Lewis Acid Catalyzed *trans*-Allylsilylation of Unactivated Alkynes

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Abstract: The addition of different substituted allylsilanes **2** to unactivated alkynes **1** in the presence of catalytic amounts of $HfCl_4$ or the $EtAlCl_2$−TMSCl catalyst system produced in high yields the silylated 1,4-dienes **3** regio- and stereoselectively. The exclusive trans manner of addition was confirmed by analysis of crude reaction mixtures by ^1H NMR and capillary GLC methods. Good agreement of relative reactivities of reaction of various allylsilanes **2a**−**e** toward phenylacetylene (**1a**) in the presence of $HfCl_4$ with the relative reaction rates of **2a**−**e** with carbenium ions supported the involvement of cationic species **11** as a reaction intermediate. The mechanisms for the $HfCl_4$ and $EtAlCl_2$−TMS catalyzed *trans*-allylsilylation of alkynes are proposed.

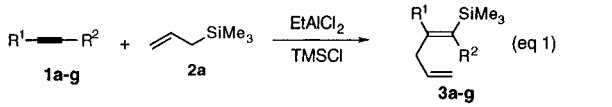
Introduction

Since the first example of carbometalation demonstrated by Ziegler and Bähr,[1] a number of additions of organometallics to carbon−carbon multiple bonds have been reported.[2] The allylmetalation of activated alkynes, such as alkynyl ketones (Michael acceptors) and alkynols (functionally substituted alkynes), in both intramolecular and intermolecular versions proceeds smoothly with various allylmetals.[2,3] However, the allylmetalation of simple unactivated alkynes is not easy, and only a limited number of allylmetals can serve for this purpose.[2,4] Recently we have communicated the first example of *trans*-allylsilylation of unactivated alkynes **1** in the presence of the $EtAlCl_2$−TMSCl catalyst system (eq 1).[5] Now we report the $HfCl_4$-catalyzed *trans*-allylsilylation of unactivated alkynes, which is more efficient than the $EtAlCl_2$−TMSCl-catalyzed allylsilylation, along with a detailed study on the $EtAlCl_2$−TMSCl catalyst system.

Results and Discussion

Allylsilylation of Alkynes Catalyzed by the $EtAlCl_2$−TMSCl Catalyst System. As we have previously shown,[5] the addition of allyltrimethylsilane (**2a**) to unactivated alkynes **1** is catalyzed by the $EtAlCl_2$−TMSCl catalyst system to give the corresponding *trans*-silylated 1,4-dienes **3** in good to high yields (eq 1, Table 1). The reaction of phenylacetylene (**1a**) with allyltrimethylsilane (**2a**) catalyzed by $EtAlCl_2$ in the presence of 20 equiv of TMSCl gave the *trans*-carbosilylation product **3a** regio- and stereoselectively in 93% yield (entry 1). Neither the stereoisomer of **3a** (*cis* addition product) nor the regioisomer of **3a** was produced.[6] The reaction of 4-ethynyltoluene (**1b**) gave **3b** in 95% yield (entry 2), whereas the addition to 3-phenyl-1-propyne (**1c**) afforded **3c** in 57% yield along with the desilylated product **4c** as a byproduct (entry 3). Very trace amounts of desilylated products were also detected by ^1H NMR of the crude products in entries 1 and 2. Reactions of 1-octyne (**1d**) and 1-dodecyne (**1e**) gave **3d** and **3e**, respectively, in high yields (entries 4 and 5). The *trans*-allylsilylation of the enyne **1f** and internal acetylene **1g** also proceeded smoothly to give the corresponding alkenylsilanes **3f** and **3g**, respectively, in high

Table 1. Allylsilylation of Alkynes in the Presence of the $EtAlCl_2$−TMSCl Catalyst System



a : R^1= Ph, R^2= H **d** : R^1= $CH_3(CH_2)_5$, R^2= H **f** : R^1=  , R^2= H

b : R^1= *p*-Me-C_6H_4, R^2= H **e** : R^1= $CH_3(CH_2)_9$, R^2= H **g** : R^1= Ph, R^2= Me

c : R^1= $PhCH_2$, R^2= H

entry	**1**	R^1	R^2	**3**	product yield %[a]
1	**1a**	Ph	H	**3a**	93
2	**1b**	*p*-$CH_3C_6H_4$	H	**3b**	95
3	**1c**	$PhCH_2$	H	**3c**	57[b,c]
4	**1d**	$CH_3(CH_2)_5$	H	**3d**	90[b]
5	**1e**	$CH_3(CH_2)_9$	H	**3e**	85[b,d]
6	**1f**	1-cyclohexenyl	H	**3f**	73[b,e]
7	**1g**	Ph	Me	**3g**	88

[a] Isolated yield, except for where otherwise indicated. [b] Yield determined by ^1H NMR with *p*-xylene as an internal standard. [c] $PhCH_2(CH_2{=}CHCH_2)C{=}CH_2$ (**4c**) was produced in 13% yield. [d] $CH_3(CH_2)_9(CH_2{=}CHCH_2)C{=}CH_2$ (**4e**) was produced in 5% yield. [e] 1-(1,4-Pentadien-2-yl)cyclohexene (**4f**) was produced in 5% yield.

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) Ziegler, K.; Bähr, K. *Chem. Ber.* **1928**, *61*, 253.

(2) For reviews, see: (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841 (organo Li, Mg, Zn, B, Al, and Cu compounds). (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38 (stoichiometric organo Li, Mg, and Zn and catalytic Ni, Pd, Pt compounds). (c) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333 (organo Al/Ti and Al/Zr systems). (d) Knochel, P. *Comprehensive Organometallic Chemistry II*; Able, E. W., Stone, F. G. A., Wilkinson, G.; Eds.; Pergamon Press: Oxford, 1995; Vol. 11, p 159 (organo Li, Mg, Zn, B, Al, Cu, Hg/Pd, Ni, and Mn compounds). (e) Knochel, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p 865. (f) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207 (organo Li, Mg, Zn, B, and Al compounds).

(3) Araki, S.; Imai, A.; Shimizu, K.; Yamada, M.; Mori, A.; Butsugan, Y. *J. Org. Chem.* **1995**, *60*, 1841 (allylindiums).

(4) (a) Takai, K.; Yamada, M.; Odaka, H.; Utimoto, K.; Fujii, T.; Furukawa, I. *Chem. Lett.* **1995**, 315 (allyl-Ta). (b) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Tetrahedron Lett.* **1994**, *35*, 5685 (allyl-Zr). (c) Chatani, N.; Amishiro, N.; Morii, T.; Yamashita, T.; Murai, S. *J. Org. Chem.* **1995**, *60*, 1834 (allyl-Zn). (d) Molander, G. A. *J. Org. Chem.* **1983**, *48*, 5409 (allyl-Zn). (e) Miller, J. A.; Negishi, E. *Tetrahedron Lett.* **1984**, *25*, 5863 (allyl-Al). (f) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761 (allyl-Zn). (g) Eishi, J. J.; Boleslawski, M. P. *J. Organomet. Chem.* **1987**, *334*, C1 (allyl-Ti). (h) Yeon, S. H.; Han, J. S.; Hong, E.; Do, Y.; Jung, I. N. *J. Organomet. Chem.* **1995**, *499*, 159 (allyl-Si).

(5) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4874.

(6) Jung and co-workers reported *cis*-allylsilylation of phenylacetylene (ref 4h). However, their stereochemical assignment of reaction product was not correct (see ref 5, note 7).

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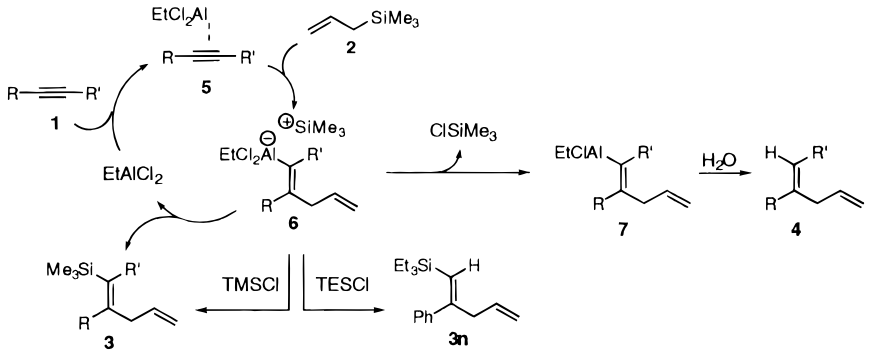
Scheme 1. Proposed Mechanism for the $EtAlCl_2$−TMSCl Catalyzed *trans*-Allylsilylation of Unactivated Alkynes

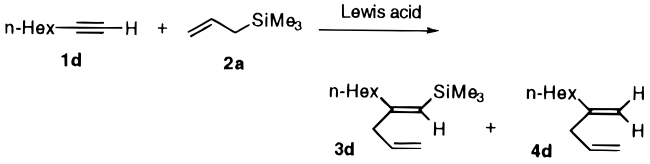


yields (entries 6 and 7). The use of other Lewis acids, such as $AlCl_3$, $AlBr_3$, and $HfCl_4$ in combination with TMSCl, also gave the allylsilylation product; however, $EtAlCl_2$ afforded the best yields of **3**. The *trans*-carbosilylation was unambiguously confirmed by the stereochemistry of the allylation product **3g**. Thus, irradiation of methyl protons attached to the double bond of **3g** enhanced both methylene protons of the allylic position (5.7% NOE) and a vinyl proton at the C-5 position (1.4% NOE), whereas irradiation of protons of the TMS group did not noticeably enhance these protons.

A plausible mechanism for the $EtAlCl_2$-catalyzed *trans*-allylsilylation is shown in Scheme 1. The coordination of $EtAlCl_2$ to **1** would produce the π-complex **5**. Allyltrimethylsilane would attack the electron-deficient triple bond from the side opposite to the Lewis acid to produce the aluminum−ate complex **6** stereoselectively. Transmetalation of aluminum halide by the trimethylsilyl group would afford **3** and regenerate the catalyst. On the other hand, the coupling between the chloro and silyl group would produce Me_3SiCl and the alkenylaluminum derivative **7**, which would afford the minor byproduct **4** upon hydrolysis. An excess amount of TMSCl is needed to drive the equilibrium over in favor of replacing aluminum with silicon. In fact, in the reaction of 1-octyne, the use of 1 equiv of TMSCl gave a 31:69 ratio of **3d**:**4d**, and the ratio changed to 5:95 in the absence of TMSCl. Furthermore, when the reaction of **1a** was carried out in the absence of TMSCl and quenched with D_2O, the deuterated alkene (*Z*)-Ph(CH_2═$CHCH_2$)C═CHD was obtained, clearly indicating that an alkenylaluminum intermediate is involved.[7] To clarify the intramolecular *vs* intermolecular character of the last silylation step (**6** to **3**), a competition experiment with another trapping agent was performed. Thus, the use of triethylchlorosilane (TESCl) instead of TMSCl afforded the triethylsilyl analogue **3n** in moderate chemical yield (Scheme 1). The test experiments indicated that no reaction took place between **1a** and allyltriethylsilane in the presense of TESCl (10 equiv). Taken together, these two facts unambigously support the intermolecular mechanism of the silylation step, and serve as an additional support for ate-complex **6** as a key intermediate in this *trans*-allylsilylation reaction (Scheme 1).

Allylsilylation of Alkynes Catalyzed by $HfCl_4$. Although *trans*-allylsilylation of unactivated alkynes catalyzed by an $EtAlCl_2$−TMSCl catalyst system has importance from a mechanistical point of view as the first example of the *trans*-carbosilylation of alkynes, the synthetic utility of this methodology is limited by the fact that a great excess of TMSCl is needed. Thus, it is doubtful that this method could be applied for preparative scale syntheses. This prompted us to search for a more synthetically useful catalyst system for this unprecedented Lewis acid catalyzed *trans*-allylsilylation reaction. Thus, we examined the addition of allyltrimethylsilane (**2a**) to 1-octyne (**1d**) in the presence of various Lewis acids (eq 3, Table 2).

Table 2. Lewis Acid Catalyzed Addition of Allyltrimethylsilane to **1d**



(eq 2)

entry	Lewis acid	solvent	temp (°C)	yield (**3d** + **4d**, %)[a]	ratio **3d**:**4d**[b]
1	$EtAlCl_2$	toluene	−78 → 0	20	5:>95[c]
2	$AlCl_3$	toluene	−78 → 0	40	24:76
3	$AlBr_3$	toluene	−78 → 0	50	15:85
4	$HfCl_4$	toluene	−78 → 0	9	>95:5[d]
5	$HfCl_4$	hexane	−78 → 0	trace	*e*
6	$HfCl_4$	CH_2Cl_2	−78 → 0	50	>95:5[d]
7	$HfCl_4$	CH_2Cl_2	0	88[f]	>95:5[d]

[a] The yield was determined by ^{1}H NMR with *p*-xylene as an internal standard. [b] The ratio was determined by 270 MHz ^{1}H NMR. [c] **3d** was not detected by ^{1}H NMR. [d] **4d** was not detected by ^{1}H NMR. [e] Not determined. [f] Isolated yield.

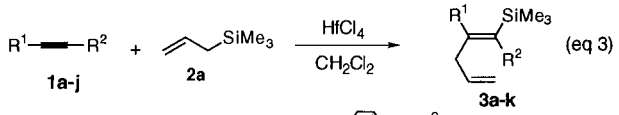
As mentioned above,[5] the addition of allyltrimethylsilane to **1d** in the presence of only $EtAlCl_2$ gave a 5:>95 mixture of **3d**:**4d** with 20% overal yield (entry 1). The reaction in the presence of $AlCl_3$ provided a 24:76 mixture of **3d** and **4d** in 40% yield (entry 2). The use of $AlBr_3$ gave rise to a combined yield of **3d** and **4d** up to 50%; however, the ratio of products was also shifted in favor of the desilylated **4d** (entry 3). Although allylsilylation in the presence of $HfCl_4$ gave a very low combined yield (9%), the only silylated adduct **3d** was detected as a reaction product (entry 4). We found this result promising and briefly optimized $HfCl_4$-catalyzed reaction conditions (entries 5−7). Thus, the $HfCl_4$-catalyzed allylsilylation of **1d** in dichloromethane at 0 °C afforded **3d** as a single reaction product in 88% isolated yield (Table 2, entry 7).[8] We further examined the $HfCl_4$-catalyzed addition of allyltrimethylsilane to various alkynes **1a**−**j** (eq 3). The results are summarized in Table 3. Addition of allyltrimethylsilane (**2a**) to alkyl- (entries 3−5), aryl- (entries 1, 2, 7, and 8), and alkenyl-substituted (entry 6) alkynes **1a**−**h** in the presence of 50 mol % $HfCl_4$ proceeded smoothly, giving regio- and stereoselectively the corresponding allylsilylated products **3a**−**h** in good to excellent yields.[9]

(7) Negishi reported *cis*-allylalumination of unactivated acetylenes in the presence of Zr catalyst (ref 4e). The present addition proceeds in a *trans* manner. Accordingly, it seems that the allylaluminium species is not involved as a reactive intermediate.

(8) Other Lewis acids such as $ZrCl_4$, $TiCl_4$, $SnCl_4$, BF_3·Et_2O, $ZnCl_2$, and $B(C_6F_5)_3$ did not catalyze the addition reaction of allyltrimethylsilane to **1d**.

(9) It is worth noting that 20 mol % of $HfCl_4$ also catalyzed these reactions; however, the yields of **3** in these cases were usually slightly lower.

Table 3. $HfCl_4$-Catalyzed Addition of Allyltrimethylsilane to Alkynes **1a**−**j**[a]

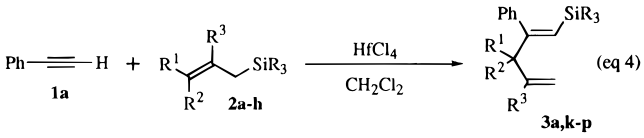


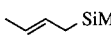
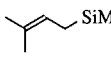
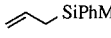
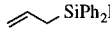
a : R^1= Ph, R^2= H
b : R^1= *p*-Me-C_6H_4, R^2= H
c : R^1= $PhCH_2$, R^2= H
d : R^1= $CH_3(CH_2)_5$, R^2= H
e : R^1= $CH_3(CH_2)_9$, R^2= H
f : R^1= , R^2= H
g : R^1= Ph, R^2= Me
h : R^1= Ph , R^2= Et
i : R^1= H , R^2= TMS
j : R^1= t-Bu , R^2= H

entry	alkyne	R^1	R^2	product	yield(%)[b]
1	**1a**	Ph	H	**3a**	95
2	**1b**	*p*-$CH_3C_6H_4$	H	**3b**	97
3	**1c**	$PhCH_2$	H	**3c**	73
4	**1d**	$CH_3(CH_2)_5$	H	**3d**	87
5	**1e**	$CH_3(CH_2)_9$	H	**3e**	86
6	**1f**	1-cyclohexenyl	H	**3f**	42
7	**1g**	Ph	Me	**3g**	90
8	**1h**	Ph	Et	**3h**	82
9	**1i**	H	TMS	**3i**	65[c,d]
10	**1j**	t-Bu	H	**3j**	10[b]

[a] All reactions were carried out in CH_2Cl_2 at 0 °C with 50 mol % of $HfCl_4$.[9] [b] Isolated yield, except for where otherwise indicated. [c] Yield was determined by ^{1}H NMR with *p*-xylene as an internal standard. [d] The allyltrimethylsilane was added slowly *via* syringe pump in order to avoid its dimerization.[4h]

Table 4. $HfCl_4$-Catalyzed Addition of **2a**−**h** to Phenylacetylene[a]



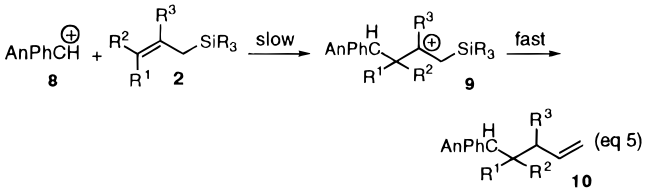
entry	allylsilane		time (min.)	product	yield (%)[b]
1		**2a**	60[c]	**3a**	95
2		**2b**	60	**3k**	96
3		**2c**	60	**3k**	90
4		**2d**	25	**3l**	92
5		**2e**	120	**3m**	97
6		**2f**	180	**3n**	73
7		**2g**	140	**3o**	76
8		**2h**	230	**3p**	51

[a] All reactions were carried out in CH_2Cl_2 at 0 °C with 50 mol % of $HfCl_4$. [b] Isolated yield. [c] In the presence of 10 equiv of TMSCl the reaction was completed in 20 min.

Desilylated products **4** were not detected by ^{1}H NMR and capillary GLC analyses of crude reaction mixtures. An exceptionally low yield of the allylsilylation of *tert*-butylacetylene (**1j**) (entry 10) might be explained by steric factors. The reverse regiochemistry of the addition of **2a** to trimethylsilylacetylene (**1i**) is in good agreement with the stabilization of a cation β to silicon in the cationic intermediate **13**, thus, directing nucleophilic attack of the allyl group to the terminal carbon atom (*vide post*).

We further examined the $HfCl_4$-catalyzed addition of different substituted allylsilanes **2a**−**h** to phenylacetylene (**1a**) (eq 4, Table 4). Although the reaction between **1a** and **2a** in the presence of 10 equiv of TMSCl proceeded more rapidly than without the chlorosilane (Table 4, entry 1, footnote *c*), the $HfCl_4$−TMSCl procedure was not applied to other substrates due to obvious synthetic inconvenience (mentioned above). The addition of allyl- (**2a**, entry 1), *E*- and *Z*-crotyl- (**2b** and **2c**, entries 2 and 3), methallyl- (**2d**, entry 4), and prenyltrimethylsilane (**2e**, entry 5) to phenylacetylene (**1a**) proceeded smoothly, affording the corresponding adducts **3a**,**k**−**m** in excellent chemical yields (90−96%). Replacement of the trimethylsilyl group in **2a** with triethylsilyl (**2f**), dimethylphenylsilyl (**2g**), and methydiphenylsilyl (**2h**) groups caused a slight decrease in the chemical yields of allylsilylated products **3n**−**p**, as well as a noticeable elongation of reaction times (Table 4, entries 6−8). It should be pointed out that in all cases only γ-addition products **3** were formed, and the formation of α-adducts was not detected by analyses of crude reaction mixtures by ^{1}H NMR and capillary GLC (Table 4, eq 4).

This kind of regiochemistry is not surprising. The γ-addition of different substituted allylsilanes to various electrophiles has been extensively studied during the past two decades and well-documented.[10] The γ-regioselectivity of this reaction has been explained by the intermediate formation of carbenium ions, which are hyperconjugatively stabilized by the carbon−silicon bond in the β-position.[11] Furthermore, the recent kinetic study on the reaction of carbenium ions with various allylsilanes accomplished by Mayr provided the methodology for quantitative determination of the nucleophilicity of the allylsilane element (eq 5).[12] Attack of the carbenium cation **8** at the γ-position of the allylsilicon compound **2** is rate determining



and leads to formation of the β-silicon-stabilized carbenium ion **9**, which subsequently transforms into product **10** *via* elimination of the silicon group (eq 5).[12]

In order to elucidate whether the relative reactivities of different substituted allylsilanes in the $HfCl_4$-catalyzed allylsilylation of alkynes are similar to those toward carbenium ions reported by Mayr,[12] we determined relative reactivities for addition of allylsilanes **2a**−**e** to phenylacetylene (**1a**) based on the measurement of half-reaction times[13] (eq 4, Figure 1).

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(11) (a) Wierchke, S. G.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) White, J. C.; Cave, R. J.; Davidson, E. R. *J. Am. Chem. Soc.* **1988**, *110*, 6308. (c) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819. (d) Eaborn, C. *J. Chem. Soc., Chem. Commun.* **1972**, 1255. (e) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. (f) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1989; Part 1, p 196. (g) McGibbon, G. A.; Brook, M. A.; Terlouw, J. K. *J. Chem. Soc., Chem. Commun.* **1992**, 360. (h) Dallaire, C.; Brook, M. A. *Organometallics* **1990**, *9*, 2873. (i) Kresge, A. J.; Tobin, J. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 721. (j) Gabelica, V.; Kresge, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3838. (k) Zhang, W.; Stone, J. A.; Brook, M. A.; McGibbon, G. A. *J. Am. Chem. Soc.* **1996**, *118*, 5764.

(12) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954.

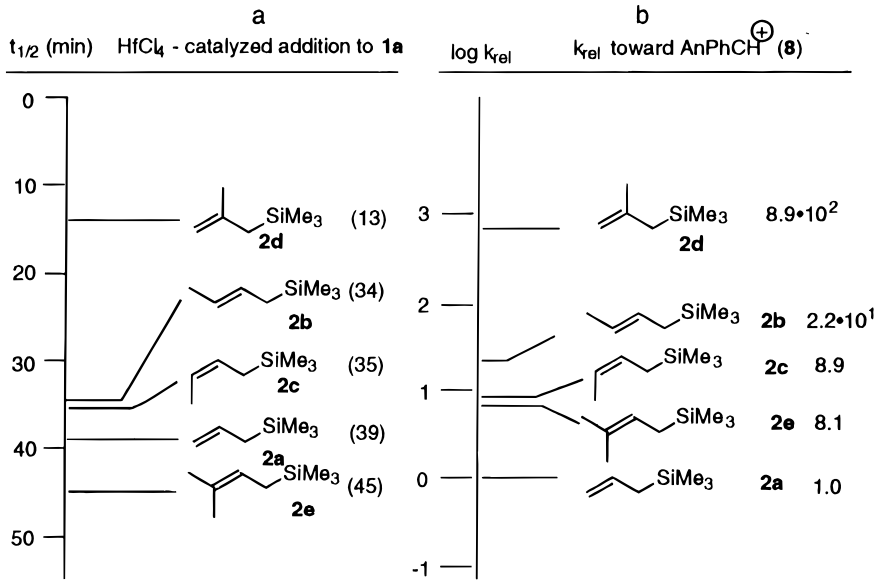
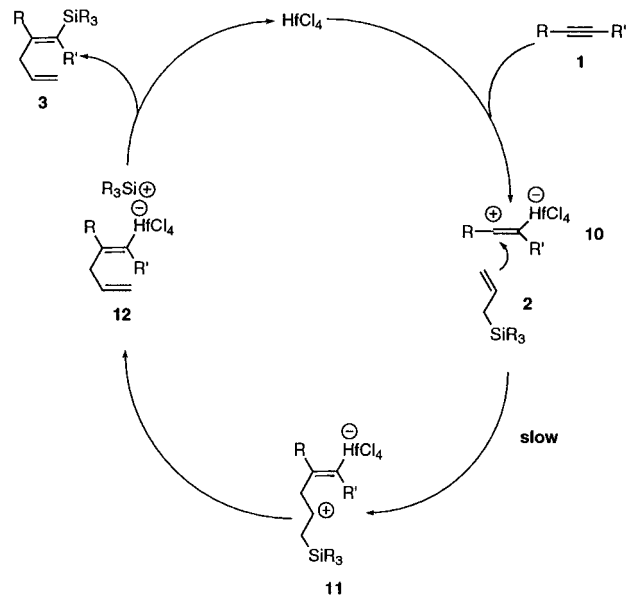


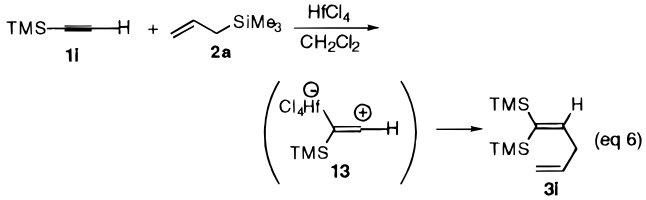
Figure 1. (a) Determined by capillary GLC with hexadecane as an internal standard. See also ref 13. (b) Relative reaction constants from ref 12. An = *p*-MeO-C_6H_4.

Scheme 2. Proposed Mechanism for the $HfCl_4$-Catalyzed *trans*-Allylsilylation of Unactivated Alkynes



We found that relative reactivities of most allylsilanes bearing trimethylsilyl groups (**2a**−**e**) in the $HfCl_4$-catalyzed addition to **1a** (Figure 1, part a) are in good agreement with relative reactivities of the same allylsilanes **2a**−**e** toward diarylcarbenium ion **8**[12] (Figure 1, part b). This finding encouraged us to consider the intermediacy of some cationic species analogous to **8** and **9** in the $HfCl_4$-catalyzed allylsilylation of alkynes, and allowed us to propose the plausible mechanism for this reaction shown in Scheme 2.

As we have previously proposed for the Lewis acid catalyzed hydro-[14] and allylstannation[15] and hydro-[16] and allylsilylation[5] of alkynes, coordination of $HfCl_4$ to the triple bond of **1** would form zwitterionic intermediate **10**, which would attack the double bond of allylsilane **2** at the γ-position affording carbenium cation **11** *trans*-selectively. The elimination of the silyl group from **11** would form ate-complex **12**, and the subsequent transmetalation of hafnium halide with silicon would produce **3** and regenerate the catalyst. This mechanism nicely explains the reverse regiochemistry upon allylsilylation of trimethysilylacetylene (**1i**), previously mentioned (Table 3, eq 3). The coordination of $HfCl_4$ to **1i** would form another regioisomer of **10**, the cationic intermediate **13**, due to β-silicon stabilization[11] (eq 6).



Subsequent reaction of zwitteronic **13** with **2a** *via* a similar transformation pathway as **10** (Scheme 2) would produce **3i** (eq 6).

Although the relative reactivities of most allyltrimethylsilanes **2a**−**e** in the $HfCl_4$-catalyzed addition to **1a** are in good agreement with relative reactivities of the same allylsilanes **2a**−**e** toward diarylcarbenium ion **8** reported by Mayr,[12] the relative reactivities of allylsilanes bearing more bulky groups at the silicon atom are completely different from Mayr's observations. Indeed, even more bulky allyltriethylsilane (**2f**) and allyldimethyl(*tert*-butyl)silane (**2i**) reacted with a carbenium ion slightly faster than allyltrimethylsilane (**2a**) ($k_{rel} = 3.13 \times 10^2$, 2.04×10^2, and 1.87×10^2 for **2f**, **2i**, and **2a**, respectively).[12] In contrast we found that the triethylsilyl analogue **2f** reacted almost two times slower than its trimethylsilyl counterpart **2a** ($t_{1/2} = 72$ and 39 min for **2f** and **2a**, respectively),[13] whereas the most hindered **2i** did not react with **1a** at all. Although our measurements of relative reactivities are a rough estimation, these results indicate the dramatic effect of the bulkiness of substituents at the silyl moiety on the overall reaction rate. Initially, we considered the transmetalation of **12** with a silyl group as a slow step, which could be dependent upon the size

(13) Although the so-called "half-reaction time" data are very approximate, they are only useful for the rough estimation of relative reactivities. For example, see: Fleming, I.; Langley, J. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1412.

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of a silyl group, thus affecting the overall reaction rate. In order to clarify the formation of **12** in the reaction of phenylacetylene (**1a**) with bulky **2i** we quenched the reaction mixture with H_2O. In the case where the ate-complex **12** is present in the reaction mixture, hydrolysis should unavoidably lead to desilylated product **4**. The experiment indicated no traces of **4** were formed. Instead, a major portion of starting **1a** was recovered, thus discounting the proposed rationale. Although the dramatic affect of steric hindrance of the silyl group on the apparent nucleophilicity of allylsilanes is not completely understood, the observed regio- and streochemistry of the $HfCl_4$-catalyzed allylsilylation of alkynes is reasonably explained by the proposed mechanism (Scheme 2).

Conclusion

We are now in position to effectively prepare (regio- and stereoselectively in high to excellent yields) various types of silylated 1,4-dienes *via* the Lewis acid catalyzed allylsilylation of unactivated alkynes. The resulting silylated 1,4-dienes are not easily available *via* the previously known methodologies and may be useful as building blocks in organic synthesis. Formation of carbocation intermediates such as **10** (and aluminum analogue) followed by allyl transfer from the side opposite Hf (or Al) can explain the regio- and stereoselectivity of the Lewis acid catalyzed allylsilylation reaction.

Experimental Section

General Information. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) instrument. IR spectra were recorded on a Shimadzu FTIR-8200A spectrometer. High-resolution mass spectra were recorded on a Hitachi M-2500S spectrometer. Capillary GLC analysis was performed on a SHIMADZU GC-14A (CPB20-M25-025 column). Column chromatography was carried out employing Merck silica gel (Kieselgel 70−230 mesh), and analytical thin layer chromatography (TLC) was performed on 0.2-mm precoated silica gel plates (Kieselgel 60 F_{254}). All manipulations were conducted under an argon atmosphere following standard Schlenk techniques. Anhydrous solvents were purchased from Kanto Chemicals. The following allylsilanes were prepared according to known procedures: (*E*)-, and (*Z*)-crotyltrimethylsilane (**b**, **c**),[17] (2-methylallyl)trimethylsilane (**2d**),[18] (3,3-dimethylallyl)trimethylsilane (**2e**),[19] allyltriethylsilane (**2f**),[10a] allyldimethylphenylsilane (**2g**),[10a] allylmethyldiphenylsilane (**2h**),[10a] and allyldimethyl(*tert*-butyl)silane (**2i**).[10a] All other compounds used were commercially available and purchased from Aldrich.

$EtAlCl_2$−TMS-Catalyzed Preparation of 3 (General Procedure). $EtAlCl_2$ (0.52 mL, 0.96 M in hexane, 0.5 mmol) was added to a mixture of allyltrimethylsilane **2** (0.19 mL, 1.2 mmol) and TMSCl (2.54 mL, 20 mmol) at −47 °C followed by addition of alkyne **1** (1.0 mmol). The reaction mixture was stirred for 2 h at −47 °C, quenched with diethylamine (2.0 mL, 19.4 mmol), and then allowed to warm to 0 °C. $NaHCO_3$(aq) was added and the mixture was extracted (Et_2O−H_2O), dried (Na_2SO_4), and concentrated. Product **3** was purified by column chromatography (silica gel).

$HfCl_4$-Catalyzed Preparation of 3 (General Procedure). Allyltrimethylsilane **2** (0.16 mL, 1.0 mmol) was added to a suspension of $HfCl_4$ (80 mg, 0.25 mmol) in dichloromethane (1 mL) at 0 °C followed by addition of alkyne **1** (0.5 mmol). The reaction temparature was kept at 0 °C and monitored by GLC analysis. After completion of the reaction diethylamine (0.5 mL) was added followed by addition of $NaHCO_3$(aq). Then mixture was extracted (Et_2O−H_2O), dried (Na_2SO_4), and concentrated. Product **3** was purified by column chromatography (silica gel).

(*Z*)-2-Phenyl-1-(trimethylsilyl)-1,4-pentadiene (3a): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.30−7.25 (m, 3H), 7.17−7.13 (m, 2H), 5.83 (ddt, J = 7.0, 9.2, 17.9 Hz, 1H), 5.59 (t, J = 1.5 Hz, 1H), 5.02−4.98 (m, 2H), 3.21 (ddd, J = 1.5, 2.7, 7.0 Hz, 2H), −0.19 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 157.4 (C), 135.9 (CH), 144.0, 127.9, 127.7, 127.0 (Ar), 116.4 (CH_2═), 46.7 (CH_2), 0.0 (Si-CH_3). IR (neat) 3078, 2953, 2897, 1639, 1610, 1595, 1490, 1248, 839 cm^{-1}. MS (EI) *m*/*z* 216 (M^+, 3), 201 ($M^+ - CH_3$, 36), 73 (100). HRMS calcd for $C_{14}H_{20}Si$ 216.1334, found 216.1290.

(*Z*)-2-(*p*-Tolyl)-1-(trimethylsilyl)-1,4-pentadiene (3b): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.17−7.03 (m, 4H), 5.83 (ddt, J = 7.0, 9.3, 17.8 Hz, 1H), 5.56 (t, J = 1.3 Hz, 1H), 5.06−4.99 (m, 2H), 3.14 (ddd, J = 1.3, 2.7, 7.0 Hz, 2H), 2.35 (s, 3H), −0.17 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 157.4 (C), 136.6, 136.1 (CH), 141.1, 128.4, 127.8, 127.6 (Ar), 116.3 (CH_2═), 46.7, 21.2 (CH_2), 0.1 (Si-CH_3). IR (neat) 2953, 1601, 1510, 1246, 841 cm^{-1}. MS (EI) *m*/*z* 230 (M^+, 12), 215 ($M^+ - CH_3$, 28), 73 (100). HRMS calcd for $C_{15}H_{22}Si$ 230.1491, found 230.1491.

(*Z*)-2-Benzyl-1-(trimethylsilyl)-1,4-pentadiene (3c): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.32−7.16 (m, 5H), 5.76 (ddt, J = 7.0, 10.3, 16.8 Hz, 1H), 5.46 (s, 1H), 5.04−4.89 (m, 2H), 3.51 (s, 2H), 2.66 (dd, J = 1.1, 7.0 Hz, 2H), 0.16 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 155.1 (C), 136.5, 128.7 (CH), 139.5, 128.3, 126.8, 126.1 (Ar), 116.3 (CH_2═), 43.0, 41.6 (CH_2), 0.4 (Si-CH_3). IR (neat) 3028, 2953, 1639, 1614, 1495, 1248, 839 cm^{-1}. MS (EI) *m*/*z* 230 (M^+, 5), 215 ($M^+ - CH_3$, 33), 73 (100). HRMS calcd for $C_{15}H_{22}Si$ 230.1576, found 230.1534.

(*E*)-2-Hexyl-1-(trimethylsilyl)-1,4-pentadiene (3d): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.88−5.73 (m, 1H), 5.19 (d, J = 1.1 Hz, 1H), 5.05−5.00 (m, 1H), 2.18 (dd, J = 1.1, 7.0 Hz, 2H), 2.14−2.08 (m, 2H), 1.38−1.29 (m, 8H), 0.89 (t, J = 7.3 Hz, 3H), 0.09 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 158.0 (C), 136.9, 124.3 (CH), 115.9 (CH_2═), 43.5, 36.3, 31.6, 29.6, 29.1, 22.7 (CH_2), 14.1 (CH_3), 0.4 (Si-CH_3). IR (neat) 3078, 2957, 2928, 2858, 1637, 1610, 1431, 1248, 837 cm^{-1}. MS (EI) *m*/*z* 224 (M^+, 2), 209 ($M^+ - CH_3$, 7), 73 (100). HRMS calcd for $C_{14}H_{28}Si$ 224.1961, found 224.1976.

(*E*)-2-Decyl-1-(trimethylsilyl)-1,4-pentadiene (3e): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.81 (ddt, J = 7.0, 9.2, 18.0 Hz, 1H), 5.20 (t, J = 1.1 Hz, 1H), 5.05−4.98 (m, 2H), 2.81 (ddd, J = 1.1, 2.6, 7.0 Hz, 2H), 2.13−2.08 (m, 2H), 1.39−1.27 (m, 16H), 0.88 (t, J = 7.0 Hz, 3H), 0.09 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 158.0 (C), 136.9, 124.3 (CH), 115.9 (CH_2═), 43.5, 36.2, 31.9, 29.9, 29.6, 29.3, 29.1, 22.7 (CH_2), 14.1 (CH_3), 0.4 (Si-CH_3). IR (neat) 3078, 2926, 2855, 1637, 1610, 1466, 1247, 837 cm^{-1}. MS (EI) *m*/*z* 280 (M^+, 3), 265 ($M^+ - CH_3$, 6), 73 (100). HRMS calcd for $C_{18}H_{36}Si$ 280.2586, found 280.2593.

(*Z*)-2-(1-Cyclohexenyl)-1-(trimethylsilyl)-1,4-pentadiene (3f): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.78 (ddt, J = 7.0, 9.2, 17.8 Hz, 1H), 5.47 (quint, J = 1.8 Hz, 1H), 5.19 (s, 1H), 5.01−4.97 (m, 2H), 2.88 (ddd, J = 1.5, 2.6, 7.0 Hz, 2H), 2.07−1.98 (m, 4H), 1.68−1.56 (m, 4H), 0.04 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 160.7, 140.5 (C), 136.6, 124.8, 124.3 (CH), 115.6 (CH_2═), 43.2, 27.0, 25.0, 22.6, 22.0 (CH_2), 0.5 (Si-CH_3). IR (neat) 2929, 1645, 1597, 1442, 1244, 916, 840 cm^{-1}. MS (EI) *m*/*z* 220 (M^+, 1), 205 ($M^+ - CH_3$, 20), 73 (100). HRMS calcd for $C_{14}H_{24}Si$ 220.1648, found 220.1682.

(*Z*)-3-Phenyl-2-(trimethylsilyl)-2,5-hexadiene (3g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27−7.21 (m, 3H), 7.09−7.07 (m, 2H), 5.72 (ddt, J = 6.4, 10.0, 17.0 Hz, 1H), 5.00−4.93 (m, 2H), 3.17 (d, J = 6.4 Hz, 2H), 1.83 (s, 3H), −0.25 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 148.6, 145.7, 134.8, 133.6, 128.9, 127.6, 126.5, 115.0, 40.4, 17.8, 0.1. IR (neat) 3076, 2952, 2895, 1952, 1891, 1815, 1637, 1593, 1247, 912, 835, 762, 702 cm^{-1}. MS (EI) *m*/*z* 230 (M^+, 29), 215 ($M^+ - CH_3$, 26), 73 (100). Anal. Calcd for $C_{15}H_{22}Si$: C, 78.19; H, 9.62. Found: C, 77.910; H, 9.374.

(*Z*)-4-Phenyl-3-(trimethylsilyl)-3,6-heptadiene (3h): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.29−7.24 (m, 3H), 7.12−7.08 (m, 2H), 5.73 (ddt, J = 6.6, 10.3, 16.9 Hz, 1H), 5.01−4.93 (m, 2H), 3.20 (dt, J = 6.6, 1.5 Hz, 2H), 2.33 (q, J = 7.5 Hz, 2H), 1.08 (t, J = 7.5 Hz, 3H), −0.21 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 149.1, 145.2, 139.9, 135.7, 129.2, 127.5, 126.5, 115.3, 40.0, 24.9, 15.2, 0.6. IR (neat) 2957, 2898, 1943, 1886, 1745, 1590, 1485, 1443, 1249, 836 cm^{-1}. MS (EI) *m*/*z* 244 (M^+, 13), 229 ($M^+ - CH_3$, 12), 73 (100). HRMS calcd for $C_{16}H_{24}Si$ 244.1646, found 244.1641.

(*Z*)-1,1-Bis(trimethylsilyl)-1,4-pentadiene (3i): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.57 (t, J = 7.0 Hz, 1H), 5.84 (ddt, J = 6.6, 10.6, 16.5 Hz, 1H), 5.08−5.01 (m, 2H), 3.03−2.69 (m, 2H), 0.17 (s, 9H), 0.09

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(s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 154.1, 141.8, 136.4, 115.4, 39.8, 1.8, 0.3. IR (neat) 2955, 1562, 1249, 991, 945, 914, 879, 839, 761, 684, 617 cm^{-1}. MS (EI) *m*/*z* 244 (M^+, 13), 229 ($M^+ - CH_3$, 12), 73 (100). HRMS calcd for $C_{11}H_{24}Si_2$ 212.1415, found 212.1432.

(*Z*)-2-(*tert*-Butyl)-1-(trimethylsilyl)-1,4-pentadiene (3j): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 5.80 (ddt, J = 7.0, 10.3, 16.9 Hz, 1H), 5.24 (s, 1H), 5.06−4.96 (m, 2H), 2.89 (ddd, J = 1.1, 2.6, 7.0 Hz, 2H), 1.13 (s, 9H), 0.15 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 165.7, 138.5, 123.8, 115.6, 41.8, 38.0, 30.4, 2.2. IR (neat) 2954, 1440, 1388, 1251, 843 cm^{-1}. MS (EI) *m*/*z* 196 (M^+, 1), 181 ($M^+ - CH_3$, 8), 73 (100). HRMS calcd for $C_{12}H_{24}Si$ 196.1645, found 196.1633.

(*Z*)-3-Methyl-2-phenyl-1-(trimethylsilyl)-1,4-pentadiene (3k): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.30−7.24 (m, 3H), 7.11−7.07 (m, 2H), 5.85 (ddd, J = 16.3, 11.2, 7.0 Hz, 1H), 5.58 (d, J = 1.1 Hz, 1H), 5.00−4.93 (m, 2H), 3.14 (quint, 1H), 1.11 (d, J = 7.0 Hz, 2H), −0.22 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 143.5, 142.1, 128.6, 127.4, 126.7, 126.0, 113.5, 48.2, 18.8, 0.0. IR (neat) 2964, 2896, 1637, 1608, 1593, 1247, 914, 871, 702 cm^{-1}. MS (EI) *m*/*z* 230 (M^+, 3), 215 ($M^+ - CH_3$, 7), 73 (100). HRMS calcd for $C_{15}H_{22}Si$ 230.1489, found 230.1480. Anal. Calcd for $C_{15}H_{22}Si$: C, 78.19; H, 9.62. Found: C, 77.961; H, 9.776.

(*Z*)-4-Methyl-2-phenyl-1-(trimethylsilyl)-1,4-pentadiene (3l): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.28−7.26 (m, 2H), 7.17−7.13 (m, 3H), 5.62 (t, J = 1.3 Hz, 1H), 4.77 (m, 1H), 4.65 (m, 1H), 3.12 (s, 1H), 1.71 (s, 3H), −0.17 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 156.4, 143.9, 142.9, 129.3, 127.9, 127.6, 126.8, 112.9, 51.4, 22.1, 0.1. IR (neat) 2925, 2854, 1639, 1608, 1465, 1247, 891, 837 cm^{-1}. MS (EI) *m*/*z* 230 (M^+, 3), 215 ($M^+ - CH_3$, 7), 73 (100). HRMS calcd for $C_{15}H_{22}Si$ 230.1490, found 230.1496. Anal. Calcd for $C_{15}H_{22}Si$: C, 78.19; H, 9.62. Found: C, 78.054; H, 9.849.

(*Z*)-3,3-Dimethyl-2-phenyl-1-(trimethylsilyl)-1,4-pentadiene (3m): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.30−7.26 (m, 3H), 7.07−7.04 (m, 2H), 5.96 (dd, J = 17.6, 10.6 Hz, 1H), 5.02 (dd, J = 10.6, 1.5 Hz, 1H), 4.98 (dd, J = 17.6, 1.5 Hz, 1H), 1.16 (s, 6H), −0.25 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 165.1, 147.2, 142.2, 130.0, 126.9, 126.4, 125.8, 111.0, 44.4, 26.7, −0.2. IR (neat) 2964, 1585, 1245, 867, 837 cm^{-1}. MS (EI) *m*/*z* 244 (M^+, 15), 229 ($M^+ - CH_3$, 8), 73 (100). Anal. Calcd for $C_{16}H_{24}Si$: C, 78.61; H, 9.90. Found: C, 78.729; H, 9.982.

(*Z*)-2-Phenyl-1-triethylsilyl-1,4-pentadiene (3n): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.28−7.24 (m, 3H), 7.17−7.14 (m, 2H), 5.83 (ddt, J = 17.6, 9.5, 7.0 Hz, 1H), 5.53 (d, J = 1.3 Hz, 1H), 5.06−4.98 (m, 2H), 3.17 (ddd, J = 7.0, 1.3, 1.3 Hz 2H), 0.81 (t, J = 7.9 Hz, 6H), 0.30 (q, J = 7.9 Hz, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 158.1, 144.3, 136.1, 127.8, 127.6, 127.0, 124.7, 116.3, 47.1, 7.5, 4.5. IR (neat) 2952, 2873, 1595, 1491, 1458, 1236, 737, 700 cm^{-1}. MS (EI) *m*/*z* 258 (M^+, 2), 229 ($M^+ - C_2H_5$, 100). Anal. Calcd for $C_{17}H_{26}Si$: C, 78.99; H, 10.14. Found: C, 77.155; H, 10.329.

(*Z*)-2-Phenyl-1-(dimethylphenylsilyl)-1,4-pentadiene (3o): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.45−7.42 (m, 2H), 7.33−7.30 (m, 3H), 7.23−7.20 (m, 3H), 7.11−7.07 (m, 2H), 5.92−5.79 (m, 1H), 5.77 (t, J = 1.5 Hz, 1H), 5.07−5.00 (m, 2H), 3.18 (ddd, J = 7.0, 2.6, 1.1 2H), 0.00 (s, 6H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 158.8, 143.6, 140.3, 135.7, 133.6, 128.5, 127.9, 127.6, 127.0, 125.7, 116.6, 46.8, −1.3. IR (neat) 3068, 2954, 1953, 1887, 1826, 1593, 1427, 1247, 1112, 837, 700 cm^{-1}. MS (EI) *m*/*z* 278 (M^+, 77), 263 ($M^+ - CH_3$, 27), 135 (100). Anal. Calcd for $C_{19}H_{22}Si$: C, 81.95; H, 7.96. Found: C, 81.945; H, 8.063.

(*Z*)-2-Phenyl-1-(diphenylmethylsilyl)-1,4-pentadiene (3p): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.47−7.41 (m, 4H), 7.34−7.27 (m, 6H), 7.17−7.12 (m, 3H), 7.05−7.02 (m, 2H), 6.02 (t, J = 1.3 Hz, 1H), 5.88 (ddt, J = 17.6, 9.5, 7.0 Hz, 1H), 5.11−5.03 (m, 2H), 3.25 (ddd, J = 7.0, 2.6, 1.3 2H), 0.06 (s, 3H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 160.3, 143.2, 138.3, 135.6, 134.5, 128.8, 127.8, 127.6, 127.1, 123.7, 123.6, 116.8, 46.9, −3.3. IR (neat) 3067, 3049, 3020, 2178, 1950, 1886, 1824, 1593, 1489, 1427, 1109, 793, 729, 700 cm^{-1}. MS (EI) *m*/*z* 340 (M^+, 69), 325 ($M^+ - CH_3$, 12), 197 (100). Anal. Calcd for $C_{24}H_{24}Si$: C, 84.65; H, 7.10. Found: C, 84.950; H, 7.269.

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