.90. **23**: pale yellow oil, bp 160 °C/0.2 Torr; IR (CCl_4) 1695 (C=O), 1617 (C=C), and 1252 (SiCH$_3$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.08 (s, 3H, Si**C**H$_3$), −0.04 (s, 3H, SiC**H**$_3$), 0.86 (t, 3H, J = 7.3 Hz, C**H**$_3$), 0.91 (t, J = 7.3 Hz, 3H, C**H**$_3$), 0.93 (s, 9H, ^{t}Bu), 1.22−1.29 (m, 4H, 2 × C**H**$_2$), 1.34 (sext, J = 7.2 Hz, 2H, C**H**$_2$), 1.40−1.48 (m, 2H, C**H**$_2$), 1.57−1.64 (m, 1H, CSiC**H**$_2$), 1.71−1.77 (m, 1H, CSiC**H**$_2$), 2.17 (t, J = 7.8 Hz, 2H, =CC**H**$_2$), 2.27 (d, J = 19.5 Hz, 1H, ring C**H**$_2$), 2.51 (d, J = 19.5 Hz, ring C**H**$_2$), 7.19 (t, J = 1.1 Hz, 1H, =C**H**); ^{13}C NMR (50 MHz, $CDCl_3$) δ −7.63 (Si**C**H$_3$), −7.45 (Si**C**H$_3$), 13.65 (**C**H$_3$), 13.77 (**C**H$_3$), 18.61 (^{t}Bu, q), 22.40 (**C**H$_2$), 23.11 (**C**H$_2$), 24.27 (**C**H$_2$), 26.49 (**C**H$_2$), 27.80 (^{t}Bu), 30.12 (**C**H$_2$), 33.72 (**C**H$_2$), 38.46 (Si**C**CH$_2$), 43.50 (ring **C**H$_2$), 144.02 (=**C**CH$_2$), 166.57 (=**C**H), 210.48 (**C**=O). Anal. Calcd for $C_{19}H_{36}OSi$: C, 73.95; H, 11.76. Found: C, 73.83; H, 11.95. **24** (tentatively assigned): pale yellow oil, bp 160 °C/0.2 Torr; IR (CCl_4) 1693 (C=O), 1595 (C=C), and 1253 (SiCH$_3$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 3H, Si**C**H$_3$), 0.08 (s, 3H, SiC**H**$_3$), 0.88 (t, J = 6.5 Hz, 3H, C**H**$_3$), 0.88 (s, 9H, ^{t}Bu), 0.94 (t, J = 7.3 Hz, 3H, C**H**$_3$), 1.22−1.34 (m, 4H, 2 × C**H**$_2$), 1.34−1.44 (m, 2H, C**H**$_2$), 1.46−1.64 (m, 4H, 2 × C**H**$_2$), 2.04 (dd, J = 1.3 and 1.1 Hz, 1H, ring C**H**Si), 2.23−2.30 (m, 1H, ring C**H**CH$_2$), 2.50 (t, J = 6.1 Hz, 2H, C**H**$_2$), 5.82 (dt, J = 1.3 and 1.3 Hz, 1H, =C**H**); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −5.72 (Si**C**H$_3$), −4.57 (Si**C**H$_3$), 13.76 (**C**H$_3$), 13.85 (**C**H$_3$), 18.32 (^{t}Bu, q), 22.42 (**C**H$_2$), 22.85 (**C**H$_2$), 27.02 (^{t}Bu), 28.39 (**C**H$_2$), 29.77 (**C**H$_2$), 34.01 (**C**H$_2$), 34.66 (**C**H$_2$), 42.94 (ring **C**H), 51.31 (ring **C**H), 126.21 (=**C**H), 188.08 (=**C**, q), 212.73 (**C**=O). **25**: pale yellow oil, 160 °C/0.2 Torr; IR (CCl_4) 1695 (C=O), 1653 (C=C), 1570 (C=C), and 1248 (SiCH$_3$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 6H, SiC**H**$_3$), 0.88 (s, 9H, ^{t}Bu), 0.94 (t, J = 7.0 Hz, 3H, C**H**$_3$), 0.96 (t, J = 7.0 Hz, 3H, C**H**$_3$), 1.40 (sext, J = 7.0 Hz, 2H, C**H**$_2$CH$_3$), 1.50 (sext, J = 7.5 Hz, 2H, C**H**$_2$), 1.52 (quint, J = 7.5 Hz, 2H, C**H**$_2$), 2.16 (dt, J = 7.5 and 7.5 Hz, 2H, =CHC**H**$_2$), 2.55 (dd, J = 7.5 and 7.5 Hz, 2H, C**H**$_2$), 3.13 (bs, 2H, ring C**H**$_2$), 6.45 (tt, J = 7.5 and 1.9 Hz, 1H, =C**H**); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −4.08 (Si**C**H$_3$), 13.88 (2 × **C**H$_3$), 17.58 (^{t}Bu, q), 21.81 (**C**H$_2$), 23.06 (**C**H$_2$), 26.77 (^{t}Bu), 30.53 (**C**H$_2$), 31.84 (**C**H$_2$), 34.24 (**C**H$_2$), 35.94 (ring **C**H$_2$), 132.77 (=**C**H), 135.76 (ring **C**=CH), 139.65 (=**C**Si), 184.08 (ring =**C**CH$_2$), 201.14 (**C**=O). Anal. Calcd for $C_{19}H_{34}OSi$: C, 74.44; H, 11.18. Found: C, 74.22; H, 11.41. **26** (*Z*:*E* = 64:36): pale yellow oil, bp 165 °C/0.2 Torr; IR (CCl_4) 1663 (C=O), 1617 (C=C), and 1248 (SiCH$_3$) cm^{-1}. (*Z*)-**26**: ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.04 (s, 6H, Si(C**H**$_3$)$_2$), 0.88 (s, 9H, ^{t}Bu), 0.90 (t, J = 7.1 Hz, 3H, C**H**$_3$), 0.92 (t, J = 7.2 Hz, 3H, C**H**$_3$), 1.28−1.49 (m, 8H, 4 × C**H**$_2$), 2.25 (dt, J = 6.8 and 6.8 Hz, 2H, C**H**$_2$), 2.29 (t, J = 7.3 Hz, 2H, C**H**$_2$), 5.67 (t, J = 1.2 Hz, =C**H**), 6.16 (dt, J = 15.8 (d) and 1.1 (t) Hz, 1H, =C**H**), 6.81 (dt, J = 15.8 (d) and 6.8 (t) Hz, 1H, =C**H**); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −5.27 (Si**C**H$_3$), 13.72 (**C**H$_3$), 13.79 (**C**H$_3$), 16.65 (^{t}Bu, q), 22.18 (**C**H$_2$), 22.98 (**C**H$_2$), 26.42 (^{t}Bu), 30.05 (**C**H$_2$), 31.68 (**C**H$_2$), 32.26 (**C**H$_2$), 38.17 (**C**H$_2$), 127.14 (=**C**H), 130.43 (=**C**H), 151.26 (=**C**HSi), 158.50 (=**C**, q), 200.63 (**C**=O); EI MS *m*/*z* 251 (M$^+$ − 57). (*E*)-**26**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (s, 6H, Si-(C**H**$_3$)$_2$), 0.90 (t, J = 6.8 Hz, 3H, CH$_3$), 0.92 (s, 9H, ^{t}Bu), 0.92 (t, J = 6.8 Hz, 3H, C**H**$_3$), 1.28−1.29 (m, 8H, 4 × C**H**$_2$), 2.25 (dt, J = 6.8 and 6.8 Hz, 2H, C**H**$_2$), 2.42 (t, J = 7.3 Hz, 2H, C**H**$_2$), 6.33 (s, 1H, =C**H**), 6.51 (dt, J = 15.6 (d) and 1.0 (t) Hz, 1H, =C**H**), 6.82 (dt, J = 15.6 (d) and 6.8 (t) Hz, 1H, =C**H**); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −4.57 (Si**C**H$_3$), 13.76 (**C**H$_3$), 13.88 (**C**H$_3$), 16.88 (^{t}Bu, q), 22.22 (**C**H$_2$), 22.98 (**C**H$_2$), 26.37 (^{t}Bu), 30.27 (**C**H$_2$), 31.68 (**C**H$_2$), 31.72 (=C**C**H$_2$), 32.34 (=C**C**H$_2$), 126.99 (=**C**H), 135.00 (=**C**HCH$_2$), 148.93 (=**C**HSi), 158.50 (=**C**, q), and 194.68 (**C**=O); EI MS *m*/*z* 251 (M$^+$ − 57).

1-Deuterio-3-(dimethylphenylsilyl)-2-phenylpropenal (2a-D$_{(formyl)}$). With $Rh_4(CO)_{12}$ (0.0060 g, 0.008 02 mmol), Me_2PhSiD (0.672 g, 4.89 mmol), **1a** (0.502 g, 4.92 mmol), and Et_3N (0.541 g, 5.35 mmol) as starting materials, **2a-D$_{(formyl)}$** was obtained analogously to **2a** as a pale yellow oily liquid (0.922 g, 71%, *Z*:*E* = 87:13, 140 °C/0.09 Torr): IR (CCl_4) 2095 (CDO), 1680 (C=O), 1615 (C=C), 1580 (C=C), and 1250 (SiCH$_3$) cm^{-1}.

3-Deuterio-3-(dimethylphenylsilyl)-2-phenylpropenal (2a-D$_{(vinyl)}$). With $Rh_4(CO)_{12}$ (0.0077 g, 0.0103 mmol), Me_2PhSiH (0.271 g, 1.99 mmol), **1a-D** (0.201 g, 1.95 mmol), and Et_3N (0.181 g, 1.78 mmol) as starting materials, **2a-D$_{(vinyl)}$** was obtained analogously to **2a** as a colorless oily liquid (0.460 g, 88%, *Z*:*E* = 57:43, bp 140 °C/0.07 Torr): IR (CCl_4) 2730 (CHO), 1690 (C=O), 1580 (C=C), and 1253 (SiCH$_3$) cm^{-1}.

Stoichiometric Reactions of $Rh_4(CO)_{12}$. Reactions in a Sample Tube for ^{1}H NMR. The weighed starting materials were charged consecutively into a ^{1}H NMR sample tube containing 0.6 mL of $CDCl_3$ under an Ar or CO atmosphere.

The resulting solution was monitored at the respective stages of the addition by ^{1}H NMR spectroscopy.

Reaction of $Rh_4(CO)_{12}$ with Me_2PhSiH (Procedure 3). A glass tube (12 mm o.d.) fitted with a stirring bar was charged with $Rh_4(CO)_{12}$ (0.0396 g, 0.0529 mmol) and $CDCl_3$ (0.6 mL) saturated with CO. The tube was placed in a 100 mL stainless steel autoclave. The reactor was pressurized by CO to 20 kg/cm^2. The contents were stirred for 20 min at ambient temperature, and then the pressurized CO was purged under a hood. Into this tube was added Me_2PhSiH (0.0274 g, 0.201 mmol) in $CDCl_3$ (0.2 mL) through a syringe needle at ambient temperature. The reactor was pressurized again by CO to 20 kg/cm^2. The contents were stirred for 14 h at 25 °C. After excess CO was purged under a hood, the reaction mixture (now cream yellow) was transferred into a sample tube for NMR spectroscopy under a CO atmosphere. A sample for an IR spectrum was prepared by an analogous procedure in hexane solution. **28a**: IR (hexane) 2102 (s), 2049 (s), 2017 (vs), and 1982 (w) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.81 (s, 6H, Si(C**H**$_3$)$_2$), 7.32−7.40 (m, 3H, Ph), 7.58−7.65 (m, 2H, Ph); ^{13}C NMR (125.7 MHz, $CDCl_3$, −55 °C, 9 mg of Cr(acac)$_3$ was added) δ 6.33 (Si**C**H$_3$), 127.64 (Ph), 128.44 (Ph), 132.56 (Ph), 142.92 (Ph, ipso), 189.37 (d, J = 65.9 Hz, **C**=O).

Preparation of a Solution of 28b and 28c. A $CDCl_3$ solution of these species was prepared according to procedure 3 for NMR spectroscopy. **28b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.46 (s, 3H, SiC**H**$_3$), 0.87−1.11 (m, 10H, Si(C**H**$_2$C**H**$_3$)$_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$, −55 °C, 9 mg of Cr(acac)$_3$ was added) δ 3.27 (Si**C**H$_3$), 8.47 (Si**C**H$_2$), 13.38 (SiCH$_2$**C**H$_3$), and 189.81 (d, J = 65.9 Hz, **C**=O). **28c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.49 (s, 6H, Si(C**H**$_3$)$_2$), 1.01 (^{t}Bu).

Preparation of 29a by Reaction of 28a with 1a under CO Pressure. Into a glass tube (28 mm o.d.) containing a CH_2Cl_2 (16 mL) solution of **28a** resulting from a reaction of $Rh_4(CO)_{12}$ (0.0643 g, 0.0860 mmol) and Me_2PhSiH (0.044 g, 0.330 mmol) by an operation similar to procedure 3 was added a CH_2Cl_2 (1 mL) solution of **1a** (0.0344 g, 0.337 mmol) through a syringe needle at ambient temperature. The reactor was pressurized by CO to 20 kg/cm^2. The contents were stirred for 24 h at 25 °C. After excess CO was purged under a hood, the volatiles were evaporated under reduced pressure. The residual oily liquid was chromatographed on silica gel using hexane/AcOEt (96/4) as an eluent to give 0.0503 g (61%) of **29a** as a pale yellow oily liquid. **29a**: IR (CCl_4) 1665 (C=O), 1585 (C=C), and 1250 (SiCH$_3$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.06 (s, 12H, 2 × Si(C**H**$_3$)$_2$), 6.77 (s, 2H, 2 × =C**H**), 7.02−7.07 (m, 4H, Ph), and 7.19−7.38 (m, 16H, Ph); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −2.21 (Si**C**H$_3$), 127.63 (Ph), 127.68 (Ph), 127.71 (Ph), 128.18 (Ph), 128.86 (Ph), 128.91 (Ph), 133.44 (Ph), 138.01 (Ph, ipso), 138.35 (Ph, ipso), 139.84 (=**C**H), 156.15 (=**C**, q), and 197.46 (**C**=O). Anal. Calcd for $C_{33}H_{34}OSi_2$: C, 78.83; H, 6.82. Found: C, 78.72; H, 6.92.

Preparation of 29b by Reaction of 28b with 1a under CO Pressure. Divinyl ketone **29b** (0.0898 g, 81%) resulted from a consecutive reaction of $Rh_4(CO)_{12}$ (0.0916 g, 0.123 mmol) with Et_2MeSiH (0.0523 g, 0.512 mmol) and **1a** (0.0558 g, 0.546 mmol) in CH_2Cl_2 (22 mL) according to the previous procedure as a pale yellow oily liquid. **29b**: IR (CCl_4) 1667 (C=O), 1610 (C=C), and 1255 (SiCH$_3$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.23 (s, 6H, 2 × SiC**H**$_3$), 0.39 (q, J = 7.8 Hz, 8H, 2 × Si(C**H**$_2$CH$_3$)$_2$), 0.82 (t, J = 7.8 Hz, 12H, 2 × Si(CH$_2$C**H**$_3$)$_2$), 6.60 (s, 2H, 2 × =C**H**), 7.14−7.17 (m, 4H, Ph), and 7.27−7.31 (m, 6H, Ph); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ −5.07 (Si**C**H$_3$), 6.05 (Si**C**H$_2$), 7.38 (SiCH$_2$**C**H$_3$), 127.66 (Ph), 128.81 (Ph), 138.63 (Ph, ipso), 140.45 (=**C**H), 155.92 (=**C**, q), and 197.76 (**C**=O); CI MS m/z 435 (M$^+$ + 1); EI MS m/z 434 (M$^+$), 419 (M$^+$ − 15), 405 (M$^+$ − 29). Anal. Calcd for $C_{27}H_{38}OSi_2$: C, 74.59; H, 8.81. Found: C, 74.51; H, 8.75.

Subsequent Reactions of $Rh_4(CO)_{12}$ with 1a and Me_2PhSiH. Into a glass tube (12 mm o.d.) containing a $CDCl_3$ (0.5 mL) solution of $Rh_4(CO)_{12}$ (5.70 mg, 0.007 62 mmol) was added **1a** (0.81 mg, 0.007 93 mmol) in $CDCl_3$ (0.2 mL) under a CO atmosphere. The resulting dark red solution was stirred for 36 h at 25 °C to form **31** and then transferred to an NMR sample tube through a syringe needle for ^{1}H NMR observation. When Me_2PhSiH (1.03 mg, 0.007 56 mmol) in $CDCl_3$ (0.1 mL) was added into this solution, (*E*)-**3** was formed almost selectively within 30 min. **31**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.00−7.30 (m, 5H, Ph) and 9.16 (quint, J = 1.0 Hz, 1H, ≡CH).

Preparation of 32a. A glass tube (25 mm i.d.) fitted with a stirring bar was charged with $Rh_4(CO)_{12}$ (0.0446 g, 0.0597 mmol) and CH_2Cl_2 (3 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 contents were stirred for 15 min at ambient temperature, and then the pressurized CO was purged under a hood. Into this tube was added **1a** (0.0134 g, 0.131 mmol) in CH_2Cl_2 (1 mL) through a syringe needle at ambient temperature. The reactor was pressurized again by CO to 20 kg/cm^2. The contents were stirred for 20 h at 25 °C. After excess CO was purged under a hood, the reaction mixture was concentrated to about 1 mL by a CO stream and diluted with 7 mL of hexane. This solution was cooled to −78 °C and kept for 12 h at the same temperature. The solid was collected on a glass filter and washed with hexane to give **32a** (0.032 g, 53%) as a yellow-brown powder. **32a**: mp 92−95 °C dec; IR (CH_2Cl_2) 2129 (m), 2111 (w), 2094 (vs), 2077 (m), 2053 (m), and 1665 (broad w) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.17 (d, J = 1.0 Hz, 1H, ≡CH), 7.21−7.41 (m, 3H, Ph), 7.42−7.51 (m, 2H, Ph); ^{13}C NMR (125.7 MHz, $CDCl_3$, −55 °C, 9 mg of Cr(acac)$_3$ was added) δ 63.91 (m, **C**H), 82.20 (m, quaternary **C**), 128.09 (Ph), 128.27 (Ph), 129.17 (Ph), 134.35 (Ph, ipso), 173.97 (d, J = 70.9 Hz, **C**=O), 182.68 (t, J = 42.4 Hz, **C**=O), 210.65 (d, J = 21.4 Hz, **C**=O), and 214.17 (d, J = 20.2 Hz, **C**=O). Anal. Calcd for $C_{15}H_6O_7Rh_2$: C, 35.75; H, 1.20. Found: C, 35.89; H, 1.20.

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