Carbosilylation of Allenes Catalyzed by Palladium Complexes: A New Efficient Route to Substituted Allylic Silanes

Ming-Yuan Wu, Feng-Yu Yang, and Chien-Hong Cheng*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, 30043

Received November 23, 1998

An aromatic or olefinic halide RX (C_6H_5I, *p*-$CH_3COC_6H_4I$, *p*-$NO_2C_6H_4I$, *p*-$CH_3OC_6H_4I$, *o*-$CH_3OC_6H_4I$, *m*-$C_2H_5OCOC_6H_4I$, (*Z*)-$C_2H_5OCOCH{=}CHI$, 3-iodocyclopent-2-en-1-one, 1-iodothiophene, 1-iodonaphthalene, 3-bromo-5,5-dimethylcyclohex-2-en-1-one, or α-bromostyrene), $Bu_3SnSiMe_3$ (**2**), and 1,1-dimethylallene (**3a**) undergo three-component coupling reaction in toluene in the presence of $Pd(dba)_2$ (dba = dibenzylideneacetone) to give an allylic silane $(Me)_2C{=}C(R)CH_2SiMe_3$ in good to excellent yields. When X = I, the yields are substantially higher than when X = Br or Cl (no reaction). This carbosilylation reaction is highly regioselective, with the R group adding to the middle carbon and the silyl group to the unsubstituted terminal carbon of **3a**. Monosubstituted allenes R″CH=C=CH_2 (R″ = cyclo-C_6H_{11}, *n*-Bu, and Ph) also undergo carbosilylation with PhI and **2**, producing R″CH=$C(Ph)CH_2SiMe_3$ stereoselectively with *Z*/*E* between 98/2 and 80/20. Bulkier organic halides and allenes give products with higher *Z*/*E* ratios. Based on known palladium−allene and −allyl chemistry, we propose a mechanism to account for this palladium-catalyzed three-component coupling reaction.

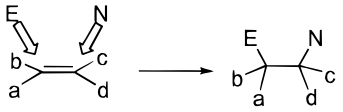
Introduction

An efficient metal-catalyzed addition of an electrophile (E) and a nucleophile (N) to a carbon−carbon double bond (Scheme 1) is greatly beneficial to organic synthesis. In the reaction, three organic units are assembled to give a product consisting of two new chemical bonds.[1] Technically, to achieve this three-component coupling reaction, it is necessary to suppress competitive reactions such as direct coupling of the electrophile and nucleophile, β-hydride elimination, and polymerization of the alkene.[2] Increasing effort in this area has led to the development of new synthetic methods. Tsuji and co-workers reported a palladium-promoted decarbonylative coupling of acid chlorides, disilanes, and 1,3-dienes to give allylic silanes (eq 1),[3] whereas Murai et al. presented an addition of trimethylsilyl and alkynyl units to acetylenes.[4]

$$\mathrm{RCOCl} + \mathrm{Me_3SiSiMe_3} + \mathrm{CH_2{=}CR'CR''{=}CH_2} \xrightarrow{\mathrm{Pd(dba)_2}} \mathrm{RCH_2CR'{=}CR''CH_2SiMe_3} + \mathrm{CO} + \mathrm{ClSiMe_3} \quad (1)$$

Allene appears to be an excellent candidate as an unsaturated organic substrate in the three-component coupling because it inserts rapidly into a metal−carbon bond and the resulting π-allyl species is relatively stable to β-hydride elimination.[5] In this paper, we report a new method for the synthesis of allylic silanes by palladium-catalyzed three-component coupling of organic halides, allenes, and organosilylstannanes (eq 2). This catalytic carbosilylation involves activation of C−X[6] and Si−Sn[7] bonds and regioselective addition of an organic and silyl groups to allenes. Allylic silanes are useful reagents in organic synthesis.[8,9] The present palladium-catalyzed reaction provides a convenient and extremely efficient new route for the synthesis of a wide range of highly substituted allylic silanes which are obtained only with difficulty according to previous methods.[3,10]

Scheme 1



(1) (a) Chatani, N.; Amishiro, N.; Morii, T.; Yamashita, T.; Murai, S. *J. Org. Chem.* **1995**, *60*, 1834−1840. (b) Ikeda, S. I.; Sato, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5975−5976. (c) Ryu, I.; Yamazaki, H.; Kusano, K.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 8558−8560. (d) Suzuki, M.; Yanagisawa, A.; Noyori, R. *J. Am. Chem. Soc.* **1988**, *110*, 4718−4726.

(2) (a) Shimizu, I.; Sugiura, T.; Tsuji, J. *J. Org. Chem.* **1985**, *50*, 537−539. (b) Negishi, E.; Noda, Y.; Lamaty, F.; Vawter, E. J. *Tetrahedron Lett.* **1990**, *31*, 4393−4396.

(3) (a) Obora, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc.* **1995**, *117*, 9814−9821. (b) Obora, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc.* **1993**, *115*, 10414−10415.

(4) Chatani, N.; Amishiro, N.; Murai, S. *J. Am. Chem. Soc.* **1991**, *113*, 7778−7780.

(5) (a) Besson, L.; Gore, J.; Cazes, B. *Tetrahedron Lett.* **1995**, *36*, 3853−3856. (b) Aniès, C.; Cazes, B.; Goré, J. *J. Chem. Res. (S)* **1996**, 116−117. (c) Vicart, N.; Cazes, B.; Gore, J. *Tetrahedron* **1996**, *52*, 9101−9110. (d) Yamamoto, Y.; Al-Masum, M.; Asao, N. *J. Am. Chem. Soc.* **1994**, *116*, 6019−6020. (e) Larock, R. C.; Tu, C.; Pace, P. *J. Org. Chem.* **1998**, *63*, 6859−6866. (f) Larock, R. C.; He, Y.; Leong, W. W.; Han, X.; Refvik, M. D.; Zenner, J. M. *J. Org. Chem.* **1998**, *63*, 2154−2160.

(6) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146−151.

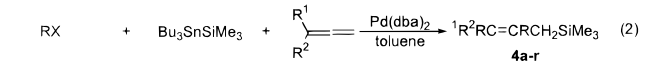
(7) (a) Obora, Y.; Tsuji, Y.; Asayama, M.; Kawamura, T. *Organometallics* **1993**, *12*, 4697−4699. (b) Murakami, M.; Morita, Y.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 428−429. (c) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868−4874. (d) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561−3566.

(8) (a) Koreeda, M.; Ciufolini, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 2308−2310. (b) Fleming, I.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1010−1011.

(9) (a) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200−206. (b) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761−786.

(10) (a) Ojima, I.; Kumagai, M.; Miyazawa, Y. *Tetrahedron Lett.* **1977**, 1385−1388. (b) Matsumoto, H.; Yako, T.; Nagashima, S.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* **1978**, *148*, 97−106. (c) Tsuji, Y.; Kajita, S.; Isobe, S.; Funato, M. *J. Org. Chem.* **1993**, *58*, 3607−3608. (d) Gilman, H.; Zuech, E. A. *J. Am. Chem. Soc.* **1959**, *81*, 5925−5928. (e) Seyferth, D.; Wursthorn, K. R.; Mammarella, R. E. *J. Org. Chem.* **1977**, *42*, 3104−3106.

10.1021/jo982307a CCC: $18.00
Published on Web 03/05/1999



1a: C_6H_5I **2** **3a**: $R^1 = R^2 = Me$

1b: p-$CH_3COC_6H_4I$ **3b**: $R^1 = H$, R^2 = cyclo-C_6H_{11}

1c: p-$NO_2C_6H_4I$ **3c**: $R^1 = H$, $R^2 = n$-Butyl

1d: p-$CH_3OC_6H_4I$ **3d**: $R^1 = H$, $R^2 = Ph$

1e: o-$CH_3OC_6H_4I$

1f: m-$C_2H_5OCOC_6H_4I$

1g: 1-I-C_4H_3S

1h:

1i: (Z)-$C_2H_5OCOCH{=}CHI$

1j:

1k: $C_6H_5(Br)C{=}CH_2$

1l: 1-I-$C_{10}H_7$

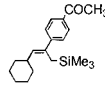
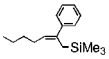
Results and Discussion

Treatment of iodobenzene (**1a**) and $Bu_3SnSiMe_3$ (**2**) with 1,1-dimethylallene (**3a**) in the presence of $Pd(dba)_2$ (5%) (dba = dibenzylideneacetone) in toluene at 80 °C led to isolation of allylic silane **4a** in excellent yield. The reaction is highly regioselective with the phenyl group adding to the middle carbon and the silyl group to the nonsubstituted terminal carbon of **3a**. No product that consists of a stannyl group attached to the allene was detected from the reaction. Under similar conditions, many substituted aryl iodides also undergo three-component coupling with **2** and **3a** (Table 1). Aryl iodides with either an electron-donating or -withdrawing functionality at the ortho, meta, or para position all appear to react smoothly to afford the corresponding allylic silanes in high yields (entries 1−6). Like **1a**, bromobenzene reacts with **2** and **3a** to afford **4a**, but in lower yield (12% yield). In contrast, chlorobenzene shows essentially no reaction with **2** and **3a** in the presence of $Pd(dba)_2$.

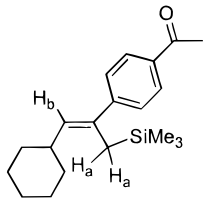
Several types of organic halides also react with **2** and **3a** to afford the corresponding allylic silanes in high yields. Thus, 2-iodothiophene gave the corresponding addition product in 85% yield. Alkenyl halides, 3-iodocyclopent-2-en-1-one (**1h**), ethyl (*Z*)-3-iodoacrylate (**1i**), 3-bromo-5,5-dimethylcyclohex-2-en-1-one (**1j**), and a-bromostyrene (**1k**) gave the corresponding allylic silanes in 61−83% yields (entries 8−11). In product **4i**, the cis stereochemistry of the acrylate group is faithfully transferred from the original (*Z*)-3-iodoacrylate.

In addition to **3a**, monosubstituted allenes **3b**, **3c**, and **3d** also undergo three-component carbosilylation with PhI and **2**, producing allylic silanes regio- and stereoselectively in 80−91% yields. The stereoselectivity of these products depends greatly on the organic halide and the substituent on the allene. Bulkier organic halides and allenes give products with higher *Z*/*E* ratios. Thus, α-iodonaphthalene and 1-cyclohexylallene using $Pd(dba)_2$ as catalyst afforded product **4l** in a *Z*/*E* ratio of 98/2. Other aryl iodides and allenes gave allylic silanes with *Z*/*E* ratios between 92/8 and 80/20. The stereochemistry of these silane products was determined using typical ^1H NMR NOE technique. For example, there are two isomers **4n** and **4n′** isolated from carbosilylation of **3b** with **1b** and **2**. The minor product **4n′** exhibits ^1H NMR signals at 1.82 and 5.15 ppm for the methylene (H_c) and olefin proton (H_d), respectively. Irradiation at the H_c signal led to increase of the intensity of H_d by 5.75%. Similarly, irradiation at the H_d signal resulted in increase of the intensity of H_c by 4.82%. In contrast, irradiation at the methylene (H_a) and at the olefin (H_b) proton signals of **4n** showed essentially no change of the intensity of H_b and H_a signals, respectively. These NOE results clearly show that the major product **4n** is a Z isomer, while **4n′** is an E product.

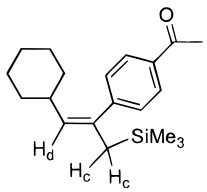
Table 1. Palladium-Catalyzed Carbosilylation of Allenes[a]

entry	RX	allene	Product		*Z*/*E*	yield/(%)[b]
1	**1a**	**3a**		**4a**		85 (91)[c]
2	**1b**	**3a**		**4b**		92
3	**1c**	**3a**		**4c**		88
4	**1d**	**3a**		**4d**		86 (93)
5	**1e**	**3a**		**4e**		83
6	**1f**	**3a**		**4f**		82
7	**1g**	**3a**		**4g**		85
8	**1h**	**3a**		**4h**		82
9	**1i**	**3a**		**4i**		78 (83)
10	**1j**	**3a**		**4j**		61
11	**1k**	**3a**		**4k**		83
12	**1n**	**3b**		**4l**	98/2	91
13	**1a**	**3b**		**4m**	92/8	85
14	**1b**	**3b**		**4n**	92/8	80
15	**1a**	**3c**		**4o**	80/20	82
16	**1a**	**3d**		**4p**	90/10	84

[a] Reaction conditions: RX (1: 1.00 mmol), $Bu_3SnSiMe_3$ (2: 1.00 mmol), allene (3: 2.00 mmol), $Pd(dba)_2$ (0.0500 mmol, 5 mol %), and toluene (3.0 mL) at 80 °C for 7 h. [b] Isolated yields. [c] Yields in parentheses were determined by NMR.



4n



4n'

To understand the effect of ligands on the catalytic activity, we tested $Pd(dba)_2$ with various phosphorus ligands in a 1/1 molar ratio for the coupling reaction of 1-cyclohexylallene with **1a** and **2**. Table 2 listed the yields, *Z*/*E* ratios, and time required for these experiments. The results clearly show that $Pd(dba)_2$ without the presence of a phosphorus ligand is most active and most stereoselective. The reaction required 7 h for completion at 80 °C using $Pd(dba)_2$ alone and gave product **4a** with a *Z*/*E* ratio of 98/2. Addition of PPh_3, $P(OEt)_3$, or dppe (1 equiv) to the reaction mixture of $Pd(dba)_2$, **1a**, and **2** greatly increases the period required for completion of reaction and decreases the *Z*/*E* ratios of the products (entries 2−6, Table 2).

A possible mechanism for the present catalytic reaction is shown in Scheme 2. The initial step likely involves oxidative addition of organic halide **1** to a Pd(0) center to give a palladium(II) intermediate. Coordination of allene **3** to the palladium(II) center followed by migration of the organic group to the central carbon of allene gives a π-allyl palladium(II) species. Transmetalation with organosilylstannane **2** followed by reductive elimination yields the final allylic silane and tributyltin halide and regenerates the palladium(0) species. Oxidative addition of an organic halide to palladium(0) species[11] and insertion of allene into a palladium(II)−carbon bond[12,13] are well established. Transmetalation of a π-allyl palladium(II) species with an organosilylstannane or disilane has been reported previously, but the intimate mechanism is not fully understood.[3a] The proposed formation of tributyltin halide was evidenced by the observation of Bu_3SnI in the ^1H NMR spectra of the product mixtures from reactions of aryl iodides with **2**. It is noteworthy that Bu_3SnI was also observed in the palladium-catalyzed reaction of 1,3-diene, aryl iodide, and **2**.[3a]

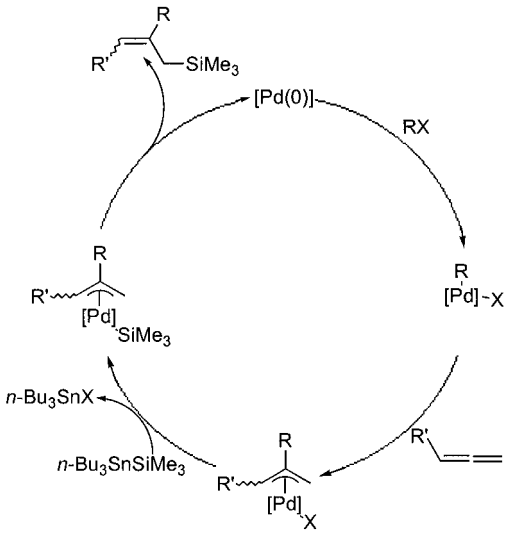
The observation that phosphorus ligands diminish the yield of allylic silanes may be understood in view of the fact that strong donor ligands are known to impede olefin coordination/insertion,[14] which is central to the success of the present three-component catalytic reaction (eq 2). The decrease in *Z*/*E* ratio for monosubstituted allene in the presence of a phosphorus ligand may be explained by the fact that donor ligands readily promote anti−syn rearrangement of π-allyl palladium(II) complexes via a σ-allyl intermediate.[15] The anti and syn forms of π-allyl palladium(II) complexes are responsible for the formation of Z and E isomers of allylic silanes, respectively.

Table 2. Effect of Phosphorus Ligands on Carbosilylation of Cyclohexylallene[a]

entry	ligand	time (h)	yield (%)[b]	Z/E[c]
1		7	85	92/8
2	P(OEt)3	14	82	77/23
3	PPh3	24	82	86/14
4	DPPF	12	20	75/25
5	DPPE	72	80	75/25
6	DPPF	72	77	75/25

[a] All reactions were carried out under the following reaction conditions: PhI (1.00 mmol); $Bu_3SnSiMe_3$ (1.00 mmol); cyclohexylallene (2.00 mmol); $Pd(dba)_2$ (0.050 mmol, 5 mol %); toluene (3.0 mL); temperature, 80 °C; ligand (1 equiv relative to Pd(dba)2); reaction time, as indicated in the table. [b] Isolated yields. [c] The Z/E ratio of the allylic silane product was determined on the basis of the 1H NMR integration method.

Scheme 2



Conclusion

We have demonstrated a new regio- and stereoselective method for the preparation of allylic silanes from allenes. Although several methods for the synthesis of allylic silanes were reported, the present methodology (eq 2) appears to be a very convenient route that can introduce a wide range of substituents to allylic silanes at the internal sp^2 carbons. Substituted allenes serve as excellent unsaturated species in the three-component coupling reactions. Further application in this direction is in progress.

Experimental Section

General Comments. All reactions were run under a nitrogen atmosphere unless otherwise mentioned. All solvents were dried according to known methods and distilled prior to use. $Pd(dba)_2$,[16] *n*-butylallene,[17] cyclohexylallene,[17] phenylallene,[17] ethyl (*Z*)-3-iodoacrylate,[18] 5,5-dimethyl-3-bromo-2-cyclohexen-1-one,[19] 3-iodo-2-cyclopenten-1-one,[19] and 3-iodo-2-cyclohexen-1-one[19] were prepared by procedures previously reported. Other reagents were commercially available and used as purchased.

(11) (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980. (b) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; Chapter 9.
(12) Shimizu, I.; Tsuji, J. *Chem. Lett.* **1984**, 233−236.
(13) Stevens, R. R.; Shier, G. D. *J. Organomet. Chem.* **1970**, *21*, 495−499.
(14) Yamamoto, Y.; Al-Masum, M.; Fujiwara, N. *Chem. Commun.* **1996**, 381−382.
(15) (a) Tibbetts, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 3031−3034. (b) Powell, J.; Shaw, B. L. *J. Chem. Soc. (A)* **1967**, 1839.
(16) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065−1066.
(17) Brandsma, L.; Verkruijisse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: New York, 1981.
(18) Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, *57*, 709−173.
(19) Piers, E.; Grierson, J. E.; Lau, C. K.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 210−223.

General Procedure for Coupling of Organic Halide (1), Silylstannane (2), and Allene (3). A 50 mL round-bottom flask containing $Pd(dba)_2$ (0.0287 g, 0.0500 mmol) was purged with nitrogen gas three times. To the flask were then added toluene (3 mL), an organic halide (1.00 mmol), allene (2.00 mmol), and **2** (1.00 mmol) via syringes. The reaction mixture was heated with stirring at 80 °C for 7 h. The solution changed color rapidly from purple red to pale yellow in the first few minutes and maintained the same color during the rest of the reaction. As the reaction approached completion, a black precipitate of palladium metal surrounding the wall of the flask appeared gradually. At the end of the reaction, the solution was filtered through Celite. The filtrate was concentrated, and the residue was separated on a silica gel column using hexane as eluent to give the desired product **4**.

Compounds **4a**−**p** were prepared according to this method. Product yields of each reaction are listed in Table 1; important spectral data of these compounds follow.

Trimethyl(3-methyl-2-phenyl-2-butenyl)silane (4a): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.20 (s, 9 H), 1.57 (s, 3 H), 1.72 (s, 3 H), 1.85 (s, 2 H), 7.10−7.23 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.94 (q), 21.09 (q), 22.07 (q), 25.71 (t), 123.81 (s), 125.70 (d), 127.67 (d), 129.16 (d), 132.40 (s), 145.11 (s); IR (neat) 3021, 2955, 845, 700 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 218 (M^+, 100), 203 (49); HRMS calcd for $C_{14}H_{22}Si$ 218.1490, found 218.1496.

(2-(4-Methoxyphenyl)-3-methyl-2-butenyl)(trimethyl)-silane (4d): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.18 (s, 9 H), 1.59 (s, 3 H), 1.72 (s, 3 H), 1.84 (s, 2 H), 3.78 (s, 3 H), 6.78 (d, J = 8.4 Hz, 2 H), 7.02 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.95 (q), 21.08 (q), 22.07 (q), 25.67 (t), 55.11 (q), 112.98 (d), 123.51 (s), 130.10 (d), 131.78 (s), 137.42 (s), 157.53 (s); IR (neat) 3031, 2929, 1245, 1174, 1039 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 248 (M^+, 100); HRMS calcd for $C_{15}H_{24}OSi$ 248.1596, found 248.1598.

Ethyl 3-(2-methyl-1-((1,1,1-trimethylsilyl)methyl)-1-propenyl)benzoate (4f): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.18 (s, 9 H), 1.37 (t, J = 7.2 Hz, 3 H), 1.56 (s, 3 H), 1.74 (s, 3 H), 1.88 (s, 2 H), 4.34 (q, J = 7.2 Hz, 2 H), 7.27−7.34 (m, 2 H), 7.81−7.85 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.91 (q), 14.27 (q), 21.05 (q), 21.99 (q), 25.67 (t), 60.82 (t), 124.79 (s), 126.97 (d), 127.66 (d), 130.07 (d), 130.14 (s), 131.56 (s), 133.78 (d), 145.37 (s), 166.82 (s); IR (neat) 2982, 1721, 1252, 1201, 1107, 850 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 290 (M^+, 100); HRMS calcd for $C_{17}H_{26}O_2Si$ 290.1695, found 290.1693.

Trimethyl(3-methyl-2-(2-thienyl)-2-butenyl)silane (4 g): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.11 (s, 9 H), 1.78 (s, 3 H), 1.82 (s, 3 H), 1.94 (s, 2 H), 6.78 (d, J = 3.6 Hz, 1 H), 6.93 (dd, J = 5.2 Hz, J = 3.6 Hz, 1 H), 7.16 (d, J = 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.13 (q), 21.70 (q), 22.55 (q), 26.76 (t), 123.27 (d), 125.14 (s), 125.69 (d), 126.14 (d), 127.08 (s), 147.04 (s); IR (neat) 3071, 2925, 1163, 973 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 224 (M^+, 72); HRMS calcd for $C_{12}H_{20}SSi$ 224.1055, found 224.1059.

3-(2-Methyl-1-((1,1,1-trimethylsilyl)methyl)-1-propenyl)-2-cyclopenten-1-one (4h): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.10 (s, 9 H), 1.68 (s, 3 H), 1.69 (s, 2 H), 1.70 (s, 3 H), 2.34−2.37 (m, 2 H), 2.61−2.65 (m, 2 H), 5.84 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.05 (q), 21.27 (t), 21.78 (q), 22.43 (q), 31.28 (t), 34.82 (t), 128.32 (s), 129.31 (s), 131.56 (d), 180.37 (s), 209.87 (s); IR (neat) 2954, 1700, 1590 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 223 (M + 1$^+$, 22); HRMS calcd for $C_{13}H_{22}OSi$ 222.1434, found 222.1444.

Ethyl (*2Z*)-5-methyl-4-((1,1,1-trimethylsilyl)methyl)-2,4-hexadienonate (4i): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.01 (s, 9 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.66 (s, 3 H), 1.69 (s, 3 H), 1.75 (s, 2 H), 4.15 (q, J = 7.2 Hz, 2 H), 5.72 (d, J = 12.4 Hz, 1 H), 6.58 (d, J = 12.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.83 (q), 14.24 (q), 20.91 (q), 21.82 (q), 22.95 (t), 59.85 (t), 119.11 (d), 126.97 (s), 127.16 (s), 147.55 (d), 165.98 (s); IR (neat) 2925, 2855, 1726, 1253, 1168 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 240 (M^+, 20), 195 (100); HRMS calcd for $C_{13}H_{24}O_2Si$ 240.1545, found 240.1549.

Trimethyl(3-methyl-2-(1-phenylvinyl)-2-butenyl)silane (4k): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.33 (s, 9 H), 1.53 (s, 2 H), 1.76 (s, 3 H), 1.77 (s, 3 H), 4.95 (d, J = 1.8 Hz, 1 H), 5.51 (d, J = 1.8 Hz, 1 H), 7.25−7.34 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.59 (q), 20.68 (t), 21.99 (q), 22.63 (q), 113.91 (t), 125.43 (s), 126.67 (d), 127.25 (d), 128.21 (d), 131.95 (s), 140.29 (s), 150.63 (s); IR (neat) 3080, 2954, 2916, 848, 780, 701 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 244 (M^+, 95); HRMS calcd for $C_{16}H_{24}Si$ 244.1641, found 244.1652.

1-(4-(*Z*)-2-Cyclohexyl-1-[(1,1,1-trimethylsilyl)methyl]-1-ethenylphenyl)-1-ethanone (4n): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.17 (s, 9 H), 1.05−1.31 (m, 5 H), 1.65−1.75 (m, 5 H), 1.98 (s, 2 H), 2.13−2.24 (m, 1 H), 0.56 (s, 3 H), 5.42 (d, J = 9.2 Hz, 1 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.84 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.05 (q), 20.32 (t), 25.93 (t), 26.01 (t), 26.48 (q), 32.92 (t), 38.13 (d), 126.72 (d), 128.28 (d), 134.37 (d), 135.21 (s), 149.95 (s), 197.82 (s); IR (neat) 2925, 2850, 1683, 1601, 846 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 314 (M^+, 48), 73 (100); HRMS calcd for $C_{20}H_{30}OSi$ 314.2058, found 314.2056.

1-(4-(*E*)-2-Cyclohexyl-1-[(1,1,1-trimethylsilyl)methyl]-1-ethenylphenyl)-1-ethanone (4n′): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.17 (s, 9 H), 1.06−1.14 (m, 5 H), 1.75−1.63 (m, 5 H), 1.82 (s, 2 H), 1.96−2.01 (m, 1 H), 2.61 (s, 3 H), 5.15 (d, J = 10 Hz, 1 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.90 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.49 (q), 25.64 (t), 25.89 (t), 26.51 (q), 29.32 (t), 33.76 (t), 37.66 (d), 128.14 (d), 138.65 (d), 133.13 (d), 134.98 (s), 135.21 (s), 148.39 (s), 197.96 (s); IR (neat) 2926, 2850, 1685, 1602, 848 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 314 (M^+, 39); HRMS calcd for $C_{20}H_{30}OSi$ 314.2058, found 314.2051.

Trimethyl((*Z*)-2-phenyl-2-heptenyl)silane (4o): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.17 (s, 9 H), 0.90 (t, J = 7.2 Hz, 3 H), 1.32−1.44 (m, 4 H), 1.96 (s, 2 H), 2.08 (q, J = 7.2 Hz, 2 H), 5.47 (t, J = 7.2 Hz, 1 H), 7.14−7.31 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.95 (q), 14.05 (q), 20.90 (t), 22.58 (t), 28.99 (t), 32.01 (t), 126.25 (d), 126.35 (d), 126.57 (d), 127.99 (d), 137.68 (s), 145.04 (s); IR (neat) 3023, 2956, 849, 753, 697 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 246 (M^+, 100); HRMS calcd for $C_{16}H_{26}Si$ 246.1803, found 246.1803.

((*Z*)-2,3-Diphenyl-2-propenyl)(trimethyl)silane (4p): ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.16 (s, 9 H), 2.31 (s, 2 H), 6.54 (s, 1 H), 7.18−7.44 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.84 (q), 21.48 (t), 125.44 (d), 126.02 (d), 126.86 (d), 127.08 (d), 128.17 (d), 128.72 (d), 138.88 (s), 141.58 (s), 145.11 (s); IR (neat) 3023, 2953, 851, 755, 697 cm^{-1}; GC−EIMS *m*/*z* (rel intensity) 266 (M^+, 98); HRMS calcd for $C_{18}H_{22}Si$ 266.1485, found 266.1491.

Acknowledgment. We thank the National Science Council of Republic of China (Grant No. NSC 87-2119-M-007-002) for support of this research.

Supporting Information Available: Spectral data for compounds **4b**−**c**, **4e**, **4j**, **4l**, and **4m** and ^{1}H NMR spectra of compounds **4a**−**p**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO982307A