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[15] New compounds were fully characterized by ^1H and ^{13}C NMR spectroscopy, FT-IR spectroscopy, EI-MS, and elemental analysis or high-resolution EI-MS.

[16] Electronic factors cannot be ruled out, and their influence is currently under investigation.

[17] a) H. Hopf in *The Chemistry of the Allenes*, *Vol. 2* (Ed.: S. R. Landor), Academic Press, New York, **1982**, pp. 536–546; b) M. Christl, S. Groetsch, K. Günther, *Angew. Chem.* **2000**, *112*, 3395–3397; *Angew. Chem. Int. Ed.* **2000**, *39*, 3261–3263.

[18] X-ray crystal data of (±)-**7a** ($C_{39}H_{76}O_2Si_4$, $M_r = 689.36$): orthorhombic space group *Pbcn*, $Z = 4$, $D_c = 0.963\ \mathrm{g\,cm^{-3}}$, $a = 14.767(5)$, $b = 11.746(4)$, $c = 27.420(13)$ Å, $V = 4756(3)$ Å^3, $Mo_{K\alpha}$ radiation, 2229 independent reflections, $2 < \theta < 20°$. Single crystals were grown at 4°C from CH_2Cl_2/MeCN. The structure was calculated by direct methods (SHELXS-86) and refined by full-matrix least-squares methods (SHELXL-93). Final $R(F) = 0.0689$, $wR(F^2) = 0.1888$ for 199 variables and 2229 observed reflections with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structures reported in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157566. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[19] M. A. Hashem, P. Weyerstahl, *Tetrahedron* **1981**, *37*, 2473–2476.

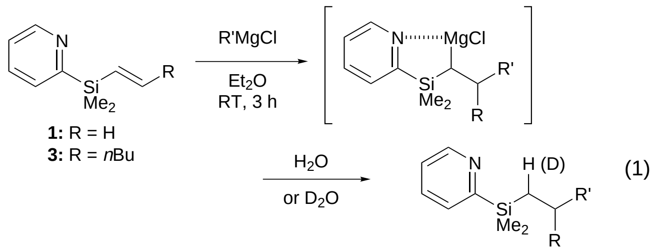
Directed Intermolecular Carbomagnesation across Vinylsilanes: 2-PyMe$_2$Si Group as a Removable Directing Group**

Kenichiro Itami, Koichi Mitsudo, and Jun-ichi Yoshida*

The addition of organolithium reagents to vinylsilanes is one of the most powerful methods for the generation of synthetically useful α-silyl carbanions.[1] Although Grignard reagents are viable alternatives for this addition reaction,[2] serious limitations are associated with the carbomagnesation methodology: 1) Activating groups on silicon (e.g., chloro, alkoxy, and amino groups) are needed for the addition (no reaction with trialkyl(vinyl)silanes); 2) substitutions at the silicon atom are often observed as unavoidable side reactions when these activating groups are used; and 3) primary alkyl Grignard reagents are not applicable in the reaction.[3, 4] These drawbacks profoundly diminish the synthetic usefulness of this otherwise attractive methodology.

Recently, we initiated a program to develop highly efficient hydro- and carbometalation reactions by utilizing the 2-pyridyldimethylsilyl (2-PyMe$_2$Si) group as a removable directing group (intramolecular ligand).[5–8] For example, highly efficient carbopalladation of vinylsilanes can be achieved with 2-PyMe$_2$Si group as a removable directing group.[6] In ongoing efforts to exploit the utility of this removable directing group in carbometalation, we investigated directed intermolecular carbomagnesation across pyridyl-substituted vinylsilanes.

2-Pyridyldimethylvinylsilane (**1**) was treated with *i*PrMgCl in Et_2O, and the mixture was stirred for 3 h at room temperature. The reaction gave the corresponding α-silyl organomagnesium compound, and **2aa** was isolated after aqueous workup in 91% yield [Eq. (1)].[9] Much milder reaction conditions and much shorter reaction times compared to the previous reported reactions with vinylsilanes clearly indicate the enhanced reactivity of **1**.[2] We assume that this carbomagnesation was facilitated by the complex-induced proximity effect (CIPE).[10] The reaction presumably involves a pre-equilibrium complex of **1** and RMgX, and this makes the subsequent carbomagnesation step intramolecular in nature. The importance of this pre-equilibrium complex was further supported by the observation of dramatic solvent effects: weakly coordinating solvents such as Et_2O favor this reaction, whereas strongly coordinating solvents such as THF disfavor it. These results may be attributed to inhibition of the formation of the pre-equilibrium complex by the coordinating solvent.[11] In addition to this kinetic preference, we assume that stabilization of the generated α-silyl organomagnesium compound by intramolecular coordination of the pyridyl group is also responsible for the efficiency of this carbomagnesation process.[8a]



2aa:	R = H	R' = *i*Pr	91%
2ba:	R = H	R' = *n*Bu	93%
2bb:	R = H	R' = *n*Bu	83% (>95% D)
2ca:	R = H	R' = Ph (PhMgBr)	73% (under reflux)
2da:	R = H	R' = $CH_2CH{=}CH_2$	94%
4ba:	R = *n*Bu	R' = *n*Bu	91%

Next we investigated the addition of a primary alkyl Grignard reagent, and found that *n*BuMgCl also adds to **1** at room temperature [Eq. (1)]. To our knowledge, this is the first example of the efficient addition of a primary alkyl Grignard reagent to a vinylsilane. In addition to secondary and primary alkyl Grignard reagents, PhMgBr[12] and $CH_2{=}CHCH_2MgCl$ also added across **1** [Eq. (1)]. The addition of $CH_2{=}CHCH_2MgCl$ was complete within 1 h even at 0°C (90%). Moreover, the addition to β-substituted vinylsilane **3**, which represents a more difficult class of substrate, also took place [Eq. (1)]. Quantitative incorporation of deuterium in the position α to silicon occurred on quenching

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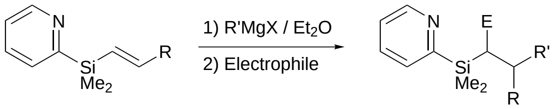
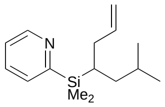
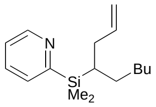
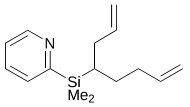
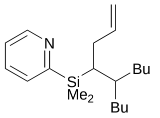
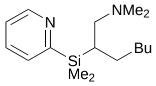
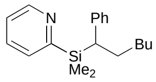
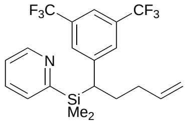
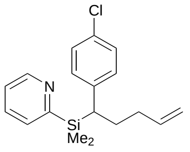
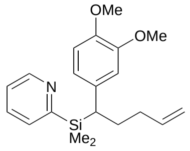
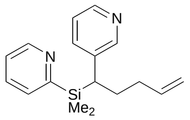
Table 1. Three-component coupling reaction of vinylsilane, Grignard reagent, and electrophile.[a]



1: R = H
3: R = *n*Bu

2: R = H
4: R = *n*Bu

Entry	Vinylsilane	Grignard reagent	Electrophile	Product	Yield [%]
1	**1**	*i*PrMgCl	$CH_2{=}CHCH_2Br$	 **2ac**	91
2	**1**	*n*BuMgCl	$CH_2{=}CHCH_2Br$	 **2bc**	93
3	**1**	$CH_2{=}CHCH_2MgBr$	$CH_2{=}CHCH_2Br$	 **2dc**	91
4	**3**	*n*BuMgCl	$CH_2{=}CHCH_2Br$	 **4bc**	90
5[b]	**1**	*n*BuMgCl	$CH_2{=}N^+Me_2I^-$	 **2bd**	93
6[c]	**1**	*n*BuMgCl	PhI (5% [Pd(PPh_3)$_4$])	 **2be**	77
7[c]	**1**	*n*BuMgCl	PhBr (5% [Pd(PPh_3)$_4$])	**2be**	66
8[c]	**1**	$CH_2{=}CHCH_2MgBr$	3,5-$(CF_3)_2C_6H_3I$ (2.5% [Pd(PPh_3)$_4$])	 **2df**	82
9[c]	**1**	$CH_2{=}CHCH_2MgBr$	4-ClC_6H_4Br (2.5% [Pd(PPh_3)$_4$])	 **2dg**	93
10[c]	**1**	$CH_2{=}CHCH_2MgBr$	3,4-$(CH_3O)_2C_6H_3Br$ (5% [Pd(PPh_3)$_4$])	 **2dh**	73
11[c]	**1**	$CH_2{=}CHCH_2MgBr$	3-bromopyridine (5% [Pd(PPh_3)$_4$])	 **2di**	72

[a] Unless otherwise noted, reactions were carried out as follows: The Grignard reagent (1.1 equiv) was added to the vinylsilane (1.0 equiv) under argon, and the mixture stirred at room temperature for 1–3 h in Et_2O. Then the electrophile (2.4 equiv) was added to the mixture, which was stirred at room temperature for 3–20 h. [b] The electrophile (1.5 equiv) was added at 0 °C, and the mixture stirred for 1 h. [c] After the addition of the Grignard reagent to the vinylsilane was complete, aryl halide, [Pd(PPh_3)$_4$] (2.5 or 5 mol%), and toluene were added, and the resulting mixture was stirred at 80–90 °C for 24 h.

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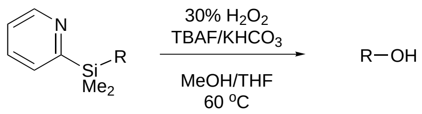
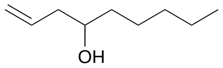
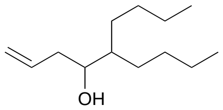
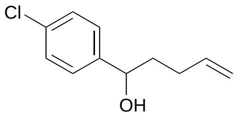
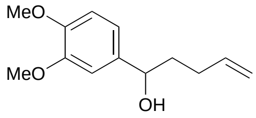
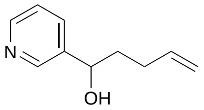
with D_2O; this indicates the reactivity of the resulting α-silyl organomagnesium compound in subsequent reactions.

Having established that intermolecular carbomagnesation across vinylsilane is efficiently directed by a 2-pyridyl group on silicon, we further investigated the three-component coupling reaction of a Grignard reagent, the vinylsilane, and an electrophile (Table 1). Electrophiles such as allyl bromide (entries 1–4) and an iminium salt (entry 5) can be used for the three-component coupling reaction. Interestingly, aryl and heteroaryl halides were also excellent electrophiles when $[Pd(PPh_3)_4]$ was used as catalyst (entries 6–11).[13]

Finally, the three-component coupling adducts were converted into the corresponding alcohols by tetrabutylammonium fluoride (TBAF) mediated H_2O_2 oxidation.[7, 14, 15] Representative results are shown in Table 2. In all cases, oxidation proceeded in good to excellent yields.

Table 2. Oxidation of the coupling products with H_2O_2.[a]



Entry	Coupling adduct	Oxidation product	Yield [%]
1	**2bc**		89
2	**4bc**		89
3	**2dg**		94
4	**2dh**		91
5	**2di**		67

[a] All reactions were performed with 30% H_2O_2 (30 equiv), TBAF (6.0 equiv), and $KHCO_3$ (2.0 equiv) in MeOH/THF (1/1) at 60 °C.

In summary, we have developed a novel strategy for intermolecular carbomagnesation across vinylsilanes by exploiting the 2-PyMe$_2$Si group as a removable directing group. By using this protocol, facile addition of primary alkyl Grignard reagents to vinylsilanes was realized for the first time. The extension to other carbometalation processes is currently under investigation.

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[1] For reviews, see a) J. S. Panek in *Comprehensive Organic Synthesis, Vol. 1* (Eds.: B. M. Trost, I. Fleming, S. L. Schreiber), Pergamon, Oxford, **1991**, p. 579; b) I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063.

[2] a) D. Seyferth, T. Wada, *Inorg. Chem.* **1962**, *1*, 78; b) M. R. Stober, K. W. Michael, J. L. Speier, *J. Org. Chem.* **1967**, *32*, 2740; c) G. R. Buell, R. Corriu, C. Guerin, L. Spialter, *J. Am. Chem. Soc.* **1970**, *92*, 7424; d) K. Tamao, R. Kanatani, M. Kumada, *Tetrahedron Lett.* **1984**, *25*, 1905; e) K. Tamao, T. Iwahara, R. Kanatani, M. Kumada, *Tetrahedron Lett.* **1984**, *25*, 1909; f) K. Tamao, R. Kanatani, M. Kumada, *Tetrahedron Lett.* **1984**, *25*, 1913; g) K. Utimoto, K. Imi, H. Shiragami, S. Fujikura, H. Nozaki, *Tetrahedron Lett.* **1985**, *26*, 2101; h) P. Kocieński, C. Love, D. A. Roberts, *Tetrahedron Lett.* **1989**, *30*, 6753.

[3] Although Buell et al. reported that the addition of primary alkyl Grignard reagents takes place to some extent with ethoxy(vinyl)silanes,[2c] we and others[2d] could not reproduce their results.

[4] Isobe et al. reported that MeMgBr adds to α-silyl-substituted vinylsulfones: A. Herunsalee, M. Isobe, Y. Fukuda, T. Goto, *Synlett* **1990**, 701, and references therein.

[5] J. Yoshida, K. Itami, K. Mitsudo, S. Suga, *Tetrahedron Lett.* **1999**, *40*, 3403.

[6] K. Itami, K. Mitsudo, T. Kamei, T. Koike, T. Nokami, J. Yoshida, *J. Am. Chem. Soc.* **2000**, *122*, 12013.

[7] K. Itami, K. Mitsudo, J. Yoshida, *J. Org. Chem.* **1999**, *64*, 8709.

[8] a) K. Itami, K. Mitsudo, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 5533; b) K. Itami, K. Mitsudo, J. Yoshida, *Tetrahedron Lett.* **1999**, *40*, 5537; c) K. Itami, T. Nokami, J. Yoshida, *Org. Lett.* **2000**, *2*, 1299.

[9] Because of the ability of 2-PyMe$_2$Si group to act as a phase tag,[5] most of the addition products were isolated simply by acid–base extraction.

[10] For a review on CIPE, see: P. Beak, A. I. Meyers, *Acc. Chem. Res.* **1986**, *19*, 356. See also: A. H. Hoveyda, D. A. Evans, G. C. Fu, *Chem. Rev.* **1993**, *93*, 1307.

[11] The same trend was observed for the deprotonation of 2-PySiMe$_3$ by *t*BuLi.[8a]

[12] Refluxing in Et_2O was required for the addition of PhMgBr.

[13] For metal-catalyzed cross-coupling reactions of α-silyl organomagnesium compounds with aryl and alkenyl halides, see: a) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958; b) K. Tamao, N. Ishida, M. Kumada, *J. Org. Chem.* **1983**, *48*, 2120.

[14] The use of KF instead of TBAF resulted in lower yield of the alcohol.

[15] For reviews on oxidative cleavage of carbon–silicon bonds, see: a) K. Tamao in *Advances in Silicon Chemistry, Vol. 3* (Ed.: G. L. Larson), JAI, Greenwich, **1996**, p. 1; b) I. Fleming, *Chemtracts: Org. Chem.* **1996**, 1; c) G. R. Jones, Y. Landais, *Tetrahedron* **1996**, *52*, 7599.

Pentacoordination of Silicon by Four Covalent Si–S Bonds and One Covalent Si–C Bond**

Reinhold Tacke,* Matthias Mallak, and Reiner Willeke

Compared to the well-established silicon–oxygen chemistry, significantly less is known about silicon–sulfur chemistry.[1, 2] Except for a preliminary report on two pentacoordinate silicates with SiO_2S_2C skeletons,[3] only tetracoordinate silicon compounds with Si–S bonds have been described. In a series of recent studies, we have realized several hitherto unknown bonding situations of pentacoordinate silicon by

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