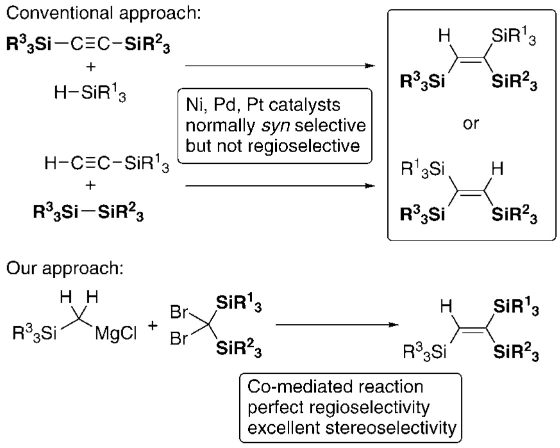
Silyl Ethenes

Regio- and Stereoselective Approach to 1,2-Di- and 1,1,2-Trisilylethenes by Cobalt-Mediated Reaction of Silyl-Substituted Dibromomethanes with Silylmethylmagnesium Reagents**

*Hirohisa Ohmiya, Hideki Yorimitsu, and Koichiro Oshima**

Vinylsilanes are useful organometallic reagents in organic synthesis because the C(sp^2)–Si bonds undergo numerous transformations.[1] Multiply silylated ethenes are thus likely to represent platforms for a variety of highly substituted ethenes. Moreover, multiply silylated ethenes themselves attract considerable attention from the viewpoint of structural organic chemistry.[2] Despite their importance, there is a limited number of access routes to multiply silylated ethenes. Hydrosilylation of silylacetylenes[3] and bissilylation of acetylenes[4] are most convenient procedures.[5] Scheme 1 (top) shows representative approaches, for instance, to trisilylethenes with three different silyl groups. However, difficulties are often encountered in such synthetic strategies in terms of regioselectivity and the occurrence of several side reactions.



Scheme 1. Conventional and novel approaches toward 1,2-di- and 1,1,2-trisilylethenes.

During the course of our studies into cobalt-mediated reactions of organic halides with Grignard reagents,[6] we

---

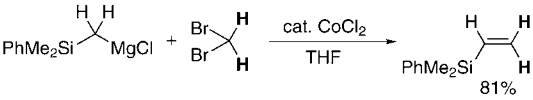
[*] H. Ohmiya, Dr. H. Yorimitsu, Prof. Dr. K. Oshima
Department of Material Chemistry
Graduate School of Engineering
Kyoto University
Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)
Fax: (+81) 75-383-2438
E-mail: oshima@orgrxn.mbox.media.kyoto-u.ac.jp

[**] This work was supported by Grants-in-Aid for Scientific Research for Young Scientists and COE Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200500576

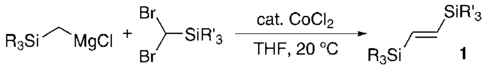
serendipitously found that the reaction of dibromomethane with dimethyl(phenyl)silylmethylmagnesium chloride in the presence of a cobalt salt provided dimethyl(phenyl)vinylsilane in excellent yield [Eq. (1)]. This observation encouraged us to explore the potential of silylated dibromomethanes[7] as precursors for multiply silylated ethenes (Scheme 1, bottom). Herein we report an inherently regioselective and, fortunately, stereoselective preparation of 1,2-di- and 1,1,2-trisilylethenes by means of a cobalt salt, thus creating a novel approach toward multiply silylated ethenes.[8,9]



(1)

After optimization of reaction conditions, the synthesis of 1,2-disilylethene proved to require cobalt(II) chloride (10 mol%) and a Grignard reagent (3 equiv). THF was the solvent of choice, while ether, dioxane, and HMPA were far inferior. The best results were found at a reaction temperature of 20 °C. Table 1 summarizes the syntheses of various 1,2-disilylethenes. All the reactions resulted in the exclusive formation of (*E*)-1,2-disilylethenes **1** in high yields. The steric hindrance of the silyl groups such as $MePh_2Si$ and $tBuMe_2Si$ had virtually no adverse influence on the synthesis. Interestingly, isopropoxy- and allyl-substituted silylmethyl Grignard reagents participated in this reaction.

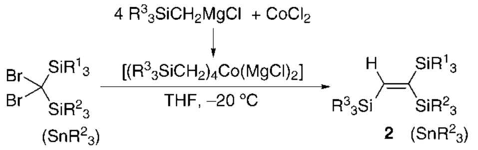
Table 1: Synthesis of (*E*)-1,2-disilylethenes **1**.



Entry	R_3Si	R′Si	1	Yield [%]
1	Me_3Si	Me_2PhSi	a	87
2	Me_3Si	$MePh_2Si$	b	86
3	Me_3Si	$tBuMe_2Si$	c	70
4	Me_2PhSi	Me_3Si	a	90
5	Me_2PhSi	Me_2PhSi	d	78
6	$(iPrO)Me_2Si$	Me_2PhSi	e	88
7	$(CH_2{=}CHCH_2)Me_2Si$	Me_2PhSi	f	79

The high efficiency of this method prompted us to examine dibromodisilylmethanes as starting materials. Contrary to our expectation, the catalytic conditions did not give satisfactory results. Instead, stoichiometric use of a cobaltate reagent $[(R^3_3SiCH_2)_4Co(MgCl)_2]$,[10,11] prepared from Co^{II} chloride and a Grignard reagent (4 equiv), allowed the efficient synthesis of 1,1,2-trisilylethenes (Table 2). The reactions of $(Me_3Si)_2CBr_2$ proceeded smoothly to afford **2a** and **2b** in good yields (Table 2, entries 1 and 2). The bulkier $MePh_2Si$- and $tBuMe_2Si$-substituted precursors were also converted into **2** in reasonable yields (Table 2, entries 3–7). The reactions were clean, and the main by-products were $(R^1_3Si)(R^2_3Si)C(H)Br$, $(R^1_3Si)(R^2_3Si)CH_2$, and $(R^1_3Si)(R^2_3Si)C{=}CH_2$, which were readily separated from the desired products by size-exclusion chromatography (see below). Gratifyingly, treatment of unsymmetrically substituted dibromodisilylmethanes under similar conditions yielded (*E*)-**2e**–**2g** with three different silyl groups stereoselectively (Table 2, entries 5–7). The reaction of a dibromosilylstannylmethane furnished the corresponding (*Z*)-1,2-disilyl-1-stannylethene **2h** with good stereoselectivity (Table 2, entry 8). There are few facile methods for the stereo- and regioselective synthesis of ethenes with different Group 14 metal substituents. Unfortunately, the attempted synthesis of tetrasilylethene from $(R_3Si)_2CBr_2$ and $(R_3Si)_2CHMgCl$ did not succeed.

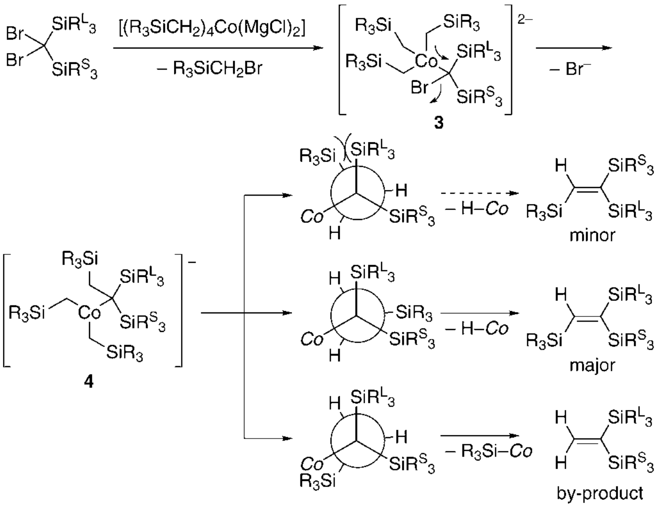
Table 2: Synthesis of 1,1,2-trisilylethenes **2**.



Entry	R^1_3Si	R^2_3Si	R^3_3Si	2	Yield [%]	*E*/*Z*
1	Me_3Si	Me_3Si	Me_3Si	a	75	–
2	Me_3Si	Me_3Si	Me_2PhSi	b	73	–
3	$MePh_2Si$	$MePh_2Si$	Me_3Si	c	55	–
4	$tBuMe_2Si$	Me_3Si	Me_3Si	d	58	100:0[a]
5	$MePh_2Si$	Me_3Si	$(iPrO)Me_2Si$	e	48	90:10[a]
6	$MePh_2Si$	Me_3Si	Me_2PhSi	f	54	94:6[a]
7	$MePh_2Si$	Me_3Si	$(CH_2{=}CHCH_2)Me_2Si$	g	53	94:6[a]
8	$MePh_2Si$	(Bu_3Sn)	Me_3Si	h	51	8:92[b]

[a] Determined by NOE experiments. [b] Judged by $J_{Sn\text{-}H}$.

We propose a mechanism for the stoichiometric reaction as shown in Scheme 2. Halogen–cobalt exchange initially takes place to produce intermediate **3**. One of the silylmethyl groups on the cobalt center migrates to generate **4** with concomitant liberation of bromide.[12] β-Hydride elimination finalizes the formation of 1,1,2-trisilylethene **2**. The major *E* stereoisomers in Table 2 would originate from the more stable eclipsed conformer upon β-hydride elimination. The formation of the by-product $(R^1_3Si)(R^2_3Si)C{=}CH_2$ can stem from β-silyl elimination.[13]



Scheme 2. Proposed mechanism for the formation of 1,1,2-trisilylethenes in the presence of stoichiometric amounts of the cobaltate complex.

In summary, we have developed a novel method for the synthesis of 1,2-di- and 1,1,2-trisilylethenes in a regio- and stereoselective manner. The products are not only useful as precursors for various alkenes but are also structurally interesting. Further improvement of this strategy will allow access to a wide range of ethenes that are multifariously substituted with Group 14 metals.

Experimental Section

General procedure (**1a**): Anhydrous cobalt(II) chloride (6.5 mg, 0.05 mmol) was placed in a 20-mL reaction flask and heated with a hair dryer in vacuo for 2 min. After the cobalt salt turned blue, anhydrous THF (3.0 mL) was added under argon. The mixture was stirred for 3 min at room temperature. Dibromo(dimethyl(phenyl)-silyl)methane (154 mg, 0.50 mmol) and a solution of trimethylsilylmethylmagnesium chloride in diethyl ether (1.0 M; 1.5 mL, 1.5 mmol) were successively added dropwise to the reaction mixture at 0 °C. While the Grignard reagent was being added, the mixture turned brown. After being stirred for 1 h at 20 °C, the reaction mixture was poured into water. The product was extracted with hexane (2 × 20 mL). The combined organic layer was dried over sodium sulfate and concentrated. Purification of the crude oil by silica-gel column chromatography (hexane) provided the corresponding (*E*)-1,2-disilylethene **1a** (102 mg, 0.43 mmol) in 87 % yield.

2b: Anhydrous cobalt(II) chloride (97.5 mg, 0.75 mmol) was placed in a 30-mL reaction flask and dried in vacuo for 2 min. Anhydrous THF (5.0 mL) was added under argon, and the mixture was stirred for 3 min at room temperature. A solution of dimethyl-(phenyl)silylmethylmagnesium chloride in diethyl ether (0.95 M; 3.16 mL, 3.0 mmol) was added dropwise to the reaction mixture at −20 °C. After the mixture was stirred for 15 min at −20 °C, dibromobis(trimethylsilyl)methane (159 mg, 0.50 mmol) was added dropwise to the reaction mixture at −20 °C. After being stirred for an additional 1 h at −20 °C, the reaction mixture was poured into water. The product was extracted with hexane (2 × 20 mL). The combined organic layer was dried over sodium sulfate and concentrated. Silica-gel column chromatography (hexane) followed by gel-permeation chromatography (toluene, to remove by-products described above) provided the corresponding 1,1,2-trisilylethene **2b** (111 mg, 0.36 mmol) in 73 % yield.

Received: February 16, 2005

Keywords: alkenes · cobalt · Grignard reagents · silicon · synthetic methods

---

[1] a) K. Oshima in *Science of Synthesis (Houben-Weyl)*, *Vol. 4* (Ed.: I. Fleming), Georg Thieme, Stuttgart, **2002**, chap. 4.4.34; b) K. Miura, A. Hosomi in *Main Group Metals in Organic Synthesis*, *Vol. 2* (Eds.: H. Yamamoto, K. Oshima), Wiley-VCH, Weinheim, **2004**, chap. 10.4; c) J. S. Panek in *Comprehensive Organic Chemistry*, *Vol. 1* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, chap. 2.5; d) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley-VCH, New York, **2000**.

[2] a) H. Sakurai, K. Ebata, K. Sakamoto, Y. Nakadaira, C. Kabuto, *Chem. Lett.* **1988**, 965 – 968; b) H. Schmidbaur, J. Ebenhoech, *Z. Naturforsch. B* **1987**, *42*, 1543 – 1548; c) M. Kira, H. Nakazawa, H. Sakurai, *J. Am. Chem. Soc.* **1983**, *105*, 6983 – 6987; d) H. Sakurai, Y. Nakadaira, H. Tobita, T. Ito, K. Toriumi, H. Ito, *J. Am. Chem. Soc.* **1982**, *104*, 300 – 302.

[3] a) T. Suzuki, P. Y. Lo, *J. Organomet. Chem.* **1990**, *391*, 19 – 25; b) E. Lukevics, Z. V. Belyakova, M. G. Pomerantseva, M. G. Voronkov, *J. Organomet. Chem. Libr.* **1977**, *5*, 1 – 179; c) I. Ojima in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**, pp. 1479 – 1526; d) *Comprehensive Handbook on Hydrosilylation* (Ed.: B. Marciniec), Pergamon, Oxford, **1992**; e) T. Hiyama, T. Kusumoto in *Comprehensive Organic Chemistry*, *Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, chap. 3.12; f) K. A. Horn, *Chem. Rev.* **1995**, *95*, 1317 – 1350.

[4] a) M. Suginome, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221 – 3256; b) J. Hibino, S. Nakatsukasa, K. Fugami, S. Matsubara, K. Oshima, H. Nozaki, *J. Am. Chem. Soc.* **1985**, *107*, 6416 – 6417; c) H. Watanabe, M. Kobayashi, M. Saito, Y. Nagai, *J. Organomet. Chem.* **1981**, *216*, 149 – 157.

[5] For the disproportionation of vinylsilane, see: a) B. Marciniec, E. Walczuk-Gusciora, P. Blazejewska-Chadyniak, *J. Mol. Catal. A* **2000**, *160*, 165 – 171; b) B. Marciniec, J. Guliñski, *J. Organomet. Chem.* **1984**, *266*, C19-C21; for Ru-catalyzed dehydrogenative silylation of vinylsilanes, see: c) Y. Seki, K. Takeshita, K. Kawamoto, *J. Organomet. Chem.* **1989**, *369*, 117 – 123.

[6] a) K. Wakabayashi, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2001**, *123*, 5374 – 5375; b) Y. Ikeda, T. Nakamura, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2002**, *124*, 6514 – 6515; c) T. Tsuji, H. Yorimitsu, K. Oshima, *Angew. Chem.* **2002**, *114*, 4311 – 4313; *Angew. Chem. Int. Ed.* **2002**, *41*, 4137 – 4139; ; d) T. Fujioka, T. Nakamura, H. Yorimitsu, K. Oshima, *Org. Lett.* **2002**, *4*, 2257 – 2259; e) K. Mizutani, H. Shinokubo, K. Oshima, *Org. Lett.* **2003**, *5*, 3959 – 3961; f) K. Mizutani, H. Yorimitsu, K. Oshima, *Chem. Lett.* **2004**, *33*, 832 – 833; g) T. Nishikawa, H. Yorimitsu, K. Oshima, *Synlett* **2004**, 1573 – 1574; h) H. Ohmiya, H. Yorimitsu, K. Oshima, *Chem. Lett.* **2004**, *33*, 1240 – 1241; i) H. Ohmiya, T. Tsuji, H. Yorimitsu, K. Oshima, *Chem. Eur. J.* **2004**, *10*, 5640 – 5648; j) Y. Ikeda, H. Yorimitsu, H. Shinokubo, K. Oshima, *Adv. Synth. Catal.* **2004**, *346*, 1631 – 1634; k) H. Shinokubo, K. Oshima, *Eur. J. Org. Chem.* **2004**, 2081 – 2091.

[7] A. Inoue, J. Kondo, H. Shinokubo, K. Oshima, *Chem. Lett.* **2001**, 956 – 957, and references therein.

[8] For the cobalt-mediated reaction of dibromocyclopropane with methyl and butyl Grignard reagents, see: Y. Nishii, K. Wakasugi, Y. Tanabe, *Synlett* **1998**, 67 – 69.

[9] We previously reported the manganese-catalyzed reaction of dibromo(silyl)methane with alkyl Grignard reagents to form 1-silyl-1-alkene, and only one example of the synthesis of 1,2-disilylethene was described. However, the reaction is not very efficient ($t\mathrm{BuMe_2SiCH{=}CHSiMe_3}$, 57 % yield by using a stoichiometric amount of a manganate complex $[(\mathrm{Me_3SiCH_2})_3\mathrm{MnMgCl}]$): a) H. Kakiya, R. Inoue, H. Shinokubo, K. Oshima, *Tetrahedron Lett.* **1997**, *38*, 3275 – 3278; b) H. Kakiya, H. Shinokubo, K. Oshima, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2139 – 2147.

[10] The exact structure of the species $[(\mathrm{R}^3{}_3\mathrm{SiCH_2})_4\mathrm{Co}(\mathrm{MgCl})_2]$ in solution is not clear. For convenience, we use this expression. Several organocobaltate(II) compounds were characterized by X-ray crystallographic analysis: R. S. Hay-Motherwell, G. Wilkinson, B. Hussain, M. B. Hursthouse, *Polyhedron* **1990**, *9*, 931 – 937.

[11] For a review on cobaltate complexes, see: T. Kauffmann, *Angew. Chem.* **1996**, *108*, 401 – 418; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 386 – 403.

[12] For examples of halogen–metal exchange between *gem*-dihaloalkane and ate complexes followed by alkyl migration, see: A. Inoue, J. Kondo, H. Shinokubo, K. Oshima, *Chem. Eur. J.* **2002**, *8*, 1730 – 1740, and references therein.

[13] a) F. Kakiuchi, A. Yamada, N. Chatani, S. Murai, N. Furukawa, Y. Seki, *Organometallics* **1999**, *18*, 2033 – 2036; b) Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, *J. Chem. Soc. Chem. Commun.* **1991**, 703 – 704; see also reference [5].