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Metathesis of silicon containing olefins

II *. Synthesis of 1,2-bis(silyl)ethenes by metathesis of vinylsilanes

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Abstract

Highly effective metathesis of vinyl-trisubstituted silanes containing two or three alkoxy groups at silicon, has permitted the synthesis of 1,2-bis(silyl)ethenes consisting either, two isomers viz., *trans-(E)* and *cis-(Z)* in a near 1/1 ratio, or favouring the *E* isomer. In consequence bis(silyl)ethenes of general formula $(RO)_nMe_{3-n}SiCH{=}CHSiMe_{3-n}(OR)_n$ (where $n = 2, 3$; $R = CH_3, C_2H_5, C_3H_7$, iso-C_3H_7) were prepared, isolated, and identified by predominantly spectroscopic methods.

Introduction

1,2-Disilylethenes have been commonly used as monomers in polymerization and copolymerization of C=C bonds as well as in hydrolysis of Si–X bonds (where X = Cl, OR) and further polycondensation. Up to now the methods that have been used for their synthesis are as follows: reactions of distannylethenes with butyllithium and chlorotrimethylsilane [1], reductive silylation of vinyltrimethylsilane by chlorotrimethylsilane in the presence of magnesium and ferric or titanium chlorides [2], the addition of chlorodimethylsilane to acetylenic silanes [3,4], the addition, of Cl_2 and Br_2 to disilylethynes catalyzed by $ZnCl_2$ [4] and the most usual the addition of disilanes to acetylene and its derivatives catalyzed by palladium(0) complexes e.g. [5–7]. Only a few studies have included the self-metathesis of alkenylsilanes and other silicon olefins. The self-metatheses gave very low conversions, usually in the presence of heterogeneous catalysts based on Re_2O_7 [8] and MoO_3 [9], or homogeneous catalysts based on WCl_6, a study which was published recently [10]. Our preliminary examinations on the metathesis of vinyltriethoxysilane [11] and vinyl-

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* For part I see ref. II.

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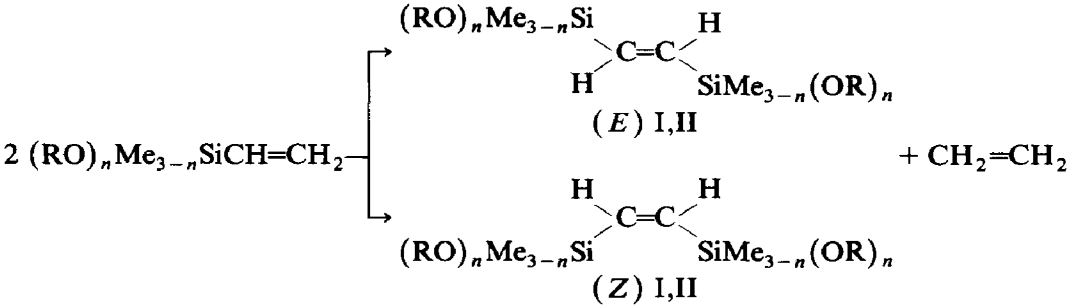
methyldiethoxysilane [12] show that a high metathetical conversion of vinylalkoxy-substituted silanes is possible in the presence of ruthenium and rhodium complexes.

Here we describe the synthetic aspects of this novel catalytic reaction which provides particularly bis(trialkoxysilyl)ethenes and bis(methyldialkoxysilyl)ethenes in very high yields.

Results and discussion

Metathesis of vinyltri(alkoxy,methyl)silanes proceeds smoothly at 80–140 °C in the presence of catalytic systems comprising ruthenium or rhodium chlorides with a Lewis acid and a hydride donor as cocatalyst e.g. $(RO)_3SiH$, R_3SiH, $LiAlH_4$ and $NaBH_4$ as well as other ruthenium or rhodium complexes as follows:



(where: Ia, R = Me, $n = 2$; Ib, R = Et, $n = 2$; Ic, R = Pr, $n = 2$;

Id, R = iso-Pr, $n = 2$; IIa, R = Me, $n = 3$; IIb, R = Et, $n = 3$; IIc, R = Pr, $n = 3$;

IId, R = iso-Pr, $n = 3$)

The metathesis products were identified from their ^1H and ^{13}C NMR, IR and Raman spectra. The analytical and spectroscopic data are listed in Table 1.

The most effective procedures for the synthesis of bis(silyl)ethenes are detailed in the Experimental section. Unfortunately, the isolation of the products of vinyltripropoxysilane was not possible because several by-products were formed during the reaction, and products oligomerized and/or decomposed during distillation. The ruthenium complex system seems to be more versatile than that of rhodium chloride since the former catalyzes the reactions of all alkoxy-substituted vinylsilanes examined, and the latter showed no metathetical activity for trialkoxy-substituted silanes under the conditions used.

On the other hand, the metathesis of the vinylmethyldialkoxysilanes takes place more readily in the presence of rhodium(I) and rhodium(III) complexes. Catalytic data on $RhCl_3$/cocatalyst are summarized in Tables 2 and 3, thus showing the influences that the various cocatalysts and the different reaction times had on the yield and selectivity of the products, viz. the bis(methyldialkoxysilyl)ethenes which formed in glass ampoules as well as under reflux.

There is no direct relationship between the type of alkoxy substituents at silicon or the kind of catalyst system used and the preferable stereoconfiguration assumed by the ethene. For the metathesis of the methoxy-substituted vinylsilanes (Ia, IIa), the *E*/*Z* ratio is predominantly close to 1/1 regardless of the catalyst and conditions used. However, when we used vinylsilanes containing higher alkoxy

Table 1

Analytical and spectroscopic data for the bis(silyl)ethenes; $(RO)_2Si(CH_3)CH{=}CHSi(CH_3)(OR)_2$ (I) and $(RO)_3SiCH{=}CHSi(OR)_3$ (II)

Compound	Substituent R	b.p. (°C/mmHg)	^{1}H NMR (δ, ppm) (TMS)				^{13}C NMR (δ, ppm) (TMS)				IR (Raman) * ν (cm^{-1})
			SiCH_3	OCH	CH_3	=CH	SiCH$_3$	OCH	CH$_3$	=CH	
Ia-(E)	CH$_3$ ^{b}	100–104/30	0.15s	3.44s		6.80s	−5.55	50.11		147.28	– ^{a}
Ia-(Z)			0.18s	3.46s		6.70s	−4.68	50.11		148.45	1575w
Ib-(E)	C$_2$H$_5$ ^{b}	78– 80/2	0.22s	3.72q	1.15t	6.95s	−4.50	58.29	18.60	148.83	– ^{a} (1570) *
Ib-(Z)			0.32s	3.75q	1.18t	6.75s	−3.59	58.29	18.54	146.67	1570w
Ic-(E)	C$_3$H$_7$ ^{c}	110–112/1.5	0.17s	3.63t	0.90t	6.59s	−3.77	64.45	10.53	146.55	– ^{a}
Ic-(Z)			0.16s	3.63t	0.90t	6.64s	−4.64	64.45	10.45	148.85	– ^{a}
Id-(E)	iso-C$_3$H$_7$ ^{b}	78– 82/1.5	0.19s	4.14m	1.15d	6.68s	−3.79	65.02	25.72	146.28	– ^{a} (1567) *
Id-(Z)			0.22s	4.17m	1.22d	6.61s	−2.55	64.82	25.72	149.03	1565w
IIa-(E)	CH$_3$ ^{b}	78– 80/4		3.46s		6.82s		50.54		145.59	– ^{a}
IIa-(Z)				3.53s		6.84s		50.54		151.36	– ^{a}
IIb-(E)	C$_2$H$_5$ ^{b}	122–125/4		3.83q	1.16t	7.05s		58.79	18.48	146.34	– ^{a} (1565) *
IIb-(Z)				3.92q	1.22t	6.96s		58.73	18.47	150.46	1600(w,br)
IId-(E)	iso-C$_3$H$_7$ ^{b}	120–123/1.5		4.27m	1.19d	6.90s		65.36	25.70	146.94	– ^{a}

[a] No sharp absorption band appeared. [b] C_6D_6 as solvent for ^{1}H and ^{13}C NMR spectroscopy. [c] CD_2Cl_2 as solvent for ^{1}H and ^{13}C NMR spectroscopy.

Table 2

Influence of the cocatalyst ($(C_2H_5O)_3SiH$, $LiAlH_4$, $NaBH_4$) on the yield and $(E)/(Z)$-isomer ratio of the products of the metathesis Ia–Id ($[RhCl_3 \cdot 3H_2O] = 10^{-4}$ mol; [ViSi] $= 10^{-2}$ mol; glass ampoules; 110 °C, air, 20 h)

Product	Yield (%) ((*E*)/(*Z*))			
	no cocatalyst	$(C_2H_5O)_3SiH$ (10^{-4} mol)	$LiAlH_4$ (10^{-3} mol)	$NaBH_4$ (5×10^{-3} mol)
Ia	traces	37 (68/32)	25 (60/40)	54 (54/46)
Ib	traces	32 (94/6)	16 (99/1)	13 (99/1)
Ic	traces	20 (99/1)	29 (99/1)	71 (99/1)
Id	0	21 (38/62)	88 (43/57)	57 (44/56)

groups, (EtO, PrO and iso-PrO) we observed that the formation of *trans*-1,2-bis(silyl)ethenes was favoured (see Tables 2 and 3), although under special conditions (catalyst, pressure of ethylene above the reaction mixture) an E/Z ratio close to 1 was seen. *Cis-trans* isomerization takes place under certain catalytic conditions, in addition to the desired metathetic conversions, probably by a catalytic cycle involving both reactions.

For this process to occur no solvents such as benzene, chlorobenzene, toluene, DMF, THF, must be present. The reasons for this inhibiting role of solvent is unclear. This effect is similar to that observed during hydrosilylation of the vinyltrialkoxysilanes by trialkoxysilanes in the presence of ruthenium complexes [13] which entails the blocking of the coordination sites of the catalyst by a solvent molecule. The formation of the four-coordinated Ru complexes in the reactions of chlororuthenium(II) complexes, with trialkoxysilanes as the hydride donors, in the absence of solvent [14] compared with the five- and seven-coordinated complexes isolated from benzene solutions [15,16] provides in direct evidence of this. Apparently, low-coordination ruthenium complexes facilitate the coordination of vinylsilane and generation of carbene-ruthenium species, thus directly initiating a metathesis chain [17]. It is noteworthy, that the activating role of small amounts of dioxygen was observed in the system under study. This effect for ruthenium-catalyzed metathesis and polymerization was reported previously and was thought to be due to the formation of epoxides and the corresponding metallooxacyclobutanes $[\overline{\text{M]OCHRC}}\text{HR}$, the cleavage of which initiates metal carbene formation [18].

Table 3

Influence of the reaction time on the yield of 1,2-bis(silyl)ethenes (Ia–Id) in the presence of $RhCl_3 \cdot 3H_2O$ as a catalyst in the presence of selected cocatalysts ($[RhCl_3 \cdot 3H_2O]$ 10^{-4} mol; [ViSi] 10^{-2} mol; under reflux, in air)

Product	Cocatalyst	$\frac{[\text{cocat.}]}{[\text{cat.}]}$	Yield (%) (*E*)/(*Z*)		
			Time 1 h	Time 2 h	Time 6 h
Ia	$NaBH_4$	50	47 (55/45)	48 (56/44)	50 (58/42)
Ib	$(C_2H_5O)_3SiH$	1	86 (95/5)	89 (94/6)	90 (93/7)
Ic	$LiAlH_4$	10	50 (32/68)	84 (46/54)	90 (43/57)
Id	$NaBH_4$	50	20 (90/10)	45 (89/11)	79 (91/9)

The metal carbene mechanism is the most plausible, and most accepted, hypothesis on metathesis, and was proposed first by Hérisson and Chauvin [19], and was specifically applied to the Wilkinson catalyst by Cardin et al. [20]. The idea is based on the formation of a metal carbene metallocyclobutane intermediate during the catalytic cycle. Further synthetic, catalytic and analytical studies may yield more data to account for the unusually high metathetical conversion of vinyl alkoxysubstituted silanes in the presence of ruthenium and rhodium complexes and thus supports the suggested reaction mechanism.

Experimental

Materials. The vinyltrialkoxysilanes and vinylmethyldialkoxysilanes were prepared by solvolysis of the corresponding chloro-substituted silanes by standard procedures.

Catalysts and cocatalysts. $RuCl_2(PPh_3)_3$ and $RhCl(PPh_3)_3$ were purchased from Strem Chemicals and Ventron. $RuCl_3 \cdot 3H_2O$ and $RhCl_3 \cdot 3H_2O$ were commercial products received from International Enzymes and Fluka, respectively. $NaBH_4$ and $LiAlH_4$ were bought from Fluka, whereas $(C_2H_5O)_3SiH$ was obtained by solvolysis of Cl_3SiH.

Equipment and analytical measurements. Infrared spectra were recorded on a Perkin–Elmer Model 180 spectrophotometer and the Raman spectra on a JEOL JRS-SI laser Raman spectrometer, ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrometer equipped with a Texas 980 B computer system. Gas chromatography was carried out with a GCHF instrument using 2 m steel columns packed with 10% SE-30 on Chromosorb P (with thermal conductivity detector).

Synthetic procedures

Syntheses of 1,2-bis(silyl)ethenes (I,II), general procedure. The catalyst ($RuCl_3 \cdot 3H_2O$, $RhCl_3 \cdot 3H_2O$, $RuCl_2(PPh_3)_3$ and $RhCl(PPh_3)_3$ were used as precursors in the presence or absence of various cocatalysts, such as triethoxysilane, $NaBH_4$, $LiAlH_4$ etc.) was placed in a glass ampoule (or in a flask equipped with a condensor) and then the vinylsilane was introduced. Sealed ampoules (or flasks) were heated at between 110–130 °C for several hours. Yields of the reaction products were calculated on the basis of GLC analysis of the reaction mixture. The 1,2-bis(silyl)ethenes (I, II) were distilled under vacuum and the (*E*)- to (*Z*)-isomer ratio was determined by GLC. Both isomers were isolated by preparative GLC.

All manipulations were carried out in dry air, in absence of solvent. All the analytical and spectroscopic data of the 1,2-bis(silyl)ethenes synthesized are listed in Table 1.

Synthesis of 1,2-bis(methyldimethoxysilyl)ethene (Ia). A mixture of vinylmethyldimethoxysilane (13.2 g, 10^{-1} mol), $NaBH_4$ (1.9 g, 5×10^{-2} mol) and $RhCl_3 \cdot 3H_2O$ (0.263 g, 10^{-3} mol) was sealed in a glass ampoule and heated at 110 °C for 20 h. The yield of product Ia (a 54/46 mixture of (*E*) and (*Z*) isomers) was found to be 54%. Isolation of the products by distillation was followed by chromatographic separation and spectroscopic identification of isomers (see Table 1).

Synthesis of 1,2-bis(methyldiethoxysilyl)ethene (Ib). A mixture of vinylmethyldiethoxysilane (16.0 g, 10^{-1} mol), $RhCl_3 \cdot 3H_2O$ (0.263 g, 10^{-3} mol) and $HSi(OC_2H_5)_3$ (0.164 g, 10^{-3} mol) was heated in reflux for 6 h. After distillation of the reaction products from the reaction mixture (90% yield based on substrate used) the preparative GLC was used. The minor product, which appeared after a shorter retention time than Ib, was identified as (*Z*)-1,2-bis(methyldiethoxysilyl)ethene (see Table 1).

A mixture of vinylmethyldiethoxysilane (8.0 g, 5×10^{-2} mole) and $RuCl_2(PPh_3)_3$ (0.48 g, 5×10^{-4} mol) was sealed in a glass ampoule and heated in an oven at 120 ° C for 24 h. After distillation, 4.83 g (66%) of isomer mixture of Ib was isolated, and a 1/1 ratio of isomers was observed.

A solution if vinylmethyldiethoxysilane (16.0 g, 10^{-1} mol) and $RuCl_3 \cdot 3H_2O$ (0.26 g, 10^{-3} mol) was placed in a reaction vessel and heated at 120 ° C for 6 h. 1,2-Bis(methyldiethoxysilyl)ethene (Ib) was synthesized in 70% yield and isolated after distillation from the reaction mixture $((E)/(Z) = 81/19)$.

Synthesis of 1,2-bis(methyldipropoxysilyl)ethene (Ic). A mixture of vinylmethyldipropoxysilane (7.53 g, 4×10^{-2} mol), $RhCl_3 \cdot 3H_2O$ (0.105 g, 4×10^{-4} mol) and $NaBH_4$ (0.76 g, 2×10^{-2} mol) was heated under reflux for 6 h. Isolation of the product from the reaction mixture was performed by distillation under reduced pressure (yield 81%, a 11/89 mixture of (*Z*) and (*E*) isomers) (see Table 1).

Synthesis of 1,2-bis(methyldiisopropoxysilyl)ethene (Id). A solution of vinylmethyldiisopropoxysilane (7.53 g, 4×10^{-2} mol), $RhCl_3 \cdot 3H_2O$ (0.105 g, 4×10^{-4} mol) and $LiAlH_4$ (0.140 g, 4×10^{-3} mol) was sealed in a glass ampoule and heated at 110 ° C for 20 h. Distillation afforded Id in 88% yield. The isomers were isolated by preparative GLC (43/57 mixture of (*Z*)- and (*E*)-isomers was found) (see Table 1).

Synthesis of 1,2-bis(trimethoxysilyl)ethene (IIa). A solution of vinyltrimethoxysilane (7.41 g, 5×10^{-2} mol), $RuCl_3 \cdot 3H_2O$ (0.130 g, 5×10^{-4} mol) and $(C_2H_5O)_3SiH$ (0.080 g, 5×10^{-4} mol) was sealed in glass ampoule and heated at 130 ° C for 3 h. The yield of product IIa was 52%. Two isomers are present in the product fraction, in a nearly 1/1 ratio (see Table 1).

Synthesis of 1,2-bis(triethoxysilyl)ethene (IIb). A solution of vinyltriethoxysilane (7.90 g, 5×10^{-2} mol) and $RuCl_2(PPh_3)_3$ (0.048 g, 5×10^{-5} mol) was refluxed for 24 h and it gave the main product, which was distilled and identified as IIb, in 82% yield. Ethylene was evolved from the mixture. On the basis of the spectroscopic data the major product was identified as (*E*)-isomer and the $(E)/(Z)$ ratio was calculated (for the resulting products mixture) to be 86/14 (see Table 1).

A mixture of vinyltriethoxysilane (1.58 g, 10^{-2} mol), $RuCl_3 \cdot 3H_2O$ (0.026 g, 10^{-4} mol) and $(C_2H_5O)_3SiH$ (0.016 g, 10^{-4} mol) was sealed and heated at 130 ° C for 1 h. The product was isolated in 60% yield.

Synthesis of 1,2-bis(tripropoxysilyl)ethene (IIc). A mixture of vinyltripropoxysilane (2.32 g, 10^{-2} mol), $RuCl_3 \cdot 3H_2O$ (0.026 g, 10^{-4} mol) and $(C_2H_5O)_3SiH$ (0.016 g, 10^{-4} mol) was sealed in a glass ampoule and heated at 130 ° C for 1 h. As the analysis of the resulting reaction mixture additionally indicates several by-products are observed in addition to the major product. All attempts to isolate this product failed. During distillation at 120 ° C/1 mm Hg, some decomposition of the products occurs.

Synthesis of 1,2-bis(triisopropoxysilyl)ethene (IId). A mixture of vinyltriisopropoxysilane (2.30 g, 10^{-2} mol), $RuCl_3 \cdot 3H_2O$ (0.026 g, 10^{-4} mol) and $(C_2H_5O)_3SiH$ (0.016 g, 10^{-4} mol) was sealed in a glass ampoule and heated at 130 ° C for 2 h. The distillation afforded IId in 45% yield, and was found to consist of only one e.i. (*E*)-isomer (see Table 1).

Catalytic tests

Metathesis examinations were carried out in sealed glass ampoules in air and in absence of solvent. The reaction mixture, containing the appropriate vinylsilane, catalyst and cocatalyst, was warmed up to the reaction temperature and kept at that temperature for several hours, and was then subjected to gas-liquid chromatography. For details see footnotes in Table 2. Although most metatheses were carried out in closed systems, some were carried out at reflux. For details see Tables 2 and 3.

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