ELSEVIER

Journal of Organometallic Chemistry 489 (1995) 215–219

Journal of Organometallic Chemistry

# Ring-opening silylformylation of oxetanes catalyzed by $[RhCl(CO)_2]_2$-amine

Yoshiya Fukumoto, Shinshi Yamaguchi, Naoto Chatani, Shinji Murai *

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*

Received 21 September 1994; in revised form 19 October 1994

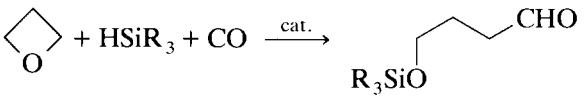
**Abstract**

With $[RhCl(CO)_2]_2$-amine as catalyst, the reaction of oxetanes with a hydrosilane and carbon monoxide results in ring-opening silylformylation to give γ-siloxy aldehydes in 42–83% yields. Addition of amines is essential for the silylformylation to proceed, and 1-methylpyrazole is the most effective additive among the amines examined. The ring-opening of 2-alkyloxetanes occurs predominantly at the primary carbon atom with regioselectivity of 95%.

*Keywords:* Rhodium; Silylformylation; Oxetane; Hydrosilane; Carbon monoxide; Aldehyde

## 1. Introduction

In the study of the transition metal-catalyzed reaction using a hydrosilane and carbon monoxide [1], we reported ring-opening silylformylation [2] of oxiranes leading to β-siloxy aldehydes in the presence of $[RhCl(CO)_2]_2$-amine [3], in which the choice of an additive was crucial. Among additives examined, 1-methylpyrazole was most effective. The ring-opening of oxiranes occurred in a *trans* manner. We had already reported that $Co_2(CO)_8$ also catalyzed ring-opening silylformylation of cyclic ethers [4]. However, the reaction required excess amounts of cyclic ethers (5 equivalents to a hydrosilane) to prevent the product aldehydes from undergoing further reactions such as silylformylation [2d,5], hydrosilylation [6], and dehydrogenative silylation [7]. In contrast, the silylformylation of oxiranes by the use of rhodium–amine catalyst can be accomplished without using the excess amounts of oxiranes. We report herein that the $[RhCl(CO)_2]_2$-amine catalyst also enabled ring-opening silylformylation of oxetanes leading to γ-siloxy aldehydes (Eq. (1)).




(1)

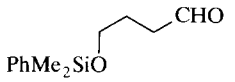
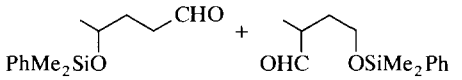
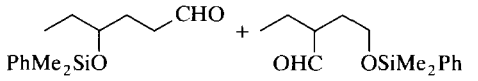
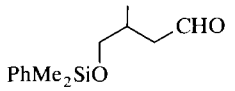
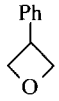
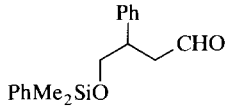
## 2. Results and discussion

The results are summarized in Table 1. To begin with, the reaction of oxetane (**1**) under the same reaction conditions as in the reaction of oxiranes was examined. Thus, the reaction of **1** (2.5 mmol) with dimethylphenylsilane (3 mmol) and carbon monoxide (50 atm, initial pressure at room temperature) in the presence of $[RhCl(CO)_2]_2$ (0.05 mmol) and 1-methylpyrazole (1 mmol) in $CH_2Cl_2$ (5 ml) at 50°C for 12 h gave 4-(dimethylphenylsiloxy)butanal (**2**) in 81% yield (run 1). The use of toluene as the solvent afforded **2** in 83% yield (run 2). Although $Et_2O$ gave a comparable yield, $CH_3CN$ and hexane were not suitable solvent for silylformylation of **1** (runs 3–5). Some other amines were moderately effective for the silylformylation of **1** ($Et_3N$: 63%, TMEDA: 10%, DBU: 3%, pyridine: 17%),

* Corresponding author.


*SSDI* 0022-328X(94)05274-3

Table 1
Rh-catalyzed ring-opening silylformylation of oxetanes [a]

| Run | Oxetane | Solvent | Product | Yield (%) [b] |
|---|---|---|---|---|
| 1 |  | $CH_2Cl_2$ |  | 81 |
| 2 | | toluene | | 83 |
| 3 | | $Et_2O$ | | 71 |
| 4 | **1** | $CH_3CN$ | **2** | 17 |
| 5 | | hexane | | 2 |
| 6 |  | toluene |  | 62 (95:5) [c] |
| | **3** | | **4a** **4b** | |
| 7 |  | toluene |  | 64 (95:5) [c] |
| | **5** | | **6a** **6b** | |
| 8 |  | toluene |  | 80 |
| | 7 | | **8** | |
| 9 |  | toluene |  | 42 [d] |
| | **9** | | **10** | |

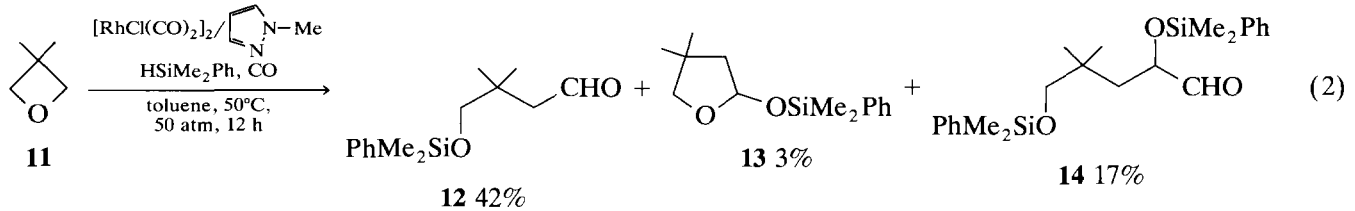
[a] Reaction conditions: oxetane (2.5 mmol), $HSiMe_2Ph$ (3.0 mmol), $[RhCl(CO)_2]_2$ (0.05 mmol), 1-methylpyrazole (1 mmol), CO (50 atm), and solvent (5 ml) at 50°C for 12 h. [b] GLC yields. [c] The ratio of regioisomers was determined by the integration of their formyl proton resonances in $^1H$ NMR. [d] 24 h.

but 1-methylimidazole was not effective as the additive. These results showed that 1-methylpyrazole is additive of choice. When the reactants and the catalyst were mixed without addition of amines, oxetane was immediately and completely consumed in minutes at room temperature even before the reaction vessel was pressurized to 50 atm of carbon monoxide. The products were 1-(dimethylphenylsiloxy)propane (40%) and 3-(dimethylphenylsiloxy)propene (17%). Although the role of 1-methylpyrazole is not clear at the present time, it is likely that the amine has not accelerated the rate of incorporation of carbon monoxide but has suppressed side reactions such as ring-opening hydrosilylation or dehydrogenative silylation of oxetane. Trialkylsilanes such as triethylsilane ($HSiEt_3$) and diethylmethylsilane ($HSiEt_2Me$) and ethoxydimethylsilane ($HSiMe_2(OEt)$) were unreactive in the present silylformylation, the starting oxetane being recovered intact.

High regioselectivity was observed in the reaction of 2-methyloxetane (**3**). The ring-opening of **3** occurred regioselectively at the primary carbon atom to give a 95:5 mixture of 4-(dimethylphenylsiloxy)pentanal (**4a**) and 4-(dimethylphenylsiloxy)-2-methylbutanal (**4b**) (run 6). The reaction of 2-ethyloxetane (**5**) gave the same result (run 7). The regioselectivity of the ring-opening of **3** or **5** is higher than that in the case of 1,2-epoxybutane [3]. The reaction of 3-methyloxetane (**7**) underwent ring-opening silylformylation effectively to give the corresponding γ-siloxy aldehyde **8** in 80% yield (run 8). In the reaction of 3-phenyloxetane (**9**), an aldehyde **10** was formed in 42% yield and 40% of the starting oxetane **9** was remained even after 24 h (run 9).

The reaction of 3,3-dimethyloxetane (**11**) afforded three products, 4-(dimethylphenylsiloxy)-3,3-dimethylbutanal (**12**), 2-(dimethylphenylsiloxy)-4,4-dimethyloxolane (**13**), and 2,5-bis(dimethylphenylsiloxy)-4,4-dimethylpentanal (**14**) which is the product of further silylformylation of **12** [2d,4,9] (Eq. (2)). No reaction took place when tetrahydrofuran was treated under the present reaction conditions.

In summary, ring-opening silylformylation of oxe-




**11** **12** 42% **13** 3% **14** 17% (2)

tanes leading to γ-siloxy aldehydes can be achieved in the presence of $[RhCl(CO)_2]_2$-amine. Only a few examples of incorporation of carbon monoxide into oxetanes have been reported [4,10], which contrasts with the well-known carbonylation of oxiranes [11]. The use of 1-methylpyrazole as an additive is effective for ring-opening silylformylation of oxetanes. 1-Methylpyrazole seems to play a role in suppressing side reactions rather than accelerating insertion of carbon monoxide.

## 3. Experimental details

### 3.1. General comments

Boiling points were uncorrected. $^1H$ NMR and $^{13}C$ NMR were recorded on a JEOL JNM-EX270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are recorded as follows: chemical shift in ppm (δ), mutiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a HITACHI 270-50 spectrometer; absorptions are reported in reciprocal centimeters ($cm^{-1}$). Mass spectra (MS) were obtained on a Shimadzu GCMS-QP 1000 with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were performed by Elemental Analyses Section of Osaka University. Analytical GLC was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Medium-pressure liquid chromatography (MPLC) was performed using 30-mm × 300-mm silica gel column (Yamazen YFLC Gel 7024) with a YAMAZEN FFLC-540 pumping system. Oxetane (**1**) and 3,3-dimethyloxetane (**11**) were purchased from Aldrich Chemical Co. and 1-methylpyrazole from Tokyo Kasei Kogyo Co. 2-Methyloxetane (**3**) [12], 2-ethyloxetane (**5**) [13], 3-methyloxetane (**7**) [14], and 3-phenyloxetane (**9**) [15] were prepared according to described methods.

### 3.2. General procedure for the rhodium-catalyzed ring-opening silylformylation of oxetanes

In a carbon monoxide purged glass vessel containing $[RhCl(CO)_2]_2$ (19.5 mg, 0.05 mmol) were placed $HSiMe_2Ph$ (0.46 ml, 3 mmol), 1-methylpyrazole (85 μL, 1 mmol), oxetane (2.5 mmol), and toluene (5 ml) in this order and the glass vessel was placed in a 50 ml stainless steel autoclave. The autoclave was charged with carbon monoxide to 50 atm at 25°C and then heated in an oil bath at 50°C for 12 h. The solvent was removed under reduced pressure. Column chromatography on Florisil (100–200 mesh) of the residue (hexane : AcOEt = 20 : 1) gave a crude product aldehyde, which was purified by MPLC (hexane : AcOEt = 50 : 1) to obtain an analytical pure sample. For GLC yield, an appropriate hydrocarbon ($C_{15}H_{32}$ or $C_{16}H_{34}$) calibrated against purified products were added before the catalytic reaction. The ratio of the regioisomers was determined by the integration of their formyl proton resonances for $^1H$ NMR spectra of the reaction mixture.

### 3.3. 4-(Dimethylphenylsiloxy)butanal (2)

$^1H$ NMR ($CDCl_3$): δ 0.38 (s, 6H, $SiCH_3$), 1.86 (quint, $J$ = 6.5 Hz, 2H, $CH_2$), 2.48 (dt, $J$ = 1.6, 6.5 Hz, 2H, $CH_2CHO$), 3.63 (t, $J$ = 6.5 Hz, 2H, $CH_2OSi$), 7.38–7.58 (m, 5H, Ph), 9.75 (t, $J$ = 1.6 Hz, 1H, CHO). $^{13}C$ NMR ($CDCl_3$): δ −2.01 ($SiCH_3$), 25.16 ($CH_2$), 40.61 ($CH_2CHO$), 61.87 ($CH_2OSi$), 127.87, 129.67, 133.39, 137.56 (Ph), 202.37 (CHO). IR (neat) 3142w, 3066w, 3008w, 2952m, 2904m, 2818m, 2730w, 1722s, 1604w, 1478w, 1429m, 1411m, 1391m, 1250s, 1180w, 1110s, 1087s, 1013m, 944m, 832s, 783s, 737s, 697m, 632w $cm^{-1}$. MS (70 eV): $m/z$ (relative intensity, %) 221 (1, $M^+$–H), 207 (14, $M^+$–$CH_3$), 145 (38), 138 (13), 137 (100), 135 (31), 131 (23), 129 (20), 121 (11), 105 (12), 99 (19), 91 (20), 77 (32), 75 (21), 61 (12). HRMS Calc. for $C_{12}H_{18}O_2Si$ ($M^+$): 222.1076, Found: 222.1059.

### 3.4. 4-(Dimethylphenylsiloxy)pentanal (4a)

The reaction mixture consisted of two regioisomers, **4a** and **4b** (95 : 5), the ratio of which was determined by the integration of their formyl proton resonances in the $^1H$ NMR spectrum of the reaction mixture (δ 9.68 **4a**, 9.62 **4b**). Purification by MPLC gave pure **4a** as a colorless oil. $^1H$ NMR ($CDCl_3$): δ 0.38 (s, 6H, $SiCH_3$), 1.12 (d, $J$ = 5.9 Hz, 3H, $CH_3$), 1.74–1.78 (m, 2H, $CH_2$), 2.42 (dt, $J$ = 1.6, 7.3 Hz, 2H, $CH_2CHO$), 3.85 (sext, $J$ = 5.9 Hz, 1H, CHOSi), 7.37–7.59 (m, 5H, Ph), 9.68 (t, $J$ = 1.6 Hz, 1H, CHO). $^{13}C$ NMR ($CDCl_3$): δ −1.31, −1.27 ($SiCH_3$), 23.56 ($CH_3$), 31.52 ($CH_2$), 40.16 ($CH_2CHO$), 67.89 (CHOSi), 127.82, 129.61, 133.46, 137.93 (Ph), 202.60 (CHO). IR (neat): 3072m, 3052m, 2958s, 2868m, 2728m, 2302m, 1726s, 1429m, 1394m, 1249s, 1138s, 1114s, 1036s, 965m, 824s, 781s, 736m, 699m $cm^{-1}$. MS (70 eV): $m/z$ (relative intensity, %) 235 (1, $M^+$–H), 221 (4, $M^+$–$CH_3$), 159 (37), 143 (12), 138 (12), 137 (100), 136 (10), 135 (66), 105 (12), 91 (11), 77 (24), 75 (42). HRMS Calc. for $C_{13}H_{20}O_2Si$ ($M^+$): 236.1233, Found: 236.1218.

### 3.5. 4-(Dimethylphenylsiloxy)hexanal (6a)

The reaction mixture consisted of two regioisomers, **6a** and **6b** (95 : 5), the ratio of which was determined by the integration of their formyl proton resonances in the $^1H$ NMR spectrum of the reaction mixture (δ 9.67 **6a**,

9.61 **6b**). Purification by MPLC gave pure **6a** as a colorless oil. $^1$H NMR ($CDCl_3$): $\delta$ 0.39 (s, 6H, $SiCH_3$), 0.84 (t, $J$ = 7.5 Hz, 3H, $CH_3$), 1.38–1.51 (m, 2H, $CH_2$), 1.61–1.87 (m, 2H, $CH_2$), 2.41 (dt, $J$ = 1.6, 5.4 Hz, 2H, $CH_2CHO$), 3.58–3.71 (m, 1H, $CH_2OSi$), 7.37–7.59 (m, 5H, Ph), 9.67 (t, $J$ = 1.6 Hz, 1H, CHO). $^{13}$C NMR ($CDCl_3$): $\delta$ −1.20 ($SiCH_3$), 9.65 ($CH_3$), 28.47 ($CH_2$), 29.76 ($CH_2$), 39.91 ($CH_2CHO$), 72.96 (CHOSi), 127.82, 129.61, 133.46, 138.04 (Ph), 202.60 (CHO). IR (neat): 3056m, 3018m, 2956s, 2926s, 2878s, 2830m, 2718m, 1725s, 1591w, 1462m, 1429s, 1411m, 1383m, 1251s, 1112s, 1057s, 1010s, 825s, 780s, 736s, 697s, 636w cm$^{-1}$. MS (70 eV): $m/z$ (relative intensity, %) 235 (22, $M^+$–$CH_3$), 173 (28), 137 (75), 136 (16), 135 (100), 105 (11), 91 (11), 77 (19), 75 (48). HRMS Calc. for $C_{14}H_{22}O_2Si$ ($M^+$): 250.1389, Found: 250.1407.

### 3.6. 4-(Dimethylphenylsiloxy)-3-methylbutanal (8)

$^1$H NMR ($CDCl_3$): $\delta$ 0.36 (s, 6H, $SiCH_3$), 0.91 (d, $J$ = 6.5 Hz, 3H, $CH_3$), 2.14–2.36 (c, 2H, CH and $CH_2CHO$), 2.44–2.58 (m, 1H, $CH_2CHO$), 3.34 (dd, $J$ = 7.6, 10.0 Hz, 1H, $CH_2OSi$), 3.53 (dd, $J$ = 4.9, 10.0 Hz, 1H, $CH_2OSi$), 7.28–7.60 (m, 5H, Ph), 9.74 (t, $J$ = 2.2 Hz, 1H, CHO). $^{13}$C NMR ($CDCl_3$): $\delta$ −2.08, −2.05 ($SiCH_3$), 16.59 ($CH_3$), 31.18 (CH), 48.12 ($CH_2CHO$), 67.46 ($CH_2OSi$), 127.84, 129.61, 133.37, 137.52 (Ph), 202.53 (CHO). IR (neat): 3072m, 3020w, 2960s, 2886m, 2720m, 1724s, 1592w, 1459m, 1428m, 1390m, 1251s, 1112s, 1086s, 1040m, 827s, 784s, 738s, 698s, 639w cm$^{-1}$. MS (70 eV): $m/z$ (relative intensity, %) 221 (14, $M^+$–$CH_3$), 159 (40), 145 (17), 143 (13), 138 (13), 137 (100), 136 (10), 135 (70), 121 (16), 113 (14), 105 (15), 91 (19), 77 (26), 75 (41). HRMS Calc. for $C_{13}H_{20}O_2Si$ ($M^+$): 236.1232, Found: 236.1236.

### 3.7. 4-(Dimethylphenylsiloxy)-3-phenylbutanal (10)

$^1$H NMR ($CDCl_3$): $\delta$ 0.31 (s, 6H, $SiCH_3$), 2.68 (ddd, $J$ = 2.2, 7.3, 16.5 Hz, 1H, $CH_2CHO$), 2.93 (ddd, $J$ = 2.2, 7.3, 16.5 Hz, 1H, $CH_2CHO$), 3.34–3.66 (m, 1H, CH), 3.60 (dd, $J$ = 8.4, 10.0 Hz, 1H, $CH_2OSi$), 3.75 (dd, $J$ = 5.1, 10.0 Hz, 1H, $CH_2OSi$), 7.15–7.52 (c, 10H, Ph), 9.72 (t, $J$ = 2.2 Hz, 1H, CHO). $^{13}$C NMR ($CDCl_3$): $\delta$ −2.15 ($SiCH_3$), 42.70 (CH), 46.56 ($CH_2CHO$), 67.28 ($CH_2OSi$), 126.99, 127.76, 127.87, 128.57, 129.70, 133.39, 137.25, 140.77 (Ph), 201.72 (CHO). IR (neat): 3184w, 3030s, 2956m, 2904m, 2864m, 2726m, 1775m, 1725s, 1605m, 1554m, 1495m, 1454m, 1428s, 1416m, 1321m, 1249s, 1112s, 1089s, 957m, 828s, 784s, 762s, 737s, 696s, 640m cm$^{-1}$. MS (70 eV): $m/z$ (relative intensity, %) 298 (1, $M^+$), 283 (1, $M^+$–$CH_3$), 268 (21), 254 (18), 221 (15), 190 (17), 165 (60), 163 (14), 137 (17), 136 (17), 135 (100), 121 (11), 91 (10). HRMS Calc. for $C_{18}H_{22}O_2Si$ ($M^+$): 298.1389, Found: 298.1389.

### 3.8. 4-(Dimethylphenylsiloxy)-3,3-dimethylbutanal (12)

$^1$H NMR ($CDCl_3$): $\delta$ 0.35 (s, 6H, $SiCH_3$), 1.01 (s, 6H, $CH_3$), 2.27 (d, $J$ = 3.0 Hz, 2H, $CH_2CHO$), 3.34 (s, 2H, $CH_2OSi$), 7.37–7.57 (m, 5H, Ph), 9.82 (t, $J$ = 3.0 Hz, 1H, CHO). $^{13}$C NMR ($CDCl_3$): $\delta$ −2.06 ($SiCH_3$), 24.58 ($CH_3$), 36.12 (C), 52.78 ($CH_2CHO$), 71.59 ($CH_2OSi$), 127.85, 129.63, 133.41, 137.61 (Ph), 203.25 (CHO). IR (neat): 3056w, 2952m, 2886m, 1722s, 1475w, 1448w, 1428s, 1398m, 1250s, 1087s, 852s, 828s, 782s, 735m, 697s cm$^{-1}$. MS: $m/z$ (relative intensity, %) 249 (1, $M^+$–H), 235 (16, $M^+$–$CH_3$), 206 (15), 173 (28), 165 (19), 163 (29), 137 (46), 135 (100), 121 (29), 107 (10), 105 (15), 103 (10), 91 (17), 77 (13), 75 (31), 70 (19), 59 (11). HRMS Calc. for $C_{14}H_{22}O_2Si$ ($M^+$): 250.1389, Found: 250.1375.

### 3.9. 2-(Dimethylphenylsiloxy)-4,4-dimethyloxolane (13)

$^1$H NMR ($CDCl_3$): $\delta$ 0.41 (s, 3H, $SiCH_3$), 0.43 (s, 3H, $SiCH_3$), 1.04 (s, 3H, $CH_3$), 1.16 (s, 3H, $CH_3$), 1.69 (dd, $J$ = 3.0, 13.0 Hz, 1H, $CH_2$), 1.89 (dd, $J$ = 5.4, 13.0 Hz, 1H, $CH_2$), 3.47 (d, $J$ = 8.1 Hz, 1H, $CH_2O$), 3.69 (d, $J$ = 8.1 Hz, 1H, $CH_2O$), 5.54 (dd, $J$ = 3.0, 5.4 Hz, 1H, CHOSi), 7.36–7.62 (m, 5H, Ph). $^{13}$C NMR ($CDCl_3$): $\delta$ −1.29, −0.82 ($SiCH_3$), 26.20, 27.82 ($CH_3$), 38.98 (C), 49.97 ($CH_2$), 79.21 ($CH_2O$), 100.25 (CHOSi), 127.75, 129.47, 133,50, 137.99 (Ph). IR (neat): 3052w, 2960s, 2866m, 2698w, 2320w, 1428m, 1367m, 1318m, 1240s, 1152s, 1113s, 1091s, 1017s, 912m, 822s, 783s, 725m, 696m, 632w cm$^{-1}$. MS: $m/z$ (relative intensity, %) 250 (9, $M^+$), 249 (18, $M^+$–H), 236 (11), 235 (57, $M^+$–$CH_3$), 205 (15), 191 (10), 173 (13), 172 (10), 165 (37), 163 (47), 157 (12): 138 (11), 137 (85), 136 (12), 135 (84), 121 (25), 107 (11), 105 (16), 104 (10), 103 (100), 91 (16), 77 (17), 75 (34), 70 (60), 55 (50). HRMS Calc. for $C_{14}H_{22}O_2Si$ ($M^+$): 250.1389, Found: 250.1371.

### 3.10. 2,5-Bis(dimethylphenylsiloxy)-4,4-dimethylpentanal (14)

$^1$H NMR ($CDCl_3$): $\delta$ 0.32 (s, 6H, $SiCH_3$), 0.41 (s, 6H, $SiCH_3$), 0.83 (s, 3H, $CH_3$), 0.86 (s, 3H, $CH_3$), 1.49 (dd, $J$ = 7.6, 14.5 Hz, 1H, $CH_2$), 1.69 (dd, $J$ = 4.6, 14.5 Hz, 1H, $CH_2$), 3.23 (s, 2H, $CH_2OSi$), 4.11 (ddd, $J$ = 1.6, 4.6, 7.6 Hz, 1H, CHOSi), 7.35–7.55 (m, 10H, Ph), 9.42 (d, $J$ = 1.6 Hz, 1H, CHO). $^{13}$C NMR ($CDCl_3$): $\delta$ −1.96, −1.92, −1.31, −1.22 ($SiCH_3$), 24.32, 25.02 ($CH_3$), 35.04 (C), 40.15 ($CH_2$), 71.61 ($CH_2OSi$), 76.52 (CHOSi), 127.76, 127.91, 129.49, 129.90, 133.42, 133.57, 136.80, 138.01 (Ph), 202.62 (CHO). IR (neat): 2954s, 1733s, 1591m, 1474s, 1420m, 1252s, 1085s, 823s, 781s, 727s, 697s, 639m cm$^{-1}$. MS: $m/z$ (relative intensity, %) 399 (3, $M^+$–$CH_3$), 385 (14), 315 (16), 234 (10), 233 (43), 219 (21), 206 (19), 178 (41), 165 (18), 163 (19), 137 (30), 136 (15), 135 (100), 104 (15), 75 (20). HRMS Calc. for $C_{23}H_{34}O_3Si_2$ ($M^+$): 414.2046, Found: 414.2051.

## Acknowledgment

We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for the use of their facilities. This work was supported in part by grants from the Ministry of Education, Science, and Culture, Japan.

## References and notes

[1] For our recent papers of this series, see: (a) N. Chatani, S. Ikeda, K. Ohe and S. Murai, *J. Am. Chem. Soc., 114* (1992) 9710; (b) N. Chatani, Y. Fukumoto, T. Ida and S. Murai, *J. Am. Chem. Soc., 115* (1993) 11615.

[2] Catalytic silylformylation of acetylenes and aldehydes by a hydrosilane and carbon monoxide has been recently reported. (a) I. Matsuda, A. Ogiso, S. Sato and Y. Izumi, *J. Am. Chem. Soc., 111* (1989) 2332; (b) I. Ojima, P. Ingallina, R.J. Donovan and N. Clos, *Organometallics, 10* (1991) 38; (c) M.P. Doyle and M.S. Shanklin, *Organometallics, 12* (1993) 11; (d) M.E. Wright and B.B. Cohren, *J. Am. Chem. Soc., 115* (1993) 2059.

[3] Y. Fukumoto, N. Chatani and S. Murai, *J. Org. Chem., 58* (1993) 4187.

[4] Y. Seki, S. Murai, I. Yamamoto and N. Sonoda, *Angew. Chem., Int. Ed. Engl., 16* (1977) 789.

[5] S. Murai, T. Kato, N. Sonoda, Y. Seki and K. Kawamoto, *Angew. Chem., Int. Ed. Engl., 18* (1979) 393.

[6] I. Ojima, in S. Patai and Z. Rappoport, (eds.), *The Chemistry of Organic Silicon Compounds*, Part 2, Wiley, New York, 1989, p. 1479.

[7] Y. Seki, S. Murai and N. Sonoda, *Angew. Chem., Int. Ed. Engl., 17* (1978) 199.

[8] M.P. García, M.A. Esteruelas, M. Martín and L.A. Oro, *J. Organomet. Chem., 47* (1994) 151.

[9] Gradysz and co-workers reported that oxetanes were transformed to 2-siloxyoxolanes (similar to **13**) and γ-siloxy aldehydes (similar to **12**) on the stoichiometric reaction of oxetanes with $(CO)_5MnSiMe_3$ and $(CO)_5MnH$. See: K.C. Brinkman and J.A. Gladysz, *Organometallics, 3* (1984) 147.

[10] (a) M. Tanaka, M. Koyanagi and T. Kobayashi, *Tetrahedron Lett.*, (1981) 3875; (b) T. Murai, K. Furuta, S. Kato, S. Murai and N. Sonoda, *J. Organomet. Chem., 302* (1986) 249; (c) M.-D. Wang, S. Calet and H. Alper, *J. Org. Chem., 54* (1989) 20; (d) Y. Watanabe, K. Nishiyama, K. Zhang, F. Okuda, T. Kondo and Y. Tsuji, *Bull. Chem. Soc. Jpn., 67* (1994) 879.

[11] I. Tkatchenko, in G. Wilkinson, F.G.A. Stone and E.W. Abel, (eds.), *Comprehensive Organometallic Chemistry*, Vol. 8, Pergamon, Oxford, 1982, p. 101; (b) H.M. Colquhoun, D.J. Thompson and M.V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*, Plenum, New York, 1991.

[12] F. Sondheimer and R.B. Woodward, *J. Am. Chem. Soc., 75* (1953) 5438.

[13] M.J. Clarke and K.A. Holbrook, *J. Chem. Soc., Faraday Trans. 1*, 73 (1977) 890.

[14] S. Searles Jr., K.A. Pollart and E.F. Lutz, *J. Am. Chem. Soc., 79* (1957) 948.

[15] P. Picard, D. Leelercq, J.-P. Bats and J. Moulines, *Synthesis.* (1981) 550.