

The effect of substituents at silicon on the cross-metathesis of trisubstituted vinylsilanes with olefins

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Abstract

Efficient cross-metathesis of vinylsilanes, carrying a large spectrum of different substituents at silicon, with various olefins in the presence of the first and second generation Grubbs catalyst and Hoveyda–Grubbs catalyst is described. On the basis of the results of equimolar reactions of vinylsilanes with ruthenium alkylidene complexes and experiments with deuterium-labelled reagents, a general, metallacarbene mechanism for the cross-metathesis of trisubstituted vinylsilanes with olefins has been suggested. Reaction was proved to be a valuable method for synthesis of unsaturated organosilicon derivatives.

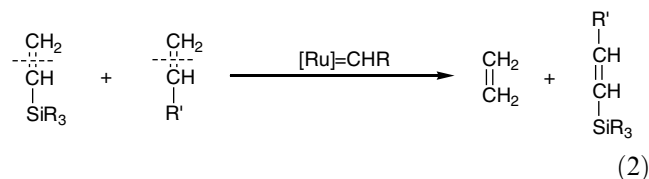
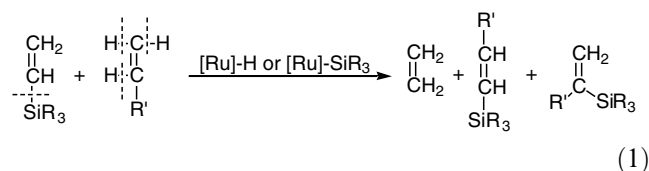
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1. Introduction

Trisubstituted vinylsilanes of the type RCH=CH(SiR₃) constitute a class of unsaturated organosilicon compounds of prospective wide applicability in organic synthesis [1], especially in the fast developing palladium-catalysed coupling of vinylsilanes with organic derivatives [2]. The main catalytic routes to silylolefins involve hydrosilylation of substituted alkynes by hydrosilanes [3], hydrogenation of alkynylsilanes [4] and silylative coupling (SC) of vinylsilanes with olefins [5]. Silylative coupling of vinylsilanes with olefins catalysed by ruthenium, rhodium and cobalt complexes containing (or generating) M–H and M–Si bonds occurs through a cleavage of the =C–Si bond of vinylsilane and =C–H bond of the olefin (Eq. (1)) and is a convenient synthetic route to vinyltrisubstituted silanes [5].

Silylative coupling is not fully regioselective and in specific systems it is accompanied by double bond migration and *cis–trans* isomerization. Moreover, this method cannot be applied for chlorosubstituted vinylsilanes [5]. In the search for new routes of effective synthesis of trisubstituted vinylsilanes, we have directed our attention to olefin metathesis (Eq. (2)).

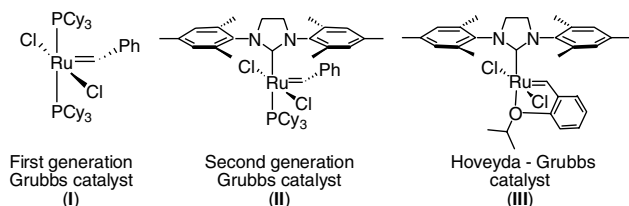


The olefin metathesis has become an important and powerful reaction in organic and polymer synthesis [6]

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as a result of development of well-defined functional group tolerant metal carbene complexes, e.g., **I**, **II** or **III**, which can act directly as metathesis initiators [7].



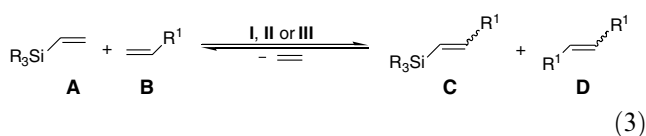
We have previously shown that Grubbs type catalysts effectively catalyse the cross-metathesis (CM) of trialkoxy-, trisiloxy- [8], trichloro- and generally electron withdrawing group substituted vinylsilanes [9] and vinylsilsesquioxanes [10] with styrenes, alkenes and numerous allyl derivatives. Metathesis of vinylsilanes with dienes and cycloalkenes catalysed by Grubbs type complexes has also been demonstrated [11].

Now, we would like to focus on the effect of substituents at silicon on the reaction, discuss advantages and drawbacks of cross-metathesis of vinylsilanes with olefins as a general synthetic method for the synthesis of vinyltrisubstituted silanes and finally search for a mechanistic scheme of catalysis of the reaction.

2. Results and discussion

2.1. Catalytic examinations

Treatment of a mixture of vinylsilane and olefin in the presence of 0.5–5 mol% of catalyst **I**, **II** or **III** gives rise to evolution of ethene and formation of trisubstituted vinylsilane (Eq. (3)). The reaction permits a synthesis of substituted silylenes with high yields and selectivities, under mild reaction conditions. The results of the catalytic studies are summarised in Table 1.



The above presented results permit drawing a comparison of reactivities of a number of vinylsilanes, olefins and catalysts used.

High yield of the reaction is obtained for styrene, 4-substituted styrenes, 1-alkenes and allyl derivatives such as allyltrimethylsilane and allyl ethers. The reactions with styrenes lead to selective formation of *E*-isomer. The cross-metathesis of vinylsilanes with 1-alkenes, allylsilanes and allyl ethers gives a mixture of *E*- and *Z*-isomers, with *E*-isomer in predominant amounts. Although the synthesis of trisubstituted olefins via cross-metathesis is possible when using catalyst **II** [12], no cross-metathesis of vinylsilanes with 1,1-disubstituted

olefins such as 1,1-diphenylethene and 1-methyl-1-phenylethene has been observed.

A significant effect of substituents at the silicon on the reactivity of vinylsilanes is observed. On the basis of substantial differences in the reactivity in metathesis, vinylsilanes can be divided into four general classes (Scheme 1).

Class **1** consists of the vinylsilanes containing three identical or different electron withdrawing substituents such as Cl, OR, OCOR, OSiMe₃, C₆H₄-CF₃-4 at silicon. The cross-metathesis of olefins with the aforementioned vinylsilanes provides the products with high yields and selectivities. The CM with olefins is usually accompanied by competitive olefin *homo*-metathesis. However, this reaction can be retarded by applying an excess of vinylsilane. Catalyst **I** permits an effective course of the cross-metathesis of olefins with H₂C=CHSi(OR)₃ or H₂C=CHSi(OSiMe₃)₃ [8a,8b]. Catalyst **I**, because of its low catalytic activity in *homo*-metathesis of styrenes, ensures high selectivities in CM of vinylsilanes with styrenes and permits the use of a small excess of styrenes, which sometimes facilitates the reaction. H₂C=CHSi(OAc)₃ or H₂C=CHSiCl₃ undergoes effective cross-metathesis in the presence of **II** or **III**. In the cross-metathesis of vinylsilanes with olefins catalysed by **I** or **II**, the formation of small amounts of *E*-1-silyl-2-phenylethene cannot be avoided. It is formed in the equimolar reaction of benzylidene complex with vinylsilanes as presented in Eqs. (4)–(6) and in Scheme 3.

The vinylsilanes containing one or two electron withdrawing groups at silicon with the remaining substituent having no electron donor properties, are substantially less active in CM with olefins. H₂C=CHSiF₂Ph in the presence of catalysts **I**, **II** or **III** and H₂C=CHSi(OEt)₂Ph or H₂C=CHSiClPh₂ in the presence of catalysts **II** or **III**, effectively react with styrene or 1-hexene. However, extended reaction time is required. H₂C=CHSi(OEt)Ph₂ and H₂C=CHSiFPh₂ undergo cross-metathesis with styrene in the presence of **II** or **III**, but afford the expected products with lower yields and selectivities. In this case competitive olefin *homo*-metathesis could not be retarded even when vinylsilane was used in excess.

Class **2** consists of the vinylsilanes active both in *homo*-metathesis [13] and cross-metathesis with olefins. Extensive search for reagents representing this type of reactivity revealed only one “substituent motif” characteristic of this class, that is H₂C=CHSiCl₂R (where R = alkyl, aryl, OSiMe₃). Cross-metathesis of H₂C=CHSiCl₂R with olefins catalysed by **II** or **III** gives the cross-metathesis products with high yields and selectivities. For these silanes, care must be taken to make a proper choice of the reaction conditions and the vinylsilane/olefin ratio because CM is accompanied by competitive *homo*-metathesis of vinylsilane and olefin [13]. However, in all reactions with dichlorosubstituted vinylsilanes, in the above specified reaction conditions,

Table 1
 Cross-metathesis of vinylsilanes with olefins

Entry	Vinylsilane SiR ₃ =	Olefin R ¹ =	Cat.	Reaction conditions	Conv. of B (%)	Yield (isolated) of C (%)	C E/Z	Yield of D (%)
1 ^a	Si(OEt) ₃	Ph	I	1:1/6/2/rt.	95	95	<i>E</i>	Trace
2	Si(OMe) ₃	Ph	I	1:1/6/2/reflux	95	94	<i>E</i>	Trace
3	Si(OSiMe ₃) ₃	Ph	I	1:1/6/2/reflux	97	95	<i>E</i>	Trace
4	SiCl ₃	Ph	I	15:1/1/0.5/reflux	0	0	–	0
5	SiF ₂ Ph	Ph	I	1:1/20/5/reflux	100	99 (80)	<i>E</i>	Trace
6	Si(OEt) ₂ Ph	Ph	I	1:1/20/5/reflux	40	40	<i>E</i>	Trace
7	Si(OEt) ₂ Me	Ph	I	1:1/6/2/rt.	10	7	<i>E</i>	2
8	Si(OEt)Ph ₂	Ph	I	1:1/3/5/reflux	0	0	–	0
9 ^b	Si(OEt)Me ₂	Ph	I	1:1/6/2/rt.	3	0	–	0
10 ^a	SiMe ₃	Ph	I	1:3/6/2/rt.	Trace	0	–	0
11	Si(OEt) ₃	Ph	II	1:1/1/2/reflux	100	80	<i>E</i>	20
12	Si(OEt) ₃	Ph	II	3:1/3/2/reflux	100	95	<i>E</i>	5
13 ^c	SiCl ₃	Ph	II	15:1/1/0.5/reflux	85	83 (70)	<i>E</i>	2
14 ^c	Si(OAc) ₃	Ph	II	15:1/1/0.5/reflux	80	75	<i>E</i>	5
15 ^c	SiCl ₂ Me	Ph	II	15:1/1/0.5/reflux	80	78 (65)	<i>E</i>	Trace
16	SiCl ₂ (OSiMe ₃)	Ph	II	1:1/1/5/reflux	100	95	<i>E</i>	Trace
17	SiCl ₂ Ph	Ph	II	1:1/1/5/reflux	100	98	<i>E</i>	Trace
18	SiCl ₂ (C ₆ H ₄ -Me-4)	Ph	II	1:1/2/5/reflux	100	95	<i>E</i>	Trace
19	SiCl ₂ (C ₆ H ₄ -CF ₃ -4)	Ph	II	4:1/1/5/reflux	100	95	<i>E</i>	0
20	SiF ₂ Ph	Ph	II	1:1/20/5/reflux	80	50	<i>E</i>	30
21	Si(OEt) ₂ Ph	Ph	II	1:1/20/5/reflux	90	88	<i>E</i>	Trace
22	Si(OEt) ₂ Me	Ph	II	1:1/3/2/reflux	10	6	<i>E</i>	2
23	Si(OEt)Ph ₂	Ph	II	1:1/3/5/reflux	100	50	<i>E</i>	50
24	Si(OEt)Me ₂	Ph	II	1:1/3/5/reflux	7	5	–	Trace
25	SiClPh ₂	Ph	II	1:1/1/5/reflux	100	99	<i>E</i>	0
26	SiFPh ₂	Ph	II	1:1/20/5/reflux	100	20	<i>E</i>	80
27	SiMe ₃	Ph	II	5:1/6/2/reflux	Trace	0	–	0
28	SiCl ₂ Me	C ₆ H ₄ -CH ₃ -4	II	1:1/1/5/reflux	100	95	<i>E</i>	Trace
29	SiCl ₂ Me	C ₆ H ₄ -Cl-4	II	1:1/1/5/reflux	100	90	<i>E</i>	10
30	SiCl ₂ Me	C ₆ H ₄ -CH ₂ Cl-4	II	1:1/1/5/reflux	100	98	<i>E</i>	Trace
31	Si(OEt) ₂ Ph	C ₆ H ₄ -Cl-4	II	3:1/20/5/reflux	95	90 (75)	<i>E</i>	Trace
32	SiClPh ₂	C ₆ H ₄ -Cl-4	II	1:1/1/5/reflux	100	97 (85)	<i>E</i>	Trace
33	SiCl ₂ Ph	C ₆ H ₄ -Cl-4	II	1:1/1/5/reflux	100	95 (78)	<i>E</i>	Trace
34	Si(OEt) ₃	Ph	III	1:1/2/5/reflux	100	85	<i>E</i>	15
35	SiCl ₃	Ph	III	1:1/1/5/reflux	100	85	<i>E</i>	15
36	SiCl ₂ Me	Ph	III	1:1/2/2/reflux	100	70	<i>E</i>	30
37 ^d	SiMe ₃	Ph	III	5:1/6/2/reflux	90	85	<i>E</i>	2
38 ^b	Si(OEt) ₃	C ₄ H ₉	I	5:1/3/5/reflux	100	75	9/1	12
39 ^b	Si(OSiMe ₃) ₃	C ₄ H ₉	I	5:1/3/5/reflux	90	72	10/1	7
40 ^c	SiCl ₃	C ₄ H ₉	I	5:1/3/5/reflux	0	0	–	0
41 ^c	SiCl ₂ Me	C ₄ H ₉	I	5:1/1/0.5/reflux	0	0	–	0
42	Si(OEt) ₃	C ₄ H ₉	II	5:1/3/5/reflux	100	99	20/1	Trace
43	Si(OSiMe ₃) ₃	C ₄ H ₉	II	5:1/3/5/reflux	100	95	20/1	Trace
44 ^c	SiCl ₃	C ₄ H ₉	II	5:1/3/5/reflux	100	100 (90)	20/1	0
45 ^c	Si(OAc) ₃	C ₄ H ₉	II	5:1/1/0.5/reflux	100	100 (70)	20/1	0
46 ^c	SiCl ₂ Me	C ₄ H ₉	II	5:1/1/0.5/reflux	100	100 (80)	20/1	0
47	SiCl ₂ (OSiMe ₃)	C ₄ H ₉	II	1:1/1/5/reflux	100	97	20/1	Trace
48	SiCl ₂ Ph	C ₄ H ₉	II	1:1/1/5/reflux	100	95	25/1	Trace
49	SiCl ₂ (C ₆ H ₄ -CF ₃ -4)	C ₄ H ₉	II	4:1/3/5/reflux	100	95	22/1	0
50	SiCl ₂ (C ₆ H ₄ -Me-4)	C ₄ H ₉	II	1:1/1/5/reflux	100	99	25/1	Trace
51	Si(OEt) ₂ Ph	C ₄ H ₉	II	1:1/1/5/reflux	90	75	25/1	12
52	SiClMe ₂	C ₄ H ₉	II	1:1/20/5/reflux	Trace	0	–	0
53	SiClPh ₂	C ₄ H ₉	II	1:1/2/5/reflux	100	90	25/1	5
54 ^c	SiPh ₃	C ₄ H ₉	II	5:1/3/2/reflux	Trace	0	–	0
55	Si(C ₆ H ₄ -Me-4) ₃	C ₄ H ₉	II	5:1/3/2/reflux	Trace	0	–	0
56 ^c	Si(C ₆ H ₄ -CF ₃ -4) ₃	C ₄ H ₉	II	5:1/3/2/reflux	100	97	>25/1	Trace
57	SiCl ₃	C ₄ H ₉	III	1:1/1/5/reflux	99	97	20/1	Trace
58	SiCl ₂ Me	C ₄ H ₉	III	1:1/6/5/reflux	90	88	<i>E</i>	Trace
59	Si(OEt) ₂ Ph	C ₄ H ₉	III	1:1/20/5/reflux	100	20	<i>E</i>	80
60 ^c	SiCl ₃	CH ₂ SiMe ₃	II	5:1/1/0.5/reflux	100	100 (92)	25/1	0
61 ^c	Si(OAc) ₃	CH ₂ SiMe ₃	II	5:1/1/0.5/reflux	100	100 (70)	25/1	0
62 ^c	SiCl ₂ Me	CH ₂ SiMe ₃	II	5:1/1/0.5/reflux	100	100 (80)	22/1	0
63	SiCl ₃	CH ₂ OC ₄ H ₉	II	1:1/1/5/reflux	100	92	8/1	8

Table 1 (continued)

Entry	Vinylsilane SiR ₃ =	Olefin R ¹ =	Cat.	Reaction conditions	Conv. of B (%)	Yield (isolated) of C (%)	C E/Z	Yield of D (%)
64	SiCl ₂ Me	CH ₂ OC ₄ H ₉	II	1:1/1/5/reflux	100	98 (75)	25/1	Trace
65	SiCl ₂ (OSiMe ₃)	CH ₂ OC ₄ H ₉	II	1:1/1/5/reflux	100	95	25/1	Trace
66	SiCl ₂ Ph	CH ₂ OC ₄ H ₉	II	1:1/1/5/eflux	100	90	E	Trace

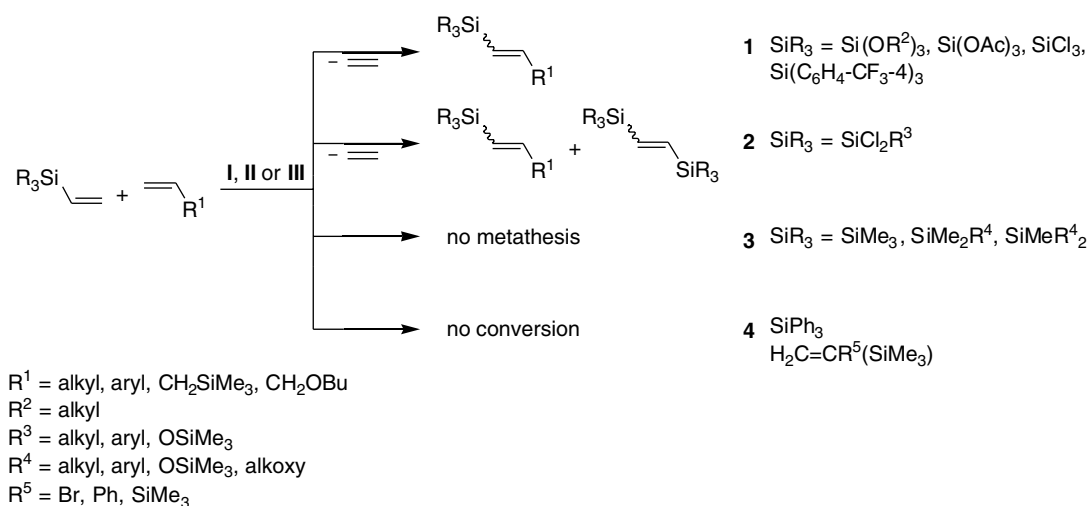
Reaction conditions: [A]:[B]/time (h)/catalyst concentration (mol%)/temp. (°C).

^a See [8a].

^b See [8b].

^c See [9].

^d Proved to be silylative coupling (see text).



Scheme 1. Reactivity of vinylsilanes in the presence of ruthenium alkylidene complexes.

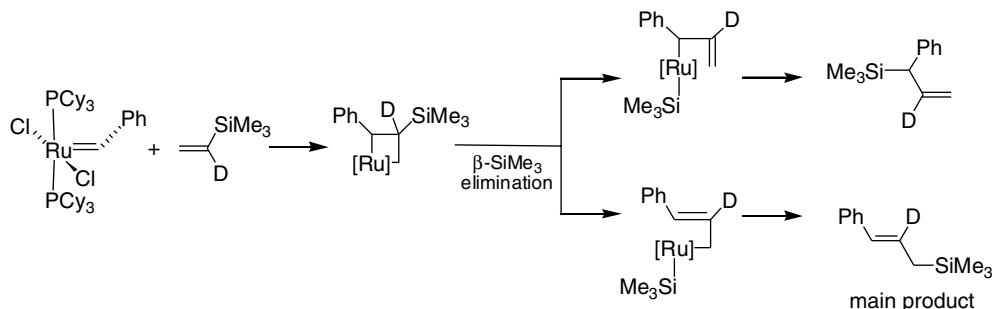
only trace amounts of 1,2-bis(silyl)ethenes have been detected.

Trimethylvinylsilane, all tested dimethylsubstituted and most monomethyl-substituted vinylsilanes belong to class 3. They do not undergo cross-metathesis with olefins in the presence of **I**, **II** or **III**. As we have reported previously, Grubbs catalyst **I** undergoes equimolar reaction with trimethylvinylsilane leading to the formation of substituted propenes and non-alkylidene ruthenium complexes. This process has been shown to proceed via formation of putative β -(trimethylsilyl) ruthenacyclobutane complex and its decomposition via β -elimination of the silyl group (Scheme 2) [14]. The same process was observed also in the presence of catalyst **II**.

The effective reaction of trimethylvinylsilane with styrene observed in the presence of Hoveyda–Grubbs catalyst **III**, leading to the effective formation of 1-(trimethylsilyl)-2-phenylethene was proved to proceed according to the non-metallacarbene mechanism.

The vinylsilanes containing substituents at C_α, e.g. H₂C=C(SiMe₃)₂ and H₂C=C(Ph)(SiMe₃), belonging to class 4 do not react with the catalyst. Presumably, a relevant ruthenacyclobutane intermediate cannot be formed because of the steric properties of 1,1-disubstituted olefins. Similarly, no activity was observed for H₂C=CHSiPh₃ under the conditions used.

Comparison of silylative coupling and cross-metathesis of vinylsilanes and olefins [5] revealed that both

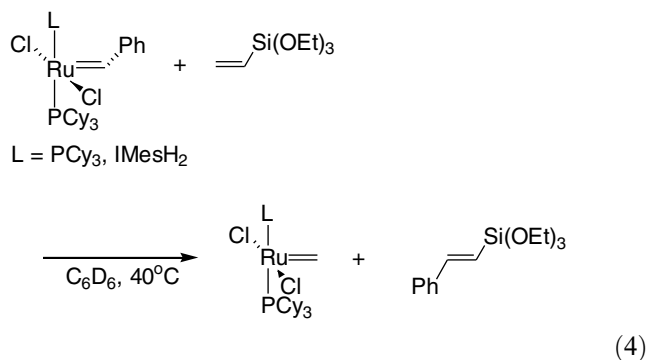


Scheme 2. Proposed mechanism of decomposition of catalyst **I** in the presence of trimethylvinylsilane [14].

methods are important synthetic tools in organosilicon chemistry and complement each other. Chlorosubstituted vinylsilanes, being most important monomers in organosilicon chemistry are effectively transformed by cross-metathesis (CM), while they are not active in silylative coupling (SC) reactions. Additionally, some vinylsilanes containing specific functional groups, e.g. $\text{H}_2\text{C}=\text{CHSiCl}_2(\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}-4)$, which is an interesting bifunctional monomer, can be converted only via metathesis. On the other hand, CM is not applicable to methylsubstituted vinylsilanes, which are easily transformed by SC.

2.2. The study of equimolar reactions

Both complexes **I** and **II** undergo equimolar metathesis with triethoxyvinylsilane. The reactions lead to selective formation of respective methylidene complex and *E*-1-phenyl-2-(triethoxysilyl)ethene (Eq. (4)). Analogously, the reaction of catalyst **III** with $\text{H}_2\text{C}=\text{CHSi}(\text{OEt})_3$ leads to the formation of *E*-1-[(2-isopropoxy)phenyl]-2-(triethoxysilyl)ethene.

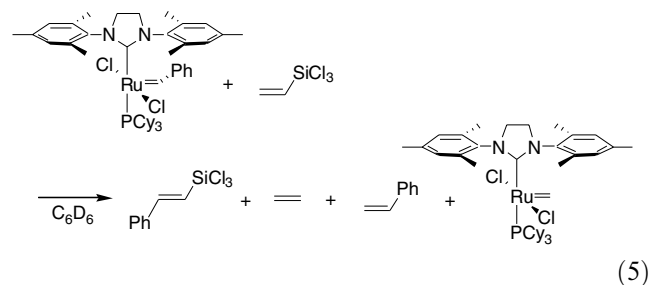


The course of the reactions was controlled by ¹H NMR spectroscopy (Fig. 1). Some differences between the reactions of **I**, **II** or **III** with $\text{H}_2\text{C}=\text{CHSi}(\text{OEt})_3$ were observed.

The reaction rate of triethoxyvinylsilane with complex **I** is slightly higher than with complex **II**. The yields of methylidene complexes (observed by ¹H NMR spectroscopy) are lower than expected on the basis of the

reaction stoichiometry. Obviously, the methylidene complexes are not stable under the conditions used. As illustrated in Fig. 1, the yield of the methylidene complex derived from **I** is much lower than that derived from **II**, suggesting a higher stability of the latter under the conditions used. In the applied reaction conditions, only ca. 15% conversion of complex **III** and no formation of methylidene complexes were observed by ¹H NMR spectroscopy after 2 h.

The reaction of **II** with trichlorovinylsilane $\text{H}_2\text{C}=\text{CHSiCl}_3$ leads to the formation of styrene, silylstyrene, ethylene and unidentified ruthenium complexes (Eq. (5)).



Identification of styrene among the reaction products suggests the formation of (silyl)methylidene complex. However, all attempts to identify it by ¹H NMR spectroscopy have failed.

Chlorosubstituted vinylsilanes react readily with complex **I** to form unidentified non-alkylidene complexes [9]. The decomposition is retarded when at least one equivalent of free PCy₃ is added to the system. Under the conditions used, the reaction of moisture traces with chlorosilane has been found to lead to rapid hydrolysis of the Si–Cl bond and to formation of HCl. The reaction is catalysed by free phosphine (which decoordinates from complex **I**). This catalytic side-reaction can significantly decrease the product yield and selectivity. Moreover, the loss of phosphine due to the reaction with HCl increases the activity of the catalyst but also accelerates its thermal decomposition. Such effects caused by “phosphine

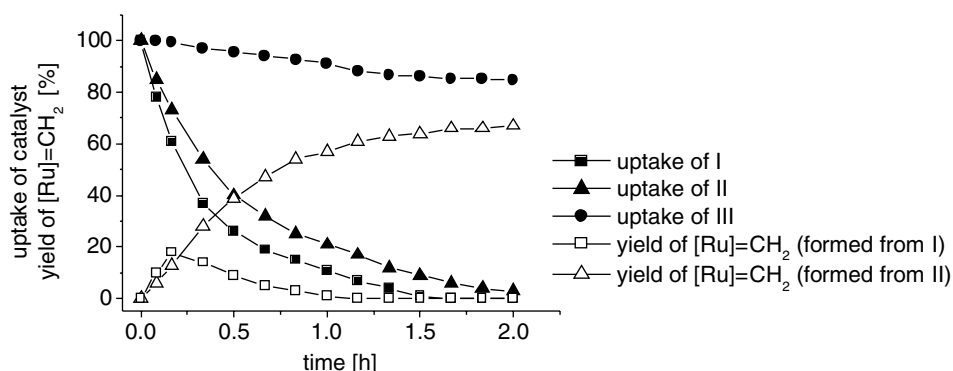
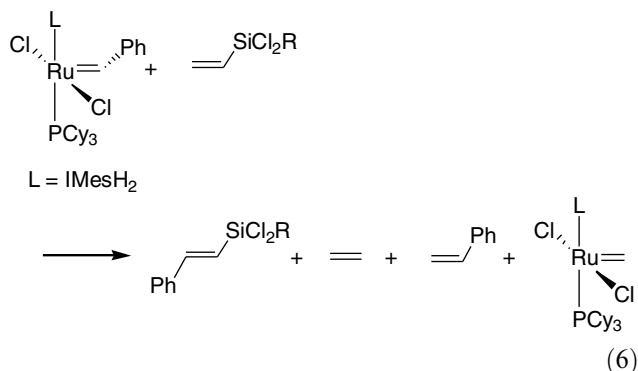


Fig. 1. Equimolar reactions of **I**, **II** or **III** with triethoxyvinylsilane (C_6D_6 , 40°C).

scavengers" (e.g. CuCl) have been documented in literature [15]. Catalysts **II** and **III** are more stable than **I** under these conditions.

Dichlorosubstituted vinylsilanes $\text{H}_2\text{C}=\text{CHSiCl}_2\text{R}$ (where $\text{R} = \text{Me}, \text{OSiMe}_3, \text{Ph}$), undergo equimolar reactions with **II**, with formation of styrene, silylstyrene, ethylene and methyldene complexes (Eq. (6)).



In the experiments performed in a standard NMR tube, no or only traces of *E*-1,2-bis(silyl)ethene were observed. Except for complex **II**, only $[\text{Cl}_2(\text{PCy}_3)(\text{IMesH}_2)\text{-Ru}(\text{=CH}_2)]$ and no other complexes of the type $[\text{Ru}]\text{=CHR}$ were detected by ^1H NMR spectroscopy. On the other hand, effective *homo*-metathesis of dichlorosubstituted vinylsilanes observed in the presence of **II** or **III** [13] indicates the formation of (silyl)methyldene complex $[\text{Ru}]\text{=CH}(\text{SiR}_3)$ as an intermediate in similar systems.

Efforts were made to confirm the formation of silylcarbene complex. To this end, the equimolar reaction of $[\text{Cl}_2(\text{PCy}_3)(\text{IMesH}_2)\text{Ru}(\text{=CH}_2)]$ with $\text{H}_2\text{C}=\text{CHSiCl}_2\text{Me}$ was investigated at different temperatures (40, room temperature, 0, -30 , -50 °C) using ^1H NMR spectroscopy. No alkylidene complex except of the starting $[\text{Ru}]\text{=CH}_2$ was detected. Also all attempts to trap the putative (silyl)methyldene complex at

-50 °C failed. Obviously, such complexes are thermally or, more likely, kinetically unstable under the conditions used.

In order to learn more on the electronic effect of the substituents at silicon on the reaction rate, a series of dichlorovinylsilanes containing 4-substituted phenyl groups $\text{H}_2\text{C}=\text{CH}[\text{SiCl}_2(\text{C}_6\text{H}_4\text{-X-4})]$ (where $\text{X} = \text{H}, \text{Me}, \text{OMe}, \text{CF}_3$) were tested in equimolar reactions with **II**. The results are presented in the form of the Hammett plot (Fig. 2).

The linearity was obtained by using σ_I parameters [16]. Slightly higher rates for vinyl dichlorosilanes carrying more electron withdrawing groups (Fig. 2, $\text{X} = \text{CF}_3, \text{OMe}$) were observed. This preliminary result does not allow us to draw reliable conclusions. According to the mechanistic scheme of metathesis catalysed by Grubbs catalysts (Eq. (7)) both k_1 and k_{-1}/k_2 contribute to the overall metathesis activity [17]. Obviously, in the system studied, the vinylsilanes containing electron withdrawing substituents compete more efficiently with phosphine for coordination to the 14-electron intermediate and in consequence, more frequently enter the catalytic cycle.

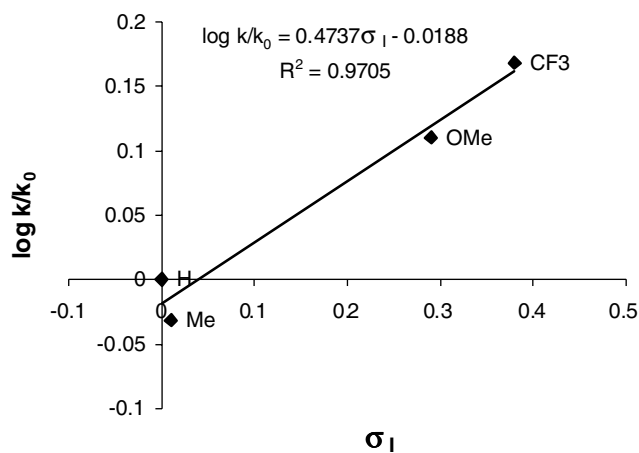
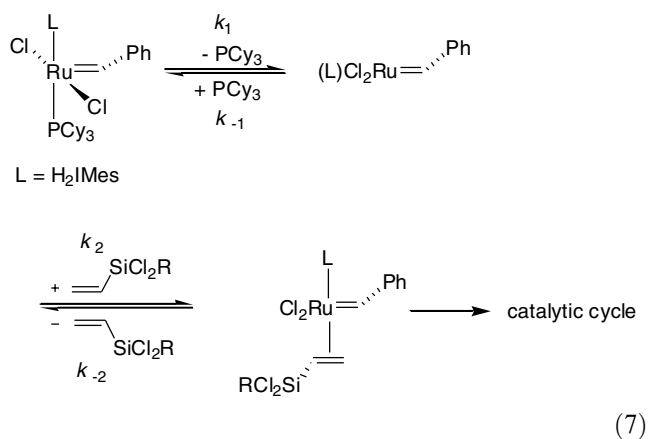
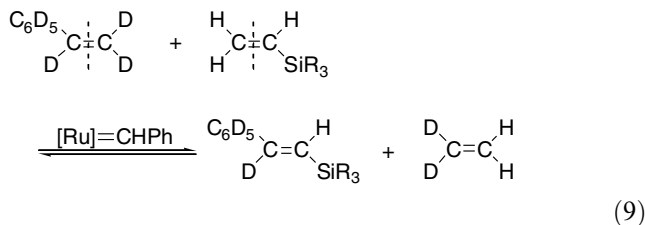
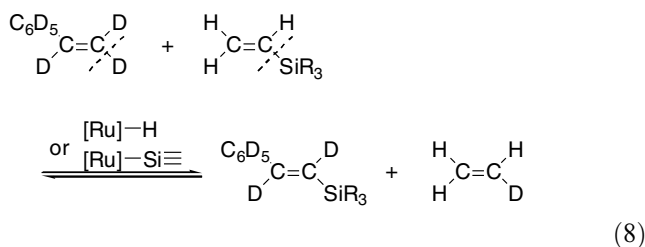


Fig. 2. Effect of the substituent at silicon on the reactions rate in stoichiometric reaction of **II** with $\text{H}_2\text{C}=\text{CHSiCl}_2(\text{C}_6\text{H}_4\text{-X-4})$ (where $\text{X} = \text{H}, \text{Me}, \text{OMe}, \text{CF}_3$) (Hammett plot).

2.3. Labelling studies

To distinguish between the non-metallacarbene mechanism (such as that observed when $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ or $[\text{RuCl}(\text{SiR}_3)(\text{CO})(\text{PPh}_3)_2]$ was used as a catalyst), and the metallacarbene mechanism, the reactions of a number of vinylsilanes with styrene- d_8 in the presence of **I**, **II** or **III** were investigated. In the case of the non-metallacarbene mechanism, the formation of silylstyrene- d_7 and ethylene- d is to be expected (Eq. (8)). In contrast, the carbene mechanism should afford silylstyrene- d_6 and ethylene- d_2 (Eq. (9))



Analysis of the products formed in the reactions of styrene- d_8 with: $\text{H}_2\text{C}=\text{CHSi}(\text{OEt})_3$ in the presence of **I** [8a], $\text{H}_2\text{C}=\text{CHSiCl}_2\text{Me}$ in the presence of **II**, and with $\text{H}_2\text{C}=\text{CHSiCl}_3$ in the presence of **II** and **III** revealed exclusive formation of *E*-1-phenyl-2-(silyl)ethene- d_6 , which strongly supports the metallacarbene mechanism of the reaction [8a]. On the other hand, the reaction of $\text{H}_2\text{C}=\text{CHSiMe}_3$ with styrene- d_8 in the presence of **III** leads to a mixture of *E*-1-phenyl-2-(silyl)ethene- d_6 and *E*-1-phenyl-2-(silyl)ethene- d_7 ,

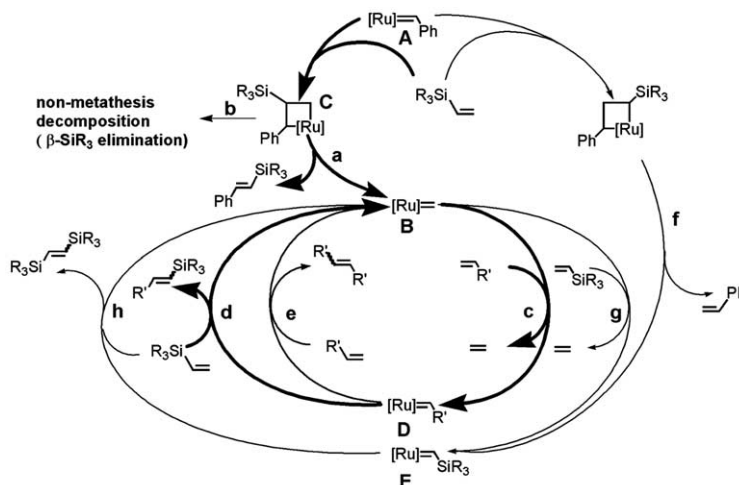
which suggests non-metallacarbene mechanism and indicates H/D exchange.

2.4. Mechanistic implications

On the basis of equimolar and catalytic reactions of vinylsilanes in the presence of ruthenium alkylidene complexes, a general scheme of reactivity was proposed (Scheme 3).

According to the scheme proposed (Scheme 3), the reaction of vinylsilanes with benzylidene complex **A** generates methylidene complex **B** and *E*-1-phenyl-2-(silyl)ethene (pathway **a**). This metathesis exchange proceeds via putative β -(silyl)ruthenacyclobutane complex **C**. In the case of methylsubstituted vinylsilanes $\text{H}_2\text{C}=\text{CHSiR}_3$ ($\text{SiR}_3 = \text{SiMe}_3, \text{SiMe}_2\text{R}, \text{SiMeR}_2$; $\text{R}^1 = \text{alkyl, aryl}$) the metathesis decomposition of β -(silyl)ruthenacyclobutane is accompanied by competitive β -(silyl)elimination, which leads to the loss of alkylidene moiety and to the formation of species inactive in metathesis (Scheme 2 and pathway **b** in Scheme 3) [14]. In the presence of olefin, methylidene complex **B** undergoes metathesis exchange leading to the formation of alkylidene complex **D** and ethene (pathway **c**). Vinylsilane competes with olefin for coordination to alkylidene complex **D**. The reaction of alkylidene complex **D** with vinylsilane $\text{H}_2\text{C}=\text{CHSiR}_3$ ($\text{SiR}_3 = \text{Si}(\text{OR}^1)_3, \text{SiCl}_3, \text{SiCl}_2\text{R}^1$) affords organosilicon product and methylidene complex **B** (pathway **d**). Stoichiometric metathesis of olefin with alkylidene complex **D** affords the olefin homo-metathesis product and regenerates methylidene complex **B** (pathway **e**). By using an excess of vinylsilanes, the olefin homo-metathesis can be avoided in most cases.

Additional pathways are available for dichlorosubstituted vinylsilanes $\text{H}_2\text{C}=\text{CHSiR}_3$ ($\text{SiR}_3 = \text{SiCl}_2\text{R}^1$). They can react with benzylidene complex **A** or methylidene complex **B** with the formation of putative (silyl)methylidene complex **E** (pathways **f** and **g**, respectively).



Scheme 3. General scheme of reactivity in the system containing Grubbs catalyst, vinylsilane and metathetically active olefin.

Homo-metathesis product [1,2-bis(silyl)ethene] and methyldiene complex **B** are formed in the reaction of complex **E** with dichlorovinylsilane (pathway **h**).

3. Experimental

3.1. General

All manipulations were carried out under dry argon using standard Schlenk techniques. ^1H - and ^{13}C NMR spectra were recorded on a Bruker AC250 spectrometer at 250 and 62.9 MHz, respectively, or on a Varian Gemini at 300 and 75 MHz. GC–MS analyses were made on Varian Saturn 2100T (DB-1, 30 m capillary column) or a HP 6890 gas chromatograph (HP-5MS 30 m capillary column) equipped with a HP 5973 mass selective detector. The chemicals (complexes **II** and **III**, decane, dodecane, CH_2Cl_2 , C_6D_6 , $\text{H}_2\text{C}=\text{CHSiCl}_2\text{Me}$) were obtained from Aldrich. The other substituted vinylsilanes were prepared by the literature methods, $\text{H}_2\text{C}=\text{CHSiCl}_2(\text{OSiMe}_3)$ [18], $\text{H}_2\text{C}=\text{CHSiCl}_2\text{Ph}$ [19], $\text{H}_2\text{C}=\text{CHSiCl}_2(\text{C}_6\text{H}_4\text{-X-4})$ (where X = Me, CF_3) were synthesised using the same methodology as in the case of $\text{H}_2\text{C}=\text{CHSiCl}_2\text{Ph}$. Catalyst **I** was prepared according to the literature procedure [20].

3.2. Catalytic tests

An oven dried 4 mL Schlenk flask with side neck closed with a septum, equipped with a condenser and a magnetic stirring bar was charged under argon with 3 mL of CH_2Cl_2 , vinylsilane (1.18×10^{-4} mol) and 10 μL of decane or dodecane (internal standard). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 43 °C). Then 0.005 g (5.89×10^{-6} mol) of ruthenium benzylidene complex **II** was added under argon. A gentle flow of argon was applied. The reaction was followed by GC. Before the chromatographic analysis, the sample of the reaction mixture was treated with an excess of absolute ethanol in the presence of pyridine in order to transform chlorosilanes into ethoxy derivatives.

3.3. Equimolar reactions of **I**, **II** or **III** with triethoxyvinylsilane

An NMR tube was charged with the catalyst (1.22×10^{-5} mol), anthracene (0.001 g, internal standard) and C_6D_6 (0.6 mL) under argon and ^1H NMR analysis was performed at 40 °C. Then triethoxyvinylsilane (1.22×10^{-5} mol) was added to the tube under argon, the tube was inserted into the spectrometer and the course of the reaction was followed at 40 °C by ^1H NMR spectroscopy.

3.4. Preliminary kinetic examinations

An NMR tube was charged with $\text{H}_2\text{C}=\text{CHSiCl}_2(\text{C}_6\text{H}_4\text{-X-4})$ (1.18×10^{-5} mol), anthracene (0.001 g, internal standard) and C_6D_6 (0.6 mL) under argon and ^1H NMR analysis was performed at 23 °C. Then the catalyst (1.18×10^{-5} mol) was added to the tube under argon. The tube was inserted into the spectrometer and the course of the reaction was followed at 23 °C by ^1H NMR spectroscopy.

3.5. Representative procedure for the reaction of vinylsilane with $\text{D}_2\text{C}=\text{C}(\text{D})\text{C}_6\text{D}_5$

In a closed system [$\text{Cl}_2(\text{PCy}_3)(\text{IMesH}_2)\text{Ru}(\text{=CHPh})$] (**II**) (0.001 g, 1.18×10^{-6} mol), C_6D_6 (0.35 mL), $\text{H}_2\text{C}=\text{CHSiCl}_2\text{Me}$ (3.0 μL , 2.3×10^{-5} mol), and styrene- d_8 (2.7 μL , 2.3×10^{-5} mol) were added under argon to an NMR tube. The sample was heated at 40 °C for 2 h and the reaction mixture was followed by NMR spectroscopy.

3.6. Procedure for the synthesis of silylolefins

An oven dried 20 mL Schlenk flask equipped with a condenser, a bubbler and a magnetic stirring bar was charged under argon with 10 mL of CH_2Cl_2 , vinylsilane (4.0×10^{-2} mol) and olefin. The reaction mixture was stirred and heated in an oil bath (50 °C) to maintain a gentle reflux. Then 2.0×10^{-3} mol of ruthenium benzylidene complex **I**, **II** or **III** was added under argon. Intensive bubbling was observed. A gentle flow of argon was applied from the top of the column. The course of the reaction was followed by gas chromatography. After a given reaction time dichloromethane was distilled off and the product was obtained by vacuum distillation with the use of a microdistillation set.

3.6.1. Analysis of selected products

(a) $\text{MeCl}_2\text{SiCH}=\text{CHCH}_2\text{OC}_4\text{H}_9$, collected fraction 119–123 °C/1 mmHg, isolated yield 75%; ^1H NMR (C_6D_6 , δ , ppm): 0.49 (s, 3H, SiMe), 0.79–0.90 (m, 3H, CH_3), 1.27–1.53 (m, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 3.15–3.23 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.63–3.68 (m, 2H, $\text{OCH}_2\text{CH}=\text{}$), 6.06 (dt, 1H, $J = 18.5$ Hz, 1.9 Hz, $=\text{CHSi}$), 6.33 (dt, 1H, $J = 18.5$ Hz, 3.6 Hz, $=\text{CHCH}_2\text{O}$); ^{13}C NMR (C_6D_6): 5.4 (SiMe), 14.3 (CH_3), 19.9 (CH_3CH_2), 32.4 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 70.9 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 71.7 ($\text{OCH}_2\text{CH}=\text{}$), 122.8 ($=\text{CHSi}$), 150.4 ($=\text{CHCH}_2\text{O}$); MS: m/z (rel. intensity) of ethoxy derivative: 61 (15), 77 (32), 89 (17), 95 (11), 101 (18), 103 (17), 105 (40), 117 (10), 119 (22), 129 (11), 131 (14), 133 (100), 134 (13), 143 (11), 145 (62), 146 (10), 147 (12), 173 (11), 189 (30), 191 (11), 205 (13), 131 (11), 233 (11), 237 (15).

(b) $\text{PhCl}_2\text{SiCH}=\text{CH}(\text{C}_6\text{H}_4\text{-Cl-4})$, isolated by crystallisation from CH_2Cl_2 , isolated yield 78%; ^1H NMR (C_6D_6 , δ , ppm): 6.30 (d, 1H, $J=18.6$ Hz, $=\text{CHSi}$), 7.17 (d, 1H, $J=18.6$ Hz, $=\text{CH}$), 6.86 (d, 2H, $J=9.0$ Hz, $\text{C}_6\text{H}_4\text{Cl}$), 7.10 (d, 2H, $J=9.0$ Hz, $\text{C}_6\text{H}_4\text{Cl}$), 7.08–7.14, 7.22–7.35, 7.79–7.85 (m, 5H, Ph); ^{13}C NMR (C_6D_6): 120.8 ($=\text{CHSi}$), 149.5 ($=\text{CH}$), 134.8, 129.0, 128.9, 135.8 ($\text{C}_6\text{H}_4\text{Cl}$), 132.2, 134.1, 128.7, 132.0 (Ph); MS: m/z (rel. intensity) of ethoxy derivative: 45 (26), 104 (19), 105 (16), 165 (10), 179 (10), 180 (22), 196 (18), 214 (20), 215 (100), 216 (20), 254 (13), 288 (11), 317 (10), 332 (M^+ , 11).

(c) $\text{Ph}_2\text{ClSiCH}=\text{CH}(\text{C}_6\text{H}_4\text{-Cl-4})$, isolated by crystallisation from CH_2Cl_2 , isolated yield 85%; ^1H NMR (C_6D_6 , δ , ppm): 6.65 (d, 1H, $J=19.3$ Hz, $=\text{CHSi}$), 6.77–6.80 (m, 2H, $\text{C}_6\text{H}_4\text{Cl}$), 6.97–7.03 (m, 2H, $\text{C}_6\text{H}_4\text{Cl}$), 7.01 (d, 1H, $J=19.3$ Hz, $=\text{CH}$), 7.15–7.23 (m, 6H, Ph), 7.79–7.84 (m, 4H, Ph); ^{13}C NMR (C_6D_6): 125.3 ($=\text{CHSi}$), 128.3, 128.4, 128.9, 130.4, 134.5, 135.3, 136.1, 136.4 ($\text{C}_6\text{H}_4\text{Cl}$, Ph) 147.5 ($=\text{CH}$); MS: m/z (rel. intensity) of ethoxy derivative: 45 (73), 50 (33), 51 (47), 53 (14), 63 (13), 73 (11), 74 (10), 75 (24), 76 (11), 77 (15), 78 (50), 79 (16), 101 (10), 102 (24), 103 (26), 104 (38), 105 (100), 106 (62), 107 (10), 123 (22), 149 (17), 150 (20), 151 (12), 152 (12), 157 (15), 165 (15), 178 (12), 179 (48), 180 (41), 181 (31), 182 (25), 183 (16), 184 (30), 185 (15), 200 (13), 208 (12), 209 (16), 215 (14), 228 (28), 242 (20), 243 (28), 244 (21), 245 (11), 253 (38), 254 (13), 286 (10), 287 (43), 288 (26), 289 (19), 319 (18), 320 (20), 321 (38), 322 (13), 323 (11), 365 (M^+ , 71), 366 (23), 367 (16).

(d) $\text{Ph}(\text{OEt})_2\text{SiCH}=\text{CH}(\text{C}_6\text{H}_4\text{-Cl-4})$ collected fraction 204–207 °C/1 mmHg, isolated yield 75%; ^1H NMR (C_6D_6 , δ , ppm): 1.18 (t, 6H, $J=6.8$ Hz, OCH_2CH_3), 3.81 (q, 4H, $J=6.8$ Hz, OCH_2CH_3), 6.33 (d, 1H, $J=19.2$ Hz, $=\text{CHSi}$), 7.12 (d, 1H, $J=19.2$ Hz, $=\text{CH}$), 6.88–7.05 (m, 4H, $\text{C}_6\text{H}_4\text{Cl}$), 7.26–7.34 (m, 3H, Ph), 7.86–7.92 (m, 2H, Ph); ^{13}C NMR (C_6D_6): 18.9 (OCH_2CH_3), 59.1 (OCH_2CH_3), 122.6 ($=\text{CHPh}$), 147.6 ($=\text{CH}$), 128.3, 128.4, 128.9, 130.6, 134.0, 134.6, 135.2, 136.6 ($\text{C}_6\text{H}_4\text{Cl}$, Ph); MS: m/z (rel. intensity): 45 (17), 104 (12), 105 (13), 165 (10), 178 (11), 179 (19), 195 (17), 214 (100), 215 (45), 216 (44), 217 (16), 254 (18), 255 (15), 288 (10), 317 (16), 332 (M^+ , 16).

(e) $\text{PhF}_2\text{SiCH}=\text{CHPh}$, isolated by column chromatography, isolated yield 80%; ^1H NMR (C_6D_6 , δ , ppm): 6.29 (dt, 1H, $J=19.5$ Hz, $J=3.0$ Hz, $=\text{CHSi}$), 7.37 (d, 1H, $J=19.5$ Hz, $=\text{CHPh}$), 7.10–7.31, 7.41–7.43, 7.72–7.78, 7.92–7.98 (m, 10H, Ph); ^{13}C NMR (C_6D_6): 115.2 ($=\text{CHSi}$), 152.8 ($=\text{CHPh}$), 128.9, 134.5, 128.6, 132.2 (SiPh), 136.8, 127.5, 128.6, 129.9 (Ph); ^{19}F NMR (C_6D_6): –140.3; MS: m/z (rel. intensity): 102 (9), 103 (7), 165 (9), 178 (6), 179 (10), 180 (24), 181 (22), 227 (20), 228 (15), 245 (8), 246 (M^+ , 100), 247 (21).

4. Conclusions

A variety of vinylsilanes have been tested in equimolar and catalytic reactions in the presence of Grubbs catalysts. Pronounced influence of the properties of substituents at silicon on the reactivity of vinylsilanes in metathesis was demonstrated. Chemo- and stereoselective course of cross-metathesis of vinylsilanes with styrenes, 1-alkenes and numerous allyl derivatives was indicated. In optimised conditions the products required were synthesised with high yields and selectivities. The carbene mechanism of the reaction was confirmed. The reaction was proved to be a valuable method for synthesis of unsaturated organosilicon derivatives.

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