[2 + 1] Carbenoid Insertion Reaction of Fischer Carbene Complexes with Silanes: A Synthesis of Allylsilanes

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Fischer carbene complexes undergo mild insertion reactions with organosilanes to give methoxysilanes in good yields. The effects of catalysts, solvents, and metals have been investigated. The insertion reactions of alkenyl carbene complexes provide a convenient route for the synthesis of allylsilanes.

Introduction

Fischer carbene complexes have been shown to be versatile synthetic reagents in organic synthesis in promoting cycloaddition reactions and metal-mediated reactions.[1] One aspect of the metal-mediated reactions of Fischer carbene complexes is the carbenoid [2 + 1] insertion reaction into Sn—H,[2] Si—H,[3] C—H,[4] and C—C[5] bonds. The applications of the insertion reactions in organic synthesis, however, have not been fully investigated. Given the mild and neutral reaction conditions of these insertion reactions,[3] a facile entry into valuable organic intermediates could be developed. Until recently, studies have been concentrated only on the aryl carbene complexes (eq 1).[3] By virtue of these advantages, this strategy can be extended to the alkenylcarbene complexes in the insertion with silanes so as to elaborate the preparative methods and categories of allylsilanes.
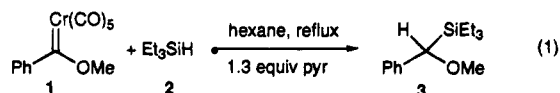
The use of allylsilanes as reagents and as intermediates in organic synthesis[6] has become a field of considerable importance, especially for C—C bond formation *via* the reaction with electrophiles. Although such chemistry of allylsilanes was recognized more than 40 years ago by Sommer and Whitmore,[7] the real impact of the allylsilane was disclosed around the mid 1970s as a result of the pioneering research efforts of Calas,[8] Corriu,[9] Sakurai,[10]

and Fleming.[11] There are, in general, two important reactions involving allylsilanes. One is the C—C bond formation *via* regiospecific reactions with carbon electrophiles. The other is [3 + 2] annulation strategy for the synthesis of 5-membered carbocycles or heterocycles with the allylsilane serving as a 3-carbon component.[12]

Allylsilanes can be synthesized mainly from the silylation of the allyllithiums or magnesiums.[11b] A recent report on the cross-coupling of vinyl triflates[13] with tris-(trimethylsilylmethyl)aluminum catalyzed by Pd(0) adds an efficient and chemoselective route to allylsilanes since the functionalities on the vinyl triflates remain intact even with excess alane reagent. Apart from the above methods, there are still other preparative methods[14] for the synthesis of allylsilanes. However, most of them involve very harsh conditions and strict temperature control, and some of the procedures are not simple. Furthermore, the availability of the starting material may be a problem. Therefore, the insertion pathway to allylsilanes *via* alkenyl Fischer carbene complexes may add a facile alternative. We now report our full report in applying the [2 + 1] insertion of alkenyl Fischer carbene complexes with triorganosilanes to give allylsilanes in good yields.[15]

Results and Discussion

Effect of Catalysts. We first examined the insertion reaction of phenyl carbene complex **1** with silane **2** to search the optimum reaction condition. Complex **1** has been reported by Connor[3b] to react with triethylsilane in hexane in the presence of pyridine (1.3 equiv) to give (α-methoxybenzyl)triethylsilane (**3**) in 82% yield. The effects of the catalyst were then examined. Catalytic amounts of chloroplatinic acid, dirhodium tetraacetate, and tetrakis(triphenylphosphine)palladium(0) increased the reaction rate slightly and almost to the same extent but had varying effects on the yields. The most efficient catalyst was dirhodium tetraacetate which gave the yield of the reaction comparable to the reaction without the catalyst (Table 1). Since the catalytic effect was not drastic, the insertion was best performed without catalyst.

Effect of Metals (Table 2). The effect of metal of aryl carbene **1** follows the reactivity reported by Fischer with

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Table 1. Effect of Catalyst on the Insertion Complex 1 with 2
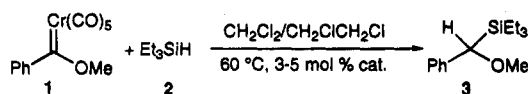
catalyst	in CH_2Cl_2		in CH_2ClCH_2Cl	
	time/h	% yield	time/h	% yield
H_2PtCl_6	1.5	49	1	48
$Rh_2(OAc)_4$	1	67	3/4	75
$Pd(Ph3P)_4$	1	25		
none	3	65	2	64

Table 2. Effect of Metal on the Insertion Reaction of Aryl Complex
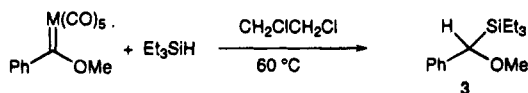
M	time	% yield
Cr, 1	2 h	65
Mo, 4	1/2 h	60
W, 5	12 d	15

Table 3. Effect of Solvent on the Insertion Reaction of Aryl Complex
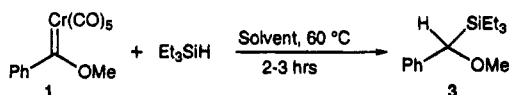
solvent	time	% yield
THF	3	58
CH_3CN	2.5	62
CH_2Cl_2	3	65
CH_2ClCH_2Cl	2	64
hexane	3	93
toluene	2	95
benzene	2.5	94

the reactivity order as follows: Mo > Cr ≫ W. This trend parallels the rate of CO dissociation of group 6 metal carbonyl.[16] The same reactivity pattern was also observed in styryl carbene complexes **6** and **7** to give allylsilane **8** with the Cr complex much more reactive than the W complex, though the yields differed little (eq 2).
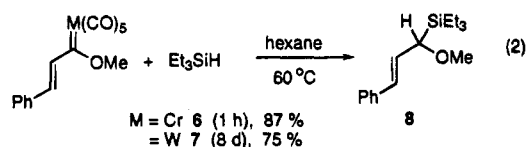
Effect of Solvents (Table 3). The insertion reaction of complex 1 with triethylsilane (2) was studied in both coordinating polar and noncoordinating nonpolar solvents at 60 °C. The best solvents were found to be the noncoordinating and nonpolar solvents: hexane, toluene and benzene. It is likely that coordinating solvents compete with triethylsilane for the electrophilic carbene carbon, thus lower yields due to side reactions and longer reaction time resulted.[17] Hexane was concluded to be the solvent of choice due to its lower boiling point.

For alkenyl carbene complexes, faster rates and higher yields were similarly observed in noncoordinating sol-

Table 4. Effect of Solvent on the Insertion of Alkenyl Complex
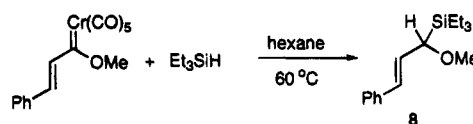
solvent	time	% yield
THF	7 d	trace
CH_3CN	7 h	6
CH_2ClCH_2Cl	20 h	41
hexane	45 min	66
hexane/CO	44 h	12
benzene	45 min	66

vents such as hexane and benzene. In polar coordinating solvents such as THF and CH_3CN, the yields of allylsilane **8** were below 10% (Table 4). These coordinating ligands reduced the rate of reaction of silane with carbene complexes, probably by forming weak complexes with the CO-dissociated tetracarbonyl carbene complex.[17-19] Consistent with this rationale, only 12% of allylsilane **8** was isolated in hexane under 1 atm of CO which reduced the equilibrium concentration of the tetracarbonyl complex.[18] Added pyridine did not increase neither the rate nor the yield significantly.[3] In summary, the optimum insertion reaction was found to be in hexane without additives.

Synthesis of Allylsilane. Alkenyl carbene complexes were all prepared from literature methods directly from alkenyllithiums **6**, **9**, and **10** (eq 3),[20,21] via 1,4-addition of MeOH to alkynyl complex **11**[22] (eq 4) and the Diels—Alder reactions of cyclopentadiene with alkynyl complexes **11** and **13** (eq 5).[23]
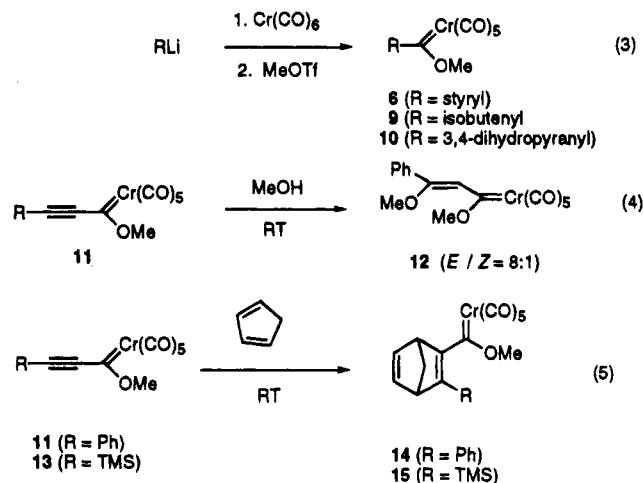
The alkenyl carbene complexes all underwent smooth insertion reaction with triethylsilane (2) in hexane at 60 °C to give allylsilanes (Table 5). The reaction is chemoselective at the metal—carbene bond without any significant hydrosilyation at the alkenyl site. The insertion is

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Table 5. Insertion of Alkenyl Fischer Carbene Complexes with Silanes

R	R′	reaction time	product	% yield
6	Et	1 h	8	68
9	Et	25 min	16	57
10	Et	30 min	17	47
12	Et	15 h	18	63
14	Et	20 h	19	40[a]
15	Et	7 h	20	69[b]
6	Ph	30 min	21	87
9	Ph	30 min	22	64

[a] Mixtures of diastereoisomers. [b] Mixtures of diastereoisomers and *exo* double bond isomers.

Table 6. Chemical Shift (δ/ppm) of the Methoxy Methine Proton in Allylsilanes

entry	allylsilane	R_3Si (R =)	δ/ppm
1	8	Et	3.74
2	16	Et	3.75
3	17	Et	4.20
4	18	Et	3.60
5	19a,b	Et	4.29, 4.21
6	20a–c[a]	Et	4.00, 3.98, 1.45
7	21	Ph	4.46
8	22	Ph	4.42

[a] 20c is a vinylsilane.

stereospecific with the retention of the *E* geometry of the double bond for complex **6** as evidenced from the *trans* coupling constant of **8** (16.0 Hz) supporting the likely concertedness of the reaction.[2,17]

The use of triphenylsilane instead of triethylsilane increased the rate by about 10 times and the yields of reaction by 20%. The reaction took only 30 min at 60 °C. Despite earlier kinetic studies by Connors that Et₃SiH is more reactive than Ph₃SiH, the better hydrolytic stability of the triphenylsilane might account for the higher yields.

Both sterically bulky complexes **14** and **15** and the more electron rich β-methoxy carbene complex **12** were slower in the rate of the insertion presumably due to the steric hindrance and the decrease in electrophilicity of the carbene carbon respectively as evidenced by the carbene carbon chemical shifts.[20,24] However, for strained carbene complexes **14** and **15**, we observed some double-bond isomerization to *exo*-cyclic olefins forming alkenyl silanes probably due to the release of ring strain of the bicyclic skeletons.

According to Table 5, alkenyl carbene complexes **6**, **9**, and **10** underwent [2 + 1] insertion reactions with much faster rates than the alkenyl carbene complexes **12**, **14**, and **15**. The rate difference may be attributed to the electronic and steric effects on the carbene complexes. For the carbene complex **12**, the electron-donating β-methoxy group may decrease the electrophilicity of the carbene carbon and also the rate of the insertion reaction.[20,22] On the other hand, the alkenyl carbene complexes **14** and **15** are sterically bulky, thus the carbene carbon on these two carbene complexes may be less susceptible to nucleophilic attack by the triorganosilanes.

The allylsilanes were easily identified by the characteristic methoxy methine proton resonances (Table 6). Replacement of Ph₃Si by the Et₃Si group (allylsilane **8** and **21** or **16** and **22**) results in a downfield shift of the methine proton resonance from 3.74 to 4.46 ppm in a

manner consistent with the greater positive inductive effect of the allyl group.

For the alkenyl carbene complexes **14** and **15**, more than one insertion product was found for the reaction with triethylsilane (Table 6) (entries 5 and 6). In fact, for the carbene complex **14** (entry 5), a mixture of two diastereomers, allylsilanes **19a** and **19b**, was produced after the insertion reaction (eq 6) as demonstrated by the appearance of two methine proton resonances.

$$(6)$$
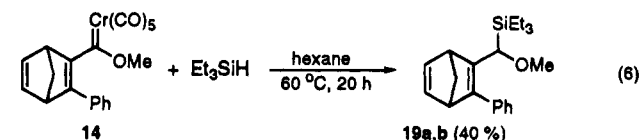
Similarly, carbene complex **15** also gave two diastereomers, allylsilanes **20a** and **20b**, with two different methine proton resonances. However, the additional isomer **20c** (Table 6) (entry 6) was produced after the insertion reaction and the ratio of isomer **20c** to the diastereomers **20a** and **20b** was 5:1 (eq 7). According to the ¹H NMR spectrum, this isomer does not have a similar value of methine proton resonance as compared with the chemical shift of the diastereomers of other allylsilanes (Table 6, entry 6). Nevertheless, the proton signal of isomer **20c** is very similar to that of its diasteromers **20a** and **20b** except for a doublet at δ 1.45. Besides, the mass spectrum for this isomer indicated that it has a molecular mass identical to its diastereomers (M⁺ = 322). Therefore we rationalized that there may be a 1,3-hydrogen migration (vinylsilane formation) during the reaction of complex **15** with triethylsilane (eq 7). The doublet at δ 1.45 ppm may be due to the methine proton α to the Me₃Si group of the vinylsilane **20c**.

$$(7)$$

$$(8)$$

(24) Wulff, W. D.; Chan, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 5229.
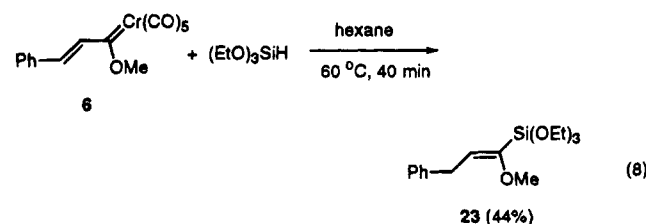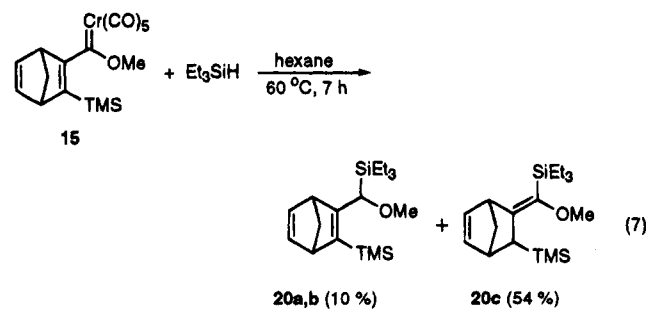
The 1,3-shift did not occur in the reaction of carbene complex **14** with silane **2** and the reason is unclear. However, the vinylsilane formation was also observed in the reaction of carbene complex **6** with triethoxysilane (eq 8) to give vinylsilane **23** whose structure was elucidated by the ^{1}H NMR spectrum. There was a doublet at δ 3.52 for the methylene protons and a triplet at δ 5.50 for the olefinic proton. The coupling constant for these multiplicities is also 7.2 Hz. Therefore, vinylsilane formation is both dependent on the structures of the carbene complexes and the silanes used. Possible metal-mediated 1,3-shift might faciliate the rearrangement.

Conclusion

We have shown that the [2 + 1] carbenoid insertion reactions of silanes with Fischer alkenyl carbene complexes is a versatile method for the preparation of allylsilanes under neutral medium and at mild reaction temperature. By appropriate variation of the alkenyl carbene complex and triorganosilanes, allylsilanes should be capable of wide variation. The ease of preparation of diverse range of alkenyl Fischer carbene complexes, high tolerance of the functionalities, and the ease of operations for such reactions constitute important features for this [2 + 1] carbenoid insertion reaction.

Experimental Section

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. THF and diethyl ether were distilled from sodium benzophenone ketyl immediately prior to use. Hexane was distilled over calcium chloride and toluene was distilled from sodium. Fischer carbene complexes **1, 4, 5,**[21] **6,**[20] **7,**[20a] **9,**[20b] **10,**[21] **12,**[22] **14,**[23] and **15**[23] were prepared according to literature procedures. For reactions involving carbene complexes the reaction mixtures were deoxygenated by the freeze−thaw−pump method (−196 to 25 °C, three cycles). All column chromatography was carried out under air by the flash method described by Still[25] with silica gel (230−400 mesh). All reactions were monitored by thin layer chromatography (TLC) performed on silica gel plates, and compounds were visualized under UV light or with a spray of 5% w/v dodecamolybdophosphoric acid in ethanol and subsequent heating. All melting points were incorrected.

Routine proton NMR spectra were recorded in CDCl$_3$ (residual CHCl$_3$ δ = 7.24 ppm) with tetramethylsilane as internal standard. Chemical shifts are reported in part per million (ppm) on the δ scale downfield from TMS. Coupling constants (*J*) are reported in hertz (Hz). ^{13}C NMR spectra were obtained at 62.9 MHz (residual CHCl$_3$ δ 77.00 ppm). Infrared spectra were recorded on a FT-IR spectrophotometer as neat films on KBr. Low and high resolution mass spectra were obtained in the EI mode. Elemental analyses were carried out by Medac Ltd, U.K. or Shanghai Institute of Organic Chemistry, China.

(α-Methoxybenzyl)triethylsilane[3b] **(3): General Procedure for Solvent Effect.** Triethylsilane (45 mg, 0.39 mmol) and (CO)$_5$CrC(OMe)Ph (**1**) (0.10 g, 0.32 mmol) were dissolved in a solvent (8 mL). The mixture was deoxygenated by the freeze−thaw−pump method (3 cycles) and then heated to 60 °C and stirred under nitrogen. After the deep red reaction mixture had changed to brownish-yellow in color (³/₄ h to 1.5 h), the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel with hexane as the eluent to afford a colorless liquid: R_f = 0.24 (hexane); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.46 (q, 6 H, *J* = 7.9 Hz), 0.83 (t, 9 H, *J* = 7.9 Hz), 3.19 (s, 3 H), 3.99 (s, 1 H), 7.04−7.10 (m, 3 H), 7.16−7.24 (m, 2 H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 1.61, 7.26, 58.97, 79.06, 125.64, 125.87, 128.10, 141.75; mass

(25) Still, W. C.; Kahn, M.; Metra, A. *J. Org. Chem.* **1978**, *43*, 2923.

spectrum, *m/e* (relative intensity) 221 (46), 115 (46), 87 (100), 59 (53). The spectral data were consistent with the values published in the literature.[3b]

The procedure and the spectroscopic data for the studies of metal and catalyst effect were similar to the one described above.

[2 + 1] Carbenoid Insertion Reaction of Alkenylmethoxy Carbene Complexes and Triorganosilanes. Preparation of Allylsilanes. Allylsilane 8. Triethylsilane (29 mg, 0.25 mmol) and carbene complex **6** (65 mg, 0.19 mmol) were mixed in hexane (8 mL). The deep red mixture was deoxygenated by the freeze−thaw−pump method (3 cycles) and then heated to 60 °C and stirred under nitrogen. After an hour, the brownish-yellow suspension was concentrated. Then it was purified by flash chromatography on silica gel with hexane as the eluent to afford the allylsilane **8** as a colorless liquid (34 mg, 68%): R_f = 0.22 (hexane); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.57−0.67 (m, 6 H), 0.98 (t, *J* = 7.9 Hz, 9 H), 3.35 (s, 3 H), 3.74 (d, 1 H, *J* = 7.3 Hz), 6.24 (dd, 1 H, *J* = 7.3, 16.0 Hz), 6.43 (d, 1 H, *J* = 16.0 Hz), 7.19−7.38 (m, 5 H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 2.02, 7.39, 59.10, 77.60, 126.05, 126.81, 127.43, 128.55, 130.28, 137.83; IR (neat) 2935, 2913, 2876, 2813, 1077, 1018, 967, 739, 721 cm^{-1}; mass spectrum, *m/e* (relative intensity) 262 (M[+], 1), 247 (88), 233 (33), 161 (7), 147 (6), 131 (13), 115 (58), 87 (100). Anal. Calcd for C$_{16}$H$_{26}$OSi: C, 73.28; H, 9.92. Found: C, 73.35; H, 10.18.

For the tungsten alkenyl carbene complex **7**, the time required was 8 d and the yield of the insertion product was 75%.

Allylsilane 16. A mixture of Et$_3$SiH (70 mg, 0.60 mmol) and carbene complex **9** (0.10 g, 0.35 mmol) was stirred at 60 °C under N$_2$ for 25 min. Purification by flash chromatography on silica gel with an eluent of hexane afforded the allylsilane **16** (43 mg, 57%) as a colorless liquid: R_f = 0.27 (hexane); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.49−0.59 (m, 6 H), 0.93 (t, 9 H, *J* = 7.9 Hz), 1.61 (br s, 3 H), 1.73 (br s, 3 H), 3.19 (s, 3 H), 3.75 (d, 1 H, *J* = 10.7 Hz), 5.15 (d, 1 H, *J* = 10.7 Hz); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 1.98, 7.37, 18.22, 25.92, 58.14, 72.63, 124.75, 132.63; IR (neat) 2954, 2934, 2915, 2877, 2809, 1078, 1012, 732, 719 cm^{-1}; mass spectrum, *m/e* (relative intensity) 199 (51), 178 (14), 115 (61), 103 (10), 97 (16), 87 (100), 71 (34), 59 (52), 57 (63), 43 (61). Anal. Calcd for C$_{12}$H$_{26}$OSi: C, 67.29; H, 12.15. Found: C, 67.61; H, 12.25.

Allylsilane 17. A mixture of Et$_3$SiH (44 mg, 0.38 mmol) and carbene complex **10** (0.10 g, 0.32 mmol) was stirred at 60 °C under N$_2$ for 30 min and the mixture was purified by flash chromatography on silica gel with an eluent of a mixture of hexane/ethyl acetate (40:1) to afford the allylsilane **17** (36 mg, 47%) as a colorless liquid: R_f = 0.24 (hexane/ethyl acetate = 40:1); ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 0.94−1.07 (m, 6 H), 1.33 (t, 9 H, *J* = 7.7 Hz), 1.69−1.77 (m, 2 H), 2.08−2.12 (m, 2 H), 3.49 (s, 3 H), 3.60 (s, 1 H), 3.83−3.91 (m, 1 H), 4.01−4.07 (m, 1 H), 4.87 (t, 1 H, *J* = 3.7 Hz); ^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ 3.47, 8.42, 21.27, 23.71, 59.05, 66.53, 77.35, 96.35, 154.33; IR (neat) 2952, 2916, 2876, 2849, 2817, 1463, 1237, 1095, 1062, 1018, 1009, 735 cm^{-1}; mass spectrum, *m/e* (relative intensity) 242 (M[+], 5), 227 (75), 189 (5), 171 (17), 115 (38), 87 (100), 59 (65); calcd for C$_{13}$H$_{26}$O$_2$Si *m/e* 242.1695, measd *m/e* 242.1811; calcd for C$_{12}$H$_{23}$O$_2$Si (M[+] − CH$_3$) *m/e* 227.1461, measd *m/e* 227.1370.

Allylsilane 18. A mixture of Et$_3$SiH (50 mg, 0.45 mmol) and carbene complex **12** (0.11 g, 0.30 mmol) was stirred at 60 °C under N$_2$ for 15 h and the mixture was purified by flash chromatography on silica gel with an eluent of hexane/ethyl acetate (40:1) to afford the allylsilane **18** (55 mg, 63%) as a colorless liquid: R_f = 0.34 (hexane/ethyl acetate = 40:1); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.56−0.66 (m, 6 H), 0.95−1.01 (m, 9 H), 3.31 (s, 3 H), 3.49 (s, 3 H), 4.20 (d, 1 H, *J* = 10.7 Hz), 5.26 (d, 1 H, *J* = 10.6 Hz), 7.28−7.45 (m, 5 H); ^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ 3.28, 8.45, 58.42, 59.42, 71.56, 115.29, 127.41, 128.85, 129.38; IR (neat) 2985, 2952, 2914, 2876, 2800, 1460, 1449, 1094, 1076, 1062, 1018, 772, 761, 733, 719, 698 cm^{-1}; mass spectrum, *m/e* (relative intensity) 292 (M[+], 0.2), 277 (100), 177 (48), 151 (52), 115 (24), 87 (55), 77 (10), 59 (31). Anal. Calcd for C$_{16}$H$_{28}$O$_2$Si: C, 69.86; H, 9.56. Found: C, 70.04; H, 9.78.

Allylsilane 19. A mixture of Et$_3$SiH (50 mg, 0.44 mmol) and carbene complex **14** (90 mg, 0.22 mmol) was stirred at 60 °C under N$_2$ for 20 h and the mixture was purified by flash chromatography on silica gel with an eluent of hexane/ethyl

acetate (30:1) to give the allylsilanes **19a,b** (29 mg, 40%) as colorless liquids: R_f = 0.27 and 0.22 (hexane/ethyl acetate = 30:1). Spectral data for isomer **19a** (R_f = 0.27): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.36–0.58 (m, 6 H), 0.79–0.86 (m, 9 H), 1.97–2.01 (m, 1 H), 2.11–2.15 (m, 1 H), 3.29 (s, 3 H), 3.73–3.74 (m, 2 H), 4.29 (s, 1 H), 6.78–6.82 (m, 1 H), 6.90–6.92 (m, 1 H), 7.15–7.33 (m, 5 H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 2.81, 7.37, 52.12, 56.44, 58.91, 70.77, 73.54, 126.08, 126.25, 128.16, 138.08, 142.31, 142.82, 147.75, 149.80. Spectral data for isomer **19b** (R_f = 0.22): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.61–0.73 (m, 6 H), 0.96–1.02 (m, 9 H), 1.95–2.00 (m, 1 H), 2.09–2.12 (m, 1 H), 2.86 (s, 3 H), 3.73–3.74 (m, 2 H), 4.21 (s, 1 H), 6.85–6.89 (m, 1 H), 6.90–6.92 (m, 1 H), 7.14–7.36 (m, 5 H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 2.92, 7.47, 54.07, 55.50, 59.79, 70.22, 72.06, 126.17, 126.23, 128.14, 137.84, 141.31, 142.90, 148.34, 150.75; IR (neat) (mixture of isomers) 2955, 2933, 2915, 2876, 2808, 1493, 1460, 1444, 1076, 1013, 801, 763, 753, 738, 696, 659 cm^{-1}; mass spectrum (mixture of isomers), m/e (relative intensity) 326 (M$^+$, 2), 311 (100), 245 (25), 211 (9), 179 (28), 145 (19), 115 (53), 87 (95), 59 (55). Anal. Calcd for C$_{21}$H$_{30}$OSi: C, 77.30; H, 9.20. Found (from the mixture of isomers): C, 77.23; H, 9.26.

Allylsilane 20. A mixture of Et$_3$SiH (0.12 g, 1.03 mmol) and carbene complex **15** (0.25 g, 0.63 mmol) was stirred at 60 °C under N$_2$ for 7 h and the mixture was purified by flash chromatography on silica gel with an eluent of hexane to afford the allylsilanes **20a,b** (20 mg, 10%) and vinylsilane **20c** (0.11 g, 54%) as colorless liquids. R_f = 0.25, 0.19, and 0.08 (hexane). Spectral data for diastereomer **20a** (R_f = 0.25): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.10 (s, 9 H), 0.46–0.62 (m, 6 H), 0.89–1.24 (m, 9 H), 1.81 (br s, 2 H), 3.19 (s, 3 H), 3.63–3.68 (m, 2 H), 4.00 (s, 1 H), 6.61–6.64 (m, 2 H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ –0.70, 2.66, 7.51, 54.35, 54.72, 59.38, 70.88, 74.83, 141.98, 142.35, 144.20, 168.08; IR (neat) 2954, 2932, 2913, 2876, 2825, 1247, 1075, 1018, 874, 836, 734, 690 cm^{-1}; mass spectrum, m/e (relative intensity) 322 (M$^+$, 2), 307 (18), 241 (100), 189 (15), 161 (17), 141 (9), 115 (27), 87 (16), 73 (17), 59 (13). Anal. Calcd for C$_{18}$H$_{34}$OSi$_2$: C, 67.08; H, 10.56. Found: C, 66.77; H, 10.53. Spectral data for diastereomer **20b** (R_f = 0.19): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.08 (s, 9 H), 0.52–0.70 (m, 6 H), 0.92–1.00 (m, 9 H), 1.75–1.84 (m, 2 H), 2.99 (s, 3 H), 3.60 (br s, 2 H), 3.98 (s, 1 H), 6.59–6.62 (m, 1 H), 6.68–6.72 (m, 1 H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ –0.55, 2.86, 7.56, 52.61, 55.17, 58.44, 71.73, 75.03, 141.64, 143.01, 144.92, 166.68; IR (neat) 2955, 2932, 2877, 2809, 1248, 1075, 1019, 873, 737, 690 cm^{-1}; mass spectrum, m/e (relative intensity) 322 (M$^+$, 2), 307 (37), 241 (97), 161 (15), 115 (81), 87 (93), 73 (100), 59 (76). Anal. Calcd for C$_{18}$H$_{34}$OSi$_2$: C, 67.08; H, 10.56. Found: C, 66.72; H, 10.66. Spectral data for vinylsilane **20c** (with exocyclic double bond) (R_f = 0.08): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.10 (s, 9 H), 0.58–0.68 (m, 6 H), 0.84–0.97 (m, 9 H), 1.22–1.33 (m, 2 H), 1.45 (d, 1 H, J = 2.7 Hz), 3.02 (br s, 1 H), 3.44 (s, 3 H), 3.81 (br s, 1 H), 5.94–5.98 (m, 1 H), 6.08–6.12 (m, 1 H); ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ

0.11, 3.91, 7.38, 30.33, 46.24, 46.45, 46.60, 60.49, 135.94, 151.48; IR (neat) 2955, 2875, 2820, 1074, 837, 732 cm^{-1}; mass spectrum, m/e (relative intensity) 322 (M$^+$, 9), 272 (8), 189 (75), 161 (38), 115 (50), 87 (59), 73(81), 59 (53); calcd for C$_{18}$H$_{34}$OSi$_2$ m/e 322.2139, measd m/e 322.2387. Anal. Calcd for C$_{18}$H$_{34}$OSi$_2$: C, 67.08; H, 10.56. Found: C, 66.48; H, 10.63.

Allylsilane 21. A mixture of Ph$_3$SiH (0.20 g, 0.77 mmol) and carbene complex **6** (0.13 g, 0.39 mmol) was stirred at 60 °C under N$_2$ for 30 min and the mixture was purified by flash chromatography on silica gel with an eluent of hexane/ethyl acetate (60:1) to give the allylsilane **21** (0.14 g, 87%) as transparent prismlike crystals: R_f = 0.21 (hexane/ethyl acetate = 60:1); mp 123–124 °C (CHCl$_3$/hexane); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 3.46 (s, 3 H), 4.46 (d, 1 H, J = 6.3 Hz), 6.26 (dd, 1 H, J = 6.4, 16.0 Hz), 6.37 (d, 1 H, J = 16.2 Hz), 7.22–7.62 (m, 20 H); IR (neat) 3069, 3060, 3025, 2814, 1494, 1428, 1111, 1073, 969, 910, 730, 700 cm^{-1}; mass spectrum, m/e (relative intensity) 406 (M$^+$, 0.3), 391 (17), 259 (100), 181 (11), 105 (7). Anal. Calcd for C$_{28}$H$_{26}$OSi: C, 82.76; H, 6.40. Found: C, 82.70; H, 6.47.

Allylsilane 22. A mixture of Ph$_3$SiH (0.31 g, 1.24 mmol) and carbene complex **9** (0.18 g, 0.62 mmol) was stirred at 60 °C under N$_2$ for 1 h and the mixture was purified by flash chromatography on silica gel with an eluent of hexane/ethyl acetate (70:1) to afford the allylsilane **22** (0.14 g, 64%) as a white solid: R_f = 0.20 (hexane/ethyl acetate = 70:1); mp 50–52 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.16 (s, 3 H), 1.60 (s, 3 H), 3.30 (s, 3 H), 4.42 (d, 1 H, J = 10.7 Hz), 5.33 (≈dh, 1 H, J = 1.4, 10.7 Hz), 7.25–7.60 (m, 15 H); IR (neat) 3070, 3050, 2975, 2917, 2810, 1428, 1111, 1073, 735, 699 cm^{-1}; mass spectrum, m/e (% relative intensity) 343 (31), 259 (100), 181 (17), 105 (8). Anal. Calcd for C$_{24}$H$_{26}$OSi: C, 80.45; H, 7.26. Found: C, 80.34; H, 7.30.

Vinylsilane 23. A mixture of (EtO)$_3$SiH (72 mg, 0.44 mmol) and carbene complex **6** (0.10 g, 0.30 mmol) was stirred at 60 °C under N$_2$ for 40 min and the mixture was purified by flash chromatography on silica gel with an eluent of hexane/ethyl acetate (30:1) to afford the vinylsilane **23** (40 mg, 44%) as a colorless liquid: R_f = 0.45 (hexane/ethyl acetate = 30:1); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.23 (t, 9 H, J = 7.0 Hz), 3.52 (d, 2 H, J = 7.2 Hz), 3.73 (s, 3 H), 3.85 (q, 6 H, J = 7.0 Hz), 5.50 (t, 1 H, J = 7.2 Hz), 7.16–7.29 (m, 5 H); ^{13}C NMR (CHCl$_3$, 62.9 MHz) δ 18.07, 31.08, 58.28, 58.50, 58.72, 125.66, 126.55, 128.28, 128.40, 141.27, 153.48; IR (neat) 2976, 2928, 2890, 2841, 1495, 1454, 1391, 1167, 1130, 1102, 1080, 963, 783, 748, 726 cm^{-1}; mass spectrum, m/e (relative intensity) 310 (M$^+$, 2), 295 (35), 163 (43), 115 (100), 79 (34), 63 (21). Anal. Calcd for C$_{16}$H$_{26}$O$_4$Si: C, 61.94; H, 8.39. Found: C, 61.96 ; H, 8.42.