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Stereoselective Synthesis of (*E*) and (*Z*)-Vinylsilane by the Addition Reaction of Organometallic Reagent to Silyl-substituted Fischer-type Carbene Complex

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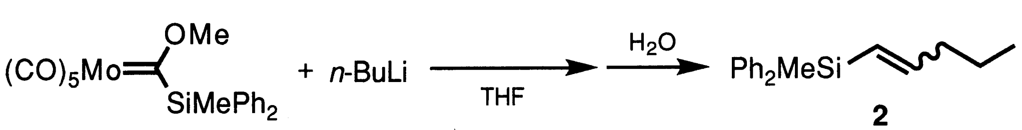
The addition reaction of organolithium or Grignard reagents to pentacarbonyl[methoxy(methyldiphenylsilyl)carbene]molybdenum is examined, and either (*E*)- or (*Z*)-vinylsilanes are obtained with high selectivities depending on the reaction conditions.

The addition reaction of organolithium or Grignard reagents to Fischer-type carbene complexes is rarely studied because deprotonation of the α-proton of carbene-carbon occurs preferentially due to its high acidity whenever such a proton is available.[1] Several examples were reported for the addition reaction of organolithium reagents to phenyl-substituted carbene complex including the original report by Fischer,[2] and in these cases, olefinic compounds were obtained by the hydrogen migration of the intermediate non-heteroatom-stabilized carbene complexes.[3] However, geometry of the olefinic products was not made obvious and its utility as a synthetic tool was not exploited. In this paper is reported a new method for the stereoselective synthesis of (*E*) and (*Z*)-vinylsilanes by utilizing the addition reaction of organolithium or Grignard reagents to a silyl-substituted carbene complex.

In the first place, pentacarbonyl[methoxy(methyldiphenylsilyl)carbene]molybdenum[4] **1** was treated with butyllithium in THF at -78 °C for a few minutes, and then pH 7 phosphate buffer was added at this temperature. Usual extractive work-up of the reaction mixture afforded vinylsilane **2**, which is supposed to be produced via a butyl(silyl)carbene complex, in 63% yield in high (*E*)-selectivity (96:4).[5] (Conditions A) On the other hand, when the reaction mixture was slowly warmed up to room temperature and stirred overnight, followed by the addition of pH 7 phosphate buffer, vinylsilane **2** was obtained in 36% yield in good (*Z*)-selectivity (92:8).[5] (Conditions B)



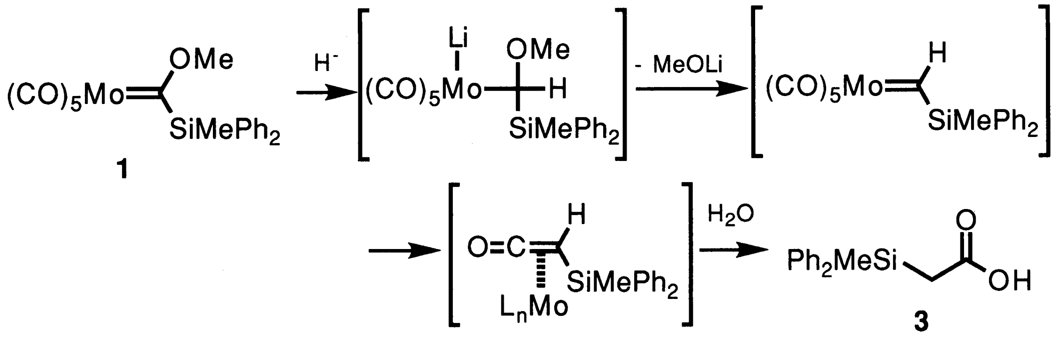
1

2

Conditions A: -78 °C, then H_2O, 63% yield, *E*:*Z*=96 : 4
Conditions B: -78 °C ~ rt, then H_2O, 36% yield, *E*:*Z*=8 : 92

Scheme 1.

Close examination of the above reactions revealed that considerable amounts of α-silyl acetic acid **3** was produced, which was presumably formed by hydride reduction of the carbene complex with butyllithium as



Scheme 2.

shown in Scheme 2. As it is supposed to be necessary to suppress this hydride reduction to improve the yield of the vinylsilane **2**, we first examined the effect of various additives on the reaction at low temperature (Conditions A) by the use of butyllithium or butylmagnesium bromide as a nucleophile.

As shown in Table 1, increase of the yield was realized by using a mixed reagent of butyllithium and cerium(III) chloride[6)] and vinylsilane **2** was obtained in 86% yield without decrease in its (*E*)-selectivity. Although somewhat lower yield, Grignard reagent also gave vinylsilane **2**, and the use of cerium(III) chloride as an additive increased the yield of the vinylsilane to 60%. In each case, the stereoselectivity of the vinylsilane was no less than 96:4 (Table 1).

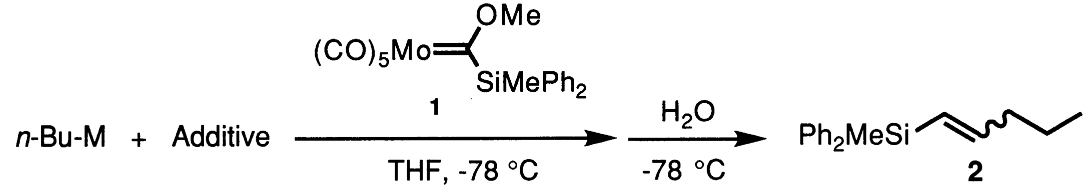


Table 1. Effect of additives (Conditions A: Low temperature procedure)

M	Additive	Yield /%	$E:Z$
Li[a)]	—	63	96 : 4
Li[a)]	HMPA[e)]	49	96 : 4
Li[b)]	$CeCl_3$	86	96 : 4
MgBr[c)]	—	40	96 : 4
MgBr[d)]	$CeCl_3$	60	97 : 3

Mole ratio: a) *n*-BuLi : **1** =1:1, b) *n*-BuLi : $CeCl_3$: **1** = 2 : 3 : 1, c) *n*-BuMgBr : **1** = 3 : 1, d) *n*-BuMgBr : $CeCl_3$: **1** = 3 : 5 : 1. e) HMPA(hexamethylphosphoric triamide) was employed in large excess.

Next, the reaction was examined to obtain (*Z*)-vinylsilane selectively (Conditions B). The use of butyllithium-cerium(III) chloride reagent increased the yield of vinylsilane **2** to 58% (*E*:*Z*=9:91). Further examination of various additives in this reaction revealed that when HMPA was added after the addition of butyllithium-cerium(III) chloride reagent at -78 °C and then the reaction mixture was warmed up to room temperature, the yield of the product increased to 79% without loss of the (*Z*)-selectivity (*E*:*Z*=7:93). When Grignard reagent was used instead of butyllithium without HMPA, vinylsilane **2** was obtained in 46% yield. However, the use of HMPA as an additive gave a complex mixture of products in this case (Table 2).

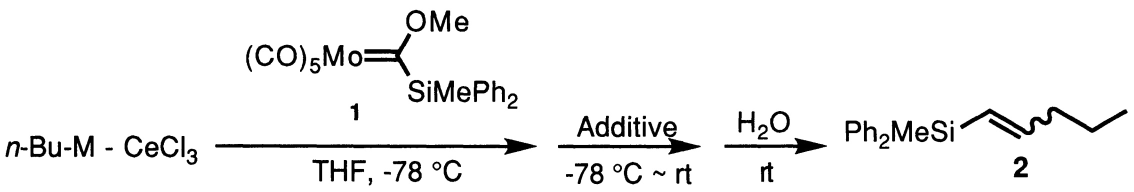


Table 2. Effect of additives (Conditions B: Room temperature procedure)

M	Additive	Yield /%	*E*:*Z*
Li[a]	—	58	9 : 91
Li[a]	HMPA[c]	79	7 : 93
MgBr[b]	—	46	8 : 92
MgBr[b]	HMPA[c]	trace	—

Mole ratio: a) *n*-BuLi : $CeCl_3$: **1** = 2 : 3 : 1, b) *n*-BuMgBr : $CeCl_3$: **1** = 3 : 5 : 1.
c) HMPA was employed in large excess.

The reactions of various organolithium and Grignard reagents were examined for the preparation of various vinylsilanes and the results are summarized in Table 3. As shown in this Table, either isomer of vinylsilanes can be prepared in good to high selectivity depending on the reaction conditions.

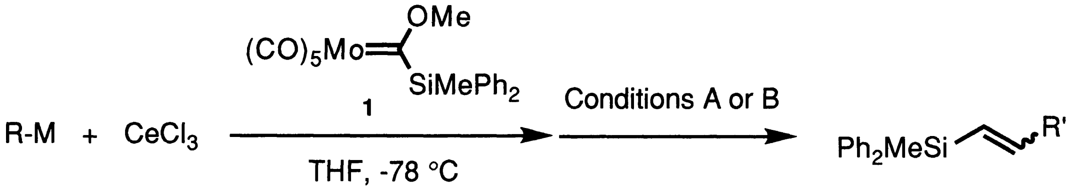
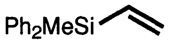
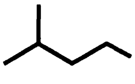
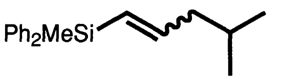
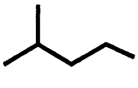
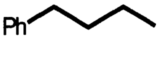
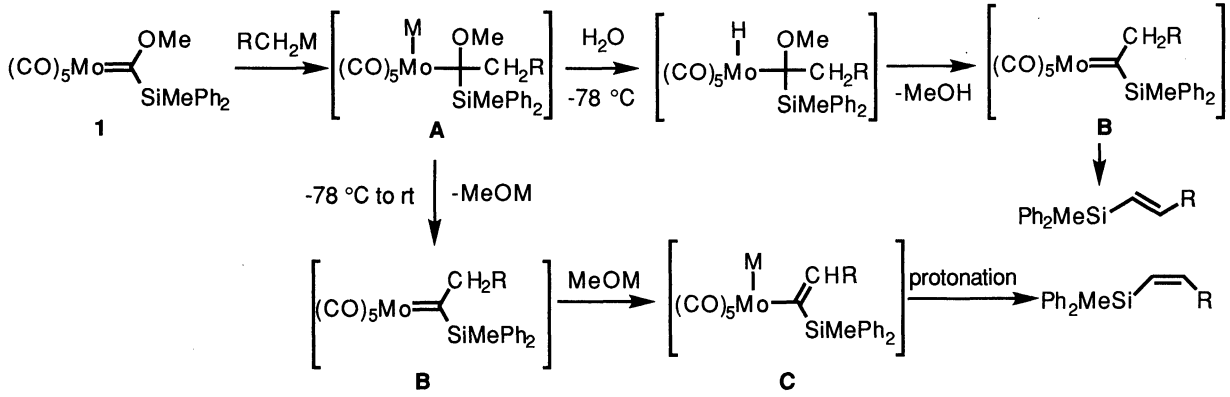


Table 3. Synthesis of (*E*)- and (*Z*)-vinylsilane

R-M	Conditions	Product	Yield /%	*E*:*Z*
MeLi[a]	A		92	—
EtLi[b]	A B		76 57	98 : 2 7 : 93
n-BuLi[b]	A B		86 79	96 : 4 7 : 93
 Li[b]	A B		94 76	96 : 4 8 : 92
 MgBr[c]	A B		85 61	97 : 3 7 : 93
 MgBr[c]	A B		85 76	97 : 3 8 : 92

Conditions A: After the addition of alkyllithiums or Grignard reagents, the reaction was quenched with pH 7 phosphate buffer at -78 °C. Conditions B: After the addition of alkyllithiums or Grignard reagents, excess amount of HMPA was added at -78 °C and the mixture was slowly warmed up to rt and stirred overnight. Then, the reaction was quenched with pH 7 phosphate buffer at rt. Mole ratio: a) MeLi : **1** = 1 : 1 ($CeCl_3$ was not used), b) RLi : $CeCl_3$: **1** = 2 : 3 : 1, c) RMgBr : $CeCl_3$: **1** = 3 : 5 : 1.

We at present suppose the pathway of this reaction as follows: Organolithium or Grignard reagents add to the carbene complex at -78 °C to give the addition product A. When the reaction is quenched at this temperature, the addition product A would give alkyl(silyl)carbene complex B by the elimination of methanol and then hydrogen migration occurs to give (*E*)-olefin selectively. On the other hand, when the reaction mixture is warmed up to room temperature, elimination of LiOMe(or BrMgOMe) occurs in the reaction medium to give alkyl(silyl)carbene complex B, and then deprotonation of this carbene complex by LiOMe(or BrMgOMe) occurs to give metalated complex C. Protonation of this complex would give (*Z*)-olefin selectively.[7]



Scheme 3.

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References

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2) E. O. Fischer and W. Held, *J. Organomet. Chem.*, **112**, C59 (1976).

3) C. P. Casey and W. R. Brunsvold, *Inorg. Chem.*, **16**, 391 (1977).

4) Silylcarbene complex **1** was prepared by the reaction of silyllithium and $Mo(CO)_6$ followed by methylation with methyl trifluoromethanesulfonate according to the procedure described in the following reference: E. O. Fischer, H. Hollfelder, P. Friedrich, F. R. Kreissl, and G. Huttner, *Chem. Ber.*, **110**, 3467 (1977). For the chemistry of silyl-substituted Fischer-type carbene complex, see: U. Schubert, *J. Organomet. Chem.*, **358**, 215 (1988).

5) The geometry of the double bond was determined by measuring NOESY spectra. Isomer ratio was determined by measuring 500 MHz ^{1}HNMR spectra.

6) Cerium(III) chloride is well known to enhance the nucleophilicity of the organolithium reagents. See for example: T. Imamoto, Y. Sugiura, and N. Takiyama, *Tetrahedron Lett.*, **25**, 4233 (1984).

7) Preferential formations of (*Z*)-enol ethers or enol esters by base-induced or thermal decomposition of the corresponding alkoxycarbene or acyloxycarbene complexes have been reported in several cases. See Ref. 3) and the following references: B. C. Söderberg and M. J. Turbeville, *Organometallics*, **10**, 3951 (1991); C. A. Challener, W. D. Wulff, B. A. Anderson, S. Chamberlin, K. L. Faron, O. K. Kim, C. K. Murray, Y-C. Xu, D. C. Yang, and S. D. Darling, *J. Am. Chem. Soc.*, **115**, 1359 (1993).

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