A New Catalytic Route to Monoalkynyl-Functionalized Di- and Trivinyl-Substituted Cyclosiloxanes and Divinylcyclosilazanes

Beata Dudziec and Bogdan Marciniec*

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

Received April 24, 2008

Series of alkynyltrimethyldivinylcyclotrisiloxanes and -trisilazanes, and of alkynyltetramethyltrivinylcyclotetrasiloxanes have been synthesized by means of a new catalytic coupling of the appropriate tri- and tetra-vinylcyclosiloxanes (**1**, **2**) and trivinylcyclosilazane (**3**) with terminal alkynes R-C≡C−H (where R = $SiEt_3$, $SiMe_2Ph$, $GeEt_3$, or alkyl) in the presence of a ruthenium hydride complex [$RuHCl(CO)(PCy_3)_2$] (**I**), as a catalyst. Twenty-one new functionalized monoalkynyl-substituted cyclosiloxanes and cyclosilazanes were isolated in high to moderate (70−95%) yields and characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. Selected alkynyldivinyl- and alkynyltrivinyl-cyclic products have been further functionalized by silylative coupling of the remaining vinyl groups with styrene to give cyclosiloxanes and cyclosilazanes containing one alkynyl and two or three styryl substituents at silicon in high yields and selectivity ((*E*)-styryl products).

Introduction

Functionalized cyclosiloxanes and cyclosilazanes have been used as the basic substrates for anionic and cationic ring opening polymerization (copolymerization) to yield the respective large class of modified silicon polymers (polysiloxanes, siloxane-containing block polymers polysilazanes) that find wide use as basic siloxane materials (coatings, resists liquid crystal membranes, etc.).[1] Various substituted cyclosiloxanes and cyclosilazanes also have been applied as novel π-ligands in transition metal complexes[2] or as a key material for ladder oligosiloxanes,[3] direct potential precursors of miscellaneous silsesquioxanes. Simultaneously, alkenyl (vinyl, aryl)-cyclosiloxanes can be used as a core for carbosilane (siloxane) dendrimers.[4] Moreover, those silicon compounds that possess π-conjugated systems have been considered to be potential precursors of optoelectronic materials, particularly candidates for electronic devices.[5]

The presently available methods for direct functionalization of cyclosiloxanes and cyclosilazanes are limited. Apart from the hydrosilylation process,[6] the main procedure for modification of these compounds, such functionalized organosilicon materials have been synthesized via hydrolysis and amonolysis of functionalized monomeric silanes.[7] However, these methods have some limitations, for example, difficulty in introducing functional groups sensitive to moisture.[8]

However, alkynyl-silicon derivatives can be prepared by various procedures involving classical stoichiometric routes using organometallic reagents[9] as well as by metal-catalyzed silylation of terminal alkynes.[10]

The well-known transition-metal (TM)-catalyzed reactions (developed by our group) of vinyl-substituted silicon compounds with olefins, called silylative coupling (*trans*-silylation), are based on the activation of the sp^2-hybridized carbon−hydrogen bond (=C_{vinyl}-H) and sp^2-hybridized carbon−silicon bond (=C_{vinyl}-Si≡) (for a recent review, see ref 11). This process seems to be complementary to olefin metathesis (for comparison of these reactions, see ref 12) but proceeds according to the following general scheme (Scheme 1) in the presence of metal (Ru, Rh, Ir, Co, and Fe) complexes initially containing or generating M-H and/or M-Si bonds. [11,12]

* Corresponding author. Fax: (+48) 61-8291-508. E-mail: marcinb@amu.edu.pl.

(1) (a) *Silicon-Containing Polymers*; Jones, R. G., Ando, W., Chojnowski, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000. (b) *Silicon in Organic, Organometallic and Polymer Chemistry*; Brook, M. A., Ed.; John Wiley & Sons: New York, 2000. (c) *Progress in Organosilicon Chemistry*; Marciniec, B., Chojnowski, J., Eds.; Gordon and Breach Publishers: Amsterdam, 1995.

(2) (a) Maciejewski, H.; Kubicki, M.; Marciniec, B.; Sydor, A. *Polyhedron* **2002**, *21*, 1261–1265. (b) Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *J. Organomet. Chem.* **2000**, *605*, 221–225. (c) Harrod, J. F.; Shaver, A.; Tucka, A. *Organometallics* **1985**, *4*, 2166–2170. (d) Rybinskaya, M. I.; Rybin, L. V.; Pogrebnyak, A. A.; Nurtdinova, G. V.; Yur'ev, V. P. *J. Organomet. Chem.* **1981**, *217*, 373–383.

(3) Unno, M.; Chang, S.; Matsumoto, H. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1105–1109.

(4) Kim, C.; Park, J. *J. Organomet. Chem.* **2001**, *629*, 194–200.

(5) (a) Ding, L.; Wong, H.; Xiang, H.; Poon, S.; Karasz, F. E. *Synth. Met.* **2006**, *156*, 110–116. (b) Majchrzak, M.; Ludwiczak, M.; Bayda, M.; Marciniak, B.; Marciniec, B. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 127–128.

(6) (a) Alonso, B.; González, B.; Garcia, B.; Ramirez-Olivia, E.; Zamora, M.; Casado, C. M.; Cuadrado, I. *J. Organomet. Chem.* **2001**, *637−639*, 642–652. (b) Zhang, Z.; Lyons, L. J.; Jin, J. J.; Amine, K.; West, R. *Chem. Mater.* **2005**, *17*, 5646–5650.

(7) (a) Makarova, N. N.; Volkova, L. M.; Matukhina, E. V.; Kaznacheev, A. V.; Petrovskii, P. V. *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 1610–1620. (b) Ronchi, M.; Pizzotti, M.; Orbelli Biroli, A.; Macchi, P.; Lucenti, E.; Zucchi, C. *J. Organomet. Chem.* **2007**, *692*, 1788–1798. (c) Veith, M.; Rammo, A.; Huppert, J.; David, J. C. R. *Chimie* **2003**, *6*, 117–124. (d) Abe, Y.; Suyama, K.; Gunji, T. *Chem. Lett.* **2006**, *35*, 114–115.

(8) Birkofer, L.; Stuhl, O. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rapport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 1, Chapter 10.

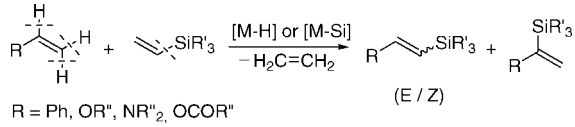
(9) (a) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981; p 165. (b) Brandsma, L.; Verkruijsse, H. D. *Synthesis* **1999**, 1727–1728.

(10) (a) Anreev, A. A.; Konshin, V. V.; Komarov, N. V.; Rubin, M.; Brouwer, C.; Gevorgyan, V. *Org. Lett.* **2004**, *6*, 421–424. (b) Yang, L.-M.; Huang, L.-F.; Luh, T.-Y. *Org. Lett.* **2004**, *6*, 1461–1463. (c) Shimizu, R.; Fuchikami, T. *Tetrahedron Lett.* **2000**, *41*, 907–910. (d) Fürstner, A. Mathes, Ch. *Org. Lett.* **2001**, *3*, 221–223. (e) Fletcher, M. D. In *Comprehensive Organic Functional Group Transformations II*; Katritzky, A. R., Taylor, R. J. K., Eds.; Elsevier: Amsterdam, 2005; Vol. 2, pp 1181−1189 and references therein.

(11) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374–2390.

10.1021/om800361k CCC: $40.75
Publication on Web 10/09/2008

Scheme 1. Silylative Coupling of Olefins with Vinyl-Substituted Organosilicon Compounds

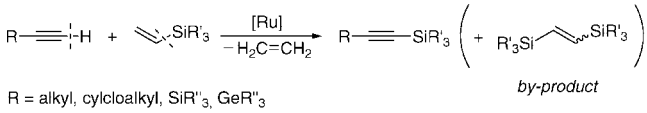


R = Ph, OR", NR"$_2$, OCOR"

R' = alkyl, aryl, alkoxyl

M = Ru, Rh, Ir

Scheme 2. Silylative Coupling of Terminal Alkynes with Organosilicon Compounds



R = alkyl, cylcloalkyl, SiR''$_3$, GeR''$_3$

R' = alkyl, alkoxyl

product of homocoupling of vinylsilane

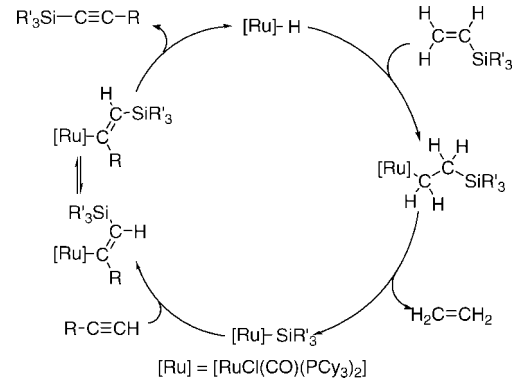
Silylative coupling of vinylsiloxanes and cyclosilazanes with various olefins, that is, selective synthesis of functionalized products,[13] constitutes an alternative synthetic route to cross-metathesis, which cannot be applied to methylvinyl-substituted silicon compounds (MeViSiR^{1}R^2).[11,12]

We have also reported the activation of *sp*-hybridized carbon−hydrogen bonds (≡CH) in reaction with vinylsilicon compounds.[14] This process (see Scheme 2), the cross-coupling of alkynes with vinylsilicon compounds, requires the presence of ruthenium complexes containing [Ru]-H and/or [Ru]-Si bonds. Only in some cases were the desired substituted alkynylsilanes accompanied by product of homocoupling of the vinylsilicon compounds when they were used in excess.

This new catalytic activation of *sp*-hybridized carbon−hydrogen bonds by the vinylsilicon compounds proceeds via mechanistic pathways, which are well documented for the silylation of olefins,[11,12] that is, the insertion of the alkyne into the Ru−Si bond (via a route proposed earlier[14,15]), β-H elimination to give the substituted alkynylsilanes and recovery of the [Ru]-H complex, and a well-known insertion of the vinylsilicon compound into the Ru−H bond followed by the β-Si elimination of ethylene. Dissociation of the phosphine ligand is postulated to generate the active ruthenium catalyst (Scheme 3).

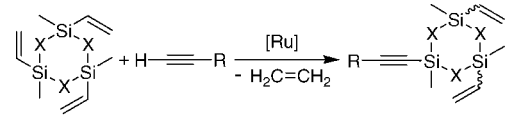
In this article, we report examples of effective regio- and chemoselective silylative coupling of methylvinyl-substituted cyclosiloxanes D_3^{Vi} (**1**) and D_4^{Vi} (**2**) as well as trimethyltrivinylcyclotrisilazane (**3**) with selected terminal alkynes. These reactions are catalyzed by a ruthenium hydride complex, [RuHCl(CO)(PCy$_3$)$_2$] (**I**), which has been found to be the most active and selective catalyst.[14] To the best of our knowledge, there are no reported examples of alkynyl-substituted cyclosiloxanes or cyclosilazanes that have been prepared by any previously known method.

Scheme 3. Mechanism of Coupling of Alkynes with Vinylsilicon Compounds



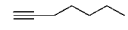
[Ru] = [RuCl(CO)(PCy$_3$)$_2$]

Table 1. Reaction of D_3^{Vi} (1) and 1,3,5-Trimethyl-1,3,5-trivinylcyclotrisilazane (3) with Terminal Alkynes (t = 24 h)



X = O (**1**)

X = NH (**3**)

Alkyne	Substrate	Molar Ratio Catalyst: Substrate: Alkyne	Conversion of Alkyne [%]	Isolated Product Yield[%]
HC≡CSiEt$_3$	1[a]	0.01:1.5:1	89	80
	3[b]	0.02:2:1	80	75
HC≡CSiMe$_2$Ph	1[a]	0.02:1.3:1	85	80
	3[b]	0.02:2:1	81	74
HC≡CGeEt$_3$	1[a]	0.02:1.4:1	82	76
	3[b]	0.02:2:1	80	73
	1[a]	0.02:1.5:1	85	76
	3[b]	0.02:2:1	85	75
	1[a]	0.02:1.5:1	82	74
	3[b]	0.02:2:1	78	70
	1[a]	0.02:1.3:1	100	90
	3[b]	0.02:2:1	94	85
	1[a]	0.01:1.5:1	100	95
	3[b]	0.01:1.5:1	96	90

[a] Toluene [0.25 M], T = 110 °C accompanied by traces of dialkynyl-substituted cyclotrisiloxane. [b] Toluene [0.5 M], T = 120 °C.

Results and Discussion

The functionalization of trimethyltrivinylcyclotrisiloxane D_3^{Vi} (**1**) and trimethyltrivinylcyclotrisilazane (**3**) with selected terminal alkynes (Table 1) was effectively catalyzed by [RuHCl(CO)(PCy$_3$)$_2$] (**I**) at 1−2 mol% loading and was highly regio- and chemoselective to produce the monoalkynyl-substituted cyclotrisiloxane and cyclotrisilazane. Only for D_3^{Vi} was the desired product accompanied by trace amounts of dialkynyl-substituted cyclosiloxane. The conversion of the cyclotrisilazane (**3**) was slightly lower than that for cyclotrisiloxane (**1**) because of possible coordination of the nitrogen atom to the ruthenium center that could be responsible for reduction of the catalytic

(12) (a) Marciniec, B.; Pietraszuk, C.; Kownacki, I.; Zaidlewicz, M. Vinyl- and Arylsilicon, Germanium, and Boron Compounds. In *Comprehensive Organic Functional Group Transformations II*; Katritzky, A. R., Taylor, R. J. K., Eds.; Elsevier: Amsterdam, 2005; Vol. 1, pp 941−1024. (b) Marciniec, B.; Pietraszuk, C. *Curr. Org. Chem.* **2003**, *7*, 691–735. (c) Marciniec, B.; Pietraszuk, C. Metathesis of Silicon-containing Olefins. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Verlag Chemie, 2003; Chapter *2.13*, pp 455−482.

(13) (a) Itami, Y.; Marciniec, B.; Kubicki, M. *Organometallics* **2003**, *22*, 3717–3722. (b) Marciniec, B.; Waehner, J.; Pawluc, P.; Kubicki, M. *J. Mol. Catal.* **2007**, *265*, 25–31.

(14) Marciniec, B.; Dudziec, B.; Kownacki, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 8180–8184.

(15) Marciniec, B. *Acc. Chem. Res.* **2007**, *40*, 943–952.

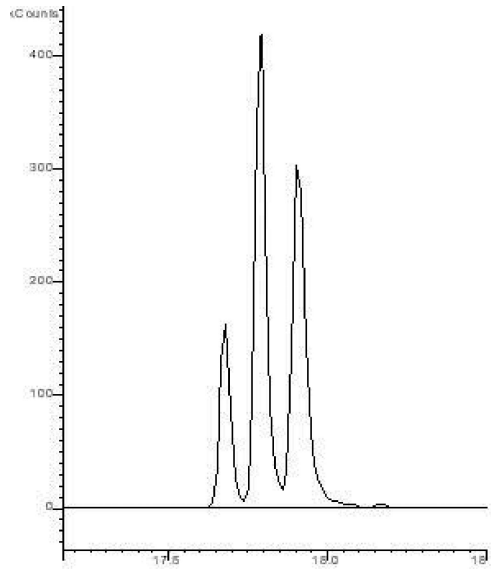


Figure 1. GCMS chromatogram of the products of silylative coupling of (**1**) and (**3**) with terminal alkynes.

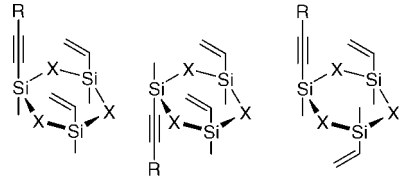


Figure 2. Possible isomers of monoalkynyl-substituted divinylcyclotrisiloxane (divinylcyclotrisilazane).

activity. In some examples, a larger excess (2 equiv) of cyclotrisilazane (**3**) was required to achieve satisfying product yields.

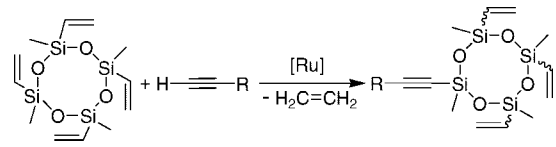
The trisiloxane D_3^{Vi} (**1**) and trimethyltrivinylcyclotrisilazane (**3**) consist of two isomers (*cis* and *trans*), which are inseparable, and consequently, the products of the silylative coupling of vinylcyclotrisiloxane (cyclotrisilazane) with selected terminal alkynes also are a mixture of diastereoisomers. Three diastereoisomers were obtained in each of these reactions (Figure 1), and this is consistent with the number of theoretically possible isomers (Figure 2).

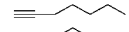
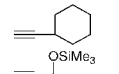
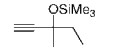
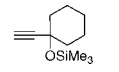
Similar to the silylative coupling reactions of trivinyl-substituted silicon compounds with selected terminal alkynes described above, catalyst (**I**) was the most effective also in the case of tetramethyltetravinylcyclotetrasiloxane D_4^{Vi} (**2**), and high conversions of (**2**) were observed (Table 2). The reactions were regio- and chemoselective to give monoalkynyl-substituted trivinylcyclotetrasiloxanes.

Because the D_4^{Vi} was a mixture of geometrical isomers (impossible to isolate), the resulting product, monoalkynyl-substituted cyclotetrasiloxane, also was a mixture of at least four diastereoisomers (broad peak) (Figure 3). Albeit in this case, the theoretical prediction gives five diastereoisomers (Figure 4). (The broad peak of the GCMS chromatogram may suggest that these are more likely not completely resolved five singlets rather than four, as is presented below.)

trans-Silylation of D_3^{Vi}, D_4^{Vi}, and tetramethyltetravinylcyclotetrasilazane with styrene was reported previously to be an effective and selective route to (*E*) tri- and tetrastyryl-substituted cyclosiloxanes and cyclosilazanes.[13] We tried to exploit this technique to perform further functionalization of the remaining

Table 2. Reaction of D_4^{Vi} with Terminal Alkynes (t = 24 h; toluene [0.25 M]; T = 110 °C)



Alkyne	Molar Ratio Catalyst: Substrate: Alkyne	Conversion of Alkyne [%]	Isolated Product Yield [%]
HC≡CSiEt$_3$	0.02:1.3:1	80	70
HC≡CSiMe$_2$Ph	0.02:1.3:1[a]	80	74
HC≡CGeEt$_3$	0.02:1.3:1[a]	100	94
	0.02:1.3:1	100	93
	0.02:1.3:1	89	82
	0.02:1.4:1	98	90
	0.01:1.1:1	100	90

[a] T = 120 °C.

vinyl groups at the silicon atoms of alkynyl-vinyl-substituted cyclic products. Selected monoalkynyl-substituted divinylcyclotrisiloxanes, divinylcyclotrisilazanes, and trivinylcyclotetrasiloxanes were successfully used in the silylative coupling reaction with styrene in the presence of ruthenium catalyst (**I**), yielding alkynyl-(*E*)-styryl-functionalized cyclic derivatives (Table 3). Since the substrates were a mixture of geometrical isomers, the resulting products also are a mixture of isomers.

All of these isolated products were characterized by ^{1}H, ^{13}C NMR spectroscopy, and the coupling constants of protons at carbon double bond atoms (J_{H-H} = 19 Hz) give evidence of the (*E*) geometry of the sp^2-hybridized carbon−carbon bonds (C═C).

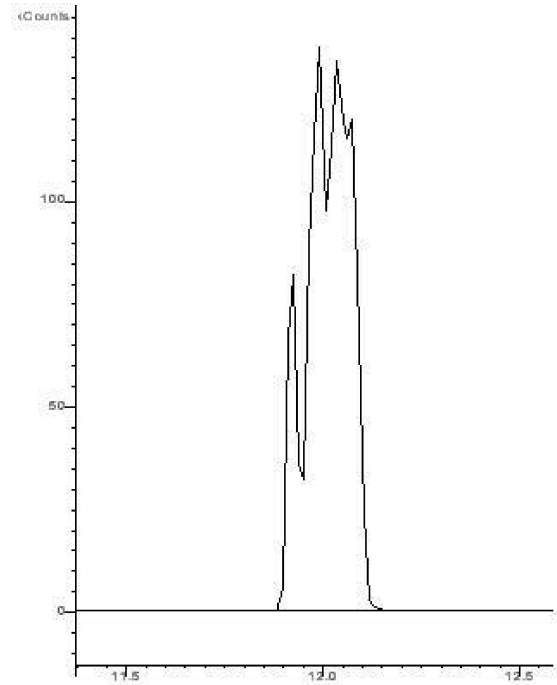


Figure 3. GCMS chromatogram of the products of silylative coupling of (**2**) with terminal alkynes.

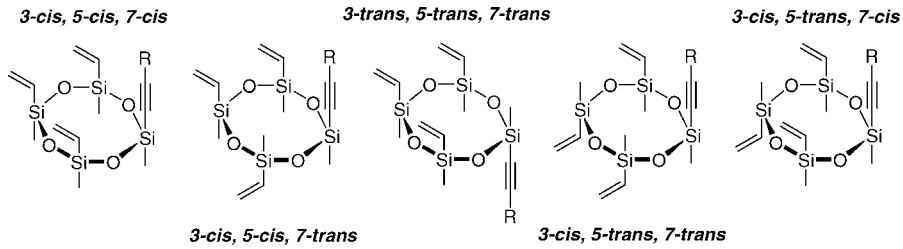
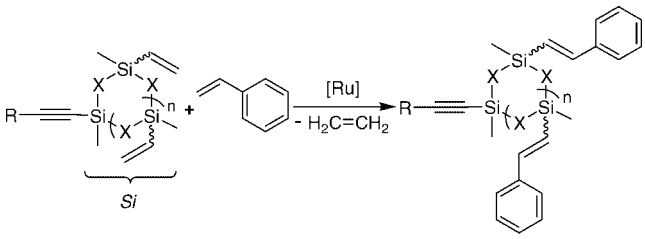
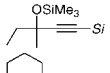
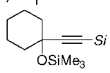
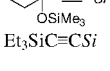


Figure 4. Possible isomers of monoalkynyl-substituted trivinylcyclotetrasiloxane.

Table 3. Reaction of Monoalkynyl-Substituted Divinylcyclotrisiloxanes, Divinylcyclotrisilazanes, and Trivinylcyclotetrasiloxanes with Styrene (t = 24 h; toluene [0.5 M]; T = 90 °C)



RC≡C*Si*	X, n	Molar Ratio Catalyst: RC≡C*Si* : Styrene	Conversion [%]	Isolated Product Yield [%]
$Et_3GeC{\equiv}CSi$	O, 1	0.01:1:6	95	90
	O, 1	0.01:1:6	98	92
	NH, 1	0.01:1:6	90	85
	O, 2	0.01:1:9	97	90
$Et_3SiC{\equiv}CSi$	O, 2	0.01:1:9	95	89

Conclusions

This article describes a new effective functionalization of vinyl-substituted cyclosiloxanes and cyclosilazanes via their regioselective silylative coupling reaction with terminal alkynes, catalyzed by [RuHCl(CO)(PCy_3)$_2$] (**I**), to yield monoalkynyl-substituted organosilicon compounds. Selected products of these reactions were applied to further modification of the remaining vinyl groups attached to the silicon atoms by *trans*-silylation with styrene.

Experimental Section

General Procedures. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian XL 300 MHz spectrometer in $CDCl_3$ solution. Chemical shifts are reported in δ (ppm) with reference to the residual portion solvent (CH_3Cl) peak for ^{1}H, ^{13}C, and Si(CH_3)$_4$ for ^{29}Si. Gas chromatographic (GC) analyses were performed on a Varian 3300 with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra of the reagents and products were obtained by GCMS analysis (Varian Saturn 2100T, equipped with a CP-SIL 6CB column (30 m × 0.25 mm) and an ion trap detector). Column chromatography was conducted with silica gel 60 (70−230 mesh, Fluka), deactivated by hexamethyldisilazane prior to use, when needed. Toluene and pentane were dried by distillation from sodium hydride, and similarly, hexane was distilled from calcium hydride under argon. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon. All of the reactions were carried out under dry argon.

Materials. The chemicals were obtained from the following sources: toluene, decane, pentane, and hexane (Fluka); 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (D_3^{Vi}, Gelest); 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^{Vi}, Gelest); 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane (Fluka); triethyl(ethynyl)silane (Gelest); ethynylcyclohexane (Sigma-Aldrich); 1-heptyn (Sigma-Aldrich); 1-ethynylcyclohexanol (Sigma-Aldrich); 3-methyl-1-pentyn-3-ol (Sigma-Aldrich); chlorodimethyl(phenyl)silane (Gelest); bromotriethylgermane (Gelest); 0.5 M THF solution of ethynylmagnesium bromide (Sigma-Aldrich). The triethyl(ethynyl)germane was prepared according to the literature procedure.[16] The ruthenium complex [RuHCl(CO)(PCy_3)$_2$] (**I**) was prepared according to the literature procedure.[17] All liquid substrates were also dried and degassed by bulb-to-bulb distillation under argon prior to use. All of the reactions were carried out under dry argon.

Preparation of Terminal Alkynes. Ethynyldimethylphenylsilane. This compound was prepared in a manner similar to that used for triethyl(ethynyl)silane, according to the literature procedure;[16] yield, 83%. Analytic data: ^{1}H NMR $CDCl_3$; δ (ppm): 0.46 (s, 6H, SiCH_3); 2.53 (s, 1H, Si−C≡CH); 7.39−7.67 (m, 5H, C_6H_5). ^{13}C NMR $CDCl_3$; δ (ppm): −0.99 (SiCH$_3$); 88.14 (Si-C≡CH); 94.74 (Si−C≡CH); 127.85, 129. 49, 133.52 (C_6H$_5$); 136.07 (c_i-C_6H$_5$).

1-Ethynyl-1-(trimethylsilyloxy)cyclohexane. A solution of 80 mL of dried and deoxidized tetrahydrofuran (THF), 5 g (40.26 mmol) of 1-ethynyl-1-cyclohexanol, and 10.08 mL (48.32 mmol) of hexamethyldisilazane (HMDS) was placed into a flame-dried two-necked, 250 mL round-bottomed flask equipped with a magnetic stirring bar, rubber septum cap, a condenser, and an argon bubbling tube. Then, 7.65 mL (60.39 mmol) of chlorotrimethylsilane was added dropwise to the above solution. The mixture was heated at reflux on stirring until the disappearance of the 1-ethynyl-1-cyclohexanol (confirmed by GC). The crude product was purified by distillation (bp 50 °C/0.5 mmHg) yielding 5.93 g (82%) of 1-ethynyl-1-(trimethylsilyloxy)cyclohexane. The compound was synthesized according to the modified literature procedure.[18]

^{1}H NMR ($CDCl_3$) δ (ppm): 0.19 (s, 9H, OSi(CH_3)$_3$); 1.17−1.21 (m, 2H, C_6H_{10}); 1.46−1.67 (m, 4H, C_6H_{10}); 1.84−1.88 (m, 4H, C_6H_{10}); 2.48 (s, 1H, C≡CH). ^{13}C NMR ($CDCl_3$) δ (ppm): 2.19 (Si(CH$_3$)$_3$); 23.12 (C_6H_{10}); 25.28 (C_6H_{10}); 41.16 (C_6H_{10}); 69.82 (c_i-C_6H_{10}); 73.27(C≡CH); 87.98 (C≡CH). MS (70 eV) m/z (%): 181 (100) [M^+ − CH_3], 167 (11), 153 (29), 105 (3), 91 (4), 79 (15), 73 (24), 45 (11).

3-Methyl-3-(trimethylsilyloxy)pent-1-yne. This compound was prepared as described above, yielding 86% of pure product. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.18 (s, (CH_3)$_3$SiO); 0.96−1.01 (tr, J_{H-H} = 7.4 Hz, CH_3CH$_2$C); 1.44 (s, CH_3C); 1.60−1.67 (qu, J_{H-H} = 7.1 Hz, CH$_3$CH_2C); 2.42 (s, C≡CH). ^{13}C NMR ($CDCl_3$) δ (ppm): 1.89 ((CH_3)$_3$SiO); 8.89 (CH$_3$CH$_2$C); 30.60 (CH$_3$C); 37.81 (CH$_3$$CH_2$); 69.79 (CH$_3$$C$); 72.17 (C≡$C$H); 87.93 ($C$≡CH). MS (70 eV) m/z (%):155 (45) [M^+ − CH_3], 141 (100) [M^+ − CH_2CH_3], 129 (21), 83 (14), 73 (40), 45 (16).

(16) Marciniec, B.; Ławicka, H.; Dudziec, B. *Organometallics* **2007**, *26*, 5188–5192.

(17) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043–2045.

(18) Medvedeva, A. S.; Novokshonov, V. V.; Mareev, A. V.; Borisova, A. I. *Russ. J. Org. Chem.* **2003**, *39*, 336–339.

Representative Procedures for Catalytic Reactions. Synthesis of 1-alkynyl-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane, 1-alkynyl-1,3,5-trimethyl-3,5-divinylcyclotrisilazane, and 1-alkynyl-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane: In a typical experiment, the ruthenium catalyst [RuHCl(CO)(PCy_3)$_2$] (**I**) (1−2 mol%) was dissolved in toluene and placed in a glass ampule under argon. The reagents and decane (as internal standard, 5% by volume of all components), vinylcyclosiloxane, or vinylcyclosilazane and the acetylene (usually used in the molar ratio [Ru]:[H_2C═CHSi]:[HC≡CR] = (0.01−0.02):(1.1−2):1) were added. Subsequently, the ampule was heated to 110 °C or to 120 °C and maintained at that temperature for 24 h. The progress of the reaction was monitored by GC and GCMS. The final products were separated from the residues of the catalyst and reactants by purification on an SiO_2 column (modified with 15% of Et_3N when needed) with hexane as eluent. All products of catalytic transformation of terminal alkynes with vinylcyclosiloxanes and vinylcyclotrisilazane were colorless or pale yellow oily liquids.

Silylative Coupling of 1-Alkynyl-vinyl-Substituted Cyclosiloxanes and Cyclosilazane with Styrene. In a typical experiment, the ruthenium catalyst [RuHCl(CO)(PCy_3)$_2$] (**I**) (1 mol%) was dissolved in toluene and placed in a glass ampule under argon. Subsequently, the reagents were added (used in the molar ratio [Ru]:[H_2C═CHSi]:[H_2C═CH(C_6H_5)] = 0.01:1:3 (per each vinyl group at silicon). Then, the ampule was heated to 90 °C and maintained at that temperature for 24 h; the progress of the reaction was monitored by GC and GCMS. The final product was separated from the residues of the catalyst and the remains of styrene by purification on an SiO_2 column (modified with 15% of Et_3N, when needed) with hexane as eluent.

Analytic Data of Isolated Products. (1) The spectroscopic data of 1-alkynyl-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane, 1-alkynyl-1,3,5-trimethyl-3,5-divinylcyclotrisilazane, and 1-alkynyl-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane, obtained for the mixture of isomers (the name of each compound excludes the presence of diastereoisomers), are presented in three groups.

(a). 1-Alkynyl-1,3,5-trimethyl-3,5-divinylcyclotrisiloxanes. 1-[(Triethylsilyl)ethynyl]-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.25, 0.27, 0.29, 0.30, 0.34, 0.36 (s, CH_3Si); 0.56−0.66 (m, CH_3CH_2); 0.90−1.03 (m, CH_3CH_2); 5.91−6.06 (m, H_2C═CHSi). ^{13}C NMR ($CDCl_3$) δ (ppm): −0.96 (CH_3Si); 4.22 (CH_3CH_2); 7.43 (CH_3CH_2); 109.98, 110.78 (C≡C); 134.32−135.22 (H_2C═CHSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −37.35; −37.56; −37.68; −19.10. MS (70 eV) *m*/*z* (%): 341 (76) [M^+-CH_2CH_3], 314 (78), 285 (100), 259 (9), 93 (23), 59 (14), 45 (11). Anal. Calcd. for $C_{15}H_{30}O_3Si_4$: C, 48.59; H, 8.16. Found: C, 48.64; H, 8.23.

1-[(Dimethylphenylsilyl)ethyny]l-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.25, 0.26, 0.28, 0.30, 0.34, 0.36, 0.38, 0.40, 0.41, 0.43, 0.44 0.46 (s, CH_3Si, Si(CH_3)$_2$Ph); 5.89−6.08 (m, H_2C═CHSi); 7.35−7.65 (C_6H_5Si). ^{13}C NMR ($CDCl_3$) δ (ppm): (−1.01)−1.13 (CH_3Si, Si(CH_3)$_2$Ph); 110.04, 111.24 (C≡C); 127.60−139.69 (H_2C═CHSi, C_6H_5Si). ^{29}Si NMR ($CDCl_3$) δ (ppm): −37.28; −37.65; −37.77; −19.46. MS (70 eV) *m*/*z* (%): 390 (10) [M^+-CH_3], 375 (100), 347 (43), 297 (10), 247 (11), 193 (14), 135 (7), 73 (7), 45 (10). Anal. Calcd. for $C_{17}H_{26}O_3Si_4$: C, 52.26; H, 6.71. Found: C, 52.35; H, 6.84.

1-[(Triethylgermyl)ethynyl]-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.24, 0.26, 0.28, 0.30, 0.32, 0.34, 0.36, 0.37 (s, CH_3Si); 0.82−0.91 (m, CH_3CH_2Ge); 1.03−1.12 (m, CH_3CH_2Ge); 5.87−6.07 (m, H_2C═CHSi). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.94)−1.45 (CH_3Si); 5.66−5.99 (CH_3CH_2Ge); 8.99−9.07 (CH_3CH_2Ge); 109.67, 110.74 (C≡C); 133.21−136.24 (H_2C═CHSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −37.28; −37.65; −37.77. MS (70 eV) *m*/*z* (%): 387 (31) [(M^++H)-CH_2CH_3], 359 (100), 329 (25), 301 (7), 203 (8), 192 (6), 177 (6). Anal. Calcd. for $C_{15}H_{30}GeO_3Si_3$: C, 43.38; H, 7.28. Found: C, 43.42, H, 7.32.

1-(1-Heptynyl)-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.22, 0.24, 0.26, 0.27, 0.28, 0.30, 0.32 (s, CH_3Si); 0.32−2.25 (m, $CH_3CH_2CH_2CH_2CH_2$); 5.83−6.12 (m, H_2C═CHSi). ^{13}C NMR ($CDCl_3$) δ (ppm): −0.84−1.59 (CH_3Si); 13.81−31.01 (C_5H_{11}); 81.36, 106.27 (C≡C); 134.23−135.32 (H_2C═CHSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −37.22; −37.63; −37.70; −37.80. MS (70 eV) *m*/*z* (%): 298 (8) [M^+-CH_2CH_3], 270 (56), 255 (58), 242 (21), 232 (20), 217 (85), 205 (100), 189 (43), 179 (38), 163 (32), 119 (10), 93 (10). Anal. Calcd. for $C_{14}H_{26}O_3Si_3$: C, 51.48; H, 8.02. Found: C, 51.52; H, 8.08.

1-(Cyclohexylethyny)l-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.22, 0.23, 0.25, 0.28, 0.30, 0.33, 0.32 (s, CH_3Si); 1.25−2.45 (m, C_6H_{11}); 5.87−6.12 (m, H_2C═CHSi). ^{13}C NMR ($CDCl_3$) δ (ppm): −0.97−1.42 (CH_3SiOSiCH_3); 24.60−32.75 (C_6H_{11}); 80.98, 110.13 (C≡C); 134.37−135.41 (H_2C═CHSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −37.33; −37.68; −37.73. MS (70 eV) *m*/*z* (%): 338 (73) [M^+], 323 (69), 295 (100), 283 (24), 267 (73), 257 (70), 253 (25), 241 (14), 230 (58), 217 (94), 205 (55), 189 (52), 178 (37), 163 (37), 147 (13), 133 (12), 103 (11), 91 (11), 55 (10). Anal. Calcd. for $C_{15}H_{26}O_3Si_3$: C, 53.20; H, 7.74. Found: C, 53.27; H, 7.78.

1-[3-Methyl-3-(trimethylsilyloxy)pent-1-ynyl]-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.17, 0.19, 0.20, 0.23, 0.26, 0.28, 0.30, 0.32, 0.34, 0.35 (s, CH_3Si, (CH_3)$_3$SiO); 0.93−1.01 (m, CH_3CH_2C); 1.41−1.44 (m, CH_3C); 1.58−1.72 (m, CH_3CH_2C); 5.82−6.10 (m, H_2C═CHSi). ^{13}C NMR ($CDCl_3$) δ (ppm): −1.02−1.14 (CH_3SiOSiCH_3); 1.90 (CH_3SiO); 8.89 (CH_3CH_2C); 30.38 (CH_3C); 37.69 (CH_3CH_2C); 69.96 (CH_3C); 85.29, 107.81−107.86 (C≡C); 133.48, 135.34 (CH_2═CHSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −37.22; −37.66; −37.77; 16.53. MS (70 eV) *m*/*z* (%): 385 (14) [M^+-CH_3], 371 (100), 278 (16), 265 (18), 251 (8), 231 (6), 145 (13), 73 (28), 45 (16). Anal. Calcd. for $C_{16}H_{32}O_4Si_4$: C, 47.95; H, 8.05. Found: C, 48.03; H, 8.16.

1-[(1-Trimethylsiloxy-1-ethynyl)cyclohexyl]-1,3,5-trimethyl-3,5-divinylcyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.18, 0.20, 0.22, 0.24, 0.25, 0.28, 0.30, 0.31, 0.33, 0.34, 0.36 (s, CH_3Si, (CH_3)$_3$SiO); 1.22−1.87 (m, (C_6H_{10})C≡); 5.83−6.10 (m, H_2C═CHSi). ^{13}C NMR ($CDCl_3$) δ (ppm): 0.92−1.22 (CH_3SiOSiCH_3); 2.07 (CH_3SiO); 23.04−69.99 ((C_6H_{10})C≡); 86.54, 107.92−108.25 (C≡C); 134.43, 135.32 (CH_2═CHSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −37.66; −37.17; −37.78; 16.26. MS (70 eV) *m*/*z* (%): 411 (32) [M^+-CH_3], 397 (47) [M^+-CH_2CH_3], 306 (26), 294 (25), 278 (31), 252 (46), 203 (30), 192 (20), 179 (18), 92 (6), 73 (100), 45 (48). Anal. Calcd. for $C_{18}H_{34}O_4Si_4$: C, 50.65; H, 8.03. Found: C, 50.77; H, 8.15.

(b). 1-Alkynyl-1,3,5-trimethyl-3,5-divinylcyclotrisilazanes. 1-[(Triethylsilyl)ethynyl]-1,3,5-trimethyl-3,5-divinylcyclotrisilazane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.17, 0.19, 0.20, (s, CH_3Si); 0.82−0.87 (m, CH_3CH_2Si, SiN*H*Si); 1.06−1.12 (m, CH_3CH_2Si); 5.85−6.05 (m, H_2C═CHSi). ^{13}C NMR ($CDCl_3$) δ (ppm): 2.03−2.41 (CH_3Si); 4.41 (CH_3CH_2Si); 7.47−7.54 (CH_3CH_2Si); 109.52, 110.75 (C≡C); 130.99−141.14 (H_2C═CHSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −27.55; −27.18; −19.52; −20.09. MS (70 eV) *m*/*z* (%): 352 (100) [M^+-CH_3], 338 (12), 324 (16), 295 (11), 262 (10), 193 (5), 70 (5), 45 (4). Anal. Calcd. for $C_{15}H_{33}N_3Si_4$: C, 48.99; H, 9.04; N, 11.43. Found: C, 49.02; H, 9.12; N, 11.38.

1-[(Triethylgermyl)ethynyl]-1,3,5-trimethyl-3,5-divinylcyclotrisilazane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.17, 0.20, 0.22, 0.25, 0.26, 0.27, 0.30 (s, CH_3Si); 0.82−0.93 (m, CH_3CH_2Ge, SiN*H*Si); 0.95−1.12 (m, CH_3CH_2Ge); 5.78−6.15 (m, H_2C═CHSi). ^{13}C NMR ($CDCl_3$) δ (ppm): 0.71−2.29 (CH_3Si); 4.97−5.98 (CH_3CH_2Ge); 9.00−9.15 (CH_3CH_2Ge); 94.97, 105.83 (C≡C); 132.18−141.12 (H_2C═CHSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −27.45; −27.28;

−18.88. MS (70 eV) *m/z* (%): 396 (100) [M^+ -CH_3], 382 (12), [M^+ -CH_2CH_3], 370 (22), 356 (19), 266 (29), 252 (17), 101 (6). Anal. Calcd. for $C_{15}H_{33}GeN_3Si_3$: C, 43.69; H, 8.07; N, 10.19. Found: C, 43.73; H, 8.12; N, 10.06.

1-(1-Heptynyl)-1,3,5-trimethyl-3,5-divinylcyclotrisilazane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.17, 0.18, 0.20, 0.22, 0.24, 0.27, 0.29 (s, CH_3Si); 0.69−2.57 (m, SiN*H*Si, CH_3CH_2CH_2CH_2CH_2); 5.77−6.17 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.42)−2.29 (*C*H_3Si); 14.07−31.75 (*C*$_5$H$_{11}$); 83.12, 106.15 (*C*≡*C*); 131.06−141.34 (H_2C=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −27.51; −27.17; −19.51. MS (70 eV) *m/z* (%): 308 (100) [M^+-CH_3], 214 (12), 197 (4), 185 (4), 156 (3). Anal. Calcd. for $C_{14}H_{29}N_3Si_3$: C, 51.95; H, 9.03; N, 12.98. Found: C, 51.99; H, 9.09; N, 12.91.

1-(Cyclohexylethynyl)-1,3,5-trimethyl-3,5-divinylcyclotrisilazane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.16, 0.17, 0.18 (s, CH_3Si); 0.63 (m, SiN*H*Si); 1.28−2.38 (m, C_6H_{11}); 5.71−6.22 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): 2.02−2.12 (*C*H_3Si); 24.87−32.83 (*C*$_6$H$_{11}$); 85.09, 109.17 (*C*≡*C*); 131.00 - 141.32 (CH_2=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −27.41; −27.07; −19.61. MS (70 eV) *m/z* (%): 320 (100) [M^+-CH_3], 275 (3), 199 (5), 186 (5), 101 (2). Anal. Calcd. for $C_{15}H_{29}N_3Si_3$: C, 53.67; H, 8.71; N, 12.52. Found: C, 53.74; H, 8.77; N, 12.48.

1-[3-Methyl-3-(trimethylsiloxy)-1-pentynyl]-1,3,5-trimethyl-3,5-divinylcyclotrisilazane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.07, 0.10, 0.13, 0.16, 0.18, 0.21, 0.23, 0.24, 0.27, 0.28 (s, CH_3Si, (CH_3)$_3$SiNH); 0.94−1.00 (m, CH_3CH$_2$C, SiN*H*Si); 1.40−1.44 (m, CH_3C); 1.59−1.65 (m, CH$_3$CH_2C); 5.71−6.07 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): 1.02−1.99 (NHSi*C*H$_3$, *C*H$_3$SiO); 9.03 (*C*H$_3$CH$_2$C); 30.61 (*C*H$_3$C); 37.81 (CH$_3$*C*H$_2$C); 70.09 (CH$_3$*C*); 89.23, 107.25 (*C*≡*C*); 131.36, 141.11 (*C*H$_2$=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −27.55; −27.30; −19.11; 15.96. MS (70 eV) *m/z* (%): 382 (61) [M^+-CH_3], 368 (100) [M^+-CH_2CH_3], 351 (13), 311 (11), 291 (15), 274 (67), 259 (27), 247 (16), 228 (59), 211 (16), 200 (24), 189 (12), 173 (12), 73 (75), 45 (42). Anal. Calcd. for $C_{16}H_{35}N_3OSi_4$: C, 48.31; H, 8.87; N, 10.56. Found: C, 48.30; H, 8.89; N, 10.50.

1-[(1-Trimethylsiloxy-1-ethynyl)cyclohexyl]-1,3,5-trimethyl-3,5-divinylcyclotrisilazane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.01, 0.03, 0.10, 0.13, 0.16, 0.20, 0.23, 0.27, 0.30, 0.33 (s, CH_3SiNH, (CH_3)$_3$SiO); 0.64−1.83 (m, (C$_6$H$_{10}$)C≡, SiN*H*Si); 5.71−6.23 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): 1.00−5.35 (*C*H$_3$SiNH; (*C*H$_3$)$_3$SiO); 23.12−70.09 ((*C*$_6$H$_{10}$)C≡); 90.89, 107.23 (*C*≡*C*); 131.10−141.21 (*C*H$_2$=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −27.61; −27.37; −19.11; 15.69. MS (70 eV) *m/z* (%): 408 (54) [M^+-CH_2CH_3], 391 (34), 380 (24), 363 (12), 302 (42), 290 (51), 274 (79), 259 (26), 248 (15), 228 (86), 216 (15), 200 (28), 189 (10), 173 (11), 73 (100), 45 (46). Anal. Cal. for $C_{18}H_{37}N_3OSi_4$: C, 51.01; H, 8.80; N, 9.91 Found: C, 51.13; H, 8.82; N, 9.88.

1-[(Dimethylphenylsilyl)ethynyl]-1,3,5-trimethyl-3,5-divinylcyclotrisilazane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.16, 0.18, 0.21, 0.24, 0.29, 0.38, 0.45, 0.57, 0.78, 1.03, 1.27 (s, CH_3SiNH, Si(CH_3)$_2$Ph); 0.89−1.00 (s, SiN*H*Si); 5.76−6.07 (m, H_2C=C*H*Si); 7.26−7.60 (C$_6$H$_5$Si). ^{13}C NMR ($CDCl_3$) δ (ppm): (−1.10)−1.15 (*C*H$_3$SiNH, Si(*C*H$_3$)$_2$Ph); 106.35, 110.24 (*C*≡*C*); 127.55−138.55 (H_2C=*C*HSi, *C*$_6$H$_5$Si). ^{29}Si NMR ($CDCl_3$) δ (ppm): −37.24; −37.55; −37.69; −19.48; −20.02. MS (70 eV) *m/z* (%): 390 (1), 372 (100), 355 (25), 344 (6), 294 (3), 100 (2), 70 (2), 45 (2). Anal. Calcd. for $C_{17}H_{29}N_3Si_4$: C, 52.65; H, 7.54; N, 10.84. Found: C, 52.70; H, 7.64; N, 10.76.

(c). 1-Alkynyl-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxanes. 1-[(Triethylsilyl)ethynyl]-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.16, 0.17, 0.18, 0.21, 0.23, 0.24, 0.26, 0.27 (s, CH_3Si); 0.57−0.67 (m, CH$_3$CH_2Si); 0.93−1.02 (m, CH_3CH$_2$Si); 5.85−6.05 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.99)−1.15 (*C*H$_3$Si); 4.25−4.42 (CH$_3$*C*H$_2$Si); 7.44−7.55 (*C*H$_3$CH$_2$Si); 108.98, 111.59 (*C*≡*C*); 133.37−136.16 (H_2C=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −47.86; −47.76; −47.67; −47.46; −20.12. MS (70 eV) *m/z* (%): 456 (4) [M^+], 441 (30) [M^+-CH_3], 427 (100) [M^+-CH_2CH_3], 413 (20), 400 (36), 371 (19), 341 (7), 290 (8), 272 (8), 73 (12), 59 (36), 45 (19). Anal. Calcd. for $C_{18}H_{36}O_4Si_5$: C, 47.32; H, 7.94. Found: C, 47.38; H, 8.02.

1-[(Dimethylphenylsilyl)ethynyl]-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.16, 0.20, 0.25, 0.28, 0.30, 0.34, 0.36, 0.40, 0.41, 0.43, 0.48 (s, CH_3Si, Si(CH_3)$_2$Ph); 5.79−6.07 (m, H_2C=C*H*Si); 7.34−7.66 (C$_6$H$_5$Si). ^{13}C NMR ($CDCl_3$) δ (ppm): (−1.16)−1.03 (*C*H$_3$Si, Si(*C*H$_3$)$_2$Ph); 19.04, 112.33 (*C*≡*C*); 127.70−139.81 (H_2C=*C*HSi, *C*$_6$H$_5$Si). ^{29}Si NMR ($CDCl_3$) δ (ppm): −47.88; −47.79; −47.69; −47.44; −19.38. MS (70 eV) *m/z* (%): 476 (53) [M^+], 461 (100) [M^+-CH_3], 449 (34), 433 (71), 421 (20), 407 (13), 383 (22), 356 (13), 320 (15), 308 (16), 274 (17), 264 (14), 248 (18), 192 (22), 181 (12), 134 (28), 121 (13), 73 (22), 59 (24), 45 (21). Anal. Cal. for $C_{20}H_{32}O_4Si_5$: C, 50.37; H, 6.76 Found: C, 50.44; H, 6.79.

1-[(Triethylgermyl)ethynyl]-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.16, 0.18, 0.19, 0.20 (s, CH_3Si); 0.82−0.87 (m, CH$_3$CH_2Ge); 1.06−1.12 (m, CH_3CH$_2$Ge); 5.85−6.05 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.97)−1.27 (*C*H$_3$Si); 5.70−5.99 (CH$_3$*C*H$_2$Ge); 8.99−9.08 (*C*H$_3$CH$_2$Ge); 109.82, 110.85 (*C*≡*C*); 134.27−135.30 (H_2C=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −47.82; −47.74; −47.69; −47.42. MS (70 eV) *m/z* (%): 471 (29) [M^+ -CH_2CH_3], 445 (100), 416 (35), 384 (7), 293 (8), 280 (8), 254 (9), 131 (10), 115 (8), 101 (14). Anal. Calcd. for $C_{18}H_{36}GeO_4Si_4$: C, 43.11; H, 7.24. Found: C, 43.24; H, 7.29.

1-(1-Heptynyl)-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.17, 0.19, 0.20, 0.22, 0.24, 0.25, 0.26 (s, CH_3Si); 0.87−2.24 (m, CH_3CH_2CH_2CH_2CH_2); 5.77−6.10 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.92)−1.36 (*C*H$_3$Si); 14.81−31.04 (*C*$_5$H$_{11}$); 82.18, 105.25 (*C*≡*C*); 133.06−136.23 (H_2C=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −47.43; −47.48; −47.64; −47.72. MS (70 eV) *m/z* (%): 397 (25) [M^+-CH_3], 369 (21), 289 (36), 278 (40), 216 (12), 355 (30), 342 (22), 328 (36), 314 (43), 275 (100), 264 (30), 250 (660, 235 (45), 203 (19), 191 (18), 93 (23), 67 (10), 55 (10), 45 (10). Anal. Cal. for $C_{17}H_{32}O_4Si_4$: C, 49.47; H, 7.81 Found: C, 49.52; H, 7.84.

1-(Cyclohexaethynyl)-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.18, 0.19, 0.20, 0.21, 0.23 (s, CH_3Si); 1.30−2.40 (m, C_6H_{11}); 5.85−6.09 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.72)-(−0.68) (*C*H$_3$Si); 24.80−32.29 (*C*$_6$H$_{11}$); 81.77, 109.04 (*C*≡*C*); 133.24−136.26 (H_2C=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −47.85; −47.75; −47.71; −47.41. MS (70 eV) *m/z* (%): 409 (21) [M^+-CH_3], 381 (22), 353 (20), 339 (15), 327 (21), 313 (19), 301 (25), 291 (59), 275 (93), 265 (84), 251 (100), 235 (47), 193 (16), 91 (18), 67 (24), 45 (17). Anal. Calcd. for $C_{18}H_{32}O_4Si_4$: C, 50.89; H, 7.59. Found: C, 50.92; H, 7.63.

1-[3-Methyl-3-(trimethylsiloxy)-1-pentynyl]-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.12, 0.14, 0.15, 0.17, 0.19, 0.20, 0.23, 0.24, 0.26, 0.27 (s, CH_3Si, (CH_3)$_3$SiO); 0.95−1.01 (m, CH_3CH$_2$C); 1.41−1.43 (m, CH_3C); 1.59−1.66 (m, CH$_3$CH_2C); 5.97−6.02 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): −1.04−1.14 (*C*H$_3$SiOSi*C*H$_3$); 1.90 ((*C*H$_3$)$_3$SiO); 8.92 (*C*H$_3$CH$_2$C); 30.40 (*C*H$_3$C); 37.67 (CH$_3$*C*H$_2$C); 69.95 (CH$_3$*C*); 85.97, 107.34 (*C*≡*C*); 133.44, 136.17 (*C*H$_2$=*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −47.88; −47.79; −47.69; −47.44; 16.38. MS (70 eV) *m/z* (%): 471 (10) [M^+-CH_3], 457 (100) [M^+-CH_2CH_3], 289 (15), 251 (20), 177 (11), 145 (25), 97 (11), 85 (13), 73 (62), 59 (17), 45 (19). Anal. Cal. for $C_{19}H_{38}O_5Si_5$: C, 46.87; H, 7.87 Found: C, 46.89; H, 7.92.

1-[(1-Trimethylsiloxy-1-ethynyl)cyclohexyl]-1,3,5,7-tetramethyl-3,5,7-trivinylcyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.19, 0.23, 0.25, 0.26, 0.28, 0.29, 0.30, 0.31 (s, CH_3Si, (CH_3)$_3$SiO); 1.26−1.86 (m, (C$_6$H$_{10}$)C≡); 5.79−6.14 (m, H_2C=C*H*Si). ^{13}C NMR ($CDCl_3$) δ (ppm): 1.15−1.23 (*C*H$_3$SiOSi*C*H$_3$); 2.21 ((*C*H$_3$)$_3$SiO); 23.08−70.00 ((*C*$_6$H$_{10}$)C≡);

87.07, 107.11 (*C*≡*C*); 133.39, 136.06 (*C*H_2═*C*HSi). ^{29}Si NMR ($CDCl_3$) δ (ppm): −47.33; −47.39; −47.67; −47.79; 16.32. MS (70 eV) *m*/*z* (%): 498 (14) [M^+-CH_3], 470 (30), 456 (18), 428 (11), 338 (10), 290 (21), 279 (21), 275 (15), 267 (13), 252 (20), 203 (14), 171 (31), 159 (13), 147 (10), 97 (17), 85 (25), 73 (100), 59 (28), 45 (39). Anal. Calcd. for $C_{21}H_{40}O_5Si_5$: C, 49.17; H, 7.86. Found: C, 49.25; H, 7.94.

(2) The spectroscopic data of the products of silylative coupling of 1-alkynyl-vinyl-substituted cyclosiloxanes and cyclosilazane with styrene, obtained for the mixture of isomers, are described below.

1-[3-Methyl-3-(trimethylsiloxy)pent-1-ynyl]-1,3,5-trimethyl-3,5-di[(*E*)-styryl]cyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.08, 0.12, 0.16, 0.20, 0.23, 0.27, 0.29, 0.33, 0.35, 0.37, 0.40, 0.43 (s, C*H*$_3$Si, (C*H*$_3$)$_3$SiO); 0.86−1.03 (m, C*H*$_3$CH$_2$C); 1.34−1.47 (m, C*H*$_3$C); 1.56−1.68 (m, CH$_3$C*H*$_2$C); 6.30−7.27 (m, (C$_6$H$_5$)*H*C═C*H*Si); 7.28−7.48 (m, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.56)−1.94 (*C*H$_3$SiOSi*C*H$_3$, *C*H$_3$SiO); 8.89−8.92 (*C*H$_3$CH$_2$C); 29.70−30.44 (*C*H$_3$C); 37.64−37.66 (CH$_3$*C*H$_2$C); 69.95 (CH$_3$*C*); 85.05−85.44, 107.88−108.10 (*C*≡*C*); 123.72 ((C$_6$H$_5$)CH═*C*HSi); 123.83 (*o*-*C*$_6$H$_5$); 126.78 (*m*-*C*$_6$H$_5$); 128.49 (*p*-*C*$_6$H$_5$); 137.50 (*c*$_i$-*C*$_6$H$_5$); 146.97 ((C$_6$H$_5$)*C*H═CHSi).

1-[(Triethylgermyl)ethynyl]-1,3,5-trimethyl-3,5-di[(*E*)-styryl]cyclotrisiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.29, 0.31, 0.33, 0.37, 0.39, 0.40, 0.42, 0.44, (s, C*H*$_3$Si,); 0.79−0.95 (m, CH$_3$C*H*$_2$Ge); 0.97−1.14 (m, C*H*$_3$CH$_2$Ge); 6.30−7.30 (m, (C$_6$H$_5$)*H*C═C*H*Si); 7.31−7.49 (m, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.89)−1.32 (*C*H$_3$Si); 5.55 (CH$_3$*C*H$_2$Ge); 8.85−8.96 (*C*H$_3$CH$_2$Ge); 109.89, 111.08 (*C*≡*C*); 123.84 ((C$_6$H$_5$)CH═*C*HSi); 123.99 (*o*-*C*$_6$H$_5$); 126.78 (*m*-*C*$_6$H$_5$); 128.56 (*p*-*C*$_6$H$_5$); 137.60 (*c*$_i$-*C*$_6$H$_5$); 146.91 ((C$_6$H$_5$)*C*H═CHSi).

1-[(1-Trimethylsiloxy-1-ethynyl)cyclohexyl]-1,3,5,7-tetramethyl-3,5,7-tri[(*E*)-styryl]cyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.18, 0.19, 0.22, 0.24, 0.27, 0.29, 0.32, 0.35, 0.37, 0.39, 0.40, 0.41 (s, C*H*$_3$Si, (C*H*$_3$)$_3$SiO); 1.28−1.61 (m, (C$_6$*H*$_{10}$)C≡); 6.32−6.45, 7.09−7.20 (m, (C$_6$H$_5$)*H*C═C*H*Si); 7.22−7.52 (m, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.23)−2.23 (*C*H$_3$SiOSi*C*H$_3$, *C*H$_3$SiO); 23.09−70.01 ((*C*$_6$H$_{10}$)C≡); 87.27, 107.44 (*C*≡*C*); 124.69−124.95 ((C$_6$H$_5$)CH═*C*HSi); 125.00−125.08 (*o*-*C*$_6$H$_5$); 126.62 (*m*-*C*$_6$H$_5$); 128.25−128.47 (*p*-*C*$_6$H$_5$); 137.69−137.74 (*c*$_i$-*C*$_6$H$_5$); 145.93−146.06 ((C$_6$H$_5$)*C*H═CHSi).

1-[(Triethylsilyl)ethynyl]-1,3,5,7-tetramethyl-3,5,7-tri[(*E*)-styryl]cyclotetrasiloxane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.12, 0.14, 0.15, 0.17, 0.19, 0.21, 0.22, 0.23, 0.24 (s, C*H*$_3$Si); 0.48−0.67 (m, CH$_3$C*H*$_2$Si); 0.84−1.04 (m, C*H*$_3$CH$_2$Si); 6.28−7.15 (m, (C$_6$H$_5$)*H*C═C*H*Si); 7.24−7.47 (m, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$) δ (ppm): (−0.55)-(−0.19) (*C*H$_3$Si); 4.08−4.35 (CH$_3$*C*H$_2$Si); 7.24−7.45 (*C*H$_3$CH$_2$Si); 109.22, 111.72 (*C*≡*C*); 124.76−124.94 ((C$_6$H$_5$)CH═*C*HSi); 125.15 (*o*-*C*$_6$H$_5$); 126.70 (*m*-*C*$_6$H$_5$); 128.34−128.50 (*p*-*C*$_6$H$_5$); 137.78−137.84 (*c*$_i$-*C*$_6$H$_5$); 145.96−146.15 ((C$_6$H$_5$)*C*H═CHSi)

1-[(1-Trimethylsiloxy-1-ethynyl)cyclohexyl]-1,3,5-trimethyl-3,5-di[(*E*)-styryl]cyclotrisilazane. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.09, 0.11, 0.14, 0.17, 0.19, 0.22, 0.26, 0.29, 0.31, 0.32, 0.33 (s, C*H*$_3$Si, (C*H*$_3$)$_3$SiO); 0.74−2.17 (m, (C$_6$*H*$_{10}$)C≡, SiN*H*Si); 6.39−7.24 (m, (C$_6$H$_5$)*H*C═C*H*Si); 7.26−7.47 (m, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$) δ (ppm): 1.15−4.77 (*C*H$_3$SiNHSi*C*H$_3$; *C*H$_3$SiO); 23.23−70.14 ((*C*$_6$H$_{10}$)C≡); 90.83, 107.13 (*C*≡*C*); 126.48 (*o*-*C*$_6$H$_5$); 127.93 (*m*-*C*$_6$H$_5$); 128.12 ((C$_6$H$_5$)CH═*C*HSi); 128.40 (*p*-*C*$_6$H$_5$); 138.24 (*c*$_i$-*C*$_6$H$_5$); 144.10 ((C$_6$H$_5$)*C*H═CHSi).

Acknowledgment. This work was supported by the project of the Ministry of Science and High Education PZB-KBN 118/T09/17.

OM800361K