Organometallics **2003,** *22,* 3717−3722

Functionalization of Vinyl-Substituted Cyclosiloxane and Cyclosilazane via Ruthenium-Catalyzed Silylative Coupling Reaction

Yujiro Itami, Bogdan Marciniec,* and Maciej Kubicki

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

Received May 9, 2003

A new type of functionalization of cyclosiloxane and cyclosilazane is reported. Commercially available vinyl-substituted cyclosiloxane and cyclosilazane can be converted chemo- and regioselectively to styryl- and β-alkoxyvinyl-substituted derivatives via respective silylative coupling reactions with styrene and vinyl alkyl ethers catalyzed by $RuHCl(CO)(PCy_3)_2$. The obtained *cis*-tristyrylcyclotrisiloxane showed a unique arrangement of the three styryl groups through face-to-face and side-by-side $\pi-\pi$ interactions. Pd-catalyzed Hiyama coupling reaction of synthesized β-*n*-butoxyvinyl-substituted cyclosiloxane with iodobenzene was also performed to afford β-*n*-butoxystyrene regioselectively.

Introduction

Organofunctional polysiloxanes and polysilazanes have been widely utilized as basic silicone materials (coatings, resists, liquid crystals, membranes, etc.) and as preceramic materials, respectively, with unique characteristics due to the strength and flexibility of the Si−O and Si−N bonds, as well as to a variety of functional groups at the silicon atom.[1] Cyclosiloxanes and cyclosilazanes have been used as the basic substances for anionic and cationic ring-opening polymerization (copolymerization) to obtain respective organofunctional silicon polymers (polysiloxanes, siloxane-containing block-copolymers, and polysilazanes).[1] Alkenyl-(vinyl,aryl)-substituted cyclosiloxanes have also been applied recently as a core for the carbosilane dendrimers[2] or as synthetic reagents for organic compounds via Pd-catalyzed coupling (Hiyama coupling) reaction[3] and also as novel π-ligands for transition metal complexes.[4]

Besides the hydrosilylation process, which has been the main method for the direct functionalization of cyclosiloxanes and cyclosilazanes,[1,5] they have been synthesized via hydrolysis or ammonolysis of functionalized monomeric silanes. However, these methods also have limitations, e.g., impossible to introduce functional groups sensitive to moisture or acidic/basic media.[6]

In the past decade, we have developed a new type of transition metal-catalyzed reaction, i.e., silylative coupling reaction of olefins with vinylsilanes, as a useful alternative reaction for the functionalization of organosilicon compounds to give novel and well-known silicon-containing olefins (for recent reviews see ref 7). This reaction occurs via cleavage of the =C−H bond of the olefin and the =C−Si bond of vinylsilane (Scheme 1),[8] in contrast to the cross-metathesis, which starts with the same substrates and ends with the same products through cleavage of the C=C bonds.[9] However, alkyl-substituted vinylsilanes appear to be quite inactive in ruthenium-catalyzed cross-metathesis.[10]

The catalytic cycle of this new type of silylolefin conversion involves a migratory insertion of olefin into the M−Si bond (which is formed via insertion of vinylsilane into the M−H bond and β-Si transfer with elimination of ethylene) followed by β-H transfer to the metal with elimination of products.[11] A notable pecu-

---

* Corresponding author. Tel: +48-61-8291366. Fax: +48-61-8291508. E-mail: marcinb@main.amu.edu.pl.

[1] *Silicon-Containing Polymers*; Jones, R. G., Ando, W., Chojnowski, J., Eds.: Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000. *Silicon in Organic, Organometallic and Polymer Chemistry*: Brook, M. A., Eds.: John Wiley & Sons: New York, 2000. Kendrick, T. C.; Parbhoo, B.; White, J. W. In *The Chemistry of Organic Silicon Compounds*: Patai, S., Rappoport, Z., Eds.: John Wiley & Sons: New York, 1989; Vol. 2, Chapter 21.

[2] Kim, C.; Park, J. *J. Organomet. Chem.* **2001**, *629*, 194, and references therein.

[3] Denmark, S.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073. Denmark, S.; Wang, Z. *J. Organomet. Chem.* **2001**, *624*, 372. Mori, A.; Suguro, M. *Synlett* **2001**, *6*, 845.

[4] Maciejewski, H.; Kubicki, M.; Marciniec, B.; Sydor, A. *Polyhedron* **2002**, *21*, 1261. Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *J. Organomet. Chem.* **2000**, *605*, 221. Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6*, 191. Harrod, J. F.; Shaver, A.; Tucka, A. *Organometallics* **1985**, *4*, 2166. Rybinskaya, M. I.; Rybin, L. V.; Pogrebnyak, A. A.; Nurtdinova, G. V.; Yure'v, V. P. *J. Organomet. Chem.* **1981**, *217*, 373.

[5] Alonso, B.; González, B.; Garcia, B.; Ramirez-Olivia, E.; Zamora, M.; Casado, C. M.; Cuadrado, I. *J. Organomet. Chem.* **2001**, *637−639*, 642. Michalczyk, M. J.; Simonsick, W. J., Jr.; Sharp. *J. Organomet. Chem.* **1996**, *521*, 261. Sonnek, G.; Jancke, H.; Pasynkiewicz, S.; Ziemkowska, W. *J. Organomet. Chem.* **1990**, *389*, 289.

[6] Birkofer, L.; Stuhl, O. In *The Chemistry of Organic Silicon Compounds*: Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 1, Chapter 10.

[7] Marciniec, B. *Appl. Organomet. Chem.* **2000**, *14*, 527. Marciniec, B. In *Applied Homogeneous Catalysis with Organometallic Compounds*: Cornils, B., Herrmann, W. A., Eds.: Wiley-VCH: New York, 2002; Vol. 1, p 491.

[8] (a) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320. Marciniec, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003. (b) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703.

[9] Pietraszuk, C.; Marciniec, B.; Fischer, H. *Organometallics* **2000**, *19*, 913. Kujawa-Welten, M.; Pietraszuk, C.; Marciniec, B. *Organometallics* **2002**, *21* 840. Pietraszuk, C.; Fischer, H.; Kujawa, M.; Marciniec, B. *Tetrahedron Lett.* **2001**, *42*, 1175.

[10] Pietraszuk, C.; Fischer, H. *J. Chem. Soc., Chem. Commun.* **2000**, 2463.

[11] (a) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *Organometallics* **2000**, *19*, 1677. (b) Marciniec, B.; Kujawa, M.; Pietraszuk, C. *New J. Chem.* **2000**, *24*, 671.

10.1021/om0303505 CCC: $25.00
Publication on Web 07/26/2003

Scheme 1. Silylative Coupling Reaction of Vinylsilanes with Olefins

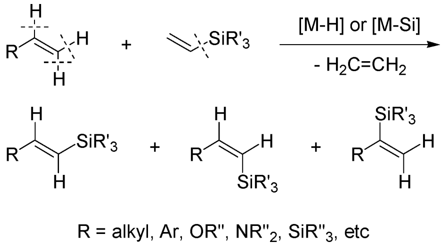
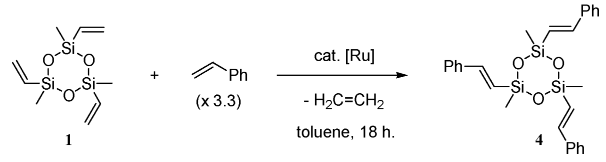


Table 1. Reaction of D_3^{Vi} (1) with Styrene



[Ru]	mol %[a]	temp (°C)	conversion[b] (%)	yield (%)
I	0.1	80	>99	95
II	1	40	10[c]	

[a] To vinylsilyl group. [b] Calculated by GC and NMR. [c] Mono only.

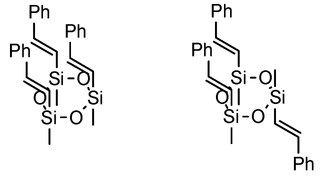
liarity of this reaction is the silylation of vinyl alkyl ethers with vinylsilanes[8b,11] to give β-alkoxy-substituted vinylsilanes, which are difficult to synthesize via other transition metal-catalyzed reactions, e.g., hydrosilylation and cross-metathesis.[12]

In this paper we report examples of effective regio- and stereoselective silylative coupling of vinylmethyl-substituted cyclosiloxanes D_3^{Vi} (**1**) and D_4^{Vi} (**2**) as well as with vinyltetramethylcyclotetrasilazane (**3**) with styrene and with vinyl alkyl ethers catalyzed by ruthenium hydride complex $RuHCl(CO)(PCy_3)_2$ (**I**), which has been found as an active and selective catalyst for silylative coupling reaction,[13] in comparison with the catalytic activity of Grubbs' catalyst $Cl_2Ru(=CHPh)(PCy_3)_2$ (**II**) in the respective cross-metathesis reactions.

Results and Discussion

At first, we have investigated a functionalization of trivinylcyclotrisiloxane D_3^{Vi} (**1**) with styrene (Table 1). The reaction catalyzed by **I** occurs quite efficiently even at a low catalyst loading (0.1 mol %) and regio-, stereo-, and chemoselectively (without homocoupling of vinylcyclosiloxane) to give exclusively a *trans*-styryl product. The styryl-substituted product (**4**) was isolated in a high yield (95%) after recrystalization from pentane. In contrast, the cross-metathesis with Grubbs' catalyst (**II**) was ineffective. This seems to be due to the decomposition of ruthenium carbene species via β-silyl migration in a metathetical intermediate, ruthenacyclobutane, which occurs in the cross-metathesis of vinylsilanes having one or more alkyl groups at the silicon atom.[10]

As a substrate D_3^{Vi} (**1**) already consists of two geometrical isomers (*trans* and *cis*), which are impossible to isolate. The isolated product **4** also consists of two geometrical isomers (**4-*trans*** and **4-*cis***, Figure 1 and Figure 2; **4-*trans***:**4-*cis*** = 3.15:1). Both of these isomers (isomers A and B) were successfully isolated by fractional recrystallization from hexane (Figure 2).



4-*cis* **4-*trans***

Figure 1. Geometrical isomers of **4**.

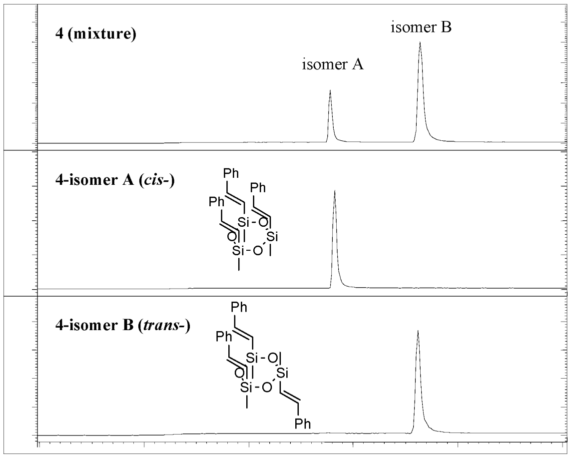


Figure 2. Gas chromatograph of **4** and two isolated isomers, A and B.

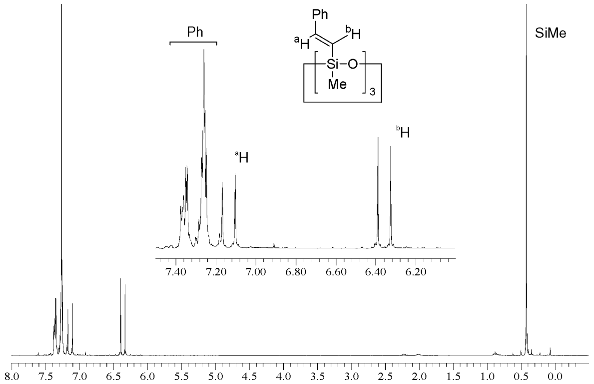


Figure 3. ^1H NMR spectrum of isomer A (**4-*cis***).

From the ^1H NMR spectrum, the isomer A (Figure 2) was identified as **4-*cis*** due to only one pair of vinylene signals and a single singlet from the methyl group (Figure 3). ^1H NMR spectrum of isomer B (Figure 2) showed good correspondence to the structure of **4-*trans***, having two independent pairs of vinylene signals and two methyl group singlets (Figure 4).

The X-ray crystal structure of the *cis*-isomer (**4-*cis***) is shown in Figure 5, and a unique arrangement of styryl groups has been found that occupy quasi-axial positions while the methyl substituents are in quasi-equatorial ones. The mean distance between β-carbons of the styryl groups (α-carbon at silicon atoms) was 4.32 Å, which was much shorter than that between the carbon atoms of the methyl groups (5.23 Å). A structure with a similar arrangement of phenyl groups has been reported for *cis*-1,3,5-trimethyl-1,3,5-triphenylcyclotri-

---

(12) Only one example for the construction of β-butoxy vinylsilane has been reported. See: Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 3890.

(13) Itami, Y.; Marciniec, B.; Majchrzak, M.; Kubicki, M. *Organometallics* **2003**, *22*, 1835. Yi, C.-S.; He, Z.; Lee, D.-W. *Organometallics* **2000**, *19*, 2036.

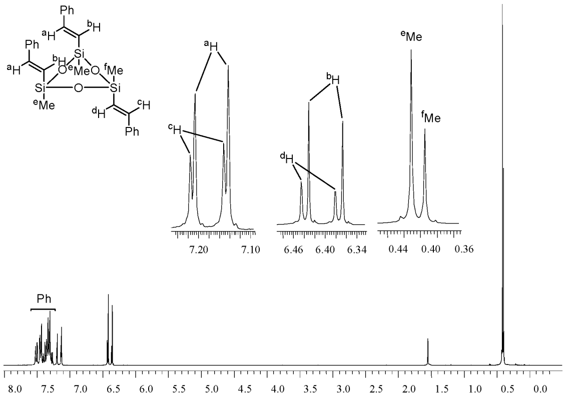


Figure 4. ^{1}H NMR spectrum of isomer B (**4-*trans***).

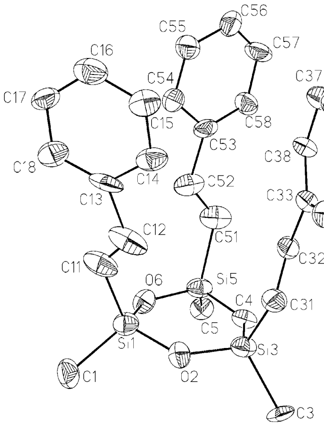


Figure 5. X-ray crystal structure of **4-*cis***.

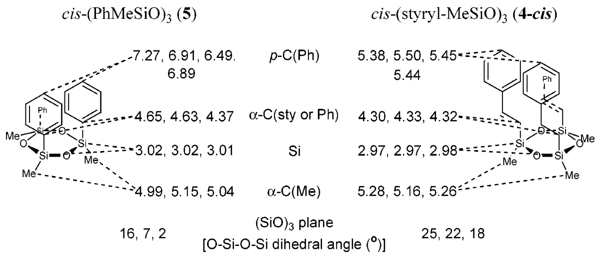


Figure 6. Arranged structure of *cis*-(PhMeSiO)$_3$ (**5**) and **4-*cis***.

siloxane (**5**)[14] with a longer mean distance between *ipso*-carbons, 4.54 Å, than that of **4-*cis*** and shorter distances between the methyl carbons, 5.06 Å (Figure 6).

Possible intramolecular π−π interactions between the styryl groups approaching one another have been suggested from the very close distances between the *para*-phenyl carbon atoms (5.44 Å mean value), much closer than that of **5** (6.89 Å mean value) and from the short distances between the midpoints of the vinylene groups (4.04 Å mean value). Actually, two out of the three styryl groups (**A** and **B**) face each other, which may have π−π interactions (Figure 7). Interestingly, another one (**C**) turns next to **A** at a slight angle, and two α-vinylene H atoms are located nearly at a distance of 1.98 Å, despite their repulsion. For this structure to be stable, some interaction has to surmount this H−H repulsion.

MO calculations of the obtained X-ray crystal structure (with the HF/LAND2DZ basis set) have revealed quite interesting π−π interactions between the three styryl groups. Molecular orbital presentations of **4-*cis*** are shown in Figure 8. As expected, face-to-face π−π interactions between **A** and **B** were found in the LUMO+1, HOMO, and HOMO-2. However, the interaction is not as strong as expected, and this face-to-face arrangement of **A** and **B** can be the result of crystal packing forces or repulsion minimalization. Moreover, a strong side-by-side π−π interaction has been found between the two vinylene groups of **A** and **C** in the LUMO and HOMO-2, resulting in repulsion between H−H. The angle between **A** and **C** releases the H−H repulsion and enables this π−π interaction between the π-orbitals of the vinylene groups.

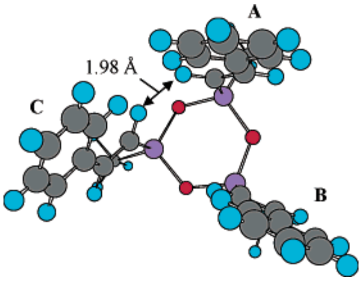


Figure 7. Alternative view of the X-ray crystal structure of **4-*cis*** from the top.

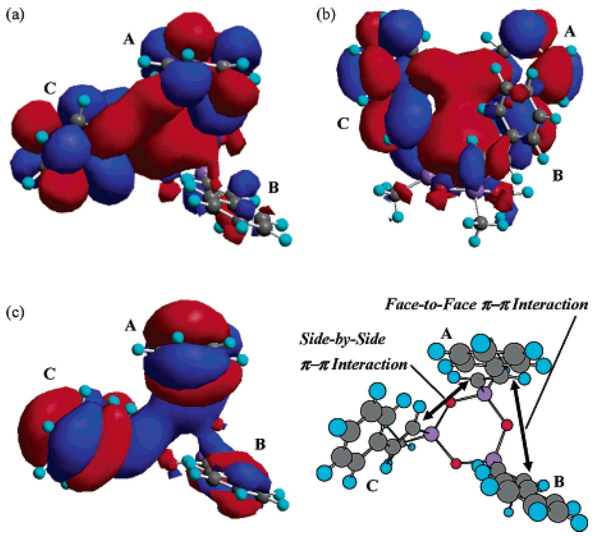


Figure 8. MO presentations of **4-*cis*** calculated with the HF/LAND2DZ basis set: (a) top view of LUMO; (b) side view of LUMO; (c) top view of HOMO-2.

The cyclosiloxy ring in **4-*cis*** adopts a flattened chair conformation with a mean dihedral angle of 22°, while *cis*-triphenylcyclotrisiloxane (**5**) has a more flattened, nearly planar conformation, with a mean dihedral angle of 8°. It seems that the cyclotrisiloxane ring, which usually tends to be flat, is distorted to a flattened chair conformation in **4-*cis*** due to the above-mentioned π−π interactions.

Catalyst **I** has also exhibited high conversion of tetravinylcyclotetrasiloxane D_4^{Vi} (**2**) and tetravinylcyclotetrasilazane (**3**) with styrene (Table 3), while metathesis has not occurred again as in the reaction of D_3^{Vi} (**1**). Cyclotetrasilazane (**3**) showed a slightly lower conversion than cyclosiloxanes (**1**, **2**), which may be due to the coordination of the nitrogen atom of silazane to ruthenium, which could reduce the reactivity of the complex.

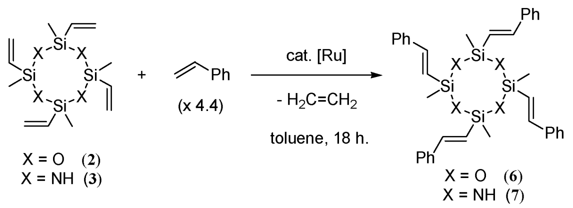
---

[14] Shklover, V. E.; Bokii, N. G.; Struchkov, Y. T.; Andrianov, K. A.; Zavin, B. G.; Svistunov, V. S. *Zh. Strukt. Khim.* **1974**, *15*, 841.

Table 2. Selected Bond Lengths [Å], Bond Angles [deg], and Torsion Angles [deg] of 4-*cis*

Si(1)−O(6)	1.630(2)	Si(1)−O(2)	1.648(2)
Si(1)−C(1)	1.831(4)		
Si(1)−C(11)	1.847(6)	Si(1)−C(11a)	1.882(19)
O(2)−Si(3)	1.610(2)	Si(3)−O(4)	1.633(2)
Si(3)−C(3)	1.828(3)		
Si(3)−C(31)	1.860(6)	Si(3)−C(31a)	1.88(4)
O(4)−Si(5)	1.637(2)	Si(5)−O(6)	1.635(2)
Si(5)−C(5)	1.837(3)	Si(5)−C(51)	1.839(3)
O(6)−Si(1)−O(2)	106.03(11)	Si(3)−O(2)−Si(1)	131.35(13)
O(2)−Si(3)−O(4)	106.62(11)	Si(3)−O(4)−Si(5)	131.70(13)
O(6)−Si(5)−O(4)	106.60(10)	Si(1)−O(6)−Si(5)	130.57(13)
O(6)−Si(1)−O(2)−Si(3)	25.1(2)	Si(1)−O(2)−Si(3)−O(4)	−21.8(2)
O(2)−Si(3)−O(4)−Si(5)	17.64(19)	Si(3)−O(4)−Si(5)−O(6)	−17.92(19)
O(2)−Si(1)−O(6)−Si(5)	−25.3(2)	O(4)−Si(5)−O(6)−Si(1)	22.5(2)

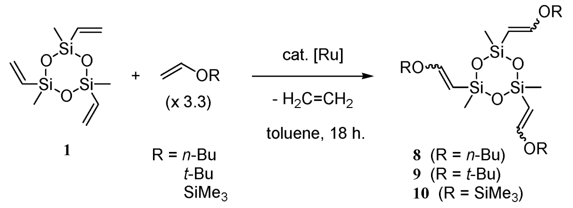
Table 3. Reaction of D_4^{Vi} (2) and Tetravinyltetracyclosilazane (3) with Styrene



substrate	[Ru]	mol %^{a}	temp (°C)	conversion^b (%)	yield (%)
2	**I**	0.1	80	>99	92
	II	1	40	10^c	
3	**I**	0.1	80	71 (>99)^d	83
	II	1	40	trace	

^{a} To vinylsilyl group. ^{b} Calculated by GC and NMR. ^{c} Mono only. ^{d} 0.2 mol % of **I**.

Table 4. Functionalization of D_3^{Vi} (1) with Vinyl Ethers



R	[Ru] (mol %^{a})	temp (°C)	conversion^b (yield, %)	*trans*/*cis*^{c}
	I (0.5)	80	>99% (77%)	58/42
n-Bu	**II** (1)	40	5%^{c}	
	II (1)	80	70%	55/45
	I (0.5)	80	>99% (85%)	72/28
t-Bu	**II** (1)	40	trace	
	II (1)	80	60%	69/31
	I (0.5)	80	>99% (53%)	37/63
SiMe$_3$	**II** (1)	40	trace	
	II (1)	80	52%	42/58

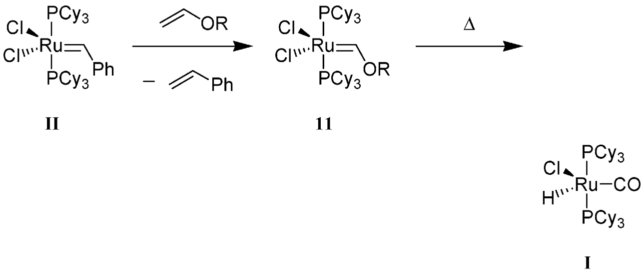
^{a} To vinylsilyl group. ^{b} Calculated by GC and NMR. ^{c} Calculated by NMR.

Table 5. Crystallographic Data for 4-*cis*

empirical formula	$C_{27}H_{30}O_3Si_3$
MW	486.78
cryst size (mm)	0.45 × 0.25 × 0.2
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.9650(7)
b, Å	11.1266(8)
c, Å	12.3097(11)
α, deg	88.446(7)
β, deg	79.827(7)
γ, deg	81.088(6)
V, Å^3	1327.2(2)
Z	2
ρ_{calcd}, g cm^{-3}	1.22
μ, mm^{-1}	1.85
R,^{a} wR2^b [$I > 2\sigma(I)$], %	5.90, 13.14

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Scheme 2. Thermal Transformation of Grubbs' Catalyst (II) with Vinyl Ethers



Analogous to tricyclosiloxane (**4**), geometrical isomers (theoretically four isomers) have been found also in cyclotetrasiloxane (**6**) and silazane (**7**), although isolation of these isomers has not succeeded.

Trivinylcyclotrisiloxane D_3^{Vi} (**1**) was successfully functionalized with various vinyl ethers (*n*-butyl, *tert*-butyl, and trimethysilyl) in the presence of ruthenium hydride complex (**I**) (Table 4), affording cyclosiloxanes bearing SiCH═CHOR fragments, which are difficult to construct in the other transition metal-catalyzed reactions.[12] Although a mixture of stereoisomers was observed in every case, functionalization occurred highly regioselectively without the α-isomer.

In the presence of ruthenium carbene complex (**II**) no reactions occurred at room temperature, as metathesis of vinyl ether did not occur due to a stable Fischer-carbene intermediate (**11**).[15,16] Notably, the reactions occurred when the reaction mixture was heated to 80 °C, due to thermal transformation of the Fischer-carbene complex (**11**) to the ruthenium carbonyl hydride complex (**I**) (Scheme 2),[11b,16] which is catalytically active in the silylative coupling reaction of vinyl ethers.[11b]

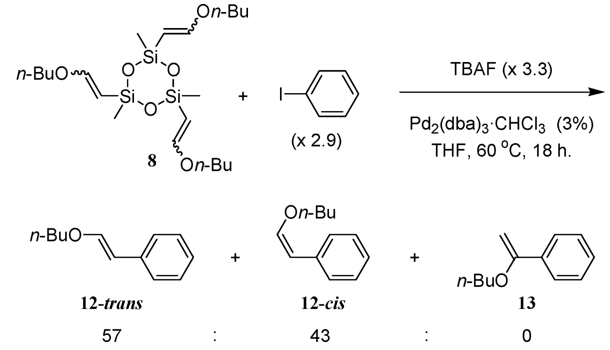
Hiyama coupling of the synthesized β-*n*-butoxyvinyl-substituted cyclotrisiloxane **8** with iodobenzene has been performed in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ as catalyst and TBAF (Scheme 3) to convert regioselectively to β-*n*-butoxystyrene (**12**).[17] The stereoselectivity of **12**

---

(15) Vinyl ethyl ether has been commonly used as quenching agent for ROMP, affording methylene-terminated polymer and inactive Fisher-carbene complex (**11**). See: Maynard, H. D.; Grubbs, R. H. *Macromolecules* **1999**, *32*, 6917.

(16) Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153. Wu, Z.; Nguyen, T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503.

Scheme 3. Hiyama Coupling Reaction of Tris(*β*-*n*-butoxyvinyl)cyclotrisiloxane (8) with Iodobenzene



was found to be 57:43 (*trans*:*cis*), equivalent to the selectivity of cyclosiloxane **8**. No α-substituted product **13** was formed, in contrast to the Mizoroki–Heck reaction between aryl iodide and butyl vinyl ether (or vinyl ethers), which generally lacks *β*-regioselectivity, giving α-substituted product selectively or giving a mixture of three isomers (*trans*, *cis*, *gem*).[18]

Conclusions

In this paper, new effective functionalizations of cyclosiloxanes and cyclosilazanes have been demonstrated via chemo- and regioselective silylative coupling reaction of vinyl-substituted initial compounds with olefins catalyzed by $RuHCl(CO)(PCy_3)_2$ (**I**), in contrast to the hydrosilylation process, which always gives a mixture of regioisomers. The reactions of vinylcyclosiloxanes and vinylcyclosilazane with styrene afforded styryl derivatives regio-, stereo-, and chemoselectively. X-ray crystal structure analysis of *cis*-1,3,5-tristyryl-1,3,5-trimethylcyclotrisiloxane (**4-*cis***) revealed a unique arranged structure, and peculiar intramolecular $\pi-\pi$ interactions in face-to-face and side-by-side manners have been found in the HOMO-1 level by MO calculations.

Trivinylcyclotrisiloxane reacted also with vinyl alkyl ethers, yielding efficiently tris(*β*-alkoxyvinyl)cyclotrisiloxanes, which are difficult to synthesize by other transition metal-catalyzed reactions. Further, Hiyama coupling reaction of the synthesized tris(*β*-*n*-butoxyvinyl)cyclotrisiloxane with iodobenzene gave *β*-*n*-butoxystyrene regioselectively.

Experimental Section

General Procedures. ^1H, ^{13}C, ^{29}Si NMR spectra were recorded on a Varian XL 300 MHz spectrometer in $CDCl_3$ or C_6D_6 solution. Chemical shifts are reported in δ ppm with reference to the residual protio-solvent ($CHCl_3$ or C_6H_6) peak for ^1H and ^{13}C and to TMS for ^{29}Si. Analytical gas chromatographic analyses were carried out on a Varian Star 3400CX gas chromatograph equipped with a DB-5 fused silica capillary column (30 m × 0.15 mm; Restock Inc.), and GC–MS with a Varian Saturn 2100T, equipped with a BD-5 30m capilary column and an ion trap detector. High-resolution desorption electron impact (DEI) mass spectra and FAB mass spectra were recorded on an AMD 402 mass spectrometer and an AMD 604 mass spectrometer (AMD Intectra GmbH.), respectively. Column chromatography was performed using silica gel 60 (70–230 mesh; Fluka) deactivated by hexamethyldisilazane prior to use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone, and toluene from sodium hydride under argon. $RuHCl(CO)(PCy_3)_2$ (**I**)[19] and $Pd_2(dba)_3{\cdot}CHCl_3$[20] were prepared according to the literature procedures, and Grubbs' catalyst ($Cl_2Ru({=}CHPh)(PCy_3)_2$; **II**, Aldrich) was purchased. 1,3,5-Trimethyl-1,3,5-trivinylcyclotrisiloxane (D_3^{Vi}, **1**, Gelest), 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^{Vi}, **2**, Gelest), 1,3,5,7-tetramethyl-1,3,5-tetravinylcyclotetrasilazane (**3**, Gelest), styrene (Fluka), *n*-butylvinyl ether (Aldrich), *tert*-butylvinyl ether (Aldrich), and trimethylsilylvinyl ether (Aldrich) were purchased, and distilled and degassed under argon prior to use. Iodobenzene (Fluka) and 1M THF solution of tetrabutylammonium fluoride (Aldrich) were purchased and used without any purification. All the reactions were carried out under an argon atmosphere.

Synthesis of 1,3,5-Trimethyl-1,3,5-tri-(*E*)-styrylcyclotetrasiloxane (4). A 7.5 mg (10.3 μmol) sample of **I**, 0.92 mL (3.44 mmol) of 1,3,5-trimethyl-1,3,5-trivinylcyclotatrasiloxane (D_3^{Vi} **1**), and 1.30 mL (11.4 mmol) of styrene were dissolved in 7 mL of toluene, and the mixture was stirred at 80 °C for 18 h. After complete conversion of the vinylsilyl groups was confirmed by ^1H NMR, volatiles were removed under vacuum. The remaining condensed oil was dissolved in 20 mL of pentane on gently heating, filtered off to remove polystyrene, evaporated to ca. 5 mL, and stored at −20 °C overnight to give a white precipitate. The precipitate was filtered off, washed by ice-cooled pentane (1 mL × 3), and dried under vacuo to afford 1.58 g (3.26 mmol) of **4** as a white powder in 95% yield. After fractional recrystallization from hexane (15 mL) at room temperature, **4-*trans*** (first fraction) and **4-*cis*** (third fraction) were isolated as a white powder (40%) and as a colorless crystal (15%), respectively.

4-*trans*. ^1H NMR ($CDCl_3$) δ (ppm): 0.42 (s, 3H), 0.44 (s, 6H), 6.41 (d, $J = 19.2$ Hz, 2H), 6.42 (d, $J = 19.5$ Hz, 1H), 7.19 (d, $J = 19.2$ Hz, 2H), 7.20 (d, $J = 19.5$ Hz, 1H), 7.27–7.44 (m, 9H), 7.52–7.55 (m, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): −0.06, 0.01, 124.06, 124.14, 126.68, 128.43, 128.48, 128.53, 128.59, 137.45, 137.49, 146.52, 146.70. ^{29}Si NMR ($CDCl_3$) δ (ppm): −20.68. HRMS: calc 486.15027, found 486.14846. Anal. Calcd for $C_{27}H_{30}O_3Si_3$: C 66.62; H 6.21. Found: C 66.43; H 6.13.

4-*cis*. ^1H NMR ($CDCl_3$) δ (ppm): 0.42 (s, 9H), 6.36 (d, $J = 19.5$ Hz, 3H), 7.14 (d, $J = 19.5$ Hz, 3H), 7.26–7.29 (m, 9H), 7.34–7.38 (m, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): −0.10, 124.10, 126.68, 128.51, 129.59 138.01, 146.61. ^{29}Si NMR ($CDCl_3$) δ (ppm): −20.55. MS (EI): 486 ($[M]^+$). Anal. Calcd for $C_{27}H_{30}O_3Si_3$: C 66.62; H 6.21. Found: C 66.54; H 6.26.

X-ray Crystal Structure Analysis of 4-*cis*. Single crystals of the complex were grown by slow evaporation from hexane solution. Accurate cell parameters were determined by a least-squares fit of 52 reflections (9° < 2θ < 78°). Diffraction data were collected by the $\omega-2\theta$ scan technique up to $2\theta = 150°$, on a KUMA KM4 four-circle diffractometer[21] with graphite-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å) at room temperature. All data were corrected for Lorentz–polarization effects[21] and absorption.[22] A total of 5479 reflections were collected, including 5249 unique ones ($R_{int} = 0.033$); of these 4476 were observed ($I > 2\sigma(I)$). The structure was solved with direct methods with SHELXS97[23] and refined by full-matrix

---

(17) *β*-Alkoxystyrene can be synthesized regioselectively via CsOH-catalyzed addition of alcohol to acetylene. Tzalis, D.; Koradin, C.; Knochel, P. *Tetrahedron Lett.* **1999**, *40*, 6193.

(18) (a) Vallin, K. S. A.; Larhed, M.; Hallberg, A. *J. Org. Chem.* **2001**, *66*, 4340. Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. Cabri, W.; Candiani, A. *Acc. Chem. Res.* **1995**, *28*, 2, and references therein. (b) *β*-Selective Heck reactions have reported for the modified (*β*-amino or *β*-phosphino) vinyl ethers, see: Larhed, M.; Anderson, C.-M.; Hallberg, A. *Tetrahedron* **1994**, *50*, 285. Badone, D.; Guzzi, U. *Tetrahedron Lett.* **1993**, *34*, 3603, and references therein.

(19) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043.

(20) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

(21) *KUMA Diffraction*, KM4 CCD diffractometer program system; Wroclaw, Poland, 1992.

least-squares procedure on F^2 with SHELXL97.[24] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined as a riding model with isotropic thermal parameters fixed at 1.2 times the U_{eq}'s of appropriate carrier atoms. Two C=C groups appeared to be disordered over two alternative positions, and site occupation factors were refined at 0.80(1)/0.20(1) for C11−C12 and 0.84(2)/0.16(2) for C31−C32. Anisotropic thermal parameters for the disordered carbon atoms were also refined.

Calculation. MO calculation of **4-*cis*** was performed using the Gaussian 98 program, with the HF/LAND2DZ basis set. Single-point energy was calculated applying geometry derived from the X-ray crystal structural data of **4-*cis***.

Synthesis of 1,3,5,7-Tetramethyl-1,3,5,7-tetra-(*E*)-styrylcyclotetrasiloxane (6). A 8.8 mg (12 μmol) sample of **I**, 1.05 mL (3.03 mmol) of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotatrasiloxane (D_4^{Vi} **2**), and 1.53 mL (13.3 mmol) of styrene were dissolved in 6 mL of toluene, and the mixture was stirred at 80 °C for 18 h. After complete conversion of the vinylsilyl groups was confirmed by ^{1}H NMR, volatiles were removed under vacuum. Then 20 mL of pentane was added to the remaining condensed oil and mixed on gentle heating. The solution was filtered off to remove polystyrene, evaporated to ca. 5 mL, and stored at −20 °C overnight. The precipitate was filtered off, washed by ice-cooled pentane (1 mL × 3), and dried under vacuo to afford 1.80 g (2.79 mmol) of **6** as a white powder in 92% yield. ^{1}H NMR δ (ppm): 0.358, 0.370, 0.376, 0.382, 0.393 (s, 12H), 6.40, 6.408, 6.411, 6.418, 6.427 (d, J = 19.5 Hz, 4H), 7.13, 7.15, 7.16, 7.18 (d, J = 19.5 Hz, 4H), 7.27−7.56 (m, 20H). ^{13}C NMR δ (ppm): −0.37, −0.32, −0.24, −0.16, 125.19, 126.72, 128.36, 128.44, 128.48, 128.53, 128.59, 137.80, 137.82, 137.89, 137.95, 145.98, 146.05, 146.11. ^{29}Si NMR δ (ppm): −30.59, −30.56, −30.45, −30.36. MS (EI, *m/z*): 648 ([M]$^+$). Anal. Calcd for $C_{36}H_{40}O_4Si_4$: C 66.62; H 6.21. Found: C 66.31; H 6.09.

Synthesis of 1,3,5,7-Tetramethyl-1,3,5,7-tetra-(*E*)-styrylcyclotetrasilazane (7). This compound was synthesized and isolated in essentially the same manner as **6** to afford **7** as a white powder in 83% yield. ^{1}H NMR (C_6D_6) δ: 0.34, 0.35, 0.36 (s, 12H), 6.57 (d, J = 19.5 Hz, 4H), 7.06−7.21 (m, J = 19.5 Hz, 3H), 7.26−7.29 (m, 16H), 7.34−7.38 (m, 8H). ^{13}C NMR (C_6D_6) δ: 2.02, 3.04, 3.20, 127.06, 127.40, 128.83, 130.71, 130.90, 131.08, 138.81, 138.88, 144.65, 144.80, 146.02. ^{29}Si NMR ($CDCl_3$) δ: 13.78. MS (FAB): 644 ([M]$^+$). Anal. Calcd for $C_{36}H_{44}N_4Si_4$: C 67.03; H 6.87. Found: C 66.87; H 6.91.

Silylative Coupling Reaction of 1,3,5-Trimethyl-1,3,5-trivinylcyclotrisiloxane (1) with Vinyl Alkyl Ethers. Synthesis of 1,3,5-Trimethyl-1,3,5-tris-(β-*n*-butoxyvinyl)-cyclotrisiloxane (8). A 7.8 mg (10.7 μmol) sample of **I**, 0.48 mL (1.79 mmol) of **1**, and 0.77 mL (5.9 mmol) of *n*-butyl vinyl ether were dissolved in 7.2 mL of toluene, and the mixture was stirred at 80 °C for 18 h. After the reaction completion was confirmed by GC, volatiles were removed under vacuum. The remaining condensed oil was passed through short-column chromatography (silica gel, hexane/CH_2Cl_2 = 1:1) to afford 0.65 g (1.38 mmol) of **8** as a colorless oil in 77% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.20, 0.21, 0.22, 0.23, 0.27, 0.28, 0.29, 0.30, 0.31 (s, 9H, CH_3Si), 0.88−0.94 (m, 9H, CH_3CH_2), 1.30−1.46 (m, 6H, $CH_2(CH_3)CH_2$), 1.54−1.67 (m, 6H, $CH_2(CH_2)CH_2$), 3.66−3.81 (m, 6H, $CH_2(CH_2)CH=$), 4.12−4.19 (m, 0.48 × 3H, =CH−Si (*cis*)), (m(d), J = 15.1 Hz, 0.52 × 3H, =CH−Si (*trans*)), 6.56−6.63 (m, 0.48 × 3H, =CH−O (*cis*)), 6.34−6.71 (m(d), J = 15.1 Hz, 0.52 × 3H, =CH−O (*trans*)). ^{13}C NMR ($CDCl_3$) δ (ppm): 0.28, 0.36, 0.40, 0.46, 0.48, 0.53, 0.65, 1.31, 1.37, 1.40, 1.46, 1.51, 1.61, 1.65, 1.77, 13.67, 13.71, 18.87, 19.12, 30.99, 31.83, 67.51, 67.60, 67.66, 67.80, 67.85, 72.21, 72.26, 72.34, 72.38, 72.41, 72.45, 72.48, 92.67, 92.98, 93.02, 93.29, 96.62, 96.71, 96.71, 96.92, 96.99, 97.26, 97.38, 158.86, 158.99, 159.16, 159.28, 159.41, 160.26, 160.34, 160.53, 160.78. ^{29}Si NMR ($CDCl_3$) δ (ppm): −23.17, −22.96, −22.92, −22.72, −22.65, −22.59, −22.57, −22.44, −22.27, −21.66, −19.68, −19.64, −19.61, −19.58, −19.39, −19.36, −19.33, −19.06. MS (EI, *m/z*): 474 ([M]$^+$). Anal. Calcd for $C_{21}H_{42}O_6Si_3$: C 53.12; H 8.92. Found: C 52.99; H 9.01.

Synthesis of 1,3,5-Trimethyl-1,3,5-tris(β-*tert*-butoxyvinyl)cyclotrisiloxane (9). This compound was synthesized and isolated in essentially the same manner as **8** to afford **9** as a colorless oil in 85% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.21, 0.22, 0.23, 0.24, 0.29, 0.30, 0.31, 0.32, 0.33, 0.34, 0.35 (s, 9H, CH_3Si), 1.24, 1.25, 1.26, 1.27, 1.28, 1.29, 1.30, 1.31, 1.32 (s, 27H, $(CH_3)_3C$), 4.17−4.21 (m(d), J = 8.5 Hz, 0.28 × 3H, =CH−Si (*cis*)), 4.58−4.69 (m(d), 0.72 × 3H, J = 14.3 Hz, =CH−Si (*trans*)), 6.68−6.74 (m(d), J = 14.3 Hz, 0.72 × 3H, =CH−O (*trans*)), 6.85−6.94 (m(d), J = 8.5 Hz, 0.28 × 3H, =CH−O (*cis*)). ^{13}C NMR ($CDCl_3$) δ (ppm): 0.53, 0.60, 0.63, 0.71, 0.96, 1.78, 1.84, 1.87, 1.98, 28.03, 28.17, 28.43, 96.07, 96.33, 96.51, 96.66, 96.73, 96.84, 97.08, 97.18, 987.68, 97.88, 98.20, 153.46, 153.62, 153.65, 153.83, 153.89, 154.05, 154.36, 154.53, 154.73, 154.82, 154.95, 155.09, 155.30. ^{29}Si NMR ($CDCl_3$) δ (ppm): −22.73, −22.69, −22.22, −21.88, −21.65, −20.19, −19.95, −19.88, −19.80, −19.65, −19.63. MS (EI, *m/z*): 474 ([M]$^+$). Anal. Calcd for $C_{21}H_{42}O_6Si_3$: C 53.12; H 8.92. Found: C 53.05; H 8.79.

Synthesis of 1,3,5-Trimethyl-1,3,5-tris(β-trimethylsiloxyvinyl)cyclotrisiloxane (10). This compound was synthesized and isolated in essentially the same manner as **8** to afford **10** as a colorless oil in 53% yield. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.22, 0.23, 0.24, 0.25, 0.26, 0.27, 0.28, 0.29, 0.30, 0.31, 0.32, 0.33, 0.34, 0.35 (s, 9H, $CH_3Si(CH=)O_2$), 1.24, 1.25, 1.26, 1.27,1.28, 1.29, 1.30, 1.31 (s, 27H, $(CH_3)_3Si$), 4.18−4.26 (m, 0.37 × 3H, =CH−Si (*cis*)), 4.59−4.70 (m(d), J = 14.4 Hz, 3H, 0.63 × 3H, =CH−Si (*trans*)), 6.68−6.75 (m(d), J = 14.4 Hz, 3H, 0.36 × 3H, =CH−O (*trans*)), 6.84−6.94 (m, 0.67 × 3H, =CH−O (*cis*)). ^{13}C NMR (C_6D_6) δ (ppm): −0.75, −0.49, −0.09, 0.41, 0.90, 1.02, 1.12, 1.88, 1.97, 2.23, 2.39, 2.52, 101.80, 102.27, 102.66, 102.97, 103.42, 103.59, 103.78, 104.03, 104.35, 152.81, 153.45, 153.72, 153.95, 154.54. MS (EI, *m/z*): 522 ([M]$^+$). Anal. Calcd for $C_{18}H_{42}O_6Si_6$: C 41.33; H 8.09. Found: C 41.51; H 7.98.

Pd-Catalyzed Coupling Reaction between 8 and Iodobenzene. A 0.45 mL (0.45 mmol) sample of THF solution (1 M) of tetrabutylammoniumfluoride was added to the THF (3.2 mL) solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (7.0 mg, 6.8 μmol), **8** (72 mg, 0.15 mmol), and iodobenzene (50 μL, 0.43 mmol), and the mixture was stirred at 60 °C for 18 h. The degree of conversion was calculated by GC and GC−MS analyses to 98%. The formation of compounds **12-*trans*** and **12-*cis*** was confirmed by ^{1}H NMR and GC−MS analyses, and their ratio was calculated to be 57:43. The absence of geminal product (**13**) was confirmed by ^{1}H NMR and ^{13}C NMR (DEPT) analyses.

Acknowledgment. We thank the Polish Committee for Scientific Research for financial support (Grant No. K012/T09).

Supporting Information Available: MO presentations of **4-*cis*** and crystallographic parameters and data for **4-*cis*** in CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0303505

---

(22) Blessing, R. H. *J. Appl. Crystallogr.* **1989**, *22*, 396−397.

(23) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

(24) Sheldrick, G. M. *SHELXL93*, Program for the refinement of crystal structures; University of Gottingen: Germany, 1993.