Novel Highly Stereoselective Approach toward (*Z*)-1,2-Bis(silyl)ethenes

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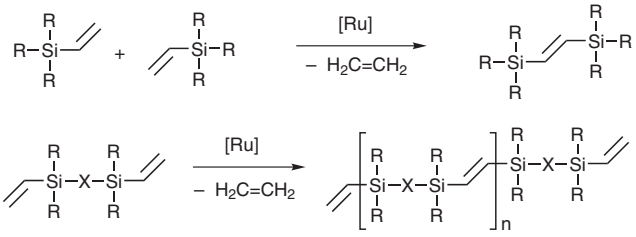
Abstract: A new flexible and stereoselective protocol for the synthesis of the compounds of the general formula, (*Z*)-$Ph_2RSiCH{=}CHSiRPh_2$ (where R is an alkyl, alkenyl or alkoxy substituent) has been developed. The title compounds have been efficiently obtained by ruthenium hydride complex $[RuHCl(CO)(PCy_3)_2]$-catalyzed (*Z*)-selective silylative coupling cyclization of 1,2-bis(diphenylvinylsiloxy)ethane or *N*,*N*′-dimethyl-*N*,*N*′-di(diphenylvinylsilyl)ethane-1,2-diamine to generate respective disilacyclic platforms, followed by their reaction with Grignard reagents or alcohols. (*Z*)-Bis(silyl)ethenes could not be synthesized by a metathesis procedure.

Key words: vinylsilanes, silylative coupling, ruthenium complex, Grignard reagent, cyclization

Vinylsilanes are a class of compounds that has attracted significant attention in recent years as important intermediates in stereocontrolled organic synthesis.[1] Over the last few decades, considerable effort has been made to find new routes for the preparation of these compounds and for their selective reaction with different electrophiles. Due to similar properties of 1,2-bis(silyl)ethenes to those of vinylsilanes, they have gained significant attention as potential precursors in organic and organosilicon syntheses.[2] Despite their importance, there is a only limited number of access routes to doubly silylated ethenes. Conventional approaches to (*Z*)-1,2-bis(silyl)ethenes involve catalytic double silylation of alkynes[3] and hydrosilylation of alkynylsilanes by hydrosilanes.[3a,4] Unfortunately, (*Z*)-1,2-bis(silyl)ethenes cannot be synthesized via *homo*-metathesis reaction due to the inactivity of vinylsilanes in this process.[5] Several independent methods, e.g. stoichiometric reaction of alkoxytitanium(IV) complexes with bis(silyl)acetylenes and silylcupration of alkynes have also been investigated.[6] However, application of these methods has been limited because of difficulties in accessing stereo- and regiodefined isomers, owing to the possibility of forming a mixture of two [β-(*Z*) and β-(*E*) in bis-silylation] or three [β-(*Z*), β-(*E*) and α- in hydrosilylation] isomeric bis(silyl)ethenes. The use of the above-mentioned methods is hampered not only by formation of a mixture of stereo- or regioisomers but also by the relatively high cost of the starting acetylenic derivatives as well as platinum or palladium complexes, which mostly catalyze these processes. Therefore, in view of the growing interest in 1,2-bis(silyl)ethenes, development of more efficient and straightforward synthetic methods is of great significance.

In the last two decades we have developed the silylative coupling reaction of vinylsilane derivatives in the presence of transition-metal complexes (e.g. ruthenium and rhodium) initially containing or generating M–H and M–Si bonds.[7] This process under optimum conditions has become an excellent method for the selective synthesis of (*E*)-1,2-bis(silyl)ethenes,[8] as well as macromolecular organosilicon compounds containing (*E*)-1,2-bis(silyl) fragments,[9] which can be used as interesting synthetic reagents for organic synthesis and polymeric materials (Scheme 1).



X = O, NH, $(CH_2)_n$, C_6H_4
[Ru] = $[RuCl_2(CO)_3]$, $[RuHCl(CO)(PCy_3)_2]$, $[RuHCl(CO)_2(PPh_3)_2]$

Scheme 1 Synthesis of (*E*)-1,2-bis(silyl)ethenes

The silylative coupling reaction of vinyl organosilicon compounds occurs by cleavage of the =C–Si bond of the vinyl-substituted silicon compound and the activation of the =C–H bond of the second vinylsilane molecule. The mechanism of this reaction involves insertion of vinylsilane into the M–H bond followed by β-silyl elimination, which generates a M–Si species and ethylene, followed by insertion of the second vinylsilane molecule into the M–Si bond. In the last stage, elimination of the isomeric bis(silyl)ethenes with regeneration of the initial M–H complex takes place.[10] During the course of our recent studies on the silylative coupling cyclization of divinyl-substituted organosilicon compounds, we have developed new facile and efficient protocols for the synthesis of alkyl-, aryl-, alkenyl- or alkoxy-substituted 1,1-bis(silyl)ethenes using cyclic silyl ether or cyclic silyl amine. These 1,1-bis(silyl)ethenes were selectively obtained by ruthenium-catalyzed silylative coupling *exo*-cyclization of divinyl-substituted monomers, followed by their reaction with Grignard[11a] reagents or alcohols[11b] (Scheme 2).

Although the silylative coupling methodology reported so far establishes a simple and convenient route for the selec-

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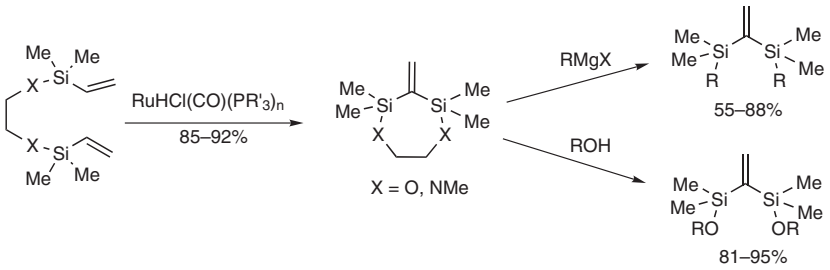
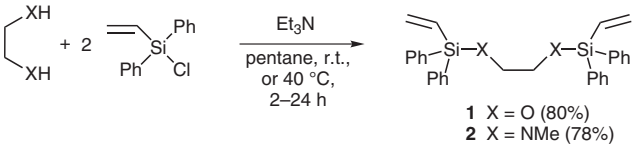


Scheme 2 Synthesis of 1,1-bis(silyl)ethenes

tive synthesis of a wide range of (*E*)-1,2- and 1,1-bis(silyl)ethenes, this particular procedure could not have been applied in the synthesis of (*Z*)-1,2-bis(silyl) derivatives which also seem to be desirable reagents in the organic and organosilicon syntheses. Very recently we have reported the first example of effective silylative coupling cyclization of 1,1′-(diphenylvinylsilyl)ferrocene to give cyclic product containing a *Z*-vinylene bond between the silicon atoms.[12] Bulky phenyl substituents have apparently been the reason for such a regioselectivity of the product isolated. However, this compound possesses a rigid structure and cannot be functionalized to produce substituted (*Z*)-1,2-bis(silyl)ethenes. Therefore, the aim of the paper is to extend the silylative coupling procedure to the stereoselective synthesis of substituted (*Z*)-1,2-bis(silyl)ethenes.

The starting 1,2-bis(diphenylvinylsiloxy)ethane (**1**) and *N*,*N*′-dimethyl-*N*,*N*′-di(diphenylvinylsilyl)ethane-1,2-diamine (**2**) were conveniently prepared by the reaction of chlorodiphenylvinylsilane with ethylene glycol and *N*,*N*′-dimethylethane-1,2-diamine, respectively in the presence of triethylamine in high yield, as outlined in Scheme 3.



Scheme 3 Synthesis of divinyl-substituted monomers

Ruthenium complexes [$RuHCl(CO)(PPh_3)_3$] (**I**), [$Ru(SiMe_3)(Cl)(CO)(PPh_3)_2$] (**II**) and [$RuHCl(CO)(PCy_3)_2$] (**III**) have recently been reported as effective catalysts for selective silylative coupling cyclization[11] and polycondensation[8a] of divinyl-substituted monomers. In view of the structural similarity of **1** and **2** to the earlier reported substrates, we expected compounds **1** and **2** to also undergo the silylative coupling cyclization. The conditions for an effective transformation of 1,2-bis(diphenylvinylsiloxy)ethane (**1**) and *N*,*N*′-dimethyl-*N*,*N*′-di(diphenylvinylsilyl)ethane-1,2-diamine (**2**) in the presence of ruthenium catalysts were optimized by catalytic screenings of the substrate conversion and the yield of cyclic product by using GC and GC-MS methods. Generally, the catalysis of the initial hexacovalent ruthe-

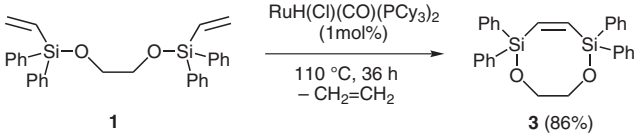
Table 1 Silylative Coupling Cyclization of **1** and **2**[a]

Catalyst	Compound **1**		Compound **2**	
	Time (h)	Yield of **3** (%)[b]	Time (h)	Yield of **4** (%)[b]
$RuHCl(CO)(PPh_3)_3$	48	0	48	0
$RuHCl(CO)(PPh_3)_3$/CuCl (5%)	24	10	24	15
$RuHCl(CO)(PPh_3)_3$/CuCl (5%)	48	14	48	18
$Ru(SiMe_3)(Cl)(CO)(PPh_3)_2$	24	30	24	16
$Ru(SiMe_3)(Cl)(CO)(PPh_3)_2$	48	56	48	25
$RuHCl(CO)(PCy_3)_2$	24	86	24	42
$RuHCl(CO)(PCy_3)_2$	36	100	48	100
$RuHCl(CO)(PCy_3)_2$[c]	24	72	48	22
$RuHCl(CO)(PCy_3)_2$[c]	36	100	36	48
$RuHCl(CO)(PCy_3)_2$/CuCl (5%)	24	88	24	45
$RuHCl(CO)(PCy_3)_2$/CuCl (5%)	48	100	48	72

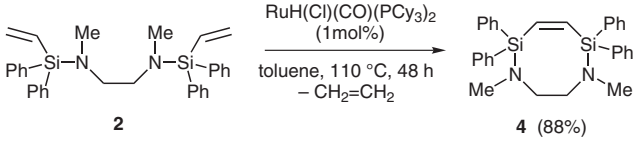
[a] Reaction conditions: toluene, 110 °C, argon atmosphere, monomer/[Ru] = 100:1.
[b] Determined by GC.
[c] Without toluene, 110 °C, glass ampoule.

nium complex **I** was less effective than in the presence of coordinatively unsaturated pentacoordinated ruthenium complexes. Unexpectedly, the cyclization of the compounds **1** and **2** did not occur in the presence of the ruthenium hydride complex **I**. At 1 mol% catalyst loading an outstanding catalytic activity was observed for the pentacoordinated ruthenium hydride complex containing tricyclohexylphosphine: $[RuHCl(CO)(PCy_3)_2]$ (**III**). However, the use of CuCl (5 mol%), reported to be an efficient co-catalyst for silylation of styrenes[13a] and vinylboranes,[13b] caused a slight increase in the catalytic activity of complex **I**, while when used with catalyst **III** it did not appreciably affect the rate i.e. the efficiency of the silylative coupling cyclization (Table 1).

The silylative coupling cyclization of **1** successfully proceeded in the presence of $[RuHCl(CO)(PCy_3)_2]$ (1 mol%), without solvent, under argon atmosphere (glass ampoule) and divinyl silyl ether **1** was exclusively transformed into cyclic product **3** (Equation 1) in 36 hours at 110 °C. However, toluene could also be employed without affecting either the activity of the catalyst or the selectivity of this process. Contrary to the above-mentioned process the silylative coupling cyclization of **2** occurred efficiently only in toluene, in the open system (Equation 2), however, it required a longer reaction time (48 h).



Equation 1 Synthesis of (*Z*)-2,2,5,5-tetraphenyl-1,6-dioxa-2,5-disilacyclooct-3-ene



Equation 2 Synthesis of (*Z*)-2,2,5,5-tetraphenyl-1,6-dioxa-2,5-disilacyclooct-3-ene

The use of this catalytic system for silylative coupling cyclization of **1** and **2** gave exclusively a disilacyclic products containing *Z*-vinylene bond between silicon atoms with perfect stereoselectivities and high yields (86–88%). The *Z*-configuration in the *endo*-cyclic vinylene bond of the cyclic products, (*Z*)-2,2,5,5-tetraphenyl-1,6-dioxa-2,5-disilacyclooct-3-ene (**3**) and (*Z*)-1,6-dimethyl-2,2,5,5-tetraphenyl-1,6-diaza-2,5-disilacyclooct-3-ene (**4**) was determined on the basis of the ^1H, ^{13}C NMR and DEPT spectra. Moreover, the cyclic silyl ether **3** proved to be a solid and yielded a crystal amenable to X-ray structure determination (Figure 1).

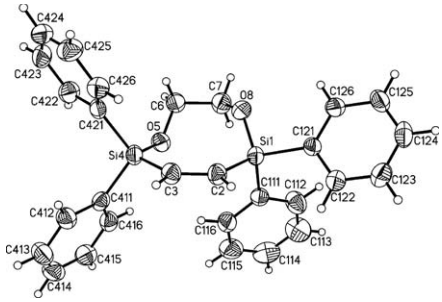
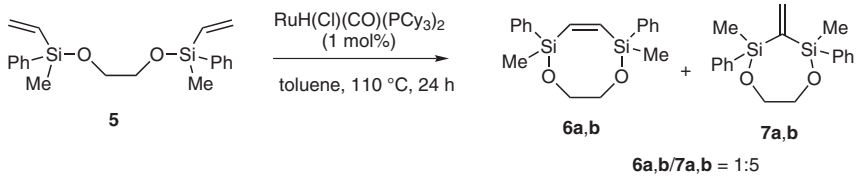


Figure 1 A perspective view of the molecule **3**. The anisotropic displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are depicted as spheres of arbitrary radii.

Figure 1 shows the perspective view of the molecule **3**.[14] The C2–C3 bond length, of 1.355(5) Å proves that this is a double bond, and the disposition of Si atoms around this bond is *cis* [the torsion angle Si–C–Si is 1.5(6)°].

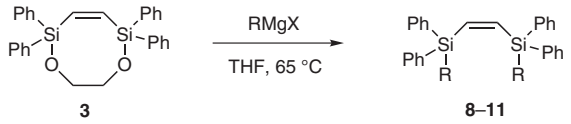
To understand the role of the phenyl group in these studies we synthesized, the analogous divinyl silyl ether (**5**) bearing the methylphenylsilyl groups instead of the diphenylsilyl fragments. We performed the silylative coupling cyclization of **5** under similar conditions as those applied for the compound **1** {$[RuHCl(CO)(PCy_3)_2]$ (1 mol%), toluene, 110 °C, 24 h}. GC-MS and NMR analyses of the products showed that silylative coupling cyclization of **5** (mixture of diastereoisomers) allows the synthesis of a mixture of cyclic products **6a** and **6b** (*meso*- and racemic mixture) containing *endo*-vinylene bond and **7a** and **7b** (*meso*- and racemic mixture) containing *exo*-methylene fragment between silicon atoms (Equation 3). Thus, the selectivity of the silylative coupling cyclization depends on the organyl group attached to silicon, producing stereoselectively the *Z*-vinylene product when the substituents are phenyl groups (presumably due to steric effects) and the mixture of products containing either *Z*-vinylene and *exo*-methylene bond when both methyl and phenyl groups are employed. It is worth noting that dimethylsilyl-substituted monomers under the same conditions led to the regioselective formation of the product containing 1,1-bis(silyl)ethene fragments.[11]

To test the synthetic utility of cyclic silyl ether **3**, we pursued transformation of the obtained product into synthetically useful (*Z*)-1,2-bis(organyldiphenylsilyl)ethenes (Equation 4). After preliminary attempts we found that



Equation 3 Silylative coupling cyclization of 1,2-bis(methylphenylvinylsiloxy)ethane

treatment of **3** with 2.5 equivalents of the corresponding Grignard reagent in THF (0.5 M concentration of the solvent) at 65 °C for 24 hours under argon atmosphere provided substituted (*Z*)-1,2-bis(silyl)ethenes in moderate to good yields (Table 2).



3 **8–11**

Equation 4 Synthesis of (*Z*)-1,2-bis(organyldiphenylsilyl)ethenes

However, when ethylmagnesium bromide was used, the reaction mixture had to be refluxed for a longer time and an increased amount of the Grignard reagents (from 2.5–3 equiv) did not appreciably affect the rate of this reaction. When phenylmagnesium bromide (3 equiv) was added to the cyclic silyl ether **3** under the same reaction conditions, no reaction occurred and the starting material was recovered unchanged. Table 2 summarizes the results of this reaction.

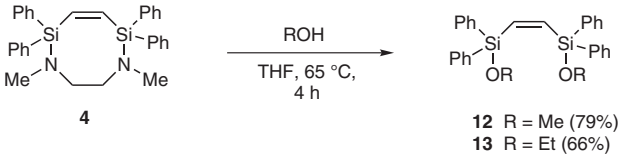
Table 2 Synthesis of (*Z*)-1,2-Bis(organyldiphenylsilyl)ethenes

Compound	R^1	X	Time (h)	Yield (%)[a]
8a	Me	I	24	78
9	Et	Br	48	63
10	$CH{=}CH_2$	Br	24	90
11	$CH_2CH{=}CH_2$	Br	24	78
–	Ph	Br	72	0[b]

[a] Isolated yields of chromatographically pure products.
[b] Exclusively recovered starting material. Reaction conditions: THF, 65 °C.

In all of the reactions examined excellent stereoselectivity was attained and no isomeric product could be detected. All products were isolated and characterized spectroscopically. Results of the spectroscopic analyses (^1H, ^{13}C NMR, DEPT and HMQC) of the products obtained in the above-mentioned reaction have confirmed the occurrence of the *Z*-vinylene carbons between silicon atoms. The *Z*-configuration of compound **8a** was additionally confirmed by preparing the geometrically defined *E*-isomer **8b** of 1,2-bis(methyldiphenylsilyl)ethene by another route, i.e. [$RuHCl(CO)(PCy_3)_2$]-catalyzed selective silylative homo-coupling of methyldiphenylvinylsilane[7] and a comparison of their spectroscopic data.

Inspired by the recently reported successful transformation of cyclic product containing SiN(Me)R functionalities into 1,1-bis(alkoxydimethylsilyl)ethenes,[11b] we envisioned compound **4** to be a good substrate candidate for the synthesis of (*Z*)-1,2-bis(silyl)ethenes containing both alkoxy and aryl substituents. We have found that the treatment of the cyclic compound **4** with 2.5 equivalents of the corresponding alcohol in THF at 65 °C for 4 hours, yielded (*Z*)-1,2-bis(alkoxydiphenylsilyl)ethenes (Equation 5) as expected.[19] Using this procedure we have synthesized two new organosilicon compounds: (*Z*)-1,2-bis(methoxydiphenylsilyl)ethene **12** (isolated yield, 79%) and (*Z*)-1,2-bis(ethoxydiphenylsilyl)ethene (**13**) (isolated yield, 66%).



4

12 R = Me (79%)
13 R = Et (66%)

Equation 5 Synthesis of (*Z*)-1,2-bis(alkoxydiphenylsilyl)ethenes

In conclusion, we have described a novel stereoselective and efficient protocol for the synthesis of (*Z*)-1,2-bis(organyldiphenylsilyl)ethenes from easily available starting materials. Otherwise difficult to synthesize compounds of the general formula (*Z*)-$RPh_2SiCH = CHSiPh_2R$, were exclusively obtained by *Z*-selective silylative coupling cyclization of divinyl-substituted monomers catalyzed by ruthenium hydride complex and subsequent treatment of the resulting cyclic bis(silyl) derivatives with various Grignard reagents or alcohols. Extension of the silylative coupling procedure to *Z*-bis(silyl) derivatives makes this particular method a universal and extremely useful route for the regio- and stereoselective synthesis of isomeric (*Z*)-1,2-, (*E*)-1,2- as well as 1,1-bis(silyl)ethenes.

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian XL 300 spectrometer using $CDCl_3$ or as a solvent. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD. 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 Finnigan Mat 800 ion trap detector. All reactions were performed under an atmosphere of deoxygenated and dried argon. Et_3N, *N*,*N*′-dimethylethane-1,2-diamine and pentane were dried over CaH_2, distilled under argon and stored over molecular sieves type 4A. THF and toluene were dried over sodium and benzophenone and freshly distilled prior to use. Ethylene glycol was dried ($CaSO_4$) and distilled under argon. Grignard reagents were synthesized via well-known procedures described in the literature. [$RuHCl(CO)(PCy_3)_2$] was prepared by adaptation of a procedure described in literature.[15]

Silylative Coupling Cyclization of 1 and 2 Using Different Catalysts (Table 1)

In a typical catalytic test, a toluene solution of the ruthenium hydride catalyst **I**, **II** or **III** was placed in a 5-mL glass mini-reactor. Then the divinyl compound **1** or **2** and dodecane as internal standard (5% by volume) were added (molar ratio: [Ru]/**1** or **2** = 1:100). After that, the reaction mixture was heated at 110 °C under the conditions shown in Table 1. The composition of the reaction mixture was analyzed by GC and identified by use of GC-MS. The progress of the reactions was monitored by GC-MS. The selectivity and yield of the reactions were calculated by using the internal standard method.

1,2-Bis(diphenylvinylsiloxy)ethane (1)

A solution of anhyd Et_3N (23.5 mL, 0.169 mol) in pyridine (500 mL) was introduced into a flame-dried three-necked, 1-L round-bottomed flask equipped with a magnetic stirring bar, rubber septum cap and argon bubbling tube. To the resulting solution was added

ethylene glycol (4.55 mL, 0.081 mol). Chlorodiphenylvinylsilane (36.0 mL, 0.162 mol) was subsequently added and the mixture was stirred under the flow of argon for 2 h at r.t. After the disappearance of the substrate was confirmed by GC, the resulting salt was filtered off and the volatiles were removed in an evaporator. Distillation under reduced pressure afforded 29.03 g (80%) of compound **1**; pale-yellow oil; bp 140 °C/0.5 mmHg.

^{1}H NMR, ($CDCl_3$): δ = 3.95 (s, 4 H, CH_2O), 5.86–5.94 (dd, *J* = 4.0, 20.1 Hz, 2 H, C*H*$_2$=CH), 6.23–6.29 (dd, *J* = 3.9, 14.8 Hz, 2 H, C*H*$_2$=CH), 6.42–6.53 (dd, *J* = 14.8, 20.1 Hz, 2 H, 2 × CH_2=C*H*), 7.36–7.66 (m, 20 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 64,8 (CH_2O), 127,7 (*C*H_2=CH), 129,8 (CH_2=*C*H), 133.3, 133.9, 134.9, 136.9 (C_6H_5).

MS (EI): *m*/*z* (%) = 451 (15), 401 (100), 357 (10), 329 (25), 279 (20), 210 (60), 183 (30), 105 (30), 77 (15), 51 (15).

Anal. Calcd for $C_{30}H_{30}O_2Si_2$: C, 75.27; H, 6.32. Found: C, 75.58; H, 6.42.

N,*N*′-Dimethyl-*N*,*N*′-di(diphenylvinylsilyl)ethane-1,2-diamine (2)

A solution of anhyd Et_3N (16.6 mL, 0.19 mol) in anhyd pentane (200 mL) was introduced into a flame-dried three-necked, 500-mL round-bottomed flask equipped with a magnetic stirring bar, rubber septum cap and argon bubbling tube. To the resulting solution was added *N*,*N*′-dimethylethane-1,2-diamine (6.0 mL, 0.057 mol). Chlorodiphenylvinylsilane (25.2 mL, 0.113 mol) was subsequently added and the mixture was stirred under the flow of argon for 4 h at 40 °C. After the disappearance of the substrate was confirmed by GC, the resulting salt was filtered off under argon and the volatiles were removed in evaporator. Distillation under reduced pressure afforded 22.32 g (78%) of compound **2**; colorless oil; bp 145–147 °C/0.5 mmHg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.46 (s, 6 H, NCH_3), 3.05 (s, 4 H, CH_2), 5.86–5.94 (dd, *J* = 3.8, 20.2 Hz, 2 H, CH=C*H*$_2$), 6.03–6.07 (dd, *J* = 3.8, 13.6 Hz, 2 H, CH=C*H*$_2$), 6.41–6.48 (dd, *J* = 13.6, 20.3 Hz, 2 H C*H*=CH_2), 7.15–7.23 (m, 4 H, C_6H_5), 7.63–7.75 (m, 16 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.9 (NCH_3), 50.2 (CH_2), 127.6 (CH=*C*H_2), 129.3 (*C*H=CH_2), 134.4, 135.4, 135.6, 136.2 (C_6H_5).

MS (EI): *m*/*z* (%) = 478 (10), 406 (30), 356 (70), 329 (70), 303 (30), 252 (100), 226 (30), 181 (45), 105 (45), 78 (50).

Anal. Calcd for $C_{32}H_{36}N_2Si_2$: C, 76.14; H, 7.19; N, 5.55. Found: C, 76.22; H, 7.31, N, 5.78.

(*Z*)-2,2,5,5-Tetraphenyl-1,6-dioxa-2,5-disilacyclooct-3-ene (3)

[$RuHCl(CO)(PCy_3)_2$] (152 mg, 2.1×10^{-4} mol) and compound **1** (10.0 g, 0.021 mol) were placed in a glass ampoule, which was sealed under argon and heated for 36 h at 110 °C. After the disappearance of the substrate was confirmed by GC, the cyclic product was isolated by recrystallization from hexane to give 8.09 g (86%) of **3**; colorless solid; bp 145–147 °C/0.5 mmHg.

^{1}H NMR ($CDCl_3$): δ = 3,88 (s, 4 H, CH_2O), 7,36 (s, 2 H, CH=CH), 7,34–7,64 (m, 20 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 65.5 (CH_2O), 127.7, 129.8, 134.7, 134.9 (C_6H_5), 149.6 (CH=CH).

MS (EI): *m*/*z* (%) = 373 (100), 330 (30), 251 (10), 182 (10), 105 (10), 77 (15), 51 (15).

Anal. Calcd for $C_{28}H_{26}O_2Si_2$: C, 74.62; H, 5.81. Found C, 74.68; H, 5.96.

(*Z*)-1,6-Dimethyl-2,2,5,5-tetraphenyl-1,6-diaza-2,5-disilacyclooct-3-ene (4)

Compound **2** (5.0 g, 0.014 mol) was added to a solution of [$RuHCl(CO)(PCy_3)_2$] (0.102 g, 1.4×10^{-4} mol) and toluene (50 mL) in a two-necked, 100-mL flask equipped with a magnetic stirring bar and a reflux condenser. The mixture was heated under the flow of argon for 24 h at 110 °C with stirring. The solvent was removed using an evaporator and the cyclic products were isolated by 'bulb-to-bulb' distillation to give 4.15 g (88%) of **4**; colorless oil; bp 145–147 °C/0.5 mmHg).

^{1}H NMR ($CDCl_3$): δ = 2.48 (s, 6 H, NCH_3), 3.16 (s, 4 H, CH_2), 7.13 (s, 2 H, CH=CH), 7.32–7.68 (m, 20 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 36.1 (NCH_3), 52.2 (CH_2), 133.4, 134.9, 137.8 (C_6H_5), 150.1 (CH=CH).

Anal. Calcd for $C_{30}H_{32}N_2Si_2$: C, 75.58; H, 6.77; N, 5.88; Found: C, 75.88; H, 6.91; N, 5.73.

1,2-Bis(methylphenylvinylsiloxy)ethane (5)

A solution of anhyd Et_3N (9.42 mL, 0.068 mol) in anhyd pentane (200 mL) was introduced into a flame-dried three-necked, 500-mL round-bottomed flask equipped with a magnetic stirring bar, rubber septum cap and argon bubbling tube. To the resulting solution was added ethylene glycol (1.82 mL, 0.032 mol). Chloromethylphenylvinylsilane (11.4 mL, 0.0624 mol) was subsequently added and the mixture was stirred under the flow of argon for 2 h at r.t. After the disappearance of the substrate was confirmed by GC, the resulting salt was filtered off and the volatiles were removed in evaporator. Distillation under reduced pressure afforded 10.18 g (89%) of compound **5**; colorless oil; bp 120 °C/0.5 mmHg.

^{1}H NMR ($CDCl_3$): δ = 0.48 (s, 6 H, CH_3), 3.79 (s, 4 H, CH_2O), 5.86–5.94 (dd, *J* = 4.4, 19.7 Hz, 2 H, C*H*$_2$=CH), 6.14–6.21 (dd, *J* = 4.4, 15.1 Hz, 2 H, C*H*$_2$=CH), 6.26–6.38 (dd, *J* = 15.1, 19.7 Hz, 2 H, CH_2=C*H*), 7.36–7.65 (m, 20 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = –3.28 (CH_3), 64.4 (CH_2O), 127,7 (*C*H_2=CH), 129.6 (CH_2=*C*H), 133.9, 134.9, 135.3, 135.9 (C_6H_5).

MS (EI): *m*/*z* (%) = 451 (15), 401 (100), 357 (10), 329 (25), 279 (20), 210 (60), 183 (30), 105 (30), 77 (15), 51 (15).

Anal. Calcd for $C_{20}H_{26}O_2Si_2$: C, 67.74; H, 7.39. Found: C, 67.89; H, 7.42

Compounds 6 and 7 (Mixture of Four Isomers)

Compound **5** (5.0 g, 0.014 mol) of was added to a solution of [$RuHCl(CO)(PCy_3)_2$] (0.102 g, 1.4×10^{-4} mol) and toluene (50 mL) in a two-necked, 100-mL flask equipped with a magnetic stirring bar and a reflux condenser. The mixture was heated under the flow of argon for 24 h at 110 °C with stirring. The solvent was removed in evaporator and the cyclic products were isolated by 'bulb-to-bulb' distillation to give 4.23 g (92%) of a mixture of compounds **6a**, **6b**, **7a**, **7b**; colorless oil; bp 112–115 °C/0.5 mmHg.

^{1}H NMR ($CDCl_3$): δ = 0.50, 0.51, 0.56, 0.57 (s, CH_3), 3.73, 3.84, 3.87, 3.88 (s, CH_2O), 6.42 (s, CH=CH), 6.46 (s, CH=CH), 7.05 (s, C=CH_2), 7.32–7.68 (m, 20 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = –2.2, –2.1, –1.4, –1.3 (CH_3), 65.4, 66.8 (CH_2O), 127.7, 127.8, 129.6, 129.7, 133.9, 134.2 (C_6H_5), 144.7, 144.8 (*C*=CH_2), 150.4 (C=*C*H_2), 152.0 (CH=CH)

MS (EI): *m*/*z* (%) = 326 (M^+, 10), 311 (60), 283 (50), 267 (60), 249 (100), 195 (70), 179 (30), 165 (35), 145 (50), 119 (45), 105 (95), 91 (45), 77 (40).

Anal. Calcd for $C_{18}H_{22}O_2Si_2$: C, 66.21; H, 6.79. Found: C, 66.41; H, 6.89.

(*Z*)-1,2-Bis(organyldiphenylsilyl)ethenes; General Procedure
A glass reactor (50-mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, argon bubbling tube and thermostated heating oil bath) was evacuated and flushed with argon. (*Z*)-2,2,5,5-Tetraphenyl-1,6-dioxa-2,5-disilacyclooct-3-ene (**3**; 2.5 g, 5.5 mmol) and THF (10 mL) were added to the reactor. Grignard reagent (molar ratio of the compound **3** to Grignard reagent was 1: 2.5) was added dropwise at r.t. The mixture was stirred under the conditions shown in Table 2. After the disappearance of the substrate was confirmed by GC, the solvent was removed in an evaporator, pentane (20 mL) was added and the resulting salt was filtered off. After evaporation the crude product was distilled under reduced pressure to afford the analytically pure product.

(*Z*)-1,2-Bis(methyldiphenylsilyl)ethene (8a)
Yield: 1.46 g (78%); colorless oil; bp 122 °C/0.5 mmHg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 6 H, CH_3), 7.32 (s, 2 H, CH=CH), 7.29–7.49 (m, 20 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.2 (CH_3), 129.0, 134.3, 134.7, 137.2 (C_6H_5), 149.1 (CH=CH).

MS (EI): *m*/*z* (%) = 405 (20), 327 (25), 265 (75), 223 (25), 197 (100), 145 (30), 105 (30).

Anal. Calcd for $C_{28}H_{28}Si_2$: C, 79.94; H, 6.71. Found: C, 79.68; H, 6.54.

(*Z*)-1,2-Bis(ethyldiphenylsilyl)ethene (9)
Yield: 1.26 g (63%); colorless oil; bp 128 °C/0.5 mmHg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.88 (q, *J* = 7.7 Hz, 4 H, CH_2), 1.48–1.53 (t, *J* = 7.9 Hz, 6 H, CH_3), 7.38 (s, 2 H, CH=CH), 7.30–7.52 (m, 20 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.4 (CH_2), 8.7 (CH_3), 129.4, 129.6, 134.4, 136.2 (C_6H_5), 150.2 (CH=CH).

MS (EI): *m*/*z* (%) = 420 (100), 372 (10), 342 (20), 314 (15), 260 (20), 184 (45), 105 (40).

Anal. Calcd for $C_{30}H_{32}Si_2$: C, 80.30; H, 7.19. Found: C, 80.62; H, 7.23.

(*Z*)-1,2-Bis(diphenylvinylsilyl)ethene (10)
Yield: 1.78 g (90%); colorless oil; bp 124 °C/0.5 mmHg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.51–5.58 (dd, *J* = 4.4, 19.5 Hz, 2 H, C*H*$_2$=CH), 5.94–6.00 (dd, *J* = 4.4, 14.6 Hz, 2 H, C*H*$_2$=CH), 6.04–6.15 (dd, *J* = 19.5, 14.7 Hz, 2 H, CH_2=C*H*), 7.28–7.60 (m, 20 H, C_6H_5), 7.56 (s, 2 H, CH=CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 129.3, 129.4 (C_6H_5), 134.3 (*C*H=CH_2), 135.5, 135.8 (C_6H_5), 136.5 (CH=*C*H$_2$), 150.1 (CH=CH).

MS (EI): *m*/*z* (%) = 417 (5), 367 (20), 340 (25), 312 (20), 259 (35), 209 (60), 183 (85), 155 (20), 131 (30), 105 (100), 77 (20), 53 (50).

Anal. Calcd for $C_{30}H_{28}Si_2$: C, 81.02; H, 6.35. Found: C, 80.78; H, 6.55.

(*Z*)-1,2-Bis(allyldiphenylsilyl)ethene (11)
Yield: 1.64 g (78%); colorless oil; bp 133 °C/0.5 mmHg.

^{1}H NMR ($CDCl_3$): δ = 1.68–1.70 (d, *J* = 5.4 Hz, 4 H, CH_2), 4.74–4.82 (m, 2 H, CH=C*H*$_2$), 4.86–4.95 (m, 2 H, CH=C*H*$_2$), 5.53–5.64 (m, 2 H, C*H*=CH_2), 7.32 (s, 2 H, CH=CH), 7.27–7.51 (m, 20 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 21.6 (CH_2), 114.4 (CH=*C*H$_2$), 127.6, 127.8, 129.3, 129.5 (C_6H_5), 133.9 (*C*H=CH_2), 135.3, 135.5 (C_6H_5), 150.3 (CH=CH).

MS (EI): *m*/*z* (%) = 472 (M^+, 5), 431 (100), 390 (95), 354 (75), 328 (20), 260 (75), 224 (20), 181 (30), 145 (20), 105 (40), 79 (10), 53 (15).

Anal. Calcd for $C_{32}H_{32}Si_2$: C, 81.30; H, 6.82. Found: C, 81.48; H, 6.56.

(*E*)-1,2-Bis(methyldiphenylsilyl)ethene (8b)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.65 (s, 6 H, CH_3), 7.07 (s, 2 H, C*H*=CH), 7.26–7.53 (m, 20 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.9 (CH_3), 127.7, 129.2, 134.7, 136.1 (C_6H_5), 150.3 (CH=CH).

MS (EI): *m*/*z* (%) = 405 (15), 327 (25), 264 (70), 223 (25), 197 (100), 145 (30), 105 (20), 53 (10).

Anal. Calcd for $C_{28}H_{28}Si_2$: C, 79.94; H, 6.71. Found: C, 79.78; H, 6.92.

(*Z*)-1,2-Bis(alkoxydiphenylsilyl)ethenes; General Procedure
A glass reactor (50-mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser and argon bubbling tube) was evacuated and flushed with argon. (*Z*)-1,6-Dimethyl-2,2,5,5-tetraphenyl-1,6-diaza-2,5-disilacyclooct-3-ene (**4**; 2.62 g, 5.5 mmol) and THF (10 mL) were added to the reactor. At r.t., the corresponding alcohol (molar ratio of the compound **4** to alcohol was 1:2.5) was added dropwise. The mixture was stirred at 65 °C for 4 h. After the reaction was complete, the excess of the alcohol and the solvent were evaporated in vacuo. After evaporation, the crude product was distilled under reduced pressure to afford the analytically pure product.

(*Z*)-1,2-Bis(methoxydiphenylsilyl)ethene (12)
Yield: 1.50 g (79%); colorless oil; bp 144 °C/0.5 mmHg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, 6 H, OCH_3), 7.06 (s, 2 H, CH=CH), 7.32–7.68 (m, 20 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 58.2 (OCH_3), 134.1, 134.9, 134.9, 137.8 (C_6H_5), 149.8 (CH=CH).

MS (EI): *m*/*z* (%) = 376 (5), 345 (70), 299 (100), 228 (30), 181 (50), 105 (45), 78 (10).

Anal. Calcd for $C_{28}H_{28}O_2Si_2$: C, 74.29; H, 6.23. Found: C, 74.47; H, 6.42.

(*Z*)-1,2-Bis(ethoxydiphenylsilyl)ethene (13)
Yield: 1.74 g (66%); colorless oil; bp 155 °C/0.5 mmHg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24–1.28 (t, *J* = 6.8 Hz, 6 H, CH_2CH_3), 3.78–3.82 (q, *J* = 6.9 Hz, 4 H, C*H*$_2$CH$_3$), 7.02 (s, 2 H, CH=CH), 7.22–7.56 (m, 20 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.2 (CH_2CH_3), 58.9 (*C*H$_2$CH$_3$) 133.8, 134.3, 134.9, 137.6 (C_6H_5), 150.1 (CH=CH).

Anal. Calcd for $C_{30}H_{32}O_2Si_2$: C, 74.95; H, 6.71. Found: C, 75.12; H, 6.98.

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