

Stereoselective formation of (*Z*)- γ -substituted allylsilanes by the titanocene(II)-promoted reaction of thioacetals with trialkyl(allyl)silanes

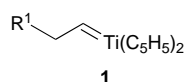
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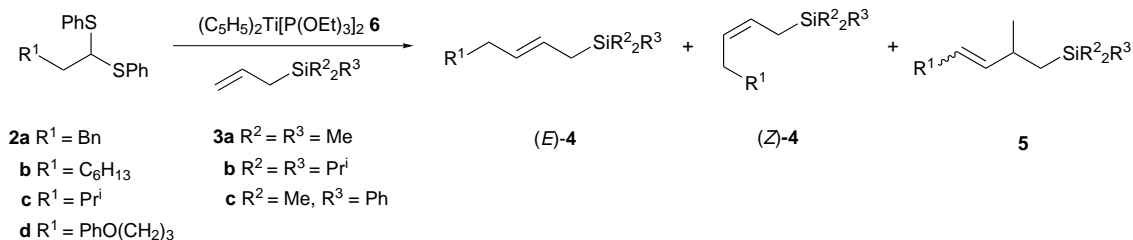
The reaction of organotitanium species prepared by the desulfurizative titanation of thioacetals with $(C_5H_5)_2Ti[P(OEt)_3]_2$ in the presence of trialkyl(allyl)silanes gives γ -substituted allylsilanes with *Z* stereoselectivity.

Since allylsilanes are useful synthetic intermediates in organic synthesis, a number of procedures for their preparation have been reported. Among them, the methods utilizing an olefination process are attractive because they enable us to prepare regioisomeric pure allylsilanes. Two types of olefination have been investigated; (i) Wittig olefination of carbonyl compounds using $Ph_3P=CHCH_2SiMe_3$,¹ and (ii) metal alkylidene catalysed olefin cross metathesis using trialkyl(allyl)silane. Crowe *et al.* showed that the cross metathesis of allyltrimethylsilane with terminal olefins using Schrock's molybdenum catalyst $PhMe_2CCH=Mo=N(2,6-Pr^i-C_6H_3)[OCMe(CF_3)_2]_2$ gave (*E*)- γ -substituted allylsilanes predominantly.² On the other hand, the stereochemistry of Grubb's ruthenium $\{Cl_2[c-C_6H_{11}]_3-P\}_2Ru=CHPh$ catalysed ring opening metathesis of strained cyclic olefins with allyltrimethylsilane is reported to be unpredictable.³

Recently we reported the titanocene(II)-promoted reactions of thioacetals with organic compounds having a multiple bond such as carbonyls,⁴ alkenes⁵ and alkynes.⁶ It was suggested that these reactions proceeded through the carbene complexes of titanium **1** formed by the desulfurization of thioacetals with low valent titanium species. Since the intermediate of olefin metathesis is assumed to be a metal alkylidene species, we expected that substituted allylsilanes would be formed by the titanocene(II)-promoted reaction of thioacetals **2** with allylsilanes **3** through the metathesis process.



As would be expected, 1-triisopropylsilyl-5-phenylpent-2-ene **4b** was produced in 50% yield along with a small amount of the homoallylsilane **5b** (7%) when the thioacetal **2a** was treated with the titanocene(II) species $(C_5H_5)_2Ti[P(OEt)_3]_2$ **6** in the presence of a two-fold excess allyltriisopropylsilane **3b** at room temperature for 48 h (Scheme 1). The starting material disappeared within a short period of time (3 h), and **4b** was obtained in a comparable yield when the reaction was carried out in refluxing THF. The yield of **4b** was increased by increasing the molar ratio of **3b** (Table 1, entry 2).[†]



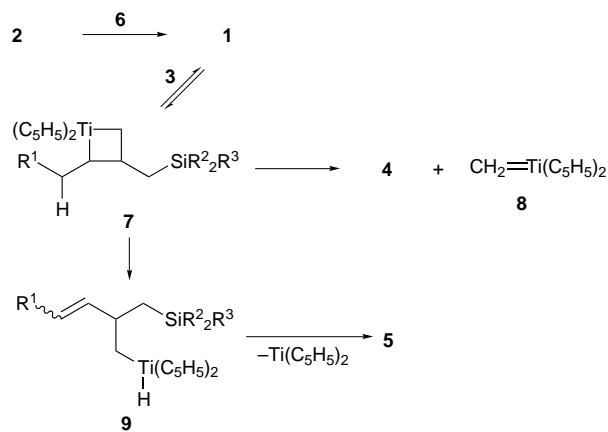
Scheme 1

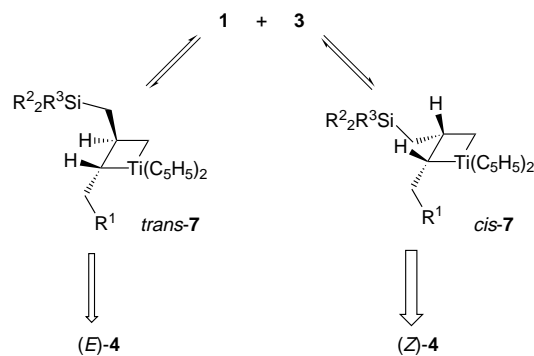
In a similar manner, the reactions of several thioacetals **2** with trialkyl(allyl)silanes **3** were performed, and the mixtures of the corresponding substituted allylsilanes **4** and the homoallylsilanes **5** were produced in a ratio of 7.1 : 1 to 1.9 : 1 depending on the alkyl substituents on silicon atom of **3** and the structure of thioacetal **2**. For example, the reaction using allyltriisopropylsilane gave substituted allylsilanes preferentially. On the other hand, in the case of the reaction using allyltrimethylsilane or allyldimethyl(phenyl)silane, a substantial amount of **5** was produced. What is striking is that

Table 1 Reaction of thioacetals **2** with trialkyl(allyl)silanes **3**^a

Entry	2	3	Products (% yield; <i>E</i> : <i>Z</i>)	
			4	5 ^b
1	2a	3a	4a (64; 13:87)	5a (13)
2	2a	3b	4b (64; 12:88)	5b (9)
3	2b	3a	4c (55; 16:84)	5c (29)
4	2b	3b	4d (85; 23:77)	5d (12)
5	2b	3c	4e (45; 14:86)	5e (23)
6	2c	3b	4f (78; 11:89)	5f (16)
7	2c	3c	4g (48; 10:90)	5g (20)
8	2d	3a	4h (44; 14:86)	5h (20)
9	2d	3b	4i (44; 14:86)	5i (18)

^a Carried out with 5 equiv. of **3**. ^b The stereochemistry was not determined.





Scheme 3

(*Z*)-allylsilanes (*Z*)-**4** were selectively produced by the present reaction regardless of the substituents on the thioacetals or allylsilanes.‡

The formation of organosilyl compounds **4** and **5** is explained by the following reaction pathway (Scheme 2), which involves the initial formation of α,β -disubstituted titanacyclobutane intermediate **7**.⁷ The metallacycle intermediate then cleaves to form a γ -substituted allylsilane **4** and titanocene methylene complex **8**. The homoallylsilane **5** is produced by elimination of the β -hydride from **7**, followed by elimination of the titanocene(II) species from the homoallyltitanium **9**. A similar process was observed in the reaction of carbene complexes with alkynes.⁶

As for the cleavage of α,β -disubstituted titanacyclobutane leading to the formation of a carbene complex and an olefin, it was shown that the configuration of the metallacycle derived from Tebbe's reagent, 3,3-dimethylcyclopropene and a norbornene diester was retained during the process.⁸ Since the *cis*- α,β -disubstituted metallacycle is much less stable than the corresponding *trans*-isomer,⁹ the preferential formation of (*Z*)-allylsilanes by the present reaction is explicable in terms of much faster cleavage of *cis*-titanacyclobutane *cis*-**7** than of *trans*-**7** (Scheme 3).

In conclusion, we have found that the reaction of titanium carbene complexes with allylsilanes affords (*Z*)-allylsilanes regio- and stereo-selectively. It should be noted that the present study first revealed the stereochemistry of the cross metathesis between an alkylidenetitanocene and an acyclic olefin. Further study on the reactions of carbene complexes formed from thioacetals with various olefins is now in progress.

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Footnotes and References

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† *Typical experimental procedure*: To a flask charged with finely powdered molecular sieves 4A (150 mg), magnesium turnings (3 mmol) and titanocene dichloride (1.5 mmol) was added THF (3 ml), triethyl phosphite (3 mmol) and trialkyl(allyl)silane (2.5 mmol) successively with stirring. After 2 h, a THF (1 ml) solution of **2** (0.5 mmol) was added and the reaction mixture was refluxed for 6 h. After being cooled to room temperature, the reaction mixture was diluted with pentane (30 ml). The insoluble materials were filtered off through Celite and the filtrate was concentrated. Purification was accomplished by preparative TLC providing a mixture of **4** and **5** as a clear, colourless oil; the excess trialkyl(allyl)silane was removed by distillation prior to purification when necessary. The yields of **4** and **5** were determined by NMR analysis.

‡ The configurations of **4a–d** were determined by comparison with authentic samples of the *E*- and *Z*-isomers. The *Z*-isomers (*Z*)-**4** were prepared by the stereoselective reduction of the corresponding prop-2-ynylsilanes with DIBAL-H reported by Rajagopalan and Zweifel,¹⁰ and *E*-isomers (*E*)-**4** were obtained by their diphenyl disulfide mediated photoisomerization¹¹ [**4a** (*E*:*Z* = 74:26), **4b** (*E*:*Z* = 83:17), **4c** (*E*:*Z* = 79:21), **4d** (*E*:*Z* = 82:18)]. The configurations of other allylsilanes were assigned on the basis of the coupling constant of their vinyl protons.

- D. Seyferth, K. R. Wursthorn and R. E. Mammarella, *J. Org. Chem.*, 1977, **42**, 3104; D. Seyferth, K. R. Wursthorn and T. F. O. Lim, *J. Organomet. Chem.*, 1979, **181**, 293; I. Fleming and I. Paterson, *Synthesis*, 1979, 446; J. G. Smith, S. E. Drozda, S. P. Petraglia, N. R. Quinn, E. M. Rice, B. S. Taylor and M. Viswanathan, *J. Org. Chem.*, 1984, **49**, 4112.
- W. E. Crowe, D. R. Goldberg and Z. J. Zhang, *Tetrahedron Lett.*, 1996, **37**, 2117. The molybdenum-catalysed cross metathesis of terminal olefins with allylstannanes has also been reported; J. Feng, M. Schuster and S. Blechert, *Synlett*, 1997, 129.
- M. F. Schneider, N. Lucas, J. Velder and S. Belchert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 257.
- Y. Horikawa, M. Watanabe, T. Fujiwara and T. Takeda, *J. Am. Chem. Soc.*, 1997, **119**, 1127.
- Y. Horikawa, T. Nomura, M. Watanabe, T. Fujiwara and T. Takeda, *J. Org. Chem.*, 1997, **62**, 3678.
- T. Takeda, H. Shimokawa, Y. Miyachi and T. Fujiwara, *Chem. Commun.*, 1997, 1055.
- The regio- and stereo-selective formation of *trans*- α,β -disubstituted titanacyclobutanes by the reaction of trimethylsilylmethylene complex $(C_5Me_5)_2Ti=CHSiMe_3$ with terminal olefins was reported; J. L. Polse, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1996, **118**, 8737.
- J. R. Stille, B. D. Santarsiero and R. H. Grubbs, *J. Org. Chem.*, 1990, **55**, 843.
- D. A. Straus and R. H. Grubbs, *J. Mol. Catal.*, 1985, **28**, 9.
- S. Rajagopalan and G. Zweifel, *Synthesis*, 1984, 113.
- A. Thalman, K. Oertle and H. Gerlach, *Org. Synth.*, 1990, **Coll. Vol. VII**, 470.

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