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Accounts

Lewis Acid-Catalyzed Hydrometalation and Carbometalation of Unactivated Alkynes

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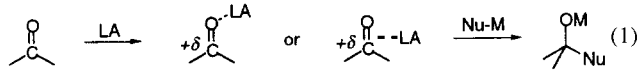
Hydrosilylation, hydrostannation, carbosilylation, and carbostannation of unactivated alkynes with organosilanes, or organostannanes proceed effectively in the presence of catalytic amounts of Lewis acids to produce the corresponding vinylsilyl or vinylstannyl compounds in a highly regio- and stereoselective way. Although it is well known that transition metal catalyzed hydrometalations and carbometalations, in general, proceed in a *cis*-manner, the Lewis acid-catalyzed reactions proceed in a *trans*-manner exclusively. The coordination of a triple bond to Lewis acids is proposed as a key step for the Lewis acid catalyzed reactions.

Electrophilic reactions catalyzed by a Lewis acid, such as Diels–Alder reactions, aldol reactions, and ene reactions, play a fundamental and important role in organic chemistry.[1] Much attention has been paid to the activation of electrophiles, such as carbonyl and imine groups, by coordinating the lone pairs of those heteroatoms of electrophiles to Lewis acids. Actually, the electrophilicity of carbonyl groups is enhanced by coordinating to Lewis acid through the lone pair of a carbonyl oxygen. However, in some cases, a carbonyl ligand coordinates to a Lewis acidic metal center preferably through their π-bond instead of their lone pair (Eq. 1).[2] In contrast, the activation of carbon–carbon multiple bonds based on the coordination to Lewis acids through their π-electrons has been much less studied. In this account we present the recent findings, in our laboratories, on the Lewis acid catalyzed hydrometalation and carbometalation of unactivated alkynes, which proceed via the coordination of the triple bond of alkynes to Lewis acids (Eq. 2).



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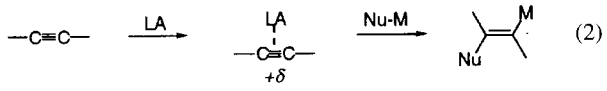

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1. Hydrometalation

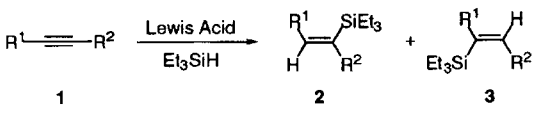
The hydrometalation of a carbon–carbon multiple bond is one of the most fundamental and straightforward methodologies for the preparation of new organometallics.[3] Particularly, the hydrometalation of unactivated alkynes is a practical method for the preparation of vinyl metals, which have great versatility as building blocks in organic synthesis. Although hydroboration and hydroalumination proceed without any activators, most hydrometalations are promoted by transition metal catalysts or by radical initiators. On the other hand, only a little attention has been paid to the utilization of a Lewis acid as an activator. We found that certain Lewis acids are quite useful activators for hydrosilylation and hydrostannation.

1-1. Hydrosilylation. **1-1-1. Hydrosilylation of Alkynes.** The great versatility of vinylsilanes as building blocks has been increased in modern synthetic organic chemistry.[4] Hydrosilylation of alkynes[5] is one of the simplest and the most straightforward preparative methods to obtain vinylsilanes. It is well known that the hydrosilylation of alkynes is induced either by radical initiator[6] or by transition metal catalysts.[7] The radical-induced procedure often provides a mixture of *trans*- and *cis*-hydrosilylation products. Although the transition metal-catalyzed reaction proceeds with high stereoselectivity via a *cis*-hydrosilylation pathway, it usually produces a mixture of two regioisomers (terminal and internal products) in the reaction with terminal alkynes.

The Lewis acid catalyzed hydrosilylation of alkenes and alkynes with chlorodialkylsilanes was first reported by Finke and Moretto in 1979.[8] Afterward, Keiji Yamamoto et al. found that the $AlCl_3$-catalyzed hydrosilylation of alkenes with chlorodialkylsilanes proceeded in a *trans* manner.[9] Recently, Jung's group reported the Lewis acid-catalyzed hydrosilylation of alkenes with trialkylsilanes.[10] AlX_3 (X: Cl or Br)-catalyzed hydrosilylation of alkynes with trialkylsilanes was found by Voronkov and his co-workers. They reported

that the stereoselectivity of hydrosilylation depended on the reaction conditions.[11]

We investigated the Lewis acid-catalyzed hydrosilylation of alkynes with trialkylsilanes systematically.[12] As previously observed by Voronkov's group, the reaction was catalyzed dramatically by Lewis acids such as $AlCl_3$ and $EtAlCl_2$. Interestingly, the $AlCl_3$- and $EtAlCl_2$-catalyzed hydrosilylation proceeded in a *trans*-fashion exclusively, regardless of the reaction conditions, in contrast to Voronkov's results (Eq. 3, Table 1). Neither a stereoisomer of **2** (*cis*-addition product) nor a regioisomer (**3**) was detected in the ^1H NMR spectra of the crude reaction product, except for the reaction of (trimethylsilyl)acetylene (Entry 7). The regiochemical difference in the hydrosilylation reaction of the alkyl- and silyl-substituted alkynes is very interesting and is discussed in the mechanistic section. The use of non-polar solvents such as toluene or hexane was essential for obtaining high stereoselectivity and chemical yield. Unlike $EtAlCl_2$, $AlCl_3$ is not soluble in such solvents, and thus the $AlCl_3$-catalyzed hydrosilylation proceeded in a heterogeneous system. The hydrosilylation of alkynes bearing a silyloxy or benzyloxy (BnO) group gave the corresponding *trans*-hydrosilylation products in good to high yields (Entries 10, 11, and 12). It is interesting that the use of 1.2 equiv of Lewis acids was essential for obtaining good chemical yields. Most probably, 1.0 equiv of the Lewis acids would be needed to form the complex with an oxygen atom of a silyloxy or benzyloxy group, and the remaining 0.2 equiv Lewis acid would act as a catalyst.



1 **2** **3** (3)

Table 1. Lewis Acid-Catalyzed Hydrosilylation of Alkynes with Et_3SiH[a)]

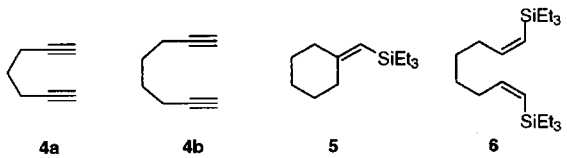
Entry	Lewis acid (equiv)	1	Alkyne R^1	Alkyne R^2	Yield/% 2	Yield/% 3
1	$AlCl_3$ (0.2)	**1a**	$C_{10}H_{21}$	H	93	0
2	$EtAlCl_2$ (0.2)	**1a**	$C_{10}H_{21}$	H	95	0
3[b)]	Et_2AlCl (0.2)	**1a**	$C_{10}H_{21}$	H	0	0
4[c)]	$AlCl_3$ (0.2)	**1a**	$C_{10}H_{21}$	H	90	0
5	$AlCl_3$ (0.2)	**1b**	$PhCH_2$	H	85	0
6	$AlCl_3$ (0.2)	**1c**	*t*-C_4H_9	H	82	0
7	$AlCl_3$ (0.2)	**1d**	Me_3Si	H	0	89
8	$EtAlCl_2$ (0.2)	**1e**	1-Cyclohexenyl	H	75	0
9	$EtAlCl_2$ (0.2)	**1f**	Ph	H	77	0
10[d)]	$EtAlCl_2$ (1.2)	**1g**	*i*-$Pr_3SiO(CH_2)_2$	H	86	0
11	$AlCl_3$ (1.2)	**1h**	*i*-$Pr_3SiO(CH_2)_4$	H	74	0
12	$EtAlCl_2$ (1.2)	**1i**	$PhCH_2O(CH_2)_2$	H	72	0
13	$AlCl_3$ (0.2)	**1j**	C_5H_{11}	C_5H_{11}	73	—
14	$AlCl_3$ (0.2)	**1k**	Ph	Ph	66	—
15	$AlCl_3$ (0.2)	**1l**	Ph	CH_3	76	10
16	$AlCl_3$ (0.2)	**1m**	Ph	C_2H_5	54	26

a) Reactions were conducted in toluene at 0 °C under Ar unless otherwise noted. b) The starting material **1a** was recovered quantitatively. c) Reaction was carried out without any solvents. d) Hexane was used as a solvent.

Table 2. Lewis Acid-Catalyzed Hydrosilylation of 1-Dodecyne **1a** with R_3SiH[a)]

Entry	Lewis acid	R_3SiH	Yield of **2** /%
1	$AlCl_3$	*t*-$BuMe_2SiH$	78
2	$AlCl_3$	(*c*-C_6H_{11})Me_2SiH	73
3	$EtAlCl_2$	Ph_3SiH	40
4	$EtAlCl_2$	Ph_2MeSiH	45
5	$EtAlCl_2$	$PhMe_2SiH$	60

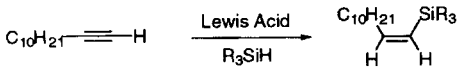
a) Reactions were conducted in toluene at 0 °C under Ar in the presence of 0.2 equiv of Lewis acids.



4a **4b** **5** **6**

Chart 1.

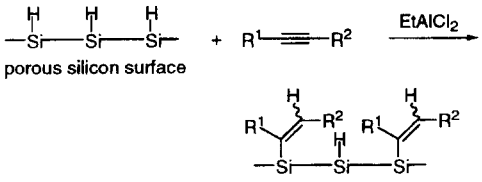
Not only Et_3SiH but also other trialkylsilanes were useful for the present reaction (Eq. 4, Table 2).



1a **2** (4)

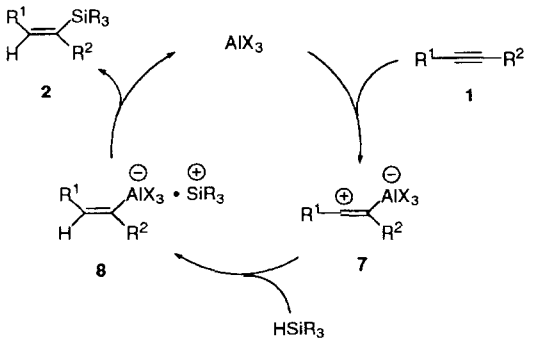
The Lewis acid-catalyzed hydrosilylation of diyne compounds was also examined. It is interesting that the $AlCl_3$-catalyzed hydrosilylation of 1,6-heptadiyne **4a** gave the six-membered cyclization product **5** in 60% yield, whereas that of 1,7-octadiyne **4b** afforded bis-hydrosilylation product **6** in 47% yield (Chart 1). The results are in marked contrast to the cyclization reaction of diyne compounds either by Ni-catalyzed-[13] or Rh-catalyzed hydrosilylation.[14]

Recently, Buriak and Allene applied our procedure to the modification of the surface of porous silicon (Eq. 5).[15] They stated that Lewis acid catalysts are suitable for the hydrosilylation of porous silicon, because transition metal catalysts have the potential for activation of the weaker Si–Si bonds on the surface instead of the Si–H bonds.



(5)

A plausible mechanism for the $AlCl_3$- or $EtAlCl_2$-catalyzed *trans*-hydrosilylation is shown in Scheme 1. The acetylenic bond of **1** would coordinate to $AlCl_3$ or $EtAlCl_2$ (AlX_3) to produce the zwitterionic intermediate **7** through a π-complex. A hydride from $HSiR_3$ would attack an electron-deficient carbon from the side opposite to AlX_3 to produce an aluminum ate-complex **8**. The intermediate **8** would undergo transmetalation from aluminum to silicon with retention of geometry to give **2** and AlX_3. This mechanism can explain the reverse regioselectivity in the hydrosilylation of (trimethylsilyl)acetylene **1d** mentioned above (Table 1, En-



Scheme 1.

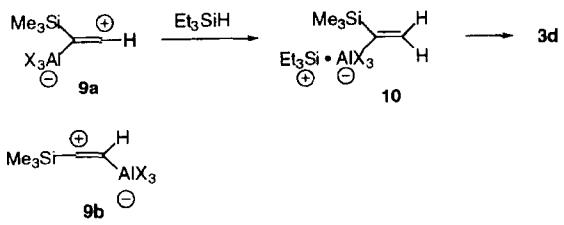


Chart 2.

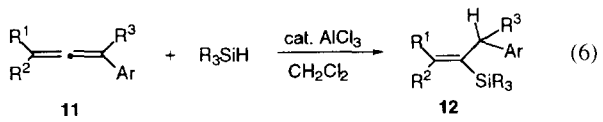
try 7). The coordination of **1d** to AlX_3 would afford the zwitterionic intermediate **9a**, instead of another regioisomer **9b** (Chart 2), since the trialkylsilyl group stabilizes a β-cationic carbon significantly and destabilizes an α-cationic carbon.[16] Subsequent reaction of **9a** with triethylsilane via a similar transformation pathway to that shown in Scheme 1 would produce **3d** through **10**.

1-1-2. Hydrosilylation of Allenes. The hydrosilylation of substituted allenes **11** was catalyzed dramatically by $AlCl_3$; the results are summarized in Table 3.[12b] The addition of trialkylsilane to the allenes occurred not only regio- but also stereoselectively to give the corresponding adducts in good to fair yields (Eq. 6) However, the allene, bearing a strong electron-withdrawing trifluoromethyl group at the *para*-position of phenyl ring, underwent no hydrosilylation reaction (Entry 4). A sterically less demanding trialkylsilane is more suitable for the hydrosilylation of allenes. Actually, the hydrosilylation of 1,3-disubstituted allenes hardly proceeded even with ethyldimethylsilane, and therefore trimethylsilane was used in those cases (Entries 5, 6, 7, 8, and 9). Very interestingly, in the case of 1,3-disubstituted allenes, the *E*-vinylsilanes were obtained stereoselectively (Entries 5, 6, and 7), and no stereoisomers were obtained. Furthermore, even the trisubstituted allene underwent regioselective hydrosilylation with trimethylsilane to give the tetrasubstituted vinylsilane in 58% yield (Entry 8). All the allenes examined in Table 3 possess an aromatic substituent (see **11**), and a hydride from $HSiR_3$ always attacks the carbon attached to the aromatic ring. However, the hydrosilylation did not proceed at all with those aliphatic allenes.

Table 3. Lewis Acid-Catalyzed Hydrosilylation of Allenes with R_3SiH[a]

Entry	Allenes **11**					R_3SiH	Yield of **12**
	R^1	R^2	R^3	Ar			%
1	H	H	H	C_6H_5	**11a**	$EtMe_2SiH$	76
2	H	H	H	*p*-Me–C_6H_4	**11b**	$EtMe_2SiH$	78
3	H	H	H	*p*-F–C_6H_4	**11c**	$EtMe_2SiH$	96
4[b]	H	H	H	*p*-CF_3–C_6H_4	**11d**	$EtMe_2SiH$	0
5	Me	H	H	*p*-Me–C_6H_4	**11e**	Me_3SiH	60
6	Me	H	H	C_6H_5	**11f**	Me_3SiH	66
7	Me	H	H	*p*-F–C_6H_4	**11g**	Me_3SiH	72
8	Me	Me	H	*p*-F–C_6H_4	**11h**	Me_3SiH	58
9	H	H	Me	*p*-F–C_6H_4	**11i**	Me_3SiH	46

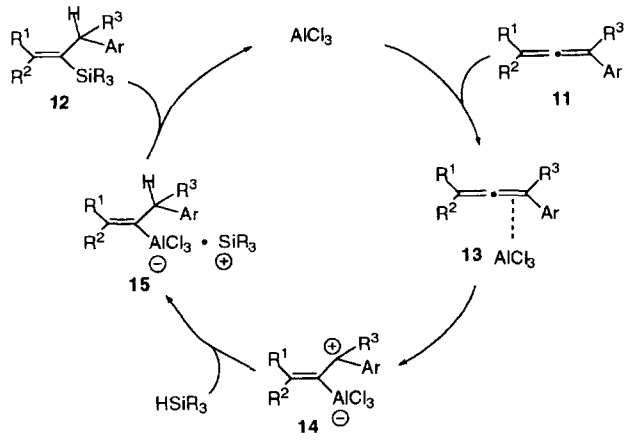
a) Reactions were conducted in CH_2Cl_2 at 0 °C in the presence of 0.2 equiv of $AlCl_3$. b) The starting material was recovered.



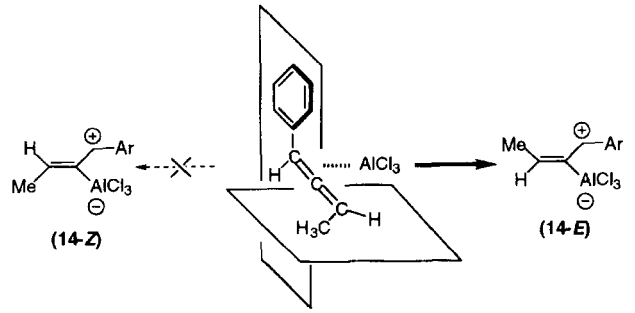
(6)

The following mechanistic rationale can explain the regio- and stereoselective hydrosilylation of allenes (Scheme 2). The double bond of an allene would coordinate to $AlCl_3$ to produce the zwitterionic intermediate **14** through π-complex **13**. Hydride transfer from $HSiR_3$ to **14** would give the ate-complex **15**, which would undergo facile transmetalation to afford the vinylsilane **12** and $AlCl_3$. Aromatic groups such as *p*-CH_3–C_6H_4 and *p*-F–C_6H_4[17,18] stabilize significantly the benzyl cation of **14**, whereas *p*-CF_3–C_6H_4 destabilizes the carbocation due to the strong electron-withdrawing effect of CF_3-group. Accordingly, the reaction did not proceed at all in the case of **11d**. In the case of allenes substituted only with aliphatic groups, the stabilization of the carbocation derived from the coordination of the double bond of the allene to $AlCl_3$ would probably be weak in comparison with that derived from aromatic allenes, and therefore the hydrosilylation did not occur with aliphatic allenes. The above mechanism also explains very nicely the regiochemistry of the hydrosilylation; Si always attaches at the central carbon of the allene, and the hydride attaches at the carbon bearing aromatic group.

In the reactions of the 1,3-disubstituted allenes (**11e—g**), the *trans*-vinylsilanes (**12e—g**) were obtained stereoselectively; such stereoselectivity can be explained by the geometry of allene double bond (Scheme 3). The double



Scheme 2.



Scheme 3.

bond of the allenes (**11e—g**) would coordinate to $AlCl_3$ as shown in Scheme 3 in order to diminish the steric congestion between methyl-group at C-3 and $AlCl_3$. The selective formation of the *trans*-vinylaluminate **14*E*** would give vinylsilanes **12e—g** stereoselectively.

1-2. Hydrostannation. 1-2-1. Hydrostannation of Alkynes. Hydrostannation[19] of acetylenes is one of the simplest and the most straightforward preparation methods for vinylstannanes, which have great versatility as building blocks in synthesis.[19,20] It is well known that the hydrostannation of acetylenes is induced by either radical initiators[21] or transition metal catalysts.[22] The radical-induced procedure often provides a mixture of the *trans*- and *cis*-hydrostannation products, since the isomerization of the alkenyltin products occurs in the presence of tin radicals.[23,24] Although the transition metal-catalyzed reaction proceeds through *cis*-hydrostannation pathway,[22] a mixture of two regioisomers (terminal and internal products) was formed in the reaction with terminal alkynes similar to the case with the transition metal-catalyzed hydrosilylation.

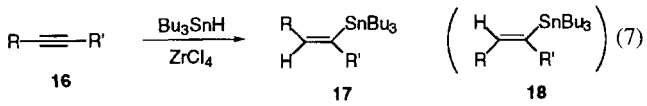
We found that the hydrostannation process was catalyzed dramatically by a Lewis acid such as $ZrCl_4$ or $HfCl_4$, and that the $ZrCl_4$-catalyzed procedure enables to produce the *trans*-hydrostannation product regio- and stereoselectively (Eq. 7, Table 4).[25] Since the hydrostannated compounds were slightly decomposed during the purification, the isolated yields were lower than those obtained by NMR. The reaction using 0.2 equiv of $ZrCl_4$ gave better results compared to that using stoichiometric amount (Entries 1 and 2). It should be noted that $ZrCl_4$ is not soluble in toluene and hexane at 0 °C and therefore the reaction is carried out in a heterogeneous system. The use of THF and CH_2Cl_2 as solvents, which dissolve the catalyst more effectively than do the non-polar solvents, gave lower stereoselectivity and chemical yield. $HfCl_4$ was also an efficient catalyst for the *trans*-hydrostannation (Entry 4), but the reaction speed via $HfCl_4$ was slightly slower than that via $ZrCl_4$. The use of a typical Lewis acid of group 13, $AlCl_3$, as a catalyst afforded a 60 : 40 mixture of **17a** and **18a** in 53% yield. The reaction of 5-(*t*-butyldimethylsilyloxy)-1-pentyne (**16d**) gave **17d** stereoselectively in high yield (Entry 7). On the other hand, the addition to 5-benzyloxy-1-pentyne (**16e**) did not take place and the starting material was recovered quantitatively (Entry 8). The BnO group can coordinate more easily to Lewis acids than the sterically demanding (*t*-Bu)-

Table 4. Lewis Acid-Catalyzed Hydrostannation of Acetylenes with Bu_3SnH[a)]

entry	Lewis acid (equiv)	Alkyne **16** R	R′		Yield of **17**[b)] %
1	$ZrCl_4$ (1.1)	C_6H_{13}	H	**16a**	30
2	$ZrCl_4$ (0.2)	C_6H_{13}	H	**16a**	76
3[c)]	$ZrCl_4$ (0.2)	C_6H_{13}	H	**16a**	89
4	$HfCl_4$ (0.2)	C_6H_{13}	H	**16a**	86
5	$ZrCl_4$ (0.2)	Ph	H	**16b**	73 (40)[d)]
6	$ZrCl_4$ (0.2)	*p*-Me-C_6H_4	H	**16c**	84
7	$ZrCl_4$ (0.2)	TBDMSO$(CH_2)_3$[g)]	H	**16d**	87 (48)
8	$ZrCl_4$ (0.2)	BnO$(CH_2)_3$[h)]	H	**16e**	0[e)]
9	$ZrCl_4$ (0.2)	C_6H_{13}	Cl	**16f**	47 (40)
10	$ZrCl_4$ (1.0)	C_5H_{11}	C_5H_{11}	**16g**	56
11	$ZrCl_4$ (1.0)	Ph	Ph	**16h**	33[f)]

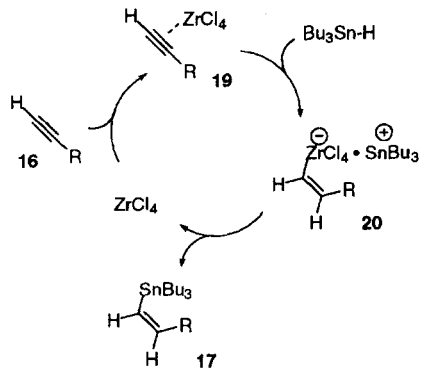
a) Reactions were conducted in toluene at 0 °C under Ar unless otherwise noted. b) Determined by ^{1}H NMR spectra of the reaction product using *p*-xylene as an internal standard. Isolated yields were in the parenthesis. c) Hexane was used as a solvent. d) Trace amount of **18** was produced. e) The starting material (**16e**) was recovered quantitatively. f) *trans*-Stilbene was obtained in 46% yield in addition to 33% yield of **17h**. g) TBDMS = *t*-$BuMe_2Si$. h) Bn = $PhCH_2$.

Me_2SiO. Therefore, it seems that $ZrCl_4$ forms the complex with BnO group of **16e**, instead of acting as a catalyst for the hydrostannation. The reactions of 6-dodecyne (**16g**) and tolan (**16h**) also proceeded smoothly, although the use of stoichiometric amounts of $ZrCl_4$ gave better results.



A plausible mechanism for the $ZrCl_4$-catalyzed *trans*-hydrostannation is shown in Scheme 4. The coordination of the acetylenic bond of **16** to $ZrCl_4$ would produce the π-complex **19**. A hydride from $HSnBu_3$ would attack an electron-deficient carbon from the side opposite to $ZrCl_4$ to produce an ate-complex **20**. The intermediate **20** would undergo transmetalation from zirconium to tin with retention of geometry to give **17** and $ZrCl_4$.

The Lewis acid-catalyzed hydrostannation with dibutyltin dihydride also proceeded smoothly to give regio- and stereodefined divinyltin derivatives **21** in good to high yields



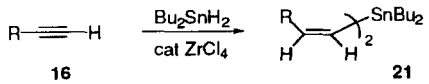
Scheme 4.

Table 5. Lewis Acid-Catalyzed Hydrostannation of Acetylenes with Bu_2SnH_2[a]

Entry	R	16	Yield/%[b]	21: Other isomers[c]
1	C_6H_{13}	**16a**	85 (60)	**21a** > 95 : 5
2	$PhCH_2$	**16i**	78 (54)	**21b** > 95 : 5
3	1-Cyclohexenyl	**16j**	76	**21c** > 95 : 5

a) Reactions were conducted using 4.0 equivalent of **16**, 1.0 equivalent of Bu_2SnH_2, and 0.2 equivalent of $ZrCl_4$ in toluene at 0 °C under Ar. b) Determined by ^1H NMR spectra of the reaction product using *p*-xylene as an internal standard. Isolated yields were in the parenthesis. c) Determined by 270 MHz ^1H NMR spectra. The stereoisomers were not detected by the NMR. The ratio, > 95 : 5, came from the limit of detection for the stereoisomer.

(Eq. 8, Table 5).[26] To avoid the formation of vinyltin hydride derivatives by the reaction of 1 equiv of Bu_2SnH_2, excess amounts of acetylenes were used.



16 21 (8)

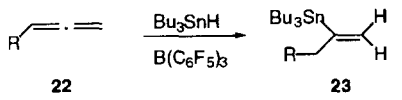
1-2-2. Hydrostannation of Allenes. Hydrostannation of allenes, in the case of controlled regiochemistry of this process, may serve as the most straightforward and universal way to both vinyl- and allylstannanes, which have great versatility as building blocks.[19,20] Since Kuivila[27] first reported the free radical addition of Me_3SnH to allenes, only a little attention has been paid to this subject. Thus, Oshima[28] showed that free radical addition of Ph_3SnH to allenes produces a complex mixture of vinyl- and allylstannanes. The only two examples of Pd-catalyzed hydrostannation of substituted allenes present in the paper[28] exhibit contradictory regiochemistry: in one case an allylstannane, and in another a vinylstannane, was formed exclusively. Shortly after Mitchell[29] reported a study on a comparison between radical and Pd-catalyzed addition of Me_3SnH to allenes. As in the previous cases[27,28] the free radical hydrostannation was characterized by an unsatisfactory degree of regio- and stereocontrol, producing a variety of products in which the tin group attached either to the central or to terminal carbon atom of allenic moiety. The Pd-catalyzed reaction was more selective, furnishing allylstannanes as a major product, however, the last were always accompanied with trace to significant amounts of isomeric vinylstannanes.[29] Taken together, it seems that due to the low degree of regio- and stereocontrol neither free radical nor Pd-catalyzed addition of Me_3SnH or Ph_3SnH to allenes could serve as a synthetically useful approach to vinyl- and allylstannanes.[30]

We found that 20 mol% of $B(C_6F_5)_3$ at low to room temperatures catalyzed the addition of Bu_3SnH to certain monosubstituted allenes **22**, leading to vinylstannanes **23** exclusively (Eq. 9, Table 6).[31] It should be pointed out that $ZrCl_4$ also catalyzed the reactions mentioned above; however, the yields of **23** in most cases were slightly lower than those via $B(C_6F_5)_3$ catalyst. The low yield of **23g** is presumably due to the strong affinity of the Lewis acid to the enol oxygen atom[32] of alkoxyallene **22g** that causes deactivation of the catalyst at low temperatures and decomposition of the starting allene when the reaction is carried out at the temperatures higher than −78 °C (Entry 7). Silyloxyallene **22h** {R = triisopropylsilyloxy (TIPSO)} reacted with Bu_3SnH in a different manner, producing allylstannanes **24** and **25** in a ratio of 85 : 15 with a total isolated yield of 52%. It is clear that replacement of the methoxy group (**22g**) with the bulky TIPSO group (**22h**) not only prevents a coordination between Lewis acid and the enol oxygen atom of **22h**, but also prevents an internal addition of the tin group to the central carbon of the allene moiety, and thus leads to the terminal addition products **24** and **25** (Chart 3).

Table 6. Lewis Acid-Catalyzed Hydrostannation of Allenes with Bu_3SnH[a]

Entry	R	22	Condition	Yield of 23/%
1[b]	C_8H_{17}	**22a**	r.t., 24 h	37
2	*c*-C_6H_{11}	**22b**	0 °C→r.t., 22 h	41
3	$PhCH_2$	**22c**	0 °C→r.t., 3 h	57
4	Ph	**22d**	0 °C→r.t., 3 h	60
5	*p*-Me–C_6H_4	**22e**	0 °C→r.t., 3 h	77
6	*p*-MeO–C_6H_4	**22f**	−70→−50 °C, 2 h	59
7	MeO	**22g**	−78 °C, 3 h	12

a) Reactions were conducted in toluene in the presence of 0.2 equivalent of $B(C_6F_5)_3$ under Ar unless otherwise noted. b) Hexane was used as solvent.



22 23 (9)

A plausible mechanism for the Lewis acid-catalyzed hydrostannation of allenes is shown in Scheme 5. The coordination of the internal double bond of **22** to $B(C_6F_5)_3$ would produce the zwitterionic intermediate **26**, which would be transformed into the ate complex **27** via hydride transfer from Bu_3SnH to the cationic center of **26**. The transmetalation from boron to tin would produce the vinylstannane **23**

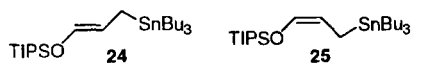
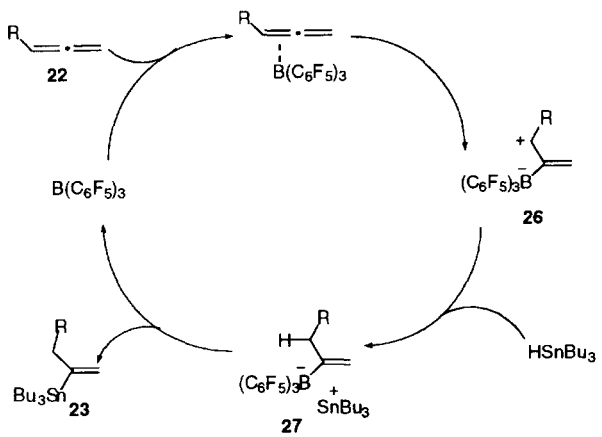


Chart 3.



Scheme 5.

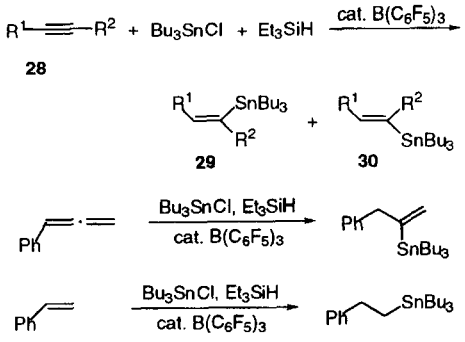
and regenerate $B(C_6F_5)_3$ catalyst. Perhaps $ZrCl_4$-catalyzed hydrostannation of allenes would proceed through a similar mechanism.

1-2-3. Hydrostannation Using Bu_3SnCl and Et_3SiH. Since the first synthesis of tributyltin hydride by Schlesinger in 1947,[33] this compound has become one of the most frequently used organometallic reagents in organic synthesis.[34] Along with wide applicability as a hydrogen source in various kinds of reductions, Bu_3SnH is the most popular hydrostannation agent for the synthesis of vinyl- and allylstannanes. The later, due to their great versatility as building blocks, are of increasing importance in modern synthetic organic chemistry. Although Bu_3SnH is commercially available, it gradually decomposes after storage in a refrigerator for a prolonged period of time;[35] consequently, distillation is needed before use. It occurred to us that in situ generation of Bu_3SnH from stable precursors would be synthetically more convenient for the hydrostannation reaction.[36] In our initial experiments, we found that simple mixing of Bu_3SnCl and Et_3SiH in toluene at room temperature did not produce any detectable amount of tin hydride. In contrast, a redistribution took place by the addition of 20 mol% $ZrCl_4$ to the same reaction mixture and noticeable amounts of Bu_3SnH were detected by ^1H NMR analysis of the reaction mixture after one hour (Eq. 10).

$$Bu_3SnCl + Et_3SiH \underset{}{\overset{ZrCl_4}{\rightleftharpoons}} Bu_3SnH + Et_3SiCl \quad (10)$$

89% 11%

Motivated by this result, we applied this method for the in situ preparation of Bu_3SnH and subsequent $ZrCl_4$-catalyzed hydrostannation of phenylacetylene; as a result the *trans*-addition product (*Z*)-*β*-(tributylstannyl)-styrene was formed in 52% yield. A brief search for a more efficient Lewis acid catalyst has located $B(C_6F_5)_3$. We found that 10 mol% of $B(C_6F_5)_3$ effectively catalyzed hydrostannation of various alkynes **28** with Bu_3SnH, generated in situ from Bu_3SnCl and Et_3SiH, producing the hydrostannation products **29** and **30** in excellent chemical yields (Eq. 11, Table 7).[37] This methodology was applicable not only to alkynes but also to phenylallene and styrene (Eqs. 12 and 13).



2. Carbometalation

Since the first carbometalation discovered by Zieglar and Bähr in 1927,[38] a number of additions of organometallics to carbon–carbon multiple bonds have been reported.[39] The carbometalation of alkynes can be used not only for preparation of vinylmetals but also for C–C bond formation. The intramolecular version of carbometalation is a useful methodology for the synthesis of carbocycles (vide post). 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.[39,40] However, the allylmetalation of simple unactivated alkynes is not easy, and only a limited number of allylmetals can serve for this purpose.[39,41]

2-1. Carbosilylation. 2-1-1. Intermolecular Allylsilylation. Among carbometalations, carbosilylation still remains unexploited due to the lack of activation of carbon–silicon bonds.[42–44] Recently, Jung's group reported the $AlCl_3$-catalyzed allylsilylation of alkenes[45] and alkynes.[41c] Hosomi's group also found that the allylsilylation of alkenes and alkynes can proceed via a radical process.[46]

We investigated the Lewis acid-catalyzed reaction of allyltrimethylsilane with unactivated alkynes **31** systematically and established that the allylsilylation proceeded in a *trans* fashion (Eq. 14, Table 8).[47] The addition of allyltrimethylsilane to 1-octyne in the presence of 0.5 equiv of $EtAlCl_2$ gave the allylation product **33** in low yield (Entry 1). However, the allylsilylated product **32a** was obtained by the addition of an excess amount of chlorotrimethylsilane (TMSCl) (Entry

Table 7. $B(C_6F_5)_3$-Catalyzed Hydrostannation of Alkynes with Bu_3SnH Generated in situ from Bu_3SnCl and Et_3SiH[a)]

Entry	Alkynes **28**		Conditions	Yield	Ratio
	R^1	R^2		**29**+**30**[b)]	**29** : **30**[c)]
1	C_6H_{13}	H	0 °C, 40 min then rt, 3h	78	> 95 : 5
2	1-Cyclohexenyl	H	0 °C, 2 h	85	86 : 14
3	$PhCH_2$	H	0 °C, 4 h	85	> 95 : 5
4	Ph	H	0 °C, 2.5 h	77	> 95 : 5
5	*p*-Me–C_6H_4	H	0 °C, 2.5 h	89	> 95 : 5
6	*p*-MeO–C_6H_4	H	−35 °C, 1.5 h	70	> 95 : 5
7	C_5H_{11}	C_5H_{11}	0 °C, 0.6 h then r.t., 3 h	90	80 : 20
8	Ph	Ph	0 °C, 0.6 h then r.t., 3 h	71	> 95 : 5

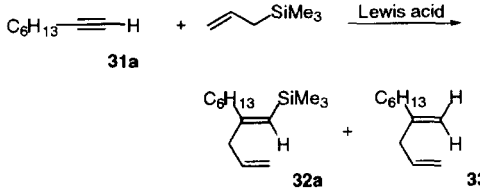
a) Reactions were conducted in toluene in the presence of 0.1 equivalent of $B(C_6F_5)_3$ under Ar unless otherwise noted. b) Isolated yield. c) Determined by ^1H NMR analysis of crude reaction mixtures.

Table 8. Lewis Acid-Catalyzed Carbosilylation of 1-Octyne **31a** with Allyltrimethylsilane[a]

Entry	Lewis acid	Solvent	Yield/%[b] **32a+33**	Ratio[c] **32a : 33**
1	$EtAlCl_2$	Toluene	20	5 : > 95[e]
2	$EtAlCl_2$	None[d]	90	> 95 : 5[f]
3	$AlCl_3$	Toluene	40	24 : 76
4	$AlBr_3$	Toluene	50	15 : 85
5	$HfCl_4$	Toluene	9	> 95 : 5[f]
6	$HfCl_4$	Hexane	Trace	[g]
7	$HfCl_4$	CH_2Cl_2	50	> 95 : 5[f]
8[h]	$HfCl_4$	CH_2Cl_2	88[i]	> 95 : 5[f]

a) Reactions were carried out at −78 to 0 °C with 0.5 equiv amount of Lewis acid unless otherwise noted. b) Determined by ^{1}H NMR spectra of the reaction product using *p*-xylene as an internal standard. c) The ratio was determined by ^{1}H NMR. d) Reaction was conducted in the presence of TMSCl (20 equiv). e) **32a** was not detected by ^{1}H NMR. f) **33** was not detected by ^{1}H NMR. g) Not determined. h) Reaction was carried out at 0 °C i) Isolated yield.

2). On the other hand, the $HfCl_4$-catalyzed allylsilylation in CH_2Cl_2 at 0 °C afforded **32a** as a single reaction product in 88% yield without TMSCl (Entry 8). The present allylsilylation was applied to various alkynes (Eq. 15, Table 9).



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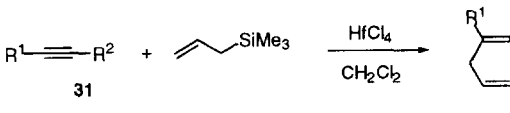


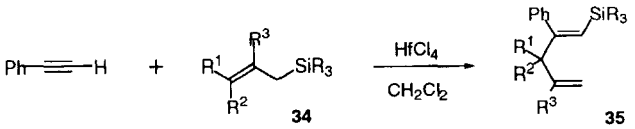
(15)

Further examination of the $HfCl_4$-catalyzed addition of different substituted allylsilanes **34a**—**h** to phenylacetylene was carried out (Eq. 16, Table 10). The addition of allyl-, *E*-, and *Z*-crotyl-, methallyl-, and prenyltrimethylsilane to phenylacetylene proceeded smoothly, affording the corresponding adducts in excellent chemical yields. Replacement of the trimethylsilyl group with triethylsilyl, dimethylphenylsilyl, and methyldiphenylsilyl groups caused a slight decrease in the chemical yields of allylsilylated products, as well as a noticeable elongation of reaction times. It should be pointed out that in all cases only γ-addition products 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 9. $HfCl_4$-Catalyzed Carbosilylation of Acetylenes with Allyltrimethylsilane[a]

Entry	**31**	R^1	R^2	**32**	Product yield/%[b]
1	**31a**	$CH_3(CH_2)_5$	H	**32a**	88
2	**31b**	Ph	H	**32b**	95
3	**31c**	*p*-$CH_3C_6H_4$	H	**32c**	97
4	**31d**	$PhCH_2$	H	**32d**	73
5	**31e**	$CH_3(CH_2)_9$	H	**32e**	86
6	**31f**	1-Cyclohexenyl	H	**32f**	42
7	**31g**	Ph	Me	**32g**	90
8	**31h**	Ph	Et	**32h**	82
9	**31i**	H	TMS	**32i**	65[c,d]
10	**31j**	*t*-Bu	H	**32j**	10[c]
11	**31k**	2-Propenyl	H	**32k**	60[c]

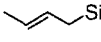
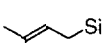
a) Reactions were carried out in CH_2Cl_2 at 0 °C with 50 mol % of $HfCl_4$. b) Isolated yield, except for where otherwise indicated. c) Yield was determined by ^{1}H NMR using *p*-xylene as an internal standard. d) The allyltrimethylsilane was added slowly via syringe pump in order to avoid its dimerization.



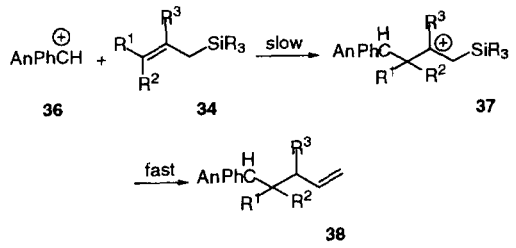
(16)

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 is well documented.[4,48] 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.[16] 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. Attack of the carbenium cation **36** at the γ-position of the allylsilicon compound **34** is rate-determining and leads to formation of the β-silicon-stabilized carbenium ion **37**, which subsequently transforms into product **38** via elimination of the silicon group (Eq. 17).[49]

Table 10. $HfCl_4$-Catalyzed Carbosilylation of Phenylacetylene with Allylsilanes

Entry	Allylsilane	**34**	Time/min	**35**	Yield/%[a]
1		**34a**	60[b]	**35a (35b)**	95
2		**34b**	60	**35b**	96
3		**34c**	60	**35b**	90
4		**34d**	25	**35c**	92
5		**34e**	120	**35d**	97
6		**34f**	180	**35e**	73
7		**34g**	140	**35f**	76
8		**34h**	230	**35g**	51

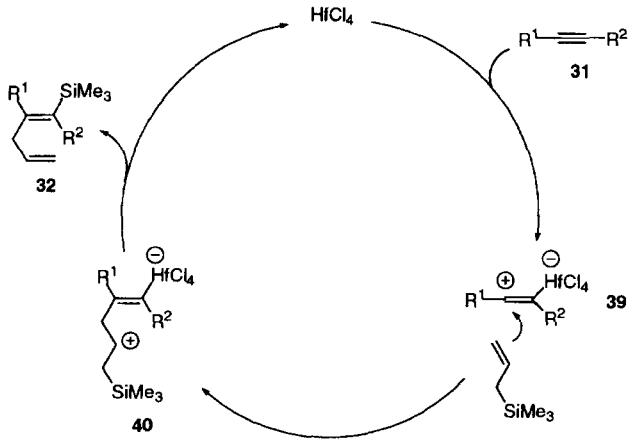
a) Reactions were carried out in CH_2Cl_2 at 0 °C with 50 mol % of $HfCl_4$. b) In the presence of 10 equiv of TMSCl, the reaction was completed in 20 mm.



(17)

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,[49] we determined relative reactivities for addition of allylsilanes **34a—e** to phenylacetylene based on the measurement of the half-reaction times.[50] We found that relative reactivities of most allylsilanes bearing trimethylsilyl groups (**34a—e**) in the $HfCl_4$-catalyzed addition to phenylacetylene (Fig. 1, part a) are in good agreement with relative reactivities of the same allylsilanes **34a—e** toward diarylcarbenium ion **36**. This finding encouraged us to consider the intermediacy of some cationic species analogous to **36** and **37** in the $HfCl_4$-catalyzed allylsilylation of alkynes, and allowed us to propose the plausible mechanism for this reaction shown in Scheme 6.

As we mentioned above, the coordination of the triple bond of **31** to $HfCl_4$ would form zwitterionic intermediate **39** through a π-complex, which would attack the double bond of allylsilane at the γ-position affording carbenium cation **40** *trans*-selectively. The elimination of the silyl group from **40** would produce **32** and regenerate the catalyst. On the other hand, the mechanism for the $EtAlCl_2$-catalyzed reaction was proposed in Scheme 7. After formation of zwitterionic intermediate **42**, transmetalation of aluminum halide by the trimethylsilyl group would afford **32** and regenerate the catalyst. On the contrary, the coupling between the chloro and silyl group would produce Me_3SiCl and the alkenylaluminum derivative **43**, which would afford **33** upon hydrolysis. An



Scheme 6.

excess amount of TMSCl is needed to drive the equilibrium over in favor of replacing aluminum with silicon. Although Jung et al. proposed a mechanism different from ours,[41c] our mechanism nicely explains not only the regio- and stereoselectivities of the present reaction but also the reason for the generation of **33**.

2-1-2. Intramolecular Allylsilylation. Carbocyclizations of alkenes and alkynes are extremely important and useful reactions for the synthesis of a variety of a carbocyclic and heterocyclic compounds.[51] Since the early report in 1943 on the ene reaction by Alder,[52] and the first systematic studies by Lehmkuhl on metallo-ene[53] versions of this reaction, the chemistry of transition metal-catalyzed carbocyclizations became a vast field and a number of transition metal-mediated[54] and -catalyzed[55] carbocyclization methodologies were developed. Carbocyclization of alkynes is of particular interest since it allows one to obtain carbo- and heterocycles with higher degrees of unsaturation.[51,56—61] Apparently, the exclusive or predominant *exo*-fashion was a general regiochemical trend for the previous intramolecular carbocyclizations of alkynes.[51] It is clear that the scope and

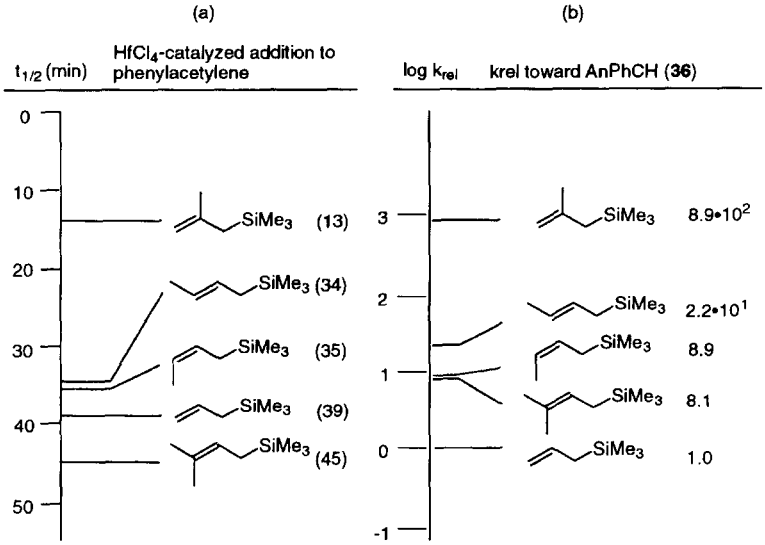
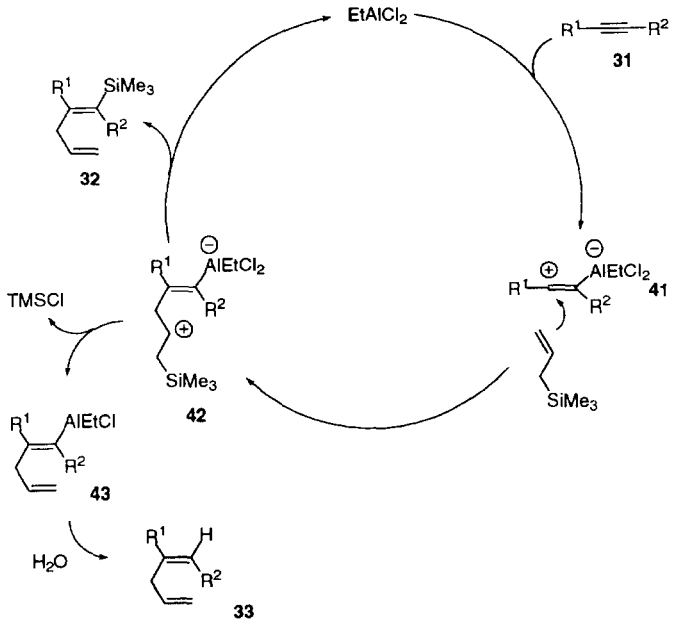
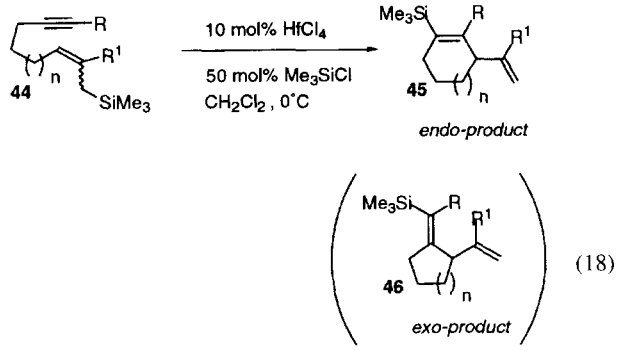


Fig. 1. a) Determined by capillary GLC with hexadecane as an internal standard. See also Ref. 50. b) Relative reaction constants from Ref. 49. An = *p*-MeO–C_6H_4.



Scheme 7.

synthetic utility of intramolecular carbocyclizations would be enhanced if methods permitting selective *endo*-cyclization could be found. As a partial solution of this problem, we reported $HfCl_4$-catalyzed intramolecular allylsilylation of unactivated alkynes, proceeding exclusively in the *endo*-fashion to give five-, six-, and seven-membered carbocycles **45** in moderate to high chemical yields with none of the *exo*-cyclization products **46** being produced (Eq. 18).[62]



(18)

The $HfCl_4$/TMSCl catalyst system was found to be effective for the intramolecular allylsilylation of carbon tethered alkynyl allylsilane, and the *endo*-cyclization product was obtained exclusively (Table 11). The cyclization of alkyl-, alkenyl-, and aryl-substituted alkynyl allylsilanes **44a—e**, which each have three methylene groups in the tether, proceeded smoothly to produce the six-membered carbocycles **45a—e** in good to nearly quantitative yields. Analogously, the cyclization of **44f—h**, having a tether chain of four methylene groups, selectively gave the seven-membered **45f—h**. In contrast to the above cases, the cyclization of **44i, j**, having a shorter carbon chain, afforded the five-membered cyclic vinylsilanes **45i, j** in rather low yields. It should be pointed out that, regardless of the size of the ring obtained, the cyclization of alkyl-, alkenyl-, and aryl-substituted alkynyl allylsilanes

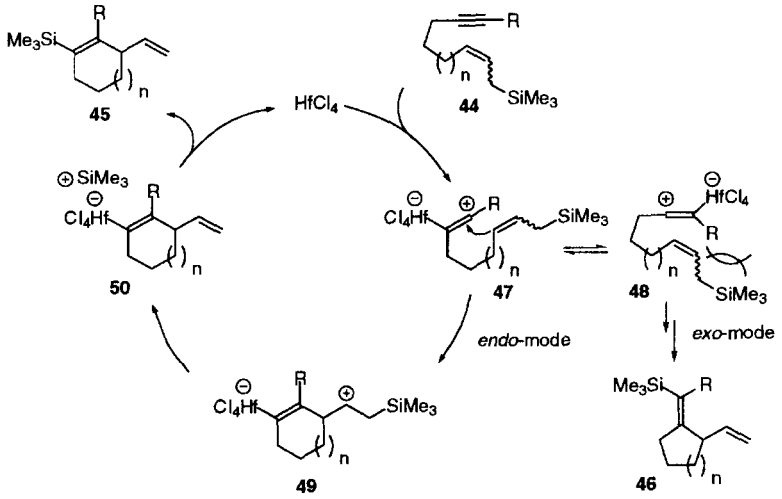
Table 11. $HfCl_4$-Catalyzed *endo*-Carbocyclization of Alkynyl Allylsilanes **44**[a]

Entry	Substrate[b]	R	R^1	*n*	Product	Yield/%[c]
1	**44a**	Ph	H	1	**45a**	61
2	**44b**	C_6H_{13}	H	1	**45b**	99
3	**44c**	1-Cyclohexenyl	H	1	**45c**	58
4	**44d**	*p*-Me–C_6H_4	H	1	**45d**	63
5	**44e**	C_6H_{13}	Me	1	**45e**	83[d]
6	**44f**	Ph	H	2	**45f**	76
7	**44g**	C_6H_{13}	H	2	**45g**	84
8	**44h**	*p*-Me–C_6H_4	H	2	**45h**	65
9	**44i**	Ph	H	0	**45i**	22[e]
10	**44j**	C_6H_{13}	H	0	**45j**	47[f,g]

a) Reactions were carried out in CH_2Cl_2 at 0 °C with 0.1 equiv amount of $HfCl_4$ and 0.5 equiv amount of TMSCl under Ar. b) A 4 : 1 mixture of *Z*- and *E*-isomers of **44** was used. c) Isolated yield. d) The *endo*-product **45e** was isolated in 83% yield along with small amount of unidentified isomeric material. e) Approximately 20% of **44i** was recovered. f) NMR yield. g) 30 mol% of $HfCl_4$ was used. The catalyst was added in three portions.

44a—j proceeded exclusively in the *endo*-fashion, and no traces of *exo*-cyclization products **46** or any other regioisomers of **45a—j** were detected by ^1H NMR and capillary GC-MS analyses of crude reaction mixtures.

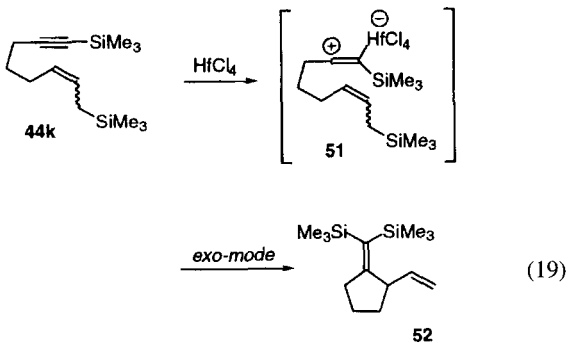
The coordination of the triple bond of **44** to $HfCl_4$ would form the zwitterionic intermediate **47** through a π-complex. The carbocation of **47** would be attacked by the double bond of internal allylsilane moiety at the γ-position affording a carbenium cation **49** via an *endo*-mode cyclization pathway. The elimination of the silyl group from **49** would form ate-complex **50**, and the subsequent transmetalation of hafnium halide with silicon would produce **45** and regenerate the catalyst (Scheme 8). Obviously, the key intermediate **47**, which is responsible for the apparent *endo*-cyclization mode, could be in equilibrium with an isomeric **48**, which would produce an *exo*-product **46** via a similar reaction pathway. The



Scheme 8.

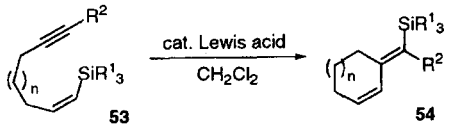
predominance of **47** over **48** could be well accounted by electronic and steric features of these vinyl cation intermediates. Indeed, in the case of the aryl- and alkenyl-substituted substrates **44a,c,d,f,h** the zwitterionic intermediate **47** would be favorable due to the higher stabilizing ability of the aryl and alkenyl group compared with that of the CH_2 group of the alkyl tether chain.[63] In contrast, the cation-stabilizing abilities of the *n*-hexyl group and that of the alkyl tether chain in **44b,e,g** would be rather similar. Perhaps even in this case the intermediate **47** would be more preferable over **48** due to the steric reasons; for a significant nonbonding interaction between an alkyl group and the allylsilane moiety in **48** would destabilize the intermediate **48**, and thus the formation of **46** would be unfavorable.

The additional support for the proposed cationic mechanism for the $HfCl_4$-catalyzed carbocyclization reaction was obtained from the cyclization of the trimethylsilyl-substituted substrates **44k** (Eq. 19). The exclusive *exo*-mode cyclization of **44k** was observed and the five-membered carbocycle **52** was obtained in 87% yield as a single product. This reversal of the reaction mode was accounted for by the stabilization effect of a cation at the β-position by the silyl group, since the intermediate **51** would be more stable due to the β-silicon stabilization, in comparison with the regioisomeric vinyl cation which leads to the formation of a six-membered carbocycle.[16]



(19)

2-1-3. Intramolecular Vinylsilylation. Despite the extensive investigation of the carbometalation reactions of alkenes and alkynes, there are very few reports on vinylmetalation, especially of alkynes. Vinylmetalation of alkynes gives new vinyl organometallics, which may exhibit a reactivity similar to that of the starting vinyl organometallic compounds. This type of carbometalation results in oligomerization or polymerization reactions. This is one of the major reasons for limiting the scope of vinylmetalation of alkynes.[64–67] We reported the first example for the intramolecular vinylsilylation of unactivated alkynes; the Lewis acid-catalyzed reaction of the carbon-tethered alkynyl vinylsilanes **53** gave the (*E*)-cyclic dienylsilanes **54** in good to high yields (Eq. 20).[68,69] The results are summarized in Table 12. Not only six-membered products but also seven-membered cyclization product was obtained in good to high yields. It is well known that the reactivity of vinylsilanes towards electrophiles is much lower than that of allylsilanes.[4,48] Accordingly, it was rather surprising for us to discover that the vinylsilylation of **53** proceeded so smoothly in the presence of Lewis acids.



(20)

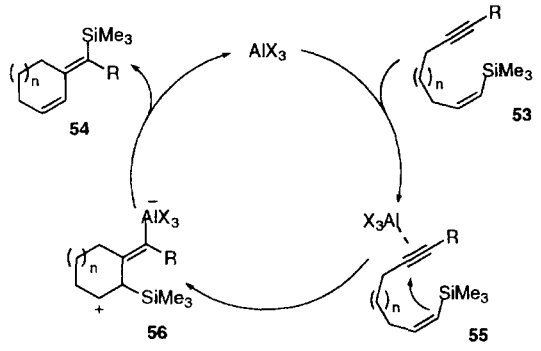
A plausible mechanism for the Lewis acid catalyzed *trans*-vinylsilylation is shown in Scheme 9. The coordination of the triple bond of **53** to a Lewis acid would form π-complex **55**. The α-carbon of vinylsilane moiety would attack the electron-deficient triple bond from the side opposite to the Lewis acid to produce an aluminum ate complex **56** stereoselectively. The transfer of trimethylsilyl group to the aluminate center would afford **54** and regenerate the Lewis acid.

A zwitterionic intermediate such as **57** may intervene in the step from **55** to **56** (Chart 4). Obviously, when the vinylsilyl group approaches the electron-deficient carbon of the alkenylaluminate, a sterically demanding R group would hamper the approach of the vinylsilyl group (see **57**). This is the reason why the reaction of **53c**, having hexyl substituted

Table 12. Lewis Acid-Catalyzed Carbocyclization of **53**[a]

Entry		Substrate **53**			Lewis acid (equiv)	Temp	Yield of **54**	
	n	R^1	R^2			°C		%[b]
1	1	Me	H	**53a**	$EtAlCl_2$ (0.5)	−78	**54a**	69
2	1	Me	H	**53a**	$AlCl_3$ (0.5)	−78	**54a**	67
3	1	Me	H	**53a**	$AlBr_3$ (0.5)	−78	**54a**	56
4	1	Me	H	**53a**	$EtAlCl_2$ (1.1)	−78	**54a**	61
5	1	Me	H	**53a**	$EtAlCl_2$ (0.2)	−78	**54a**	92
6	1	Me	H	**53a**	$EtAlCl_2$ (0.1)	−78 to 0	**54a**	49[c]
7	1	Me	H	**53a**	$AlCl_3$ (0.1)	−78 to −30	**54a**	84
8[d]	1	Me	H	**53a**	$EtAlCl_2$ (0.2)	−78	**54a**	91
9	1	Et	H	**53b**	$EtAlCl_2$ (0.2)	−78 to −20	**54b**	85
10[e]	1	Me	C_6H_{13}	**53c**	$EtAlCl_2$ (0.5)	r.t.	**54c**	31
11[e]	1	Me	$SiMe_3$	**53d**	$EtAlCl_2$ (0.5)	r.t.	**54d**	85
12	2	Me	H	**53e**	$AlCl_3$ (0.2)	−78 to −5	**54e**	89

a) Reactions were conducted in CH_2Cl_2 at the indicated temperature within 1h, except for where otherwise mentioned. The reactions were quenched by adding excess amounts of Et_2NH and saturated aq $NaHCO_3$ solution at the reaction temperature. b) Isolated yield. c) The starting material **53a** was recovered in 23% yield. d) Hexane was used as a solvent. e) Reaction was conducted for 1 d.



Scheme 9.

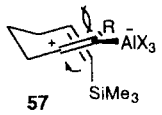
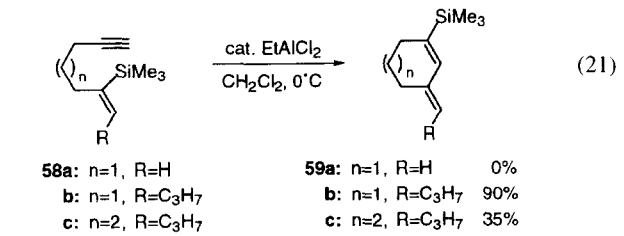


Chart 4.

internal alkyne (R = C_6H_{13}), was sluggish and the cyclization product was obtained in low yield (Table 12, Entry 10). On the other hand, the smooth cyclization of **53d** can be accounted for by the well-known β-silyl effect: the carbocation beta to trimethylsilyl group is stabilized significantly.[16] The *Z*-vinylsilane reacts with retention of configuration, which is the normal stereochemistry for the electrophilic substitution of a vinylsilane, whereas the *E*-isomer has to undergo inversion, which it is reluctant to do.[70] Indeed, no cyclization product was obtained when (*E*)-isomer of **53a** was treated with a catalytic amount of $AlCl_3$.

We further examined the cyclization of differently substituted vinylsilanes **58**. Although no cyclization product was obtained in the reaction of **58a**, this is normal for electrophilic attack on a vinylsilane of this type. However, the cyclizations of **58b** and **58c** took place in the presence of catalytic amounts of $EtAlCl_2$ and the *trans*-vinylsilylation products **59b** and **59c** were obtained, respectively (Eq. 21), because the carbocation of **61a** is stabilized by the substituent R (**58b,c**, R = C_3H_7) (vide infra). Interestingly, these products were produced via an *endo*-mode cyclization, in contrast to the reactions of **53**, which proceeded in an *exo*-mode fashion. These results can be accounted for by the following mechanistic rationale (Scheme 10). When the α-carbon of vinylsilane attacks the terminal acetylenic carbon of the complex **60** (route a, *endo*-mode), which was formed from **58** and Lewis acid, no significant steric repulsion would be produced (**62a** and **63a**) (Chart 5), although the terminal acetylenic carbon should be electronically deficient. In contrast, *exo*-mode cyclization (route b) proceeds via a vinylcation on the internal acetylenic carbon, as shown in **62b** and **63b**. Serious steric repulsion between the vinylic proton and vinylsilane moiety would destabilize these intermediates. Accordingly, the *endo*-mode cyclization would take place to give **61a**, leading to **59**.



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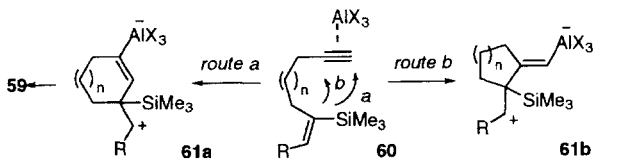


Scheme 10.

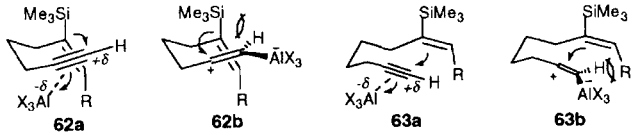
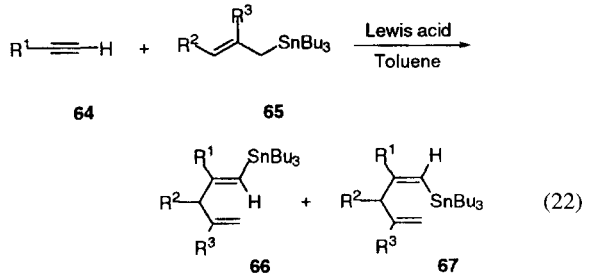


Chart 5.

2-2. Carbostannation. Although organostannanes are widely used for the carbon–carbon bond formation in organic synthesis,[3h] carbostannation of alkenes and alkynes has not been known.[71] Recently, three research groups independently developed three different methodologies for carbostannation. Hosomi's group found the allylstannation of alkenes and alkynes proceeded via a radical pathway.[72] Hiyama and coworkers reported the transition metal complex-catalyzed carbostannation of alkynes.[73] On the other hand, we reported that the allylstannation of unactivated alkynes proceeded in the presence of catalytic amounts of Lewis acids, such as $ZrCl_4$ or $EtAlCl_2$, in a trans addition manner (Eq. 22).[74]



(22)

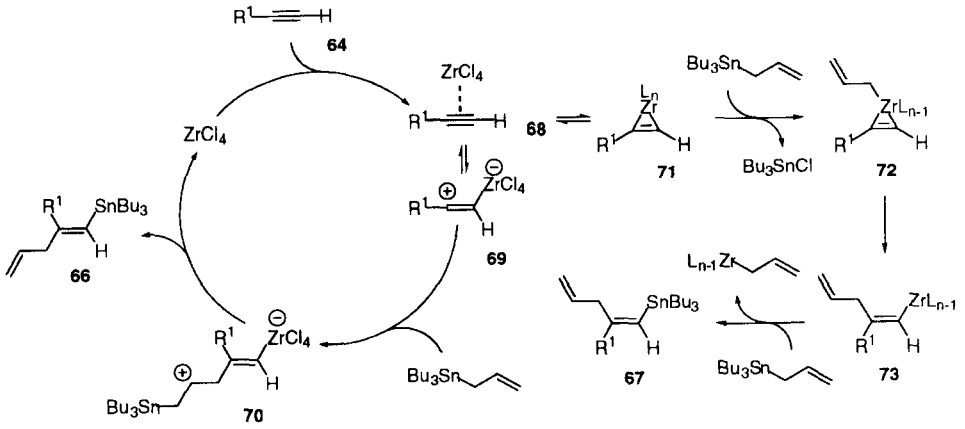
The selected $ZrCl_4$-catalyzed allylstannylation of various unactivated alkynes listed in Table 13 provides the following conclusions: 1) Reactions of the aromatic acetylenes proceed smoothly to give the corresponding *trans*-allylstannated products with very high regio- and stereoselectivity in high yields (Entries 1, 2, 3, and 4). 2) The conjugated enyne also produced the *trans*-allylstannylation product **66e** (Entry 5). 3) Stoichiometric amount of $ZrCl_4$ was needed for obtaining good yields in the reaction of the aliphatic acetylene (Entries 6 and 7). Interestingly, the *cis*-addition products were afforded predominantly in the reaction of the aliphatic acetylenes in toluene at 0 °C, in contrast to the reactions of aromatic acetylenes (Entries 7,9,11, and 12). Particularly, the reaction of cyclopentylacetylene gave the *cis*-adduct **67i** as a sole product. Without solvents, however, allyltributylstannane added to the acetylenic bonds of **64f** and **64g** with *trans*-fashion (Entries 8 and 10). Consequently, stereodivergent synthesis of (*E*)- and (*Z*)-alkenylstannanes can be carried out in the reactions of aliphatic acetylenes by changing the solvent system. 4) The reaction of 3,3-dimethyl-1-butyne **64j** did not proceed at all, perhaps owing to the steric factor of *t*-Bu group (Entry 13). 5) Stereoselective *cis*-allylstannylation was observed in the reaction of acetylene **64k** (Entry 14). The chemical yield was enhanced to 55% by the addition of 1 equiv of 1,5-cyclooctadiene (Entry 15). 6) Crotyl- and methallylstannane (**65b** and **65c**) also underwent the *trans* addition to phenylacetylene **64a** to give the corresponding alkenylstannanes (**66l** and **66m**, respectively) in reasonable yields (Entries 16 and 17). In the case of crotylstannane, only the γ-adduct was isolated.

The addition order of reagents and substrates is essential for obtaining the allylstannated products in the present reaction. Treatment of alkynes with a suspension of $ZrCl_4$ in toluene, followed by addition of allyltributylstannane to the reaction mixture, gave allylstannylation products. However, the reverse mode of the addition of the reagents and substrates gave no products; the addition of allylstannane to $ZrCl_4$ in toluene and subsequent addition of alkynes did not afford the adducts. Probably the treatment of allyltributylstannane with $ZrCl_4$ induced transmetalation to produce an allylzirconium species, which would not undergo the addition to alkynes under the reaction conditions. The interaction

Table 13. $ZrCl_4$-Catalyzed Allylstannylation of Unactivated Alkynes[a)]

Entry	$ZrCl_4$	Temp			Allyltin		Product	Yield[b)]	Ratio[c)]
	equiv	°C	Alkyne	R^1	R^2	R^3	**66 67**	%	**66 : 67**
1	0.2	−78 to 0	**64a**	Ph	H	H	**66a**	83	100 : 0
2	0.2	−78 to 0	**64b**	*p*-$CH_3C_6H_4$	H	H	**66b**	84	100 : 0
3	0.2	−78 to 0	**64c**	*p*-ClC_6H_4	H	H	**66c**	65	100 : 0
4	0.2	−78 to 0	**64d**	*p*-$CH_3OC_6H_4$	H	H	**66d**	79	100 : 0
5	0.2	−78 to 0	**64e**	1-Cyclohexenyl	H	H	**66e**	99	100 : 0
6	0.3	−78 to 0	**64f**	C_6H_{13}	H	H	**66f**	0	—
7	1.0	0	**64f**	C_6H_{13}	H	H	**66f+67f**	68	17 : 83
8[d)]	1.0	0	**64f**	C_6H_{13}	H	H	**66f**	51	100 : 0
9	1.0	0	**64g**	$C_{10}H_{21}$	H	H	**66g+67g**	70	27 : 73
10[d,e)]	1.0	0	**64g**	$C_{10}H_{21}$	H	H	**66g**	32	100 : 0
11	1.0	0	**64h**	$PhCH_2$	H	H	**66h+67h**	47	14 : 86
12	1.0	0	**64i**	Cyclopentyl	H	H	**67i**	30	0 : 100
13	1.0	0	**64j**	*t*-Bu	H	H	**66j**	0	—
14[f,g)]	1.0	0	**64k**	H	H	H	**67k**	32	0 : 100
15[f,g,h)]	1.0	0	**64k**	H	H	H	**67k**	55	0 : 100
16	0.2	−78 to 0	**64a**	Ph	Me	H	**66l**	56	100 : 0
17	0.2	−78 to 0	**64a**	Ph	H	Me	**66m**	55	100 : 0

a) Reactions were carried out with 2 equiv of allylstannane. b) Isolated yield. c) Ratio was determined by ^1H NMR. d) Reaction was carried out without solvent. e) Destannylated product was obtained in 10% yield in addition to 32% yield of alkenylstannane **66g**. f) Excess amounts of acetylene **64k** was used. g) Isolated yield based on allylstannane. h) 1,5-Cyclooctadiene (1 equiv) was added.



Scheme 11.

Table 14. $EtAlCl_2$-Catalyzed Allylstannylation of Unactivated Alkynes[a)]

Entry	Alkyne		Product	Yield[b)]	Ratio[c)]
	64	R^1	**66 67**	%	**66 : 67**
1	**64a**	Ph	**66a**	83	100 : 0
2	**64b**	*p*-$CH_3C_6H_4$	**66b**	98	100 : 0
3	**64d**	*p*-$CH_3OC_6H_4$	**66d**	62	100 : 0
4	**64e**	1-Cyclohexenyl	**66e**	54	100 : 0
5	**64f**	C_6H_{13}	**66f+67f**	50	86 : 14
6	**64g**	$C_{10}H_{21}$	**66g+67g**	51	82 : 18
7[d)]	**64k**	H	**66k**	0	—

a) Reactions were carried out with 2 equiv of allylstannane in the presence of 0.2 equiv of $EtAlCl_2$. b) Isolated yield. c) Ratio was determined by ^1H NMR. d) Excess amounts of acetylene **64k** was used.

between Lewis acidic $ZrCl_4$ and a triple bond is a key for this addition reaction; actually the color of the reaction mixture changed to orange when alkynes were added to a suspension of $ZrCl_4$ in toluene.

Consequently, a plausible mechanism for the $ZrCl_4$-catalyzed *trans*-allylstannylation is shown in Scheme 11. The coordination of alkynes to $ZrCl_4$ would produce the π-complex **68**, which would be stabilized by the π-system of R^1 group in the case of aromatic acetylenes to form the zwitterionic intermediate **69**. Allyltributylstannane would attack the electron-deficient carbon from the side opposite to the Lewis acid to produce the adduct **70** stereoselectively, which would undergo elimination of Bu_3Sn^+ and form the corresponding zirconium ate complex. Transmetalation of zirconium halide by the tributylstannyl group would afford the *trans*-allylstannated product **66** and regenerate the catalyst. On the other hand, aliphatic alkynes might produce the η^2-complex **71** because the resonance stabilization of vinyl cation by a π-system, as observed in the case of aromatic acetylenes, is not expected. Allyltributylstannane would react with zirconium (ZrL_n) of **71**, instead of reacting with the unsaturated bond, to form allyl zirconium **72**, which would undergo the regioselective intramolecular allylation to give the vinylzirconium derivative **73**. Transmetalation of zirconium halide by the tributylstannyl group would afford the *cis*-allylstannated product **67**.

We next examined the $EtAlCl_2$-catalyzed allylstannylation to various alkynes; the results are summarized in Table 14. Addition of allyltributylstannane to arylsubstituted alkynes (**64a**, **64b**, and **64d**) and the conjugated enyne **64e** in the presence of 0.2 equiv of $EtAlCl_2$ proceeded smoothly, giving regio- and stereoselectively the corresponding allylstannated products (**66a**, **66b**, **66d**, and **66e**, respectively) in good to excellent yields (Entries 1, 2, 3, and 4). In contrast to the $ZrCl_4$-catalyzed reaction, allylstannane reacted with aliphatic acetylenes even in the presence of catalytic amounts of $EtAlCl_2$ in reasonable yields and the *trans*-allylstannated products were obtained predominantly (Entries 5 and 6). On the other hand, no product was obtained in the reaction using acetylene **64k** (Entry 7). The outline of the proposed reaction mechanism for the $EtAlCl_2$-catalyzed *trans*-allylstannylation of alkynes is the same as that for the $ZrCl_4$-catalyzed *trans*-allylstannylation of aromatic alkynes.

3. Conclusion

We are now in a position to effectively prepare (regio- and stereoselectively in good to excellent yields) various types of vinylsilanes and vinylstannanes via the Lewis acid-catalyzed hydrosilylation, hydrostannation, carbosilylation, and carbostannation of unactivated alkynes. The essential mechanism behind the Lewis acid-catalyzed stereoselective *trans*-addition of the nucleophiles to alkynes is simple and straightforward: π-basic alkynes coordinate to Lewis acids, making an electron-deficient unsaturated carbon center, and nucleophiles attack that carbon from the phase opposite to the Lewis acid coordination side. The resulting vinylmetals are not easily available via any previously known methodologies and may be useful as building blocks in organic chemistry.

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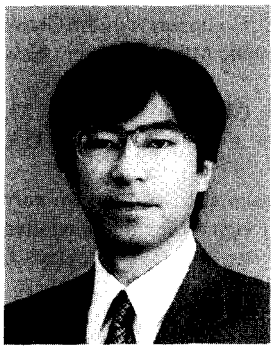

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