

Lewis Acid Catalyzed Stereoselective Carbosilylation. Intramolecular *trans*-Vinylsilylation and *trans*-Arylsilylation of Unactivated Alkynes

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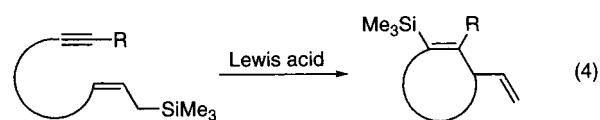
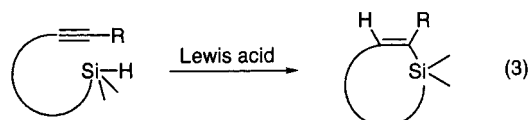
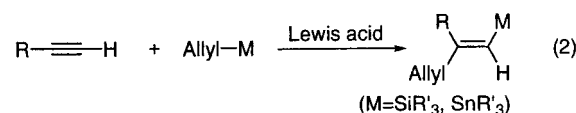
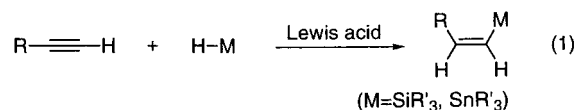
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Abstract: Intramolecular *trans*-vinylsilylation using silicon-tethered alkynylvinylsilanes **3b–c** was catalyzed dramatically by Lewis acids such as EtAlCl₂ to give the corresponding six-membered silacycles **4b–c** in high yields. The reaction proceeded *via* an *exo*-mode cyclization. In addition to the vinylsilylation, the intramolecular *trans*-arylsilylations using carbon-tethered alkynylarylsilanes **8a–b** were also catalyzed by Lewis acids such as HfCl₄ to give six- and seven-membered cyclic (*E*)-vinylsilanes **9a–b**, respectively. The cyclization of silicon-tethered substrates **13a–d** afforded five- and six-membered silacycle products **14a–d** in low to high yields. All arylsilylation reactions proceeded *via* an *exo*-mode fashion exclusively.

Introduction

The hydro- and carbometalation of a carbon–carbon multiple bond is one of the most fundamental and straightforward methodologies for the preparation of new organometallics.¹ Particularly, the hydro- and carbometalation of unactivated alkynes is a practical method for the preparation of vinylmetals, which have great versatility as building blocks in organic synthesis. Although hydroboration and hydroalumination proceed without any activators, the other hydrometalations such as hydrosilylation and hydrostannation are promoted by transition metal catalysts or by radical initiators. Only a little attention was paid to the utilization of a Lewis acid as an activator. 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. However, the allylmetalation of simple unactivated alkynes is not easy, and only a limited number of allylmetals can serve for this purpose. Here also, no attention was paid to the use of a Lewis acid as an activator for the allylmetalation of unactivated alkynes. We previously reported that Lewis acids such as AlCl₃, EtAlCl₂, ZrCl₄, HfCl₄, and B(C₆F₅)₃ catalyzed efficiently the *intermolecular* hydrosilylation,² hydrostannation,³ allylsilylation,⁴ and allylstannation⁵ of unactivated alkynes to give the corresponding *trans*-hydro- and allylmetalation products with very high stereoselectivities in high chemical yields (eqs 1 and 2).^{6,7} The *intramolecular*

version of the Lewis acid catalyzed hydro-⁸ and carbometalation⁹ produces the corresponding silacycles (eq 3) and carbocycles (eq 4), in which the hydro- and carbosilylation take place also in a *trans* manner.⁷



Despite the extensive investigation of the hydro- and 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

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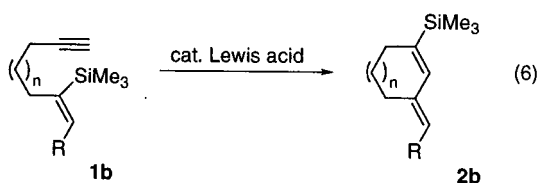
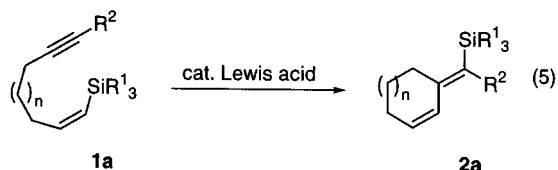
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alkynes. Although it has been known for many years that polar organometallics ($R-M$; $M = Li, Mg, Zn, \dots$) undergo intramolecular carbometalation to alkynes, the carbometalation of alkynes with organosilicon compounds is not easy due to the lack of a method for activation of stable carbon–silicon bonds.¹⁰ Concerning polar organometallics, carbometalation with allyl and alkyl reagents is more popular than that with vinyl and aryl reagents.¹¹ Recently, we communicated that the intramolecular *trans*-vinylsilylation of unactivated alkynes is catalyzed by certain Lewis acids to give the cyclic vinylsilanes in high yields (eqs 5 and 6).^{12,13} In this paper, we wish to report the Lewis acid catalyzed highly stereoselective intramolecular *trans*-arylsilylation of unactivated alkynes along with a detailed study of the intramolecular *trans*-vinylsilylation.¹⁴



Results and Discussion

1. Vinylsilylation of Alkynes. As we previously showed, the intramolecular vinylsilylation reactions using the *carbon-tethered* alkynevinylsilanes **1a,b** were catalyzed by Lewis acids such as $EtAlCl_2$ and $AlCl_3$ to afford six- or seven-membered cyclization products **2a,b** ($n = 1$ or 2) in good to high yields, respectively (eqs 5 and 6).¹² The stereostructures of the products **2** clearly showed that the vinylsilylation proceeded in a *trans*-fashion stereoselectively: the formation of the stereo and regioisomers of **2** was not observed. On the basis of these results, we examined the cyclization reactions of the *silicon-tethered* alkynevinylsilanes **3** for obtaining silacycle compounds, which have attracted interest from both pharmaceutical and synthetical

(10) For example, the mean bond dissociation energies $D(M-R)$ of representative organometallics MR_n are as follows: Si–Et, 297 ± 6 kJ/mol; Li–Et, 209 kJ/mol; Zn–Et, 145 kJ/mol; Al–Et, 242 kJ/mol. See: Becerra, R.; Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, pp 153–180. Skinner, H. A. *Adv. Organomet. Chem.* **1964**, *2*, 49–114. Aylett, B. J. *Organometallic Compounds, Vol. 1, The Main Group Elements, Part 2*; 1979.

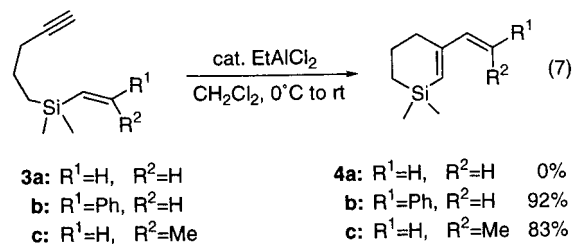
(11) To date very little is known about the intramolecular vinylmetalation and arylmetalation of unactivated alkynes. For vinylolithiation and aryllithiation, see: (a) Wu, G.; Cederbaum, F. E.; Negishi, E. *Tetrahedron Lett.* **1990**, *31*, 493–496. (b) Ovaska, T. V.; Warren, R. R.; Lewis, C. E.; Wachter-Jurcsak, N.; M.; Bailey, W. F. *J. Org. Chem.* **1994**, *59*, 5868–5870. (c) Bailey, W. F.; Wachter-Jurcsak, N. M.; Pineau, M. R.; Ovaska, T. V.; Warren, R. R.; Lewis, C. E. *J. Org. Chem.* **1996**, *61*, 8216–8228.

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(13) It is well-known that the reactivity of vinylsilanes and arylsilanes toward electrophiles is much lower than that of allylsilanes. See: (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Chemistry*; Springer-Verlag: Berlin, 1983. (c) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57–575.

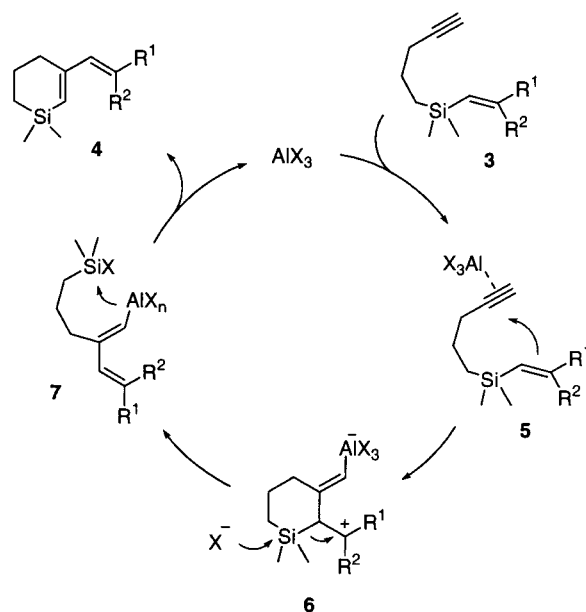
(14) During our investigation of the present work, Murai and co-workers reported one example of $PtCl_2$ -catalyzed intramolecular arylsilylation of unactivated alkynes, though both of stereoselectivity and chemical yield were low, see: Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4913–4918.

points of view (eq 7).^{15,16} While no cyclization took place in the reaction of **3a**, the cyclization reactions of **3b,c** proceeded in the presence of a catalytic amount of $EtAlCl_2$ to afford the silacycles **4b,c** in high yields, respectively, which are not easily available via the previously known methodologies.¹⁷



These results can be accounted for by the following mechanistic rationale (Scheme 1). The coordination of a Lewis acid

Scheme 1



to the triple bond of **3** would form π -complex **5**.⁷ The α -carbon of vinylsilane moiety would attack the electron deficient triple bond from the side opposite to the Lewis acid *via* an *exo*-mode fashion to produce an aluminum ate complex **6** stereoselectively. The transfer of dimethylsilyl group to the aluminate center and concomitant shift of electrons to the carbocation center would afford **4** *via* the intermediate **7** and regenerate the Lewis acid. In the reaction of **3b,c**, the developed carbocation β to the dimethylsilyl group of the intermediate **6** could be stabilized by the presence of Ph or Me group at the R^1 and R^2 position, but in the reaction of **3a**, such stabilization is not expected since both R^1 and R^2 are H. Such substituent effect in the reaction of

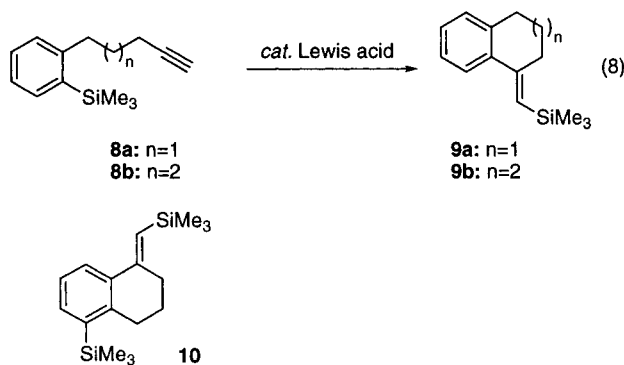
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(16) (a) Matsumoto, K.; Aoki, Y.; Oshima, K.; Utimoto, K. *Tetrahedron* **1993**, *49*, 8487–8502. (b) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1996**, *15*, 1524–1526. (c) Chauhan, B. P. S.; Tanaka, Y.; Yamashita, H.; Tanaka, M. *Chem. Commun.* **1996**, 1207. (d) Birot, M.; Pillot, J.; Dunoguès, J. *Chem. Rev.* **1995**, *95*, 1443–1477.

(17) (a) Aylett, B. J.; Sullivan, A. C. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 2, pp 45–75. (b) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2209–2230. (c) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1999**, 81–102.

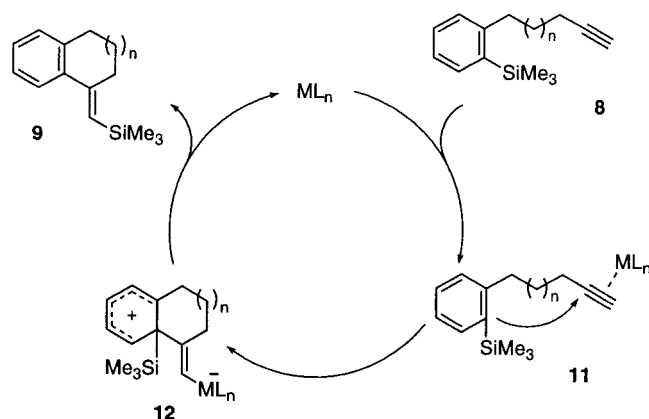
vinylsilane compounds is known,¹³ and it clearly explains why the cyclization of **3a** did not proceed at all.

2.1. Exo-Mode Arylsilylation of Alkynes (Type 1). We next turned our attention to the intramolecular arylsilylation of unactivated alkynes and found that the Lewis acid catalyzed reaction of the carbon tethered alkynylarylsilanes **8** gave cyclic (*E*)-vinylsilanes **9** in moderate to good yields (eq 8). The reaction of **8a**, having a tether chain of three methylene groups ($n = 1$), in the presence of 0.1 equiv of HfCl_4 in CH_2Cl_2 gave the *trans*-arylsilylation product **9a** regio- and stereoselectively in 48% yield accompanied with a trace amount of **10** and the desilylated starting material. We could not detect the stereo- (*cis*-addition product) and regioisomer (*endo*-cyclization product) of **9a**. Besides CH_2Cl_2 , toluene was a solvent of choice for the present arylsilylation. Optimization experiments revealed that the use of 0.2 equiv of HfCl_4 in toluene gave the best result, and **9a** was obtained in 74% yield. Other Lewis acids such as ZrCl_4 and AlCl_3 gave unsatisfactory results. The seven-membered product **9b** was obtained in 45% yield in the reaction of **8b**, having a tether chain of four methylene groups ($n = 2$), with 0.2 equiv of EtAlCl_2 in CH_2Cl_2 . The stereochemistries of the olefinic parts of **9a,b** were determined unambiguously by NOE experiments; irradiations of an alkenyl proton attached to the carbon alpha to trimethylsilyl group of **9a** or **9b** enhanced the signal of the benzene proton which was proximal to the alkenyl group (NOE: 14.7% in **9a**; 6.1% in **9b**), whereas no enhancements of any signals of methylene protons on the carbocycle were observed.¹⁸



A plausible mechanism for the Lewis acid catalyzed *trans*-arylsilylation is shown in Scheme 2. The coordination of the

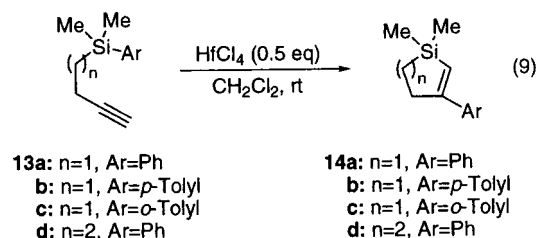
Scheme 2



(18) While the preparation of **9a** by the titanium-mediated carbonyl olefinations has been reported, the stereoselectivity was quite low (*Z/E* = 1–1.5:1), see: Petasis, N. A.; Akritopoulou, I. *Synlett* **1992**, 665–667.

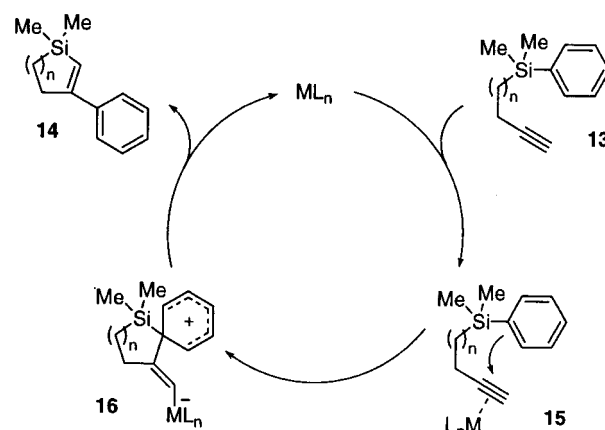
triple bond of **8** to a Lewis acid would form π -complex **11**. The carbon at the *ipso* position of arylsilane moiety would attack the electron deficient triple bond from the side opposite to the Lewis acid *via* an *exo*-fashion to produce the ate complex **12** stereoselectively.¹⁹ The transfer of trimethylsilyl group to the olefinic part would afford **9** and regenerate the Lewis acid.

2.2. Arylsilylation of Silicon-Tethered Alkynes (Type 2). The highly stereoselective *trans*-arylsilylation reactions were observed again when the cyclization reactions of differently substituted arylsilanes **13** were examined (eq 9). The corresponding five-membered silacycle product **14a** was obtained in 71% yield when the starting material **13a** was treated with 0.5 equiv of HfCl_4 . No regio- and stereoisomers of **14a** were obtained. The *p*-tolyl-substituted product **14b** was also obtained in 57% yield. Even the reaction of **13c**, bearing a bulky *o*-tolyl group as Ar, proceeded to give the corresponding product **14c** though the chemical yield was low (20% yield). While the six-membered silacycle compounds **14d** was obtained regioselectively in the reaction of **13d**, the chemical yield was low.^{20,21}



A plausible mechanism of these reactions is shown in Scheme 3. After the formation of π -complex **15** from the starting material **13** with Lewis acid, the *ipso* carbon of arylsilane of **15** would attack the internal acetylenic carbon to give an ate complex **16**.¹⁹ The cleavage of the carbon–silicon bond followed by the cyclization through the transfer of silyl group to olefinic carbon would give the cyclization product **14**. The decreased yield in the reaction of **13c** would be explained by the steric interaction of bulky *o*-tolyl group and alkyne moiety in the step from **15** to **16**.

Scheme 3



Conclusion

We are now in a position to efficiently prepare various types of silylated carbocycles and silacycles regio- and stereoselec-

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(20) The starting materials decomposed easily under the reaction conditions, and the products other than **14c,d** were not obtained.

(21) The palladium-catalyzed cycloaddition of silacyclobutane with acetylene was carried out to give **14d** in low yield, see: Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891–894.

tively *via* the Lewis acid catalyzed intramolecular vinylsilylation and arylsilylation of unactivated alkynes. The present reaction provides an easy access to a variety of five-, six-, and seven-membered cyclic compounds, which are not easily available *via* the previously known methodologies and may be useful as building blocks in organic synthesis. As observed in the Lewis acid catalyzed hydro- and allylsilylation, here also the coordination of Lewis acids to alkynes followed by the nucleophilic attack of the alkenyl and aryl groups to the electron-deficient alkynyl carbon (or vinyl cation) is a key for the present unprecedented transformation. Further studies to elucidate the precise mechanism of this reaction and to extend the scope of synthetic utility are in progress in our laboratory.

Experimental Section

Lewis Acid Catalyzed Intramolecular Vinylsilylation. The preparation of **4b** is representative. To a solution of **3b** (0.5 mmol) in CH₂Cl₂ (5 mL) was added EtAlCl₂ (0.1 mmol, 1 M in hexane) at 0 °C. The mixture was allowed to warm to room temperature gradually. After the mixture was stirred for 3 h, excess amounts of diethylamine (0.5 mL) and a saturated aqueous solution of NaHCO₃ were added

successively at 0 °C. The mixture was extracted with pentane three times. The combined extracts were dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by column chromatography (basic silica gel, hexane eluent) to give **4b** (0.46 mmol) in 92% yield.

Lewis Acid Catalyzed Intramolecular Arylsilylation. The preparation of **9a** is representative. To a suspension of HfCl₄ (64 mg, 0.2 mmol) in toluene (6 mL) was added **8a** (0.22 mL, 1.0 mmol) at -78 °C. The reaction mixture was allowed to warm to 10 °C over a period of 1 h. After the mixture was stirred for 5 min at 10 °C, excess amounts of diethylamine (0.6 mL) and saturated aqueous solution of NaHCO₃ were added successively at 0 °C. The mixture was extracted with ether. The combined ether extracts were dried (Na₂SO₄) and evaporated to leave the crude product, which was purified by column chromatography (basic silica gel, hexane eluent) to give **9a** (0.74 mmol) in 74% yield.

Supporting Information Available: A table listing optimization study data on the reactions of **8a,b** and text and figures providing identification data for all products including copies of the NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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