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Co$_2$(CO)$_8$-Catalyzed reaction of aromatic aldehydes with hydrosilanes under carbon monoxide as 1 atm: Incorporation of CO into the carbonyl carbon atom of aldehydes ☆

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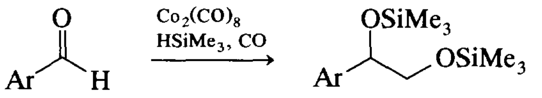
Abstract

Co$_2$(CO)$_8$-catalyzed reaction of aromatic aldehydes with hydrosilanes under CO as 1 atm results in incorporation of CO into the carbonyl carbon atom of aldehydes to give arylethane-1,2-diol disilyl ethers as the main product. The reaction of aliphatic aldehydes gives similar products, only with low yields.

Keywords: Cobalt; Silicon; Hydrosilane; Aldehyde; Carbon monoxide; Oxymethylation

1. Introduction

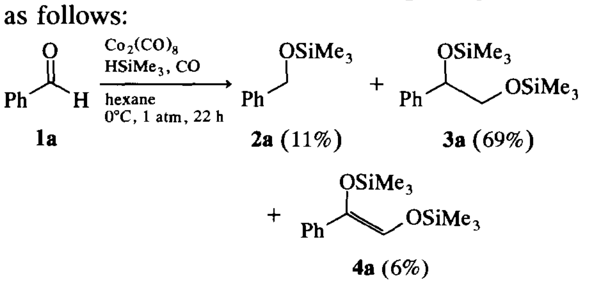
In a series of our studies on the Co$_2$(CO)$_8$-catalyzed reaction of oxygen-containing compounds with hydrosilanes and carbon monoxide at ambient reaction temperature under CO as 1 atm, new methods for the introduction of a siloxymethyl group with concomitant cleavage of a carbon–oxygen bond in various substrates such as cyclic ethers [1], sugars [2], benzylic esters [3] and cyclic ortho esters [4] have been reported. It is interesting to note that there is no report, to the best of our knowledge, describing the catalytic incorporation of CO into carbonyl compounds at ambient temperature and under CO as 1 atm [5,6], although many examples of carbonylation of various compounds under CO as 1 atm have been reported [7]. The carbonylation of a carbonyl carbon atom is not an easy task since generally a transition metal will bind preferably to the oxygen atom of carbonyl group rather than carbon atom, and this will lead to *O*-carbonylation rather than the desirable *C*-carbonylation of carbonyl group [8]. We now report that Co$_2$(CO)$_8$ can catalyze the reaction of aromatic aldehydes with hydrosilanes under CO as 1 atm with CO incorporation. The new catalytic reaction gives arylethane-1,2-diol disilyl ethers as the main product with good yields:



(1)

2. Results and discussion

The reaction of benzaldehyde (**1a**) with HSiMe$_3$ (five equivalents) in the presence of Co$_2$(CO)$_8$ (4 mol.%) is as follows:



(2)

Three kinds of product were obtained: benzyl trimethylsilyl ether (**2a**), phenylethane-1,2-diol bis(trimethylsilyl) ether (**3a**) and phenylethene-1,2-diol bis(trimethylsilyl) ether (**4a**). One molecule of CO and two molecules of HSiMe$_3$ were incorporated to give the

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☆ Dedicated to Professor Hideki Sakurai on his retirement from Tohoku University and in honor of his contribution to organometallic chemistry.

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Table 1
$Co_2(CO)_8$-catalyzed reaction of benzaldehyde with $HSiMe_3$ and CO [a]

Run	Solvent	Temperature (°C)	Time (h)	Yield [b] (%)		
				2a	3a	4a
1	Hexane	0	22	11	69	6
2		15	9	18	60	15
3	Benzene	0	37	17	50	7
4		15	10	23	47	19
5	CH_2Cl_2	0	72	4	0	0
6		15	16	40	39	16

[a] Reaction conditions: benzaldehyde, 2.5 mmol, 265 mg; $HSiMe_3$, 12.5 mmol, 1.5 ml; $Co_2(CO)_8$, 0.1 mmol, 34 mg; solvent, 5 ml.
[b] Gas-liquid chromatography (GLC) yields.

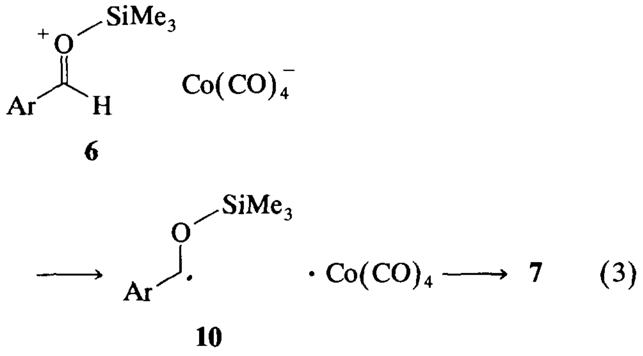
main product **3a** with a new carbon–carbon bond formation between the carbonyl carbon atom of **1a** and the carbon atom of CO. This reaction represents the first example, to our knowledge, of the carbonylation of carbonyl carbon atom using CO as 1 atm. The benzyl ether **2a** is a hydrosilylation product which is also obtainable by the catalytic reaction in the absence of CO. The formation of **4a** will be described later.

The results of changing the reaction conditions such as reaction temperatures and solvents are given in Table 1. Raising the temperature of the reaction in hexane resulted in a faster reaction rate and a poor product selectivity (run 2). The yields of both byproducts **2a** and **4a** were increased. A similar tendency was also observed in the reaction in benzene (runs 3 and 4). It was interesting to note that the reaction in CH_2Cl_2, a polar solvent, became very slow and the main course of the reaction was simple hydrosilylation, leading to **2a** (runs 5 and 6).

The results of the reaction of various aromatic aldehydes in benzene are summarized in Table 2. No distinct substitution effect both on product distribution and on reaction time was observed. *o*-Substituted benzaldehydes reacted slightly more rapidly than *p*-substituted benzaldehydes, do. The reason for these differences is not clear at the present time.

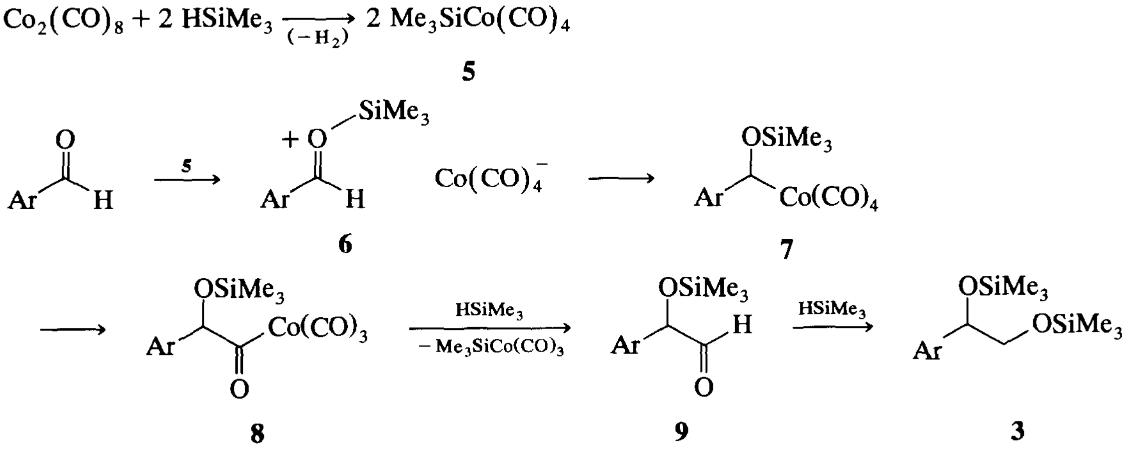
The proposed mechanism is shown in Scheme 1. The important catalytic species would be $Me_3SiCo(CO)_4$ (**5**) which is known to be formed by the reaction of $Co_2(CO)_8$ with $HSiMe_3$ [9]. The interaction of **5** with an aldehyde gives a silyloxonium ion intermediate **6**, to which the attack of $Co(CO)_4^-$ gives an α-siloxyalkylcobalt complex **7** [10]. Migratory insertion of CO into the carbon–cobalt bond in the alkylcobalt complex **7** gives an acylcobalt complex **8** [11]. Oxidative addition of $HSiMe_3$ to **8** followed by reductive elimination affords an aldehyde **9** [12], which is hydrosilylated to give the main product **3**. $Me_3SiCo(CO)_3$ reacts with CO to regenerate **5**. Byproduct **4** would be obtained by dehydrogenative silylation of **9** [13].

There are many alternative possibilities for the mechanism. The silyloxonium ion **6** could undergo a one-electron transfer process to give a free-radical pair **10** first and then couple to **7** [14]:



(3)

Oxidative addition of a hydrosilane to **8** followed by a 1,3-silicon shift would give a cobalt–carbene complex



Scheme 1.

Table 2
Cobalt-catalyzed reaction of arylaldehydes with $HSiMe_3$ and CO [a]

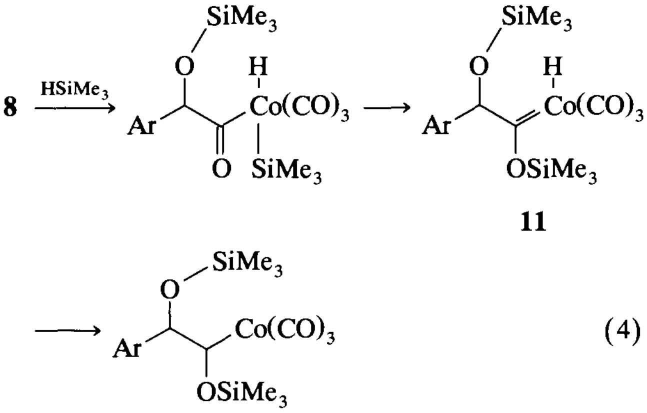
Substrate	Time (h)	Yield [b] (%)		
		2	3	4
C_6H_5CHO (**1a**)	37	17	50	7
p-$MeOC_6H_4CHO$ (**1b**)	48 [c]	20	0	0
p-ClC_6H_4CHO (**1c**)	35	17	55	8
p-FC_6H_4CHO (**1d**)	34	7	66	9
o-$MeOC_6H_4CHO$ (**1e**)	26	39	62	2
o-ClC_6H_4CHO (**1f**)	9	21	59	3
o-MeC_6H_4CHO (**1g**)	27	20	63	4

[a] Reaction conditions: arylaldehyde, 2.5 mmol; $HSiMe_3$, 12.5 mmol, 1.5 ml; $Co_2(CO)_8$, 0.1 mmol, 34 mg; C_6H_6, 5 ml; 0°C.

[b] GLC yields.

[c] Incomplete reaction. When the reaction was run at 15°C, **2b** (41% yield), **3b** (28%) and **4c** (6%) were obtained after 39 h.

11, which then give an alkylcobalt **12** by a 1,2-hydrogen shift:



11

12

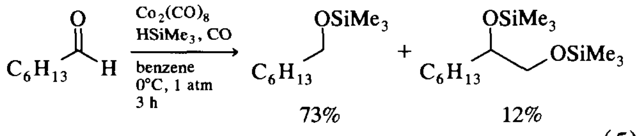
(4)

Further oxidative addition of a hydrosilane to **12** followed by reductive elimination should give the product **3**. The β-hydride elimination from **12** would account for the formation of the byproduct **4**.

The catalytic reaction was faster in hexane or in benzene than in dichloromethane. The faster rate in a non-polar solvent implies that the charge decreases in the transition state. This may suggest that the reaction of **6** with $Co(CO)_4^-$ giving directly **7** (Scheme 1) or alternatively a one-electron transfer process affording a benzylic free radical **10** (Eq. (3)) is the rate-determining step of the catalytic reaction.

The proper explanation of the product distributions is not possible at present since the mechanism of the hydrosilylation leading to **2** is not known. The two important possibilities for the process to **2** are (1) direct hydrogen atom transfer to the silyloxonium ion from $HSiMe_3$ [15] and (2) reaction of **7**, after loss of CO, with $HSiMe_3$ followed by reductive elimination. These processes may compete with various steps in Scheme 1 and/or in Eqs. (3) and (4) so that the product distributions in Tables 1 and 2 are not straightforward to rationalize.

In contrast with aromatic aldehydes, aliphatic aldehydes reacted with $HSiMe_3$ under CO as 1 atm gave only a small amount of CO-incorporated product. For example, the reaction of heptanal, using the same molar ratio of reactants as in Table 1, afforded heptanol trimethylsilyl ether as the major product:



(5)

In conclusion, the present reaction provides the first example of CO incorporation into the aldehyde carbonyl carbon atom under CO as 1 atm at ambient temperature. The results suggest new possibilities of designing or exploiting a new catalytic carbonylation reaction.

3. Experimental section

3.1. General comments

Bulb-to-bulb distillations were done on a Sibata glass tube oven GTO-250R; boiling points refer to air bath temperature and are uncorrected. ^1H NMR and ^{13}C NMR were recorded on a JEOL JMN-270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift δ, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet; c, complex), coupling constant, integration and interpretation. IR spectra were obtained on a Hitachi IR-270-50 spectrometer; absorptions are reported in reciprocal centimeters. Mass spectra were obtained on a Shimadzu GCMS-QP 1000 with an ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analyses Section of Osaka University. Analytical GLC was carried out on a Shimazu GC-14A gas chromatograph, equipped with a flame ionization detector. Preparative GLC was carried out on a Hitachi 164 gas chromatograph.

3.2. General procedure for the $Co_2(CO)_8$-catalyzed reaction of aldehydes with $HSiMe_3$ and CO

In a 10 ml reaction flask with an efficient condenser (dry-ice–CH_3OH) was placed $Co_2(CO)_8$ (0.1 mmol, 34 mg), after the flask was flashed with CO (1 atm from a stock balloon); $HSiMe_3$ (12.5 mmol, 1.5 ml) was added via a pressure syringe [16] at 25°C. After 5 min, solvent (5 ml), arylaldehyde (**1**) (2.5 mmol) and appropriate hydrocarbons (C_nH_{2n+2}) calibrated against purified products for GLC yields were added and the mixture was stirred at 0°C under CO (1 atm). Solvent was evaporated in vacuo and Kugelrohr distillation followed by preparative gas chromatography (Silicone OV-1) gave pure **3**.

*3.3. Phenylethanediol bis(trimethylsilyl) ether (**3a**)*

^{1}H NMR ($CDCl_3$): δ – 0.02 (s, 9H, Me_3Si), 0.01 (s, 9H, Me_3Si), 3.52 (dd, J = 10.3 and 5.1 Hz, 1H, CH_2O), 3.56 (dd, J = 10.3 and 6.8 Hz, 1H, CH_2O), 4.63 (dd, J = 6.8 and 5.1 Hz, 1 H, CHO), 7.15–7.29 (m, 5H, Ph) ppm. IR (neat): ν 3036w, 2964m, 2916w, 1498w, 1456w, 1252s, 1200w, 1150s, 1098m, 1028w, 968m, 842s, 752m, 698m cm^{-1}. Mass spectroscopy (MS): m/z (relative intensity) 282 (M^+, 0), 179 (M^+ – CH_2OSiMe_3, 100), 147 (23), 73 (100). Anal. Found: C, 59.63; H, 9.43. $C_{14}H_{26}O_2Si_2$ Calc.: C, 59.52; H, 9.28%.

*3.4. 4-(Methoxyphenyl)ethanediol bis(trimethylsilyl) ether (**3b**)*

^{1}H NMR ($CDCl_3$): δ 0.06 (s, 9H, Me_3Si), 0.07 (s, 9H, Me_3Si), 3.54 (dd, J = 10.5 and 4.8 Hz, 1H, CH_2O), 3.60 (dd, J = 10.5 and 7.1 Hz, 1H, CH_2O), 3.80 (s, 3H, CH_3O), 4.65 (dd, J = 7.1 and 5.3 Hz, 1H, CHO), 6.84 (d, J = 6.7 Hz, 2H, Ar), 7.25 (d, J = 6.7 Hz, 2H, Ar) ppm. ^{13}C NMR ($CDCl_3$). δ – 0.50 (Me_3Si), 0.17 (Me_3Si), 55.20 (CH_3O), 69.09 (CH_2OSi), 75.30 (CHOSi), 113.38, 127.42, 134.45, 158.85 (Ar) ppm. IR (neat): ν 2960m, 2912m, 2866w, 1616m, 1588w, 1516s, 1467w, 1367w, 1301w, 1249s, 1199m, 1171s, 1128m, 1091s, 1067m, 1038m, 969m, 889m, 841s, 749m, 686w cm.$^{-1}$ MS: m/z (relative intensity) 312 (M^+, 0), 297 (M^+ – Me, 1), 210 (18), 209 (M^+ – CH_2OSiMe_3, 100), 147 (21), 73 (60). Anal. Found: C, 57.29; H, 9.19. $C_{15}H_{28}O_3Si_2$ Calc.: C, 57.64; H, 9.03%.

*3.5. 4-(Chlorophenyl)ethanediol bis(trimethylsilyl) ether (**3c**)*

^{1}H NMR ($CDCl_3$): δ 0.03 (s, 9H, Me_3Si), 0.05 (s, 9H, Me_3Si), 3.50 (dd, J = 10.5 and 5.1 Hz, 1H, CH_2O), 3.58 (dd, J = 10.5 and 7.0 Hz, 1H, CH_2O), 4.64 (dd, J = 7.0 and 5.1 Hz, 1H, CHO), 7.24–7.29 (m, 4H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ –0.55 (Me_3Si), 0.11 (Me_3Si), 68.83 (CH_2OSi), 75.00 (CHOSi), 127.73, 128.13, 132.94, 140.93 (Ar) ppm. IR (neat): ν 2968m, 1496m, 1252s, 1132s, 1092s, 1016w, 968m, 844s, 756w, 688w cm^{-1}. MS: m/z (relative intensity) 316 (M^+ for ^{35}Cl, 0), 215 (26), 214 (12), 213 (M^+ – CH_2OSiMe_3, 71), 147 (33), 75 (10), 73 (100). Anal. Found: C, 53.08; H, 8.05. $C_{14}H_{25}ClO_2Si_2$ Calc.: C, 53.05; H, 7.95%.

*3.6. 4-(Fluorophenyl)ethanediol bis(trimethylsilyl) ether (**3d**)*

^{1}H NMR ($CDCl_3$): δ 0.04 (s, 9H, Me_3Si), 0.07 (s, 9H, Me_3Si), 3.52 (dd, J = 10.5 and 5.1 Hz, 1H, CH_2O), 3.60 (dd, J = 10.5 and 7.0 Hz, 1H, CH_2O), 4.67 (dd, J = 7.0 and 5.1 Hz, 1H, CHO), 6.96–7.03 (m, 2H, Ar), 7.26–7.32 (m, 2H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ – 0.56 (Me_3Si), 0.11 (Me_3Si), 68.92 (CH_2OSi), 74.98 (CHOSi), 114.77 (J_{C-F} = 11 Hz), 127.87 (J_{C-F} = 7 Hz), 138.10 (J_{C-F} = 3 Hz), 163.61 (J_{C-F} = 245 Hz) ppm. IR (neat): ν 2964m, 2868m, 1610m, 1514m, 1418w, 1368w, 1252s, 1224m, 1198m, 1130m, 1016w, 968m, 842s, 750m, 690w ppm. MS: m/z (relative intensity) 300 (M^+ for ^{19}F, 0), 198 (15), 197 (M^+ – CH_2OSiMe_3, 92), 147 (31), 73 (100). Anal. Found: C, 55.47; H, 8.30. $C_{14}H_{25}FO_2Si_2$ Calc.: C, 55.95; H, 8.39%.

*3.7. 2-(Methoxyphenyl)ethanediol bis(trimethylsilyl) ether (**3e**)*

^{1}H NMR ($CDCl_3$): δ 0.09 (s, 9H, Me_3Si), 0.11 (s, 9H, Me_3Si), 3.45 (dd, J = 10.3 and 7.8 Hz, 1H, CH_2O), 3.70 (dd, J = 10.3 and 3.0 Hz, 1H, CH_2O), 3.83 (s, 3H, CH_3O), 5.13 (dd, J = 7.8 and 3.0 Hz, 1H, CHO), 6.83 (d, J = 8.3 Hz, 1H, Ar), 6.96 (t, J = 8.3 Hz, 1H, Ar), 7.23 (td, J = 8.3 and 2.0 Hz, 1H, Ar), 7.49 (dd, J = 2.0 and 8.3 Hz, 1H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ –0.41 (Me_3Si), 0.16 (Me_3Si), 55.14 (CH_3O), 67.80 (CH_2OSi), 70.29 (CHOSi), 109.78, 120.44, 127.38, 128.02, 130.28, 155.80 (Ar) ppm. IR (neat): ν 2962m, 2842w, 1604m, 1592m, 1494s, 1469m, 1442m, 1369m, 1280m, 1249s, 1191m, 1173m, 1131s, 1085s, 1030m, 969s, 889s, 841s, 754s, 687w cm^{-1}. MS: m/z (relative intensity) 312 (M^+, 0), 210 (19), 209 (M^+ – CH_2OSiMe_3, 100), 147 (17), 73 (70).

*3.8. 2-(Chlorophenyl)ethanediol bis(trimethylsilyl) ether (**3f**)*

^{1}H NMR ($CDCl_3$): δ 0.09 (s, 18H, Me_3Si), 3.50 (dd, J = 10.8 and 7.3 Hz, 1H, CH_2O), 3.70 (dd, J = 10.8 and 3.5 Hz, 1H, CH_2O), 5.14 (dd, J = 7.3 and 3.5 Hz, 1H, CHO), 7.15–7.31 (m, 3H, Ar), 7.57 (dd, J = 7.8 and 1.9 Hz, 1H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ –0.45 (Me_3Si), 0.07 (Me_3Si), 67.40 (CH_2OSi), 72.43 (CHOSi), 126.72, 128.39, 128.52, 128.94, 131.73, 139.56 (Ar) ppm. IR (neat): ν 3072m, 2964s, 1628w, 1600w, 1578w, 1476m, 1444m, 1410w, 1382w, 1252s, 1198m, 1128s, 1098s, 1072s, 1048m, 1036m, 968s, 888s, 842s, 754s, 696m cm^{-1}. MS: m/z (relative intensity) 316 (M^+ for ^{35}Cl, 0), 215 (35), 214 (15), 213 (M^+ – CH_2OSiMe_3, 93), 147 (44), 73 (100). Anal. Found: C, 52.75; H, 8.06, Cl, 11.43. $C_{14}H_{25}ClO_2Si_2$ Calc.: C, 53.05; H, 7.95, Cl, 11.19%.

*3.9. 2-(Methylphenyl)ethanediol bis(trimethylsilyl) ether (**3g**)*

^{1}H NMR ($CDCl_3$): δ 0.06 (s, 18H, Me_3Si), 2.34 (s, 3H, CH_3), 3.53 (dd, J = 10.0 and 4.9 Hz, 1H, CH_2O), 3.58 (dd, $J = 10.0$ and 6.8 Hz, 1H, CH_2O), 4.93 (dd, $J = 6.8$ and 4.9 Hz, 1 H, CHO), 7.08–7.19 (m, 3H, Ar), 7.46–7.49 (m, 1H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ -0.50 (Me_3Si), 0.14 (Me_3Si), 19.24 (CH_3), 68.25 (CH_2OSi), 72.54 (CHOSi), 125.88, 126.63, 127.01, 129.87, 140.40 (Ar) ppm. IR (neat): ν 3032w, 2964m, 2868w, 1492w, 1464w, 1378w, 1252s, 1216w, 1180w, 1130s, 1086s, 1062m, 968m, 842s, 754m, 724w, 688w cm^{-1}. MS: m/z (relative intensity) 296 (M^+, 0), 194 (17), 193 ($M^+ - CH_2OSiMe_3$, 100), 147 (25), 75 (10), 73 (84). Anal. Found: C, 60.74; H, 9.53. $C_{15}H_{28}O_3Si_2$ Calc.: C, 60.75; H, 9.52%.

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[14] We found that the reaction of benzaldehyde (10 mmol) with $HSiEt_2Me$ (30 mmol) and CO (50 atm) in the presence of $Co_2(CO)_8$ (0.2 mmol) and PPh_3 (0.2 mmol) at 140°C in C_6H_6 (20 ml) gave **1a** with a 37% yield along with 1,2-diphenylethane-1,2-diol disilyl ether with a 26% yield (dl/*meso*, 1/1). This result implies the intermediacy of a benzyl radical such as **10** in the reaction.

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