Zwitterionic Rhodium(I) Complex Catalyzed Net Silylhydroformylation of Terminal Alkynes

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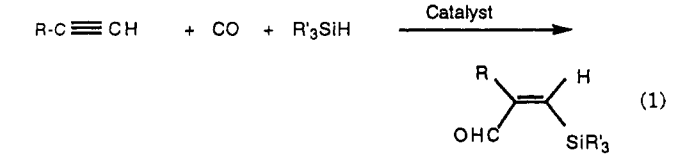
The zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-$ Rh^+(1,5-COD) is an excellent catalyst for the reaction of alkynes with hydrosilanes and synthesis gas (1:1 CO/H_2). Vinyl, allyl, and, in some cases, saturated silylaldehydes were usually isolated in greater than 60% yield using a 100:1 ratio of substrate to catalyst. The silylhydroformylation reaction is both regio- and stereoselective.

Introduction

A combination of transition-metal complexes and hydrosilanes is a useful tool for numerous synthetic transformations of alkenes, alkynes, and carbonyl compounds.[1-4] Catalytic carbonylation is also a useful process for the incorporation of CO into various unsaturated substrates.[5] As a consequence, the investigation of hydroformylation reactions in which hydrogen is replaced by a trialkylsilane has been initiated, and the reaction of "silylformylation" has been discovered by Murai.[6-8] The silylformylation of alkenes catalyzed by $Co_2(CO)_8$,[6-8] $[RhCl(CO)_2]_2$,[9] or $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$[10] gives silyl enol ethers or the homologous aldehydes as the sole products. The reaction of cyclic ethers with $CO/HSiR_3/Co_2(CO)_8$ affords $R_3SiO(CH_2)_{n+1}OSiR_3$.[11] The silylformylation of aldehydes to the corresponding α-silyloxyaldehydes is catalyzed by $Co_2(CO)_8$[6,12] or more effectively by $[Rh(COD)Cl]_2$.[13]

Addition of both carbon monoxide and trialkylsilane (eq 1) to an alkyne constitutes an organosilane counterpart to hydroformylation.[14,15]



(1)

In contrast to the silylcarbonylations described above, reactions involving alkyne, carbon monoxide, and hydrosilane give carbon-centered silanes exclusively. The silylcarbonylation of alkynes is catalyzed by $Rh_4(CO)_{12}$ or Rh-Co mixed-metal carbonyl clusters. These transformations generally occur under mild conditions and afford (*Z*)-3-silyl-2-alkenals **1** with a high degree of regiocontrol.[14,15] More recently, this method[14] was successfully applied to the silylformylation of propargyl-type alcohols,[16] propargylamine derivatives.[17,18] and 5-ethynyl-2-pyrrolidinone.[19] Finally, it should be mentioned that the silylformylation of terminal alkynes to **1** is smoothly catalyzed by rhodium(II) perfluorobutyrate.[20] In the present work, we have examined the reactions of a variety of terminal alkynes with hydrosilanes and synthesis gas in the presence of the zwitterionic rhodium(I) complex **2**, (1,5-COD)-η^6-$Rh^+PhBPh_3^-$.[21] To our knowledge, this is the first use of a mixture of $HSiR_3/CO/H_2$ in reaction with alkynes. The term "silylhydroformylation" has been used to describe these transformations.

Results and Discussion

Net Silylhydroformylation of Nonfunctionalized Terminal Alkynes. Treatment of 1-hexyne with 1.2 equiv of dimethylphenylsilane and 1:1 CO/H_2, using a catalytic amount of **2** in CH_2Cl_2, at 40 °C and 40 atm for 24 h, gave (*E*)-2-((dimethylphenylsilyl)methyl)-2-hexen-1-al (**5**) in 73% isolated yield. In the absence of hydrogen, 1-hexyne reacts with $HSiMe_2Ph/CO$/**2** to give 1-(dimethylphenylsilyl)-1-hexen-2-al (**6**) in 89% yield (Scheme 1).

The rhodium(I) cationic complex **3** and rhodium carbonyl **4** also smoothly catalyze the reaction of 1-hexyne with $HSiMe_2Ph/CO/H_2$, but unlike the zwitterionic complex **2**, these catalysts give rise to **6**, which is formed stereospecifically and in high yield (87–92%).

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Scheme 1

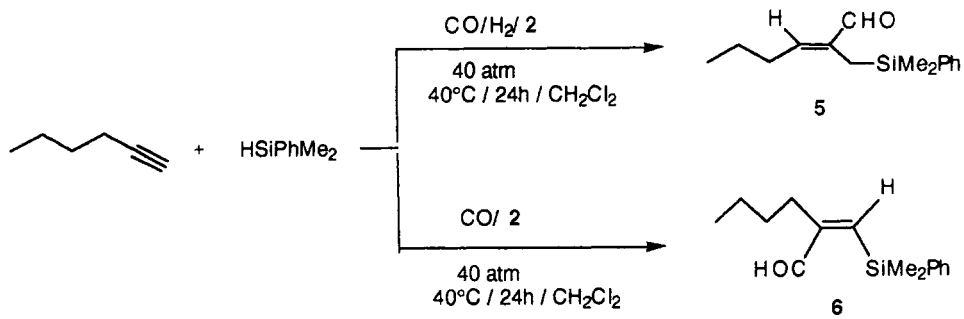
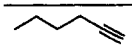
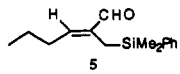
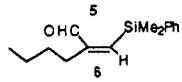
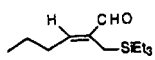
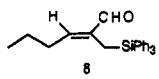
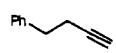
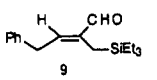
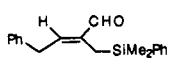
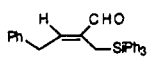
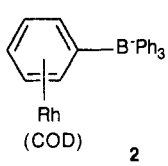


Table 1. Silylhydroformylation of Terminal Alkynes with CO/H_2 Using Rh Complexes[a]

substrate	silane	catalyst[a]	product	yield, % (isolated)
	$HSiPhMe_2$	**2**	 **5**	73
	$HSiPhMe_2$	**2**[b]	 **6**	89
	$HSiPhMe_2$	**3**	6	87
	$HSiPhMe_2$	**4**	6	92
	$HSiEt_3$	**2**	 **7**	78
	$HSiPh_3$	**2**	 **8**	62
	$HSiEt_3$	**2**	 **9**	71
	$HSiPhMe_2$	**2**	 **10**	64
	$HSiPh_3$	**2**	 **11**	54

[a] Reaction conditions: alkyne (4 mmol), silane (4.5 mmol), catalyst (0.04 mmol), CH_2Cl_2 (10 mL), CO/H_2 (1:1, 40 atm), 40 °C, 24 h. [b] Reaction in the absence of hydrogen.



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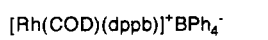

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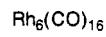
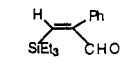
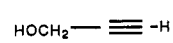
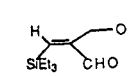
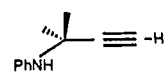
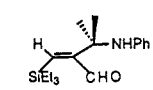
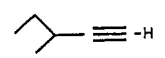
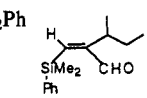
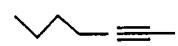


4

Therefore, catalyst **2** in the system consisting of alkyne/$HSiMe_2Ph$/CO behaves similarly to other rhodium catalysts,[14,15,19,20] while the use of **2** and synthesis gas leads to the product with different stereochemistry. When the reaction of 1-hexyne with $HSiMe_2Ph$ was carried out in a H_2 atmosphere, a complicated mixture of unidentified products was obtained. The results of the silylhydroformylation of 1-hexyne and 4-phenyl-1-butyne with different hydrosilanes catalyzed by **2** and several rhodium complexes are listed in Table 1. Triethyl- and triphenylsilane react with 1-hexyne under CO/H_2 in the presence of **2**, affording the corresponding 1-silylhexen-2-als **7** and **8** in fair yield. It should be noted that the neutral Rh(I) complex $[Rh(COD)Cl]_2$, unlike its zwitterionic and cationic counterparts, gives a complicated mixture of unidentified products. 4-Phenyl-1-butyne, under the silylhydroformylation conditions, behaves like 1-hexyne, and, upon Rh(I)-catalyzed reaction with triethyl-, dimethylphenyl-, and triphenylsilane, yields (*E*)-4-phenyl-2-(silylmethyl)-2-buten-1-als **9-11** in satisfactory yield (Table 1).

Table 2. Silylhydroformylation of Some Alkynes with $HSiR_3/CO/H_2$ Catalyzed by 2[a]

substrate	silane	product	yield, % (isolated)
	$HSiEt_3$	 **19**	87
	$HSiEt_3$	 **20**	93
	$HSiEt_3$	 **21**	91
	$HSiMe_2Ph$	 **22**	94
	$HSiMe_2Ph$	no reaction	

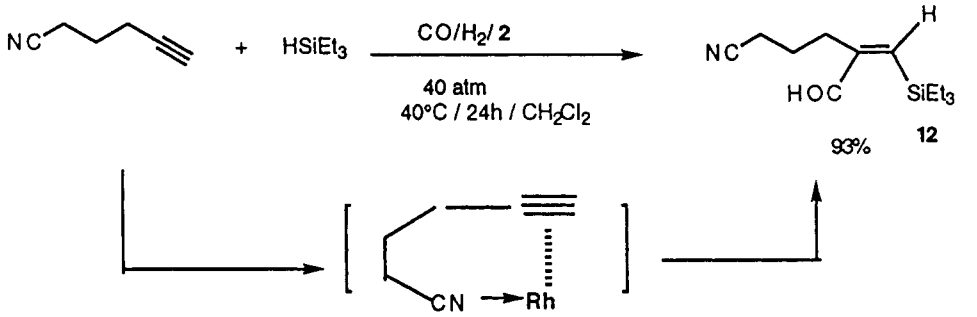
[a] For reaction conditions, see footnote *a* in Table 1.

The silylalkenals **5** and **7-11** are new compounds, and their structures and purity were established by ^1H and ^{13}C NMR spectra, mass spectra, and elemental analyses. The trans configuration was determined by ^1H NOE experiments. For example, in the case of **5**, irradiation of the olefin proton leads to a 20% enhancement of the aldehydic proton. Similarly, irradiation of the aldehydic proton induces a 22% enhancement of the olefin proton.

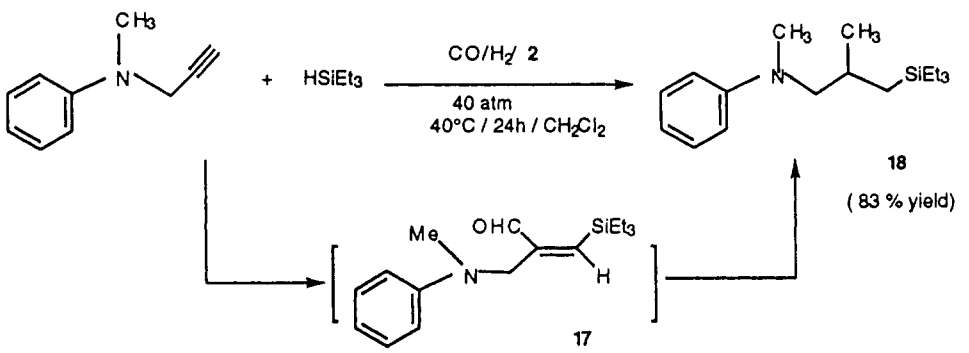
Net Silylhydroformylation of Functionally Substituted Terminal Alkynes. The results obtained in the silylhydroformylation of 1-hexyne and 4-phenyl-1-butyne indicate that similar transformations involving functionally substituted terminal alkynes could give rise to synthetically valuable multifunctionalized derivatives. For this reason, we have studied the reactions of substituted acetylenes with $HSiR_3/CO/H_2$ using **2** as the catalyst. The results on the silylhydroformylation of alkynes are summarized in Table 2. 5-Cyano-1-pentyne, structurally related to 1-hexyne, reacts with $HSiEt_3/CO/H_2$/**2** to give (*Z*)-5-cyano-1-(triethylsilyl)-1-penten-2-al (**12**) in 93% isolated yield (Scheme 2). Thus, the presence of the cyano group leads to a significant change in the reaction pathway.

It is conceivable that the cyano group interacts with the rhodium catalyst and determines the direction of the reaction (Scheme 2). In the case of 5-chloro-1-pentyne, this intramolecular coordination obviously does not take place, and the alkyne behaves similarly to 1-hexyne and

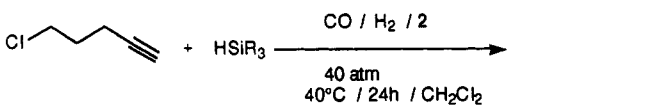
Scheme 2

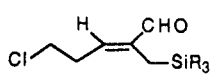


Scheme 3



affords (*E*)-5-chloro-1-(triethylsilyl)-2-penten-2-al (**13**) in fair yield under the silylhydroformylation conditions (eq 2, Table 2).





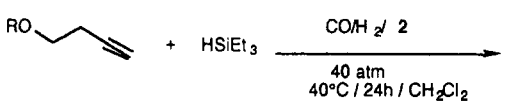
(2)

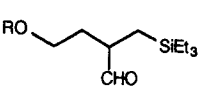
13, 14

13 R = Et 38 %

14 $HSiR_3$ = $HSiMe_2Ph$ 62 %

Use of 3-butyn-1-ol in reaction with $HSiR_3/CO/H_2$ gives a complicated mixture of unidentified products. When the hydroxyl group is protected by an acetyl or a *p*-tosyl group, the reaction yields saturated silylaldehydes **15** and **16**, probably via intermediate silylalkenals of type **12** (eq 3).





(3)

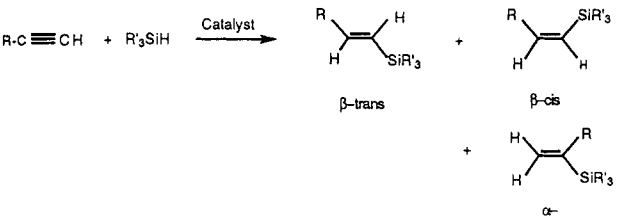
15, 16

15 R = CH_3CO- 61 %

16 R = p-Tosyl- 54 %

N-Methyl-*N*-propargylaniline, reacted under the same conditions, affords the saturated product **18** in 83% isolated yield. The reaction may occur via an intermediate silylalkenal **17**, followed by the reduction of both the C=C and C=O bonds, affording **18** (Scheme 3).

Scheme 4



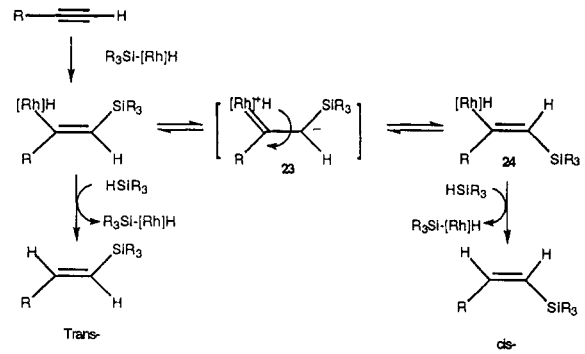
The reaction has been applied to other alkynes to assess the scope and limitations of the silylhydroformylation reaction catalyzed by the Rh(I) zwitterionic complex. Phenylacetylene, propargyl alcohol, *N*-phenyl-3,3-dimethylpropargylamine, and 3-methyl-1-pentyne behave similarly, with (*Z*)-silylalkenals **1** and **19–21** respectively, formed regiospecifically and in excellent yield (Table 2). Therefore, the presence of hydrogen does not change the reaction pathway in these cases. The outcome is the same as those for rhodium carbonyl[14–19] and Rh(II) perfluorobutyrate[20]-catalyzed silylformylations of alkynes with $HSiR_3/CO$. It should be noted that an internal alkyne, viz. 2-heptyne, does not react under identical conditions.

Mechanistic Studies. It is conceivable that the mechanism for the silylhydroformylation of alkynes is closely related to that for hydrosilylation. This well-studied transition-metal-catalyzed reaction generally can give a mixture of three products (Scheme 4).[1–4]

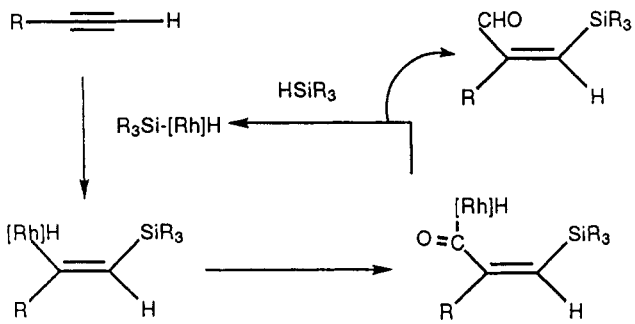
In one product, the silicon is bound to the α-carbon of the alkyne, while for the other two products, the Si is attached to the β-carbon, but Si–H addition has taken place in either a syn or an anti manner to give trans (*E*) or cis (*Z*) products, respectively. The selectivity of the hydrosilylation reaction depends on the nature of the catalyst and the structure of the alkyne. Several mechanisms may be considered for the hydrosilylation reaction.[22] A deuterium labeling study, using deuteriodimethylphenylsilane as reactant, was carried out to gain

(22) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984.

Scheme 5

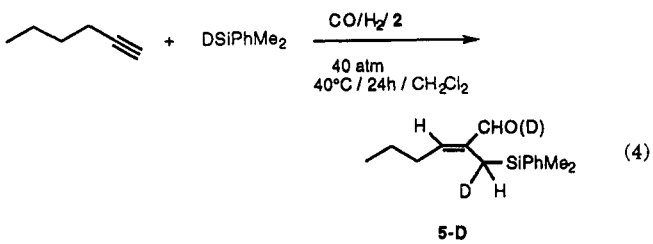


Scheme 6



some insight into the mechanism of the silylhydroformylation reaction.

Reaction of a mixture of 1-hexyne (4 mmol) with excess $DSiMe_2Ph$ (5.0 mmol) in CH_2Cl_2(10 mL) and the zwitterionic rhodium complex **2** (0.04 mmol) under CO/H_2 (1:1, 40 atm) for 24 h at 40 °C gave the partially deuterated silylalkenal **5-D** in 53% yield (eq 4). The structure of **5-D**



(4)

5-D

was confirmed by ^1H and ^2H NMR spectra, and the percent deuterium (55% at the aldehydic position and 60% at the allylic position) was determined by integrating the formyl and alkenyl protons in the ^1H NMR spectrum.

The mechanism of the rhodium-catalyzed hydrosilylation of alkynes was proposed independently by Tanke and Crabtree[22] and by Ojima and coworkers[23] to account for the formation of the β-cis adduct. A carbene-type zwitterionic rhodium complex **23** was proposed as the key intermediate, which then undergoes isomerization from a high-energy form (*Z* complex) to a lower energy form (*E* complex) **24**, followed by reductive elimination to give the cis isomer as the kinetic product (Scheme 5).[23]

A similar mechanism, involving CO insertion into the rhodium–carbon bond, may operate in the case of the silylformylation process (Scheme 6).

This mechanism accounts for the formation of (*Z*)-silylalkenals when phenylacetylene and some functionally substituted terminal alkynes were used as starting materials (see Table 2). Note that in the case of O-protected propargyl alcohol and *N*-methyl-*N*-propargylaniline (Table 2), the corresponding products **15**, **16**, and **18** result mainly from the consecutive hydrogenation of silylalkenals. Finally, the reaction of 1-hexyne with $HSiEt_3/CO$ in the absence of H_2 also gave (*Z*)-silylalkenal, i.e., according to Scheme 6. However, it is unclear why terminal alkynes such as 1-hexyne and 4-phenyl-1-butyne, under silylhydroformylation conditions, give rise to 1-silylmethyl-2-alken-1-als (see Table 1). Taking into account the results of the deuterium labeling experiment (eq 4) as well as the mechanism described above (Scheme 6), the reaction pathway shown in Scheme 7 may be proposed for the silylhydroformylation reaction.

The first three steps of this mechanism (a silicon shift to the C≡C bond, the formation of a carbene-like Rh complex **23-D**, and its isomerization to **24-D**) are identical to those shown in Scheme 5. An important intermediate, presumably responsible for the formation of the (silylmethyl)alkenal, is the rhodium–allenyl π-complex **25** which may afford the π-complex **26**. Insertion of CO into the rhodium–carbon bond may give **27**, and subsequent reductive elimination would afford the 1-(silylmethyl)-2-alkenal **28**. It should also be pointed out that (silylmethyl) alkenals [$R_3'SiCH_2C(CHO)$=CHR] do not result from silylalkenals [$RC(CHO)$=$CHSiR_3$] and vice versa. This has been shown by reacting each of these compounds with H_2 in the presence of the Rh(I) zwitterionic complex **2**.

A more detailed mechanistic study is required to rationalize the catalytic sequence. However, mechanistic aspects aside, the present novel Rh(I)-catalyzed silylhydroformylation reaction of an alkyne, hydrosilane, carbon monoxide, and hydrogen is a simple and efficient approach to vinyl, allyl, and saturated silylaldehydes which are difficult to prepare or are inaccessible by other means. In conclusion, a new catalytic system consisting of the zwitterionic rhodium(I) complex **2**, hydrosilane, and synthesis gas has been developed. Using this system for the silylhydroformylation of terminal alkynes, one can obtain a variety of multifunctional products regiospecifically and in high yield.

Experimental Section

All chemicals were purchased from commercial sources. The zwitterionic rhodium(I) complex **2** was prepared as described previously.[24] Dimethylphenyldeuteriosilane was obtained by reduction of $ClMe_2SiPh$ with $LiAlD_4$ in ether as described in the literature.[25] ^1H and ^{13}C NMR spectra were recorded on a Gemini 200 or a Varian XL-300 spectrometer using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Mass spectra were obtained on a VG 7070 E mass spectrometer. Gas chromatography was performed on a Varian Vista 6000 instrument equipped with a glass column packed with 3% OVA-17 on W-HP (100–200 mesh). Elemental analyses were carried out by MHW Laboratories (Phoenix, AZ).

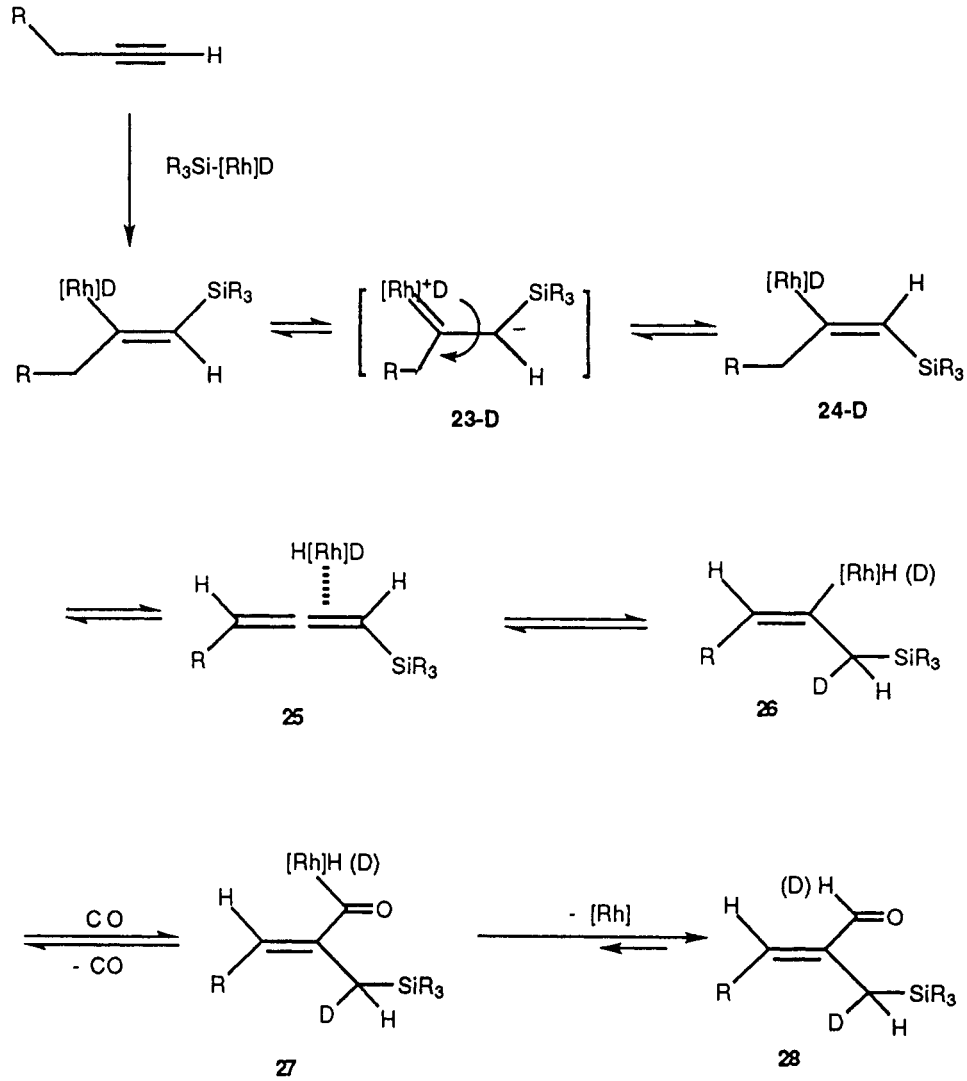
Silylhydroformylation of Alkynes. A mixture of alkyne (4 mmol), silane (4.5 mmol), and the Rh catalyst (0.04 mmol) in 10 mL of CH_2Cl_2 was placed in a 45-mL autoclave, and the reactor was pressurized to 40 atm with $CO:H_2$ (1:1). The reaction mixture was magnetically stirred at 40 °C for 24 h and then cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by silica gel chromatography using hexane/ethyl acetate (95:5) as the developer. The following compounds are new.

(23) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

(24) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339.

(25) Lukevics, E.; Gevorgyan, V. N.; Goldberg, Yu. *Tetrahedron Lett.* **1984**, *25*, 1415.

Scheme 7



(*E*)-2-((Dimethylphenylsilyl)methyl)-2-hexen-1-al (5): ^{1}H NMR δ 9.30 (s, 1H, CHO), 7.49 (m, 2H, aromatic protons), 7.32 (m, 3H, aromatic protons), 6.27 (t, 1H, CH, J = 7.4 Hz), 1.97 (q, 2H, CH_2, J = 7.4 Hz), 1.97 (s, 2H, $SiCH_2$), 1.32 (m, 2H, CH_2), 0.83 (t, 3H, CH_3, J = 7.4 Hz), 0.23 (s, 6H, $SiCH_3$); ^{13}C NMR δ 195.57, 152.47, 141.24, 138.48, 133.68, 129.12, 127.75, 31.28, 21.80, 14.35, 13.88, -2.70; **MS** (*m/e*) 246 [M$^+$]. Anal. Calcd for $C_{15}H_{22}SiO$: C, 73.17; H, 8.90. Found: C, 73.38; H, 8.67.

(*E*)-2-((Triethylsilyl)methyl)-2-hexen-1-al (7): ^{1}H NMR δ 9.28 (s, 1H, CHO), 6.22 (t, 1H, CH, J = 7.4 Hz), 2.23 (q, 2H, CH_2, J = 7.4 Hz), 1.65 (s, 2H, $SiCH_2$), 1.49 (m, 2H, CH_2), 0.88 (m, 12H, CH_3), 0.46 (q, 6H, CH_2, J = 7.4 Hz); ^{13}C NMR δ 195.08, 151.31, 142.24, 31.32, 21.91, 13.88, 9.91, 7.24, 3.70; MS (*m/e*) 226 [M$^+$]. Anal. Calcd for $C_{13}H_{26}SiO$: C, 69.00; H, 11.50. Found: C, 68.66; H, 11.21.

(*E*)-2-((Triphenylsilyl)methyl)-2-hexen-1-al (8): ^{1}H NMR δ 9.13 (s, 1H, CHO), 7.52 (m, 6H, aromatic protons), 7.37 (m, 9H, aromatic protons), 6.25 (t, 1H, CH, J = 7.4 Hz), 2.59 (s, 2H, CH_2), 1.82 (q, 2H, CH_2, J = 7.4 Hz), 1.21 (m, 2H, CH_2), 0.73 (t, 3H, CH_3, J = 7.4 Hz); ^{13}C NMR δ 194.24, 152.90, 140.63, 135.92, 134.14, 129.60, 127.74, 31.36, 21.65, 13.82, 11.77; MS (*m/e*), 370 [M$^+$]. Anal. Calcd for $C_{25}H_{26}SiO$: C, 81.08; H, 7.03. Found: C, 81.00; H, 7.32.

(*E*)-4-Phenyl-2-((triethylsilyl)methyl)-2-buten-1-al (9): ^{1}H NMR δ 9.36 (s, 1H, CHO), 7.26 (m, 5H, aromatic protons), 6.43 (t, 1H, CH, J = 7.5 Hz), 3.62 (d, 2H, CH_2, J = 7.5 Hz), 1.83 (s, 2H, CH_2), 0.95 (t, 9H, CH_3, J = 7.5 Hz), 0.53 (q, 6H, CH_2, J = 7.3 Hz); ^{13}C NMR δ 194.89, 149.01, 142.37, 139.05, 129.43, 129.21, 126.35, 37.89, 10.74, 7.98, 4.11; MS (*m/e*) 274 [M$^+$]. Anal. Calcd for $C_{17}H_{26}SiO$: C, 74.45; H, 9.49. Found: C, 74.81; H, 9.01.

(*E*)-4-Phenyl-2-((dimethylphenylsilyl)methyl)-2-buten-1-al (10): ^{1}H NMR δ 9.32 (s, 1H, CHO), 7.32 (m, 10H, aromatic protons), 6.41 (t, 1H, CH, J = 7.5 Hz), 3.23 (d, 2H, CH_2, J = 7.5 Hz), 2.05 (s, 2H, CH_2), 0.32 (s, 6H, CH_3); ^{13}C NMR δ 194.78, 150.01, 141.59, 138.61, 138.29, 133.66, 129.28, 128.69, 128.39, 127.89, 126.57, 35.12, 14.64, -2.68; MS (*m/e*) 294 [M$^+$]. Anal. Calcd for $C_{19}H_{22}SiO$: C, 77.55; H, 7.48. Found: C, 77.54; H, 7.60.

(*E*)-4-Phenyl-2-((triphenylsilyl)methyl)-2-buten-1-al (11): ^{1}H NMR δ 9.18 (s, 1H, CHO), 7.62–6.91 (m, 20H, aromatic protons), 6.42 (t, 1H, CH, J = 7.5 Hz), 3.12 (d, 2H, CH_2, J = 7.5 Hz), 2.73 (s, 2H, CH_2); ^{13}C NMR δ 194.01, 150.54, 126.56, 35.35, 12.10; MS (*m/e*) 418 [M$^+$].

(*Z*)-5-Cyano-1-(triethylsilyl)-1-penten-2-al (12): ^{1}H NMR δ 9.18 (s, 1H, CHO), 6.81 (s, 1H, CH), 2.43 (t, 2H, CH_2, J = 7.4 Hz), 2.25 (t, 2H, CH_2), 1.76 (m, 2H, CH_2), 0.97 (t, 9H, CH_3, J = 7.3 Hz), 0.68 (q, 6H, CH_2, J = 7.3 Hz); ^{13}C NMR δ 192.98, 154.96, 151.32, 119.25, 31.35, 24.29, 16.62, 7.35, 5.26; MS (*m/e*) 237 [M$^+$]. Anal. Calcd for $C_{13}H_{23}SiON$: C, 65.82; H, 9.70. Found: C, 66.07; H, 9.83.

(*E*)-5-Chloro-1-(triethylsilyl)-2-penten-2-al (13): ^{1}H NMR δ 9.34 (s, 1H, CHO), 6.29 (t, 1H, CH, J = 7.3 Hz), 3.62 (t, 2H, CH_2, J = 7.3 Hz), 2.74 (q, 2H, CH_2, J = 7.3 Hz), 1.69 (s, 2H, CH_2), 0.87 (t, 9H, CH_3, J = 7.3 Hz), 0.48 (q, 6H, CH_2, J = 7.3 Hz); ^{13}C NMR δ 194.66, 145.07, 144.28, 42.75, 32.18, 10.46, 7.27, 3.75; MS (*m/e*) 231 [M$^+$ - 15]. Anal. Calcd for $C_{12}H_{23}SiOCl$: C, 58.53; H, 9.30. Found: C, 58.82; H, 9.34.

(*E*)-5-Chloro-1-(dimethylphenylsilyl)-2-penten-2-al (14): ^{1}H NMR δ 9.33 (s, 1H, CHO), 7.45 (m, 2H, aromatic protons), 7.32 (m, 3H, aromatic), 6.27 (t, 1H, CH, J = 7.3 Hz), 3.31 (t, 2H, CH_2, J = 7.3 Hz), 2.34 (q, 2H, CH_2, J = 7.3 Hz), 1.92 (s,

2H, CH_2), 0.25 (s, 6H, CH_3); ^{13}C NMR δ 194.41, 146.07, 142.94, 137.90, 133.49, 129.22, 127.76, 42.49, 31.87, 14.83, −2.93; MS (*m/e*) 243 [M^+ − 15]. Anal. Calcd for $C_{14}H_{19}SiOCl$: C, 63.15; H, 7.14. Found: C, 63.48; H, 7.18.

3-Formyl-4-(triethylsilyl)butyl acetate (15): ^1H NMR δ 9.51 (d, 1H, CHO, J = 2.1 Hz), 4.07 (m, 2H, CH_2), 2.42 (m, 1H, CH), 2.01 (m, 1H, CH), 1.98 (s, 3H, CH_3), 1.73 (m, 1H, CH_2), 0.92 (m, 10H, CH, CH_3), 0.55 (m, 7H, CH, CH_2); ^{13}C NMR δ 203.30, 179.74, 61.96, 44.92, 30.63, 20.74, 10.53, 7.24, 3.67. Anal. Calcd for $C_{13}H_{26}SiO_3$: C, 60.46; H, 10.07. Found: C, 60.81; H, 10.19.

3-Formyl-4-(triethylsilyl)butyl tosylate (16): ^1H NMR δ 9.45 (d, 1H, CHO, J = 2.1 Hz), 7.74, (d, 2H, aromatic protons), 7.32 (d, 2H, aromatic protons), 4.04 (m, 2H, CH_2), 2.43 (m, 4H, CH, CH_3), 1.98 (m, 1H, CH), 1.75 (m, 1H, CH_2), 0.89 (t, 9H, $3CH_3$, J = 7.6 Hz), 0.79 (dd, 1H, CH, J = 15.1, 7.0 Hz), 0.50 (q, 6H, $3CH_2$, J = 7.6 Hz), 0.47 (dd, 1H, CH, J = 15.1, 7.6 Hz); ^{13}C NMR δ 202.82, 144.88, 132.78, 129.85, 128.01, 127.87, 67.95, 44.03, 30.62, 10.70, 7.30, 3.71.

3-(Methylphenylamino)-2-((triethylsilyl)methyl)propane (18): ^1H NMR δ 7.21 (m, 2H, aromatic protons), 6.69 (m, 3H, aromatic protons), 3.17 (dd, 1H, CH, J = 6.0 Hz), 2.97 (dd, 1H, CH, J = 8.9, 14.5 Hz), 2.93 (s, 3H, CH_3), 2.04 (m, 1H, CH), 0.93 (d, 3H, CH_3, J = 7.5 Hz), 0.92 (t, 9H, $3CH_3$, J = 7.7 Hz), 0.64 (dd, 1H, CH, J = 3.3, 7.5 Hz), 0.57 (q, 6H, $SiCH_2$, J = 7.5 Hz), 0.35 (dd, 1H, CH, J = 10.5, 14.9 Hz); ^{13}C NMR δ 149.76, 129.01, 115.61, 111.85, 62.91, 39.29, 28.62, 20.80, 16.80, 7.47, 4.05; HRMS calcd for $C_{17}H_{31}SiN$ 277.2281, found 277.2220.

(*Z*)-2-Formyl-3-methyl-3-(phenylamino)-1-(triethylsilyl)-1-butene (21): ^1H NMR δ 9.98 (s, 1H, CHO), 7.09 (m, 2H, aromatic protons), 6.92 (s, 1H, CH), 6.67 (m, 1H, aromatic protons), 6.54 (m, 2H, aromatic protons), 4.05 (s, 1H, NH), 1.56 (s, 6H, $2CH_3$), 0.91 (t, 9H, $3CH_3$), 0.68 (q, 6H, $SiCH_2$); ^{13}C NMR δ 193.46, 160.05, 148.44, 146.14, 128.68, 117.89, 116.13, 57.08, 28.61, 7.49, 5.17; HRMS calcd for $C_{18}H_{29}SiNO$ 303.2018, found 303.2020.

(*Z*)-1-(Dimethylphenylsilyl)-2-formyl-3-methyl-1-pentene (22): ^1H NMR 9.78 (s, 1H, CHO), 7.56 (m, 2H, aromatic protons), 7.34 (m, 3H, aromatic protons), 6.87 (s, 1H, CH), 2.72 (m, 1H, CH), 1.38 (m, 2H, CH_2), 1.02 (d, 3H, CH_3, J = 7.3 Hz), 0.84 (t, 3H, CH_3, J = 7.3 Hz), 0.52 (s, 6H, $SiCH_3$); ^{13}C NMR δ 193.32, 162.09, 146.89, 138.16, 133.51, 129.43, 128.16, 34.86, 28.87, 19.52, 11.75, 0.01; MS (*m/e*) 231 [M^+ − 15]. Anal. Calcd for $C_{15}H_{22}SiO$: C, 73.17; H, 8.9. Found: C, 72.78; H, 8.51.

Silylformylation of 1-hexyne with $HSiMe_2Ph/CO$ catalyzed by **2**, **3**, or **4** in the absence of hydrogen was carried out according to the general procedure, affording (*Z*)-1-(dimethylphenylsilyl)-2-formyl-1-hexene (**6**) in 89, 87, and 92% yields, respectively (see Table 1).

(*Z*)-1-(Dimethylphenylsilyl)-2-formyl-1-hexene (6): ^1H NMR δ 9.75 (s, 1H, CHO), 7.52 (m, 2H, aromatic protons), 7.34 (m, 3H, aromatic protons), 6.91 (s, 1H, CH), 2.26 (t, 2H, CH_2), 1.34 (m, 4H, $2CH_2$), 0.89 (t, 3H, CH_3), 0.51 (s, 6H, $2CH_3$); MS (*m/e*) 246 [M^+].

Silylhydroformylation of phenylacetylene and propargyl alcohol with $HSiEt_3/CO/H_2$ gives rise to (*Z*)-α-formyl-β-triethylsilyl)styrene (**19**)[20] and (*Z*)-2-formyl-1-(triethylsilyl)-1-propen-3-ol (**20**),[16] respectively (see Table 2). Their spectral data have not been described previously.

19: ^1H NMR δ 10.02 (s, 1H, CHO), 7.38 (m, 5H, aromatic protons), 7.12 (s, 1H, CH), 1.05 (t, 9H, $3CH_3$), 0.82 (q, 6H, $3CH_2$); ^{13}C NMR δ 192.20, 155.22, 152.19, 137.33, 128.13, 127.99, 127.93, 7.35, 5.11; MS (*m/e*) 231 [M − 15]$^+$.

20: ^1H NMR δ 9.73 (s, 1H, CHO), 6.98 (t, 1H, CH, J = 1.4 Hz), 4.28 (d, 2H, CH_2, J = 1.4 Hz), 0.95 (t, 9H, CH_3), 0.56 (q, 6H, $SiCH_2$); ^{13}C NMR δ 193.62, 155.01, 146.62, 66.20, 7.31, 5.15; **MS** (*m/e*) 165 [M − 15]$^+$.

Silylhydroformylation of 1-Hexyne with $DSiMe_2Ph$. A mixture of 1-hexyne (328 mg, 4 mmol), $DSiMe_2Ph$ (685 mg, 5.0 mmol), and the Rh(I) complex **2** (24 mg, 0.04 mmol) in 10 mL of CH_2Cl_2 was placed in an autoclave under CO/H_2 (1:1, 40 atm). The mixture was magnetically stirred at 40 °C for 24 h. The partially deuterated silylalkene **5-D** was isolated in 53% yield by column chromatography on silica gel using 95:5 hexane–ethyl acetate as eluant.

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