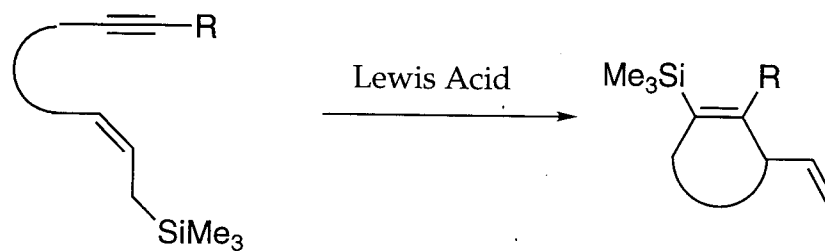
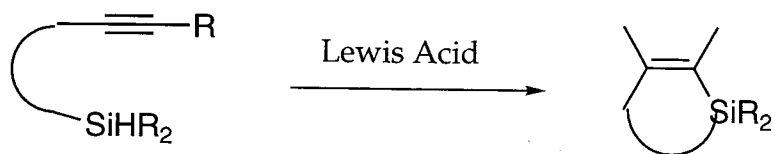
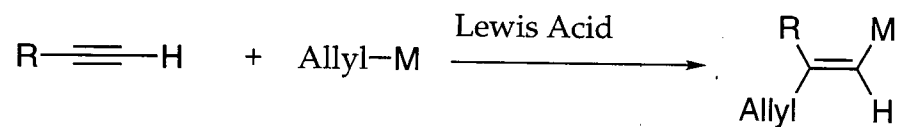
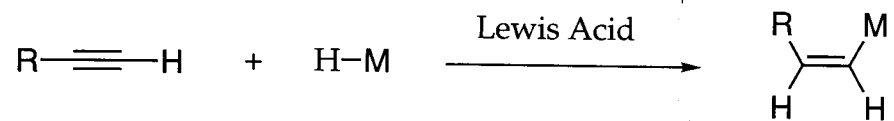


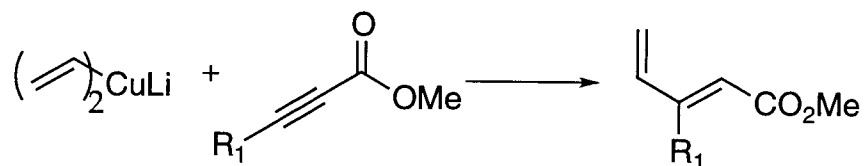
## Lewis Acid Catalyzed Hydrometalation and Carbometalation Reactions of Unactivated Alkynes



# Lewis Acid Activation of Alkynes

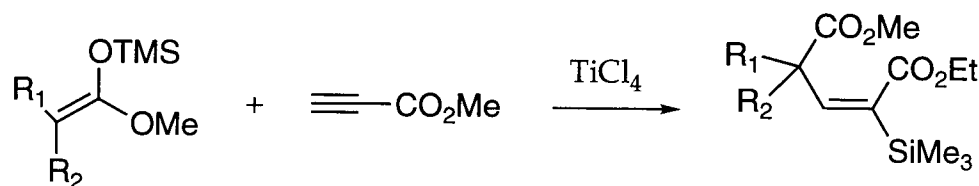
## Nucleophilic Addition Reactions with Activated Alkynes (Conjugated Addition)

### 1. organocopper reagents



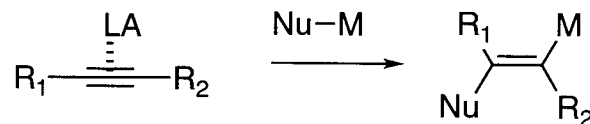
Comprehensive Organic Synthesis  
Vol4. p169  
Organocopper:  
Org. Reaction. V41, chap2

### 2. Lewis Acid Promoted



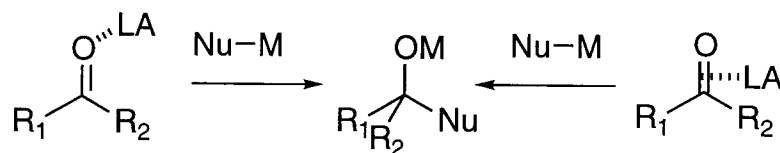
Comprehensive Organic Synthesis  
Vol4. p139

## Nucleophilic Addition Reactions with Unactivated Alkynes



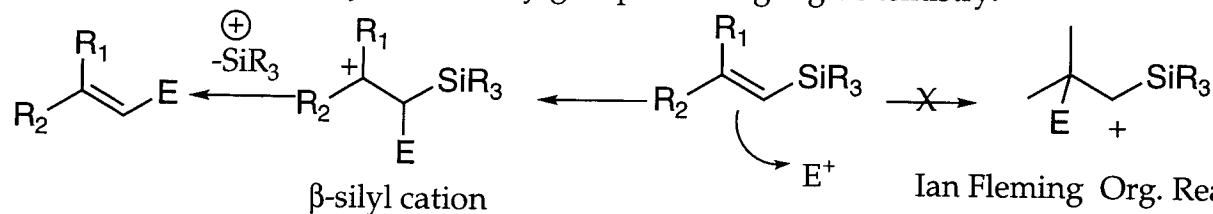
Electrophilic activation of the  $\pi$  system towards nucleophilic addition is necessary.  
Lewis acid is coordinated with the  $\pi$  electron clouds.

For carbonyl,  $\sigma$  electron coordination is common.

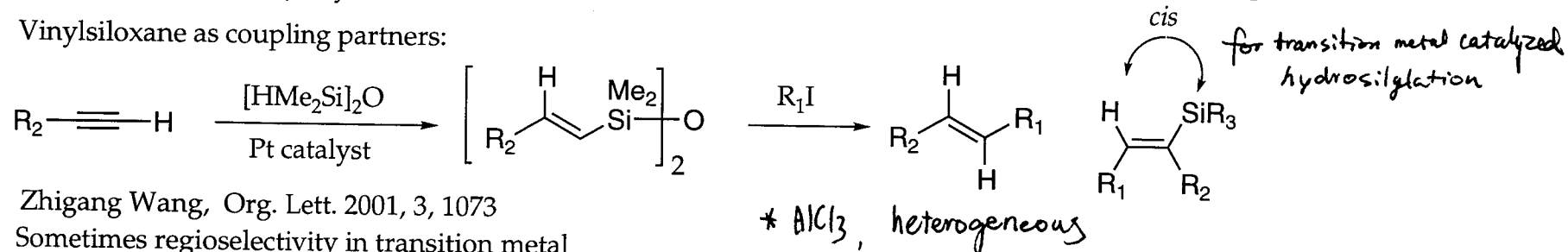


# Lewis Acid Catalyzed Hydrosilylation of Unactivated Alkynes

Vinyl silanes are useful synthons. Silylgroup directing regiochemistry.



Vinylsiloxane as coupling partners:

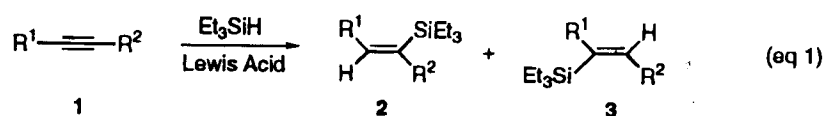


Zhigang Wang, Org. Lett. 2001, 3, 1073

Sometimes regioselectivity in transition metal catalyzed hydrosilylation can be problematic.

entry	Lewis acid (equiv)	1		yield (%)	
		R <sup>1</sup>	R <sup>2</sup>	2	3
1	ZrCl <sub>4</sub> (0.2)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	H	(1a)	trace 0
2	HfCl <sub>4</sub> (0.2)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	H	(1a)	28 0
3	AlCl <sub>3</sub> (0.2)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	H	(1a)	93 0
4	EtAlCl <sub>2</sub> (0.2)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	H	(1a)	95 0
5 <sup>b</sup>	Et <sub>2</sub> AlCl (0.2)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	H	(1a)	0 0
6 <sup>c</sup>	AlCl <sub>3</sub> (0.2)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	H	(1a)	90 0
7	AlCl <sub>3</sub> (0.2)	PhCH <sub>2</sub>	H	(1b)	85 0
8	AlCl <sub>3</sub> (0.2)	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	(1c)	82 0
9	AlCl <sub>3</sub> (0.2)	Me <sub>3</sub> Si	H	(1d)	89 0
10	AlCl <sub>3</sub> (0.2)	1-cyclohexenyl	H	(1e)	45 0
11 <sup>d</sup>	EtAlCl <sub>2</sub> (1.0)	Ph	H	(1f)	61 0
12 <sup>e</sup>	EtAlCl <sub>2</sub> (1.2)	( <i>i</i> -Pr) <sub>3</sub> SiO(CH <sub>2</sub> ) <sub>2</sub>	H	(1g)	86 0
13	AlCl <sub>3</sub> (1.2)	( <i>i</i> -Pr) <sub>3</sub> SiO(CH <sub>2</sub> ) <sub>4</sub>	H	(1h)	74 0
14	EtAlCl <sub>2</sub> (1.2)	PhCH <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub>	H	(1i)	72 0
15	AlCl <sub>3</sub> (0.2)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub>	(1j)	73
16	AlCl <sub>3</sub> (0.2)	Ph	Ph	(1k)	66
17	AlCl <sub>3</sub> (0.2)	Ph	CH <sub>3</sub>	(1l)	76 10
18	AlCl <sub>3</sub> (0.2)	Ph	C <sub>2</sub> H <sub>5</sub>	(1m)	54 26

**Table 1. Lewis Acid-Catalyzed Hydrosilylation of Acetylenes with Et<sub>3</sub>SiH<sup>a</sup>**



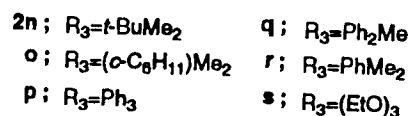
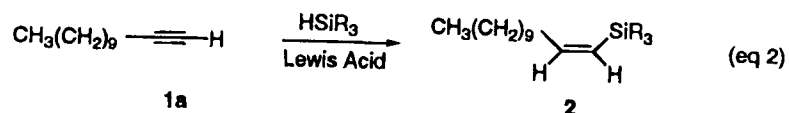
- 1, 2, and 3 a : R<sup>1</sup>=CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>, R<sup>2</sup>=H    g : R<sup>1</sup>=(*i*-Pr)<sub>3</sub>SiO(CH<sub>2</sub>)<sub>2</sub>, R<sup>2</sup>=H  
 b : R<sup>1</sup>=PhCH<sub>2</sub>, R<sup>2</sup>=H    h : R<sup>1</sup>=(*i*-Pr)<sub>3</sub>SiO(CH<sub>2</sub>)<sub>4</sub>, R<sup>2</sup>=H  
 c : R<sup>1</sup>=*tert*-C<sub>4</sub>H<sub>9</sub>, R<sup>2</sup>=H    i : R<sup>1</sup>=PhCH<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>, R<sup>2</sup>=H  
 d : R<sup>1</sup>=Me<sub>3</sub>Si, R<sup>2</sup>=H    j : R<sup>1</sup>=R<sup>2</sup>=CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>  
 e : R<sup>1</sup>=, R<sup>2</sup>=H    k : R<sup>1</sup>=R<sup>2</sup>=Ph  
 f : R<sup>1</sup>=Ph, R<sup>2</sup>=H    l : R<sup>1</sup>=Ph, R<sup>2</sup>=CH<sub>3</sub>  
 m : R<sup>1</sup>=Ph, R<sup>2</sup>=C<sub>2</sub>H<sub>5</sub>

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<sup>a</sup> Reactions were conducted in toluene at 0 °C under Ar unless otherwise noted. <sup>b</sup> The starting material 1a was recovered quantitatively. <sup>c</sup> Reaction was carried out without any solvents. <sup>d</sup> 2f was obtained in 40% yield, if 0.2 equiv of AlCl<sub>3</sub> was used as a catalyst. <sup>e</sup> Hexane was used as a solvent.

# Effects of Silanes And A Possible Mechanism

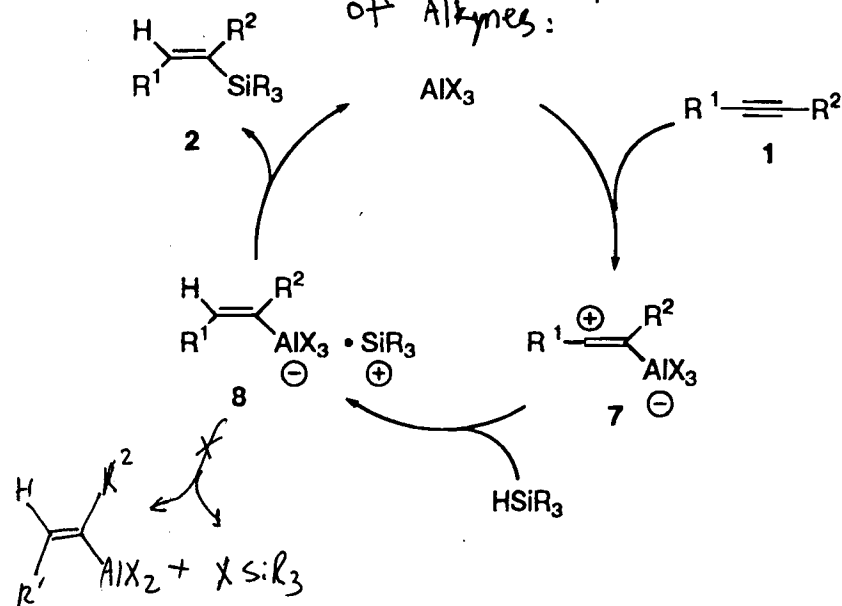
Table 2. Lewis Acid-Catalyzed Hydrosilylation of 1-Dodecyne 1a with R<sub>3</sub>SiH



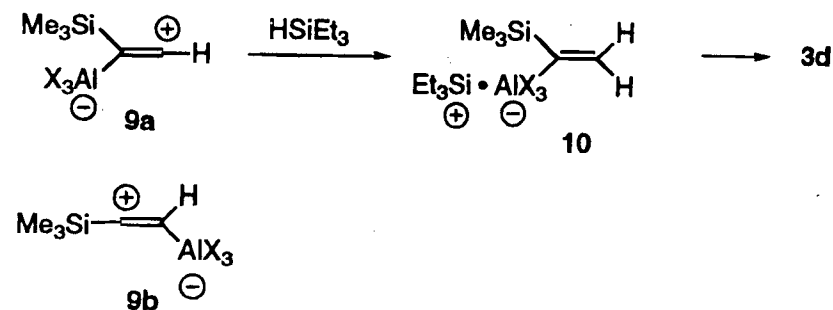
entry	Lewis acid (equiv)	R <sub>3</sub> SiH		yield (%)
1	AlCl <sub>3</sub> (0.2)	<i>t</i> -BuMe <sub>2</sub> SiH (2n)		78
2	AlCl <sub>3</sub> (0.2)	( <i>c</i> -C <sub>6</sub> H <sub>11</sub> )Me <sub>2</sub> SiH (2o)		73
3	EtAlCl <sub>2</sub> (0.2)	Ph <sub>3</sub> SiH (2p)		40
4	EtAlCl <sub>2</sub> (0.2)	Ph <sub>2</sub> MeSiH (2q)		45
5	EtAlCl <sub>2</sub> (0.2)	PhMe <sub>2</sub> SiH (2r)		60
6 <sup>a</sup>	AlCl <sub>3</sub> (0.2)	(EtO) <sub>3</sub> SiH (2s)		0

<sup>a</sup> The starting material 1a was recovered quantitatively.

Mechanism based on electrophilic activation of Alkynes:

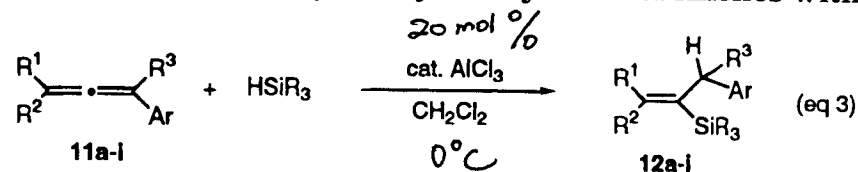


Inverted regioselectivity:



# Hydrosilylation of Aryl Substituted Allenes

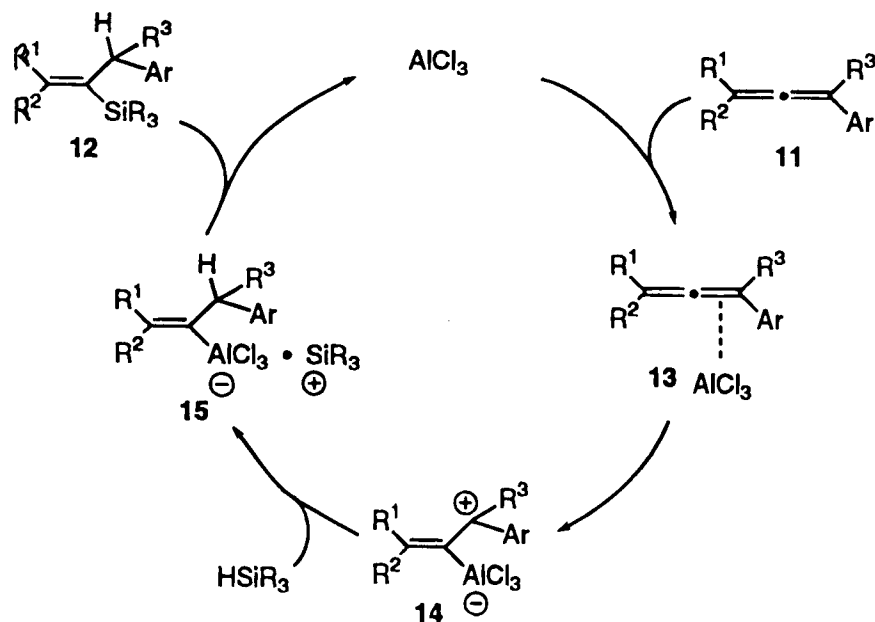
**Table 3. Lewis Acid-Catalyzed Hydrosilylation of Allenes with HSiR<sub>3</sub>**



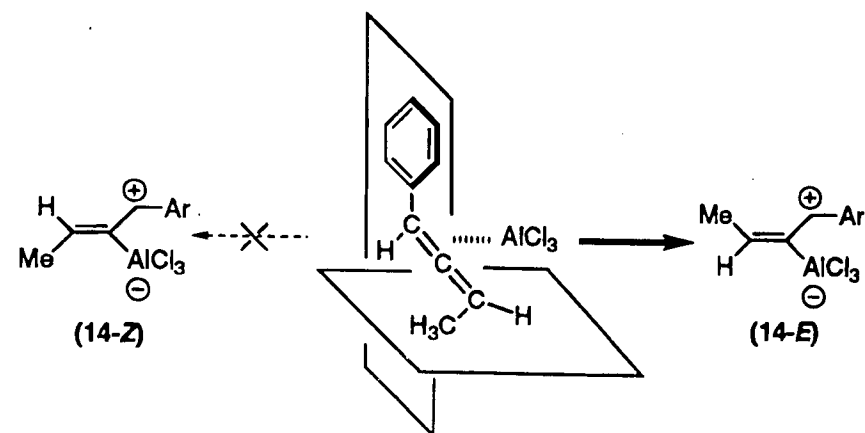
entry	11				HSiR <sub>3</sub>	product	yield (%) <sup>a,b</sup>	
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Ar				
1	H	H	H	C <sub>6</sub> H <sub>5</sub>	11a	HSiMe <sub>2</sub> Et	12a	76
2	H	H	H	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	11b	HSiMe <sub>2</sub> Et	12b	78
3	H	H	H	<i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	11c	HSiMe <sub>2</sub> Et	12c	96
4 <sup>c</sup>	H	H	H	<i>p</i> -CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	11d	HSiMe <sub>2</sub> Et	—	0
5	Me	H	H	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	11e	HSiMe <sub>3</sub>	12e	60
6	Me	H	H	C <sub>6</sub> H <sub>5</sub>	11f	HSiMe <sub>3</sub>	12f	66
7	Me	H	H	<i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	11g	HSiMe <sub>3</sub>	12g	72
8	Me	Me	H	<i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	11h	HSiMe <sub>3</sub>	12h	58
9	H	H	Me	<i>p</i> -F-C <sub>6</sub> H <sub>4</sub>	11i	HSiMe <sub>3</sub>	12i	46

<sup>a</sup> The reactions were carried out in the Wheaton microreactors with 0.5 mmol of 11 and 1.0 mmol of HSiR<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) at 0 °C in the presence of AlCl<sub>3</sub> (0.1 mmol). <sup>b</sup> Isolated yield. <sup>c</sup> The starting material 11d was recovered.

**Scheme 2**



**Scheme 3**



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# Intramolecular *Trans*-Hydrosilylation

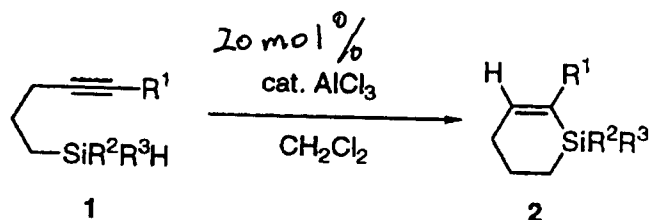
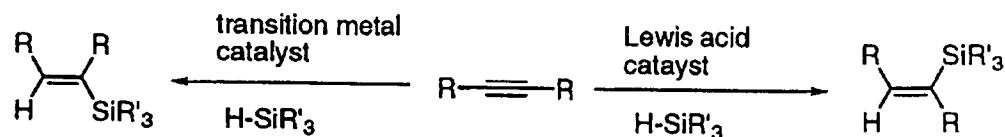
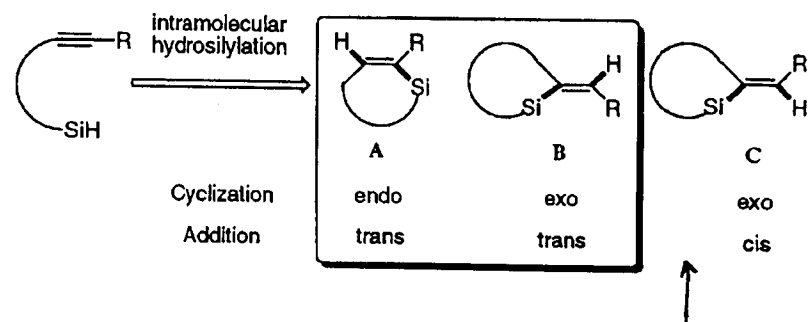


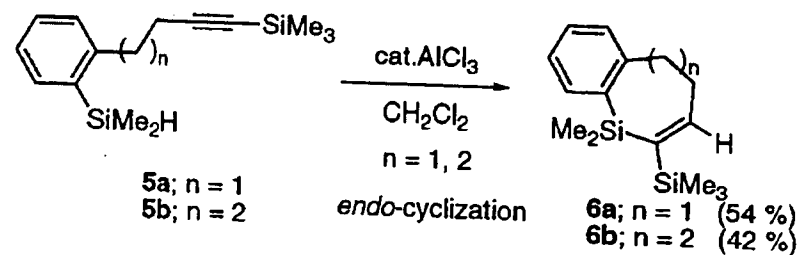
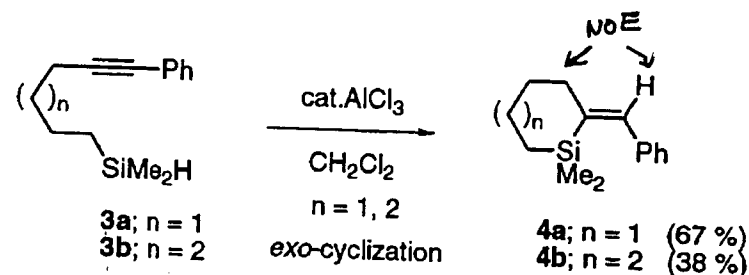
Table 1. AlCl<sub>3</sub>-Catalyzed Intramolecular *Trans*-Hydrosilylation of 1<sup>a</sup>

entry	substr	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	reaction temp, °C	time	product	yield, <sup>b</sup> %
1	1a	H	Me	Me	0	10 min	2a	70 <sup>c</sup>
2	1b	<i>n</i> -Hex	Me	Me	0	10 min	2b	78
3	1c	<i>t</i> -Bu	Me	Me	0	10 min	2c	72
4	1d	Ph	Me	Me	0	10 min	2d	78
5	1e	SiMe <sub>3</sub>	Me	Me	0	10 min	2e	96
6	1f	SiMe <sub>3</sub>	<i>i</i> -Pr	<i>i</i> -Pr	0	30 min	2f	89
7	1g	SiMe <sub>3</sub>	Me	Ph	0 to rt	1 h	2g	86
8	1h	SiMe <sub>3</sub>	Ph	Ph	0 to rt	5 h	2h	30(35) <sup>d</sup>

<sup>a</sup> The reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> (1.0 M). <sup>b</sup> Isolated yield. <sup>c</sup> NMR yield. <sup>d</sup> Yield in parentheses means recovery of the starting material 1h.

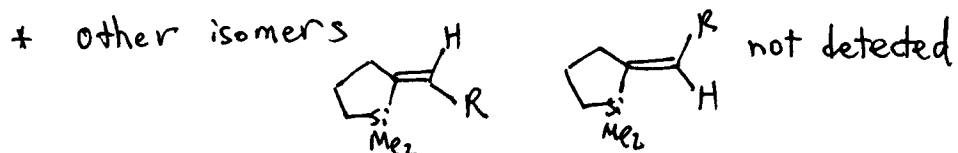


Transition metal catalyst

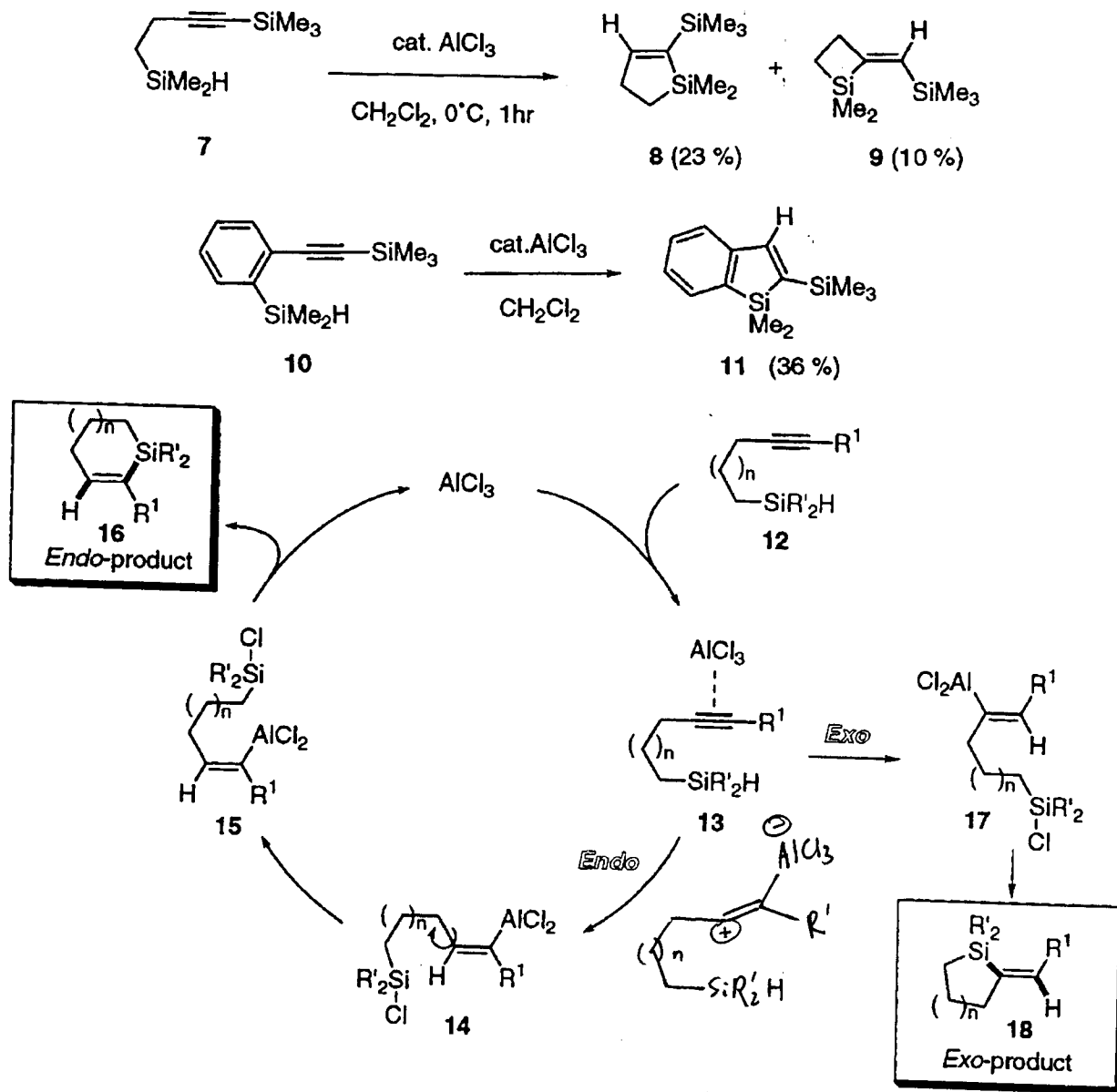


\* the rest of material not mentioned

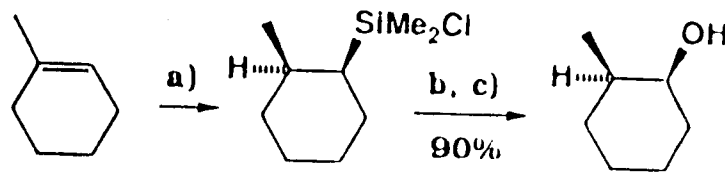
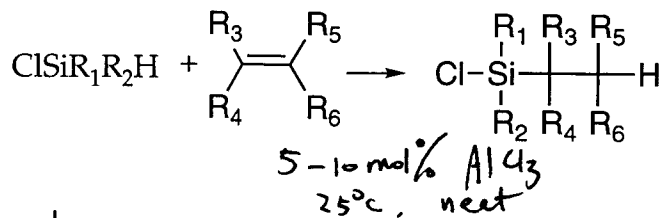
\* E+AlCl<sub>2</sub> and GaI<sub>3</sub> also effective



# Intramolecular *Trans*-Hydrosilylation

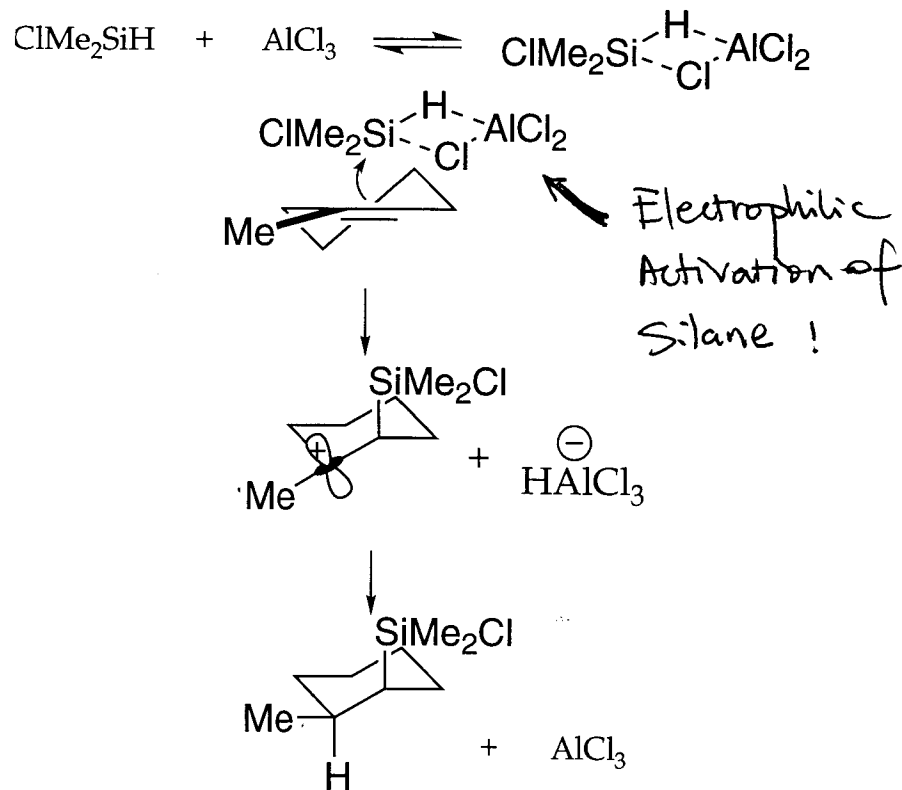


# Lewis Acid Catalyzed *trans*-Hydrosilylation of Alkenes

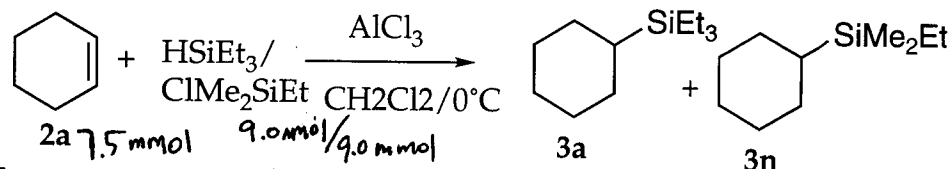
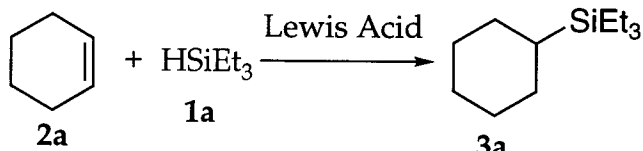


**a:** Cat.  $\text{AlCl}_3$ ,  $\text{HSiMe}_2\text{Cl}$ ; **b:**  $\text{K}_2\text{CO}_3$ ,  $\text{EtOH}$ ;  
**c:** 90%  $\text{H}_2\text{O}_2$ , TBAF,  $\text{K}_2\text{CO}_3$ , DMF, 45 °C

Silanes	Olefins <sup>9</sup>	Products (% yield <sup>b</sup> )
$\begin{array}{c} \text{Me} \\   \\ \text{Cl}-\text{Si}-\text{H} \\   \\ \text{Me} \\ \underline{4} \end{array}$		(93 %) <p style="text-align: center;"><u>6</u></p>
<u>4</u>		(80 %) <p style="text-align: center;"><u>7</u></p>
<u>4</u>		(50 %) <p style="text-align: center;"><u>8</u></p>
<u>4</u>		(67 %) <p style="text-align: center;"><u>9</u></p>
$\begin{array}{c} \text{Bu} \\   \\ \text{Cl}-\text{Si}-\text{H} \\   \\ \text{Me} \\ \underline{5} \end{array}$		(80 %) <p style="text-align: center;"><u>10</u></p>



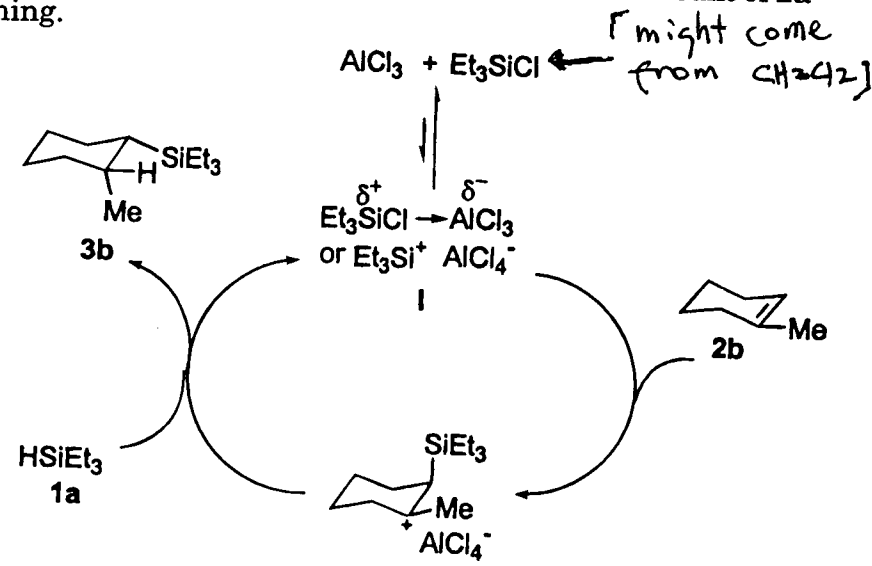
# Lewis Acid Catalyzed *trans*-Hydrosilylation of Alkenes



**Table 5. Effect of Chlorotrialkylsilane in the Hydrosilylation of 2a<sup>a</sup>**

reaction time (min)	2a <sup>c</sup>	products <sup>b</sup>	
		3a + 3n	3n/3a
1	96	3	6.3
2	86	6	5.7
4	83	10	5.5
8	72	17	5.1
16	51	32	5.0
32	17	58	4.5
60	0	70	3.9

<sup>a</sup> A 0.2 equiv amount of AlCl<sub>3</sub> was used as catalyst. <sup>b</sup> Yields were determined using decane as an internal standard. <sup>c</sup> Amount of 2a remaining.



entry no.	Lewis acid <sup>a</sup>	reaction conditions			3a (%) <sup>b</sup>
		solvent	temp (°C)	time (h)	
20	AlCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	0	3	74
21	AlCl <sub>3</sub>	CHCl <sub>3</sub> <sup>c</sup>	0	2	30
22	AlCl <sub>3</sub>	hexane <sup>d</sup>	0 to rt	9	50
23	AlCl <sub>3</sub>	neat	0 to rt	3	64
24	EtAlCl <sub>2</sub> <sup>e</sup>	CH <sub>2</sub> Cl <sub>2</sub>	0 to rt	12	7
25	AlBr <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	0	1.5	61
26	TiCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	reflux	4	trace
27	ZrCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	reflux	7	33
28	HfCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	0	5	65

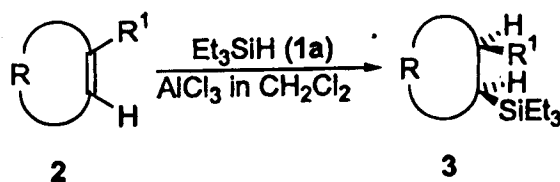
<sup>a</sup> A 0.2 equiv amount of Lewis acid was used as catalyst. <sup>b</sup> Isolated yield. <sup>c</sup> The exchange reaction between the Si-H bond of 1a and the C-Cl bond of chloroform in the presence of aluminum chloride occurred predominantly to give chlorotriethylsilane (67%). <sup>d</sup> 12% of 2a was also recovered. <sup>e</sup> 1.0 M solution in hexane.

**Table 3. Results on the Hydrosilylation of 2a with R<sub>3</sub>SiH**

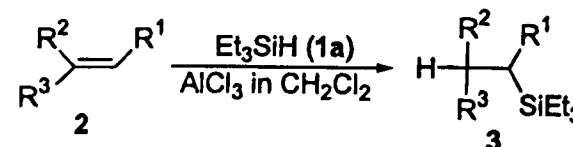
entry no.	HSiR <sub>3</sub>	AlCl <sub>3</sub> (equiv)	reaction time (h)	product <sup>a</sup>	
	1 (R <sub>3</sub> )			3	(%)
14	1a (Et <sub>3</sub> )	0.2	3	3a	74
15	1b (EtMe <sub>2</sub> )	0.2 <sup>b</sup>	0.5	3n	66
		0.1	2	3n	87
16	1c ( <sup>n</sup> C <sub>8</sub> H <sub>11</sub> Me <sub>2</sub> )	0.2	3	3o	81
17	1d (PhMe <sub>2</sub> )	0.2	1.3	3p	21
18	1e (Ph(CH <sub>2</sub> ) <sub>2</sub> Me <sub>2</sub> )	0.2	3	3q	11
19	1f ( <sup>t</sup> BuMe <sub>2</sub> )	0.2	3	3r	9

<sup>a</sup> Isolated yield. <sup>b</sup> (Trimethylsilyl)cyclohexane and (chloro(ethyl)methylsilyl)cyclohexane were obtained as byproducts.

# Lewis Acid Catalyzed *trans*-Hydrosilylation of Alkenes



2a. cyclohexene, 2b. 1-methylcyclohexene, 2c. cyclopentene  
2d. norbornene, 2e. indene



f: R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = Me  
g: R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = <sup>n</sup>Bu  
h: R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = *n*-octyl  
i: R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = CH<sub>2</sub>C<sub>6</sub>F<sub>5</sub>  
j: R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = Ph  
k: R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = *p*-ClPh  
l: R<sup>1</sup> = H, R<sup>2</sup> = Me, R<sup>3</sup> = Ph  
m: R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = Me

**Table 1. Hydrosilylation of Cycloalkenes with Et<sub>3</sub>SiH**

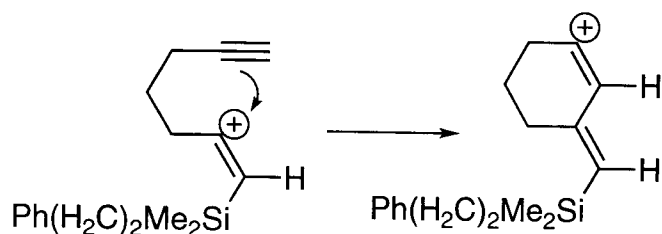
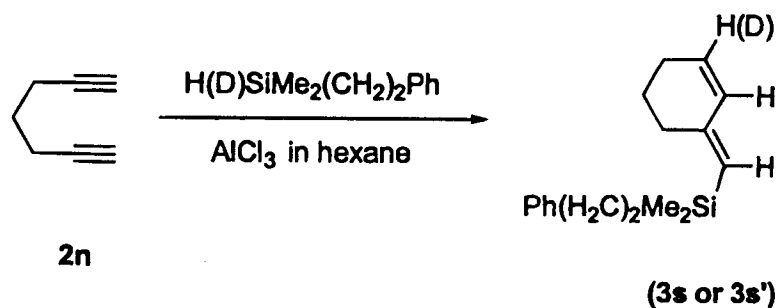
entry no.	cycloalkenes <b>2</b>	reaction conditions			product	
		AlCl <sub>3</sub> (equiv)	temp (°C)	time (h)	<b>3</b>	(%) <sup>a</sup>
1	<b>2a</b>	0.2	0	3.0	<b>3a</b>	74
2	<b>2b</b>	0.2	-20	1.0	<b>3b</b>	82
3	<b>2c</b>	0.2	0	1.5	<b>3c</b>	78
4	<b>2d</b>	0.2	0	4.0	<b>3d</b>	65
5 <sup>b</sup>	<b>2e</b>	0.1	-20	1.0	<b>3e</b>	25

<sup>a</sup> Isolated yield. <sup>b</sup> The reaction of indene in the presence of 0.2 equiv of AlCl<sub>3</sub> at 0 °C gave mostly polymeric materials.

**Table 2. Hydrosilylation of Linear Alkenes with Et<sub>3</sub>SiH**

entry no.	alkene <b>2</b>	reaction conditions		product	
		AlCl <sub>3</sub> <sup>a</sup> temp (°C)	time (h)	<b>3</b>	(%) <sup>b</sup>
6 <sup>c</sup>	<b>2f</b>	0	5.0	<b>3f</b>	66
7	<b>2g</b>	rt	4.0	<b>3g</b>	58
8	<b>2h</b>	rt	5.0	<b>3h</b>	57
9	<b>2i</b>	rt	5.0	<b>3i</b>	58
10	<b>2j</b>	-20	1.0	<b>3j</b>	57
11	<b>2k</b>	-20	1.5	<b>3k</b>	61
12 <sup>d</sup>	<b>2l</b>	-20	1.5	<b>3l</b>	55
13	<b>2m</b>	-10	1.0	<b>3m</b>	70

<sup>a</sup> A 0.2 equiv amount of AlCl<sub>3</sub> was used as catalyst. <sup>b</sup> Isolated yield. <sup>c</sup> A 2.5:1 ratio of reactants **2f** and **1a** was used, and 23% of unreacted **1a** was recovered. <sup>d</sup> **3l** decomposed during this reaction to give benzene (0.01 g) and propyltriethylsilane (0.17 g).







# B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Catalyzed Hydrostannylation Using *in situ* Generated Bu<sub>3</sub>SnH

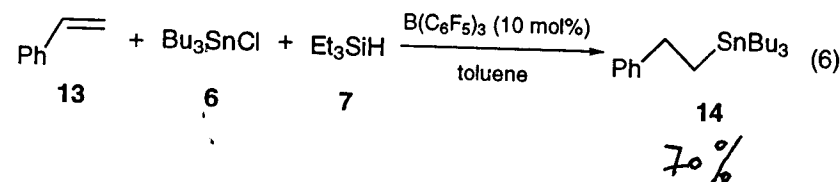
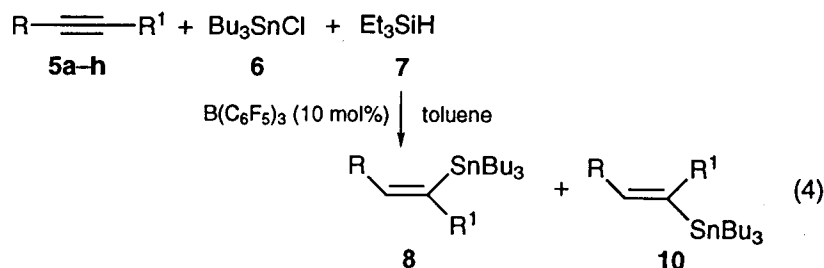
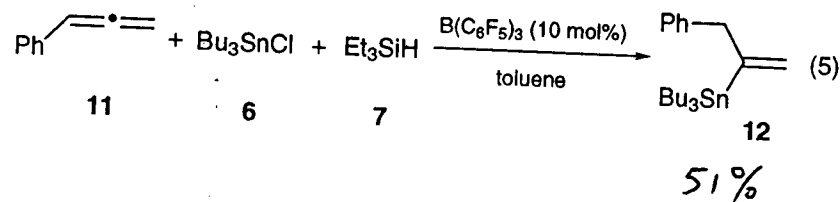
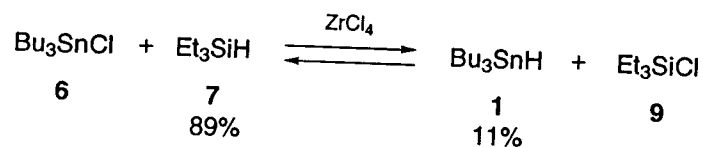


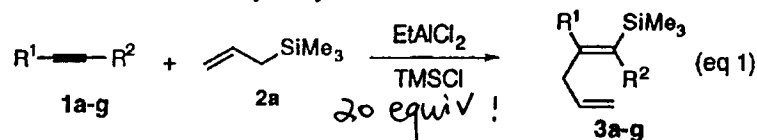
Table 1 B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed hydrostannylation of alkynes with Bu<sub>3</sub>SnH generated *in situ* from Bu<sub>3</sub>SnCl and Et<sub>3</sub>SiH

Entry	R	R <sup>1</sup>	Conditions	Yield of 8 + 10 <sup>a</sup> (%)	Ratio 8 : 10 <sup>b</sup>
1	C <sub>6</sub> H <sub>13</sub>	H	5a 40 min/0 °C 3 h/rt <sup>c</sup>	78	>95 : 5
2	Cyclohexenyl	H	5b 2 h/0 °C	85	86 : 14
3	PhCH <sub>2</sub>	H	5c 4 h/0 °C	85	>95 : 5
4	Ph	H	5d 2.5 h/0 °C	77	>95 : 5
5	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	H	5e 2.5 h/0 °C	89	>95 : 5
6	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	H	5f 1.5 h/-35 °C	70	>95 : 5
7	Pentyl	Pentyl	5g 40 min/0 °C 3 h/rt	90	80 : 20
8	Ph	Ph	5h 40 min/0 °C 3 h/rt	71	>95 : 5

<sup>a</sup>olated yield. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis of crude reaction mixtures. <sup>c</sup> rt = room temp.

# Lewis Acid Catalyzed *trans*-Carbosilylation of Simple Alkynes

**Table 1.** Allylsilylation of Alkynes in the Presence of the EtAlCl<sub>2</sub>-TMSCl Catalyst System



a : R<sup>1</sup> = Ph, R<sup>2</sup> = H      d : R<sup>1</sup> = CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>, R<sup>2</sup> = H      f : R<sup>1</sup> = , R<sup>2</sup> = H

b : R<sup>1</sup> = *p*-Me-C<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H      e : R<sup>1</sup> = CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>, R<sup>2</sup> = H      g : R<sup>1</sup> = Ph, R<sup>2</sup> = Me

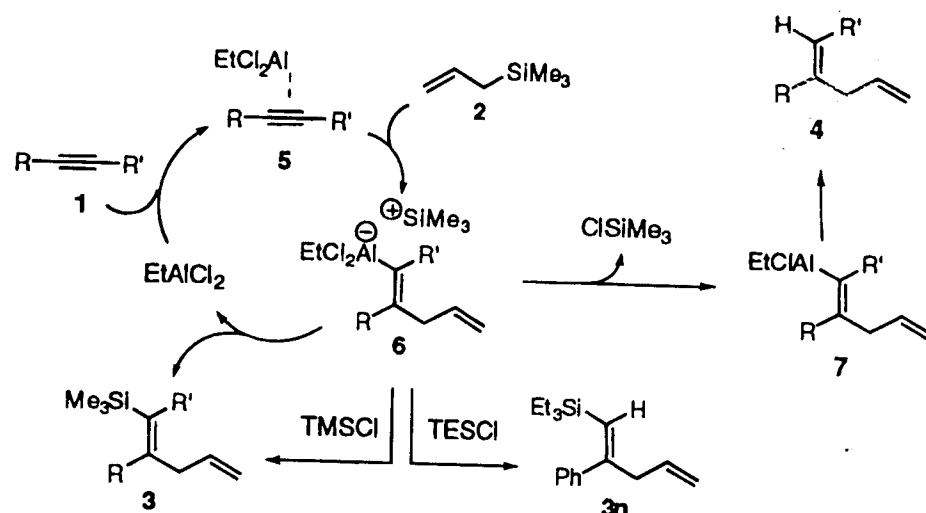
c : R<sup>1</sup> = PhCH<sub>2</sub>, R<sup>2</sup> = H

entry	1	R <sup>1</sup>	R <sup>2</sup>	3	product yield % <sup>a</sup>
1	1a	Ph	H	3a	93
2	1b	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	3b	95
3	1c	PhCH <sub>2</sub>	H	3c	57 <sup>b,c</sup>
4	1d	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	H	3d	90 <sup>b</sup>
5	1e	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	H	3e	85 <sup>b,d</sup>
6	1f	1-cyclohexenyl	H	3f	73 <sup>b,e</sup>
7	1g	Ph	Me	3g	88

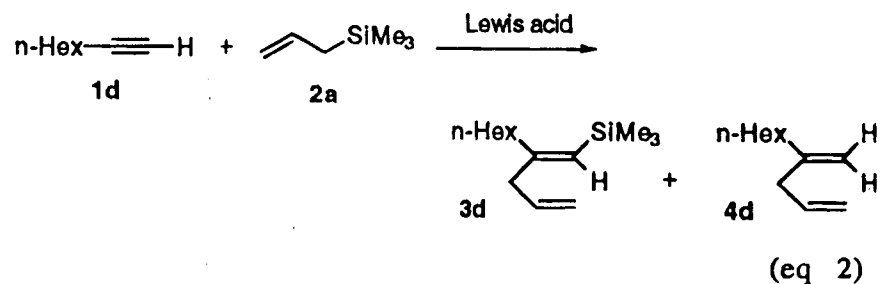
<sup>a</sup> Isolated yield, except for where otherwise indicated. <sup>b</sup> Yield determined by <sup>1</sup>H NMR with *p*-xylene as an internal standard. <sup>c</sup> PhCH<sub>2</sub>(CH<sub>2</sub>=CHCH<sub>2</sub>)C=CH<sub>2</sub> (4c) was produced in 13% yield. <sup>d</sup> CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>(CH<sub>2</sub>=CHCH<sub>2</sub>)C=CH<sub>2</sub> (4e) was produced in 5% yield. <sup>e</sup> 1-(1,4-Pentadien-2-yl)cyclohexene (4f) was produced in 5% yield.

\* large excess of TMSCl is necessary to obtain silylated product with EtAlCl<sub>2</sub> catalyst.

<sup>a</sup> The yield was determined by <sup>1</sup>H NMR with *p*-xylene as an internal standard. <sup>b</sup> The ratio was determined by 270 MHz <sup>1</sup>H NMR. <sup>c</sup> 3d was not detected by <sup>1</sup>H NMR. <sup>d</sup> 4d was not detected by <sup>1</sup>H NMR. <sup>e</sup> Not determined. <sup>f</sup> Isolated yield.



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

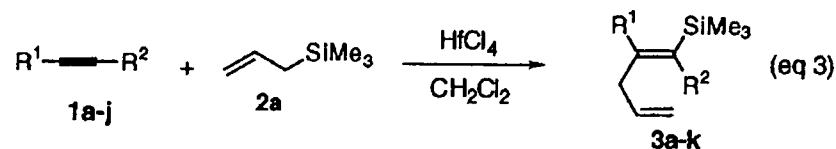


entry	Lewis acid	solvent	temp (°C)	yield (3d + 4d, %) <sup>a</sup>	ratio 3d:4d <sup>b</sup>
1	EtAlCl <sub>2</sub>	toluene	-78 → 0	20	5: >95 <sup>c</sup>
2	AlCl <sub>3</sub>	toluene	-78 → 0	40	24:76
3	AlBr <sub>3</sub>	toluene	-78 → 0	50	15:85
4	HfCl <sub>4</sub>	toluene	-78 → 0	9	>95:5 <sup>d</sup>
5	HfCl <sub>4</sub>	hexane	-78 → 0	trace	<i>e</i>
6	HfCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-78 → 0	50	>95:5 <sup>d</sup>
7	HfCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	0	88 <sup>f</sup>	>95:5 <sup>d</sup>

# HfCl<sub>4</sub> Catalyzed *trans*-Carbosilylation of Simple Alkynes

Hf: atomic number 72; atomic weight 178.49. Group number 4 [Xe]4f<sup>14</sup>5d<sup>2</sup>6s<sup>2</sup>  
 discovered 1923 at Denmark; "Hafnia" meaning "Copenhagen"

**Table 3.** HfCl<sub>4</sub>-Catalyzed Addition of Allyltrimethylsilane to Alkynes **1a-j**<sup>a</sup>

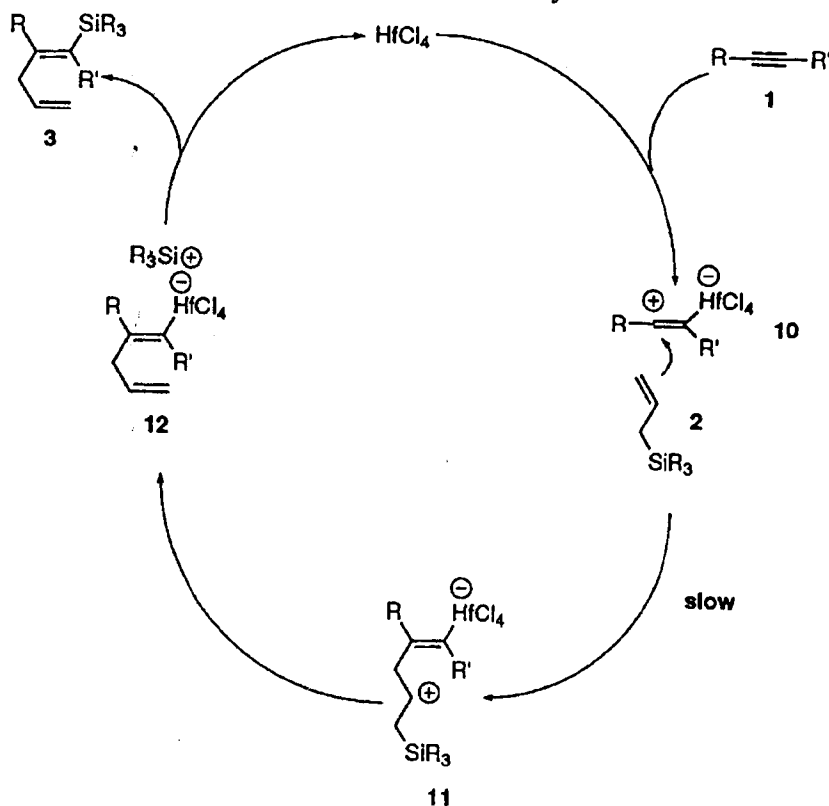


- a**: R<sup>1</sup> = Ph, R<sup>2</sup> = H      **f**: R<sup>1</sup> = , R<sup>2</sup> = H  
**b**: R<sup>1</sup> = *p*-Me-C<sub>6</sub>H<sub>4</sub>, R<sup>2</sup> = H      **g**: R<sup>1</sup> = Ph, R<sup>2</sup> = Me  
**c**: R<sup>1</sup> = PhCH<sub>2</sub>, R<sup>2</sup> = H      **h**: R<sup>1</sup> = Ph, R<sup>2</sup> = Et  
**d**: R<sup>1</sup> = CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>, R<sup>2</sup> = H      **i**: R<sup>1</sup> = H, R<sup>2</sup> = TMS  
**e**: R<sup>1</sup> = CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>, R<sup>2</sup> = H      **j**: R<sup>1</sup> = *t*-Bu, R<sup>2</sup> = H

entry	alkyne	R <sup>1</sup>	R <sup>2</sup>	product	yield(%) <sup>b</sup>
1	<b>1a</b>	Ph	H	<b>3a</b>	95
2	<b>1b</b>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	<b>3b</b>	97
3	<b>1c</b>	PhCH <sub>2</sub>	H	<b>3c</b>	73
4	<b>1d</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	H	<b>3d</b>	87
5	<b>1e</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	H	<b>3e</b>	86
6	<b>1f</b>	1-cyclohexenyl	H	<b>3f</b>	42
7	<b>1g</b>	Ph	Me	<b>3g</b>	90
8	<b>1h</b>	Ph	Et	<b>3h</b>	82
9	<b>1i</b>	H	TMS	<b>3i</b>	65 <sup>c,d</sup>
10	<b>1j</b>	<i>t</i> -Bu	H	<b>3j</b>	10 <sup>b</sup>

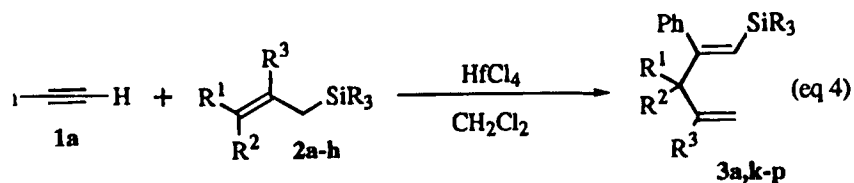
<sup>a</sup> All reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C with 50 mol % of HfCl<sub>4</sub>.<sup>9</sup> <sup>b</sup> Isolated yield, except for where otherwise indicated. <sup>c</sup> Yield was determined by <sup>1</sup>H NMR with *p*-xylene as an internal standard. <sup>d</sup> The allyltrimethylsilane was added slowly *via* syringe pump in order to avoid its dimerization.<sup>4h</sup>

**Scheme 2.** Proposed Mechanism for the HfCl<sub>4</sub>-Catalyzed *trans*-Allylsilylation of Unactivated Alkynes



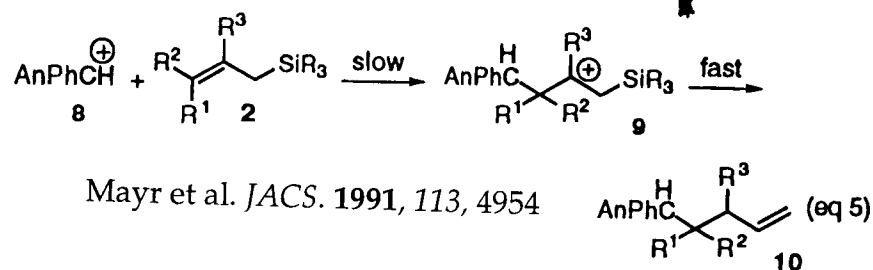
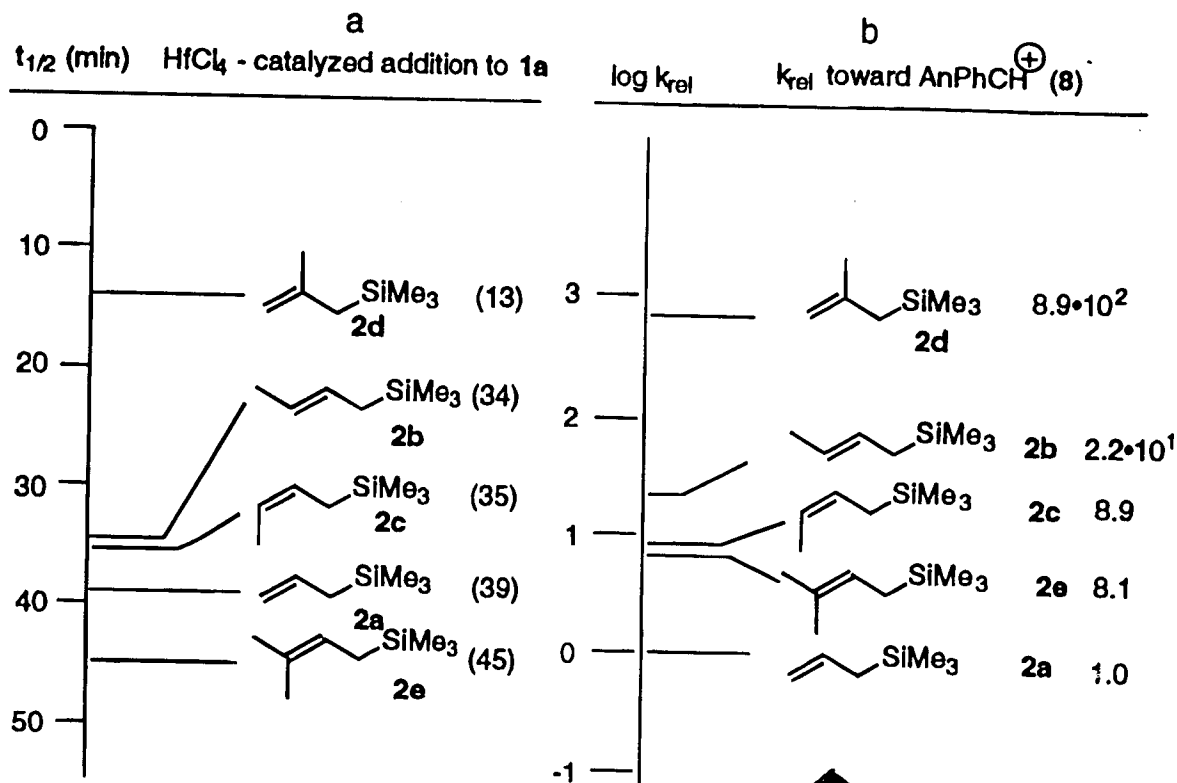
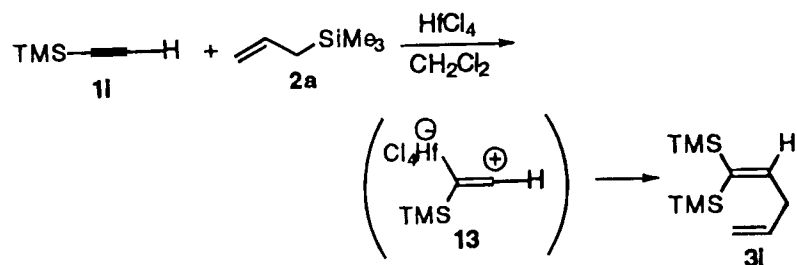
# HfCl<sub>4</sub> Catalyzed Allylsilylation of Phenylacetylene

Table 4. HfCl<sub>4</sub>-Catalyzed Addition of 2a-h to Phenylacetylene<sup>a</sup>



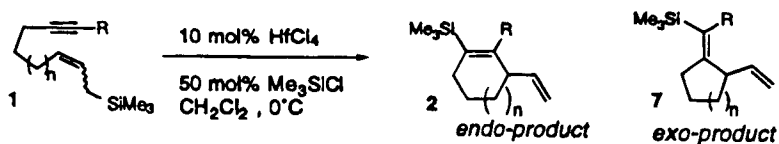
entry	allylsilane	time (min.)	product	yield (%) <sup>b</sup>
1	2a	60 <sup>c</sup>	3a	95
2	2b	60	3k	96
3	2c	60	3k	90
4	2d	25	3l	92
5	2e	120	3m	97
6	2f	180	3n	73
7	2g	140	3o	76
8	2h	230	3p	51

<sup>a</sup> All reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C with 50 mol % of HfCl<sub>4</sub>. <sup>b</sup> Isolated yield. <sup>c</sup> In the presence of 10 equiv of TMSCl the reaction was completed in 20 min.



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# HfCl<sub>4</sub> Catalyzed *Endo-dig* Cyclization



**Table 1.** HfCl<sub>4</sub>-Catalyzed *endo*-Carbocyclization of Alkynyl-Allylsilanes **1**<sup>10</sup>

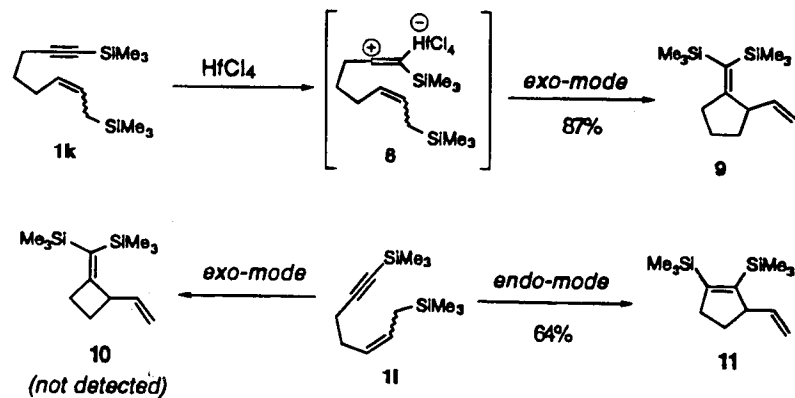
entry	substrate <sup>a</sup>	R	R <sup>1</sup>	n	product	yield, <sup>b</sup> %
1	<b>1a</b>	Ph	H	1	<b>2a</b>	61
2	<b>1b</b>	<i>n</i> -Hex	H	1	<b>2b</b>	99
3	<b>1c</b>	<i>c</i> -hexenyl	H	1	<b>2c</b>	58
4	<b>1d</b>	<i>p</i> -tolyl	H	1	<b>2d</b>	63
5	<b>1e</b>	<i>n</i> -Hex	Me	1	<b>2e</b>	83 <sup>c</sup>
6	<b>1f</b>	Ph	H	2	<b>2f</b>	76
7	<b>1g</b>	<i>n</i> -Hex	H	2	<b>2g</b>	84
8	<b>1h</b>	<i>p</i> -tolyl	H	2	<b>2h</b>	65
9	<b>1i</b>	Ph	H	0	<b>2i</b>	22 <sup>d</sup>
10	<b>1j</b>	<i>n</i> -Hex	H	0	<b>2g</b>	47 <sup>e,f</sup>

<sup>a</sup> A 4:1 mixture of *Z*- and *E*-isomers of **1** was used. <sup>b</sup> Isolated yield. <sup>c</sup> The *endo*-product **2e** was isolated in 83% yield along with small amount of unidentified isomeric material.<sup>11</sup> <sup>d</sup> Approximately 20% of **1i** was recovered. <sup>e</sup> NMR yield. <sup>f</sup> 30 mol % of HfCl<sub>4</sub> was used. The catalyst was added in three portions.

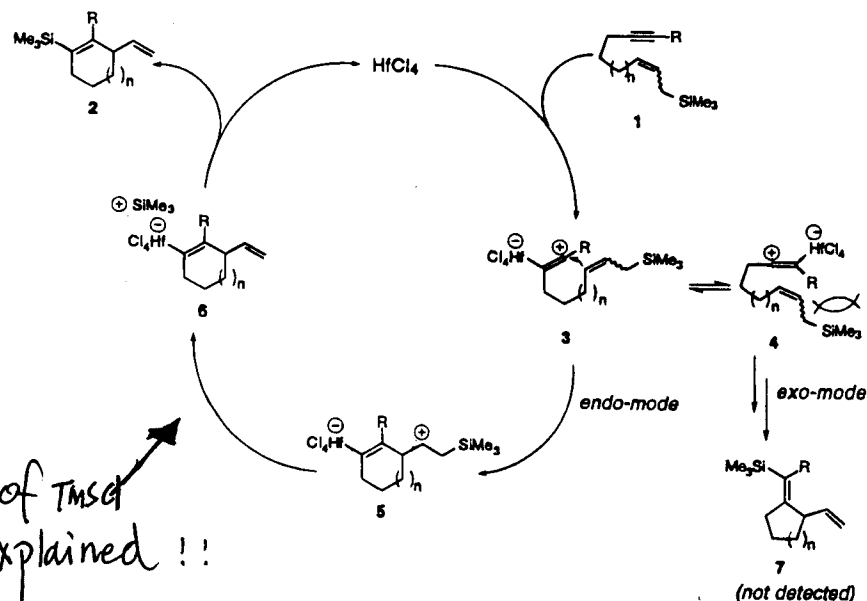
\* Me<sub>3</sub>SiCl is necessary for good yield.

\* no other isomers identified

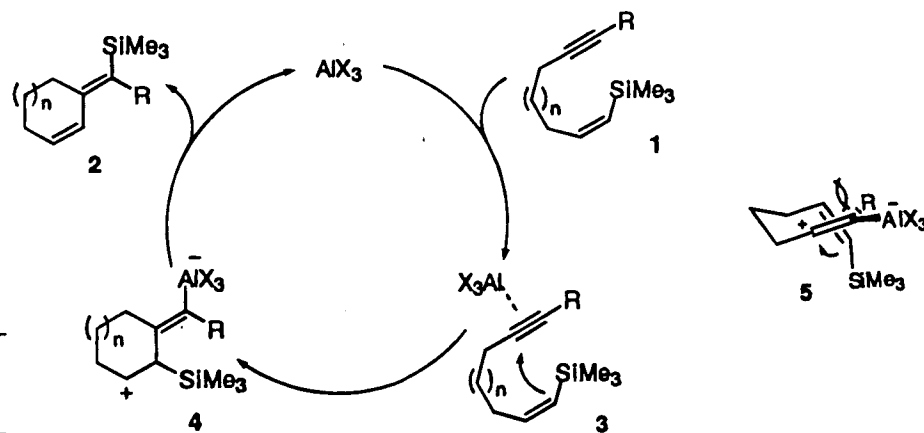
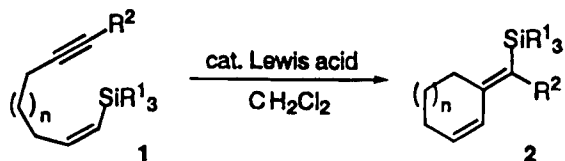
role of TmsCl  
not explained !!



**Scheme 1.** Proposed Mechanism for the HfCl<sub>4</sub>-Catalyzed *endo*-Carbocyclization of **1**



# Lewis Acid Catalyzed Intramolecular *trans*-Vinylsilylation



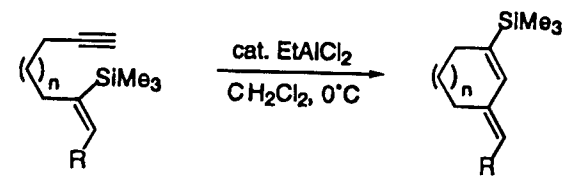
**Table 1.** Lewis Acid-Catalyzed Carbocyclization of **1**<sup>a</sup>

entry no.	substrate <b>1</b>			Lewis acid (equiv)	temp (°C)	yield of <b>2</b> (%) <sup>b</sup>	
	<i>n</i>	R <sup>1</sup>	R <sup>2</sup>			<b>1</b>	<b>2</b>
1	1	Me	H	<b>1a</b>	EtAlCl <sub>2</sub> (0.5)	-78	<b>2a</b> 69
2	1	Me	H	<b>1a</b>	AlCl <sub>3</sub> (0.5)	-78	<b>2a</b> 67
3	1	Me	H	<b>1a</b>	AlBr <sub>3</sub> (0.5)	-78	<b>2a</b> 56
4	1	Me	H	<b>1a</b>	EtAlCl <sub>2</sub> (1.1)	-78	<b>2a</b> 61
5	1	Me	H	<b>1a</b>	EtAlCl <sub>2</sub> (0.2)	-78	<b>2a</b> 92
6	1	Me	H	<b>1a</b>	EtAlCl <sub>2</sub> (0.1)	-78 to 0	<b>2a</b> 49 <sup>c</sup>
7	1	Me	H	<b>1a</b>	AlCl <sub>3</sub> (0.1)	-78 to -30	<b>2a</b> 84
8 <sup>d</sup>	1	Me	H	<b>1a</b>	EtAlCl <sub>2</sub> (0.2)	-78	<b>2a</b> 91
9	1	Et	H	<b>1b</b>	EtAlCl <sub>2</sub> (0.2)	-78 to -20	<b>2b</b> 85
10 <sup>e</sup>	1	Me	C <sub>6</sub> H <sub>13</sub>	<b>1c</b>	EtAlCl <sub>2</sub> (0.5)	rt	<b>2c</b> 31
11 <sup>e</sup>	1	Me	SiMe <sub>3</sub>	<b>1d</b>	EtAlCl <sub>2</sub> (0.5)	rt	<b>2d</b> 85
12	2	Me	H	<b>1e</b>	AlCl <sub>3</sub> (0.2)	-78 to -5	<b>2e</b> 89

<sup>a</sup> Reactions were conducted in CH<sub>2</sub>Cl<sub>2</sub> at the indicated temperature within 1 h, except for where otherwise mentioned. The reactions were quenched by adding excess amounts of Et<sub>2</sub>NH and saturated aqueous NaHCO<sub>3</sub> solution at the reaction temperature. <sup>b</sup> Isolated yield. <sup>c</sup> The starting material **1a** was recovered in 23% yield. <sup>d</sup> Hexane was used as a solvent. <sup>e</sup> Reaction was conducted for 1 d.

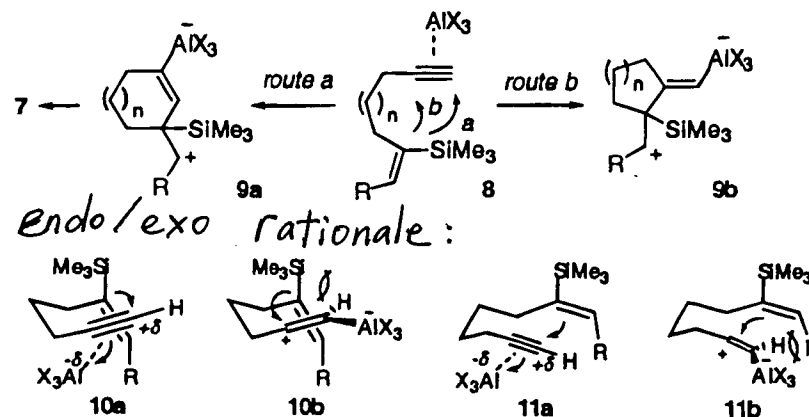
\* *E*-silane, no reaction

\* no need for Me<sub>3</sub>SiCl

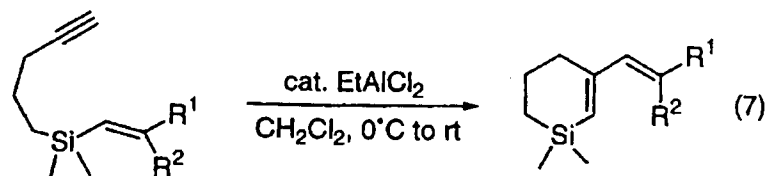


**6a:** *n*=1, R=H  
**b:** *n*=1, R=C<sub>3</sub>H<sub>7</sub>  
**c:** *n*=2, R=C<sub>3</sub>H<sub>7</sub>

**7a:** *n*=1, R=H 0%  
**b:** *n*=1, R=C<sub>3</sub>H<sub>7</sub> 90%  
**c:** *n*=2, R=C<sub>3</sub>H<sub>7</sub> 35%



# Lewis Acid Catalyzed Silyltethered Intramolecular *trans*-Vinylsilylation



3a: R<sup>1</sup>=H, R<sup>2</sup>=H

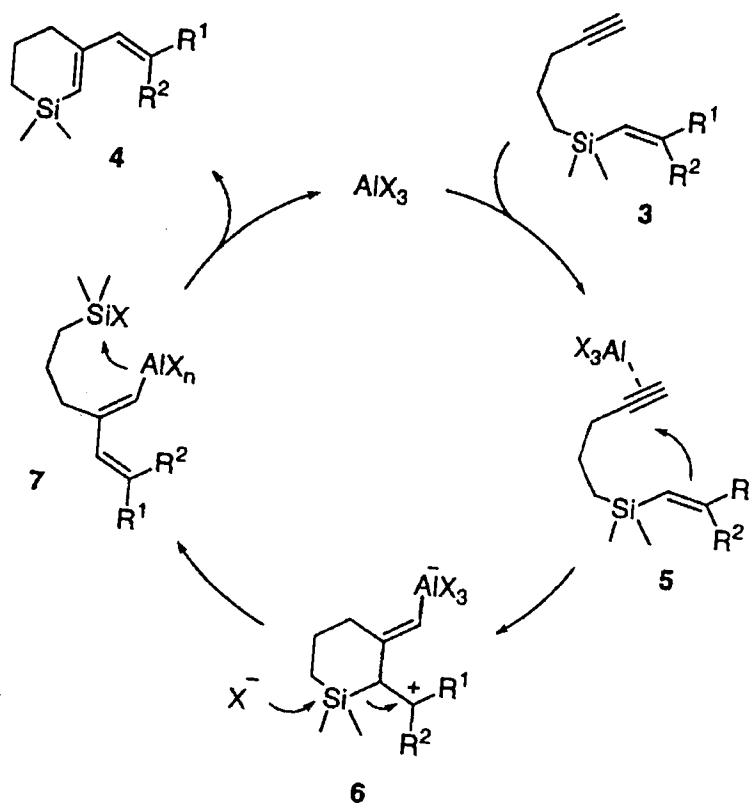
b: R<sup>1</sup>=Ph, R<sup>2</sup>=H

c: R<sup>1</sup>=H, R<sup>2</sup>=Me

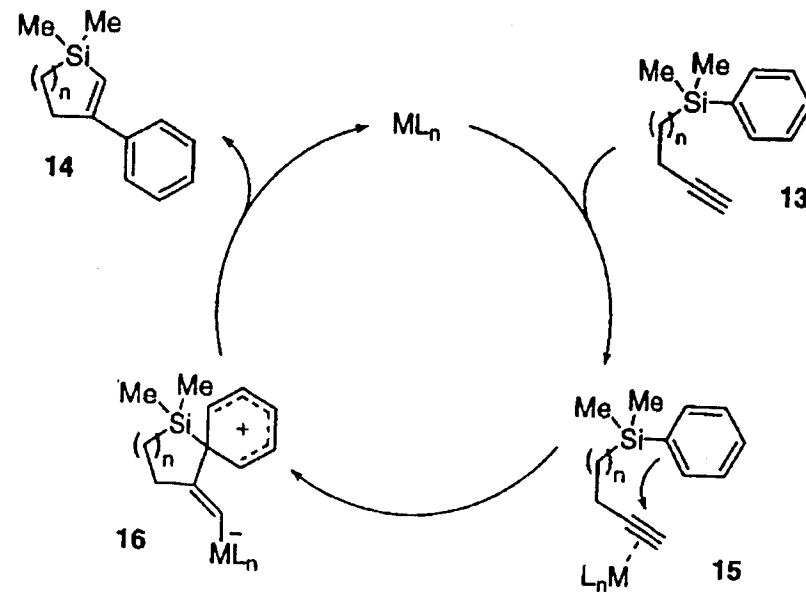
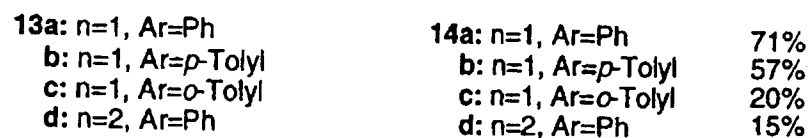
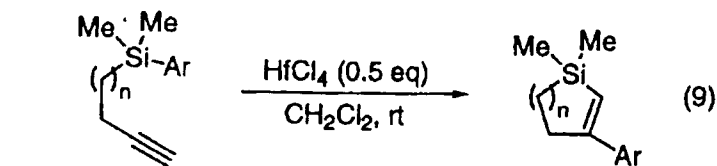
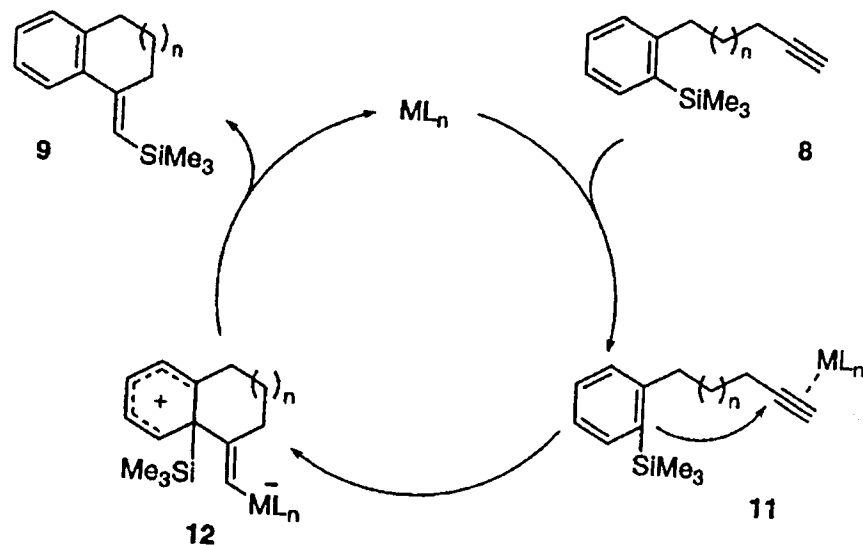
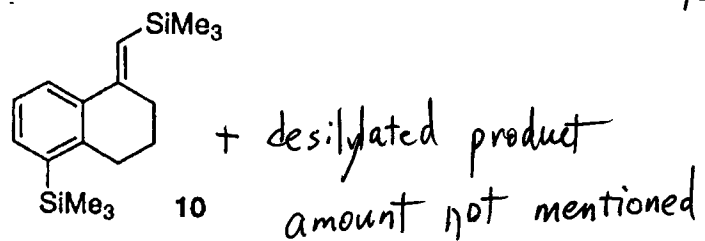
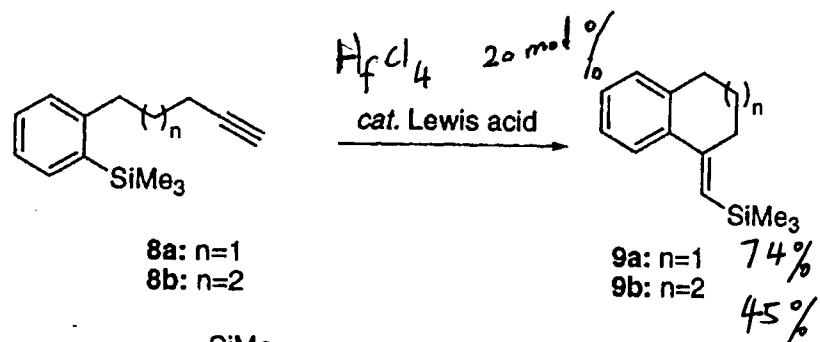
4a: R<sup>1</sup>=H, R<sup>2</sup>=H 0%

b: R<sup>1</sup>=Ph, R<sup>2</sup>=H 92%

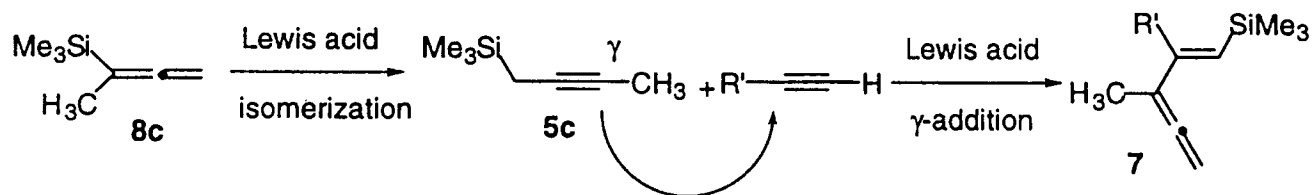
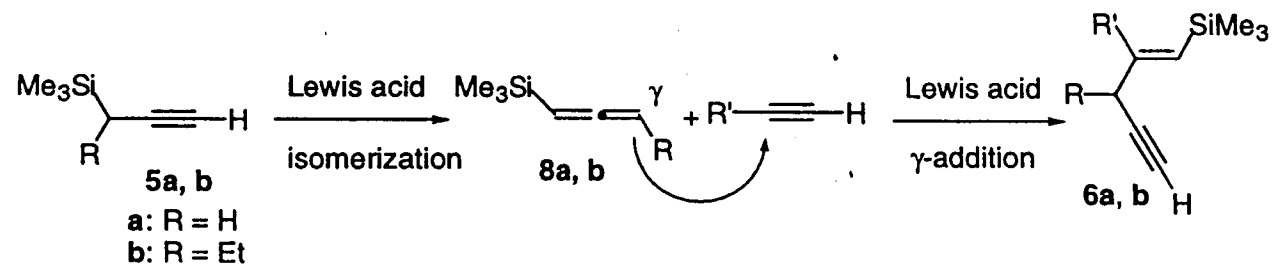
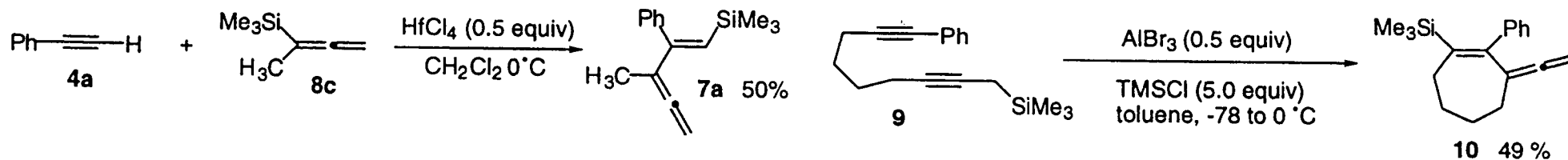
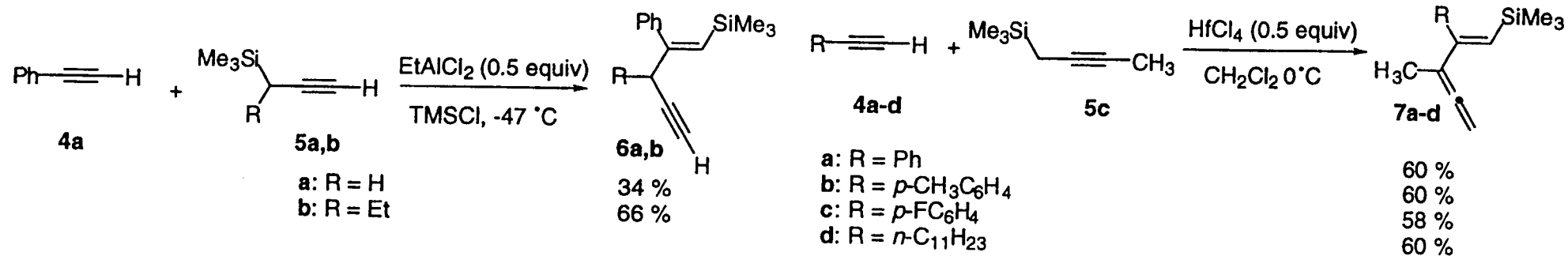
c: R<sup>1</sup>=H, R<sup>2</sup>=Me 83%



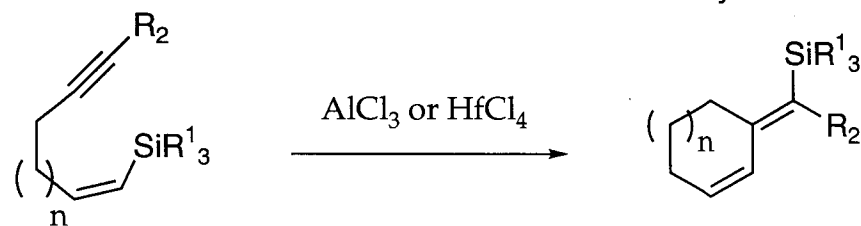
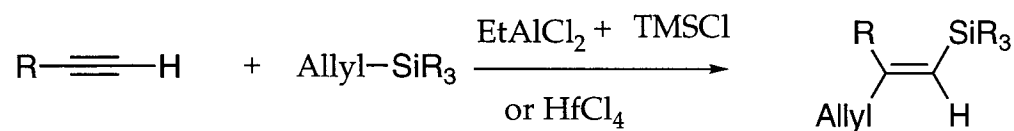
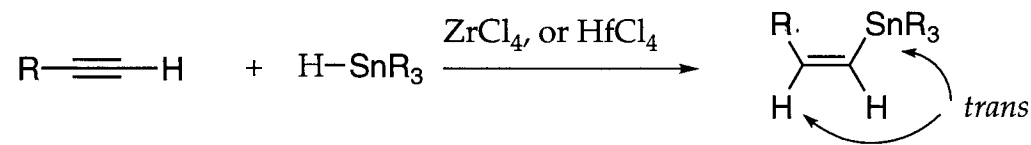
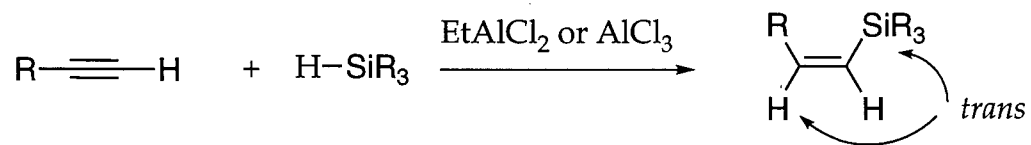
# Lewis Acid Catalyzed Intramolecular *trans*-Arylsilylation



# Lewis Acid Catalyzed Carbosilylation with propargyl- and allenylsilanes



## Summary



Mechanism is not clear yet.

Two more references on allylstannylation of alkynes:

Y. Yamamoto et al. *Tetrahedron* **1999**, 55, 3779

Y. Yamamoto et al. *Chem. Commun.* **1996**, 1513.