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Journal of Organometallic Chemistry 692 (2007) 375–381
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Silylation and alkylation of allenes using chlorosilanes and alkyl halides in the presence of palladium catalyst and Grignard reagents

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Received 28 February 2006; accepted 6 July 2006
Available online 30 August 2006

Abstract

Allenes react with Grignard reagents and chlorosilanes in the presence of a palladium catalyst giving rise to carbosilylated products bearing carbon groups from Grignard reagents at the central carbon and silyl groups at the terminal carbon. When alkyl halides were used instead of chlorosilanes, the corresponding alkylated products were obtained.

Keywords: Palladium catalyst; Allenes; Grignard reagent; Chlorosilanes; Alkyl halides

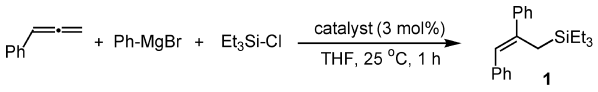
1. Introduction

Transition metal-catalyzed reactions which introduce carbon and/or silyl functionalities to C–C unsaturated compounds have been widely used for organic synthesis as useful methods for construction of organic molecules. One of our current projects is the regioselective silylation [1] and alkylation [2] of alkenes and dienes using chlorosilanes and alkyl halides by the combined use of transition metal catalysts and Grignard reagents. During the course of this study, we have found that Pd catalyzes silylation and alkylation of allenes using chlorosilanes and alkyl halides [3].

2. Results and discussions

2.1. Carbosilylation of arylallenes

A typical example is as follows. To a mixture of phenylallene (1.0 mmol), Et_3SiCl (1.3 mmol), and PhMgBr (1.3 mmol) in THF (1.3 mL) was added $Pd(dba)_2$ (dba = dibenzylideneacetone) (0.03 mmol) at 25 °C under nitrogen, and the resulting mixture was stirred for 1 h at the same temperature. The NMR analysis of the crude mixture indicated the formation of carbosilylated product **1** bearing phenyl group at the central carbon and triethylsilyl group at the terminal carbon in 92% yield and with higher than 99% regio- and stereoselectivities (Eq. (1)). The product was obtained in pure form in 67% yield by column chromatography with hexane as the eluent. In this reaction, only a trace amount of Et_3SiPh (2%) was formed as a byproduct, probably through the direct reaction of Et_3SiCl with PhMgBr. When $PdCl_2$ was used instead of $Pd(dba)_2$, **1** was obtained in 71% yield. Under the same conditions, palladium complexes bearing phosphine ligands such as $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$ and $NiCl_2$ were ineffective.



$Pd(dba)_2$	92% (*E*/*Z* = 1/99)
$PdCl_2$	71% (*E*/*Z* = 1/99)
$PdCl_2(PPh_3)_2$	2%
$Pd(PPh_3)_4$	0%
$NiCl_2$	3%

(1)

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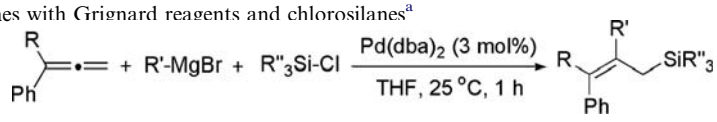
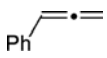
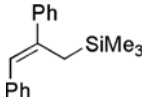
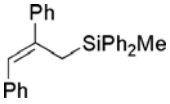
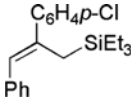
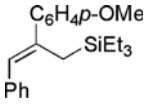
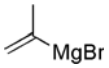
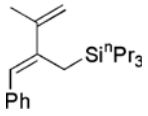
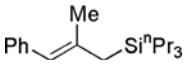
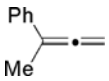
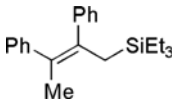
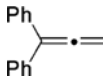
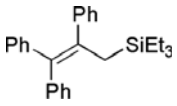
doi:10.1016/j.jorganchem.2006.08.053

Some other representative results are shown in Table 1. This reaction also proceeded efficiently when Me_3SiCl and $Ph_2MeSiCl$ were used (entries 1 and 2). Chloro and methoxy substituents on the aryl ring remained intact in this reaction system (entries 3 and 4). The use of vinyl and methyl Grignard reagents also afforded the corresponding coupling products **6** and **7** in 72% and 51% yield, respectively (entries 5 and 6) although the stereoisomers were obtained. α-Methyl and phenyl substituted phenylallenes also underwent present coupling reaction (entries 7 and 8). The reaction was sluggish with respect to alkylallenes.

Table 1
Pd-catalyzed carbosilylation of allenes with Grignard reagents and chlorosilanes[a]

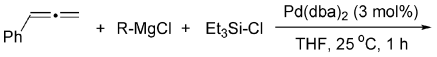


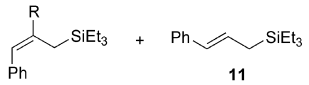
Entry	Allene	R′-MgBr	R''_3Si–Cl	Product		Yield (%)[d]	*E*/*Z*[e]
1		Ph–MgBr	Me_3Si–Cl		**2**	89	2/98
2			Ph_2MeSi–Cl		**3**	82 (68)	2/98
3		*p*-Cl–C_6H_4–MgBr	Et_3Si–Cl		**4**	90 (80)	1/99
4		*p*-OMe–C_6H_4–MgBr	Et_3Si–Cl		**5**	87 (75)	1/99
5[b]			$^nPr_3Si$–Cl		**6**	(72)	30/70
6[b]		Me–MgBr	$^nPr_3Si$–Cl		**7**	53 (51)	84/16
7[c]		Ph–MgBr	Et_3Si–Cl		**8**	84 (72)	93/7
8		Ph–MgBr	Et_3Si–Cl		**9**	50 (38)	

[a] The reaction was carried out unless otherwise stated in THF at 25 °C for 1 h using arylallene (1.0 mmol), Grignard reagent (1.3 mmol), chlorosilane (1.3 mmol), chlorosilane (1.3 mmol), and $Pd(dba)_2$ (0.03 mmol).
[b] Grignard reagent and chlorosilane were used in 1.5 mmol.
[c] The reaction was carried out for 9 h.
[d] NMR yield. Isolated yield is in parentheses.
[e] Determined by GC.

2.2. Hydrosilylation of arylallenes

When *n*-butyl Grignard reagent was used, expected carbosilylated product **10a** was obtained in 76% yield along with 8% yield of hydrosilylated product **11** (Eq. (2)). *s*-Butyl Grignard reagent gave nearly 1:1 mixture of **10b** and **11**. Hydrosilylated product was predominantly obtained when *t*-butyl Grignard reagent was employed. The yields of **11** increase in the order of primary < secondary < tertiary reflecting the number of β-hydrogens.



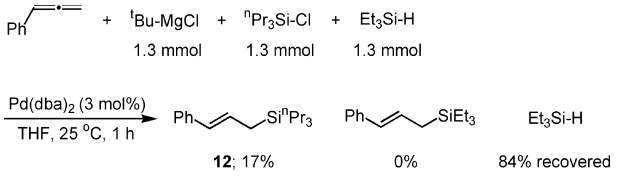


(2)

entry	R	Yield	
1	*n*-Bu	**10a**: 76% [*E*/*Z* = 4/96]	8%
2	*s*-Bu	**10b**: 30% [*E*/*Z* = 0/100]	36%
3	*t*-Bu	**10c**: 2%	62%

We carried out control experiments in order to prove the hydrogen source for the formation of **11**. When the reaction mixture of Eq. (2) using *t*-BuMgCl was quenched with D_2O before work-up, deuterated **11** was not obtained at all. This result would rule out the formation of silylmagnesation intermediates.

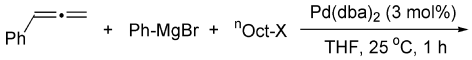
Since it is known that a palladium complex catalyzes hydrosilylation of allenes to give allylsilanes [4], we next examined whether a similar hydrosilylation process is involved in the present reaction. When a reaction similar to that in entry 3 of Eq. (2) was carried out in the presence of $^{n}Pr_3SiCl$ and Et_3SiH, only **12** having $^{n}Pr_3Si$ group was obtained as silylated product and 84% of Et_3SiH was recovered (Eq. (3)). These results suggest that hydrogen would be derived from alkyl group of Grignard reagents.

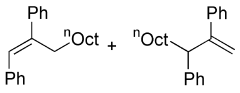


(3)

2.3. Arylalkylation of arylallenes

Use of 1-bromooctane instead of chlorosilanes yielded three component coupling products **13a** and **13b** in 24% and 51% yields, respectively (Eq. (4)). Under the same conditions, 1-chlorooctane gave low yields of coupling products. It should be noted that the present reaction proceeds efficiently in the case of alkyl fluorides with superior yields and regioselectivities compared with other halides [5].





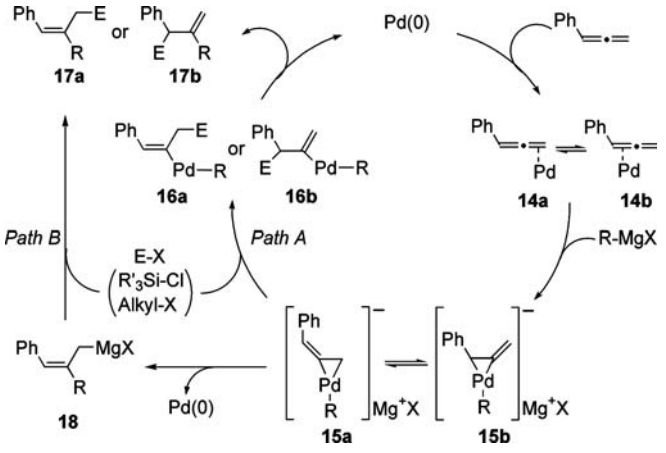
(4)

X = Br	24%	51%
X = Cl	6%	19%
X = F	11%	73%

2.4. Reaction mechanisms

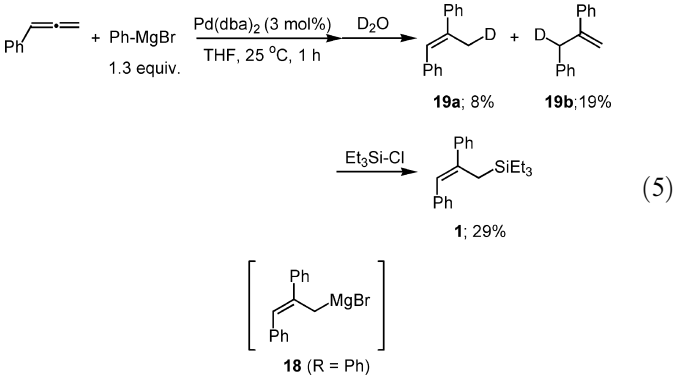
Although the detailed mechanism of present coupling reaction has not been clarified yet, plausible reaction pathways are shown in Scheme 1. The reaction of $Pd(dba)_2$ with arylallenes affords allene-palladium complexes **14** [6], which reacts with Grignard reagents to give palladate complexes **15** [7]. Direct reaction of palladate complexes **15** with chrolosilanes or alkyl halides at terminal or benzylic carbon leads to palladium (II) complexes **16** (Path A). The subsequent reductive coupling of these palladium (II) complexes **16** gives silylated or alkylated products **17** and regenerates Pd(0) to complete the catalytic cycle. Alternatively, transmetallation of **14** with Grignard reagents via **15** gives carbomagnesation product **18**, which is trapped with chlorosilanes or alkyl halides to afford **17** (Path B). Silyl groups are introduced regioselectively at the terminal position of intermediates **15** or **18** due probably to the steric effect. When alkyl Grignard reagents are used, β-hydrogen elimination of **16** leading to hydrosilylation products predominates over the reductive coupling to form **17**.

In order to confirm the validity of the plausible reaction pathways, we first tested the intermediary of carbomagnesation products **18**, which may be formed by addition of Grignard reagents toward allenes, since it is known that transition metal catalyzes carbometalation of allenes with organometallic reagents [8]. A reaction of phenylallene with phenyl Grignard reagent was carried out in the presence of $Pd(dba)_2$ under identical conditions to those of



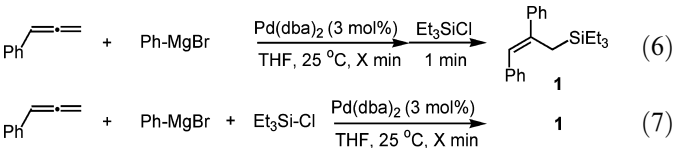
Scheme 1. Plausible pathways.

Eq. (1). Quenching the reaction mixture with D_2O gave a 30:70 mixture of arylated compounds (**19a**, **19b**) which contain a deuterium at an allylic position in 27% total yield (Eq. (5)). When reaction mixture was treated with Et_3SiCl instead of D_2O, 29% yield of carbosilylated product **1** was obtained. These results suggest the formation of carbomagnesation product **18** (R = Ph) in the present reaction, although Path B (**18** → **17**) may not be the major pathway due to the low yields of the trapped products.



(5)

Next, we examined the time course of the Pd-catalyzed reaction of phenylallene with phenyl Grignard reagent in the absence (Eq. (6)) and presence (Eq. (7)) of Et_3SiCl. Into a mixture of phenylallene (0.5 mmol) and PhMgBr (0.65 mmol) was added $Pd(dba)_2$ (0.015 mmol) and the mixture was stirred for 1, 3, 5, 7, 10 or 15 min. After trapping the formed product with Et_3SiCl at 25 °C for 1 min, the reaction was quenched with 1 N HCl. The yield of **1** for the reaction of Eq. (6) was plotted in Fig. 1 together with the result of the catalytic reaction depicted in Eq. (7) where the reaction was carried out in the presence of Et_3SiCl and quenched directly with 1 N HCl. The evidence that the yield of **1** increases linearly indicates that the rate of formation of **1** is independent on the concentration of substrates and that the reductive elimination from **16** can be the rate determining step if the reaction follows Path A. On the other hand, forming rate of **1** in Eq. (6) decreased against reaction time. At any stage of the reaction, **1** was formed more efficiently in the catalytic system than in Eq. (6). These results would indicate that the palladate complexe **15** is the active catalytic species and is more reactive than **18**.



(6)

(7)

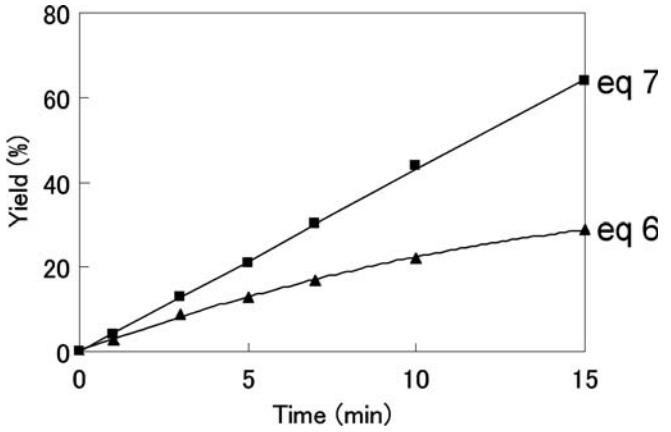


Fig. 1. Time course of the formation of **1** in Eqs. 6 and 7.

3. Conclusion

In conclusion, a new method for palladium catalyzed silylation or alkylation of arylallenes has been developed. This study provides the first example of a C–Si and C–C bond forming reaction of allenes using chlorosilanes and alkyl halides. Mechanistic details including the specific features of the palladate complex are currently under investigation.

4. Experimental

^1H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were recorded with a Perkin–Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass spectra (EI) were obtained using a JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. HPLC separations were performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent. Column chromatography was conducted using Kanto Chemical Co., Inc. silica gel 60 (63–210μm). Elemental analyses were performed on a Perkin–Elmer 240C apparatus. GC yields were determined using decane as an internal standard. Grignard reagents (Kanto Chemical Company), triethylchlorosilane, triethylsilane (Shin-Etsu Chemical Company), trimethylchlorosilane, tripropylchlorosilane, methyldiphenylchlorosilane, octyl fluoride (Aldrich Chemical Company), octyl chloride, octyl bromide, D_2O (Wako Pure Chemical Industries), $Pd(dba)_2$ (Tokyo Chemical Industry Company) were purchased and used as received. Phenylallenes were prepared according to the literature [9].

4.1. Typical procedure for palladium-catalyzed carbosilylation of phenylallene using phenyl Grignard reagent and triethylchlorosilane (Eq. (1))

To a mixture of phenylallene (114.5 mg, 0.985 mmol), triethylchlorosilane (0.22 mL, 1.3 mmol) and Ph–MgBr (1.0 M in THF, 1.3 mL, 1.3 mmol) was added $Pd(dba)_2$ (17.3 mg, 0.03 mmol) at 25 °C under nitrogen. After

stirring for 1 h, aqueous 1 N HCl was added and the products were extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated to give yellow crude products (92% yield according to NMR spectroscopy). Purification by column chromatography on silica gel with hexane as the eluent afforded 204 mg (67%) of **1**.

4.2. Spectral data

4.2.1. (*Z*)-1,2-Diphenyl-3-triethylsilyl-1-propene (*1*)

IR (NaCl): 3055, 3022, 2952, 2874, 1598, 1494, 1456, 1446, 1414, 1237, 1156, 1004, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.19 (m, 10H), 6.51 (s, 1H), 2.33 (s, 2H), 0.76 (t, $J = 8.0$ Hz, 9H), 0.34 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 145.1, 141.5, 138.7, 128.6, 128.0, 126.9, 126.7, 125.9, 125.52, 125.50, 17.0, 7.4, 4.1; MS (EI) *m*/*z* (relative intensity, %): 308 (M^+, 38), 279 (6), 116 (11), 115 (100), 107 (6), 88 (7), 87 (70), 59 (22); HRMS calcd for $C_{21}H_{28}Si$: 308.1960, found 308.1965; Anal. Calc. for $C_{21}H_{28}Si$: C, 81.75; H, 9.15. Found: C, 81.48; H, 9.21%.

4.2.2. (*Z*)-3-Methyldiphenylsilyl-1,2-diphenyl-1-propene (*3*)

IR (KBr): 3051, 3023, 2959, 1612, 1598, 1491, 1445, 1427, 1254, 1151, 1110, 989, 833, 789, 766, 735, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.09 (m, 20H), 6.57 (s, 1H), 2.84 (s, 2H), 0.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.2, 139.9, 138.2, 136.5, 134.3, 129.0, 128.5, 127.96, 127.95, 127.5, 127.0, 126.81, 126.75, 126.0, 19.5, −3.5; MS (EI) *m*/*z* (relative intensity, %): 390 (M^+, 10), 199 (5), 198 (19), 197 (100), 181 (2), 165 (2), 119 (2), 105 (4); HRMS calcd for $C_{28}H_{26}Si$: 390.1804, found 390.1801; Anal. Calc. for $C_{28}H_{26}Si$: C, 86.10; H, 6.71. Found: C, 85.81; H, 6.63%.

4.2.3. (*Z*)-2-(4-Chlorophenyl)-1-phenyl-3-triethylsilyl-1-propene (*4*)

IR (NaCl): 3055, 3024, 2953, 2874, 1618, 1598, 1494, 1456, 1414, 1237, 1156, 1093, 1014, 818, 747, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.20 (m, 9H), 6.49 (s, 1H), 2.29 (s, 2H), 0.77 (t, $J = 8.0$ Hz, 9H), 0.34 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 140.3, 138.4, 132.6, 128.6, 128.12, 128.07, 127.9, 126.1, 126.0, 16.9, 7.4, 4.1; MS (EI) *m*/*z* (relative intensity, %): 342 (M^+, 19), 313 (3), 117 (4), 116 (13), 115 (100), 88 (7), 87 (74), 59 (25); HRMS calcd for $C_{21}H_{27}ClSi$: 342.1571, found 342.1568; Anal. Calc. for $C_{21}H_{27}ClSi$: C, 73.54; H, 7.93. Found: C, 73.47; H, 7.89%.

4.2.4. (*Z*)-2-(4-Methoxyphenyl)-1-phenyl-3-triethylsilyl-1-propene (*5*)

IR (NaCl): 3021, 2952, 2874, 1607, 1510, 1464, 1415, 1285, 1247, 1179, 1038, 1004, 824, 749, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.34 (m, 6H), 7.22–7.16 (m, 1H), 6.88 (d, $J = 8.4$ Hz, 2H), 6.47 (s, 1H), 3.83 (s, 3H), 2.30 (s, 2H), 0.77 (t, $J = 8.0$ Hz, 9H), 0.35 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.6, 140.9, 138.9, 137.5, 128.6, 128.0, 127.7, 125.7, 124.4, 113.3, 55.3, 16.9, 7.4, 4.1; MS (EI) *m*/*z* (relative intensity, %): 338 (M^+, 52), 310 (2), 309 (7), 137 (6), 117 (7), 116 (12), 115 (100), 88 (8), 87 (86), 59 (29); HRMS calcd for $C_{22}H_{30}OSi$: 338.2066, found 338.2068.

4.2.5. (*Z*)-3-Methyl-1-phenyl-2-[(tripropylsilyl)methyl]-1,3-butadiene (*6*)

IR (NaCl): 3023, 2954, 2924, 2867, 1603, 1460, 1409, 1373, 1332, 1203, 1150, 1068, 1005, 888, 840, 743, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.14 (m, 5H), 6.50 (s, 1H), 5.12 (s, 1H), 5.04 (s, 1H), 2.07 (s, 2H), 2.03 (s, 3H), 1.21–1.11 (m, 6H), 0.86 (t, $J = 7.2$ Hz, 9H), 0.43–0.39 (m, 6H); NOE difference measurement: irradiation of vinyl proton at δ 6.50 caused 8.5% enhancement of methyl protons at δ 2.03, irradiation of methyl protons at δ 2.03 caused 5.2% enhancement of vinyl proton at δ 6.50; ^{13}C NMR (100 MHz, $CDCl_3$): 145.2, 140.7, 139.1, 128.8, 127.9, 125.8, 124.0, 113.2, 21.8, 20.2, 18.8, 17.4, 16.2; MS (EI) *m*/*z* (relative intensity, %): 314 (M^+, 26), 158 (11), 157 (84), 145 (8), 116 (14), 115 (100), 87 (21), 73 (38), 59 (11), 45 (16); HRMS calcd for $C_{21}H_{34}Si$: 314.2430, found 314.2437.

4.2.6. (*E*)-2-Methyl-1-phenyl-3-tripropylsilyl-1-propene (*7*)

IR(NaCl): 3022, 2954, 2925, 2868, 1640, 1493, 1454, 1409, 1374, 1333, 1202, 1158, 1068, 1008, 816, 743, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.12 (m, 5H), 6.13 (s, 1H), 1.87 (d, $J = 1.2$ Hz, 3H), 1.84 (d, $J = 0.8$ Hz, 2H), 1.30–1.20 (m, 6H), 0.90 (t, $J = 7.2$ Hz, 9H), 0.52–0.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 139.2, 137.7, 128.4, 127.9, 125.2, 122.6, 27.6, 19.7, 18.8, 17.5, 16.3; MS (EI) *m*/*z* (relative intensity, %): 288 (M^+, 17), 245 (4), 161 (5), 159 (6), 158 (12), 157 (82), 116 (12), 115 (100), 87 (21), 73 (39), 59 (13), 45 (15); HRMS calcd for $C_{19}H_{32}Si$: 288.2273, found 288.2283; Anal. Calc. for $C_{19}H_{32}Si$: C, 79.09; H, 11.18. Found: C, 79.01; H, 11.26%.

4.2.7. (*E*)-2,3-Diphenyl-1-triethylsilyl-2-butene (*8*)

IR (NaCl): 3055, 3019, 2952, 2874, 1599, 1489, 1442, 1414, 1236, 1159, 1017, 967, 762, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.06–6.91 (m, 10H), 2.13 (s, 3H), 2.10 (s, 2H), 0.82 (t, $J = 0.8$ Hz, 9H), 0.40 (t, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.9, 144.3, 135.8, 129.7, 129.3, 129.2, 127.22, 127.16, 125.4, 125.0, 21.9, 21.7, 7.4, 4.2; MS (EI) *m*/*z* (relative intensity, %): 322 (M^+, 29), 293 (7), 116 (12), 115 (100), 107 (5), 88 (8), 87 (78), 59 (26); HRMS calcd for $C_{22}H_{30}Si$: 322.2117, found: 322.2112; Anal. Calc. for $C_{22}H_{30}Si$: C, 81.92; H, 9.37. Found: C, 81.92; H, 9.28%.

4.2.8. 3-Triethylsilyl-1,1,2-triphenyl-1-propene (*9*)

IR(KBr): 3053, 3020, 2950, 2873, 1598, 1492, 1442, 1413, 1237, 1191, 1072, 1019, 762, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35–6.88 (m, 15H), 2.04 (s, 2H), 0.77 (t, $J = 8.0$ Hz, 9H), 0.33 (q, $J = 8.0$ Hz, 6H); ^{13}C

NMR (100 MHz, $CDCl_3$): 143.6, 143.5, 143.1, 138.6, 136.2, 130.6, 129.6, 129.5, 128.0, 127.4, 127.1, 126.1, 126.0, 125.2, 22.0, 7.5, 4.2; MS (EI) *m*/*z* (relative intensity, %): 384 (M^+, 34), 355 (4), 191 (5), 116 (11), 115 (100), 107 (7), 91 (6), 88 (6), 87 (66), 59 (22); HRMS calcd for $C_{27}H_{32}Si$: 384.2273, found: 384.2282.

4.2.9. (*Z*)-1-Phenyl-2-[(triethylsilyl)methyl]-1-hexene (**10a**)

IR (NaCl): 3055, 3022, 2952, 2930, 2873, 1636, 1598, 1492, 1465, 1414, 1238, 1156, 1016, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.22 (m, 4H), 7.15–7.12 (m, 1H), 6.12 (s, 1H), 2.11 (t, $J = 7.2$ Hz, 2H), 1.86 (s, 2H), 1.55–1.47 (m, 2H), 1.37 (qt, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.2$ Hz, 3H), 0.86 (t, $J = 8.0$ Hz, 9H), 0.51 (q, $J = 8.0$ Hz, 6H); NOE difference measurement: irradiation of vinyl proton at δ 6.12 caused 5.4% enhancement of methylene protons at δ 2.11 (–CH_2–^{n}Pr), irradiation of methylene protons at δ 2.11 (–CH_2–^{n}Pr) caused 5.3% enhancement of vinyl proton at δ 6.12; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 139.3, 128.5, 127.9, 125.2, 121.8, 40.1, 30.8, 22.7, 16.8, 14.3, 7.5, 4.4; MS (EI) *m*/*z* (relative intensity, %): 288 (M^+, 16), 259 (4), 117 (4), 116 (11), 115 (100), 88 (6), 87 (68), 59 (19); HRMS calcd for $C_{19}H_{32}Si$: 288.2273, found: 288.2277; Anal. Calc. for $C_{19}H_{32}Si$: C, 79.09; H, 11.18. Found: C, 78.80; H, 11.03%.

4.2.10. (*Z*)-3-Methyl-1-phenyl-2-[(triethylsilyl)methyl]-1-pentene(**10b**)

IR (NaCl): 3056, 3022, 2956, 2874, 1636, 1598, 1494, 1460, 1415, 1377, 1238, 1154, 1017, 749, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.22 (m, 4H), 7.14–7.11 (m, 1H), 6.09 (s, 1H), 2.01–1.91 (m, 2H), 1.78 (d, $J = 13.2$ Hz, 1H), 1.68–1.58 (m, 1H), 1.46–1.35 (m, 1H), 1.12 (d, $J = 6.8$ Hz, 3H), 0.93 (t, $J = 7.2$ Hz, 3H), 0.85 (t, $J = 8.0$ Hz, 9H), 0.85 (q, $J = 8.0$ Hz, 6H); NOE difference measurement: irradiation of vinyl proton at δ 6.09 caused 5.7% enhancement of methyl protons at δ 1.12 (CH_3-CH), irradiation of methyl protons at δ 1.12 (CH_3-CH) caused 2.7% enhancement of vinyl proton at δ 6.09; ^{13}C NMR (100 MHz, $CDCl_3$): 146.7, 139.5, 128.6, 127.8, 125.1, 119.5, 42.9, 29.3, 19.4, 17.7, 12.2, 7.5, 4.4; MS (EI) *m*/*z* (relative intensity, %): 288 (M^+, 16), 259 (4), 117 (4), 116 (11), 115 (100), 88 (6), 87 (65), 59 (19); HRMS calcd for $C_{19}H_{32}Si$: 288.2273, found: 288.2280; Anal. Calcd for $C_{19}H_{32}Si$: C, 79.09; H, 11.18. Found: C, 78.80; H, 11.15%.

4.2.11. (*E*)-1-Phenyl-3-tripropylsilyl-1-propene (**12**)

IR (NaCl): 2954, 2867, 1641, 1599, 1496, 1460, 1408, 1332, 1146, 1067, 960, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.10 (m, 5H), 6.24–6.21 (m, 2H), 1.68 (m, 2H), 1.36 (tq, $J = 7.3$, 7.1 Hz, 6H), 0.96 (t, $J = 7.1$ Hz, 9H), 0.58–0.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 128.3, 128.0, 127.9, 126.0, 125.3, 20.2, 18.8, 17.6, 15.3; MS (EI) *m*/*z* (relative intensity, %): 274 (M^+, 13), 157 (90), 115 (100), 87 (24), 73 (43); HRMS calcd for $C_{18}H_{30}Si$: 274.2117, found: 274.2108; Anal. Calc. for $C_{18}H_{30}Si$: C, 78.75; H, 11.02. Found: C, 78.58; H, 10.92%.

4.2.12. (*E*)-1,2-Diphenyl-1-undecene (**13a**)

IR (NaCl): 3053, 3021, 2954, 2854, 1598, 1494, 1465, 1443, 1074, 1029, 918, 759, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.23 (m, 10H), 6.69 (s, 1H), 2.69 (t, $J = 7.6$ Hz, 2H), 1.45–1.38 (m, 2H), 1.28–1.21 (m, 12H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 142.9, 138.2, 128.6, 128.2, 128.1, 127.9, 126.9, 126.4, 126.3, 32.0, 30.3, 29.8, 29.6, 29.5, 29.4, 28.8, 22.8, 14.3; MS (EI) *m*/*z* (relative intensity, %): 306 (M^+, 100), 194 (93), 193 (84), 179 (43), 178 (38), 129 (14), 117 (21), 116 (40), 115 (70), 103 (13), 91 (68); HRMS calcd for $C_{23}H_{30}$: 306.2348, found: 306.2352.

4.2.13. 2,3-Diphenyl-1-undecene (**13b**)

IR (NaCl): 3080, 3023, 2924, 2852, 1626, 1600, 1493, 1451, 1074, 1028, 899, 777, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.13 (m, 10H), 5.37 (s, 1H), 5.17 (s, 1H), 3.75 (t, $J = 7.6$ Hz, 1H), 1.93–1.85 (m, 1H), 1.81–1.73 (m, 1H), 1.43–1.22 (m, 12H), 0.86 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 143.5, 142.5, 128.03, 127.95, 127.8, 126.9, 126.6, 125.9, 113,0 50.5, 35.3 32.0, 29.8, 29.6, 29.4, 28.1, 22.8, 14.3; MS (EI) *m*/*z* (relative intensity, %): 306 (M^+, 10), 195 (16), 194 (100), 193 (45), 179 (14), 178 (14), 117 (9), 115 (31), 105 (9), 103 (9), 91 (45); HRMS calcd for $C_{23}H_{30}$: 306.2348, found: 306.2343; Anal. Calc. for $C_{23}H_{30}$: C, 90.13; H, 9.87. Found: C, 89.88; H, 9.60%.

4.2.14. CAS registry numbers of other compounds known in the literature

Compound **2**, 221280-63-3 and Compound **11**, 63522-98-5.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (Nos. 15036241 and 16033237, "Reaction Control of Dynamic Complexes") from Ministry of Education, Culture, Sports, Science and Technology, Japan and Industrial Technology Research Grant Program in 2006 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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