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Synthesis of Disilacycloalkenes by Ruthenium Alkylidene Catalyzed Ring-Closing Metathesis (RCM) Reaction of α,ω-Bis(allyldimethylsilyl)-Substituted Compounds[1)]

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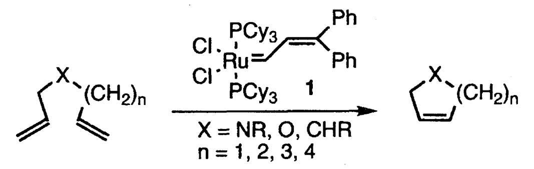
Ruthenium-catalyzed ring-closing metathesis (RCM) reactions of various α,ω-bis(allyldimethylsilyl)-, bis(dimethylvinylsilyl)-, and bis(dimethylvinyloxysilyl)-substituted compounds are examined. The steric and electronic influences of the substrates on the RCM reaction were discussed. Although the successful ring-closing reactions are limited to seven- and eight-membered rings, disilacycloalkene derivatives constructed with $-SiMe_2-CH_2-SiMe_2-$, $-SiMe_2-(CH_2)_2-SiMe_2-$, $-SiMe_2-O-SiMe_2-$, $-SiMe_2-N(Ph)-SiMe_2-$, and a vinylene unit in the ring system were obtained in good to reasonable yields under the mild reaction conditions. The limitation of the reactions is mainly ascribed to Si–C and Si–Si bonds being longer than the C–C bond in the ring system.

Cyclic organosilicon compounds are an interesting class of compounds because of their unique reactivities and structures. Synthesis as well as structures and modes of reaction of these compounds thus have attracted much attention in recent years.[2)] In particular, the cyclic systems composed of the carbon–carbon multiple bonds are quite interesting due to the highly reactive carbon π bond(s). Silacycloalkenes, which include a vinylene unit in the ring system, have attracted growing interest, especially in the field of polymer chemistry. For example, silacycloalkenes are applied to monomers of the ring-opening polymerization for the highly ordered alternating poly(silylenevinylene)copolymers.[3)] Because many potential applications are proposed to the silicon polymers, the electronic and geometric features of the vinylene unit should add additional functions to the usefulness of the silicon polymers.[4)]

Several attempts at preparing the silacycloalkene derivatives exist. Among them, the bis-silylation reaction to the carbon–carbon triple bond occupies an interesting position, since it is employed as one of the most popular methods.[5)] However, the cyclization products thus prepared are limited only to cyclic disilaalkenes, in which a vinylene unit is directly connected to silylene units in the ring system. In order to establish a general methodology for the preparation of unsaturated disilacycloalkene derivatives, it is important to look for a complementary process as an alternative to the bis-silylation reaction.

We wish herein to report the ruthenium alkylidene-catalyzed ring-closing metathesis (RCM) reaction of several α,ω-unsaturated silaalkadienes as the first application of the RCM reaction to the preparation of silacycloalkene derivatives. The ruthenium alkylidene complex **1**, which has recently been synthesized by Grubbs et al., is an efficient catalyst for the ring closure of functionalized dienes to afford the corresponding cycloalkenes (Eq. 1).[6)] Indeed recently, several cyclic natural products[7)] and heterocyclic compounds[8)] have been prepared by means of the Grubbs's RCM reaction.



(1)

In this paper, the synthetic feasibility of the RCM reaction for preparing disilacycloalkenes was investigated on various α,ω-bis(allyldimethylsilyl)-, bis(dimethylvinylsilyl)-, and bis(dimethylvinyloxysilyl)-substituted compounds **2**—**10** (Fig. 1). The accessible ring-size of the cyclization products was first investigated by using alkylene-bridged α,ω-bis(allyldimethylsilyl)compounds **2**—**6**, which should be precursors of possible five-, six-, seven-, eight-, and nine-membered cyclic silaalkenes **11**—**15**. In addition to the experimental survey, the semi-empirical PM3 conformational analyses were also carried out to deepen the understanding of the reaction mechanism especially of the accessible ring-size.[9)]

The RCM reaction was also applied to the oxygen- or nitrogen-bridged bis(allyldimethylsilyl)methane derivatives **7** and **8** for the preparation of the unsaturated silicon heterocycles **16** and **17**. Although the accessible products were limited to seven- and eight-membered rings, the disilacycloalkenes constructed with $-SiMe_2-CH_2-SiMe_2-$, $-SiMe_2-(CH_2)_2-SiMe_2-$, $-SiMe_2-O-SiMe_2-$, and $-SiMe_2-N(Ph)-SiMe_2-$ have been successfully obtained under the mild reaction conditions. The scope and limitation of the

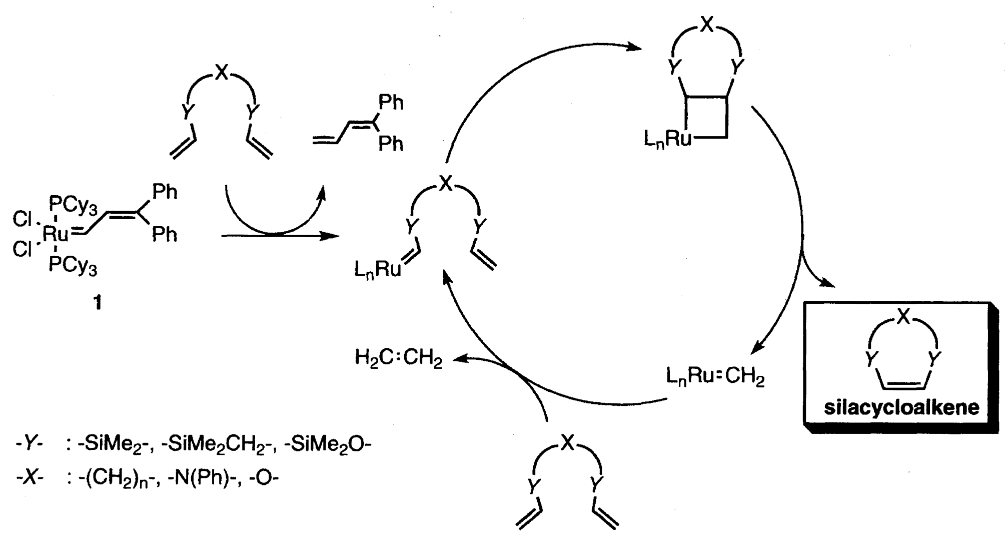


Fig. 1. Catalytic cycles of the ruthenium alkylidene catalyzed RCM reaction providing silacycloalkene derivatives.

reaction as applied to synthesis of the disilacycloalkenes are also discussed on the basis of steric and electronic properties of substrates **9** and **10**. After completion of our present work, we became aware of a closely related study about RCM reaction of α,ω-bis(vinylsilyl)compounds involving a silyl transfer mechanism.[10)]

Experimental

General. ^{1}H (300.1 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.6 MHz) NMR spectra were measured on a Bruker DPX-300 NMR spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to internal $CDCl_3$ (^{1}H $\delta = 7.24$; ^{13}C $\delta = 77$) relative to Me_4Si at 0 ppm. ^{29}Si chemical shifts were relative to Me_4Si at 0 ppm. Low resolution mass spectra were obtained on a Finnigan Mat GCQ mass spectrometer. High-resolution mass spectra were obtained on a JEOL JMS DX-300 mass spectrometer. GLC analysis was conducted by using a Shimadzu 8A gas chromatograph with a 4 mm × 1.5 m glass column (5% or 15% SE-30 on Celite 545) or a Shimadzu 17A gas chromatograph with a CBP 0.25 nm × 30 m capillary column. Semi-empirical MO calculations were performed using the PM3 method in the MOPAC installed on a Macintosh PowerBook 5300cs. The ruthenium complex **1** was prepared from $[RuCl_2(PPh_3)_3]$ according to published procedures.[6m)] α,ω-Bis(allyldimethylsilyl)-, bis(dimethylvinylsilyl)-, and bis(dimethylvinyloxysilyl)-substituted compounds were prepared by conventional methods from the corresponding chlorosilanes.

General Procedure for the Ruthenium-Catalyzed Ring-Closing Metathesis (RCM) Reactions of α,ω-Bis(allyldimethylsilyl) Compounds. The following is a typical example of the RCM reaction. Under an argon atmosphere, bis(allyldimethylsilyl)methane **4** (5.0 g, 2.4×10^{-2} mol) was added to a solution of the ruthenium complex **1** (0.38 g, 4.1×10^{-4} mol) in 100 ml dry benzene. After the solution was stirred at room temperature for 2 h, GPC examination revealed that **4** was completely consumed to produce the corresponding cyclization product **13**. The solvent of the reaction mixture was removed under reduced pressure and the residue was purified by silica-gel column chromatography to afford the essentially pure product **13** (3.85 g, 87% yield).

Spectral data and physical properties of the cyclization products are as follows.

4,4,6,6-Tetramethyl-4,6-disilacycloheptene (13). ^{1}H NMR (C_6D_6) $\delta = -0.20$ (s, 2H), 0.15 (s, 12H), 1.59 (d, $J = 8.9$ Hz, 4H), 5.70 (t, $J = 8.9$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 0.6$, 5.2, 18.4, 124.6; ^{29}Si NMR ($CDCl_3$) $\delta = 4.4$. HRMS Calcd for $C_9H_{20}Si_2$: M, 184.1104. Found: *m/z* 184.1102.

4,4,7,7-Tetramethyl-4,7-disilacyclooctene (14). ^{1}H NMR (C_6D_6) $\delta = 0.11$ (s, 12H), 0.74 (s, 4H), 1.57 (d, $J = 7.3$ Hz, 4H), 5.58 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -2.7$, 8.3, 17.6, 123.3; ^{29}Si NMR ($CDCl_3$) $\delta = 4.1$. HRMS Calcd for $C_{10}H_{22}Si_2$: M, 198.1260. Found: *m/z* 198.1231.

4,4,6,6-Tetramethyl-5-oxa-4,6-disilacycloheptene (16). ^{1}H NMR ($CDCl_3$) $\delta = 0.11$ (s, 12H), 1.55 (d, $J = 7.1$ Hz, 4H), 5.64 (t, $J = 7.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 0.5$, 20.0, 126.3; ^{29}Si NMR ($CDCl_3$) $\delta = 5.0$. HRMS Calcd for $C_8H_{18}OSi_2$: M, 186.090. Found: *m/z* 186.089.

***N*-Phenyl-4,4,6,6-tetramethyl-5-aza-4,6-disilacycloheptene (17).** The RCM reaction of *N*,*N*-bis(allyldimethylsilyl)aniline **8** was carried out according to the general procedure. However, the reaction scale (3.0×10^{-4} mol) was too small to isolate the pure cyclization product **17**. The formation of the cyclization product **17** was thus confirmed only by a low-resolution mass spectrometer. The reaction yield was determined by capillary GLC analysis on the basis of octane as an internal standard; GC-MS, *m/z* (%) 261 (M^+; 79), 246 (M^+-Me; 100).

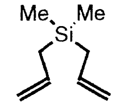
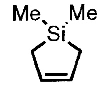
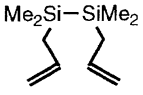
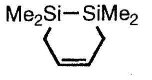
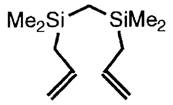
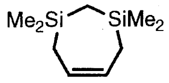
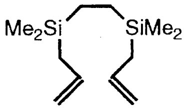
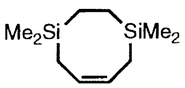
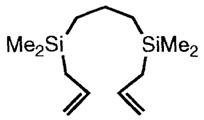
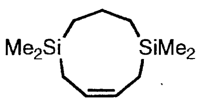
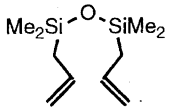
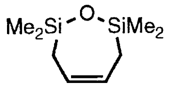
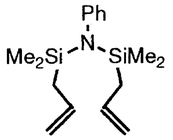
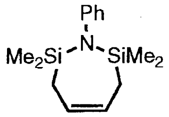
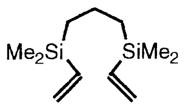
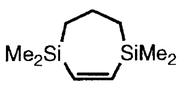
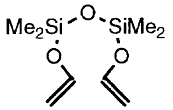
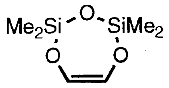
Results and Discussion

Accessible Ring-Size in the RCM Reaction for Preparing Disilacycloalkenes. The ruthenium catalyst **1** used in the cyclization reaction was prepared according to Grubbs's method.[6m)] The RCM reactions were generally carried out in benzene with 2 mol% **1** unless otherwise noted, all the results being listed in Table 1.

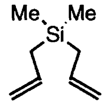
Initially, we have examined the accessible ring-size in the ring-closing metathesis (RCM) reaction for preparing silacycloalkenes from alkylene-bridged α,ω-bis(allyldimethylsilyl)-substituted compounds **2**—**6**, which should provide the corresponding five-, six-, seven-, eight-, and nine-membered cyclic silaalkenes **11**—**15** (Chart 1).

The RCM reaction of diallyldimethylsilane **2**, which should be the precursor of a five-membered silacycloalkene **11**, did not occur at all and **2** was recovered quantitatively. 1,2-Diallyl-1,1,2,2-tetramethyldisilane **3** also did not pro-

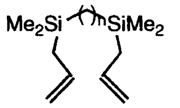
Table 1. Ruthenium-Catalyzed Ring-Closing Metathesis (RCM) Reactions of α,ω-Bis(allyldimethylsilyl)-, Bis(dimethylvinylsilyl)-, and Bis(dimethylvinyloxysilyl)-Substituted Compounds (2 mol% **1**, C_6H_6)

Substrate		Product		Condition	Yield (%)
	**2**		**11**	80 °C 12 h	No reaction
	**3**		**12**	80 °C 12 h	No reaction
	**4**		**13**	R.T. 2 h	87
	**5**		**14**	65 °C 21 h[a)]	51
	**6**		**15**	R.T. 2 h	No reaction
	**7**		**16**	R.T. 2 h	66
	**8**		**17**	R.T. 2 h	49[b)]
	**9**		**18**	R.T. 2 h	No reaction
	**10**		**19**	R.T. 2 h	No reaction

a) 11 mol% **1**. b) Determined by GLC analysis.



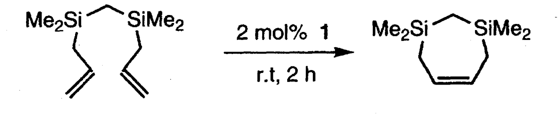
2



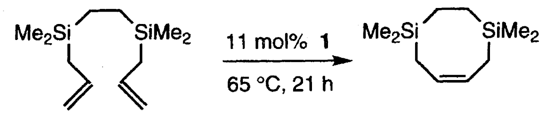
3: n = 0, **4**: n = 1
5: n = 2, **6**: n = 3

Chart 1.

vide a six-membered cyclization product **12**, and remained unchanged during the attempted reaction. In contrast, when the ring-size of the expected cyclization product was increased once more to the seven-membered ring, the reactivity changed dramatically in favor of the RCM reaction. Thus, bis(allyldimethylsilyl)methane **4** gave the seven-membered cyclic disilaalkene **13** in 87% isolated yield under the mild conditions of room temperature for 2 h (Eq. 2). Although somewhat severe conditions such as larger amount of the catalyst (11 mol% **1**), longer reaction time (21 h), and higher temperature (65 °C) were required to complete the reaction, the eight-membered cyclic disilaalkene **14** was also obtained from 1,2-bis(allyldimethylsilyl)ethane **5** in 51% isolated yield (Eq. 3). These facile cyclization reactions demonstrate that the RCM reaction can be applied to the preparation of various seven- and eight-membered disilacycloalkene derivatives. The RCM reaction, however, became completely suppressed again recovering the substrate **6**, when the ring-size was further increased to a nine-membered cyclic disilaalkene **15**.



4 13, 87% (2)

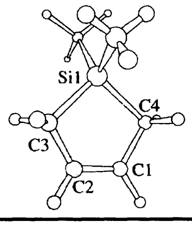


5 14, 51% (3)

Semi-Empirical PM3 Conformational Analysis of the RCM Reaction. Within our present survey, the accessible cyclization products were consequently limited to seven- and eight-membered cyclic disilaalkenes **13** and **14**. Contrary to our expectations, the five- and six-membered cyclic silaalkenes **11** and **12** were not obtained at all, although cyclopentene and cyclohexene are especially accessible cyclization products in view of the ring size of the carbon compounds. We thought that the Si–C (ca. 1.90 Å) and Si–Si bonds (ca. 2.34 Å), which are much longer than C=C (ca. 1.33 Å) and C–C bonds (ca. 1.54 Å), considerably distorted the ring skeletons to suppress the RCM reactions. Then we have examined the optimized structures of the cyclized products by the semi-empirical PM3 method.[11]

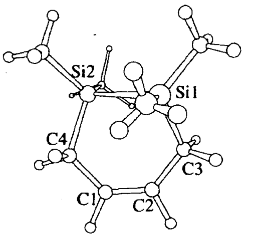
The semi-empirical PM3 calculations show that the optimized five-membered ring **11** is a highly strained structure including unusually narrow bond angles, Si1–C3–C2 (102.5°), Si1–C5–C1 (102.5°), and C3–Si1–C4 (95.1°), in the ring skeleton (Table 2). The optimized six-membered ring **12** is also highly distorted form a normal hexagonal structure (Table 3) with the Si1–Si2 bond length (2.423 Å) stretched by about 0.9 Å from a typical Si–Si single bond. The Si–Si–C bond angles (av. 96.1°) are also significantly narrowed from the normal values. In seven- and eight-membered cyclic disilaalkenes **13** and **14**, however, the three kinds of bond lengths, Si–C, C–C, and C=C, lie in normal values to construct suitable cyclic geometry (Tables 4 and 5), so that the RCM reactions should proceed smoothly to provide the corresponding cyclization products. It should be noted that the distortion of the ring skeleton is also absent in the nine-membered ring **15**, because all the bond lengths and bond angles in the optimized structure are within ranges of normal values (Table 6). The fact that the reaction did not take place to form the nine-membered ring suggests that the entropy factor must play an important role in the reaction. Grubbs also has reported that eight-membered cycloalkenes could not always be produced by the RCM reactions, whereas smaller (five- to seven-membered) rings can be successfully obtained.[6i] The RCM reaction for preparing silacycloalkenes is rather specific due to longer Si–C or Si–Si bonds in the ring system.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of **11** Optimized by PM3



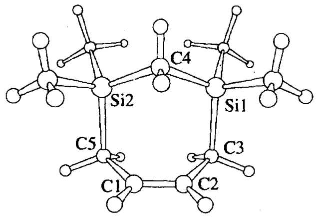
	Bond lengths		
Si1–C3	1.911	Si1–C5	1.910
C1–C2	1.339	C1–C4	1.482
C2–C3	1.482		
	Bond angles		
Si1–C3–C2	102.5	Si1–C5–C1	102.5
C1–C2–C3	112.0	C2–C1–C4	112.0
C3–Si1–C4	95.1		

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of **12** Optimized by PM3



	Bond lengths		
Si1–Si2	2.423	Si1–C3	1.891
Si2–C4	1.891	C1–C2	1.335
C1–C4	1.473	C2–C3	1.473
	Bond angles		
Si1–Si2–C4	96.3	Si2–Si1–C3	95.8
Si1–C3–C2	116.6	Si2–C4–C1	117.1
C1–C2–C3	131.3	C2–C1–C4	131.5

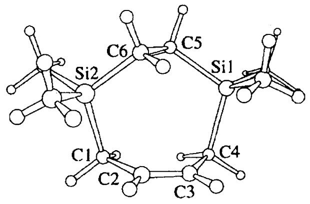
Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of **13** Optimized by PM3



	Bond lengths		
Si1–C3	1.921	Si1–C4	1.878
Si2–C4	1.878	Si2–C5	1.921
C1–C2	1.342	C1–C5	1.469
C2–C3	1.469		
	Bond angles		
Si1–C3–C2	108.6	Si1–C4–Si2	110.3
Si2–C5–C1	108.6	C1–C2–C3	122.2
C2–C1–C5	122.2	C3–Si1–C4	112.5
C4–Si2–C5	112.5		

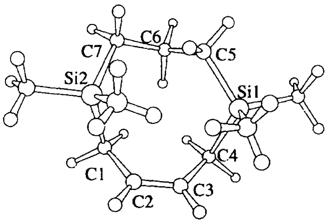
Application to the Synthesis of Unsaturated Silicon Heterocycles. Because it was disclosed that the RCM reaction could be applied in the preparation of seven- and

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) of **14** Optimized by PM3



	Bond lengths		
Si1–C4	1.914	Si1–C5	1.915
Si2–C6	1.913	Si2–C1	1.913
C1–C2	1.469	C2–C3	1.341
C3–C4	1.469	C5–C6	1.496
	Bond angles		
Si1–C4–C3	109.2	Si1–C5–C6	112.7
Si2–C1–C2	108.0	Si2–C6–C5	112.3
C1–C2–C3	123.6	C1–Si2–C6	111.9
C2–C3–C4	123.6	C4–Si1–C5	110.8

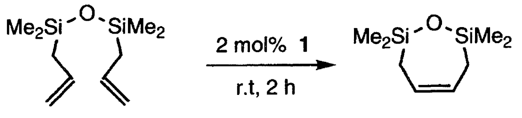
Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) of **15** Optimized by PM3



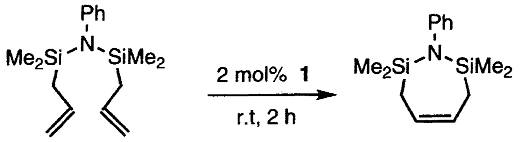
	Bond lengths		
Si1–C4	1.918	Si1–C5	1.920
Si2–C1	1.921	Si2–C7	1.918
C1–C2	1.468	C2–C3	1.341
C3–C4	1.469	C6–C5	1.511
C6–C7	1.510		
	Bond angles		
Si1–C4–C3	109.7	Si1–C5–C6	114.1
Si2–C1–C2	110.3	Si2–C7–C6	111.3
C1–Si2–C7	107.8	C1–C2–C3	124.1
C2–C3–C4	124.3	C4–Si1–C5	112.3
C5–C6–C7	113.1		

eight-membered silacycloalkenes, next we applied the RCM reaction to the preparation of seven-membered unsaturated silicon heterocycles from bis(allyldimethylsilyl)methane derivatives containing $-SiMe_2-O-SiMe_2-$ or $-SiMe_2-N-(Ph)-SiMe_2-$ units instead of $-SiMe_2-CH_2-SiMe_2-$. Silicon heterocycles have been expected to be valuable in the application to the precursors for silicon-based hybrid materials, some of them being already produced on a commercial basis. Thus, the synthesis of unsaturated cyclic disiloxane and disilazane is a useful extension of this methodology.

1,3-Diallyl-1,1,2,2-tetramethyldisiloxane **7** gave the corresponding cyclic disiloxane derivative **16** in 66% isolated yield under mild conditions without any problems (Eq. 4). The RCM reaction of *N*,*N*-bis(allyldimethylsilyl)aniline **8** also proceeded smoothly to give the corresponding cyclic disilazane compound **17** by a similar procedure in 49% GLC analytical yield (Eq. 5).



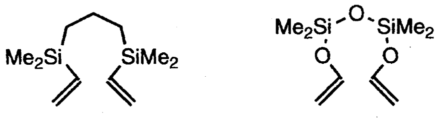
7 **16**, 66% (4)



8 **17**, 49% (5)

Steric and Electronic Influence over the RCM Reaction. Finally, scope and limitations of the RCM reaction as applied to preparing disilacycloalkenes were investigated from viewpoints of steric and electronic properties of substrates. Investigations of steric and electronic influences over the RCM reaction were carried out with 1,3-bis(dimethylvinylsilyl)propane **9** and 1,3-bis(dimethylvinyloxy)-1,1,2,2-tetramethyldisiloxane **10**, precursors of the seven-membered disilacycloheptene **18** and trioxadisilacycloheptene **19**, respectively, because the seven-membered ring, as mentioned above, proved to be the preferred size for the RCM reaction of disilacycles (Chart 2).

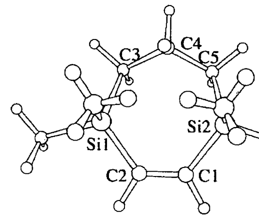
In the cyclization reaction of 1,3-bis(dimethylvinylsilyl)propane **9**, which is a structural isomer of the effective substrate **4**, the RCM reaction did not proceed at all to give the corresponding cyclization product. The thermodynamic properties of the expected cyclization product **18**, in terms of ring strain, should be similar to that of **13**, because the ring skeleton of **18** is a seven-membered ring composed of the same units as **13**. The PM3 calculation also suggests that bond lengths and bond angles in the optimized structure of **18** are rather normal (Table 7). Probably the RCM reaction of **9** was suppressed by the steric bulk of four methyl groups neighboring to the reaction sites (Eq. 6). Thus, **9** failed to give the cyclization product despite the possible formation of the expected seven-membered ring. Although the result is somewhat disappointing in that the synthetic potentials of this methodology for disilacycles are limited to some extent, there is a possibility of using the RCM reaction if it is applied to less sterically hindered vinylsilanes. For example, the reaction may be applied to 1-(allyldimethylsilyl)-2-(dimethylvinylsilyl)ethane, $CH_2=CHCH_2(Me_2)SiCH_2CH_2Si(Me_2)-CH=CH_2$, in which one side of (dimethylvinylsilyl)methyl groups of the inert substrate **9** is replaced by an isomeric al-



9 **10**

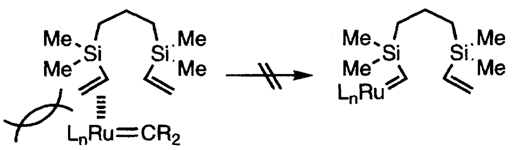
Chart 2.

Table 7. Selected Bond Lengths (Å) and Bond Angles (deg) of **18** Optimized by PM3

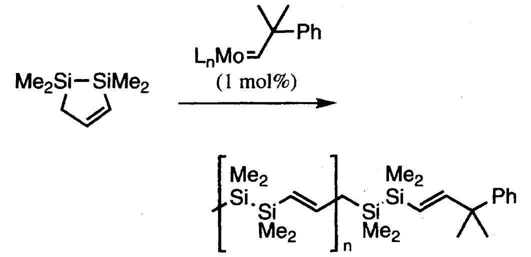


Bond lengths			
Si1–C2	1.844	Si1–C3	1.910
Si2–C1	1.844	Si2–C5	1.908
C1–C2	1.318	C3–C4	1.508
C4–C5	1.507		
Bond angles			
Si1–C2–C1	126.6	Si1–C3–C4	112.9
Si2–C1–C2	126.7	Si2–C5–C4	112.9
C1–Si2–C5	113.7	C2–Si1–C3	113.5
C3–C4–C5	113.7		

lyldimethylsilyl group to reduce the steric hindrance. In this respect, it is interesting to note that Sita et al. have recently reported the facile ring-opening metathesis polymerization of disilacyclopentene (Eq. 7).[3a)]



(6)



(7)

Not only steric bulk, but also electronic influence around the reaction sites should affect the reactivity of the RCM reaction. The reaction of 1,3-bis(vinyloxy)-1,1,3,3-tetramethyldisiloxane **10** did not give the corresponding cyclization product **19**, the starting material being recovered quantitatively. Although **10** is structurally similar to the effective substrate **7**, electronic properties of the reaction sites are very different due to the electron donation from the oxygen atom through the resonance effect. Because the ruthenium catalyst **1** is a Schrock-type alkylidene complex, in which the metal–carbon bond is polarized in a mode of $M^{\delta +}=C^{\delta -}$ (Fig. 2),[12)] the catalytic species in the RCM reaction should be destabilized electronically by the oxygen atom on the alkylidene carbon. Thus, the catalytic cycle did not progress and the formation of the cyclization product failed. In this connection, it is interesting to note that bis(allyloxy)diphenylsilane derivatives undergo the successful RCM reaction to give seven-membered products.[13)] We became aware of the result after completion of the manuscript.

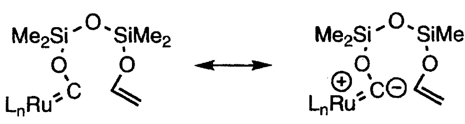


Fig. 2. The resonance structures of Schrock-type alkylidene complex.

In conclusion, we have demonstrated the application of the ruthenium alkylidene catalyzed RCM reactions to preparing the silacycloalkene derivatives for the first time. Although the accessible ring-size was limited to seven and eight, the disilacycloalkenes composed of $-SiMe_2-CH_2-SiMe_2-$, $-SiMe_2-(CH_2)_2-SiMe_2-$, $-SiMe_2-O-SiMe_2-$, and $-SiMe_2-N(Ph)-SiMe_2-$ units have been successfully obtained under the mild reaction conditions.

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