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Articles

Trans-Silylation vs Cross-Metathesis of Styrene with 2,2,4,4,6,6,8,8-Octamethyl-1,5-dioxo-2,4,6,8-tetrasila-3,7-*exo*-dimethylenecyclooctane Catalyzed by Ruthenium Complexes

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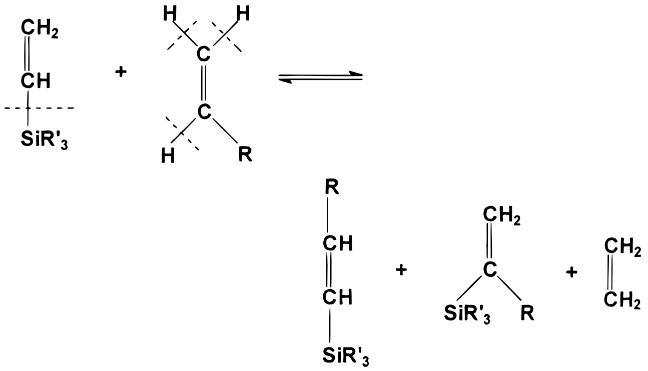
2,2,4,4,6,6,8,8-Octamethyl-1,5-dioxo-2,4,6,8-tetrasila-3,7-*exo*-dimethylenecyclooctane (**1**) (whose X-ray structure has been determined) is a good model to study the reactivity of an exocyclic vinyl bond at silicon with styrene occurring in the presence of RuHCl(CO)(PPh$_3$)$_3$ (**I**). Two products are formed initially: the linear **2** by ring opening of **1** and the cyclic **3** by condensation with evolution of ethylene. In the presence of an excess of styrene, **2** undergoes consecutive reactions giving subsequent styryl derivatives. Effective catalysis by **I** and the lack of activity of Ru−carbenes (**II**) for the reaction were examined. An MS study of the products ($\mathbf{2_D}$ and $\mathbf{3_D}$) of the reaction of deuterated styrene with **1** provides convincing evidence for a mechanism that does not involve a metallacarbene. A sequential insertion−elimination mechanism is proposed for the catalytic process.

Introduction

Results of recent experiments on the disproportionation (metathesis) of monovinyl-substituted silanes[1] and siloxanes[2] and their codisproportionation (cross-metathesis) with alkenes[3] and styrene[4] occurring in the presence of Ru and Rh complexes provide convincing evidence for a new type of catalytic conversion of olefins, namely silylation of olefins with vinyl-substituted silicon compounds, as presented in Scheme 1.[5]

Scheme 1. Trans-Silylation of Olefins by Vinylsilanes



The reaction proceeds through cleavage of the =C−Si bond of the vinyl-substituted silicon compound and the =C−H bond of the olefin via a mechanism involving the insertion of the olefin into the Ru−Si bond and that of the vinylsilane into the Ru−H bond, followed by β-H and β-Si elimination, giving an alkenylsilane and ethene, respectively.

In contrast to the case for other alkenylsilanes, metathetical conversion of vinylsilanes as well as acyclic diene metathesis (ADMET) polymerization of divinyl-substituted silicon compounds does not occur in the presence of W and Mo carbene complexes, presumably due to steric hindrance of two silyl groups in the metallacyclobutane intermediates.[5c]

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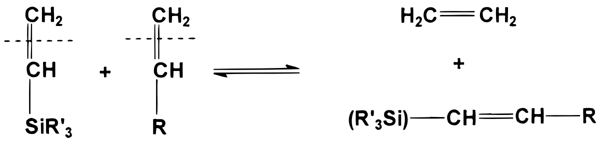
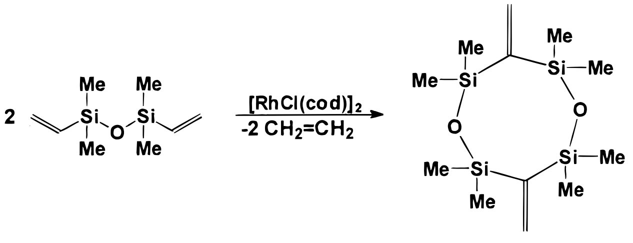
10.1021/om990061+ CCC: $15.00

Scheme 2. Cross-Metathesis of Olefins with Vinylsilanes



Scheme 3. Ring Closing of 1,3-Divinyltetramethyldisiloxane



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However, some recent experiments suggest the occurrence of cross-metathesis of divinylsilsesquioxanes[6] with olefins and of cometathesis polymerization of divinyldimethylsilane with 1,9-decadiene[7] in the presence of W and Mo carbenoids. Scheme 2 illustrates the process, which could occur via C═C bond cleavage of the initially used substrate.

On the other hand, similar to the case for monovinyl-substituted silanes, divinyl-substituted silanes or siloxanes undergo acyclic diene polycondensation (ADPOL) in the presence of a variety of ruthenium and rhodium complexes, giving, respectively, poly(silylene−vinylene)[8] and poly(siloxylene−vinylene)s,[9] according to the non-metallacarbene mechanism. The ADPOL proceeds via initial formation of cyclic and linear oligomers (dienes, trimers, etc.). Surprisingly, when using $[Rh(cod)(\mu\text{-}Cl)]_2$ as a catalyst, a condensation (ring closure) of two monomers of divinyltetramethyldisiloxane takes place (Scheme 3) to yield 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxo-2,4,6,8-tetrasila-3,7-*exo*-dimethylenecyclooctane (**1**).[10]

1 is a very attractive model to follow the reaction of an exocyclic vinyl group at silicon, occurring in the presence of ruthenium complexes, in terms of the two above-mentioned catalytic mechanisms. The aim of this work was to determine the structure of **1** and to follow its reaction with styrene using $RuHCl(CO)(PPh_3)_3$ (**I**) vs ruthenium−carbene (**IIa, IIb**) complexes.

Experimental Section

General Methods and Materials. All syntheses and manipulations were performed under argon using Schlenk and high-vacuum-line techniques unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 VS spectrometer in C_6D_6 at 350 and 75 MHz, respectively. ^{29}Si NMR spectra were recorded on the same instrument. Infrared spectra (KBr plates) were recorded using a Bruker FT-IR IFS-113v instrument. The mass spectra of the products and substrates were determined by GC-MS analysis (Varian 3300 gas chromatography equipped with a DB-1, 30 m capillary column, and a ITD 800 Finnigan MAT ion trap detector). GC analysis were carried out on a Varian 3300 gas chromatograph.

Chemicals were received from the following sources: 1,3-divinyltetramethyldisiloxane from ABCR, styrene from Fluka, hexane from Merck, and benzene-d_6 and styrene-d_8 from Dr. Glasser AG Basel. All solvents were dried over CaH_2 prior to use and stored under argon.

Synthesis of Ruthenium and Rhodium Complexes. The Grubbs ruthenium−carbene $(PPh_3)_2Cl_2Ru═CHCH═CPh_2$ (**IIa**) was prepared by the method reported in ref 11; $RuCl_2(p\text{-cymene})(PCy_3)$ was synthesized under argon by slow addition of PCy_3 in CH_2Cl_2 to $[(p\text{-cymene})RuCl_2]_2$ according to the literature.[12] Such a catalyst precursor was activated by addition of (trimethylsilyl)diazomethane (TMSD from Aldrich Chemical Co.; ratio of Ru to diazo compound 1:4) to form Ru−carbene **IIb** in situ.[12] $RuHCl(CO)(PPh_3)_3$ (**I**) was purchased from Aldrich and used without further purification. $[Rh(cod)(\mu\text{-}Cl)]_2$ (**III**)[13] and $[Rh(cod)(\mu\text{-}OSiMe_3)]_2$ (**IV**)[14] were prepared according to the previously reported methods.

Synthesis of 2,2,4,4,6,6,8,8-Octamethyl-1,5-dioxo-2,4,6,8-tetrasila-3,7-*exo*-dimethylenecyclooctane (1). 1 was synthesized according to the modified method described in ref 10. 1,3-Divinyltetramethyldisiloxane (25 mL, 109 mmol) and rhodium catalyst **III** (1.1 mmol) were placed in a reaction flask and heated at 130 °C for 3 weeks. The soluble part of the catalyst was removed using an SiO_2 column with hexane as eluent. Hexane was removed by vacuum rotary evaporation. The cyclic dimer **1** was isolated from the mixture of oligomers by vacuum distillation to give 5 mL of product in 30% yield; bp 84 °C (1 mmHg); mp 23 °C. ^1H NMR (300 MHz, C_6D_6; δ (ppm)): 0.22 (s, $-CH_3$), 6.16 (s, $═CH_2$). ^{13}C NMR (75 MHz, C_6D_6; δ (ppm)): 1.72 ($-CH_3$), 140.39 ($═CH_2$ at quaternary carbon atom), 157.13 (quaternary carbon atom). ^{29}Si NMR (59 MHz, C_6D_6; δ (ppm)): −0.38 (s). IR (cm^{-1}): 3006 (═CH), 2959, 2927, 2901 (−CH aliphatic), 1573 (C═C), 1413 (of C−H of $-CH_3$ group), 1253 ($SiOC(CH_3)_2$ group), 1085 (Si−O−Si), 844 ($SiOC(CH_3)_2$ group), 672 (═CH).

Synthesis of 1-Styryl-3-vinyl-1,1,3,3-tetramethyldisiloxane (5). $[Rh(cod)(\mu\text{-}Cl)]_2$ (0.0220 g, 4.4×10^{-5} mol), benzene (0.75 mL), 1,3-divinyltetramethyldisiloxane (1 mL, 0.0044 mol), and styrene (5 mL) were placed in a glass ampule, which was sealed and heated at 90 °C for 18 h. The reaction mixture was added in small drops to 100 mL of hexane to precipitate polystyrene. The mixture was then heated at reflux for 1 h. Hexane was removed by vacuum rotary evaporation. The soluble part of the catalyst was removed using SiO_2 column with hexane as eluent. Hexane was removed at reduced pressure, and the product was distilled (bp 89 °C, 1 mmHg) to get 1-styryl-3-vinyl-1,1,3,3-tetramethyldisiloxane in 70% yield. Anal. Calcd for $C_{14}H_{22}OSi_2$: C, 64.06; H, 8.45. Found: C, 64.09; H, 8.59. ^1H NMR (300 MHz, C_6D_6; δ (ppm)): 0.22 (s, $-CH_3$ at silicon in vinyl group), 0.29 (s, $-CH_3$ at silicon in styryl group), 6.49 (d, $J_{H-H} = 19.23$ Hz, ═CH at silicon atom at styryl group), 7.07 (d, $J_{H-H} = 19.23$ Hz, ═CH at styryl group), 7.11, 7.34 (m, styryl group), 5.75−6.28 (m, vinyl group). ^{13}C NMR (75 MHz, C_6D_6; δ (ppm)): 1.14 ($-CH_3$ at silicon in vinyl group), 1.49 ($-CH_3$ at silicon at styryl group), 127.45 (═CH at silicon atom at styryl group), 145.63 (═CH at styryl group), 140.23 (═CH at vinyl group), 128.92, 129.10 (styryl group), 132.42 ($═CH_2$), 139.11 (quaternary carbon atom). ^{29}Si NMR (59 MHz, C_6D_6; δ (ppm)): −1.93 (s, at styryl group), −2.79 (s, at vinyl group). MS (EI; *m/z* (relative intensity)): 262 $(M)^+$, 247 $(M - Me)^+$, 235 $(M - Vi)^+$, 220 $(M - Me - Vi)^+$, 159 $(M - PhCHCH)^+$, 73 $(SiMe_3)^+$.

Synthesis of 1,3-Distyryl-1,1,3,3-tetramethyldisiloxane

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(6). $[Rh(cod)(\mu\text{-}OSiMe_3)]_2$ (0.0264 g, 4.4×10^{-5} mol), benzene (0.75 mL), 1,3-divinyltetramethyldisiloxane (1 mL, 0.0044 mol), and styrene (5 mL) were placed in a glass ampule, which was sealed and heated at 90 °C for 18 h. The reaction mixture was subsequently worked up by the method described above. 1,3-Distyryl-1,1,3,3-tetramethyldisiloxane was isolated after distillation (bp 156 °C, 1 mmHg) in 80% yield. Anal. Calcd for $C_{20}H_{26}OSi_2$: C, 70.95; H, 7.74. Found: C, 70.97; H, 7.74. ^1H NMR (300 MHz, C_6D_6; δ (ppm)): 0.34 (s, $-CH_3$), 6.52 (d, J_{H-H} = 19.68 Hz, =CH at silicon group), 7.11 (d, J_{H-H} = 19.20 Hz, =CH at styryl group), 7.10, 7.32 (m, styryl group). ^{13}C NMR (75 MHz, C_6D_6; δ (ppm)): 1.63 ($-CH_3$), 127.46, 129.28 (=CH at silicon group), 145.65 (=CH at styryl group), 138.95 (quaternary carbon atom), 139.11 (styryl group). ^{29}Si NMR (59 MHz, C_6D_6; δ (ppm)): −1.79 (s). MS (EI; *m/z*): 338 $(M)^+$, 323 $(M - Me)^+$, 248 $(M - PhCH)^+$, 235 $(M - PhCHCH)^+$, 220 $(M - Me - PhCHCH)^+$, 73 $(SiMe_3)^+$.

GC-MS Analysis of Products. MS (EI; *m/z*): 1-(3-vinyl-1,1,3,3-tetramethyldisiloxanyl)-1-(3-styryl-1,1,3,3-tetramethyldisiloxanyl)ethene (**2**), 420 $(M)^+$, 405 $(M - Me)^+$, 393 $(M - Vi)^+$, 317 $(M - PhCHCH)^+$, 73 $(SiMe_3)^+$; 2,2,4,4,6,6,8,8-octamethyl-3-benzylidene-7-methylene-1,5-dioxo-2,4,6,8-tetrasilacyclooctane (**3**), 92 $(M)^+$, 377 $(M - Me)^+$, 289 $(M - PhCHCH)^+$, 73 $(SiMe_3)^+$; 1,1-bis(3-styryl)-1,1,3,3−tetramethydisiloxanylethene (**4**), 496 $(M)^+$, 481 $(M - Me)^+$, 393 $(M - PhCHCH)^+$, 73 $(SiMe_3)^+$.

X-ray Crystallography. A colorless crystal of **1** of approximate dimensions 0.4 × 0.3 × 0.3 mm was used for data collection. X-ray diffraction data were collected at 250 K on a KUMA KM4 κ-geometry diffractometer,[15] using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. The unit cell dimensions were calculated by the least-squares fit to 30 automatically centered reflections ($9.9^0 \leq 2\theta \leq 29.0°$). The $2\theta-\theta$ scan method and a variable scan speed ranging from 1.2 to 11°/min, depending on reflection intensity, were applied to 2412 reflections up to $2\theta = 46°$ ($0 \leq h \leq 7$, $-8 \leq k \leq 9$, $-13 \leq l \leq 14$). Three control reflections were measured after every 100 current measurements; they showed slight decomposition of the crystal (up to 6% intensity loss), and appropriate correction was applied. Intensity data were collected for Lorentz and polarization effects.[15] The structure was solved by direct methods, using the SHELXS86 program.[16] The full-matrix least-squares method was used for refinement with SHELXL93.[17] Scattering factors incorporated in SHELXL93 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = \sigma^2(F_o)^2 + 0.0653P^2 + 0.21P$ (where $P = \mathrm{Max}(F_o^2, 0) + 2F_c^2/3$). The positions of hydrogen atoms were found in subsequent ΔF maps, and both positional and isotropic thermal parameters of hydrogen atoms were refined. Five reflections were excluded from the reflection file for **1**, and **3** for **2**, due to their large ($|F_o^2| - |F_c^2|$) differences. A final refinement of 275 parameters converged at $R(F) = 0.031$, $R(F^2) = 0.0914$, and $S = 1.06$. On the final difference Fourier map the largest peak was 0.36 e Å^{-3} and the deepest hole was −0.20 e Å^{-3}. Crystallographic data: $C_{12}H_{28}O_2Si_4$, M_r = 316.70, triclinic, space group $P\bar{1}$, a = 8.842(2) Å, b = 9.052(2) Å, c = 13.124(3) Å, α = 77.57(3)°, β = 77.74(3)°, γ = 69.85(3)°, V = 952.0(4) Å^3, Z = 2, d_{exptl} = 1.105 g cm^{-3}, μ(Mo Kα) = 0.307 mm^{-1}.

General Procedure for Catalytic Examinations. In a typical catalytic reaction with the ruthenium complex, **1**, decane (internal standard), styrene, and 4-methoxyphenol (as an inhibitor of radical polymerization) were placed in glass ampules filled with argon at various ratios **1**:styrene ratios (1:1 to 1:4) and **1**:[Ru] ratios (1:(10^{-2}) to 1:(2×10^{-2})). The sealed ampules were heated at the required temperature (usually 130 °C) and for an appropriate time (24−120 h). The progress of the reaction was monitored and analyzed by GC-MS. The yields and selectivities were calculated by GC using an internal standard.

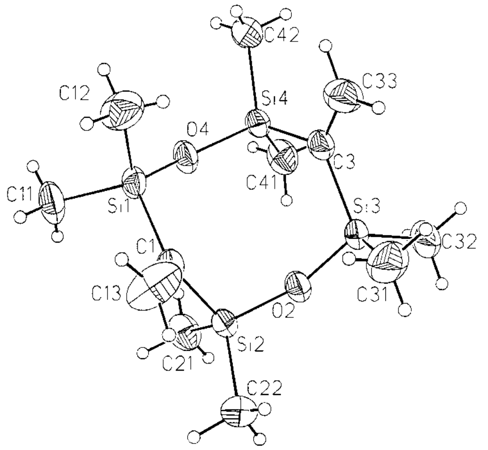

Figure 1. Thermal ellipsoid representation of a molecule together with a labeling scheme.[14] The ellipsoids are drawn at the 50% probability level, and hydrogen atoms are drawn as spheres of arbitrary radii.

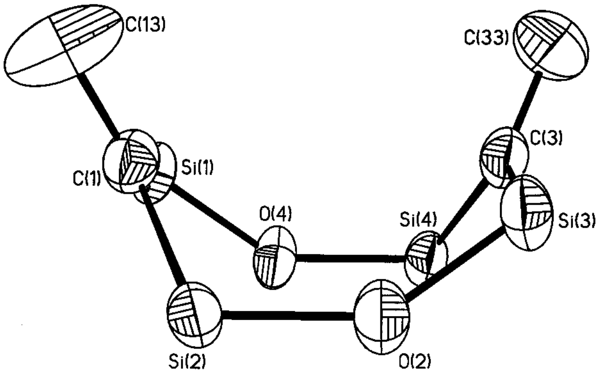

Figure 2. Perspective view of the ring of **1** with Me groups removed for clarity.

Reaction of 1 with $CD_2{=}CDC_6D_5$ Catalyzed by $RuHCl(CO)(PPh_3)_3$. The catalyst **I** (20 mg), **1** (33 mL), and $CD_2{=}CDC_6D_5$ (40 μL), as well as decane (as an internal standard) and 4-methoxyphenol (as an inhibitor of radical polymerization) were introduced into a glass vial (Supelco). The vial was heated at 90 °C. The progress of the reactions was followed by GC-MS.

Results and Discussion

X-ray Structure of 1. The product **1** was characterized by ^1H NMR and ^{13}C NMR spectroscopy. Additionally, its ^{29}Si NMR and IR spectra are reported here. The X-ray structure of molecule **1** is shown in Figures 1 and 2. Selected bond lengths, bond angles, and torsion angles are listed in Table 1. The molecule is close to a boat conformation, with O(2), Si(2), O(4), and Si(4) atoms perfectly coplanar (maximum deviation from the least-squares plane of 0.002(1) Å), and other ring atoms displaced in the same direction from this plane. These displacements are equal to the following: Si(1), 0.943(2) Å; Si(3), 0.920(2) Å; C(1), 1.245(2) Å; C(3), 1.255(3) Å. The bond length and angle patterns are both quite typical, with weighted mean bond length values Si−O = 1.631(1) Å and $Si-CH_3$ = 1.850(1) Å. Very wide Si−O−Si angles, ca. 143°, make an interesting geometrical feature. However, such large values were found

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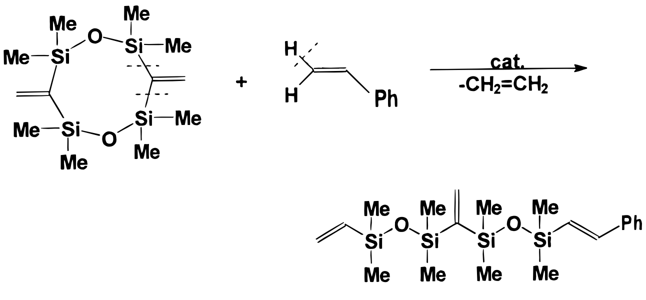
Table 1. Bond Lengths (Å), Bond Angles (deg), and Selected Torsion Angles (deg) with Esd's in Parentheses

Si(1)−O(4)	1.631(2)	O(2)−Si(3)	1.627(2)
Si(1)−C(12)	1.849(3)	Si(3)−C(32)	1.851(3)
Si(1)−C(11)	1.849(3)	Si(3)−C(31)	1.852(3)
Si(1)−C(1)	1.866(2)	Si(3)−C(3)	1.863(2)
C(1)−C(13)	1.317(4)	C(3)−C(33)	1.325(3)
C(1)−Si(2)	1.863(2)	C(3)−Si(4)	1.869(2)
Si(2)−O(2)	1.630(2)	Si(4)−O(4)	1.635(2)
Si(2)−C(21)	1.844(3)	Si(4)−C(41)	1.846(3)
Si(2)−C(22)	1.856(3)	Si(4)−C(42)	1.852(3)
O(4)−Si(1)−C(12)	109.79(14)	O(2)−Si(3)−C(32)	107.1(2)
O(4)−Si(1)−C(11)	107.64(12)	O(2)−Si(3)−C(31)	109.2(2)
C(12)−Si(1)−C(11)	110.5(2)	C(32)−Si(3)−C(31)	110.9(2)
O(4)−Si(1)−C(1)	108.64(10)	O(2)−Si(3)−C(3)	108.35(10)
C(12)−Si(1)−C(1)	111.3(2)	C(32)−Si(3)−C(3)	109.76(14)
C(11)−Si(1)−C(1)	108.92(13)	C(31)−Si(3)−C(3)	111.34(14)
C(13)−C(1)−Si(2)	119.7(2)	C(33)−C(3)−Si(3)	119.3(2)
C(13)−C(1)−Si(1)	118.8(2)	C(33)−C(3)−Si(4)	119.6(2)
Si(2)−C(1)−Si(1)	121.47(11)	Si(3)−C(3)−Si(4)	121.10(12)
O(2)−Si(2)−C(21)	107.24(13)	O(4)−Si(4)−C(41)	106.88(14)
O(2)−Si(2)−C(22)	108.73(13)	O(4)−Si(4)−C(42)	108.54(13)
C(21)−Si(2)−C(22)	109.7(2)	C(41)−Si(4)−C(42)	110.3(2)
O(2)−Si(2)−C(1)	109.43(10)	O(4)−Si(4)−C(3)	108.70(9)
C(21)−Si(2)−C(1)	110.85(13)	C(41)−Si(4)−C(3)	110.92(13)
C(22)−Si(2)−C(1)	110.84(13)	C(42)−Si(4)−C(3)	111.36(13)
Si(3)−O(2)−Si(2)	143.70(11)	Si(1)−O(4)−Si(4)	142.82(10)
C(1)−Si(2)−O(2)−Si(3)	28.9(2)		
Si(2)−O(2)−Si(3)−C(3)	−70.2(2)		
O(2)−Si(3)−C(3)−Si(4)	−31.9(2)		
Si(3)−C(3)−Si(4)−O(4)	73.6(2)		
C(3)−Si(4)−O(4)−Si(1)	29.1(2)		
C(1)−Si(1)−O(4)−Si(4)	−2.0(2)		
O(4)−Si(1)−C(1)−Si(2)	29.0(2)		
Si(1)−C(1)−Si(2)−O(2)	71.7(2)		

Scheme 4. Silylation of Styrene with 1



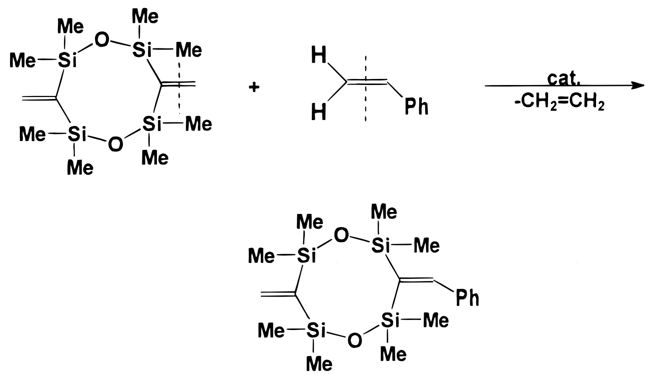
2

in similar eight-membered rings in the crystal structure of 2,2,4,4,5,5,8,8,9,9,11,11-dodecamethyl-3,7,10-trioxa-2,4,6,8,9,11-hexasilabicyclo[3.3.3]undecane.[18] In the crystal molecules are held together mainly by means of van der Waals forces; there are no unusually close intermolecular contacts.

Catalytic Studies. The reaction of styrene with **1** was chosen as a model reaction to distinguish between two mechanisms, i.e., silylation of the olefin (styrene) leading, in the presence of Ru−H complexes, to the ring opening of **1** (cleavage of one Si−C bond at the beginning; Scheme 4) and/or cross-metathesis of **1** with styrene giving cyclic derivatives (cleavage of one C=C bond at the beginning) in the presence of ruthenium carbene catalysts (Scheme 5).

The reaction was followed by the GC-MS technique. The conversion of **1** and the yield of the particular products formed with time are illustrated in Tables 2 and 3.

Scheme 5. Cross-Metathesis of Styrene with 1



3

Table 2. Conversion of 1 and Selectivity of Products (2−7) of the Reaction of 1 with Styrene Catalyzed by RuHCl(CO)(PPh$_3$)$_3$[a]

reacn time (h)	conversn of **1** (%)	product selectivity (%)					
		2	**3**	**4**	**5**	**6**	**7**
24	6	52	48				
48	9	35	50	15			
72	19	18	38	15	15	14	1
96	36	10	29	28	16	15	2
120	50	6	24	34	16	18	2

[a] Reaction conditions: temperature, 130 °C; [Ru]:[**1**]:[styrene] = (10^{-2}):1:2; sealed ampules.

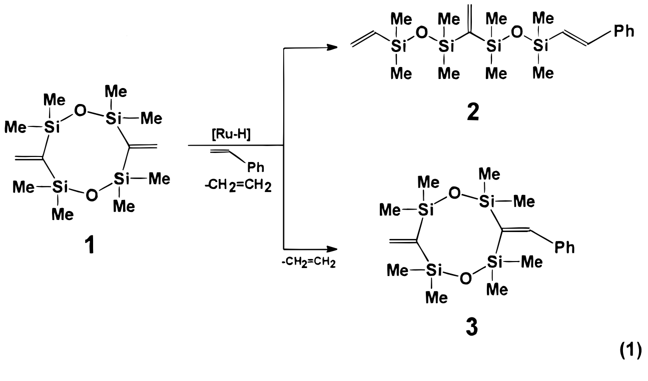
Table 3. Conversion of 1 and Selectivity of Products (2−7) of the Reaction of 1 with Styrene Catalyzed by RuHCl(CO)(PPh$_3$)$_3$[a]

1:styrene	conversn of **1** (%)	product selectivity (%)				
		2	**3**	**4**	**5**	**6**
2:1	6	22	75	2		
1:1	9	29	59	6	traces	6
1:2	19	9	17	63	traces	11
1:4	36	4	18	61	1	16

[a] Reaction conditions: time, 24 h; temperature, 130 °C; [Ru]:[**1**] = (10^{-2}):1; sealed ampules.

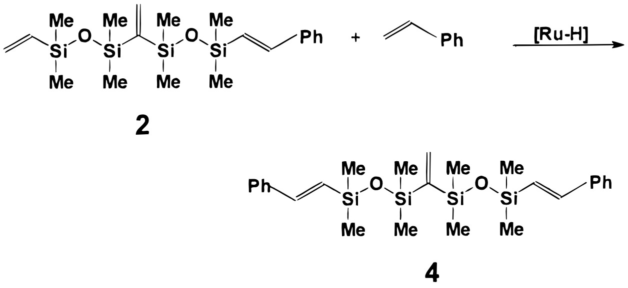
All products (**2**−**7**) formed during the reaction were identified by mass spectroscopy. Some of the products, i.e., **5**−**7** (see Experimental Section) were also identified by comparison with standard samples. The conversion of **1** with time and the successive formation of the particular products (**2**−**7**) are shown in Table 2.

In the initial step (at low conversion (6%) in 24 h) only two products, **2** and **3,** were observed at a ratio of about 52:48. This initiating step suggested that two parallel reactions are taking place, i.e., cross-metathesis to yield **3** and silylation to give **2** (eq 1). After the next 24 h at



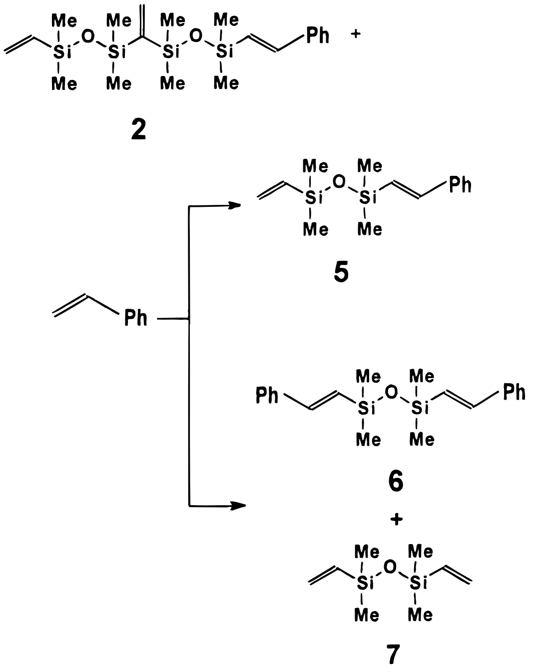
(1)

a conversion of 9%, the consecutive reaction of **2** with an excess of styrene (silylation or metathesis of styrene by the terminal vinyl group of **2**) proceeds to give **4** according to eq 2.



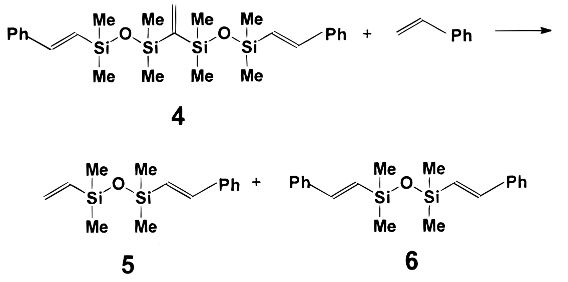
(2)

Further heating for 3 days at 130 °C furnishes the new products **5**−**7** (eq 3), which apparently are a result of the cleavage of the terminal vinyl group and the internal C=C bonds of 1,1-bis(silyl)ethene in the reaction with styrene.



(3)

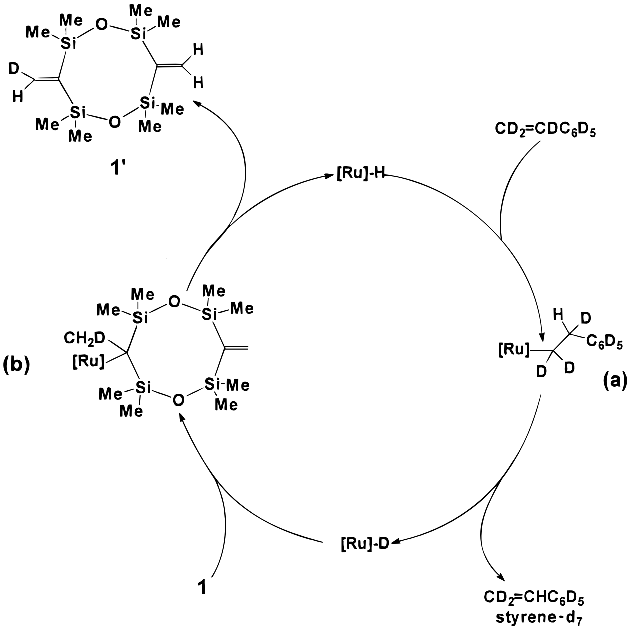
Formally, products **5** and **6** can also be the result of the following consecutive reaction, the silylation of styrene with **4** (eq 4). Alternatively, products **5** and **6** can be ascribed to the reaction of **7** with styrene.



(4)

No product of the silylation of styrene by the two *exo*-vinylic groups of **1** was observed.

Scheme 6. Catalytic H/D Exchange of 1 with Styrene-d_8 in the Presence of RuHCl(CO)(PPh$_3$)$_3$



The effect of the ratio of **1** to styrene in the reaction catalyzed by RuHCl(CO)(PPh$_3$)$_3$ is illustrated in Table 3.

The reaction was carried out under a concentration ([Ru]:**1** = 1:50) of the catalyst **I** that was higher than in the previously discussed experiments. The results have shown that in the presence of an excess of **1** basically only two products, **2** and **3,** are formed, with a clear preference for the cyclic product **3**. However, in the presence of an excess of styrene it is noteworthy that practically all the terminal vinyl groups left after ring opening of **1**, i.e., those in intermediate products **2**, **5**, and **7,** react with styrene to give styryl derivatives (**4** and **6**). A preference of the catalytic reaction for terminal vinyl groups over internal C=C groups of **2** is revealed by the high ratio of **4** to **6** (61:16). No bis(styryl) derivatives of **1** were observed, even when a large excess of styrene was used. A separate study of the catalysis of the cross-metathesis of **1** with styrene by the well-defined Ru−carbene complex of Grubbs (60, 80, and 130 °C)[11] or the catalytic system [RuCl$_2$(p-cymene)]$_2$ + PCy$_3$ + Me$_3$SiCHN$_2$ (60, 80, and 130 °C)[12] resulted in formation of neither cyclic nor linear products. This clearly indicates that there is no metathesis activity of ruthenium carbenoids in the conversion of vinyl-substituted silicon derivatives under the conditions studied.[19] The conclusion is that **3** cannot be a product of the direct metathetical conversion of **1** with styrene.

Isotopic Labeling Experiments. To find additional proof for the mechanistic pathways of the reaction, a few series of catalytic experiments were performed by replacing C$_6$H$_5$CH=CH$_2$ with C$_6$D$_5$CD=CD$_2$. The aim of the test was to confirm some individual steps of the silylative cross-coupling of **1** with styrene to distinguish between the preliminary linear product **2** and the cyclic **3**.

The spectra of the initial substance **1** and styrene recorded after 30 min show signals attributed to styrene-

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[19] Schrock, R. R. *Organometallics* **1990**, *9*, 2262.

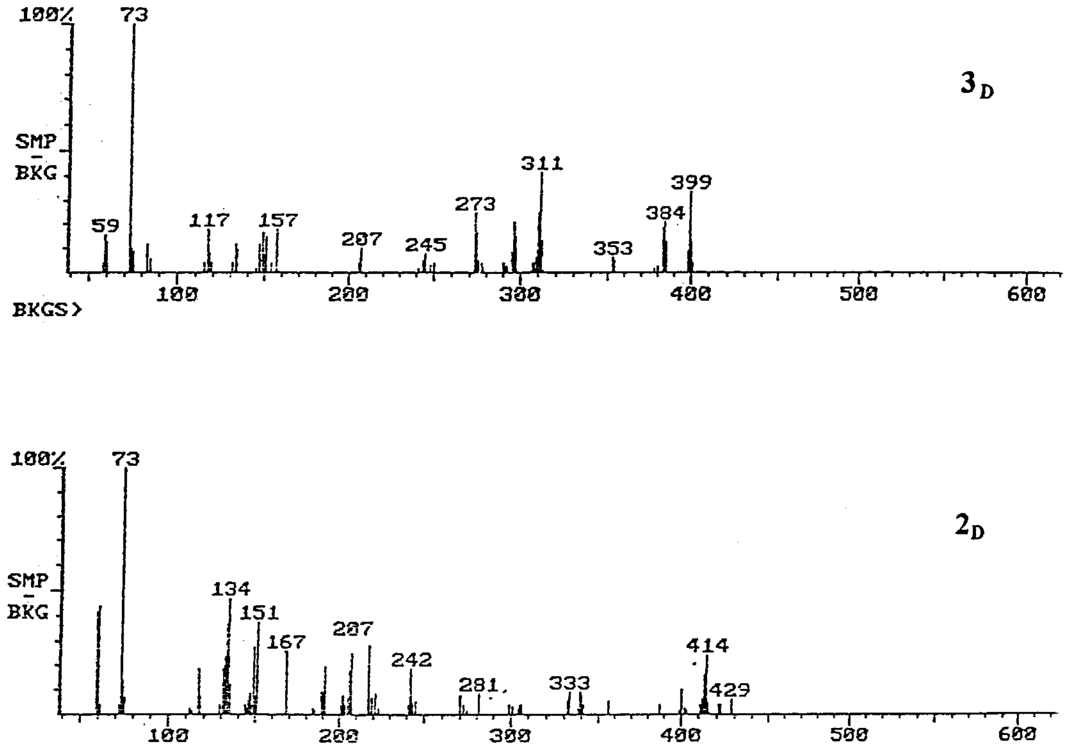
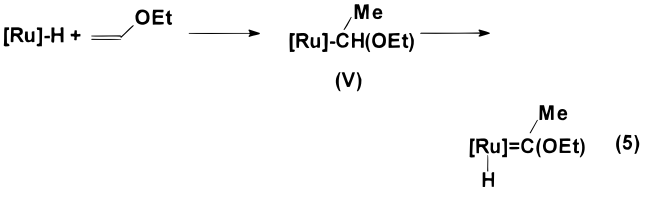


Figure 3. Mass spectrograms of the products 2_D and 3_D of the reaction of $C_6D_5CD{=}CD_2$ with **1** after 30 min.

d_7 (m/z 111) and the substance **1′** (i.e., **1** containing one deuterium atom; m/z 302 ($M^+ - CH_3$)). Thus, they provide evidence of a fast, simultaneous exchange of one atom of hydrogen in **1** with deuterium of the styrene-d_8 occurring in the presence of the Ru−H catalyst. This catalytic H/D exchange can be explained by the individual insertion−elimination process of Ru−H (D) with styrene-d_8 and one vinyl group of **1**, as shown in Scheme 6.

While the mode of the addition of the Ru−H bond to the C=C bond of styrene-d_8 is quite obvious and results in the formation of the styrene-d_7 product, the unconventional direction of the addition of Ru−D to **1** requires more comment. Such a regiochemistry of Ru−H addition to a vinyl ether at 25 °C to form RuHCl[C(Me)OEt]L_2 (**V**) was revealed very recently by Caulton et al.[20] Such a rearrangement is very rare[21] and presumably is due to the presence of two nonequivalent anionic ligands at Ru.[22] In the case of the vinyl ether, the carbyl complex **V** is formed. The Ru atom goes to the relatively uncharged internal carbon (of the vinylic carbon atoms)[20] to finally form hydrido−carbene complexes according to the eq 5. A similar regiochemistry was

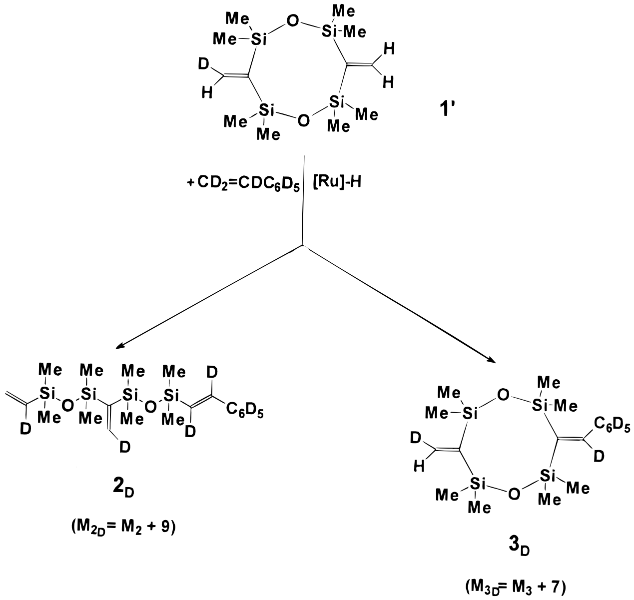


proposed to rationalize the formation of $L_2Cl_2Ru[{=}C(H)\text{-}Me]$ from $RuHCl(H_2)L_2$ and $HClC{=}CH_2$.[23]

In case of cyclic **1**, the second step, i.e., a formation of Ru−carbene, is not possible, but the character of the internal carbon in **1** is similar to the respective one in the vinyl ether and, therefore, formation of intermediate **b** (see Scheme 6) can be rationally proposed, particularly if we assume the boat confirmation of **1** (Figure 2).

This conformation enables simultaneous reaction of exocyclic $=CH_2$ bonds of **1** opposite to =CHD with the catalytic silylation reaction with styrene.

Scheme 7. Initial Products of the Reaction of 1′ with Styrene-d_8 in the Presence of $RuHCl(CO)(PPh_3)_3$



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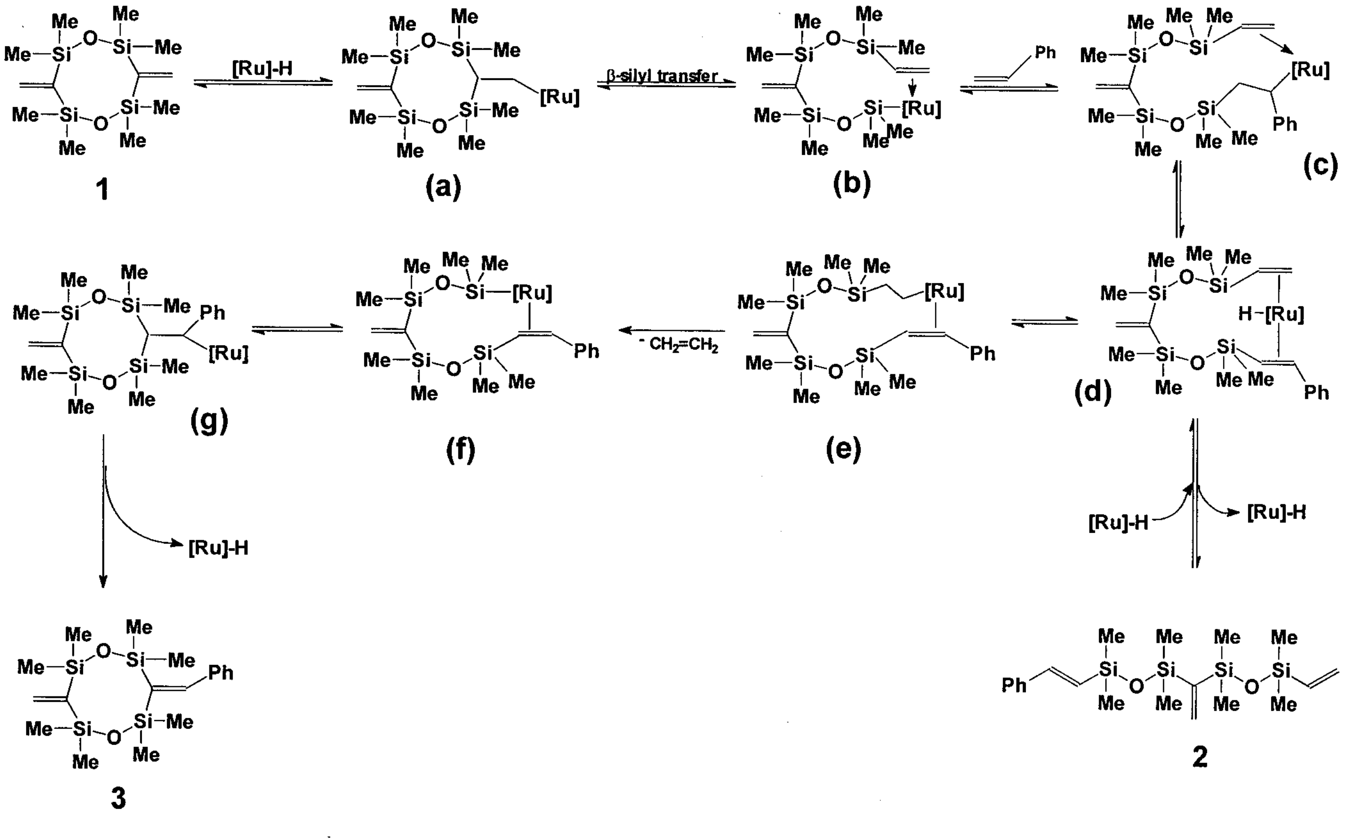
[20] Coalter, J. N., III; Spivak, G. J.; Gerard, H.; Clot, E.; Davidson, E. R.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 100.

[21] (a) Freundlich, J. S.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476. (b) de los Rios, I.; Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997,** *114*, 6529. (c) Olivan, M.; Clet, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 309.

[22] Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974.

Scheme 8. Catalysis of the Reaction of 1 with Styrene



when [Ru] = RuCl(CO)(PPh$_3$)$_2$

Mass spectrograms of the deuterated **2** and **3** (**2_D**, **3_D**) are given in Figure 3.

The peak at *m*/*z* 414 ($M^+ - CH_3$) for **2_D** and the peak at *m*/*z* 399 ($M^+ - CH_3$) for **3_D** were observed after 30 min of the reaction of **1** with styrene-d_8 catalyzed by **I** (90 °C) and provide convincing evidence for the formation of the two initial products containing nine (**2_D**) and seven (**3_D**) deuterium atoms, as presented in Scheme 7:

Although the structure of **2_D** is a proof for the nonmetathetical reaction, the **3_D** structure cannot be used as a basis to distinguish between the two mechanisms discussed.

Mechanistic Considerations. Catalytic efficiency of Ru–H (**I**) and the lack of reactivity of Ru–carbenes (**IIa**, **IIb**) show that the reaction of one of the exocyclic vinylic bonds of **1** with styrene occurs via a nonmetallacarbene mechanism. In addition, the isotopic labeling study revealed a fast preliminary H/D exchange in the catalytic system **1** + styrene-d_8 → **1_D** + styrene-d_7, giving the product **1_D**, which undergoes subsequent (or simultaneous) insertion–elimination as proposed in Scheme 8.

Both stoichiometric reactions of styrene with the Ru–silyl bond and the reversible equimolar reactions of styrylsilanes with the Ru–H bond of complex **I,** as well as the respective MS study of the products of styrene-d_8 with vinylsilanes, reported previously,[4] together with earlier results of Wakatsuki[1c] and our group[1e] on the insertion of ethylene and vinylsilane into the Ru–Si bond provide the basis for the nonmetallacarbene mechanism of the reaction **1** with styrene.

The formation of the initial pentacoordinate Ru–H intermediate proceeds via oxidative elimination of a triphenylphosphine ligand. Apart from the unconventional regioselective addition of Ru–H to **1** proposed in Scheme 6 for H/D exchange, the only predominant process is an insertion of **1** into the Ru–H bond to give **a** (see Scheme 8) followed by subsequent β-silyl elimination to form **b**. The next step **b** → **c** requires the regiospecific insertion of styrene into the Ru–Si bond of the opened cyclocarbosiloxane **b**, which still involves a vinyl group on another silicon π-bonded to ruthenium. The β-hydrogen elimination from the β-siloxy(α-phenyl)-ethyl ligand to ruthenium regenerates Ru–H, a species with π-bonded chelate styryl–vinyl–carbosiloxane ligands (**d**). This is an intermediate which can eliminate **2** and/or initiate the back-closing reaction of the macrochelate via the addition of Ru–H to a vinyl group **d** → **e** followed by the well-known process of Ru–Si bond formation **e** → **f** with elimination of ethylene. In the intermediate **f**, the regiochemistry of the insertion of the C=C of the styryl group into the Ru–Si bond again causes ring closure of the carbosiloxane **f** → **g**, yielding finally product **3**.

As we have already mentioned, the competitive, reversible reaction of intermediate **d**, namely, elimination of **2** and/or the addition of Ru–H to the coordinated vinylic group, is directly responsible for the final distribution of the observed products. When there is an excess of styrene, the consecutive reactions of **2** with styrene (to yield **4**–**7**) shift the coordination–elimination **d** → **2** step toward a decreased amount of cyclic product **3** in the final product distribution.

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(23) Wilhelm, T. E.; Beldorrain, T. R.; Grown, S. R.; Grubbs, R. H.; *Organometallics* **1997**, *16*, 3867.

In view of the results of the isotopic labeling studies, deuterium atoms found in the internal and exocyclic vinylic groups of $\mathbf{2_D}$ and $\mathbf{3_D}$, respectively, come from the H/D exchange presented in Scheme 6. The presence of two deuterium atoms in the styryl group of **2a** proves that the reaction has occurred according to the insertion−elimination mechanism described earlier.[4a] The presence of a deuterium atom at the α-carbon of the terminal vinyl group of **2a** is an effect of Ru−D addition to **1** in the first step because the initial step starts from a Ru−D bond instead of a Ru−H bond, in the 100-fold excess of styrene-d_8.

Acknowledgment. This work was supported by Grant No. 13T0A074 from the State Committee for Scientific Research.

Supporting Information Available: Figures giving additional GC and mass spectra and tables and figures giving X-ray crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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