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Generation of a Silylethylene−Titanium Alkoxide Complex. A Versatile Reagent for Silylethylation and Silylethylidenation of Unsaturated Compounds

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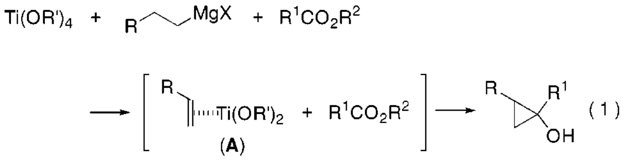
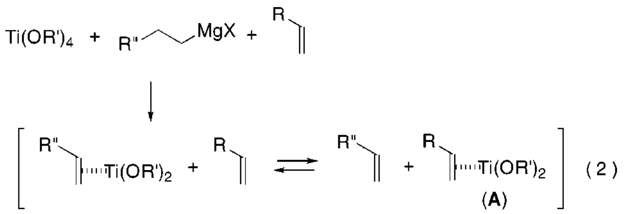
(Trimethylsilyl)ethylene−titanium alkoxide complex (**1**) was generated from trimethyl(vinyl)silane, Ti(O-*i*-Pr)$_4$, and *i*-PrMgCl as a preformed alkene−titanium complex and reacted with several unsaturated compounds such as aldehyde, imine, other vinylsilane, and acetylene to give the corresponding coupling products **4a**−**f**, **6**, **8**, and **10a**−**d** in a regioselective manner. Both of the two carbon−titanium bonds of the complex **1** reacted successively with esters to afford silylcyclopropanols **11a**−**j**, **13**, and **15**, some synthetic applications of which were illustrated in the preparation of β-silyl ketones **16** and cyclopropenes **17**. Asymmetric addition of **1** to a chiral acyloxazolidinone **19** gave optically active cyclopropanol (+)-**11a** of 50% ee.

Introduction

Alkene−titanium alkoxide complex **A**, originally reported by Kulinkovich et al. in 1989,[1−3] has attracted much attention recently, because it has realized a unique preparation of cyclopropanols from carboxylic esters as shown in eq 1.[1,4−6] While complex **A** was initially generated from a titanium alkoxide and 2 equiv of an appropriate Grignard reagent according to eq 1,[1a,b,4a−c] later, it was generated via the olefin exchange reaction as shown in eq 2,[1c,4d,6] in which two alkene−titanium complexes, **A** and another one derived from the Grignard reagent, are basically under equilibrium. It should be noted that, in both methods, complex **A** has been always generated as a transient species in the presence of the acceptor (esters). However, the coupling reaction with other substrates that are not compatible with the conditions for the concomitant generation of **A** should require the preformed complex prior to their reaction.





This time, we found that silylethylene complex **1** can be generated as a preformed species, satisfying the above argument, to enable reactions with a variety of coupling partners other than esters (eq 3 in Scheme 1).[7] In addition, this complex underwent the aforementioned Kulinkovich cyclopropanol formation as efficiently as other nonsilylated alkene−titanium alkoxide complexes

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(1) (a) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A.; Pritytskaya, T. S. *Zh. Org. Khim.* **1989**, *25*, 2244−2245. (b) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevski, D. A. *Synthesis* **1991**, 234. (c) Kulinkovich, O. G.; Savchenko, A. I.; Sviridov, S. V.; Vasilevskii, D. A. *Mendeleev Commun.* **1993**, 230−231.

(2) Sato, F.; Urabe, H.; Okamoto, S. *Pure Appl. Chem.* **1999**, *71*, 1511−1519. Sato, F.; Urabe, H.; Okamoto, S. *Synlett* **2000**, 753−775.

(3) For review on relevant Group 4 metalocene−olefin complexes, see: Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723−742. Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058. Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 1163−1184. Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696−1701. Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124−130. Maier, M. In *Organic Synthesis Highlights II*; Waldmann, H., Ed.; VCH: Weinheim, 1995; pp 99−113. Ohff, A.; Pulst, S.; Lefeber, C.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. *Synlett* **1996**, 111−118. Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755−769. Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119−129.

(4) For earlier reports, see: (a) de Meijere, A.; Kozhushkov, S. I.; Spaeth, T.; Zefirov, N. S. *J. Org. Chem.* **1993**, *58*, 502−505. (b) Corey, E. J.; Rao, A.; Noe, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 9345−9346. (c) Lee, J.; Kim, H.; Cha, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 9919−9920. (d) Lee, J.; Kang, C. H.; Kim, H.; Cha, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 291−292.

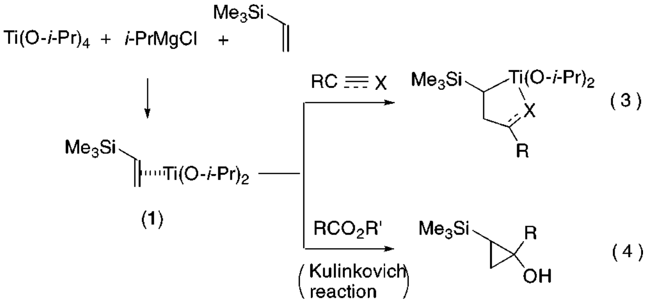
(5) For latest reports, see: (a) Epstein, O. L., Kulinkovich, O. G. *Tetrahedron Lett.* **1998**, *39*, 1823−1826. (b) Williams, C. M.; Chaplinski, V.; Schreiner, P. R.; de Meijere, A. *Tetrahedron Lett.* **1998**, *39*, 7695−7698. (c) Lee, K. L.; Kim, S.-I.; Cha, J. K. *J. Org. Chem.* **1998**, *63*, 9135−9138. (d) Sung, M. J.; Lee, C.-W.; Cha, J. K. *Synlett* **1999**, 561−562. (e) Epstein, O. L.; Savchenko, A. I.; Kulinkovich, O. G. *Tetrahedron Lett.* **1999**, *40*, 5935−5938. (f) Chevtchouk, T. A.; Isakov, V. E.; Kulinkovich, O. G. *Tetrahedron* **1999**, *55*, 13205−13210. (g) Park, S.-B.; Cha, J. K. *Org. Lett.* **2000**, *2*, 147−149. (h) Cho, S. Y.; Cha, J. K. *Org. Lett.* **2000**, *2*, 1337−1339.

(6) For the contribution from our group, see: (a) Kasatkin, A.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 6079−6082. (b) Kasatkin, A.; Kobayashi, K.; Okamoto, S.; Sato, F. *Tetrahedron Lett.* **1996**, *37*, 1849−1852. (c) Okamoto, S.; Iwakubo, M.; Kobayashi, K.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 6984−6990. (d) Hikichi, S.; Hareau, G. P−J.; Sato, F. *Tetrahedron Lett.* **1997**, *38*, 8299−8302. (e) Mizojiri, R.; Urabe, H.; Sato, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2666−2669; *Angew. Chem.* **1998**, *110*, 2811−2814. (f) Mizojiri, R.; Urabe, H.; Sato, F. *Tetrahedron Lett.* **1999**, *40*, 2557−2560.

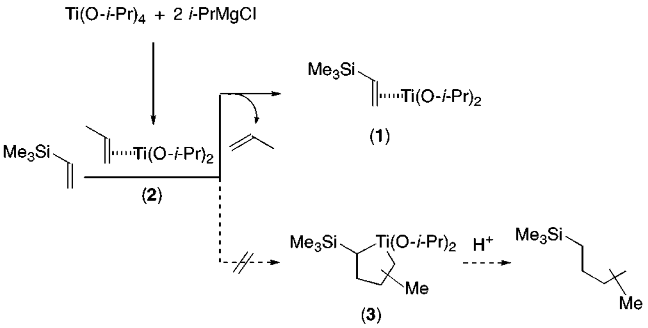
(7) Although the reactivity of various alkene complexes of Group 4 metals has been investigated, that of silylalkene complexes has not been studied (see ref 3).

10.1021/jo000925x CCC: $19.00

Scheme 1. Generation and Reactions of Silylethylene−Titanium Alkoxide Complex



Scheme 2. Generation of Silylethylene−Titanium Alkoxide Complex

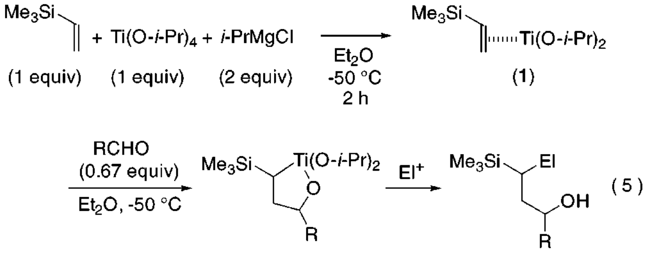


to give silylcyclopropanols, which are otherwise tedious to prepare, in good yields (eq 4 in Scheme 1).[8] From the synthetic point of view, complex **1** should become a convenient reagent to impart a silylated moiety to organic molecules, based on the fact that organosilicon compounds are versatile intermediates in organic synthesis.[9] Herein, we disclose our findings on the generation of the silylethylene−titanium alkoxide complex **1** and its behavior toward unsaturated compounds that has not been previously reported.

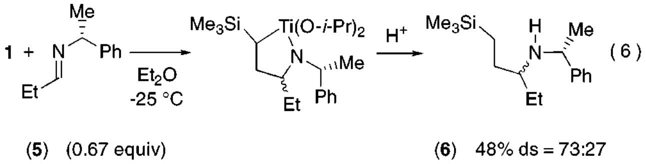
Results and Discussion

(Trimethylsilyl)ethylene−titanium alkoxide complex **1** can be readily generated via the ligand exchange reaction between the added vinylsilane and (η^2-propene)Ti(O-*i*-Pr)$_2$ (**2**) that is generated from Ti(O-*i*-Pr)$_4$ and *i*-PrMgCl[2] (Scheme 2). All steps are carried out in situ and in one pot. Thus, in practice, *i*-PrMgCl (2.0 equiv) was added to a mixture of vinylsilane (1.0 equiv) and Ti(O-*i*-Pr)$_4$ (1.0 equiv) in ether at −78 °C, and the mixture was stirred at −50 °C for 2 h to give **1** ready for a subsequent reaction. Two points are noteworthy in this process. (i) This method enables the clean generation of olefin complex **1** *as a preformed species before the subsequent reaction*; that is, the equilibration exclusively shifted from **2** to **1**.[10] (ii) The titanacycle **3**, which may act as an equivalent of the olefin complex **1** with the dissociation of the propene unit, was not formed, as evidenced by the detection of only a negligible amount of trimethyl(pentyl)silanes upon hydrolysis of the reaction mixture.

The preformed complex **1** reacted with cyclohexanecarbaldehyde to give γ-silyl alcohol **4b** in good yield (eq 5).[11,12] Propylation of the aldehyde with remaining *i*-PrMgCl and/or **2**[13] was not observed at all, confirming the complete exchange of the ligating propene of **2** with the added vinylsilane to give cleanly **1**. As far as the regioselectivity is concerned, the γ-silyl alcohol was exclusively produced with >99% selectivity. The reaction with other aldehydes gave the corresponding alcohols **4a**−**f** in a similar manner as shown in eq 5. The presence of the intermediate oxatitanacycles was verified by deuteriolysis and iodinolysis (to give **4c** and **4d**), which, at the same time, demonstrated the successive introduction of two different electrophiles to **1**. Although chiral imine **5** shown in eq 6 seemed to be less reactive than aldehydes and required a higher reaction temperature, it behaved like an aldehyde to afford γ-silylamine **6**. The coupling reaction again proceeded with virtually complete regioselection and with an appreciable diastereoselectivity of around 3:1.



R =	El =		
C$_7$H$_{15}$	H	(**4a**)	63%
c-C$_6$H$_{11}$	H	(**4b**)	87%
"	D	(**4c**)	85% (97%d)ds = 77:23
"	I	(**4d**)	87% ds = 70:30
t-Bu	H	(**4e**)	66%
Ph	H	(**4f**)	34%



Treatment of complex **1** with a different vinylsilane **7** gave 1,4-disilylbutane **8** as the cross-coupling product after hydrolysis (eq 7). Neither the homo-coupling products nor the regioisomers were detected in this reaction. This result illustrates a successful example of *cross*-coupling reaction of two olefins mediated by the titanium alkoxide species, even though the attempted coupling of

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[8] This part has appeared in a preliminary form. See ref 6f.

[9] (a) Weber, W. P. In *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (b) Colvin, E. W. In *Silicon in Organic Synthesis*; Butterworth: London, 1981. (c) Fleming, I.; Dunoguès, J.; Smithers, R. In *Organic Reactions*; Kende, A. S., Ed.; Wiley: New York, 1989; Vol. 37, pp 57−575. (d) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063-2192.

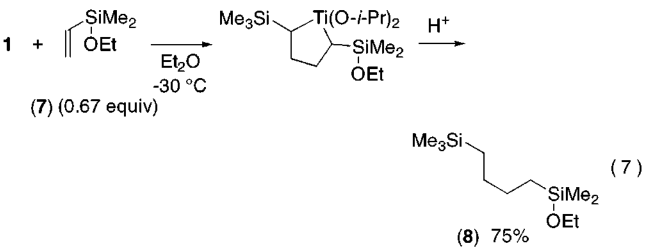
[10] To investigate the coupling reaction of **1** with aldehydes or imines (vide infra), the generation of **1** as a preformed species is critical; otherwise, the added aldehyde or imine is consumed by the remaining *i*-PrMgCl or **2**.

[11] The same reaction, silylethylation of aldehydes, was previously carried out with Me$_3$SiCH$_2$CH$_2$Li or -MgBr generated via unstable Me$_3$SiCH$_2$CH$_2$Br prepared from vinylsilane and HBr. Wilson, S. R.; Shedrinsky, A. *J. Org. Chem.* **1982**, *47*, 1983−1984.

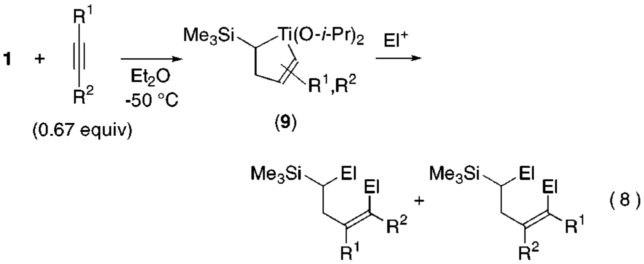
[12] Addition of other types of nonsilylated alkene-Group 4 metal complexes to aldehydes, ketones, and imines is known. Cohen S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006−1014. Mashima, K.; Haraguchi, H.; Ohyoshi, A.; Sakai, N.; Takaya, H. *Organometallics* **1991**, *10*, 2731−2736. Takahashi, T.; Suzuki, N.; Hasegawa, M.; Nitto, Y.; Aoyagi, K.; Saburi, M. *Chem. Lett.* **1992**, 331−334. Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771−1773. Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630−8641.

[13] For control, complex **2** generated from Ti(O-*i*-Pr)$_4$ and *i*-PrMgCl (−50 °C, 2 h) (ref 2) undergoes the smooth coupling reaction with aldehyde to give propyl carbinol.

1 with other terminal alkenes such as styrene, ethyl acrylate, or ethyl vinyl ether only resulted in the formation of a product mixture.

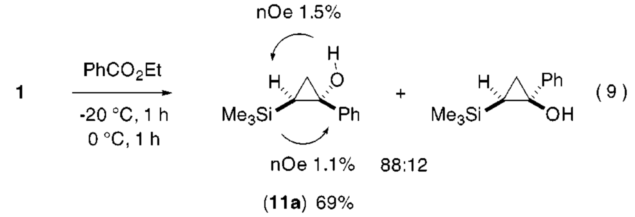


The coupling of **1** with 4-octyne proceeded also in a highly regioselective manner to give stereodefined (β-silylethyl)alkene (**10a**), a homoallylsilane,[14] in good yield after hydrolysis as shown in eq 8.[15,16] The presence of the intermediate titanacyclopentene **9** ($R^1 = R^2 =$ Pr) was verified by deuteriolysis that shows a high degree of deuterium incorporation. A few terminal acetylenes afforded the expected products as well, but a mixture of regioisomers with respect to the reacting acetylene was obtained. Sterically demanding Me_3Si and *t*-Bu substituents decreased the product yields and increased the proportion of the regioisomer in which they are placed at the α position of the titanacycle.



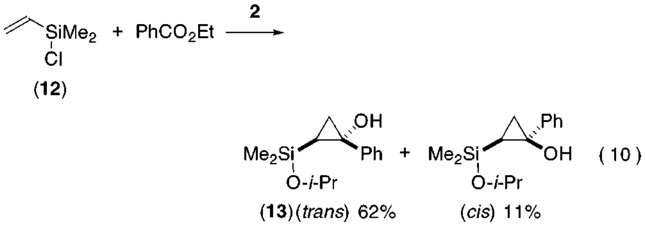
R^1 = Pr	R^2 = Pr	El = H(D)	(**10a**) 87%	-- (94%d, 94%d)
C_6H_{13}	H	H	(**10b**) 80%	76 : 24
Me_3Si	H	H	(**10c**) 44%	68 : 32
t-Bu	H	H	(**10d**) 41%	47 : 53

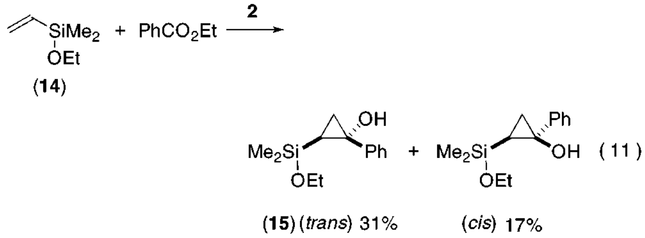
The above results are the first examples of the cross-coupling reaction of titanium alkoxide complex **1** with a variety of unsaturated compounds such as aldehyde, imine, vinlysilane, and acetylene. As one of the most unique reactions of alkene−titanium alkoxide complexes should be the formation of cyclopropanols upon reaction with esters as mentioned in the introductory part (see Scheme 1), we next turned our attention to the feasibility of this reaction starting with **1**. Gratifyingly, the silylated olefin complex **1** was found to participate in the coupling reaction with ethyl benzoate as well to afford the corresponding silylcyclopropanol **11a** (eq 9). The diastereoselection of the product favored the trans relationship between the silyl and hydroxy groups.



Although the reaction of eq 9 started with preformed olefin complex **1**, an alternative method where complex **1** was generated as a transient species and was trapped by the ester as it formed was possible.[8] In fact, this transformation could be carried out just by the addition of a mixture of an ester and vinylsilane to **2**. The latter method appears to attain somewhat higher product yields than the former one (cf. the yields of **11a** in eq 9 and entry 1 of Table 1). Table 1 displays the preparation of a variety of cyclopropanols by the latter method. In all cases, the corresponding silylated cyclopropanols were obtained without any complications. Both aromatic and aliphatic esters gave the desired products. The presence of an additional functional group in the esters such as olefin, alkyl bromide, and phenyl ether does not interfere with the reaction at all. To our surprise, methyl 6-heptenoate did undergo the intermolecular reaction to give the corresponding silylcyclopropanol without any complication, even though it was reported that this unsaturated ester gave a bicyclic cyclopropanol in the intramolecular reaction promoted by an olefin−titanium alkoxide complex.[4d,6a] As far as the diastereoselectivity of the reaction is concerned, the selectivity generally falls within a good range, favoring trans relationship between the silyl and hydroxy groups in most cases where the alkyl side chain is not sterically demanding (all entries except entry 6) and, contrarily, cis for a sterically encumbered *tert*-butyl substituent (entry 6) (vide infra).

Besides trimethyl(vinyl)silane, chloro- and alkoxysilanes **12** or **14** gave the corresponding (alkoxysilyl)cyclopropanols **13** or **15**[17] as shown in eqs 10 and 11. If the chlorosilane was used, the chloride was most likely displaced by the isopropoxide anion in situ to give the observed product (eq 10).





The relative stereochemistry of a few silylcyclopropanols shown in Figure 1 has been unambiguously

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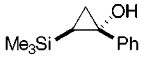
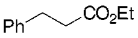
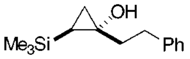
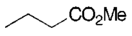
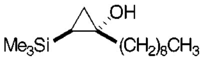
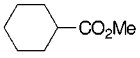
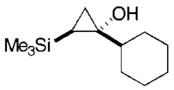
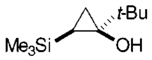
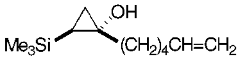
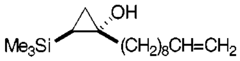
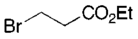
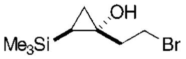
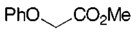
[14] For synthetic utility of homoallylsilanes, see: (a) ref 9a, p 178. (b) Sarkar, T. K.; Ghorai, B. K.; Das, S. K.; Gangopadhyay, P.; Rao, P. S. V. S. *Tetrahedron Lett.* **1996**, *37*, 6607−6610. For the basis of the reactivity of homoallylsilanes, see: (c) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677−2689.

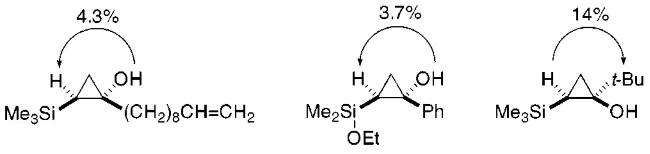
[15] The unsuccessful coupling of nonsilylated alkene complex **2** with acetylenes has been reported. Harada, K.; Urabe, H.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 3203−3206.

[16] For the coupling of an acetylene−titanium alkoxide complex with vinylsilane, that is, a reversal combination of eq 8, see: Urabe, H. *J. Synth. Org. Chem. Jpn.* **1999**, *57*, 492−502. Alternatively, that a mixture of an internal alkyne and vinylsilane was treated with Cp_2ZrBu_2 to give a coupling product was reported. Takahashi, T.; Xi, Z.; Rousset, C. J.; Suzuki, N. *Chem. Lett.* **1993**, 1001−1004.

Table 1. Synthesis of Silylcyclopropanols via Titanium(II)-Mediated Coupling of Trimethyl(vinyl)silane and Esters[a]

Entry	Ester	Major isomer of the product		*Trans*/*cis* ratio of crude product[b]	Isolated yield of major isomer (%)
1	$PhCO_2Et$		(**11a**)	93 : 7	88
2			(**11b**)	81 : 19	76
3			(**11c**)	87 : 13	80
4	$CH_3(CH_2)_8CO_2Me$		(**11d**)	88 : 12	74
5			(**11e**)	81 : 19	62
6	*t*-$BuCO_2Me$		(**11f**)	7 : 93	82
7	$CH_2{=}CH(CH_2)_4CO_2Me$		(**11g**)	88 : 12	62
8	$CH_2{=}CH(CH_2)_8CO_2Me$		(**11h**)	87 : 13	81
9			(**11i**)	77 : 23	42
10			(**11j**)	88 : 12	55

[a] See text and Experimental Section. [b] Determined by ^1H NMR spectroscopy. Trans/cis refers to the relationship between the silyl and hydroxy groups.



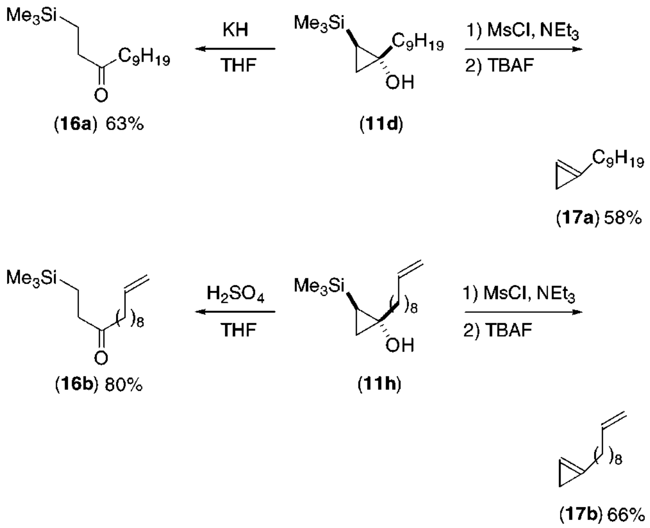
(**11h**) (**15**) (**11f**)

Figure 1. Values in % refer NOE enhancements.

determined by measurements of the nuclear Overhauser effects in the ^1H NMR spectra. As the major isomers **11b**–**e**,**g**,**i**–**j** and **13** (Table 1 and eq 10) as well as **11a**,**h** and **15** (eq 9 and Figure 1) of the established structures always behaved as the more polar component upon silica gel chromatography (TLC or preparative) than the minor isomers (as readily expected based on the degree of steric shielding of the hydroxy group), the stereochemical assignments for the major and minor isomers of the former products were made as shown in Table 1 by analogy. This fact also indicates that the stereoisomers were successfully separated by flash chromatography on silica gel to yield pure fractions (of the major isomers).

Cyclopropanols and their derivatives are useful intermediates in organic synthesis.[18] To disclose the synthetic application of silylated cyclopropanols,[19] their transformations are exemplified in Scheme 3. The treatment of silylcyclopropanols **11d** and **11h** with potassium hydride or sulfuric acid effected the regioselective ring-opening of cyclopropane to give the *β*-silyl ketones **16a** and **16b**.[20] The silyl group appears to control the regioselective cleavage of the carbon–carbon bond under both acidic

Scheme 3. Synthetic Application of Silylcyclopropanol



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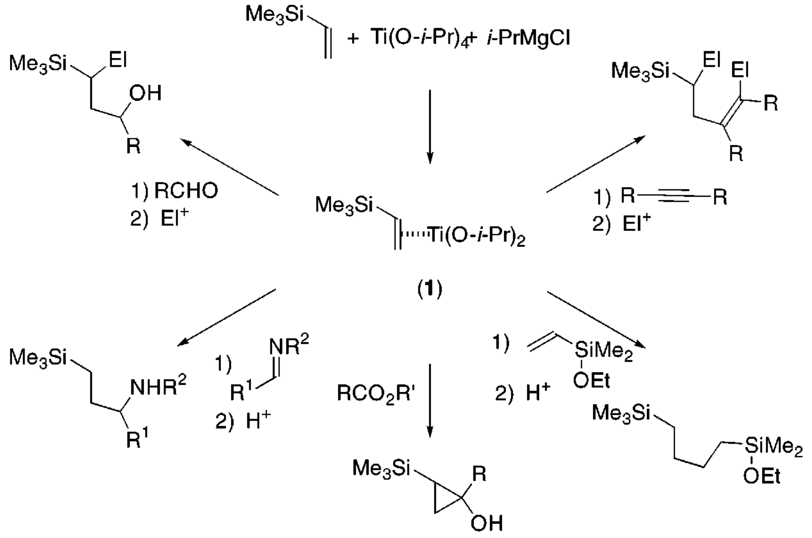
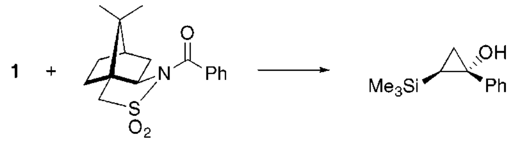
(17) An alkoxysilyl group could be stereospecifically converted to a hydroxy group. Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599–7662.

Scheme 4. Reactions of Silylethylene−Titanium Alkoxide Complex 1

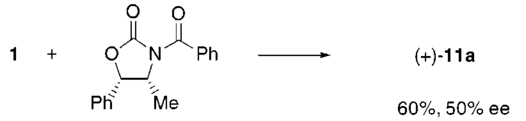


and basic reaction conditions.[14c] Another example is the preparation of cyclopropenes **17a** and **17b** via the Peterson-like olefination consisting of mesylation followed by treatment with a fluoride anion in good yield.[21]

A few carboxylic acid derivatives having a chiral auxiliary were examined in order to develop a substrate-controlled asymmetric synthesis of silylcyclopropanols.[22] Oppolzer's acylcamphorsultam **18**[23] afforded the desired cyclopropanol **11a** in good yield but, unfortunately, without any detectable chiral induction (eq 12). On the other hand, a chiral amide **19** derived from Evans's oxazolidinone[24] furnished optically active (+)-silylcyclopropanol **11a** of 50% ee (eq 13). Its absolute configuration has not yet been determined.



(**18**) (**11a**) 80%, 0% ee (12)



(**19**) 60%, 50% ee (13)

Conclusion

The silylethylene−titanium alkoxide complex undergoes carbon−carbon bond formation and subsequent functionalization with a variety of unsaturated compounds as shown in Scheme 4, which should be informative regarding the behavior of Group 4 metal−alkene complexes. Since the reagents, vinylsilane, Ti(O-*i*-Pr)$_4$, and the Grignard reagent, are inexpensive and readily available, this new silylethylation method with possible introduction of an additional electrophile could find application in organic synthesis.

Experimental Section

Generation of Preformed (Trimethylsilyl)ethylene−Titanium Complex 1. To a solution of Ti(O-*i*-Pr)$_4$ (0.45 mL, 1.5 mmol) and trimethyl(vinyl)silane (0.22 mL, 1.5 mmol) in Et$_2$O (10 mL) was added *i*-PrMgCl (2.0 mL of a 1.5 M ethereal solution, 3.0 mmol) at −78 °C to give a yellow homogeneous mixture. The solution was warmed to −50 °C over 30 min, during which period its color turned brown. After stirring for 2 h at −50 °C to −55 °C, the generation of silylethylene−titanium complex **1** was complete, and it was ready for the next reaction without isolation.

Generation of (Trimethylsilyl)ethylene−Titanium Complex 1 in Situ. Typical Procedure for the Preparation of Silylcyclopropanols in Table 1. (1*RS*,2*SR*)-1-Phenyl-2-(trimethylsilyl)cyclopropanol (11a). To a stirred solution of Ti(O-*i*-Pr)$_3$Cl (1.5 mL of a 1.0 M solution in hexane, 1.5 mmol) in Et$_2$O (10 mL) was added *i*-PrMgCl (2.2 mL of a 1.3 M solution in ether, 2.9 mmol) at −60 °C. Ten minutes later, a mixture of trimethyl(vinyl)silane (0.22 mL, 1.5 mmol) and ethyl benzoate (0.14 mL, 1.0 mmol) was added to the solution. The reaction mixture was then warmed to −25 °C over 30 min and was stirred at −25 °C to −20 °C for 1 h and finally at 0 °C for 1 h. After water (0.5 mL) in THF (2.0 mL) was added at room temperature, the heterogeneous mixture was stirred for 0.5 h. The resultant suspension was filtered through a pad of Celite, which was subsequently washed with ether. The combined filtrate and ethereal fractions were concentrated in vacuo to afford a crude oil, ^{1}H NMR analysis of which showed the diastereomeric ratio to be 93:7. Purification by column chromatography on silica gel (pretreated with 1% NEt$_3$ in

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(18) Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *250*, 121−133. Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165−198. Kuwajima, I.; Nakamura, E. *Top. Curr. Chem.* **1990**, *155*, 1−39. Kuwajima, I.; Nakamura, E. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 7, pp 441−454. Ryu, I.; Murai, S. In *Houben-Weyl Methods of Organic Chemistry*; de Meijere, A., Ed.; Thieme: Stuttgart, 1997; Vol. E 17c, pp 1985−2040.

(19) Reactivity of silylcyclopropanols has not been elucidated. Reference 18 and Paquette, L. A. *Chem. Rev.* **1986**, *86*, 733−750.

(20) For synthetic utility of β-silyl ketones, see: Tanino, K.; Sato, K.; Kuwajima, I. *Tetrahedron Lett.* **1989**, *30*, 6551−6554.

(21) For the preparation of cyclopropenes via dehalosilylation, see: Chan, T. H.; Massuda, D. *Tetrahedron Lett.* **1975**, *16*, 3383−3386. Billups, W. E.; Haley, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 5084−5085. Haley, M. M.; Biggs, B.; Looney, W. A.; Gilbertson, R. D. *Tetrahedron Lett.* **1995**, *36*, 3457−3460. Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, 1987; Vol. 2, pp 1223−1339.

(22) For preparation of optically active cyclopropanols via substrate-controlled synthesis, see ref 6e. For the reagent (titanium species)-controlled asymmetric synthesis, see ref 4b.

(23) Oppolzer, W.; Barras, J.-P. *Helv. Chim. Acta* **1987**, *70*, 1666−1675.

(24) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127−2129.

hexane and eluted with hexane/ether 8:1) afforded pure **11a** as a colorless oil (182 mg, 88%).

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Supporting Information Available: Typical procedures for the preparation of **4a**, **4d**, **6**, **8**, **10a**, **11a** (from preformed **1**), **13**, **16**, **17a**, **19**, and (+)-**11a** and the characterization data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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