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New cyclic and macrocyclic silaolefins *via* ring-closing metathesis of 1,1-bis(silyl)ethene-tethered dienes

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Abstract

Dialkenyl-substituted 1,1-bis(silyl)ethenes of the general formulae $(CH_2{=}CH(CH_2)_nMe_2Si)_2C{=}CH_2$ and $(CH_2{=}CH(CH_2)_nOMe_2Si)_2C{=}CH_2$, (where $n = 1$–3) have been successfully converted into new silacyclic or silamacrocyclic compounds in the presence of ruthenium–benzylidene complex (first generation Grubbs catalyst). The structures of both macrocyclic silaolefins have been confirmed using X-ray diffraction.

Keywords: Silacyclic compounds; 1,1-Bis(silyl)ethenes; Ring-closing metathesis; Grubbs catalyst; Cyclization

1. Introduction

Among the most notable and commonly employed synthetic methods leading to functionalized silacyclic compounds, the ring-closing metathesis (RCM) of dialkenyl-substituted organosilicon compounds is of unique importance [1].

In the last decade, the synthetic potential of ring-closing metathesis of organosilicon dienes (except divinyl derivatives) in the presence of molybdenum and ruthenium alkylidene complexes has been well recognized as a mild and effective method for the synthesis of unsaturated silacyclic compounds containing *endo*-cyclic bonds [1,2]. Although divinyl-substituted organosilicon compounds carrying electron-withdrawing substituents at silicon have been recently proved to be valuable substrates in the cross-metathesis with olefins [3], there is no data available on the reactivity of these compounds towards the RCM process. On the other hand, divinyl-substituted organosilicon compounds in the presence of ruthenium and rhodium complexes containing or generating M–H and M–Si (M = Ru, Rh) bonds, undergo competitive silylative coupling polycondensation [2,4–7] and cyclization [2,8–13] to give organosilicon oligomers or silicon-containing *exo*-methylenes, which cannot be prepared *via* ring-closing diene metathesis.

Unsaturated functionalized silacyclic compounds are versatile platforms for the construction of acyclic organic synthons because they can undergo a variety of highly selective Si–C bond cleavage transformations [14]. They can serve as hydroxyl or alkenyl surrogates *via* well-known stereospecific oxidation under Tamao/Fleming conditions [15–19] or Peterson elimination [20], producing unsaturated alcohols or alkenes, respectively. In addition, they are direct precursors for the preparation of substituted oxygenated heterocycles, e.g. tetrahydrofurans and tetrahydropyrans [21]. The application of a sequential ring-closing metathesis of silicon-containing dienes and silicon-assisted cross-coupling protocols has become a powerful synthetic strategy for the construction of functionalized organic derivatives, e.g. unsaturated aryl-substituted alcohols [22,23] and medium-sized cyclic dienes possessing hydroxy [24] or alkoxy [25] functionalities.

We have recently reported a new facile and efficient route for the synthesis of dialkenyl- and dialkenyloxy-substituted 1,1-bis(silyl)ethenes using cyclic silyl ether [9]

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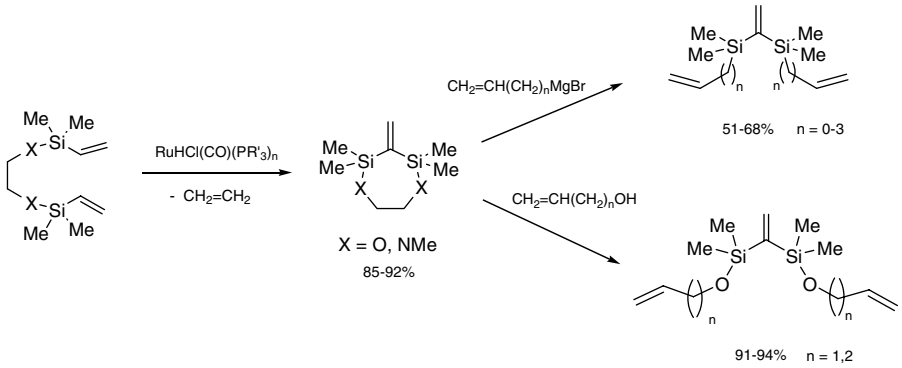


Scheme 1. Synthesis of dialkenyl-substituted 1,1-bis(silyl)ethenes.

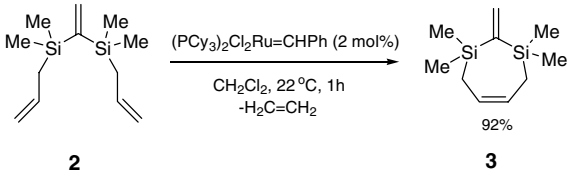
or cyclic silyl amine [10] selectively obtained *via* ruthenium catalyzed deethenative silylative coupling cyclization of divinyl-substituted monomers, followed by their reaction with alkenyl Grignard reagents or alkenols (Scheme 1).

Silicon-tethering ring-closing metathesis of dialkenyl- and dialkenyloxy-substituted compounds has been recently developed as a powerful tool for the enantioselective synthesis of symmetrical diols [26], polyols [27] and a wide range of natural products [28–30].

Therefore, the aim of this work was to study the reactivity of the easily accessible *gem*-bis(silyl)ethene-tethered dienes towards the first generation Grubbs catalyst and synthesis of new unsaturated silacyclic compounds containing easily modified Si–C or Si–OR bonds.

2. Results and discussion

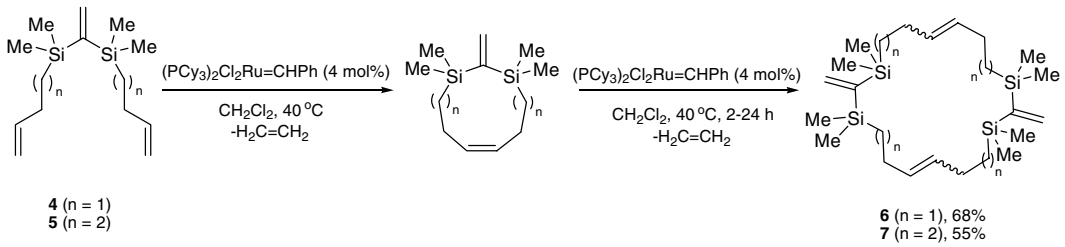
The starting 1,1-bis(alkenyldimethylsilyl)ethenes were prepared according to our previously reported procedure [9]. In a preliminary experiment, we studied the ring-closing metathesis of 1,1-bis(dimethylvinylsilyl)ethene (**1**). This particular compound appears to be inactive in ruthenium–benzylidene complex-catalyzed ring-closing metathesis and ruthenium-hydride complex [Ru(H)(Cl)(CO)-$(PCy_3)_2$] – catalyzed silylative coupling cyclization and the analysis of the crude reaction mixtures revealed the presence of starting material only and none of the desired cyclic product. Next we studied the ring-closing metathesis of 1,1-bis(allyldimethylsilyl)ethene (**2**) in the presence of the first generation Grubbs catalyst. Treatment of a solution of **2** in dichloromethane by a catalytic amount of [$(PCy_3)_2Cl_2$-Ru=CHPh] (2 mol%) at 22 °C led to the selective formation of the 7-membered cyclic carbosilane – (*Z*)-1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclohept-5-ene (**3**). After optimisation, a nearly quantitative yield (92%) of compound **3** was isolated after 1 h (Scheme 2).



Scheme 2. Ring-closing metathesis of 1,1-bis(allyldimethylsilyl)ethene.

Similarly, we performed the RCM of 1,1-bis(3-butenyldimethylsilyl)ethene (**4**) and 1,1-bis(4-pentenyldimethylsilyl)ethene (**5**) under the conditions indicated above. Detailed GCMS studies have shown, that after preliminary formation of the 9- or 11-membered carbosilane derivatives, their further metathetical cyclodimerization took place (Scheme 3). Such a cyclodimerization of dialkenyl-substituted organometallic reagents under RCM conditions has been previously reported for dialkenylsilanes [31] and more recently for bis(alkenyl)niclocenes [32]. Reactions of **4** with ruthenium–benzylidene catalyst in CH_2Cl_2 after 2 h gave an equilibrium mixture including the substrates, 9-membered carbosilane and cyclodimer isomers in the ratio 44:31:25 (Fig. 1).

The GCMS monitoring of the RCM reaction of **5** shows that a similar equilibrium mixture is generated after 0.5 h, in which the monomer, 11-membered carbosilane and



Scheme 3. Ring-closing metathesis of 1,1-bis(3-butenyldimethylsilyl)ethene and 1,1-bis(4-pentenyldimethylsilyl)ethene.

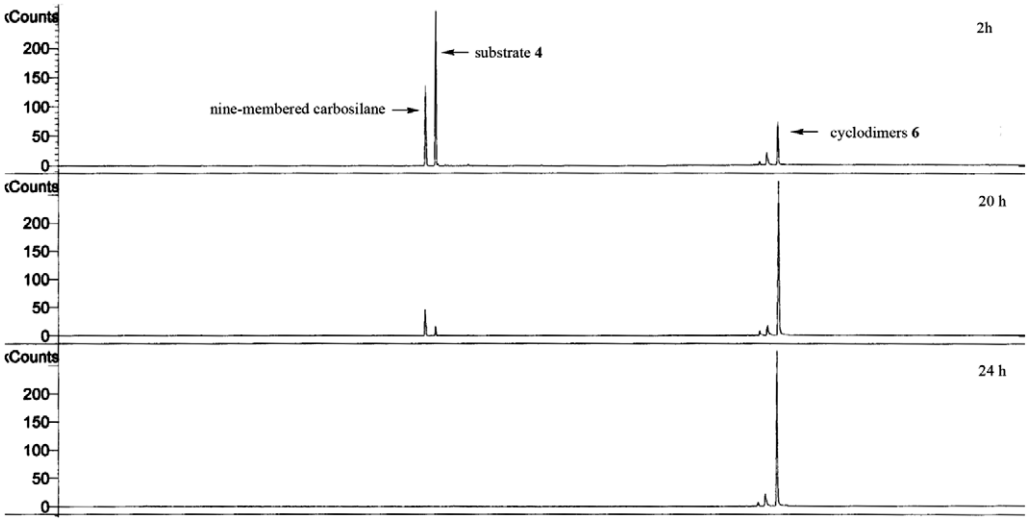


Fig. 1. GC monitoring of the RCM reaction of **4**.

cyclodimer may be identified and their ratio is about 10:40:50. The ruthenium–benzylidene complex present in these reaction mixtures catalyzed the ring-opening metathesis of the ring strained (*Z*)-1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclonon-6-ene (formed from **4**) or (*Z*)-1,1,3,3-tetramethyl-2-methylene-1,3-disilacycloundec-7-ene (formed from **5**), to give a mixture of stereoisomeric 18-membered 1,1,3,3,10,10,12,12-octamethyl-2,11-dimethylene-1,3,10,12-tetrasilacyclo-octadeca-6,15-dienes (**6**) or a mixture of 22-membered 1,1,3,3,12,12,14,14-octamethyl-2,13-dimethylene-1,3,12,14-tetrasilacyclodocosa-7,18-dienes (**7**), respectively (Scheme 3). Although the (*E*),(*E*)-isomeric cyclodimers were found as the predominant products (>90%), small amounts of the (*Z*),(*Z*)- and (*E*),(*Z*)-isomers were also detected (Table 2). Application of $[(PCy_3)_2Cl_2Ru{=}CHPh]$ (2–4 mol%) in dichloromethane for RCM of dialkenyl-substituted silicon derivatives **2**, **4** and **5** under dilution conditions ([monomer] = 0.22 M) gave exclusively cyclic or macrocyclic products accompanied by only trace amounts of oligomers (^{1}H NMR analysis of the crude reaction mixture) formed *via* ADMET and no cross-metathesis products were observed.

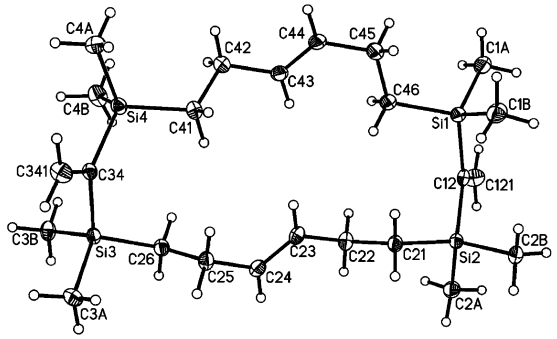


Fig. 2. A perspective view of the molecule **6** together with the numbering scheme. The anisotropic displacement ellipsoids are drawn at 50% probability level and hydrogen atoms are shown as spheres of arbitrary radii.

The (*E*),(*E*)-isomers of macrocyclic carbosilanes **6** and **7** proved to be solids and yielded crystals amenable to X-ray structure determination. Perspective views of these molecules are shown in Figs. 2 and 3.

In **7**, the 18-membered ring is non-symmetrical. Both C=C double bonds are *trans* (C22–C23–C24–C25 and C42–C43–C44–C45 torsion angles are 179.7(2)° and 178.7(2)°, respectively). The environments of these two double bonds display different conformations, and these

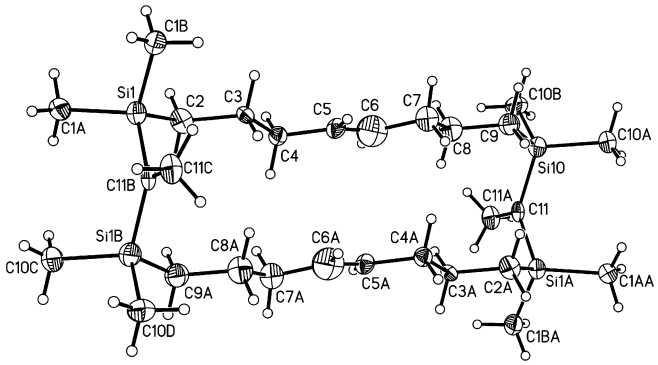


Fig. 3. A perspective view of the molecule **7** together with the numbering scheme. The anisotropic displacement ellipsoids are drawn at 50% probability level and hydrogen atoms are shown as spheres of arbitrary radii. For clarity, only one alternative position of the disordered C3–C7 part is shown.

Table 1a
Torsion angles (in degrees, with s.u.'s in parentheses) along 18-membered ring in **6**

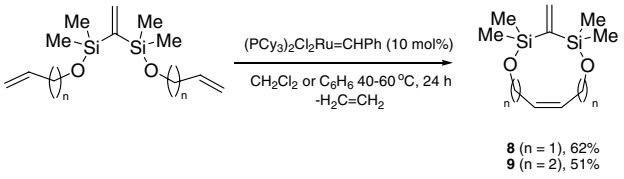
Si1–C12–Si2–C21	49.0(1)	Si3–C34–Si4–C41	−70.4(1)
C12–Si2–C21–C22	68.7(1)	C34–Si4–C41–C42	173.4(1)
Si2–C21–C22–C23	−171.1(1)	Si4–C41–C42–C43	−177.0(1)
C21–C22–C23–C24	−118.4(2)	C41–C42–C43–C44	−121.8(2)
C22–C23–C24–C25	179.7(2)	C42–C43–C44–C45	178.7(2)
C23–C24–C25–C26	108.4(2)	C43–C44–C45–C46	1.0(3)
C25–C26–Si3–C34	−178.9(1)	C44–C45–C46–Si1	−177.9(1)
C26–Si3–C34–Si4	47.4(2)	C45–C46–Si1–C12	174.5(1)

Table 1b
Torsion angles (in degrees, with s.u.'s in parentheses) along 22-membered ring in **7**

Si1–C2–C3–C4	164.7(8); −179.3(9)	C7–C8–C9–Si10	168.7(6); −167.7(6)
C2–C3–C4–C5	178.9(10); −175.2(11)	C8–C9–Si10–C11	−53.9(4)
C3–C4–C5–C6	−167.7(15); 163.0(15)	C9–Si10–C11–Si1A	−66.5(3)
C4–C5–C6–C7	173.4(13); −171.9(12)	Si10–C11–Si1A–C2A	63.9(3)
C5–C6–C7–C8	−178.8(15); 166.0(14)	C11–Si1A–C2A–C3A	–68.9(8); −82.3(8)
C6–C7–C8–C9	−172.8(9); −178.1(7)		

Two alternative values are given for two disordered molecules; A denotes the symmetry operation $-x+1, -y, -z+2$.

differences are the main reason for the loss of the approximately two-fold axis of symmetry of the molecule as a whole (Tables 1a and 1b lists the torsion angles along the 18-membered ring). The geometrical features are typical. The Si–C bond lengths can be divided into two groups: Si–CH_3 (mean value 1.871(3) Å), Si–CH_2 and Si–C=CH_2 (1.883(3) Å). Also the C=C double bonds are essentially different: the C=CH_2 bond lengths are 1.334(3) Å and 1.338(3) Å, while the CH=CH bonds (intra-annular) are shorter, of 1.319(2) Å and 1.316(2) Å. In contrast, **7** lies at the centre of symmetry and the molecule as a whole has the C_i symmetry. Due to the disorder, the quality of the data is poor, but the conformation of the molecule can be analyzed: the C=C double bonds are also *trans* (C4–C5–C6–C7 torsion angles are 173.4(13)° and −171.9 (12)° for both alternative positions). A comparison of the torsion angles (Tables 1a and 1b) shows that while for the 22-membered ring the longer arms of the macrocycle are in extended conformation, the shorter arms in **6** are more folded. In both structures, the crystal packing is determined by weak van der Waals forces.

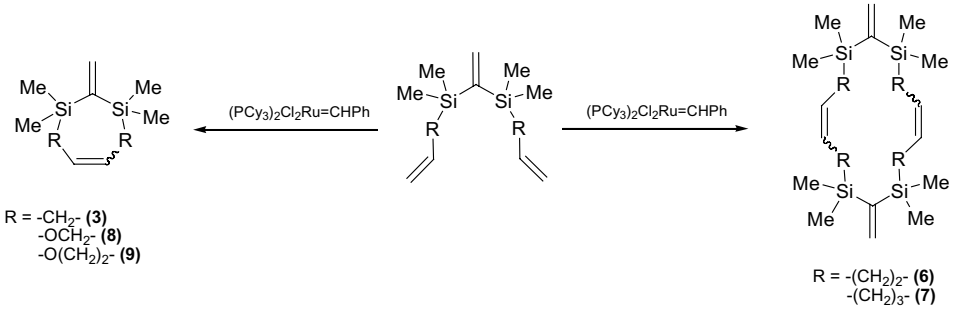


Scheme 4. Ring-closing metathesis of 1,1-bis(alkenyloxydimethylsilyl)-ethenes.

The encouraging results achieved for dialkenyl-substituted 1,1-bis(silyl)ethenes, which were efficiently converted into cyclic carbosilanes, prompted us to prepare a series of unsaturated cyclic silyl ethers *via* RCM of the corresponding 1,1-bis(alkenyloxy-dimethylsilyl)ethenes (Scheme 4). The starting 1,1-bis(alkenyloxydimethylsilyl)ethenes were prepared according to our previously reported procedure [10].

Ring-closure of 1,1-bis(alkenyloxydimethylsilyl)ethenes leading to the corresponding cyclic silyl ethers occurred readily but required an increase in the catalytic load of

Table 2
Ring-closing metathesis of dialkenyl-substituted 1,1-bis(silyl)ethenes



R	Mol% of catalyst	Solvent	Temperature (°C)	Time (h)	Product	Yield (%)[a]	*Z*/*E*
–	10	CH_2Cl_2	40	24	–	0[c]	–
–CH_2–	2	CH_2Cl_2	22	1	**3**	92	>99:1
–$(CH_2)_2$–	4	CH_2Cl_2	40	24	**6**	68[b]	Complex mixture[d]
–$(CH_2)_3$–	4	CH_2Cl_2	40	2	**7**	55[b]	Complex mixture[e]
–OCH_2–	10	C_6H_6	60	24	**8**	62	96:4
–$O(CH_2)_2$–	10	CH_2Cl_2	40	24	**9**	51	93:7

[a] Isolated yields of chromatographically pure products.
[b] Formation of dimeric macrocyclic product.
[c] Exclusively recovered starting material.
[d] (*E*),(*E*)-: (*E*),(*Z*)-: (*Z*),(*Z*)- = 90:8:2.
[e] (*E*),(*E*)-: (*E*),(*Z*)-: (*Z*),(*Z*)- = 93:5:2.

Grubbs catalyst to 10 mol% and extended reaction time (24 h) in order to achieve good yield (Table 2). Using this procedure we have synthesized two new cyclic organosilicon compounds – 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disila-cyclonon-7-ene (**8**) (isolated yield 62%) and 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disila-cycloundec-8-ene (**9**) (isolated yield 51%). For the cyclic silyl ethers obtained, the (*Z*)-isomer definitely predominated, although 4–7% (GCMS ratio) of a second stereoisomer assigned as the (*E*)-product was also observed. Similarly to the previously reported ruthenium–carbene catalyzed RCM of dialkenyloxy-substituted organosilicon compounds [26,27], the metathetical conversion of 1,1-bis(alkenyloxy-dimethylsilyl)ethenes lead to the cyclic products without the formation of the respective cyclodimers. Higher concentration of the catalyst is required due to non-metathetical decomposition of Grubbs catalyst (particularly ruthenium–methylidene intermediate) in the presence of alkenyloxy-substituted silanes occurring *via* oxygen interaction with ruthenium or ruthenium center. A detailed ^{1}H NMR analysis of the by-products of the reaction discussed revealed the presence of a small amount (less than 8%) of oligomeric products (formed *via* ADMET), however, they can be easily separated by column chromatography. Table 2 summarizes the results of all RCM reactions examined.

3. Conclusion

The reactivity of 1,1-bis(alkenyldimethylsilyl)ethenes and 1,1-bis(alkenyloxydimethylsilyl)ethenes towards the ruthenium-based ring-closing metathesis catalyst has been examined. Depending on the structure of the substrate, new 7-, 9- and 11-membered silacyclic or 18- and 22-membered silamacrocyclic products containing both 1,1-bis(silyl)ethene and vinylene fragments can be selectively synthesized with moderate to high yields.

4. Experimental

4.1. Analytical equipment

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Varian XL 300 spectrometer using $CDCl_3$ as a solvent. Mass spectra of the products were determined by GC-MS analysis on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and a Finigan Mat 800 ion trap detector. Elemental analyses were carried out by Vario EL III. Column chromatography was carried out on silica gel, particle size 60 μm, using hexane as eluent.

4.2. Materials

First generation Grubbs catalyst [$(PCy_3)_2Cl_2Ru$=CHPh] was purchased from Aldrich. Organic solvents were received from OBR Plock (Poland). Dichloromethane and benzene were dried over CaH_2, distilled under argon and stored with molecular sieves type 3 Å. THF was dried over sodium and benzophenone and freshly distilled prior to use. Dialkenyl- and dialkenyloxy-substituted 1,1-bis(silyl)ethenes (except 1,1-bis(4-pentenyldimethylsilyl)ethene) were synthesized according to the previously reported procedure [9,10]. All reactions were carried out under deoxygenated and dried argon.

4.3. X-ray crystallographic analysis

Data for a colourless crystals of **6** ($0.3 \times 0.15 \times 0.05$ mm) and **7** ($0.2 \times 0.2 \times 0.05$ mm) were collected at 100(1) K on a KUMA KM4CCD. **6**: $C_{24}H_{48}Si_4$, $M = 448.98$, monoclinic, *Pn*, $a = 9.0836(6)$, $b = 7.5736(5)$, $c = 20.8726(13)$ Å, $\beta = 96.515(5)°$, $V = 1426.67(16)$ Å^3, $Z = 2$, R (4855 data with $I \geqslant 2\sigma(I)$; θ_{max} 30.0°) = 0.028, wR (all 5720 data) = 0.057. **7**: $C_{28}H_{58}Si_4$, $M = 507.10$, triclinic, $P\bar{1}$, $a = 6.8896(13)$, $b = 8.8575(16)$, $c = 14.705(4)$ Å, $\alpha = 73.59$ (2)°, $\beta = 78.73$ (2)°, $\gamma = 72.484(16)°$, $V = 814.9(3)$ Å^3, $Z = 1$, R (1542 data with $I \geqslant 2\sigma(I)$; θ_{max} 27.0°) = 0.075, wR (all 2998 data) = 0.169. Programs used: CRYSALIS CCD [33], CRYSALIS RED [34], SHELXS-97 [35], SHELXL-97 [36] and XP [37]. In (**7**) a disorder along one of the arms of macrocycle was found, soft constraints were applied for the geometry of disordered part.

4.4. Synthesis of 1,1-bis(4-pentenyldimethylsilyl)ethene (5)

A solution of 2.0 g (0.01 mol) of 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane [9] in 20 mL dry THF was introduced into a flame-dried, two-necked, 100 mL round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, rubber septum cap and argon bubbling tube. Then, a 0.025 mol amount of 4-pentenylmagnesium bromide in dry THF was added dropwise. The reaction mixture was refluxed under argon for 72 h. The excess amount of Grignard reagent was quenched by adding MeOH/diethyl ether solution and the mixture was extracted from ether/H_2O. The ethereal phase was dried over $MgSO_4$ and filtered, the volatiles removed in evaporator and the mixture was passed through a silica gel column (eluent-hexane). After isolation by "bulb to bulb" distillation 1.44 g of compound **5** was afforded in 52% yield as colourless liquid.

^{1}H NMR($CDCl_3$) δ (ppm): 0.08 (s, 12H, $SiCH_3$), 0.56–0.62 (m, 4H, $SiCH_2CH_2$), 1.30–1.41 (m, 4H, $SiCH_2CH_2$), 2.03–2.11 (m, 4H, $SiCH_2CH_2CH_2$), 4.92–5.03 (m, 4H, CH_2=CH), 5.75–5.84 (dd, 2H, $J = 10.2$ Hz, $J = 17.0$ Hz, CH_2=CH), 6.31 (s, 2H, C=CH_2). **^{13}C NMR**, ($CDCl_3$) δ (ppm): −2.2 ($SiCH_3$), 15.3 ($SiCH_2CH_2$), 23.5 ($SiCH_2CH_2$), 37.7 ($SiCH_2CH_2CH_2$), 114.5 (CH=CH_2), 138.9 (CH=CH_2), 140.9 (C=CH_2), 152.4 (C=CH_2). **MS** (EI) *m*/*z*: 228 (20%), 211 (10), 183 (20), 169 (15), 155 (20), 127 (100), 113 (35), 99 (25), 85 (35), 73 (75), 59 (15). Anal. Calc. for $C_{16}H_{32}Si_2$: C, 68.49; H, 11.49; Found: C, 68.70, H, 11.66%.

4.5. Synthesis of (Z)-1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclohept-5-ene (3)

One gram (4.46×10^{-3} mol) of 1,1-bis(allyldimethylsilyl)ethene was added to the solution of 0.073 g $(PCy_3)_2Cl_2Ru(=CHPh)$ (8.93×10^{-5} mol) and 20 mL CH_2Cl_2 in the two-necked, 50 mL flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was stirred under the flow of argon for 1 h at room temperature. After the substrate disappearance the solvent was evaporated in vacuo and the residue was passed through a silica gel column (eluent-hexane) to give 0.76 g of compound **3** in 92% yield as a colourless liquid.

^{1}H NMR($CDCl_3$) δ (ppm): 0.06 (s, 12H, $SiCH_3$), 1.52 (d, 4H, CH_2), 5.53–5.58 (t, 2H, CH=CH), 6.25 (s, 2H, CH_2=C). **^{13}C NMR** ($CDCl_3$) δ (ppm): −2.3 ($SiCH_3$), 17.6 (CH_2), 124.3 (*C*H=*C*H), 139.8 (*C*H_2=C), 155.0 (CH_2=*C*). **MS** (EI) *m*/*z* (rel. int.): 196 (M^+, 30%), 181 (100), 168 (10), 153 (15), 127 (35), 97 (10), 73 (20). Anal. Calc. for $C_{10}H_{10}Si_2$: C, 61.14; H, 10.26. Found: C, 61.66; H, 10.42%.

4.6. Synthesis of 1,1,3,3,10,10,12,12-octamethyl-2,11-dimethylene-1,3,10,12-tetrasila-cyclooctadeca-6,15-diene (6)

One gram (3.97×10^{-3} mol) of 1,1-bis(3-butenyldimethylsilyl)ethene was added to the solution of 0.131 g $(PCy_3)_2Cl_2Ru(=CHPh)$ (1.59×10^{-4} mol) and 18 mL CH_2Cl_2 in the two-necked, 50 mL flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was stirred under the flow of argon for 24 h at 40 °C. After the substrate disappearance the solvent was evaporated in vacuo and the residue was passed through a silica gel column (eluent-hexane) to give 0.61 g of compound **6** in 68% yield as a white solid.

^{1}H NMR($CDCl_3$) δ (ppm): 0.08, 0.07, 0.09, 0.10 (s, 24H, $SiCH_3$), 0.61–0.67 (m, 8H, $SiCH_2$), 1.86-1.92 (m, 8H, $SiCH_2CH_2$), 5.42–5.44 (m, 4H, CH=CH), 6.31, 6.32, 6.33 (s, 4H, CH_2=C). **^{13}C NMR** ($CDCl_3$) δ (ppm): −2.5, −2.1, −2.0 ($SiCH_3$), 16.2, 16.8, 17.1, ($SiCH_2$), 26.5, 29.8 ($SiCH_2CH_2$), 131.3, 131.4 (CH=CH), 141.3, 141.2 (*C*H_2=C), 152.2 (CH_2=*C*). **MS** (EI) *m*/*z* (rel. int.): 448 (M^+, 10%), 361 (10), 281 (40), 207 (90), 181 (35), 143 (40), 97 (25), 73 (100). Anal. Calc. for $C_{24}H_{48}Si_4$: C, 64.20; H, 10.78. Found: C, 64.09; H, 10.91%.

4.7. Synthesis of 1,1,3,3,12,12,14,14-octamethyl-2,13-dimethylene-1,3,12,14-tetrasila-cyclodocosa-7,18-diene (7)

One gram (3.57×10^{-3} mol) of 1,1-bis(4-pentenyldimethylsilyl)ethene was added to the solution of 0.147 g $(PCy_3)_2Cl_2Ru(=CHPh)$ (1.79×10^{-4} mol) and 16 mL CH_2Cl_2 in the two-necked, 50 mL flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was stirred under the flow of argon for 2 h at 40 °C. After the substrate disappearance, the solvent was evaporated in vacuo and the residue was passed through a silica gel column (eluent-hexane) to give 0.49 g of compound **7** in 55% yield as a colourless liquid.

^{1}H NMR ($CDCl_3$) δ (ppm): 0.06, 0.07 (s, 24H, $SiCH_3$), 0.54–0.61 (m, 8H, $SiCH_2$), 1.26–1.38 (m, 8H, $SiCH_2CH_2$), 1.99–2.07 (m, 8H, $SiCH_2CH_2$ CH_2), 5.34–5.37 (m, 4H, CH=CH), 6.27, 6.29, 6.31 (s, 4H, CH_2=C). **^{13}C NMR** ($CDCl_3$) δ (ppm): −2.2, −2.1, −2.0, −1.9 ($SiCH_3$), 15.7, 15.8, 15.9, 16.0, 16.2 ($SiCH_2$), 23.9, 24.0, 24.1, 24.2, ($SiCH_2CH_2$), 36.4, 36.5, 36.6, 36.6, ($SiCH_2CH_2CH_2$), 129.8, 130.4, 130.5 (CH=CH), 140.8, 140.9, 141.0 (*C*H_2=C), 152.3, 152.5 (CH_2=*C*). **MS** (EI) *m*/*z*: 505 ($[M + H]^+$, 5%), 490 (5), 477 (5), 464 (5), 416 (15), 355 (15), 341 (20), 310 (10), 281 (25), 223 (25) 209 (50), 183 (20), 169 (30), 157 (85) 143 (80), 125 (75), 111 (70), 97 (100) 73 (100), 59 (50). Anal. Calc. for: $C_{28}H_{56}Si_4$: C, 66.58; H, 11.18. Found: 66.72, H, 11.30%.

4.8. Synthesis of (Z)-2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacyclonon-7-ene (8)

One gram (3.91×10^{-3} mol) of 1,1-bis(allyloxydimethylsilyl)ethene was added to the solution of 0.32 g $(PCy_3)_2Cl_2Ru(=CHPh)$ (3.91×10^{-4} mol) and 20 mL C_6H_6 in the two-necked, 50 mL flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was stirred under the flow of argon for 24 h at 60 °C. After the substrate disappearance, the solvent was evaporated in vacuo and the residue was passed through a silica gel column (eluent-hexane) to give 0.55 g of compound **8** in 62% yield as a colourless liquid.

^{1}H NMR($CDCl_3$) δ (ppm): 0.27 (s, 12H, $SiCH_3$), 4.24–4.25 (d, 4H, CH_2O), 5.59–5.62 (m, 2H, CH=CH), 6.30 (s, 2H, CH_2=C). **^{13}C NMR** ($CDCl_3$) δ (ppm): −0.5 ($SiCH_3$), 59.4 (CH_2O), 131.4 (*C*H=*C*H), 142.7 (*C*H_2=C), 154.1 (CH_2=*C*). **MS** (EI) *m*/*z* (rel. int.): 229 ($[M + H]^+$, 3%), 213 (30%), 187 (25), 159 (30), 143 (85), 133 (100), 117 (20), 97 (25), 73 (35). Anal. Calc. for $C_{10}H_{20}O_2Si_2$: C, 52.58; H, 8.82. Found: C, 52.63; H, 8.89%.

4.9. Synthesis of (Z)-2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloundec-8-ene (9)

One gram (3.97×10^{-3} mol) of 1,1-bis(3-butenyloxydimethylsilyl)ethene was added to the solution of 0.30 g $(PCy_3)_2Cl_2Ru(=CHPh)$ (3.97×10^{-4} mol) and 20 mL CH_2Cl_2 in the two-necked, 50 mL flask equipped with a magnetic stirring bar and a reflux condenser. The reaction mixture was stirred under the flow of argon for 24 h at 40 °C. After the substrate disappearance, the solvent was evaporated in vacuo and the residue was passed through a silica gel column (eluent-hexane) to give 0.45 g of compound **9** in 51% yield as a colourless liquid.

^{1}H NMR ($CDCl_3$) δ (ppm): 0.31 (s, 12H, $SiCH_3$), 2.32–2.40 (m, 4H, CH_2CH_2O), 3.64–3.66 (t, 4H, CH_2CH_2O), 5.56–5.61 (m, 2H, CH=CH), 6.53 (s, 2H, CH_2=C). **^{13}C NMR** ($CDCl_3$) δ (ppm): −0.6 ($SiCH_3$), 36.9 (CH_2CH_2O), 63.2 (CH_2CH_2O), 129.2 (*C*H=*C*H), 142.9 (*C*H_2=C),

152.5 (CH_2=*C*). **MS** (EI) *m*/*z* (rel. int.): 241 (65%), 211 (25), 173 (10), 158 (30), 143 (100), 133 (25), 75 (30), 76 (30), 59 (30), 45 (30). Anal. Calc. for: $C_{12}H_{24}O_2Si_2$: C, 56.19; H, 9.43. Found: C, 56.46; H, 9.31%.

5. Supplementary material

CCDC 609243 and 637462 contain the supplementary crystallographic data for **6** and **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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