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Mechanistic studies on the hydrosilylation of an acetylene cobalt complex; trapping an active catalyst $Co_2(CO)_6$ causing olefin-isomerization and *O*-silylation

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This article is dedicated to Professor Yoshito Kishi for his Tetrahedron Prize

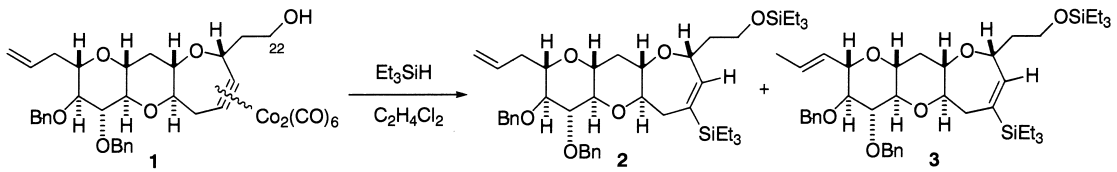
Abstract—We have recently reported a hydrosilylation reaction of acetylene cobalt complexes to produce the corresponding vinylsilanes. It has become clear that olefin-isomerization and *O*-silylation occurred under some hydrosilylation conditions. To avoid these side reactions, we found that hydrosilylation should be carried out in the presence of bis(trimethylsilyl)acetylene. The $Co_2(CO)_6$, which would cause side reactions, migrates to bis(trimethylsilyl)acetylene to form an acetylene cobalt complex. Mechanisms of olefin-isomerization and *O*-silylation are also discussed.

1. Introduction

Biscobalthexacarbonyl complexes of acetylenes are becoming increasingly important in synthetic organic chemistry, not only as protection of intermediate-triple bonds[1] but also as bond formation reactions,[2] and sometimes as a key step in natural product synthesis.[3] We have already reported a reductive decomplexation of these acetylene cobalt complexes with trialkylsilane to produce the corresponding vinylsilanes (hydrosilylation).[4] From our recent research, it became clear that some side reactions, such as olefin-isomerization and *O*-silylation, occurred during this hydrosilylation. In the current paper, we propose several conditions for hydrosilylation in the presence of bis(trimethylsilyl)acetylene to avoid the side reactions. Mechanisms of the side reactions are also discussed.

In our synthetic studies[5] on Ciguatoxin[6] (CTX-1B), the hydrosilylation of acetylene cobalt complex **1** occasionally turned out to be problematic in larger scales;[7] thus, hydrosilylation of **1** was conducted with Et_3SiH by heating at 60°C in 1,2-dichloroethane. This hydrosilylation reaction provided the vinylsilanes regioselectively together with an inseparable mixture of *O*-silylated **2** (50–80%) and *O*-silylated **3** (10–30%), the terminal olefin of the latter being isomerized into an inner olefin, unexpectedly (Scheme 1). The alcohol at C-22 was completely silylated under this condition. If large excess of EtOH was added as a co-solvent, it was possible to prevent the *O*-silylation.[4] We, however, could not control the olefin-isomerization at all. The amounts of the olefin-isomerization were remarkably dependent on the reaction scale; thus, the larger scale, the more side reaction.

It is known that the reaction of R_3SiH with $Co_2(CO)_8$ takes place smoothly even at room temperature to give $HCo(CO)_4$ and $R_3SiCo(CO)_4$ (step *a* in the following equation).[8,9] In the presence of excess amount of R_3SiH, $HCo(CO)_4$ reacts with R_3SiH to give $R_3SiCo(CO)_4$ and molecular hydrogen (step *b*).



Scheme 1.

Keywords: acetylene cobalt complex; hydrosilylation; olefin-isomerization; *O*-silylation; bis(trimethylsilyl)acetylene.

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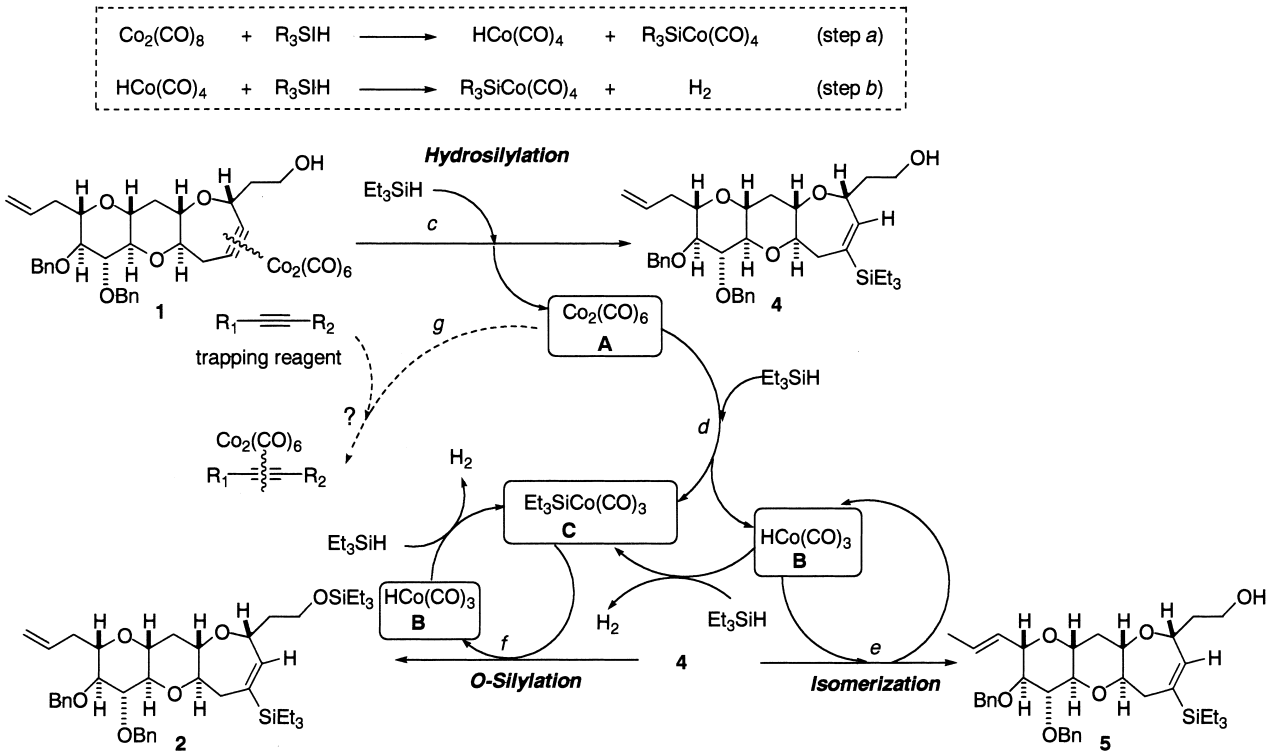
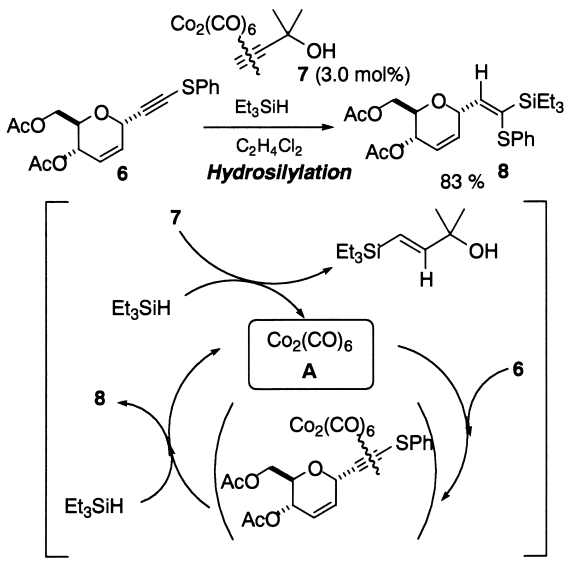


Scheme 2.



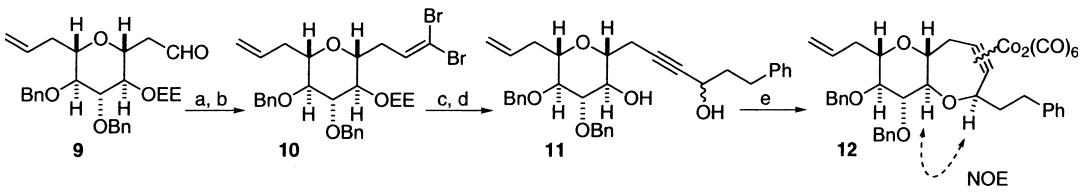
Scheme 3.

Many reactions have been reported to occur under various combinations of $Co_2(CO)_8$ and R_3SiH; for example, hydrosilylation of olefins,[8,10] *O*-silylation,[11] isomerization[8,12] and polymerization.[11,12] In these reactions, $HCo(CO)_4$ and $R_3SiCo(CO)_4$ play important roles.

On the basis of these published reports, we made a working hypothesis of the olefin-isomerization and *O*-silylation during the hydrosilylation as shown in Scheme 2. The hydrosilylation of acetylene cobalt complex **1** generated a desired vinylsilane **4** and $Co_2(CO)_6$ species **A** (step *c* in Scheme 2). This species **A** was assumed to be the active catalyst of the catalytic hydrosilylation reactions[13] (Scheme 3) and to be identical with the active species of catalytic Pauson–Khand reactions.[14] This **A** reacted with Et_3SiH to give $HCo(CO)_3$ **B** and $Et_3SiCo(CO)_3$ **C** (step d in Scheme 2). It is likely that the olefin-isomerization should occur by **B** (step *e*, insertion and β-elimination) and the O-silylation by **C** (step *f*). It would be possible to diminish the side reactions (*O*-silylation and olefin-isomerization) by trapping the $Co_2(CO)_6$ **A** with additives (step *g*).

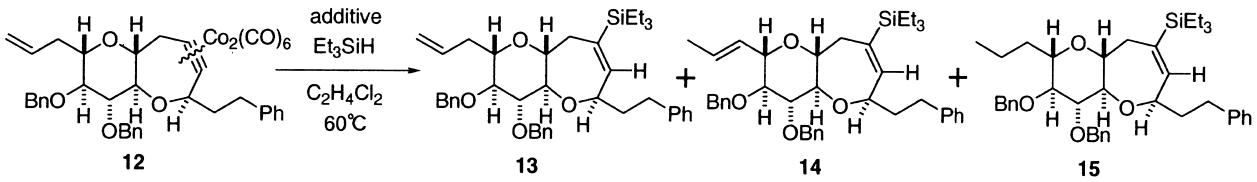
2. Results and discussion

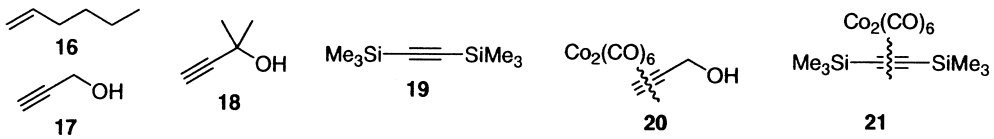
We became interested in finding some trapping reagents of the $Co_2(CO)_6$ **A** to avoid these side reactions with a simpler model compound **12**, which possessed the same *endo*-cobalt



Scheme 4. (a) CBr_4, PPh_3/CH_2Cl_2; (b) EVE, PPTS/CH_2Cl_2, 82% in 2 steps; (c) **10**, *n* BuLi/THF then hydrocinnamaldehyde; (d) Amberlyst-15E/MeOH, 76% in 2 steps; (e) $Co_2(CO)_8/CH_2Cl_2$ then $BF_3{\cdot}OEt_2$ 94%. EVE=ethyl vinyl ether, PPTS=pyridinium *p*-toluenesulfonate.

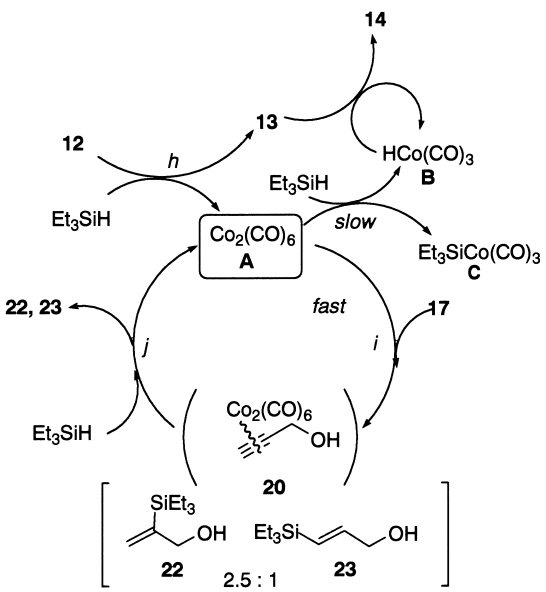
Table 1.





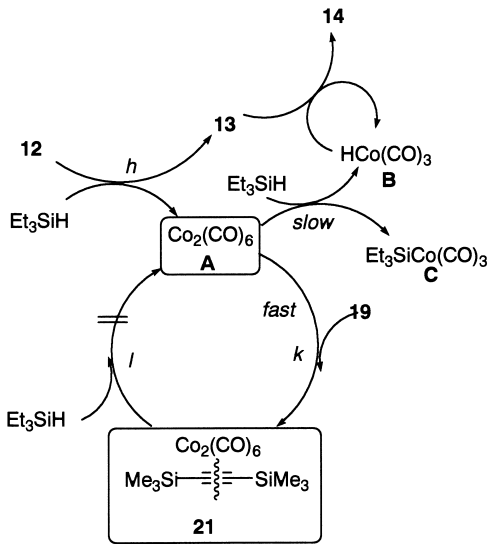
Entry	Et_3SiH	Additive	Time (h)	Yield (%)			
				12 (recovery)	**13**	**14**	**15**
1	5 equiv.	None	2	–	77	19	–
2	5 equiv.	None	24	–	–	–	80
3	1.3 equiv.	None	24	18	18	53	–
4	5 equiv.	**16** (50 equiv.)	2	–	90	9	–
5	4 equiv.	**17** (6 equiv.)	1.5	–	86	–	–
6	3 equiv.	**17** (6 equiv.)	24	–	92	–	–
7	2 equiv.	**17** (4 equiv.)	2.5	28	64	–	–
8	6 equiv.	**17** (3 equiv.)	2	16	16	64	–
9	2 equiv.	**18** (4 equiv.)	2	26	64	–	–
10	4 equiv.	**18** (6 equiv.)	2.5	–	94	–	–
11	5 equiv.	**19** (2 equiv.)	1.5	–	90	–	–
12	5 equiv.	**19** (2 equiv.)	24	–	95	–	–
13	2 equiv.	**19** (1.1 equiv.)	2	–	96	–	–

complex and terminal olefin. This model **12** was synthesized as summarized in Scheme 4. The aldehyde **9**[7] was converted into dibromoolefin **10**.[15] Treatment of the dibromoolefin **10** with 2.2 equiv. of *n*-BuLi generated the corresponding acetylide, which was mixed with hydrocinnamaldehyde to give the coupling product. After deprotection of the hydroxyl group, it was successively treated with $Co_2(CO)_8$ and then $BF_3{\cdot}OEt_2$ in one-pot to afford the cyclization product **12** as a single stereoisomer having *syn* relationship.[16]



Scheme 5.

With the model compound **12** in hand, hydrosilylation was performed under various conditions to check whether the side reactions took place or not in the presence of additives. The results are summarized in Table 1. When the reaction was run without any additive and interrupted after 2 h, the products were a mixture of the vinylsilane **13** and its isomer **14** (entry 1), while when the reaction was prolonged to 24 h, the product was exclusive to give **15** (entry 2). It was expected that **14** might transform into **15** by the participation of large excess Et_3SiH. In fact, when small excess Et_3SiH (1.3 equiv.) was added to the cobalt complex **12**, **15** was not observed (entry 3). Next, large excess 1-hexene **16** was added as a dummy terminal olefin to prevent the isomerization of **13**, but the olefin-isomerization reaction was only partly diminished (entry 4). These results showed the importance of trapping the active species **A** to prevent the primary product **13** from isomerization. As a candidate to trap **A**, propargyl alcohol **17** was chosen to add to the reaction mixture. This choice turned out to be right; addition of **17** prevented **13** from the isomerization completely, even though the reaction was prolonged to 24 h (entries 5, 6). It is noteworthy that the vinylsilane (**22**, **23**) was derived from the trapping reagent **17** to be isolated (Scheme 5). The formation of these vinylsilanes (**22**, **23**) suggested that reagent **17** could trap the active species **A** (step *i* in Scheme 5), then cobalt complex **20** also hydrosilylated into vinylsilane **22** or **23** (step *j*). Since Et_3SiH was consumed by **20** (step *j*), more than 3 equiv. of Et_3SiH is necessary to complete the reaction (entry 7 in Table 1); thus, the competition between step *h* and step *j*. Apparently, it was necessary to add more excess trapping reagent **17** than Et_3SiH to stop the isomerization and to complete the reaction (entry 8). If the rate of step *j* is much slower than

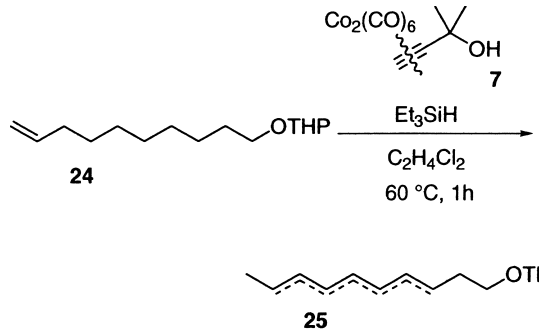


Scheme 6.

step h, it would be possible to complete the reaction with less than 3 equiv. of Et_3SiH. Then sterically hindered 2-methyl-3-butyn-2-ol **18** was selected as a trapping reagent because of its slower reactivity with Et_3SiH. Although **18** was effective to stop the isomerization, it was still necessary to add more than 4 equiv. of Et_3SiH to complete the reaction as the same efficiency as **17** (entries 9, 10). Finally, a much bulky acetylene, bis(trimethylsilyl)acetylene **19** was the best choice as a trapping reagent because of our recent finding that it would be difficult to hydrosilylate the cobalt complex **21** into vinylsilane (Scheme 6, step *l*). The effect of bis(trimethylsilyl)acetylene **19** as trapping reagent was almost perfect as shown in short or long reaction time (entries 11–13). There was no side product under this condition. It is noted that cobalt complex **21**, which came from the trapping reagent **19**, was isolated from the reaction mixture. It means that the $Co_2(CO)_6$ in **12** migrates to **19** to form cobalt complex **21**.[17] This cobalt complex **21** provided strong evidence for the existence of the active species $Co_2(CO)_6$ **A**.

We employed this condition for the synthesis of the desired vinylsilane **4** (Scheme 7). It was clear that the trapping reagent **19** played important roles in stopping the side reactions. No olefin-isomerization and *O*-silylation were observed. In spite of our previous report,[4] EtOH was not necessary as a co-solvent to prevent the alcohol at C-22 from *O*-silylation because of the presence of a trapping reagent. This result indicated that the *O*-silylation also occurred by the participation of $Co_2(CO)_6$ **A**. Until now, this hydrosilylation reaction was performed in a higher scale

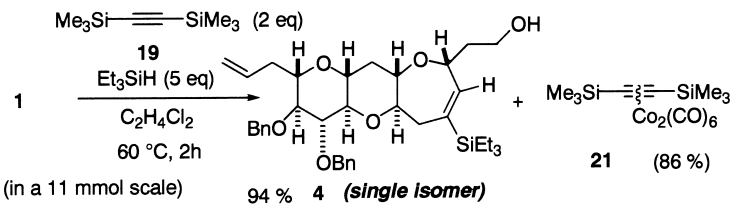
Table 2.



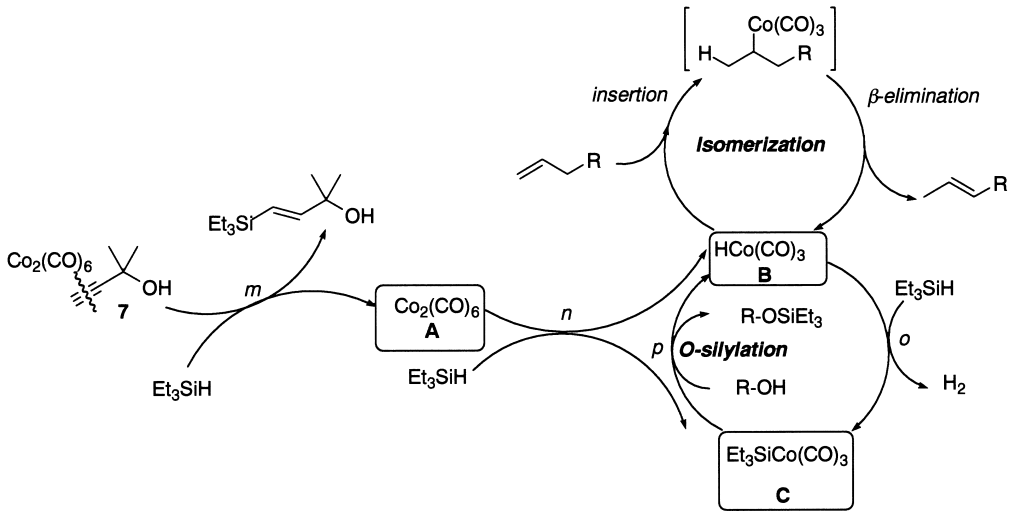
Entry	**7** (equiv.)	Et_3SiH (equiv.)	Additive	**24/25**
1	1	1	–	50:50
2	1	2	–	0:100
3	1	4	–	21:79
4	1	10	–	55:45
5	0.5	1	–	18:82
6	0.5	1	EtOH (5 equiv.)	0:100
7	0.5	1	**19** (2 equiv.)	100:0

than 11 mmol scale under this condition. In this scale, we were successful in getting **4** (94% yield) along with **21** (86% yield of the theoretical value). Since **21** is a nonpolar compound, it is easy to separate **4** from **21** by silica gel column chromatography.

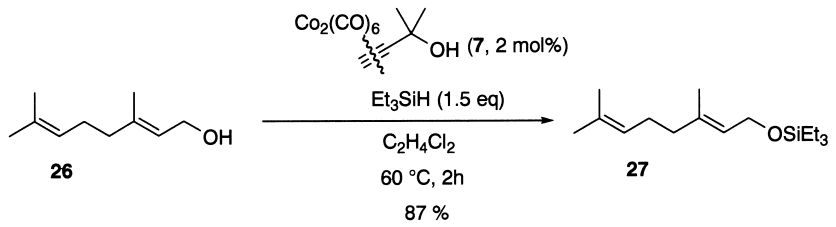
Thus, we could successfully control the side reactions using trapping reagents, and our attention was turned to the mechanisms of these side reactions. To investigate the validity of this olefin-isomerization mechanism (Scheme 2, working hypothesis), subsequent experiments were carried out with a simple terminal olefin **24**. For this propose, acetylene cobalt complex **7**[13,14] was selected as a source of $Co_2(CO)_6$ **A** due to the fact that **7** is easy to prepare and is shelf stockable crystal. The results are summarized in Table 2. Under these conditions, olefin-isomerization went on to give **25** in quantitative yield as a mixture of olefin-regioisomers. At first, an effect of Et_3SiH/**7** ratio was examined (entries 1–4). Taking into account the supposed mechanism of isomerization in Scheme 8, 2 mol of Et_3SiH to 1 mol of **7** would be a best ratio to generate the $HCo(CO)_3$ **B** (steps *m* and *n*) that is supposed to be a real catalyst of olefin-isomerization. Actually, the olefin-isomerization under that condition (Et_3SiH/**7**=2) is faster than other ratio (entry 2). If the ratio Et_3SiH/**7** is more than 2, part of $HCo(CO)_3$ **B** is supposed to transform into $Et_3SiCo(CO)_3$ **C** (step o). Next, EtOH was added to transform $Et_3SiCo(CO)_3$ **C** into $HCo(CO)_3$ **B** (step p, R=Et). As compared with entry 5, adding EtOH surely accelerate the isomerization



Scheme 7.



Scheme 8.



Scheme 9.

(entry 6). It should be noted that these isomerization did not occur at all if bis(trimethylsilyl)acetylene **19** was added (entry 7). These results would support the working hypothesis. It appears that $HCo(CO)_3$ **B** is unstable species at 60°C, because the olefin-isomerization gradually became slow with the elapsing of time and finally stopped.

Subsequent experiments were carried out to investigate the validity of the *O*-silylation mechanism (Scheme 2). If the working hypothesis is correct, this condition would be applicable to **7** for a catalytic *O*-silylation (Scheme 8, step p). For this propose, 1.5 equiv. of Et_3SiH and 2 mol% of **7** was added to geraniol **26** in 1,2-dichloroethane at 60°C to generate the $Et_3SiCo(CO)_3$ **C** that was supposed to be a real catalyst of *O*-silylation. In this case, excess Et_3SiH would transform $HCo(CO)_3$ **B** into $Et_3SiCo(CO)_3$ **C** (step o). As we expected, **7** catalyzed *O*-silylation proceeded to give **27** (Scheme 9). It is noteworthy that *O*-silylation did not occur at all if bis(trimethylsilyl)acetylene **19** was added. These results also support the working hypothesis.

Thus, we have successfully developed a hydrosilylation reaction of an acetylene cobalt complex in the presence of a trapping reagent of the active species **A**. Although bis(trimethylsilyl)acetylene **19** is recommended as the trapping reagent, cheaper acetylenic additives **17** and **18** were also effective to stop the side reactions. The formation of the cobalt complex **21** should provide the evidence that the active species **A** should be '$Co_2(CO)_6$'. Further studies on the improvement and limitation of **7** catalyzed olefin-isomerization and *O*-silylation are now in progress.

3. Experimental

3.1. General

Infrared spectra (IR) were recorded on a JASCO FT/IR-8300 spectrophotometer and are reported in wave number (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on Brucker ARX-400 (400 MHz) and Varian Gemini-2000 (300 MHz) spectrometers. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Brucker ARX-400 (100 MHz) and Varian Gemini-2000 (75 MHz) spectrometers. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. Mass spectra were recorded on a Micromass Q-TOF (ESI), and are reported in *m/z*. Elemental analyses were performed by Analytical Laboratory at School of Bioagricultural Sciences, Nagoya University. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel coated glass plates $60F_{254}$ (Cica Merck, Art 1.05715) using UV light as visualizing agent and 7% ethanolic phosphomolybdic acid, or *p*-anisaldehyde solution as developing agents. Cica Merck silica gel 60 (particle size 0.063–0.2 mm ASTM) was used for open-column chromatography. Unless otherwise noted, nonaqueous reactions were conducted in oven-dried (200°C) or flame-dried glassware under inert atmosphere of dry nitrogen or argon. Dry THF was distilled from potassium metal with benzophenone. Dry CH_2Cl_2 was distilled from CaH_2 under nitrogen atmosphere. $BF_3{\cdot}OEt_2$ were distilled from CaH_2. All other commercially available reagents were used as received. Hyflo Super-Cel® (nacalai tesque) was used as filter aid.

3.1.1. Dibromoolefin (10). To a solution of CBr_4 (5.78 g, 17.4 mmol) in 24 mL of CH_2Cl_2 was added a solution of PPh_3 (9.14 g, 34.8 mmol) in 10 mL of CH_2Cl_2 at 0°C. After stirring for 10 min at 0°C, aldehyde **9** (2.04 g, 4.36 mmol) in 10 mL of CH_2Cl_2 was added and the resulting mixture was stirred for 30 min at 0°C. Then the reaction mixture was poured into an ice-cold sat. $NaHCO_3$ solution and extracted with CH_2Cl_2 (×2). The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo, which was filtered through a silica gel short column.

To a solution of the above dibromoolefin in 44 mL of CH_2Cl_2 were successively added ethyl vinyl ether (1.25 mL, 13.1 mmol) and pyridinium *p*-toluenesulfonate (50 mg). After stirring for 6 h at room temperature, the reaction mixture was poured into an ice-cold sat. $NaHCO_3$ solution. The resulting mixture was extracted with CH_2Cl_2 (×2). The combined extract was dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane=5:95) to give the dibromoolefin **10** (2.21 g, 82% in 2 steps). IR (KBr) ν_{max} 2980, 2900, 2360, 1498, 1455, 1359, 1121, 1090, 1056, 1028, 993, 735, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.06, 1.21 (total 3H, t, J=7.0 Hz, $-OCH_2CH_3$), 1.24, 1.35 (total 3H, d, J=5.0 Hz, $-OCH(O)CH_3$), 2.16–2.29 (2H, m, H-8a, 14a), 2.51–2.63 (1H, m, H-8b), 2.76 (1H, ddd, J=16.0, 7.5, 3.0 Hz, H-14b), 3.18–3.62 (6H, m, H-9, 10, 11, 12, 13, $-OCH_2CH_3$), 3.82, 3.89 (total 1H, q, J=7.0 Hz, $-OCH_2CH_3$), 4.61, 4.63 (total 1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.75–5.03 (4H, m, $-OCH(CH_3)O-$, $-OCH_2Ph$, $-OCH_2Ph$, $-OCH_2Ph$), 5.08 (1H, dm, J=12.0 Hz, H-6a), 5.09 (1H, dm, J=16.0 Hz, H-6b), 5.80–5.96 (1H, m, H-7), 6.55 (1H, ddd, J=7.0, 6.0, 1.0 Hz, H-15), 7.22–7.39 (10H, m, aromatic). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.2, 15.4, 20.5, 21.2, 35.6, 35.7, 35.8, 61.7, 63.1, 75.1, 75.3, 75.5, 77.2, 78.0, 78.5, 78.8, 81.8, 82.0, 86.0, 87.2, 89.4, 101.6, 101.7, 117.1, 117.2, 127.4, 127.5, 127.6, 127.7, 127.9, 128.3, 128.5, 134.6, 134.9, 135.8, 138.1, 138.5. Anal. Calcd for $C_{29}H_{36}Br_2O_5$: C, 55.78; H, 5.81. Found: C, 55.78; H, 5.80.

3.1.2. Diol (11). To a solution of the dibromoolefin **10** (1.27 g, 2.04 mmol) in 20 mL of THF was added a solution of *n*-BuLi (1.59 M in hexane, 2.94 mL, 4.68 mmol) at −78°C. After stirring for 15 min at −78°C, hydrocinnamaldehyde (0.32 mL, 2.65 mmol) in 2.7 mL of THF was added and the resulting mixture was stirred for 60 min at −78 to 0°C. Then the reaction mixture was poured into an ice-cold sat. NH_4Cl solution and extracted with ether (×3). The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

To a solution of the above coupling product in 20 mL of MeOH was added Amberlyst-15E (300 mg). After stirring for 90 min at room temperature, the reaction mixture was filtered through a pad of Super-Cel®, the resin was washed thoroughly with ethyl acetate. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/hexane=30:70) to give **11** (0.82 g, 76% in 2 steps). IR (KBr) ν_{max} 3406, 2913, 2862, 1643, 1604, 1497, 1455, 1359, 1087, 1028, 1002, 915, 750, 737, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.79 (1H, d, J=5.0 Hz, $-OH$), 1.94–2.06 (2H, m, H-18a, 18b), 2.18 (1H, d, J=1.5 Hz, $-OH$), 2.22–2.34 (1H, m, H-8a), 2.53 (1H, dm, J=17.0 Hz, H-14a), 2.57–2.62 (1H, m, H-8b), 2.68 (1H, dm, J=17.0 Hz, H-14b), 2.79 (2H, t, J=8.0 Hz, H-19a, 19b), 3.26–3.53 (5H, m, H-9, 10, 11, 12, 13), 4.35 (1H, br, H-17), 4.66 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.75 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.86 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.96 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 5.02 (1H, dm, J=10.0 Hz, H-6a), 5.09 (1H, dm, J=17.0 Hz, H-6b), 5.92 (1H, ddt, J=17.0, 10.0, 6.0 Hz, H-7), 7.16–7.38 (15H, m, aromatic). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.3, 31.3, 35.7, 39.4, 61.9, 73.4, 75.0, 75.3, 76.9, 78.6, 81.5, 81.8, 82.8, 86.6, 117.1, 126.0, 127.9, 128.0, 128.4, 128.6, 128.7, 134.6, 138.1, 138.5, 141.5. Anal. Calcd for $C_{34}H_{38}O_5$: C, 77.54; H, 7.27. Found: C, 77.53; H, 7.29.

3.1.3. Cyclic acetylene cobalt complex (12). To a solution of the diol **11** (489 mg, 0.93 mmol) in 47 mL of CH_2Cl_2 was added a solution of $Co_2(CO)_8$ (635 mg, 1.86 mmol) in 3.0 mL of CH_2Cl_2. After stirring for 30 min at room temperature, $BF_3{\cdot}OEt_2$ (0.12 mL, 0.93 mmol) was added at 0°C. After stirring for 15 min at 0°C, the reaction mixture was poured into an ice-cold sat. $NaHCO_3$ solution and extracted with CH_2Cl_2 (×3). The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/hexane=5:95) to give **12** (686 mg, 93%) as a dark red oil. $[\alpha]_D^{27}=-72°$ (*c* 0.155, $CHCl_3$). IR (KBr) ν_{max} 2360, 2343, 2094, 2053, 2026, 1085, 698, 519 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.08 (1H, ddt, J=13.0, 9.5, 6.5 Hz, H-18a), 2.19 (1H, ddt, J=13.0, 9.5, 6.5 Hz, H-18b), 2.20–2.26 (1H, m, H-8a), 2.55–2.62 (1H, m, H-8b), 2.84 (2H, td, J=9.5, 6.5 Hz, H-19a, 19b), 2.92 (1H, dd, J=16.0, 9.0 Hz, H-14a), 3.31 (1H, t, J=9.0 Hz, H-10), 3.32–3.34 (1H, m, H-9), 3.42 (1H, td, J=9.0, 4.5 Hz, H-13), 3.49 (1H, t, J=9.0 Hz, H-12), 3.63 (1H, dd, J=16.0, 4.5 Hz, H-14b), 3.64 (1H, t, J=9.0 Hz, H-11), 4.53 (1H, t, J=6.5 Hz, H-17), 4.64 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.87 (2H, d, J=11.0 Hz, $-OCH_2Ph$), 4.99 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 5.08 (1H, dm, J=7.0 Hz, H-6a), 5.09 (1H, dm, J=17.5 Hz, H-6b), 5.88 (1H, ddt, J=17.5, 10.0, 7.0 Hz, H-7), 7.26–7.40 (15H, m, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.2, 36.0, 39.1, 39.4, 75.0, 75.7, 76.0, 77.9, 81.1, 81.6, 85.9, 87.9, 93.9, 101.4, 117.2, 126.0, 127.5, 127.6, 127.7, 127.8, 128.2, 128.4, 134.6, 138.2, 138.8, 141.4, 199.1, 199.5. ESI Q-TOF MS calcd for $C_{40}H_{37}Co_2O_{10}$ $[M+H]^+$ 795.105, found 795.107.

3.1.4. Vinylsilane (13); hydrosilylation in the presence of bis(trimethylsilyl)acetylene. To a solution of the acetylene cobalt complex **12** (39.2 mg, 49.3 μmol) and bis(trimethylsilyl)acetylene (22.3 μL, 98.6 μmol) in 0.5 mL of 1,2-dichloroethane was added Et_3SiH (39.4 μL, 0.25 mmol). After stirring for 1.5 h at 60°C, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane=5:95) to give the vinylsilane **13** (30.8 mg, 99%). $[\alpha]_D^{24}=+29°$ (*c* 0.48, $CHCl_3$). IR (KBr) ν_{max} 2361, 2343, 2054, 1600, 1508, 1457, 1087, 697, 669 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.61 (6H, q, J=8.0 Hz, $-SiCH_2CH_3$), 0.93 (9H, t, J=8.0 Hz, $-SiCH_2CH_3$), 1.89 (1H, dddd, J=14.0, 9.0, 7.0, 5.0 Hz, H-18a), 2.03 (1H, dtd, J=14.0, 9.0, 5.5 Hz, H-18b), 2.25 (1H, m, H-8a), 2.47–2.60

(3H, m, H-8b, 14a, 14b), 2.73 (1H, ddd, J=14.0, 9.0, 7.0 Hz, H-19a), 2.82 (1H, ddd, J=14.0, 9.0, 5.5 Hz, H-19b), 2.98 (1H, ddd, J=10.0, 8.5, 3.0 Hz, H-13), 3.32 (1H, t, J=8.5 Hz, H-10), 3.33–3.37 (1H, m, H-9), 3.54 (1H, t, J=8.5 Hz, H-12), 3.64 (1H, t, J=8.5 Hz, H-11), 4.00 (1H, dt, J=9.0, 5.0 Hz, H-17), 4.12 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.32 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.40 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 5.05 (1H, dm, J=10.0 Hz, H-6a), 5.07 (1H, dm, J=17.0 Hz, H-6b), 5.08 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 5.89 (1H, ddt, J=17.0, 10.0, 6.0 Hz, H-7), 6.07 (1H, dd, J=5.0, 2.5 Hz, H-16), 7.13–7.38 (15H, m, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 2.5, 7.5, 31.8, 36.0, 36.3, 37.8, 75.0, 75.2, 75.9, 78.4, 81.4, 85.6, 88.6, 116.8, 125.8, 127.5, 127.6, 127.7, 127.9, 128.4, 128.5, 134.7, 138.5, 138.9, 140.5, 141.9, 146.6. Anal. Calcd for $C_{40}H_{52}O_4Si$: C, 76.88; H, 8.39. Found: C, 76.89; H, 8.51.

3.1.5. Vinylsilane olefin isomer (14). $[\alpha]_D^{24}=+43°$ (c 0.55, $CHCl_3$). IR (KBr) ν_{max} 2951, 2904, 2873, 2360, 2343, 1560, 1498, 1455, 1087, 1029, 748, 736, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.60 (6H, q, J=8.0 Hz, $-SiCH_2CH_3$), 0.92 (9H, t, J=8.0 Hz, $-SiCH_2CH_3$), 1.74 (3H, d, J=7.5, 1.5 Hz, $-CH_3$), 1.84–1.95 (1H, m, H-18a), 1.98–2.20 (1H, m, 18b), 2.48 (1H, ddd, J=14.5, 9.0, 2.0 Hz, H-14a), 2.60 (1H, dd, J=14.5, 2.5 Hz, H-14b), 2.68–2.90 (2H, m, H-19a, 19b), 3.04 (1H, td, J=9.0, 2.5 Hz, H-13), 3.31 (1H, t, J=9.0 Hz, H-10), 3.53 (1H, t, J=9.0 Hz, H-9), 3.63 (1H, t, J=9.0 Hz, H-12), 3.72 (1H, t, J=9.0 Hz, H-11), 3.98 (1H, dt, J=9.0, 4.5 Hz, H-17), 4.61 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.76 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.85 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 5.05 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 5.44 (1H, ddd, J=15.0, 7.5, 1.5 Hz, H-8), 5.87 (1H, dq, J=15.0, 7.5 Hz, H-7), 6.07 (1H, dd, J=4.5, 2.0 Hz, H-16), 7.13–7.40 (15H, m, aromatic). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 2.3, 7.4, 18.0, 31.7, 36.4, 37.8, 74.9, 75.1, 76.1, 76.7, 80.2, 82.3, 84.9, 88.3, 125.8, 127.5, 127.7, 127.9, 128.2, 128.4, 128.6, 128.8, 130.9, 138.4, 139.0, 140.3, 142.0, 146.9. Anal. Calcd for $C_{40}H_{52}O_4Si$: C, 76.88; H, 8.39. Found: C, 76.89; H, 8.64.

3.1.6. Vinylsilane saturated olefin (15). $[\alpha]_D^{26}=+26°$ (c 0.67, $CHCl_3$). IR (KBr) ν_{max} 2955, 2910, 2874, 2360, 2343, 2054, 2029, 1498, 1456, 1074, 1029, 1005, 733, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.59 (6H, q, J=8.0 Hz, $-SiCH_2CH_3$), 0.87–0.93 (3H, m, $-CH_3$), 0.92 (9H, t, J=8.0 Hz, $-SiCH_2CH_3$), 1.30–1.41 (1H, m, H-8a), 1.47–1.57 (2H, m, H-7a, 7b), 1.72–1.79 (1H, m, H-8b), 1.88 (1H, dddd, J=14.0, 9.5, 7.0, 4.5 Hz, H-18a), 2.04 (1H, dtd, J=14.0, 9.0, 5.5 Hz, H-18b), 2.48 (1H, ddd, J=14.5, 9.5, 2.5 Hz, H-14a), 2.55 (1H, dd, J=14.5, 3.5 Hz, H-14b), 2.72 (1H, ddd, J=14.0, 9.0, 7.0 Hz, H-19a), 2.82 (1H, ddd, J=14.0, 9.5, 5.5 Hz, H-19b), 2.96 (1H, td, J=9.5, 3.5 Hz, H-13), 3.19–3.23 (1H, m, H-9), 3.24 (1H, t, J=9.0 Hz, H-10), 3.54 (1H, t, J=9.0 Hz, H-12), 3.62 (1H, t, J=9.0 Hz, H-11), 3.98 (1H, dt, J=9.0, 4.5 Hz, H-17), 4.61 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.81 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.89 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 5.07 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 6.06 (1H, dd, J=4.5, 2.5 Hz, H-16), 7.03–7.42 (15H, m, aromatic). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 2.5, 4.5, 6.5, 7.4, 14.0, 18.7, 31.8, 34.0, 36.5, 37.8, 74.8, 75.1, 75.2, 75.9, 76.5, 78.8, 82.4, 85.7, 88.8, 125.8, 127.4, 127.6, 127.8, 127.9, 128.3, 128.5, 138.5, 139.0, 140.7, 142.0, 146.6. ESI Q-TOF MS calcd for $C_{40}H_{54}O_4SiNa$ $[M+Na]^+$ 649.369, found 649.373.

3.1.7. Vinylsilane (4) and acetylene cobalt complex (21); hydrosilylation in the presence of bis(trimethylsilyl)-acetylene. To a solution of the acetylene cobalt complex **1** (8.42 g, 10.6 mmol) and bis(trimethylsilyl)acetylene (4.82 mL, 21.3 mmol) in 200 mL of 1,2-dichloroethane was added Et_3SiH (8.46 mL, 53.0 mmol). After stirring for 2 h at 60°C, the reaction mixture was filtered through Super-Cel® and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane=100) to give the acetylene cobalt complex **21** (4.17 g, 86%) and (ethyl acetate/hexane=25:75) to give the vinylsilane **4** (6.28 g, 94%)

Acetylene cobalt complex **21**: IR (KBr) ν_{max} 2085, 2042, 2015, 1544, 1249, 839, 521. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.29 (18H, s, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.9, 92.8, 201.0. Anal. Calcd for $C_{14}H_{18}O_6Co_2$: C, 36.85; H, 3.98. Found: C, 36.91; H, 3.97.

Vinylsilane **4**: $[\alpha]_D^{24}=+21°$ (c 0.57, $CHCl_3$). IR (KBr) ν_{max} 3484, 3067, 3032, 2953, 2908, 2874, 2053, 2028, 1456, 1362, 1327, 1074, 1029, 1003, 913, 733, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.63 (6H, q, J=7.5 Hz, $-SiCH_2CH_3$), 0.95 (9H, t, J=7.5 Hz, $-SiCH_2CH_3$), 1.58 (1H, q, J=11.5 Hz, H-14a), 1.83 (1H, ddt, J=14.5, 6.5, 4.0 Hz, H-21a), 1.95 (1H, dddd, J=14.5, 9.5, 6.5, 4.5 Hz, H-21b), 2.25 (1H, dt, J=14.5, 7.5 Hz, H-8a), 2.37 (1H, dt, J=11.5, 4.0 Hz, H-14b), 2.50–2.60 (2H, m, H-8b, 17a), 2.62 (1H, dd, J=14.5, 3.0 Hz, H-17b), 2.98 (1H, ddd, J=11.5, 8.5, 3.0 Hz, H-16), 3.12 (1H, t, J=8.5 Hz, H-12), 3.12–3.16 (1H, m, H-13), 3.28 (1H, dd, J=9.5, 8.5 Hz, H-10), 3.37 (1H, ddd, J=9.5, 7.5, 3.0 Hz, H-9), 3.51 (1H, ddd, J=11.5, 8.5, 4.5 Hz, H-15), 3.60 (1H, t, J=8.5 Hz, H-11), 3.78–3.82 (2H, m, H-22a, 22b), 4.24 (1H, ddd, J=9.5, 4.5, 4.0 Hz, H-20), 4.62 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.75 (1H, d, J=11.5 Hz, $-OCH_2Ph^*$), 4.93 (1H, d, J=11.0 Hz, $-OCH_2Ph$), 4.95 (1H, d, J=11.5 Hz, $-OCH_2Ph^*$), 5.05 (1H, dm, J=10.5 Hz, H-6a), 5.07 (1H, dm, J=17.5 Hz, H-6b), 5.86 (1H, dddd, J=17.5, 10.5, 7.5, 6.5 Hz, H-7), 6.02 (1H, dd, J=4.5, 2.5 Hz, H-19), 7.26–7.38 (10H, m, aromatic). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 2.3, 7.4, 35.9, 36.5, 37.0, 37.9, 60.9, 73.9, 75.1, 75.2, 78.9, 80.9, 82.5, 82.9, 84.2, 117.1, 127.8, 128.0, 128.2, 128.4, 128.5, 134.6, 139.4, 138.8, 141.2, 145.9. Anal. Calcd for $C_{37}H_{52}O_6Si$: C, 71.57; H, 8.44. Found: C, 71.57; H, 8.58.

3.1.8. Decene-1-ol olefin iosmers (25). To a solution of the olefin **24** (21.1 mg, 87.8 μmol) in 1.8 mL of 1,2-dichloroethane were added Et_3SiH (28 μL, 0.18 mmol) and acetylene cobalt complex **7** (32.5 mg, 87.8 μmol). After stirring for 1 h at 60°C, the reaction mixture was filtered through Super-Cel® and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ether/hexane=1:20) to give the olefine-isomers **25** (20.4 mg, 97%). IR (KBr) ν_{max} 2929, 2856, 1455, 1201, 1138, 1121, 1079, 1035, 966, 870 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.20–2.10 (22H, m, $-CH_2-$), 3.38 (1H, dt, J=9.5, 7.0 Hz, $-OCH_2-$), 3.46–3.54 (1H, m, $-OCH_2-$), 3.73 (1H, dt, J=9.5, 7.0 Hz, $-OCH_2-$), 3.83–

3.92 (1H, m, $-OCH_2$), 4.57 (1H, dd, $J=4.5$, 3.0 Hz, $-OCH(CH_2-)-O-$), 5.30–5.50 (2H, m, olefinic). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.8, 19.6, 25.4, 26.1, 26.7, 29.0, 29.1, 29.3, 29.5, 29.7, 30.7, 32.5, 62.3, 67.7, 98.9, 123.7, 124.6, 130.9, 131.7.

3.1.9. Silyl ether (27). To a solution of geraniol **26** (227 mg, 1.47 mmol) in 3.8 mL of 1,2-dichloroethane were added Et_3SiH (0.35 mL, 2.20 mmol) and acetylene cobalt complex **7** (10.9 mg, 29.4 μmol). After stirring for 2 h at 60°C, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ether/hexane=1:20) to give **27** (344 mg, 87%). IR (KBr) ν_{max} 2956, 2937, 2913, 2877, 1458, 1379, 1239, 1104, 1067, 1008, 776, 745 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.61 (6H, q, $J=8.0$ Hz, $-SiCH_2CH_3$), 0.96 (9H, t, $J=8.0$ Hz, $-SiCH_2CH_3$), 1.60 (3H, s, $-CH_3$), 1.63 (3H, d, $J=1.0$ Hz, $-CH_3$), 1.68 (3H, d, $J=1.0$ Hz, $-CH_3$), 1.98–2.14 (total 4H, m, $-CH_2-$), 4.18 (2H, dq, $J=6.5$, 1.0 Hz, $-CH_2O-$), 5.10 (1H, tt, $J=7.0$, 1.5 Hz, *olefinic*), 5.33 (1H, tq, $J=6.5$, 1.0 Hz, *olefinic*). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 4.4, 6.8, 16.2, 17.6, 25.6, 26.3, 39.5, 59.8, 124.2, 124.3, 131.6, 137.2. Anal. Calcd for $C_{16}H_{32}OSi$: C, 71.57; H, 12.01. Found: C, 71.45; H, 12.19.

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