

# Stereoselective synthesis of esters with vinylsilicon functionality via ruthenium carbene catalyzed cross-metathesis

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Received 22 December 2001; accepted 29 January 2002

## Abstract

A new catalytic route for the synthesis of unsaturated organosilicon compounds with vinylic functionality based on cross-metathesis of vinyltrialkoxy- and vinyltris(trimethylsiloxy)-silanes with allyl esters of carboxylic acids catalyzed by ruthenium carbenes (Grubbs catalysts):  $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(\text{=CHPh})]$  (**I**),  $[\text{Cl}_2(\text{PCy})_3(1,3\text{-dimesityl-4,5-dihydroimidazol-2-ylidene})\text{Ru}(\text{=CHPh})]$  (**II**) is reported. The efficient reaction can be extended to alkyl esters of unsaturated acids, e.g., of methyl 3-butenolate.

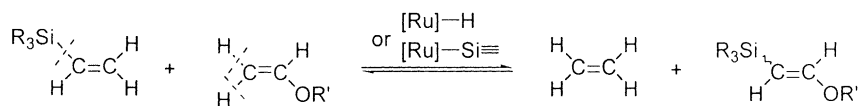
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**Keywords:** Cross-metathesis; Grubbs catalysts; Vinylsilanes; Allyl esters

## 1. Introduction

Silyl olefins, particularly vinyl- and allylsilanes have become one of the most common silyl reagents used in regio- and stereoselective organic synthesis [1]. Substituted vinylsilanes have been prepared using traditional methods such as silylation of vinylalkenes with halogenotrimethylsilane in the presence of organomagnesium [2] and organolithium [3] compounds as well as hydrosilylation of alkyne derivatives with Pt catalyst [4] and hydrogenation of silyl alkyne using palladium catalyst [5].

In the last decade, the method of silylative coupling (*trans*-silylation) of vinyltrisubstituted silanes with olefins catalyzed by ruthenium, rhodium, cobalt and iridium complexes was efficiently developed to lead to the novel and well-known silicon-containing olefins (for recent reviews see [6–9]). Recently, the silylative coupling of vinyl alkyl ethers with vinylsilanes catalyzed by ruthenium complexes involving or generating  $[\text{Ru}]\text{-H}$  and  $[\text{Ru}]\text{-Si}$  bond led to a very effective method for the synthesis of 1-silyl-2-(alkoxy)ethenes [10,11]. This reaction occurs according to the following equation:



where:  $\text{SiR}_3 = \text{SiMe}_3, \text{SiMe}_2\text{Ph}$ ,  $\text{R}' = \text{alkyl, aryl}$

(1)

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where  $\text{SiR}_3 = \text{SiMe}_3, \text{SiMe}_2\text{Ph}; \text{R}' = \text{alkyl, aryl}$ .

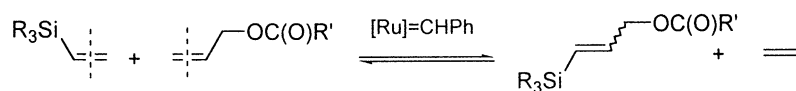
On the other hand, generation of olefins with vinylic functionality through the use of the cross-metathesis

reaction has met with limited success (for recent reviews see [12–16]). Very recent reports on the activity of well-defined functional group tolerant molybdenum complexes in the ring opening/cross-metathesis (AROM/CM) of norbornene [17] and ruthenium carbenes in RCM of acyclic silyl ether dienes [18], cross-metathesis of vinyl substituted silsesquioxanes with alkenes [19] and above all highly efficient cross-metathesis of vinyltrialkoxo- and vinyltris(trimethylsiloxy)-silanes with styrene [20], *p*-substituted styrenes, 1-alkenes and allyl derivatives [21], particularly allyl alkyl ethers [22], as well as 5-hexene-1-yl acetate [16] and degradation of 1,4-polybutadiene [23] have opened a new opportunity for common use of the olefin cross-metathesis in the synthesis of unsaturated organosilicon compounds.

Stoichiometric reactions of the Grubbs carbene complex with vinylmethyl-substituted silanes provided the first evidence for  $\beta$ -silyl migration in a metallacyclobutane followed by reductive elimination of an allylsilane. This whole process constitutes a terminating step in the Ru carbene catalyzed cross-metathesis of olefins with methyl-substituted vinylsilanes [24]. Therefore, in this paper we report new examples of effective cross-metathesis of vinyltrialkoxo- and vinyltrisiloxysilane with a variety of allyl esters catalyzed by Grubbs complexes (I) and (II).

## 2. Results and discussion

The reactions of vinyltrisubstituted silanes with allyl esters of carboxylic acids proceeded in the presence of ruthenium benzylidene according to the following equation:



R = OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, OSi(CH<sub>3</sub>)<sub>3</sub>  
R' = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, CH<sub>2</sub>CH<sub>2</sub>Cy, C(CH<sub>3</sub>)=CH<sub>2</sub>, Ph

The catalytic data on the reaction of vinyltriethoxysilane and vinyltris(trimethylsiloxy)silane with various allyl esters of saturated acids and methacrylic acid (2-methylpropenoate) are presented in Table 1. Exemplary products were isolated and characterized spectroscopically.

The yields were predominantly close to the conversion of the allyl ester used. Minor amounts of products of self-metathesis of allyl esters were observed as by-products. Most reactions proceeded highly stereoselectively with a strong preference for the formation of the *E*-isomer. Ten-fold excess of vinylsilane was used to exclude even traces of by-products (products of self-metathesis of allyl esters), although the final yield was slightly decreased. On the other hand, catalysis by more active “*super*”-Grubbs (II) catalyst gives rise to similar total yields of the main products yet obtained in a shorter time (1 h vs 3 h). Moreover, it is observed that a long-time heating of the reaction mixture allows exclusive isolation of the *E*-isomer due to *Z* → *E* isomerization of the products catalyzed by ruthenium complexes containing [Ru]–H bond formed by decomposition of ruthenium carbenes [25]. Allyl 3-(cyclohexyl)propionate was selected for the catalytic reaction with two other vinylsubstituted silanes, vinyltrimethoxysilane and vinyltris(trimethylsiloxy)-silane, to show similar yields and selectivities.

In contrast to the generally unsuccessful cross-metathesis of vinyl alkyl ethers and acrylonitrile [26] in the presence of ruthenium benzylidene, the latter appeared effective in the reaction of vinyltriethoxysilane with hexen-2-yl-acetate (the yield 81%, *E/Z* = 11/1) [16], but with the functional acetate group being far from the vinylic silicon. Therefore, high efficiency of (I) in the reaction of vinylsilanes with allyl esters offers an interesting route to a whole family of esters of the R'COOCH<sub>2</sub>CH=CHSiR<sub>3</sub> formula, where R' = alkyl, alkenyl, aryl; R = alkoxy, siloxy, which can provide useful pathway of synthesis for further reactions such as palladium



catalyzed cross-coupling with alkenyl and aryl halides [27,28].

The respective silylative coupling of allyl esters with vinyl-substituted silanes does not proceed at the usually used conditions (80–110 °C, 24 h, benzene, [RuH(Cl)(CO)(PPh<sub>3</sub>)<sub>3</sub>]), but according to the general

Table 1  
Cross-metathesis of allyl esters with selected vinylsilanes<sup>a</sup>

CH <sub>2</sub> =CHSiR <sub>3</sub>	R'COOCH <sub>2</sub> CH=CH <sub>2</sub>	Conversion of allyl ester (%)	Yield of ( <i>E</i> + <i>Z</i> ) (isolated yield of <i>E</i> ), R'COOCH <sub>2</sub> CH=CHSi(OEt) <sub>3</sub> (%)	<i>E/Z</i>	Yield of by-products (%)
R = OC <sub>2</sub> H <sub>5</sub>	R' = CH <sub>3</sub>	100	90 (87)	12/1	10
R = OC <sub>2</sub> H <sub>5</sub>	R' = C <sub>2</sub> H <sub>5</sub>	99	94	14/1	5
R = OC <sub>2</sub> H <sub>5</sub>	R' = <i>n</i> -C <sub>3</sub> H <sub>7</sub>	95	93 (89)	13/1	2
		75 <sup>b</sup>	75	8/1	0
		90 <sup>c</sup>	90	11/1	0
		91 <sup>d</sup>	90	4/1	1
R = OC <sub>2</sub> H <sub>5</sub>	R' = C <sub>6</sub> H <sub>5</sub>	85	80	2/1	5
R = OC <sub>2</sub> H <sub>5</sub>	R' = CyCH <sub>2</sub> CH <sub>2</sub>	95	90	<i>E</i>	5
R = OCH <sub>3</sub>		92	88	<i>E</i>	4
R = OSi(CH <sub>3</sub> ) <sub>3</sub>		96	90	8/1	6
R = OC <sub>2</sub> H <sub>5</sub>	R' = H <sub>2</sub> C=C(CH <sub>3</sub> )	92	90	3/1	2

<sup>a</sup> Reaction conditions: [Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru(=CHPh)]:[silane]:[ester] = 5 × 10<sup>-2</sup>:5:1, CH<sub>2</sub>Cl<sub>2</sub>, reflux, 3 h, argon.

<sup>b</sup> [Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru(=CHPh)]:[silane]:[ester] = 5 × 10<sup>-2</sup>:10:1, 3 h, argon.

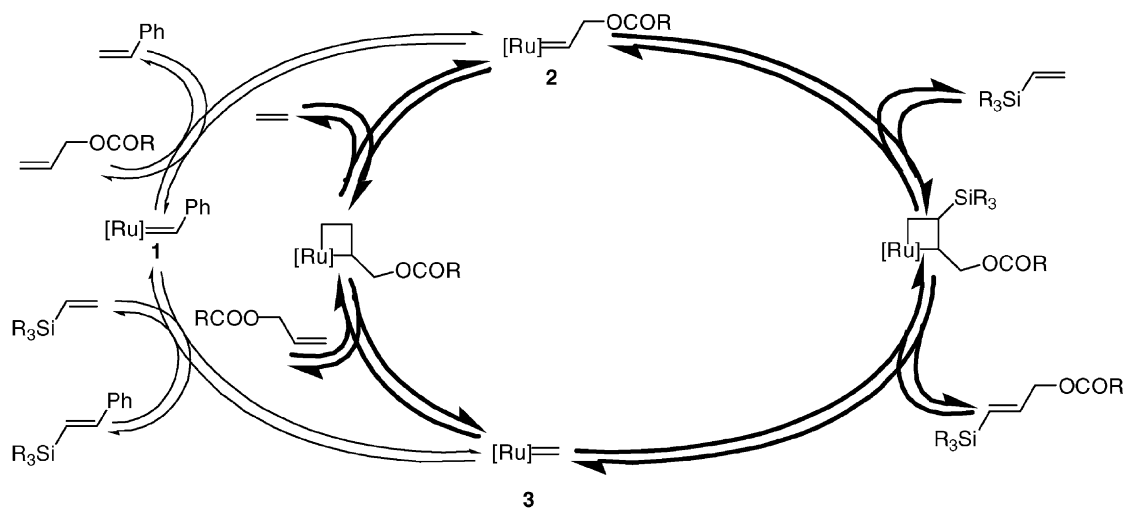
<sup>c</sup> [Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru(=CHPh)]:[silane]:[ester] = 5 × 10<sup>-2</sup>:10:1, 4 h, argon.

<sup>d</sup> [Cl<sub>2</sub>(PCy<sub>3</sub>)(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)Ru(=CHPh)]:[silane]:[ester] = 5 × 10<sup>-2</sup>:5:1, 1 h, argon.

mechanism, an olefin isomerization (C=C bond migration) is observed instead. The isomerization is a well-known process to be catalyzed by complexes containing Ru–H bonds. However, under the conditions used, in the cross-metathesis, i.e., when the ruthenium carbene is initially used, neither allyl ester nor the cross-metathesis product isomerization was observed, which confirms that ruthenium hydride complexes have not been generated.

The results of the catalytic studies and those of the study of cross-metathesis of vinylsilanes, with olefins [20,21], in particular with allyl alkyl ethers [22] reported previously, have led us to propose a reasonable mechanism for the reaction with allyl esters of carboxylic acids in the presence of ruthenium carbenes (Scheme 1).

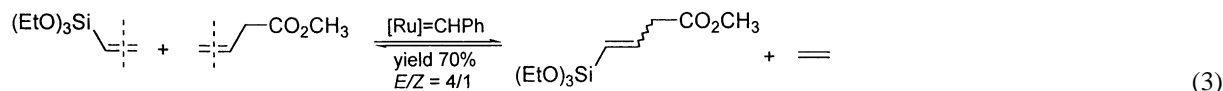
Both substrates react competitively with the active complex (1) generated after dissociation of PCy<sub>3</sub> from



Scheme 1.

the initial complex (**I**) to give ruthenium carbene (**2**) and (**3**). However, under the conditions used, i.e., in at least 5-fold excess of vinylsilanes, the reaction of (**2**) with vinylsilane is a crucial step in the catalytic cycle ensuring high selectivity of the cross-metathesis process. It was previously reported that the competitive reaction of (**3**) with vinyltrialkoxysilanes leads to the exchange of the methylidene unit but does not produce silylcarbene complex [20].

For comparison, the exemplary reaction of cross-metathesis of *C*-allyl analogue of *O*-allyl esters (e.g., methyl 3-butenolate) with vinyltriethoxysilane was shown to occur under the same conditions according to the following equation:



The product was isolated and characterized spectroscopically.

It can be finally concluded that ruthenium carbenes (Grubbs complexes) catalyze effectively the cross-metathesis of vinyltrialkoxy- and vinyltrisiloxysilanes with *O*-allyl esters and *C*-allyl analogue (as an example of alkyl ester of unsaturated acid) to yield under the optimum conditions (5–10 excess of vinylsilane) esters with vinylsilicon functionality of the general formula  $(\text{RO})_3\text{SiCH}=\text{CHCH}_2\text{OCOR}'$  and  $(\text{RO})_3\text{SiCH}=\text{CHCH}_2\text{COOR}'$  (where R = alkoxy, siloxy; R' = alkyl, aryl) with high preference of *E*-isomer which is illustrated by exclusive isolation of *E*-isomer. The compounds synthesized play an important role in stereoselective organic synthesis.

### 3. Experimental

#### 3.1. General methods and chemicals

All syntheses and catalytic tests were carried out under argon.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of isolated products were recorded in  $\text{C}_6\text{D}_6$  on a Varian Gemini 300 VT spectrometer (300 and 75 MHz, respectively). When necessary for a correct signal assignment, COSY ( $^1\text{H}$ ,  $^1\text{H}$ ) correlation spectra were recorded. The mass spectra of the products and substrates were determined by GC–MS analysis (Varian

Saturn 2100T, equipped with a DB-5, 30 m capillary column and TCD detector). GC analyses were performed on a Hewlett-Packard HP 5890 Series II with a 30 m Megabore HP-1 column and TCD.

The chemicals were obtained from the following sources: allyl acetate, allyl methacrylate, allyl cyclohexanepropionate, methyl 3-butenolate, allyl propionate and allyl butyrate from Aldrich, vinyltri(alkoxy, siloxy) from ABCR, benzene- $\text{d}_6$  from Dr. Glaser A.G.,  $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(\text{=CHPh})]$  (**I**) and  $[\text{Cl}_2(\text{PCy}_3)(1,3\text{-dimesityl-4,5-dihydroimidazol-2-ylidene})\text{Ru}(\text{=CHPh})]$  (**II**) was purchased from Strem Chemicals, dodecane from Aldrich, and dichloromethane from POCh (Poland).

Prior to use all solvents were dried and distilled over  $\text{CaH}_2$  in argon. All liquid reagents were distilled, dried with molecular sieves, and degassed by repeated freeze–pump–thaw cycles.

#### 3.2. General procedure for the catalytic cross-metathesis

An oven-dried flask equipped with a condenser and a magnetic stirrer bar was charged under argon with  $\text{CH}_2\text{Cl}_2$  (5 ml), dodecane (internal standard), vinylsilane ( $3.14 \times 10^{-3}$  mol) and a respective allyl ester ( $6.28 \times 10^{-4}$  mol). The reaction mixture was stirred and heated in water bath to maintain a gentle reflux.

Then ruthenium benzylidene complex (**I**) ( $3.14 \times 10^{-5}$  mol) was added and the reaction was controlled by GC. Analyses were made before and 3 h after the addition of the complex.

#### 3.3. Representative procedure for the synthesis of new products of cross-metathesis

The reaction was carried out with catalyst, reagents and solvent in 10 times greater amounts as described above. No standard was added. The reaction time was 3 h. The solvent was removed under atmospheric pressure. The product was isolated by vacuum distillation with the use of an efficient column (yields are included in Table 1).

### 3.4. Analytical data of the selected new products

(*E*)-(EtO)<sub>3</sub>SiCH=C(H)CH<sub>2</sub>OC(O)CH<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm, coupling constants in Hz), δ: 1.15 (t, 9H) (CH<sub>3</sub>), 1.66 (s, 3H) (CH<sub>3</sub>CO), 3.77 (q, 6H) (CH<sub>2</sub>), 4.46 (dd, 2H) (*J* = 4.8 Hz) (OCH<sub>2</sub>CH=CH), 5.78 (dt, 1H) (*J* = 19.2 Hz) (OCH<sub>2</sub>CH=CH), 6.43 (dt, 1H) (*J* = 18.9 Hz) (OCH<sub>2</sub>CH=CH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ppm), δ: 18.88 (OCH<sub>2</sub>CH<sub>3</sub>), 20.83 (CH<sub>3</sub>), 59.09 (OCH<sub>2</sub>CH<sub>3</sub>), 66.31 (OCH<sub>2</sub>CH=CH), 122.66 (OCH<sub>2</sub>CH=CH), 146.24 (OCH<sub>2</sub>CH=CH), 170.15 (CO). MS, *m/z* (%): 263 (M, 28), 216 (100), 191 (58), 163 (74), 135 (44), 119 (74), 79 (45). Anal. Calcd. for C<sub>11</sub>H<sub>22</sub>O<sub>5</sub>Si: C, 50.35; H, 8.45. Found: C, 50.42; H, 8.46. b.p. = 92 °C/1 mm Hg.

(*E*)-(EtO)<sub>3</sub>SiCH=C(H)CH<sub>2</sub>OC(O)C<sub>3</sub>H<sub>7</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm, coupling constants in Hz), δ: 0.75 (t, 3H) (CH<sub>3</sub>), 1.18 (t, 9H) (OCH<sub>2</sub>CH<sub>3</sub>), 1.44–1.56 (m, 6H) (CH<sub>2</sub>), 2.04 (t, 2H) (CH<sub>2</sub>CO), 3.81 (q, 2H) (OCH<sub>2</sub>CH<sub>3</sub>), 4.52 (dd, 2H) (*J* = 4.8 Hz) (OCH<sub>2</sub>CH=CH), 5.86 (dt, 1H) (*J* = 18.9 Hz) (OCH<sub>2</sub>CH=CH), 6.51 (dt, 1H) (*J* = 18.9 Hz) (OCH<sub>2</sub>CH=CH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ppm), δ: 18.52 (OCH<sub>2</sub>CH<sub>3</sub>), 19.68 (CH<sub>3</sub>), 35.91 (CH<sub>2</sub>), 35.96 (CH<sub>2</sub>CO), 58.63 (OCH<sub>2</sub>CH<sub>3</sub>), 65.57 (OCH<sub>2</sub>CH=CH), 121.86 (OCH<sub>2</sub>CH=CH), 145.72 (OCH<sub>2</sub>CH=CH), 172.05 (CO). MS, *m/z* (%): 289 (M, 2), 244 (76), 191 (73), 174 (72), 163 (100), 135 (45), 119 (70). Anal. Calcd. for C<sub>13</sub>H<sub>26</sub>O<sub>5</sub>Si: C, 53.76; H, 9.02. Found: C, 53.70; H, 9.04. b.p. = 125 °C/1 mm Hg.

(*E*)-(EtO)<sub>3</sub>SiCH=C(H)CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm, coupling constants in Hz), δ: 1.16 (t, 3H) (CH<sub>3</sub>), 3.30 (s, 3H) (OCH<sub>3</sub>), 3.78 (q, 2H) (CH<sub>2</sub>), 4.46 (dd, 2H) (*J* = 4.5 Hz) (SiCH=CHCH<sub>2</sub>), 5.89 (dt, 1H) (*J* = 18.9 Hz) (SiCH=CHCH<sub>2</sub>), 6.46 (dt, 1H) (*J* = 19.2 Hz) (SiCH=CHCH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ppm), δ: 18.68 (CH<sub>3</sub>), 54.43 (OCH<sub>3</sub>), 58.80 (CH<sub>2</sub>), 69.19 (SiCH=CHCH<sub>2</sub>), 122.61 (SiCH=CHCH<sub>2</sub>), 145.01 (SiCH=CHCH<sub>2</sub>), 155.86 (CO). MS, *m/z* (%): 263 (M, 2), 233 (100), 203 (71), 163 (40), 145 (24), 119 (33), 101 (19). Anal. Calcd. for C<sub>11</sub>H<sub>22</sub>O<sub>5</sub>Si: C, 50.35; H, 8.45. Found: C, 50.40; H, 8.46. b.p. = 102 °C/1 mm Hg, the isolated yield is 65%.

### Acknowledgements

This work was supported by grant No. K012/T09/2000 from the State Committee for Scientific Research

(Poland). The authors thank Dr. S. Krompiec for synthesizing allyl benzoate.

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