A Facile Synthesis of 1,1-Bis(silyl)ethenes[†]

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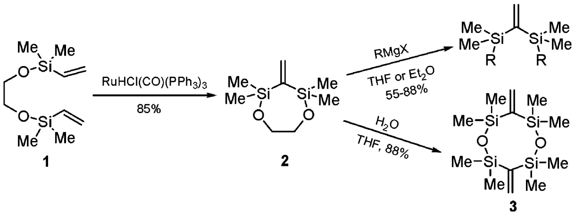

Symmetrical 1,1-bis(silyl)ethenes have been easily prepared via ruthenium complex-catalyzed silylative coupling cyclization of 1,2-bis(dimethylvinylsiloxy)ethane to give 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane with excellent selectivity and good yield, followed by its reaction with Grignard reagents. The cyclic product can also be effectively transformed into cyclic carbosiloxane, 2,2,4,4,6,6,8,8-octamethyl-3,7-dimethylene-1,5-dioxa-2,4,6,8-tetrasilacyclooctane.

Alkenylsilanes, especially vinyl- and allylsilanes are well established in regio- and stereoselective organic synthesis.[1] The properties of 1,1-bis(silyl)alkenes are similar to those of vinylsilanes, and the former compounds have recently been shown to be interesting intermediates in organic and organosilicon synthesis.[2] Although it is already known to be possible to apply 1,1-bis(silyl)alkenes as synthetic tools, their synthesis is complicated.[3] 1,1-Bis(silyl)alkenes have been mostly prepared by multistep reactions involving commercially unavailable dihalodisilylmethanes; however, several independent methods, e.g., Peterson olefination of carbonyl compounds with the use of LiC(SiMe$_3$)$_3$[3a] and reaction of esters with phenyldimethylsilyllithium,[3c] have also been investigated. Oshima and co-workers reported the synthesis of 1,1-bis(silyl)ethenes via lithium trimethylmagnesate-induced monomethylation of dibromodisilylmethanes followed by dehydrobromination of the resulting 1-bromo-1,1-disilylethanes with DBU.[3h] Chromium(II) chloride-mediated reaction of aldehydes with dibromodisilylmethane reported by Hodgson and co-workers provides an alternative route to vinylbis(silanes).[2c] 1,1-Bis(silyl)alkenes can be also prepared from 1-alkynylsilanes by hydroalumination−halogenolysis followed by replacement of the halide atom in the resulting 1-halovinylsilane by a silyl group using alkyllithium.[3e,g]

In the last 15 years, we have developed the silylative coupling reaction of vinylsilane derivatives in the presence of ruthenium, rhodium, cobalt, and iridium complexes containing or generating M−H and M−Si bonds (e.g., [RuHCl(CO)(PPh$_3$)$_3$], [RuCl$_2$(CO)$_3$]$_2$, or [Rh(μ-Cl)(cod)]$_2$).[4] The silylative coupling reaction of monovinyl organosilicon compounds proceeds through cleavage of the =C−Si bond of the vinyl-substituted silicon compound and the activation of the =C−H bond of the second vinylsilane molecule.[4] The mechanism of this reaction involving β-silyl elimination and insertion of a C=C double bond into the resulting M−Si bond has been proved by insertion of ethylene and vinylsilane into M−Si (where M = Ru, Rh, Co) bonds as well as by a series of elaborate mass-spectrometric studies with deuterated styrene and vinylsilanes (Scheme 1).[5]

In this reaction divinyl-substituted silanes, siloxanes and silazanes undergo efficient silylative coupling condensation to yield a mixture of linear oligomers and cyclic dimers and trimers containing *exo*-cyclic methylene bonds (Scheme 2). The unique feature of this silylative coupling reaction, distinguishing this reaction from cross-metathesis, is the formation of 1,1-bis(silyl)ethene fragment in given conditions.[6]

Herein we disclose a new facile and rapid synthetic protocol for synthesis of 1,1-bis(silyl)ethenes using alkyl-(aryl) or alkenyl Grignard reagents and 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane selectively obtained via ruthenium-catalyzed silylative coupling cyclization.

The starting 1,2-bis(dimethylvinylsiloxy)ethane **1** could be easily prepared by the reaction of commercially

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[†] Dedicated to Professor Mieczysław Mąkosza on the occasion of his 70th birthday in recognition of his significant contribution to organic chemistry.

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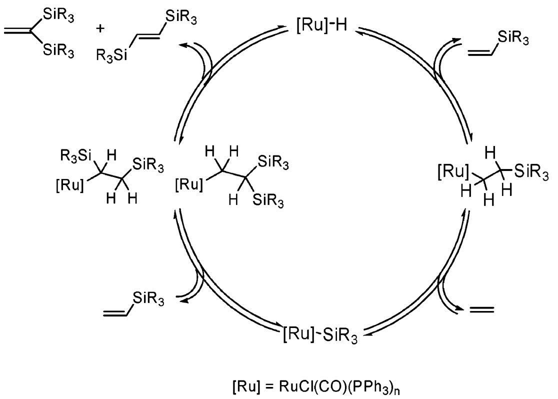
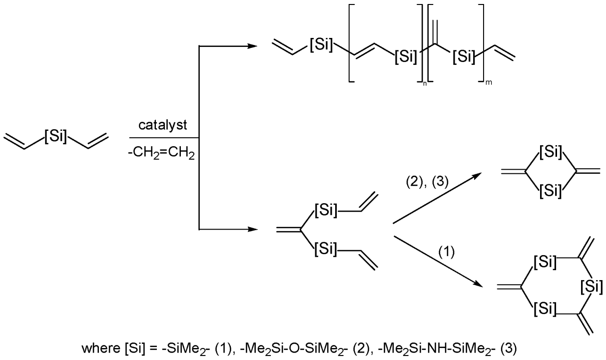
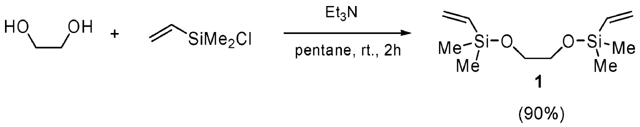
SCHEME 1. Silylative Coupling Reaction Mechanism



SCHEME 2. Silylative Coupling Reaction of Divinyl-Substituted Organosilicon Compounds



SCHEME 3. Synthesis of 1,2-Bis(dimethylvinylsiloxy)ethane



available chlorodimethylvinylsilane and ethylene glycol in the presence of triethylamine in high yield (90%) as outlined in Scheme 3.

Silylative coupling cyclization of 1,2-bis(dimethylvinylsiloxy)ethane was effectively catalyzed by [RuHCl(CO)(PPh_3)$_3$] (1 mol %), and the divinyl compound was completely consumed within 1 h at 80 °C. The reaction occurred even at a lower catalyst loading (0.2 mol %), but in a longer time (24 h).

The cyclization reaction successfully proceeded without the solvent under air, but toluene or benzene could also be employed without affecting either the activity of the catalyst or the selectivity of this process. Application of this catalytic system for silylative coupling cyclization of 1,2-bis(dimethylvinylsiloxy)ethane gives exclusively a disilacyclic product containing *exo*-methylene bond between two silicon atoms in the molecule with perfect regioselectivity and high yield (85%) (Scheme 4). It is worth adding that the cyclic product was easily isolated only by the "bulb to bulb" distillation from the reaction flask.

The existence of the *exo*-methylene unit in the product was unambiguously determined on the basis of the ^{13}C NMR and NMR DEPT spectra.

SCHEME 4. Synthesis of 2,2,4,4-Tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane

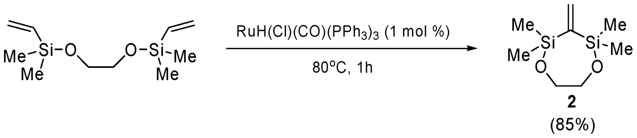
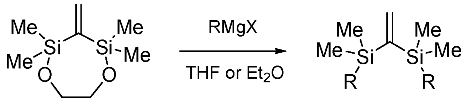


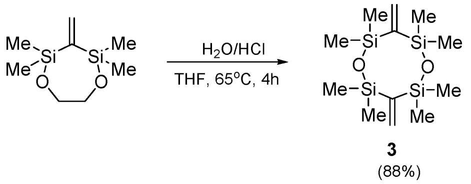
TABLE 1. Synthesis of 1,1-Bis(dimethylsilyl)ethenes[a]



entry	R	X	time (h)	yield (%)[c]
I	Me	I	24	76
II	Et	Br	24	73
III	Ph	Br	24	88
IV	−CH=CH_2	Br	24	62
V	−CH_2CH=CH_2	Br	48[b]	68
VI	−(CH_2)$_2$CH=CH_2	Br	72	55

[a] Reaction conditions: THF, 65 °C. [b] Diethyl ether, 40 °C. [c] Isolated yields of chromatographically pure products

SCHEME 5. Synthesis of 2,2,4,4,6,6,8,8-Octamethyl-3,7-dimethylene-1,5-dioxa-2,4,6,8-tetrasilacyclooctane



At the next stage, we investigated the reaction of 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane with Grignard reagents. After preliminary attempts, we found that the treatment of the silylative coupling cyclization product **2** with 2.5 equiv of the corresponding Grignard reagent in THF or diethyl ether (0.5 M concentration of the solvent) at reflux under an Ar atmosphere provided substituted 1,1-bis(silyl)ethenes in moderate to good yields. In all cases, excellent regioselectivity was attained; however, when the allyl- and 3-butenylmagnesium bromide were used, the reaction mixture had to be refluxed for a longer time and an increased amount of the Grignard reagents (from 2.5 to 3 equiv) did not appreciably affect the rate of this reaction. Table 1 summarizes the results of this reaction.

Results of the spectroscopic analyses (^{13}C NMR and DEPT) of the products obtained in the above-mentioned reaction have confirmed the occurrence of the quaternary carbon atoms and methylene groups.

Compound **2** was also found to be a good starting material for synthesis of cyclic tetrasilacarbosiloxane **3** containing two *exo*-methylene bonds between silicon atoms in the molecule (Scheme 5). This compound has been obtained previously via silylative coupling cyclization of 1,3-divinyltetramethyldisiloxane in the presence of [RhX(cod)]$_2$ (where X = Cl, $OSiMe_3$), and its structure has been determined by the X-ray method.[5d,6a] However, the cyclization was accompanied by linear polycondensation of 1,3-divinyltetramethyldisiloxane and the isolated yield of the cyclic product was rather low (30%). In contrast to the above-mentioned synthetic method, the hydrolysis of compound **2** in the presence of catalytic amount of HCl proceeded directly to afford exclusively 2,2,4,4,6,6,8,8-octamethyl-3,7-dimethylene-1,5-dioxa-2,4,6,8-tetrasilacyclooctane in 88% yield.

In conclusion, we have shown that through ruthenium-catalyzed selective *exo*-cyclization of 1,2-bis(dimethylvinylsiloxy)ethane and subsequent coupling of the cyclic product with varying the structure of the Grignard compounds, a wide range of alkyl-, aryl-, or alkenyl-substituted 1,1-bis(silyl)ethenes should be available. Our current investigation focuses on the application of the resulting alkyl- and alkenyl-substituted 1,1-bis(silyl)-ethenes in the synthesis of new unsaturated silacyclic and silamacrocyclic compounds as well as unsaturated organic derivatives.

Experimental Section

Synthesis and Characterization of Compound 2. $RuHCl(CO)(PPh_3)_3$ (0.828 g, 8.7×10^{-4} mol) and 20.0 g (0.087 mol) of 1,2-bis(dimethylvinylsiloxy)ethane were placed in a two-necked, 50 mL flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was heated for 1 h at 80 °C with stirring. The cyclic product was isolated by "bulb to bulb" distillation to give 14.93 g of **2** (0.074 mol) in 85% yield as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.25 (s, 12H), 3.65 (s, 4H), 6.20 (s, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): −1.5, 66.6, 139.7, 157.7. Anal. Calcd for $C_8H_{18}O_2Si_2$: C, 47.47; H, 8.96. Found: C, 47.51; H, 9.14.

General Procedure for Synthesis of 1,1-Bis(silyl)ethenes. The glass reactor (100 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, argon bubbling tube, and thermostated heating oil bath) was evacuated and flushed with argon. Compound **2** and the solvent were added to the reactor. At room-temperature, Grignard reagent (molar ratio of compound **2**:Grignard reagent was 1:2.5) was added dropwise. The reaction mixture was stirred under the conditions shown in Table 1. After the reaction was completed, the excess amount of the Grignard reagent was quenched by adding MeOH and pentane; the suspended salt was filtered off, and the volatiles were evaporated in vacuo. After evaporation, the crude product was chromatographed on silica gel and distilled under reduced pressure to afford the analytically pure product.

Synthesis and Characterization of Compound 3. Compound **2** (3.0 g, 0.015 mol) in 10 mL of THF was placed in a two-necked, 50 mL flask equipped with a magnetic stirring bar and a reflux condenser. Then, 0.29 mL (0.016 mol) of water and several drops of aqueous solution of HCl were added. The reaction mixture was refluxed for 4 h with stirring. The solvent was evaporated in vacuo, and the cyclic product was isolated by distillation under reduced pressure (68 °C/0.5 mmHg) to give 2.06 g of **3** in 88% yield. ^{1}H NMR, ($CDCl_3$, 300 MHz) δ (ppm): 0.28 (s, 24H), 6.19 (s, 4H). ^{13}C NMR, ($CDCl_3$) δ (ppm): 1.6, 139.9, 156.6. Anal. Calcd for $C_{12}H_{28}O_2Si_4$: C, 45.60; H, 8.86. Found: C, 45.56; H, 8.81.

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Supporting Information Available: Detailed experimental procedures and characterization data of all compounds prepared in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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