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# Cobalt-Catalyzed Isomerization of 1-Alkenes to (*E*)-2-Alkenes with Dimethylphenylsilylmethylmagnesium Chloride and Its Application to the Stereoselective Synthesis of (*E*)-Alkenylsilanes

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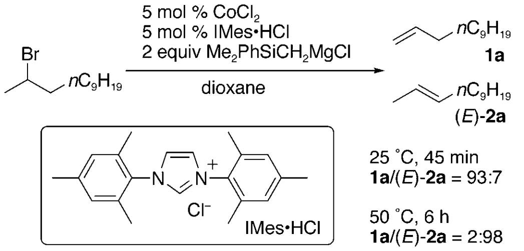
**Abstract:** Treatment of 1-alkenes with dimethylphenylsilylmethylmagnesium chloride in the presence of a cobalt-NHC complex in dioxane at 50 °C or higher provides the corresponding (*E*)-2-alkenes selectively. The isomerization is applicable to the stereoselective synthesis of (*E*)-crotylsilanes and (*E*)-1-propenylsilanes from the corresponding homoallylsilanes and allylsilanes, respectively.

**Keywords:** alkenes • alkenylsilanes • cobalt • Grignard reagents • isomerization

## Introduction

Transition-metal-catalyzed isomerization of alkenes is a simple and well-studied transformation in organic chemistry.[1] However, highly selective isomerization of 1-alkenes to (*E*)-2-alkenes is still difficult[2] because additional isomerization reactions into 3-alkenes and other possible isomers are often problematic. Most of the isomerization reactions suffer from lack of *E*/*Z* selectivity and narrow substrate scope.

During the course of our studies on cobalt-catalyzed reactions,[3,4] we recently reported cobalt-catalyzed dehydrohalogenation of 2-haloalkanes which yields 1-alkenes (Scheme 1).[5] In this report, we disclosed that (*E*)-2-dodecene [(*E*)-**2a**] was selectively obtained when the elimination reaction of 2-bromododecane was performed at 50 °C for 6 h. Apparently, the reaction initially afforded **1a** within 45 min, and prolonged heating induced cobalt-catalyzed gradual isomerization to (*E*)-**2a**. It is worth noting that further isomerization to 3-dodecene and other internal dodecenes was negligible, probably because of the sufficient bulkiness of the cobalt catalyst. In light of the importance of the isomerization of terminal alkenes, we report herein detailed studies on the cobalt-catalyzed selective isomerization of 1-alkenes to (*E*)-2-alkenes.[6]



Scheme 1. Previous results.

## Results and Discussion

On the basis of the previous observation in Scheme 1, treatment of 1-tetradecene (**1b**) with $Me_2PhSiCH_2MgCl$ (0.50 equiv) in the presence of $CoCl_2$ and IMes·HCl (both 5 mol %) in dioxane at 50 °C for 6 h afforded (*E*)-2-tetradecene [(*E*)-**2b**] with high selectivity (Table 1, entry 1). Trace amounts of (*Z*)-2-tetradecene [(*Z*)-**2b**] and 3-tetradecene (**3b**) were observed.

The choice of the Grignard reagent is quite important. The use of the smaller $Me_3SiCH_2MgCl$ yielded the larger amount of **3b** (Table 1, entry 2). Simple Grignard reagents such as butyl-, methyl-, phenyl-, and allylmagnesium bromide promoted isomerization with lower regio- and stereoselectivities (Table 1, entries 3–6).

The use of an N-heterocyclic carbene (NHC) ligand[7] is essential to achieve the selective isomerization. The reaction by using IPr·HCl provided (*E*)-**2b** stereoselectively, albeit

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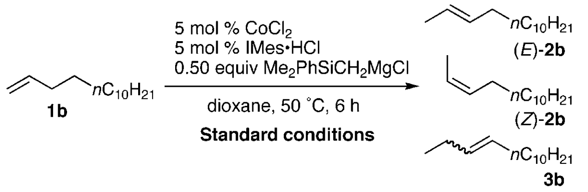
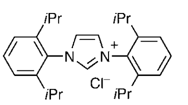
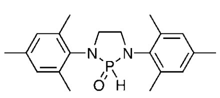
Table 1. Isomerization of 1-tetradecene.[a]



| Entry | Deviation from standard conditions | **1b** recov. [%] | (*E*)-**2b** [%] | (*Z*)-**2b** [%] | **3b** [%][b] |
|---|---|---|---|---|---|
| 1 | none | 3 | 79 | 2 | 2 |
| | Grignard reagent | | | | |
| 2 | $Me_3SiCH_2MgCl$ | 3 | 88 | 1 | 8 |
| 3 | *n*BuMgBr | 0 | 62 | 19 | 2 |
| 4 | MeMgBr | 0 | 67 | 14 | 19 |
| 5 | PhMgBr | 0 | 64 | 8 | 28 |
| 6 | $CH_2{=}CHCH_2MgCl$ | 0 | 76 | 3 | 19 |
| | (Pre)Ligand | | | | |
| 7 | IPr·HCl[c] | 2 | 78 | 4 | 16 |
| 8 | Mes·HASPO[c] | 2 | 48 | 18 | 3 |
| 9 | $Ph_3P$ | 10 | 32 | 27 | 8 |
| 10 | *t*Bu$_3$P | 0 | 43 | 16 | 16 |
| 11 | $(cC_6H_{11})_3P$ | 0 | 55 | 22 | 12 |
| 12 | $Ph_2PCH_2CH_2PPh_2$ | 11 | 52 | 21 | 6 |
| 13 | $Me_2NCH_2CH_2NMe_2$ | 43 | 27 | 11 | 6 |
| 14 | absence of ligand | 1 | 40 | 15 | 19 |
| | Metal salt | | | | |
| 15 | $PdCl_2$ | 80 | 4 | 3 | 0 |
| 16 | $NiCl_2$ | 85 | 2 | 2 | 0 |
| 17 | $CuCl_2$ | 89 | 0 | 0 | 0 |
| 18 | $MnCl_2$ | 91 | 0 | 0 | 0 |
| 19 | $FeCl_3$ | 80 | 8 | 0 | 0 |
| 20 | no transition metal | 97 | 0 | 0 | 0 |

[a] Yields were determined by $^1$H NMR analysis. [b] The *E*/*Z* ratios could not be determined. [c]


IPr·HCl


Mes·HASPO

with lower regioselectivity (Table 1, entry 7). Mes·HASPO[8] as well as phosphine ligands were inferior to NHC ligands (Table 1, entries 8–11). Bidentate ligands failed to serve well (Table 1, entries 12 and 13), and no selectivity was observed in the absence of ligand (entry 14).

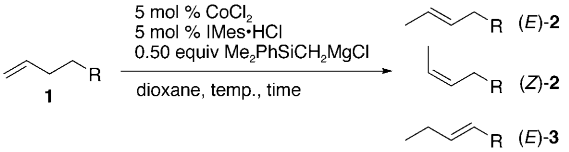
Only a cobalt salt could catalyze the isomerization. Other transition-metal salts such as $NiCl_2$ and $FeCl_3$ were ineffective (Table 1, entries 15–19). No reaction took place without a cobalt salt (Table 1, entry 20).

**Abstract in Japanese:**

*コバルト-N-ヘテロサイクリックカルベン錯体触媒存在下、1-アルケンに対して塩化ジメチルフェニルシリルメチルマグネシウムをジオキサン中50 °C以上で作用させると、(E)-2-アルケンが選択的に得られる。ホモアリルシランやアリルシランを出発物質とすると、それぞれ(E)-クロチルシランや(E)-1-プロペニルシランが立体選択的に生じる。*

Several terminal olefins were treated under the cobalt catalysis (Table 2). The isomerization of *tert*-butyldimethylsilyl 10-undecenyl ether (**1c**) proceeded smoothly to yield the corresponding (*E*)-9-undecenyl ether (*E*)-**2c** with good selectivity (Table 2, entry 1). However, protection of 10-undecen-1-ol by a benzyl or tetrahydropyranyl (THP) group led to lower regioselectivity (Table 2, entries 2 and 3). THP ether **1e** did not react at 50 °C, requiring a higher temperature. Protection of the hydroxy group by a bulky mesitylcarbonyl group was suitable, and the reaction of **1f** proceeded with high selectivity without decomposition of the ester bond (Table 2, entry 4). The less bulky benzoyl protection was not compatible. Tosylamide **1g** participated in the selective isomerization in boiling dioxane (Table 2, entry 5). The curious effect of the functional groups in the substrates is not clear.

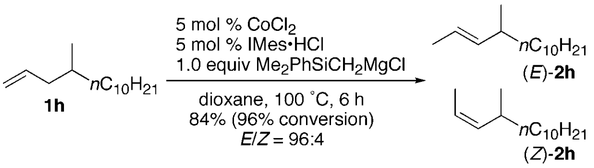
Table 2. Cobalt-catalyzed isomerization of terminal olefins.



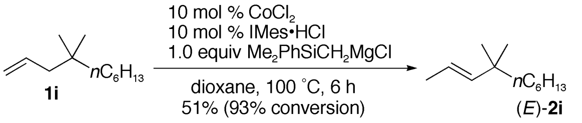
| Entry | R | Temp. [°C], time [h] | (*E*)-**2**, [%] | (*Z*)-**2**, [%] | (*E*)-**3**, [%] |
|---|---|---|---|---|---|
| 1 | (CH$_2$)$_7$OSi*t*BuMe$_2$ (**1c**) | 50, 6 | (*E*)-**2c**, 81 | (*Z*)-**2c**, 2 | (*E*)-**3c**, 5 |
| 2 | $(CH_2)_7OBn$ (**1d**) | 50, 6 | (*E*)-**2d**, 85 | (*Z*)-**2d**, 0 | (*E*)-**3d**, 15 |
| 3 | $(CH_2)_7OTHP$ (**1e**) | 100, 6 | (*E*)-**2e**, 65 | (*Z*)-**2e**, 0 | (*E*)-**3e**, 18 |
| 4[a] | $(CH_2)_7OC({=}O)Mes$ (**1f**) | 100, 8 | (*E*)-**2f**, 80 | (*Z*)-**2f**, 0 | (*E*)-**3f** 4 |
| 5[a] | $CH_2N(Bn)Ts$ (**1g**) | 100, 8 | (*E*)-**2g**, 61 | (*Z*)-**2g**, 0 | (*E*)-**3g**, 0 |

[a] $CoCl_2$ (10 mol %), IMes·HCl (10 mol %), and $Me_2PhSiCH_2MgCl$ (1.0 equiv) were used.

The isomerization reaction was sensitive to the steric environment around the double bond. The reaction of 4-methyl-1-tetradecene (**1h**) in the presence of the cobalt catalyst (5 mol %) and $Me_2PhSiCH_2MgCl$ (0.50 equiv) at 50 °C failed to proceed to completion within a reasonable reaction time. A temperature as high as 100 °C and one equivalent of the Grignard reagent were essential to attain acceptable conversion of **1h** [Eq. (1)]. The isomerization of alkene **1i** having a quaternary carbon atom in proximity to the double bond was sluggish, affording (*E*)-**2i** in 51 % yield with remaining **1i** (4 %) and unidentified by-products [Eq. (2)].

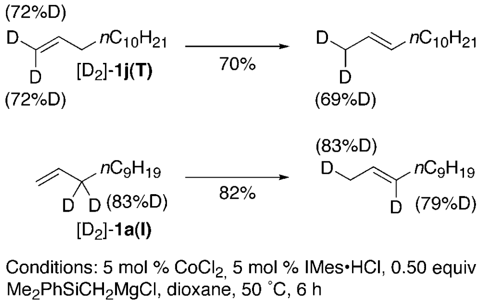


(1)



(2)

To gain information about the reaction mechanism of the isomerization, two deuterated alkenes [$D_2$]-**1j(T)** and [$D_2$]-**1a(I)** were prepared and subjected to the isomerization (Scheme 2). Terminally deuterated [$D_2$]-**1j(T)** was isomerized into the corresponding (*E*)-2-alkene, leaving the deuterium atoms untouched. In addition, internally deuterated [$D_2$]-**1a(I)** was isomerized with deuterium transposition to yield (*E*)-1,3-dideuterio-2-dodecene.



Scheme 2. Isomerization of deuterated 1-alkenes.

We tentatively propose the reaction mechanism as follows (Figure 1). Low-valent cobalt **4** would be generated from cobalt chloride, IMes·HCl, and $Me_2PhSiCH_2MgCl$. Terminal olefin **1** would then coordinate to **4** to yield cobaltacyclopropane **5**.[9] Complex **5** would undergo β-hydride elimination to yield cobalt(allyl)hydride **6**,[10] which is followed by reductive elimination to afford 2-alkene **2**. We presume that one (or two) dimethylphenylsilylmethyl group(s) would be located on the cobalt atom since the size of the triorganosilyl group has an influence on the selectivity (Table 1, entries 1 and 2). Degrees of steric repulsion in the transition states of the β-hydride elimination account for the stereoselective formation of (*E*)-2-alkenes. The β-hydride elimination should proceed via a *syn* periplanar conformation **5a** or **5b**.[11] The former is more preferable, minimizing the total steric repulsion.

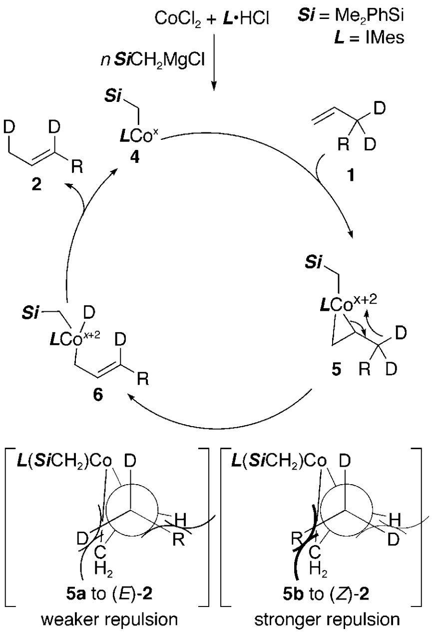
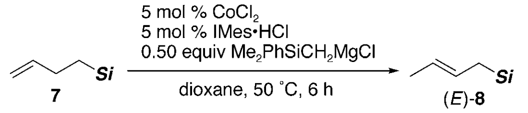


Figure 1. Plausible reaction mechanism.

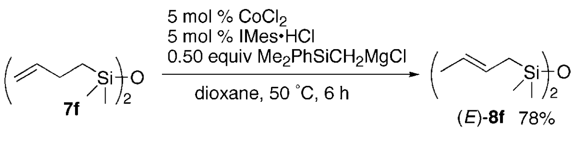
Stereoselective synthesis of (*E*)-crotylsilanes has been attracting much attention.[12] The cobalt-catalyzed isomerization is applicable to the synthesis of (*E*)-crotylsilanes from homoallylsilanes (Table 3).[13] Exceptionally, the silyl group of homoallylsilane **7e** is so bulky that **7e** failed to undergo highly selective isomerization (Table 3, entry 5). Whereas the reaction of **7e** at 50 °C resulted in recovery of **7e**, the reaction at 100 °C yielded a mixture of isomers. Disiloxane **7f** underwent the isomerization to (*E*)-**8f** with exclusive *E* selectivity without affecting the Si–O bonds [Eq. (3)].

Table 3. Isomerization of homoallylsilanes into (*E*)-2-crotylsilanes.



| Entry | *Si* | **7** | **7** recov. [%] | (*E*)-**8**, [%][a] |
|---|---|---|---|---|
| 1 | $SiMe_2Ph$ | **7a** | 6 | (*E*)-**8a**, 74 |
| 2 | $SiMe_2C_6F_5$ | **7b** | 0 | (*E*)-**8b**, 63[b] |
| 3 | $SiMe_2C_6H_4$-*m*-$CF_3$ | **7c** | 0 | (*E*)-**8c**, 77[c] |
| 4 | $Si(SiMe_3)_3$ | **7d** | 5 | (*E*)-**8d**, 70 |
| 5[d] | $SiMePh_2$ | **7e** | 0 | **8e**[e], 51 |

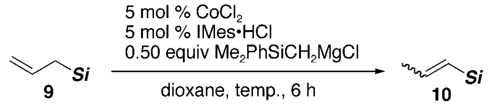
[a] *E*/*Z* ratios are greater than 99:1 unless otherwise noted. [b] $CoCl_2$ (10 mol %), IPr·HCl (10 mol %), and $Me_3SiCH_2MgCl$ (1.0 equiv) were used. [c] Stereoisomer (*Z*)-**8c** and the corresponding (*E*)-1-butenylsilane were obtained in 1 % and 3 % yields, respectively. [d] Catalyst (10 mol %), Grignard reagent (1.0 equiv), 100 °C, 6 h. [e] *E*/*Z* = 75:25. Contaminated with the corresponding (*E*)-1-butenylsilane (4 % yield).



(3)

Allylsilanes were successfully converted into the corresponding (*E*)-1-propenylsilanes (Table 4). Each reaction showed high *E* selectivity. It is worth noting that all the reactions did not proceed to completion, leaving small amounts of the starting allylsilanes. Neither prolonged reaction time nor higher loadings of the catalyst and/or the Grignard reagent could improve conversion. We confirmed by the following experiment [Eq. (4)] that the reaction reached equilibrium between allylsilane and 1-propenylsilane under the reaction conditions. Treatment of **10b** (*E*/*Z* = 42:58) under the isomerization conditions afforded a mixture of **10b** (74 %, *E*/*Z* = 94:6) and allylsilane **9b** (13 %).

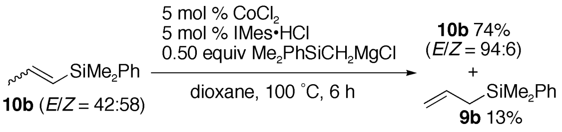
Table 4. Isomerization of allylsilanes into (*E*)-1-propenylsilanes.



| Entry | *Si* | **9** | Temp. [°C] | **10**, [%] | *E*/*Z* | **9** recov. [%] |
|---|---|---|---|---|---|---|
| 1[a] | $SiMePh_2$ | **9a** | 50 | **10a**, 74 | 99:1 | 3 |
| 2 | $SiMe_2Ph$ | **9b** | 100 | **10b**, 55 | 95:5 | 9 |
| 3[b] | $SiMe_2C_6H_4$-*m*-$CF_3$ | **9c** | 100 | **10c**, 71 | 96:4 | 13 |
| 4 | $SiMe_2(OnC_7H_{15})$ | **9d** | 50 | **10d**, 85 | 95:5 | 15 |

[a] IPr·HCl and $Me_3SiCH_2MgCl$ were used instead of IMes·HCl and $Me_2PhSiCH_2MgCl$. [b] $CoCl_2$, IMes·HCl (10 mol% each), and $Me_2PhSiCH_2MgCl$ (1.0 equiv) were used.

The isomer distribution is essentially the same as that of entry 2 in Table 4.



(4)

## Conclusions

Cobalt-catalyzed $Me_2PhSiCH_2MgCl$-mediated isomerization of 1-alkenes has emerged as a method for the selective synthesis of (*E*)-2-alkenes. The bulky Grignard reagent and NHC ligand realize high regio- and stereoselectivities. The isomerization reaction is applicable to the stereoselective synthesis of (*E*)-crotyl- and (*E*)-1-propenylsilanes.

In some cases, conversions of 1-alkenes were not perfect, which would render isolation of the desired (*E*)-2-alkenes difficult. However, further transformation of the alkene moieties such as epoxidation should allow for selective formation or separation of the desired final products.

## Experimental Section

**General**: $^1H$ NMR (500 MHz) and $^{13}C$ NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous $CoCl_2$ was purchased from Wako Pure Chemicals and was used after removal of water. Specifically, in each experiment, $CoCl_2$ was dried in a reaction flask carefully under reduced pressure (0.5 torr) by heating with a hair dryer for 2 min immediately before use. Imidazolium salts, IMes·HCl was purchased from Strem Chemicals. Dimethylphenylsilylmethylmagnesium chloride was prepared from magnesium metal and the corresponding (chloromethyl)dimethylphenylsilane in THF. Dioxane was dried over slices of sodium. All reactions were carried out under argon atmosphere.

**Typical procedure for cobalt-catalyzed isomerization of 1-alkenes to (*E*)-2-alkenes**: The reaction of 1-tetradecene is representative (Table 1, entry 1). Under argon atmosphere, cobalt(II) chloride (6.5 mg, 0.05 mmol), 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (17.0 mg, 0.05 mmol), and dioxane (1.0 mL) were placed in a 20 mL reaction flask. Dimethylphenylsilylmethylmagnesium chloride (1.0 M THF solution, 0.5 mL, 0.5 mmol) was added to the suspension at 25 °C. After the resulting mixture was stirred for 2 min, 1-tetradecene (0.20 g, 1.0 mmol) in dioxane (1.0 mL) was added. After the mixture was heated at 50 °C for 6 h, ammonium chloride solution was added. The products were extracted with hexane three times. The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Silica gel column purification provided a mixture of 1-tetradecene, (*E*)-2-tetradecene, (*Z*)-2-tetradecene, and (*E*)-3-tetradecene in 86% combined yield (172.0 mg, 0.86 mmol) in a ratio of 4:92:2:2.

**Characterization data of new starting material**: Compounds **1a**, **1b**, and **1j** are commercially available. Compounds **1c**,[14] **1d**,[15] **1e**,[15] **1g**,[5] **7a**,[16] **7f**,[17] **9a**,[18] and **9b**[18] were prepared and showed the spectra identical with those shown in the literature.

**10-Undecenyl 2,4,6-trimethylbenzoate (1f)**: Oil. IR (neat): $\tilde{\nu} = 2927$, 2855, 1726, 1612, 1436, 1265 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 1.25$–1.45 (m, 12 H), 1.73 (dt, $J = 17.0$, 7.0 Hz, 2 H), 2.00–2.08 (m, 2 H), 2.29 (s, 9 H), 4.30 (t, $J = 7.0$ Hz, 2 H), 4.93 (d, $J = 10.0$ Hz, 1 H), 4.99 (d, $J = 17.0$ Hz, 1 H), 5.81 (ddt, $J = 10.0$, 17.0, 7.0 Hz, 1 H), 6.85 ppm (s, 2 H); $^{13}C$ NMR ($CDCl_3$): $\delta = 19.9$, 21.3, 26.2, 28.9, 29.1, 29.3, 29.4, 29.6 (two signals merge), 34.0, 65.2, 114.3, 128.5, 131.5, 135.1, 139.3, 139.3, 170.4 ppm; HRMS (DI-EI$^+$): *m*/*z*: observed: 316.2408 ($\Delta = +1.8$ ppm), calcd for $C_{21}H_{32}O_2$ [$M^+$]: 316.2402.

**4-Methyl-1-tetradecene (1h)**: Oil. IR (neat): $\tilde{\nu} = 3077$, 2855, 1641, 1456, 910 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 0.86$ (d, $J = 7.0$ Hz, 3 H), 0.88 (t, $J = 7.0$ Hz, 3 H), 1.03–1.17 (m, 1 H), 1.20–1.34 (m, 17 H), 1.42–1.53 (m, 1 H), 1.87 (dddq, $J = 7.0$, 7.0, 14.3, 3.0 Hz, 1 H), 2.06 (dddq, $J = 7.0$, 7.0, 14.3, 3.0 Hz, 1 H), 4.95–5.02 (m, 2 H), 5.78 ppm (ddt, $J = 10.0$, 17.0, 7.0 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): $\delta = 14.3$, 19.7, 22.9, 27.3, 29.6, 29.9 (three signals merge), 30.2, 32.2, 33.0, 36.8, 41.7, 115.5, 138.0 ppm. Elemental analysis (%) found: C 85.63, H 14.37; calcd for $C_{15}H_{30}$: C 85.67, H 14.58.

**4,4-Dimethyl-1-decene (1i)**: Oil. IR (neat): $\tilde{\nu} = 3076$, 2930, 1639, 1469, 1366, 912 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 0.84$ (s, 6 H), 0.88 (t, $J = 7.0$ Hz, 3 H), 1.10–1.35 (m, 10 H), 1.93 (d, $J = 7.5$ Hz, 2 H), 4.94–5.04 (m, 2 H), 5.80 ppm (ddt, $J = 9.0$, 17.5, 7.5 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): $\delta = 14.3$, 23.0, 24.2, 27.2, 30.5, 32.2, 33.3, 42.2, 46.7, 116.6, 136.2 ppm. Elemental analysis (%) found: C 85.82, H 14.67; calcd for $C_{12}H_{24}$: C 85.63, H 14.37.

**(3-Butenyl)dimethyl(pentafluorophenyl)silane (7b)**: Oil. IR (neat): $\tilde{\nu} = 2916$, 1642, 1517, 1458, 1285, 1087 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 0.41$ (dd, $J = 2.0$, 2.0 Hz, 6 H), 0.98 (t, $J = 8.5$ Hz, 2 H), 2.05–2.12 (m, 2 H), 4.90 (ddt, $J = 1.5$, 10.0, 1.5 Hz, 1 H), 4.99 (ddt, $J = 1.5$, 17.0, 1.5 Hz, 1 H), 5.84 ppm (ddt, $J = 10.0$, 17.0, 6.0 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta = -1.5$, 15.2, 27.8, 110.2, 113.7, 137.4 (dm), 140.7, 142.1 (dm), 149.2 ppm (dm); HRMS (DI-EI$^+$): *m*/*z*: observed: 280.0702 ($\Delta = -1.6$ ppm), calcd for $C_{12}H_{13}F_5Si$ [$M^+$]: 280.0707.

**(3-Butenyl)dimethyl(3-trifluoromethylphenyl)silane (7c)**: Oil. IR (neat): $\tilde{\nu} = 2959$, 1640, 1410, 1320, 1126, 1074 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 0.31$ (s, 6 H), 0.88 (t, $J = 8.5$ Hz, 2 H), 2.02–2.11 (m, 2 H), 4.90 (ddt, $J = 1.5$, 10.0, 1.5 Hz, 1 H), 4.98 (ddt, $J = 1.5$, 17.0, 1.5 Hz, 1 H), 5.86 (ddt, $J = 10.0$, 17.0, 7.5 Hz, 1 H), 7.47 (t, $J = 7.0$ Hz, 1 H), 7.60 (d, $J = 7.0$ Hz, 1 H), 7.68 (d, $J = 7.0$ Hz, 1 H), 7.72 ppm (s, 1 H); $^{13}C$ NMR ($CDCl_3$): $\delta = -3.0$, 14.8, 28.0, 113.3, 124.6 (q, $J = 271$ Hz), 125.8 (q, $J = 3.8$ Hz), 128.2, 130.1 (q, $J = 3.8$ Hz), 130.1 (q, $J = 31.5$ Hz), 137.1, 140.9, 141.3 ppm; HRMS (DI-EI$^+$): *m*/*z*: observed: 258.1051 ($\Delta = -0.1$ ppm), calcd for $C_{13}H_{17}F_3Si$ [$M^+$]: 258.1052.

**(3-Butenyl)tris(trimethylsilyl)silane (7d)**: Solid. IR (nujol): $\tilde{\nu} = 2949$, 1640, 1442, 1245, 834 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta = 0.17$ (s, 27 H), 0.81–0.89 (m, 2 H), 2.08–2.15 (m, 2 H), 4.89 (dt, $J = 10.0$, 1.5 Hz, 1 H), 4.98 (dt, $J = 17.0$, 1.5 Hz, 1 H), 5.88 ppm (ddt, $J = 10.0$, 17.0, 7.5 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): $\delta = 1.4$, 7.4, 33.3, 112.9, 142.1 ppm; HRMS (DI-EI$^+$): *m*/*z*: observed: 302.1735 ($\Delta = -1.0$ ppm), calcd for $C_{13}H_{34}Si_4$ [$M^+$]: 302.1738. M.p. 57–60 °C.

**(3-Butenyl)diphenylmethylsilane (7e)**: Oil. IR (neat): $\tilde{\nu}=3069$, 3049, 1428, 1252, 1113, 699 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.71$ (s, 3H), 1.29–1.37 (m, 2H), 2.22–2.32 (m, 2H), 5.04 (dd, $J=1.5$, 10.0 Hz, 1H), 5.14 (dd, $J=1.5$, 17.0 Hz, 1H), 5.97–6.09 (m, 1H), 7.44–7.53 (m, 6H), 7.63–7.70 ppm (m, 4H); $^{13}$C NMR (CDCl$_3$): $\delta=-4.2$, 13.4, 28.0, 113.2, 128.0, 129.4, 134.6, 137.2, 141.4 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 252.1339 ($\Delta=+1.8$ ppm), calcd for $C_{17}H_{20}Si$ [$M^+$]: 252.1334.

**Dimethyl(2-propenyl)(3-trifluoromethylphenyl)silane (9c)**: Oil. IR (neat): $\tilde{\nu}=3093$, 2961, 1631, 1600, 1321 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.32$ (s, 6H), 1.77 (ddd, $J=1.3$, 1.3, 8.0 Hz, 2H), 4.84–4.87 (m, 1H), 4.87–4.90 (m, 1H), 5.74 (ddt, $J=9.5$, 18.0, 8.0 Hz, 1H), 7.47 (t, $J=7.5$ Hz, 1H), 7.61 (d, $J=7.5$ Hz, 1H), 7.68 (d, $J=7.5$ Hz, 1H), 7.73 ppm (s, 1H); $^{13}$C NMR (CDCl$_3$): $\delta=-3.4$, 23.6, 114.2, 124.6 (q, $J=271$ Hz), 125.9 (q, $J=3.9$ Hz), 128.2, 130.2 (q, $J=31.5$ Hz), 130.2 (q, $J=3.8$ Hz), 134.1, 137.2, 140.3 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 244.0895 ($\Delta=0.0$ ppm), calcd for $C_{12}H_{15}F_3Si$ [$M^+$]: 244.0895.

**Dimethylheptyloxy(2-propenyl)silane (9d)**: Oil. IR (neat): $\tilde{\nu}=2929$, 2858, 1632, 1255, 1098 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.11$ (s, 6H), 0.88 (t, $J=7.0$ Hz, 3H), 1.21–1.34 (m, 8H), 1.47–1.56 (m, 2H), 1.62 (ddd, $J=1.0$, 1.0, 8.0 Hz, 2H), 3.58 (t, $J=7.0$ Hz, 2H), 4.83–4.92 (m, 2H), 5.79 ppm (ddt, $J=15.0$, 17.0, 8.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta=-2.3$, 14.3, 22.8, 24.6, 26.0, 29.3, 32.0, 32.9, 63.2, 113.7, 134.3 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 213.1684 ($\Delta=+4.5$ ppm), calcd for $C_{12}H_{26}OSi$ [$(M-H)^+$]: 213.1675.

**Characterization data of products**: Compounds (*E*)-**2b**,[19] (*E*)-**8a**,[20] **10a**,[21] and **10b**[22] showed the spectra identical with those shown in the literature. The assignment of *E*/*Z* geometry was performed by focusing on either the coupling constants of the vinylic protons or the chemical shifts of the terminal allylic methyl groups.[19]

***tert*-Butyldimethylsilyl (*E*)-9-undecenyl ether ((*E*)-2c)**: Oil. IR (neat): $\tilde{\nu}=2928$, 2856, 1463, 1256, 1100, 965 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.04$ (s, 6H), 0.89 (s, 9H), 1.23–1.36 (m, 10H), 1.46–1.55 (m, 2H), 1.64 (d, $J=5.0$ Hz, 3H), 1.91–2.06 (m, 2H), 3.59 (t, $J=6.5$ Hz, 2H), 5.36–5.46 ppm (m, 2H); $^{13}$C NMR (CDCl$_3$): $\delta=-5.1$, 18.1, 18.6, 26.0, 26.2, 29.3, 29.6, 29.7, 29.8, 32.8, 33.1, 65.5, 124.7, 131.9 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 284.2545 ($\Delta=+3.2$ ppm), calcd for $C_{17}H_{36}OSi$ [$M^+$]: 284.2535.

**Benzyl (*E*)-9-undecenyl ether ((*E*)-2d)**: Oil. IR (neat): $\tilde{\nu}=2927$, 2855, 1454, 1102, 965, 733 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=1.25$–1.42 (m, 10H), 1.61 (dt, $J=1.0$, 7.5 Hz, 2H), 1.64 (dd, $J=1.0$, 3.5 Hz, 3H), 1.94–2.08 (m, 2H), 3.48 (t, $J=6.5$ Hz, 2H), 4.52 (s, 2H), 5.34–5.49 (m, 2H), 7.27–7.32 (m, 1H), 7.32–7.39 ppm (m, 4H); $^{13}$C NMR (CDCl$_3$): $\delta=18.1$, 26.4, 29.3, 29.6, 29.7, 29.8, 30.0, 32.8, 70.7, 73.0, 124.7, 127.6, 127.8, 128.5, 131.8, 138.9 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 260.2141 ($\Delta=+0.5$ ppm), calcd for $C_{18}H_{28}O$ [$M^+$]: 260.2140.

**2-Oxacyclohexyl (*E*)-9-undecenyl ether ((*E*)-2e)**: Oil. IR (neat): $\tilde{\nu}=2927$, 1454, 1353, 1201, 1184, 966 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=1.22$–1.38 (m, 10H), 1.48–1.62 (m, 6H), 1.64 (dd, $J=1.0$, 4.0 Hz, 3H), 1.68–1.75 (m, 1H), 1.78–1.88 (m, 1H), 1.92–2.07 (m, 2H), 3.33–3.39 (m, 1H), 3.48 (t, $J=7.0$ Hz, 1H), 3.68–3.74 (m, 1H), 3.85 (t, $J=10.5$ Hz, 1H), 4.55 (s, 1H), 5.26–5.45 ppm (m, 2H); $^{13}$C NMR (CDCl$_3$): $\delta=19.9$, 25.7, 26.4, 29.3, 29.5, 29.6, 29.7, 29.9, 30.9, 32.7, 32.8, 62.5, 67.8, 99.0, 124.7, 131.8 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 254.2245 ($\Delta==-0.1$ ppm), calcd for $C_{16}H_{30}O_2$[$M^+$]: 254.2246.

**(*E*)-9-Undecenyl 2,4,6-trimethylbenzoate ((*E*)-2f)**: Oil. IR (neat): $\tilde{\nu}=2927$, 2855, 1725, 1612, 1435, 1266 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=1.22$–1.46 (m, 10H), 1.65 (dd, $J=1.0$, 3.0 Hz, 3H), 1.74 (dt, $J=7.0$, 15.0 Hz, 2H), 1.94–2.04 (m, 2H), 2.30 (s, 9H), 4.31 (t, $J=6.5$ Hz, 2H), 5.37–5.47 (m, 2H), 6.85 ppm (s, 2H); $^{13}$C NMR (CDCl$_3$): $\delta=18.1$, 19.9, 21.3, 26.2, 28.8, 29.2, 29.4, 29.5, 29.7, 32.7, 65.2, 124.8, 128.5, 131.4, 131.7, 135.1, 139.3, 170.5 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 316.2407 ($\Delta=+1.5$ ppm), calcd for $C_{21}H_{32}O_2$ [$M^+$]: 316.2402.

***N*-Benzyl-*N*-(*E*)-3-pentenyl-*p*-toluenesulfonamide ((*E*)-2g)**: Oil. IR (neat): $\tilde{\nu}=2920$, 1455, 1339, 1161, 1092, 656 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=1.54$ (dd, $J=1.5$, 6.5 Hz, 3H), 1.96–2.03 (m, 2H), 2.44 (s, 3H), 3.10 (t, $J=7.5$ Hz, 2H), 4.33 (s, 2H), 5.10 (dtq, $J=15.0$, 7.0, 1.5 Hz, 1H), 5.27 (dtq, $J=15.0$, 6.5, 1.0 Hz, 1H), 7.25–7.34 (m, 7H), 7.71–7.76 ppm (m, 2H); $^{13}$C NMR (CDCl$_3$): $\delta=18.1$, 21.6, 31.6, 47.9, 52.0, 127.2, 127.3, 127.6, 127.8, 128.4, 128.7, 129.8, 136.6, 137.3, 143.3 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 329.1452 ($\Delta=+0.7$ ppm), calcd for $C_{19}H_{23}NO_2S$ [$M^+$]: 329.1449.

**4-Methyl-2-tetradecene (2h, *E*/*Z*=96:4)**: Oil. IR (neat): $\tilde{\nu}=2924$, 2855, 1454, 1378, 966 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.88$ (t, $J=7.0$ Hz, 3H), 0.94 (d, $J=7.0$ Hz, 3H), 1.18–1.33 (m, 18H), 1.60 (dd, $J=1.8$, 6.8 Hz, 0.04×3H), 1.64 (dd, $J=1.8$, 6.8 Hz, 0.96×3H), 1.92–2.09 (m, 1H), 5.28 (ddq, $J=6.0$, 15.0, 1.5 Hz, 1H), 5.36 ppm (dq, $J=15.0$, 6.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$) for *E* isomer, $\delta=14.3$, 18.2, 21.0, 22.9, 27.6, 29.6, 29.8, 29.9 (two signals merge), 30.0, 32.2, 36.9, 37.4, 122.8, 138.0 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 210.2344 ($\Delta=-1.9$ ppm), calcd for $C_{15}H_{30}$ [$M^+$]: 210.2348.

**(*E*)-4,4-Dimethyl-2-decene (2i)**: Oil. IR (neat): $\tilde{\nu}=3025$, 2859, 1455, 1362, 971, 911 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.88$ (t, $J=7.0$ Hz, 3H), 0.93 (s, 6H), 1.10–1.35 (m, 10H), 1.66 (dd, $J=1.0$, 6.0 Hz, 3H), 5.28 (dq, $J=15.5$, 6.0 Hz, 1H), 5.37 ppm (dq, $J=15.5$, 1.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta=14.3$, 18.3, 22.9, 24.8, 27.6, 30.4, 32.2, 35.8, 43.6, 120.3, 141.8 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 168.1878 ($\Delta=-0.2$ ppm), calcd for $C_{12}H_{24}$ [$M^+$]: 168.1878.

**[(*E*)-2-Butenyl]dimethyl(pentafluorophenyl)silane ((*E*)-8b)**: Oil. IR (neat): $\tilde{\nu}=2962$, 1642, 1517, 1458, 1256, 1087 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.38$ (t, $J=1.5$ Hz, 6H), 1.62 (d, $J=4.5$ Hz, 3H), 1.76 (d, $J=6.0$ Hz, 2H), 5.26–5.39 ppm (m, 2H); $^{13}$C NMR (CDCl$_3$): $\delta=-2.0$, 18.2, 21.7, 110.0, 124.9, 125.6, 137.4 (dm), 142.1 (dm), 149.2 ppm (dm); HRMS (DI-EI$^+$): $m/z$: observed: 280.0702 ($\Delta=-1.8$ ppm), calcd for $C_{12}H_{13}F_5Si$ [$M^+$]: 280.0707.

**[(*E*)-2-Butenyl]dimethyl(3-trifluoromethylphenyl)silane ((*E*)-8c)**: Oil. IR (neat): $\tilde{\nu}=2960$, 1327, 1320, 1166, 1126, 841 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.32$ (s, 6H), 1.66 (d, $J=6.5$ Hz, 3H), 1.69 (d, $J=8.0$ Hz, 2H), 5.26–5.35 (m, 1H), 5.35–5.46 (m, 1H), 7.48 (t, $J=7.5$ Hz, 1H), 7.62 (d, $J=7.5$ Hz, 1H), 7.70 (d, $J=7.5$ Hz, 1H), 7.77 ppm (s, 1H); $^{13}$C NMR (CDCl$_3$): $\delta=-3.3$, 18.2, 21.5, 124.7 (q, $J=271$ Hz), 124.8, 125.8 (q, $J=3.8$ Hz), 125.9, 128.1, 130.0 (q, $J=31.5$ Hz), 130.3 (q, $J=3.8$ Hz), 137.2, 140.6 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 258.1053 ($\Delta=+0.6$ ppm), calcd for $C_{13}H_{17}F_3Si$ [$M^+$]: 258.1052.

**[(*E*)-2-Butenyl]tris(trimethylsilyl)silane ((*E*)-8d)**: Solid. IR (nujol): $\tilde{\nu}=2331$, 837, 404 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.15$ (s, 27H), 1.60 (ddt, $J=2.0$, 6.0, 2.0 Hz, 3H), 1.66 (ddq, $J=2.0$, 8.0, 2.0 Hz, 2H), 5.21–5.30 (m, 1H), 5.38–5.48 ppm (m, 1H); $^{13}$C NMR (CDCl$_3$): $\delta=1.2$, 13.0, 18.1, 122.0, 130.8 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 302.1740 ($\Delta=+0.7$ ppm), calcd for $C_{13}H_{34}Si_4$ [$M^+$]: 302.1738. M.p. 58–60 °C.

**(2-Butenyl)diphenylmethylsilane (8e, *E*/*Z*=75:25)**: Oil. IR (neat): $\tilde{\nu}=3069$, 2916, 1428, 1250, 1113, 699 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.54$ (s, 3H), 1.48 (d, $J=6.5$ Hz, 0.25×3H), 1.61 (d, $J=6.5$ Hz, 0.75×3H), 1.98 (d, $J=8.0$ Hz, 0.75×2H), 2.04 (d, $J=8.0$ Hz, 0.25×2H), 5.28–5.50 (m, 2H), 7.32–7.41 (m, 6H), 7.46–7.56 ppm (m, 4H); $^{13}$C NMR (CDCl$_3$) for *E* isomer, $\delta=-4.5$, 18.2, 20.3, 125.0, 127.9, 129.4, 134.7, 135.0, 137.1 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 252.1325 ($\Delta=-3.5$ ppm), calcd for $C_{17}H_{20}Si$ [$M^+$]: 252.1334.

**1,1,3,3-Tetramethyl-1,3-bis[(*E*)-2-butenyl]disiloxane ((*E*)-8f)**: Oil. IR (neat): $\tilde{\nu}=3015$, 2857, 1306, 1253, 1041, 798 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.05$ (s, 12H), 1.43 (d, $J=8.0$ Hz, 4H), 1.65 (dd, $J=1.5$, 6.0 Hz, 6H), 5.23–5.32 (m, 2H), 5.34–5.43 ppm (m, 2H); $^{13}$C NMR (CDCl$_3$): $\delta=0.2$, 18.3, 24.5, 123.9, 126.5 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 241.1442 ($\Delta=-0.9$ ppm), calcd for $C_{12}H_{26}OSi_2$ [$(M-H)^+$]: 241.1444.

**Dimethyl(1-propenyl)(3-trifluoromethylphenyl)silane (10c, *E*/*Z*=96:4)**: Oil. IR (neat): $\tilde{\nu}=2929$, 2855, 1620, 1319, 841 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.35$ (s, 6H), 1.72 (dd, $J=1.5$, 6.0 Hz, 0.04×3H), 1.87 (dd, $J=1.5$, 6.0 Hz, 0.96×3H), 5.66 (dq, $J=14.0$, 1.5 Hz, 0.04×1H), 5.78 (dq, $J=18.0$, 1.5 Hz, 0.96×1H), 6.17 (dq, $J=18.0$, 6.0 Hz, 0.96×1H), 6.58 (dq, $J=14.0$, 6.0 Hz, 0.04×1H), 7.46 (t, $J=7.5$ Hz, 1H), 7.60 (d, $J=7.5$ Hz, 1H), 7.70 (d, $J=7.5$ Hz, 1H), 7.75 ppm (s, 1H); $^{13}$C NMR (CDCl$_3$) for *E* isomer, $\delta=-2.5$, 22.9, 124.6 (q, $J=271$ Hz), 125.7 (q, $J=3.8$ Hz), 128.1, 128.4, 130.0 (q, $J=31.5$ Hz), 130.3 (q, $J=3.8$ Hz), 137.4, 140.9, 145.2 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 244.0899 ($\Delta=+1.7$ ppm), calcd for $C_{12}H_{15}F_3Si$ [$M^+$]: 244.0895.

**Dimethylheptyloxy[(*E*)-1-propenyl]silane ((*E*)-10d)**: Oil. IR (neat): $\tilde{\nu}=2930$, 1621, 1445, 1251, 1097, 838 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta=0.14$ (s, 6H), 0.87 (t, $J=8.0$ Hz, 3H), 1.21–1.34 (m, 8H), 1.46–1.56 (m, 2H), 1.82 (dd, $J=2.0$, 6.0 Hz, 3H), 3.55 (t, $J=7.0$ Hz, 2H), 5.65 (dq, $J=18.5$, 2.0 Hz, 1H), 6.18 ppm (dq, $J=18.5$, 6.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta=-1.7$, 14.3, 22.7, 22.8, 26.0, 29.3, 32.1, 32.9, 63.1, 129.4, 144.6 ppm; HRMS (DI-EI$^+$): $m/z$: observed: 213.1685 ($\Delta=+4.7$ ppm), calcd for $C_{12}H_{26}OSi$ $[(M-H)^+]$: 213.1675.

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[1] a) W. A. Herrmann, M. Prinz in *Applied Homogeneous Catalysis with Organometallic Compounds*, *Vol. 3*, *2nd ed.* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, Germany, **2002**, p. 1119; b) D. V. McGrath, R. H. Grubbs, *Organometallics* **1994**, *13*, 224–235 and references therein; c) H. Wakamatsu, M. Nishida, N. Adachi, M. Mori, *J. Org. Chem.* **2000**, *65*, 3966–3970 and references therein; d) M. Akita, H. Yasuda, K. Nagasuna, A. Nakamura, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 554–558.

[2] a) T. J. Donohoe, T. J. C. O'Riordan, C. P. Rosa, *Angew. Chem.* **2009**, *121*, 1032–1035; *Angew. Chem. Int. Ed.* **2009**, *48*, 1014–1017; b) M. Arisawa, Y. Terada, M. Nakagawa, A. Nishida, *Angew. Chem.* **2002**, *114*, 4926–4928; *Angew. Chem. Int. Ed.* **2002**, *41*, 4732–4734 and references cited therein; c) M. Mirza-Aghayan, R. Boukherroub, M. Bolourtchian, *Appl. Organomet. Chem.* **2006**, *20*, 214–219; d) M. Arisawa, Y. Terada, K. Takahashi, M. Nakagawa, A. Nishida, *J. Org. Chem.* **2006**, *71*, 4255–4261.

[3] a) H. Yorimitsu, K. Oshima, *Pure Appl. Chem.* **2006**, *78*, 441–449; b) H. Shinokubo, K. Oshima, *Eur. J. Org. Chem.* **2004**, 2081–2091; c) H. Someya, H. Ohmiya, H. Yorimitsu, K. Oshima, *Tetrahedron* **2007**, *63*, 8609–8618; d) H. Someya, H. Ohmiya, H. Yorimitsu, K. Oshima, *Org. Lett.* **2007**, *9*, 1565–1567; e) H. Yasui, T. Nishikawa, H. Yorimitsu, K. Oshima, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1271–1274; f) H. Hamaguchi, M. Uemura, H. Yasui, H. Yorimitsu, K. Oshima, *Chem. Lett.* **2008**, *37*, 1178–1179; g) K. Oshima, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1–24.

[4] Reviews for cobalt-catalyzed reactions: a) C. Gosmini, J.-M. Bégouin, A. Moncomble, *Chem. Commun.* **2008**, 3221–3233; b) A. Rudolph, M. Lautens, *Angew. Chem.* **2009**, *121*, 2694–2708; *Angew. Chem. Int. Ed.* **2009**, *48*, 2656-2670; c) M. Jeganmohan, C.-H. Cheng, *Chem. Eur. J.* **2008**, *14*, 10876–10886; d) W. Hess, J. Treutwein, G. Hilt, *Synthesis* **2008**, 3537–3562.

[5] T. Kobayashi, H. Ohmiya, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2008**, *130*, 11276–11277.

[6] Isomerization of 1-decene to (*E*)-2-decene catalyzed by a CO-stabilized cobalt catalyst was reported. N. Satyanarayana, M. Periasamy, *J. Organomet. Chem.* **1987**, *333*, C33–C36.

[7] a) A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534; b) L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49–54.

[8] a) L. Ackermann, *Synthesis* **2006**, 1557–1571; b) L. Ackermann, *Synlett* **2007**, 0507–0526.

[9] 1,6-Diynes were proposed to undergo oxidative addition to a low-valent cobalt-NHC complex to form cobaltacyclopentadienes: N. Saino, D. Kogure, S. Okamoto, *Org. Lett.* **2005**, *7*, 3065–3067.

[10] a) K. R. Sawyer, E. A. Glascoe, J. F. Cahoon, J. P. Schlegel, C. B. Harris, *Organometallics* **2008**, *27*, 4370–4379; b) K. Fujita, H. Yorimitsu, H. Shinokubo, K. Oshima, *J. Am. Chem. Soc.* **2004**, *126*, 6776–6778; c) R. Uma, C. Crevlsy, R. Gree, *Chem. Rev.* **2003**, *103*, 27–51; d) R. J. Batchelor, F. W. B. Einstein, R. H. Jones, J.-M. Zhuang, D. Sutton, *J. Am. Chem. Soc.* **1989**, *111*, 3468–3469 and references therein.

[11] I. Kovacs, F. Ungváry, L. Markó, *Organometallics* **1994**, *13*, 1927–1933.

[12] a) T. K. Sarkar in *Science of Synthesis (Houben-Weyl)*, *Vol. 4* (Ed.: I. Fleming), Georg Thieme Verlag, Stuttgart, **2002**, chap. 4.4.40; b) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, Hoboken, NJ, **2000**; c) L. Birkofer, O. Stuhl, *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, Hoboken, NJ, **1989**, chap. 10; d) K. Miura, A. Hosomi in *Main Group Metals in Organic Synthesis* (Eds.: H. Yamamoto, K. Oshima), Wiley-VCH, Weinheim, Germany, **2004**, chap. 10.3.

[13] Rhodium- and iridium-catalyzed isomerization leading to (*E*)-2-alkenylsilanes: I. Matsuda, T. Kato, S. Sato, Y. Izumi, *Tetrahedron Lett.* **1986**, *27*, 5747–5750.

[14] J. R. Vyvyan, J. A. Meyer, K. D. Meyer, *J. Org. Chem.* **2003**, *68*, 9144–9147.

[15] M. J. Cryle, N. J. Matovic, J. J. De Voss, *Org. Lett.* **2003**, *5*, 3341–3344.

[16] R. J. Smith, M. Pietzsch, T. Waniek, C. Syldatk, S. Bienz, *Tetrahedron: Asymmetry* **2001**, *12*, 157–165.

[17] G. Manuel, P. Mazerolles, J.-C. Florence, *J. Organomet. Chem.* **1971**, *30*, 5–19.

[18] Z. Li, X. Cao, G. Lai, J. Liu, Y. Ni, J. Wu, H. Qiu, *J. Organomet. Chem.* **2006**, *691*, 4740–4746.

[19] M. Feldhues, H. J. Schäfer, *Tetrahedron* **1985**, *41*, 4213–4235.

[20] I. Fleming, D. Higgins, N. J. Lawrence, A. P. Thomas, *J. Chem. Soc. Perkin Trans. 1* **1992**, 3331–3349.

[21] M. D. Curtis, L. Messerle, J. J. D'Errico, W. M. Butler, M. S. Hay, *Organometallics* **1986**, *5*, 2283–2294.

[22] A. Chénedé, I. Fleming, R. Salmon, M. C. West, *J. Organomet. Chem.* **2003**, *686*, 84–93.

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