

Coupling vs. metathesis of vinylsiloxanes catalyzed by Ru-complexes

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Abstract

Effective disproportionation of vinylsiloxanes (vinylmethylbis(trimethylsiloxy)silane (**I**) and vinyltris(trimethylsiloxy)silane (**II**)) proceeds in the presence of ruthenium(II) complexes, e.g., $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and $\text{RuCl}_2(\text{PPh}_3)_3$ in air to yield new *E*-bis(siloxy)ethenes, (except the $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ catalyzed reaction of (**I**) giving 1:1 mixture of *E*-1,2-bis(siloxy)ethene and 1,1-bis(siloxy)ethene). The reaction can be regarded as a molecular model of a new method of poly(methyl, vinyl)siloxanes cross-linking. Cross-coupling of the two vinylsiloxanes (**I**) and (**II**) with styrene also effectively catalyzed by Ru-complexes allows a synthesizing of new *E*-1-phenyl-2-(siloxy)ethenes. Mechanistic implications following from the previous works assume the involvement of Ru–H and Ru–Si intermediates responsible for catalytic reactions. β -Si transfer to metal from a β -siloxyethyl ligand bonded to Ru atom is a key step in the homocoupling of vinylsiloxane and its heterocoupling with olefin (styrene). © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Vinylsiloxanes; Ruthenium complexes; Coupling; Cross-linking

1. Introduction

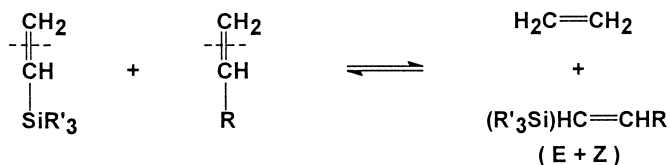
Results of the last decade investigation of the metathetical conversion of silicon-containing olefins have shown that allyl- and butenyl-silanes can be effectively catalyzed by $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3 + \text{Sn}$ (or $\text{Pb})\text{R}_4$ [1,2] system as well as WCl_6 -based catalytic system [3,4]. Acyclic diene metathesis (ADMET) polymerization of dialkenylsilanes also occurs in the presence of highly active W and Mo alkylidene catalysts [5,6]. However, vinyl-substituted silicon compounds appeared to be quite inactive in the presence of classical W, Mo and Re–carbene complexes in any metathetical conversion presumably due to steric effects and the relative stability of the silyl-substituted metallacarbenes [7].

On the other hand, vinyl-substituted silanes undergo a very effective disproportionation and co-disproportionation with olefins in the presence of Ru-complexes [8–12].

It has been shown that the reaction referred to as metathesis of vinylsilanes and their co-metathesis with olefins does not involve a process of C=C bond cleavage, which is formally characteristic of the

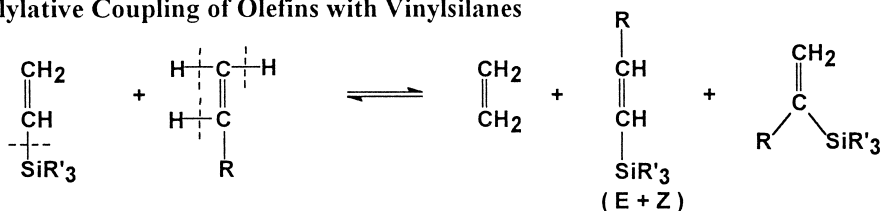
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A. Metathesis of Olefins with Vinylsilanes



Activation of $\text{C}=\text{C}$ bond

B. Silylative Coupling of Olefins with Vinylsilanes



Activation of $\text{C}=\text{C}-\text{H}$ and $\text{C}=\text{C}-\text{Si}$ bond

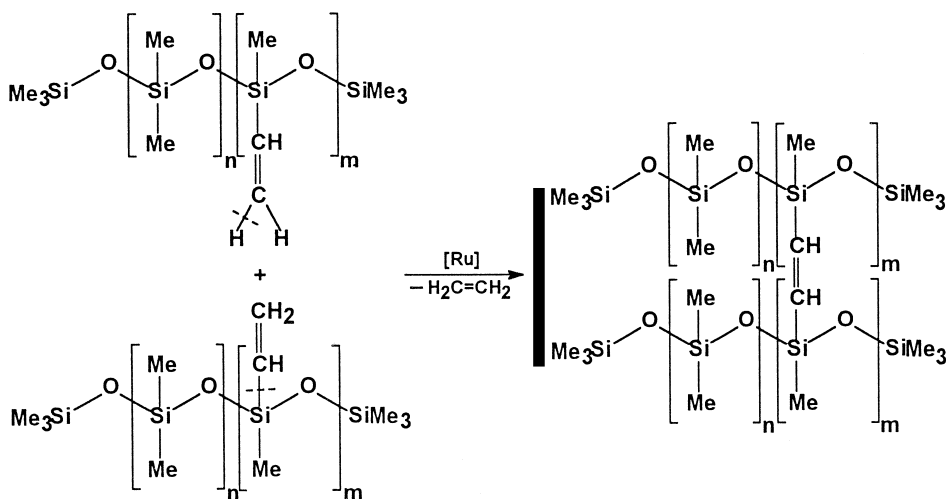
Scheme 1. Metathesis vs. silylative coupling of olefins with vinylsilanes.

olefin metathesis (Scheme 1A), and instead a new type of olefin conversion was revealed, that is the silylative dehydrocoupling of olefins by vinylsilane (Scheme 1B) [13–15].

The reaction proceeds through $\text{C}=\text{Si}$ and $\text{C}=\text{H}$ bond cleavage.

The aim of this paper is to make an attempt at the use of mono-vinylsubstituted siloxanes in the Ru-complex catalyzed reactions of homocoupling (disproportionation) and heterocoupling with styrene.

The disproportionation of vinylsiloxanes can be a good molecular model for cross-linking of polydimethylsiloxanes containing internal vinyl substituents at silicon, which can occur according to Scheme 2. At present, Pt-catalyzed hydrosilylation is a common reaction for cross-linking of poly(methyl, vinyl)siloxanes by poly(methyl, hydro)siloxanes [16]. There is only one report on the

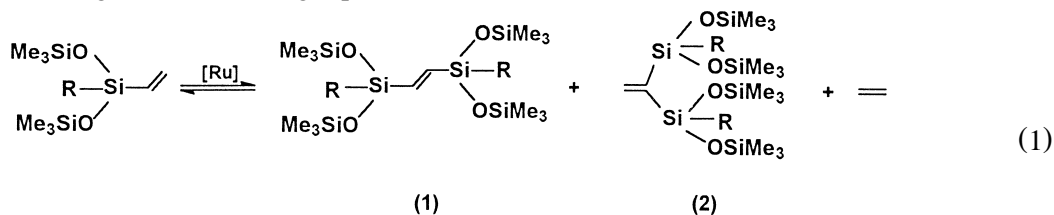


Scheme 2. Cross-linking of polyvinyl dimethylsiloxanes via their homo coupling.

cross-linking of hexenyl silicone polymers via the olefin metathesis catalyzed by $WCl_6/Sn(M)_4$ system based also on the molecular reaction of metathesis of hexenylsiloxane [17]. However, commercially available vinyl silicone polymers similar to vinyl silicon monomers do not undergo such a metathetical conversion.

2. Results

Vinylmethylbis(trimethylsiloxy)silane (**I**) and vinyltris(trimethylsiloxy)silane (**II**) undergo disproportionation according to the following equation:



The catalytic data are presented in Tables 1 and 2.

A very high conversion of vinylmethylbis(trimethylsiloxy)silane (**I**) and yield of bis(siloxy)ethenes (**1 + 2**) were observed if ruthenium(II) complexes were used as the initial catalysts in the reaction occurring in glass ampoules as well as in the open system. It is worth pointing out that in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$, (**I-1**) can be stereoselectively synthesized (see Section 4), whereas in the presence of the complex initially containing Ru–H, both isomers (**I-1 + I-2**) can be formed at a ratio close to

Table 1
Disproportionation of vinylmethylbis(trimethylsiloxy)silane (**I**) catalyzed by ruthenium complexes

Catalyst	Conversion of vinylsiloxane (I) (%)	Yield of bis(siloxy)ethenes (I-1 + I-2) (%)	(I-1)/(I-2) isomer ratio
$\text{RuCl}_2(\text{PPh}_3)_3$	70	60	25:1
$\text{Ru}_3(\text{CO})_{12}$	20	15	<i>E</i>
$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$	72	67	1:0.9
Reaction conditions: 130°C, 24 h, [Ru]:[ViSi≡]=10 ⁻² :1, sealed glass ampoules			
$\text{RuCl}_2(\text{PPh}_3)_3$	70	65	30:1
$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$	92	88	1:1
Reaction conditions: reflux, 24 h, [Ru]:[ViSi≡]=10 ⁻² :1, open system			

Table 2
Disproportionation of vinyltris(trimethylsiloxy)silane (**II**) catalyzed by ruthenium complexes

Catalyst	Conversion of vinylsiloxane (II) (%)	Yield of bis(siloxy)ethene (II-1) (%)
$\text{RuCl}_2(\text{PPh}_3)_3$	25	22
$\text{Ru}_3(\text{CO})_{12}$	5	2
$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$	42	40
Reaction conditions: 130°C, 24 h, [Ru]:[ViSi≡]=10 ⁻² :1, sealed glass ampoules		
$\text{RuCl}_2(\text{PPh}_3)_3$	10	7
$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$	75	72
Reaction conditions: reflux, 24 h, [Ru]:[ViSi≡]=10 ⁻² :1, open system		

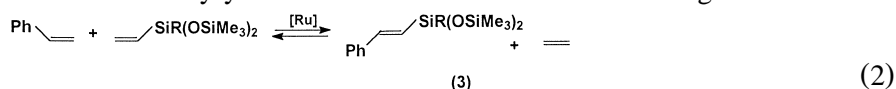
Table 3
Silylative coupling of styrene by siloxanes (I) and (II) catalyzed by various ruthenium complexes

Catalyst	Conversion of vinylsiloxane (%)		Yield of styrylsiloxane (%)	
	(I)	(II)	(I-3)	(II-3)
RuCl ₂ (PPh ₃) ₃	69	33	65	30
Ru ₃ (CO) ₁₂	0	0	0	0
RuHCl(CO)(PPh ₃) ₃	75	36	72	32
RuCl(SiMe ₃)(CO)(PPh ₃) ₂	72	23	70	22
Reaction conditions: 100°C, 6 h, [Ru]:[ViSi≡]:[styrene]=10 ⁻² :1:5; sealed glass ampoules				
RuCl ₂ (PPh ₃) ₃	92	78	90	76
RuHCl(CO)(PPh ₃) ₃	88	83	86	82
Reaction conditions: 100°C, 24 h, [Ru]:[ViSi≡]:[styrene]=10 ⁻² :1:5, open system				

1:1. The two catalysts enabled us to synthesize and identify, for the first time, both main products of disproportionation of (I). GC-MS analyses of all products have shown that (I-1) and (I-2) are accompanied by traces of 1,4-bis(siloxy)butenes.

Steric hindrance caused by three siloxy groups at vinylic silicon in (II) (Table 2) is the main reason for its lower conversion and high stereoselectivity to yield exclusively (II-1). Much higher yield of (II-2) in the initial presence of Ru–H complex evidences the involvement of dehydrocoupling. Separate studies of the use of a well-defined Ru–carbene (PPh₃)₂Cl₂Ru=CH–CH=CPh₂ complex (Grubbs catalyst) showed no metathesis reaction of vinyltrisubstituted silanes and siloxanes under the conditions examined.

Our study of the dehydrogenative silylation of styrene by various vinyl-substituted silanes in the presence of Ru-complexes has markedly extended the available methods for obtaining numerous styrylsilanes effectively and selectively in a one-step process [15]. The aim of this work is also to find an efficient method for synthesis of new styrylsiloxanes on the basis of the following reaction:



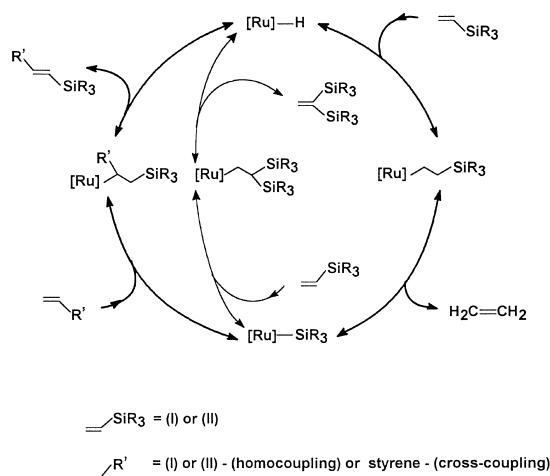
where R = Me (I) and (OSiMe₃) (II)

The catalytic data given in Table 3 show that the reaction of styrene with (I) and (II) occurs in the presence of Ru(II) complexes in glass ampoules and, much more efficiently, in an open system, to allow for ethylene evolution.

The reaction is regio- and stereo-selective regardless of the initial complex used. Both products—styrylsiloxanes—were isolated and characterized by ¹H and ¹³C NMR spectroscopy.

3. Discussion

Recent reports on the striking evidence for the insertion of ethylene [13], styrene [15], and vinylsilanes [14] into a Ru–Si bond (and/or migration of the silyl ligand to vinylsilane bonded to the ruthenium complexes) as well as inactivity of metallocarbenes in the metathesis of vinylsilanes [7] and vinylsiloxanes have shown that the reactions of vinylsubstituted silicon compounds with olefins occur via the insertion of vinylsilane into Ru–H bond and the olefin (also vinylsilane in the homocoupling) into Ru–Si bond, followed by β-Si and β-H elimination, respectively, to give as products 1,2- and 1,1-bis(silyl)ethenes (and respective alkenylsilanes) as well as ethene.



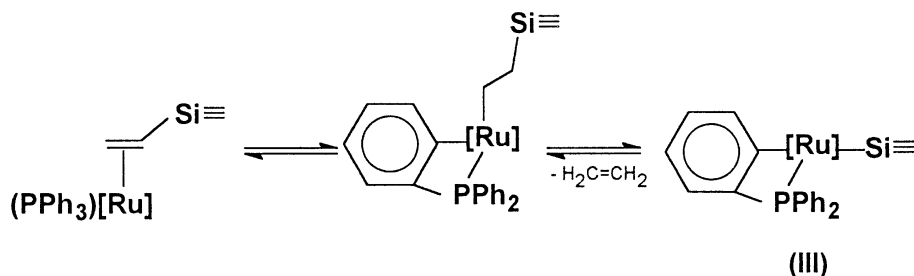
Scheme 3. Mechanism of silylative coupling of olefins by vinylsiloxane catalyzed by Ru–H and Ru–Si complexes.

In the case of vinylsiloxanes examined, the catalytic scheme is as shown in Scheme 3.

Catalysis of vinylsilane disproportionation by ruthenium phosphine complexes containing initially no Ru–H bond, e.g., $\text{RuCl}_2(\text{PPh}_3)_3$ was proposed to be a result of the orthometallation of ruthenium triphenylphosphine complexes [11,18], followed by direct insertion of vinylsilane into Ru–H bond and β -Si transfer to Ru according to Scheme 4.

Orthometallation of transition metal complexes is a well-known reversible step in some stoichiometric and catalytic reactions [19,20]. In case of the complex containing arylphosphine ligands coordinated to the metal, this process occurs via formation of agostic $\text{C}_{\text{aryl}}\text{--H} \rightarrow \text{M}$ bond and/or formal intramolecular addition of $\text{C}_{\text{aryl}}\text{--H}$ bond to form C–M–H systems [21]. Orthometalated transition metal complexes of the type **(III)** cause an enhancement of catalytic activity of ruthenium phosphine and phosphite complex in catalyzed hydrogenation of olefins [19]. Apparently, the geometry induced by the process of orthometallation governs, the insertion of **(I)** to such Ru(IV)–Si complex **(III)** stereoselectively to get almost exclusively *E*-bis(siloxy)ethene. In this case, however, we cannot exclude partial catalysis by Ru–carbene species formed in situ under the conditions studied.

Contrary to the reaction with $\text{RuCl}_2(\text{PPh}_3)_3$, vinylsiloxane is directly inserted to $\text{RuHCl}(\text{CO})(\text{PPh}_3)_2$ complex which results in the formation of $\text{Ru}(\text{siloxy})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ of approximately square–pyramidal geometry [15,22,23] in the air. The next insertion of **(I)** into Ru–Si of such a complex proceeds in both fashions to get 1,2-*E* and 1,1-bis(siloxy)ethenes.



Scheme 4. Mechanism of orthometallation of $\text{RuCl}_2(\text{PPh}_3)_3$ in the presence of vinylsubstituted silicon compounds.

Vinylsiloxane (**II**) with the substituents at vinylic silicon more crowded than those in (**I**), as well as styrene in the cross-coupling with (**I**) and (**II**) have been inserted into Ru–Si bond stereoselectively regardless of the initial ruthenium complex used.

4. Experimental

4.1. General methods and chemicals

All syntheses and catalytic tests were carried out in the air. ^1H and ^{13}C NMR spectra of isolated products were recorded in C_6D_6 on a Varian Gemini 300 VT spectrometer (300 and 75 MHz, respectively). When needed, DEPT and HETCOR spectra were also recorded. GLC analyses were performed on a Hewlett Packard HP 5890 Series II with 30 m megabore column HP-1 and TCD. Infrared spectra (KBr/film) were recorded using FT-IR Bruker IFS-113v.

The chemicals were obtained from the following sources: vinylmethylbis(trimethylsiloxy)silane and vinyltris(trimethylsiloxy)silane from ABCR, styrene from Fluka, benzene from Lachema (Czech Rep.), toluene from R&D Center, Petrochemia Płock, Poland, benzene d_6 from Dr. Glaser, Basel. $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ was purchased from Aldrich, $\text{Ru}_3(\text{CO})_{12}$ from Strem Chemicals and used without further purification: $\text{RuCl}_2(\text{PPh}_3)_3$ was prepared by standard procedure and $\text{RuCl}(\text{SiMe}_3)(\text{CO})(\text{PPh}_3)_2$ according to procedures described in Ref. [13]. Grubbs ruthenium–carbene complex $(\text{PPh}_3)_2\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$ was prepared by the method reported in Ref. [24]. All solvents were dried prior to use over CaH_2 and stored under argon.

5. Synthesis

5.1. Synthesis of *E*-1,2-bis[methyl(trimethylsiloxy)silyl]ethene (**I-1**)

The following substances: 0.1291 g (1.35×10^{-4} mol) $\text{RuCl}_2(\text{PPh}_3)_3$, 4 cm^3 of toluene, 4 cm^3 (1.35×10^{-2} mol) of vinylmethylbis(trimethylsiloxy)silane and 0.3 cm^3 (1.54×10^{-3} mol) of *n*-decane (an internal standard) were placed in a 20 cm^3 flask. The mixture was heated in oil bath at 130°C for 24 h. The product was isolated by vacuum distillation as the fraction boiling at 71–74°C/3 mm Hg, in the amount of 1.8 g and of 98% purity, which gives a yield of 56%. ^1H NMR (C_6D_6) (δ , ppm): 6.85(s, 2H) CHSi, 0.25 (s, 6H) SiMe, 0.19 (s, 36H) OSiMe₃; ^{13}C NMR (C_6D_6) (δ , ppm): 150.14 CHSi, –0.03 SiMe, 2.49 OSiMe₃; IR (cm^{-1}): 2959(m), 2900(vw), 1635(l), 1411(l), 1252(m), 1171(w), 1088(s), 871(m), 842(m), 792(m), 755(m), 627(w).

5.2. Synthesis of the mixture of isomers: *E*-1,2-bis[methyl(trimethylsiloxy)silyl]ethene and 1,1-bis[methyl(trimethylsiloxy)silyl]ethene (**I-1** + **I-2**)

The substances: 0.1286 g (1.35×10^{-4} mol) $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, 4 cm^3 of toluene, 4 cm^3 (1.35×10^{-2} mol) of vinylmethylbis(trimethylsiloxy)silane and 0.3 cm^3 (1.54×10^{-3} mol) of *n*-decane (an internal standard) were placed in a 20 cm^3 glass flask. The contents were heated at 130°C for 24 h. The mixture of products was isolated by distillation in vacuum collecting the fraction boiling at 71–75°C/3 mmHg.

The mixture of the two products of 98% purity was obtained in the amount of 2.58 g, which gives a yield of 80%. The molar ratio of the obtained isomers was ca. 1:1.

NMR spectrum of (**I-2**) was identified by a comparison of the spectrum of the mixture with that of the pure (**I-1**). The isomer structures were confirmed by DEPT analysis. NMR data for (**I-2**) ^1H NMR (C_6D_6) (δ , ppm): 6.57 (s, 2H) $\text{H}_2\text{C}=\text{}$, 0.33 (s, 6H) SiMe, 0.21 (s, 36H) OSiMe₃; ^{13}C NMR (C_6D_6) (δ , ppm): 143.71 $\text{H}_2\text{C}=\text{}$, 152.51 $=\text{C}(\text{SiR}_3)_2$, 1.83 SiMe, 2.63 OSiMe₃.

5.3. Synthesis of *E-1,2-bis[tris(trimethylsiloxy)silyl]ethene (II-1)*

The substances: 0.1022 g (1.07×10^{-4} mol) $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, 4 cm³ of toluene, 4 cm³ (1.07×10^{-2} mol) of vinyltris(trimethylsiloxy)silane and 0.3 cm³ (1.54×10^{-3} mol) of *n*-decane (an internal standard) were placed in a 20 cm³ flask.

The mixture was heated in oil bath at 130°C for 24 h. The product isolated by distillation in vacuum was the fraction boiling at 85–88°C/3 mmHg. The amount of the 96% pure product was 2.03 g which corresponds to a yield of 59%. ^1H NMR(C_6H_6) (δ , ppm): 6.86 (s, 2H) CHSi, 0.24(s, 54H) OSiMe₃; ^{13}C NMR (C_6D_6) (δ , ppm): 147.7 CHSi, 2.40 OSiMe₃; IR (cm^{-1}): 2959(m), 2900(vw), 1635(l), 1418(l), 1261(m), 1252(m), 1177(w), 1087(s), 865(m), 842(m), 766(m), 756(m), 687(w), 636(w), 627(w), 595(w).

5.4. Synthesis of *E-1-phenyl-2-[methylbis(trimethylsiloxy)silyl]ethene (I-3)*

The substances: 0.0969 g (1.01×10^{-4} mol) $\text{RuCl}_2(\text{PPh}_3)_3$, 3 cm³ of toluene, 3 cm³ (1.01×10^{-2} mol) of vinylmethylbis(trimethylsiloxy)silane, 5.8 cm³ (5.06×10^{-2} mol) of styrene and 0.3 cm³ (1.54×10^{-3} mol) of *n*-decane (an internal standard) were placed in a 20 cm³ flask.

The mixture was heated in oil bath at 100°C for 24 h.

The product was isolated by distillation in vacuum as the fraction boiling at 92–94°C/3 mm Hg. The amount of the product of 97% purity was 2.8 g which corresponds to a yield of 82% taking into account the vinylsiloxane used. ^1H NMR (C_6D_6) (δ , ppm): 6.40(d, $J_{\text{HH}} = 19.2$ Hz, 1H) CHSi; 7.14(d, $J_{\text{HH}} = 19.2$ Hz, 1H) CHPh; 0.29 (s, 6H) SiMe; 0.18 (s, 18H) OSiMe₃; ^{13}C NMR (C_6D_6) (δ , ppm) 127.07 CHSi; 146.33 CHPh; 0.95 SiMe; 2.69 OSiMe₃; IR (cm^{-1}): 3080(vw), 3060(vw), 3026(vw), 2959(m), 2900(vw), 1607(w), 1576(w), 1495(w), 1448(w), 1260(m), 1252(m), 1084(s), 991(w), 871(m), 843(m), 813(m), 784(m), 754(m), 733(m), 689(w), 637(w), 627(w).

5.5. Synthesis of *E-1-phenyl-2-[tris(trimethylsiloxy)silyl]ethene (II-3)*

The substances: 0.0771 g (8.04×10^{-5} mol) $\text{RuCl}_2(\text{PPh}_3)_3$, 3 cm³ of toluene, 3 cm³ (8.04×10^{-3} mol) of vinyltris(trimethylsiloxy)silane, 4.6 cm³ (4.01×10^{-2} mol) of styrene and 0.3 cm³ (1.54×10^{-3} mol) of *n*-decane (an internal standard) were placed in a 20 cm³ flask.

The mixture was heated in oil bath at 100°C for 24 h. The product was isolated by distillation in vacuum as the fraction boiling at 112–116°C/3 mmHg. The amount of the 96% pure product was 2.2 g which corresponds to a yield of 66% taking into account the vinylsiloxane used. ^1H NMR (C_6D_6) (δ , ppm): 6.27(d, $J_{\text{HH}} = 18.9$ Hz, 1H) CHSi; 7.20(d, $J_{\text{HH}} = 18.9$ Hz, 1H) CHPh; 0.16(s, 27H) OSiMe₃; ^{13}C NMR (C_6D_6) (δ , ppm): 123.37 CHSi; 147.36 CHPh; 2.63 OSiMe₃; IR (cm^{-1}): 3080(vw), 3060(vw), 3028(vw), 2959(m), 2900(vw), 1611(w), 1575(w), 1495(w), 1448(w), 1261(m), 1252(m), 1091(s), 991(w), 843(m), 797(w), 755(m), 736(m), 689(w), 627(w), 601(w).

5.6. Catalytic examinations

In a typical catalytic test a benzene solution of the ruthenium catalyst was placed in glass ampoules or in a glass reactor (20 cm³) equipped with a condenser, heating coat and magnetic stirrer in the air. Vinylsiloxane (**I**) or (**II**) (as well as styrene in case of the heterocoupling) and decane as the internal standard were then added. The sealed ampoules were heated at a given temperature (100–130°C) (6–24 h). The mixture in the glass reactor was refluxed or heated at a given temperature in an open system. The conversion of substrates and the yield of products were determined by GLC using an internal standard method.

6. Conclusions

(1) Vinylsiloxanes type (**I**) and (**II**) undergo effective disproportionation in the presence of ruthenium(II) complexes to yield stereoselectively new *E*-1,2-bis(siloxy)ethenes or a mixture (1:1) of *E*-1,2- and 1,1-bis(siloxy)ethenes.

(2) The catalytic disproportionation of (**I**) and (**II**) can be regarded as a molecular model for cross-linking of polymethylsiloxanes containing internal vinyl substituents at silicon.

(3) *E*-1-phenyl-2-(siloxy)ethenes can be efficiently synthesized by silylative dehydrocoupling of styrene with vinylsiloxane (**I**) and (**II**) catalyzed by RuCl₂(PPh₃)₃ and RuHCl(CO)(PPh₃)₃.

(4) The catalytic cycles for homocoupling of vinylsiloxanes and heterocoupling of styrene with vinylsiloxanes involve the competitive–consecutive insertion reactions of the olefins examined into Ru–H and/or Ru–Si bond followed by β -Si and β -H transfer from β -siloxyethyl ligand bound to Ru atom, eliminating unsaturated siloxanes—products and ethylene.

Acknowledgements

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