

# Ruthenium catalyzed cross-metathesis versus silylative coupling of vinyl and allyl sulfides with vinylsilanes

Bogdan Marciniec<sup>a,\*</sup>, Dariusz Chadyniak<sup>a</sup>, Stanisław Krompiec<sup>b</sup>

<sup>a</sup> Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

<sup>b</sup> Faculty of Chemistry, Silesian University of Technology, Ks. M. Strzody 9, 44-100 Gliwice, Poland

Received 23 March 2004; received in revised form 1 July 2004; accepted 5 July 2004

Available online 22 October 2004

The paper is dedicated to Professor Józef J. Ziółkowski in recognition of his significant contribution to homogeneous catalysis and coordination chemistry.

## Abstract

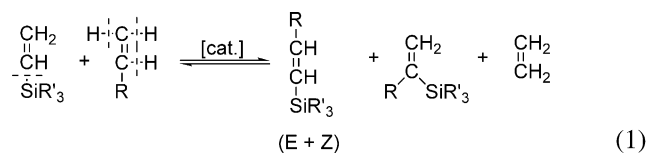
A new catalytic route for synthesis of unsaturated organosilicon compounds with vinylic functionality (R'O)<sub>3</sub>SiCH=CH(CH<sub>2</sub>)<sub>n</sub>SR (where R = *t*-Bu, Ph, R' = Me, Et, Me<sub>3</sub>Si *n* = 0, 1), based on cross-metathesis of vinyltrialkoxo- and vinyltris(trimethylsiloxy)silanes with vinyl and allyl, *t*-butyl (phenyl) sulfides catalyzed by the second generation Grubbs catalyst Cl<sub>2</sub>(PCy<sub>3</sub>)(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)Ru(=CHPh)(**II**) is reported. The silylative coupling reactions of the substrates performed in the presence of Ru–H(**III**) and Ru–Si(**IV**) give no products which is explained by formation of the ruthenium sulfide species Ru–S–*t*-Bu that appear to be catalytically inactive towards the silylative coupling reactions since there is no insertion of olefin into Ru–S bond.

© 2004 Elsevier B.V. All rights reserved.

## 1. Introduction

Substituted vinylsilanes have become a commonly used class of organosilicon reagents in organic synthesis. They have been usually prepared by traditional methods, such as hydrosilylation and silylmethallation and/or carbosilylation of alkynes or hydromethallation and hydrogenation of alkynylsilanes (for reviews see [1–4]). In the last 15 years we have developed a new type of transition metal catalyzed reaction of vinyl-substituted organosilicon monomers and polymers with a variety of olefins called the silylative coupling, *trans*-silylation or silyl group transfer which has become a useful process for the synthesis of novel and well-known silicon-containing alkenes (for reviews see [5–9]). The reaction proceeds via cleavage of the =C–H bond of alkene and the C–Si bond of the vinylsilane, in contrast to the cross-metathesis,

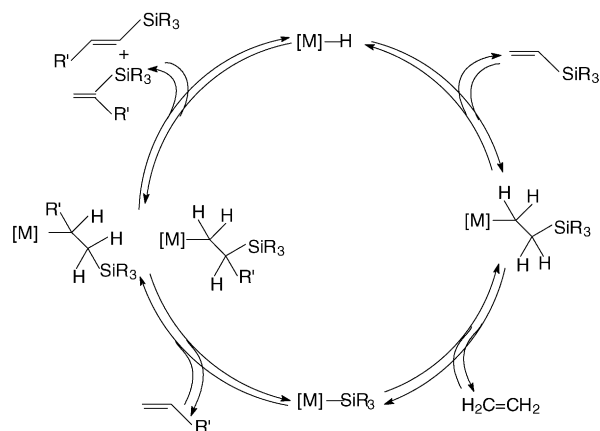
which, using the same substrates, yields the same or similar isomeric products.



The reaction of silylative coupling occurs via active intermediates containing M–Si (silicometallics) and M–H (where M = Ru, Rh, Ir, Co) bonds. The insertion of alkene into M–Si bond and vinylsilanes into M–H bonds, followed by elimination of vinylsilane and ethene, respectively, are the key steps in this new process (Scheme 1) [10–15].

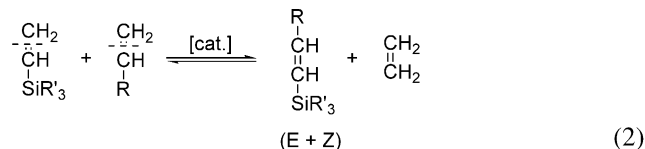
On the other hand, although well-defined or in situ generated metallacarbenes are inactive for self-metathesis of vinyl-substituted silanes and siloxanes, we have recently proved a high catalytic activity of Grubbs catalysts of both generations in cross-metathesis of vinylsilanes with electron-withdrawing (e.g. alkoxy, siloxy [16–19] as well as chloro [20]) substituents (for reviews see [5,6]).

\* Corresponding author. Tel.: +48 61 8291366; fax: +48 61 8291508.  
E-mail address: [marcinb@main.amu.edu.pl](mailto:marcinb@main.amu.edu.pl) (B. Marciniec).



M = Ru, Rh, Ir, Co, Fe

Scheme 1.

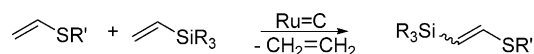


The two catalytic reactions provide a universal route towards synthesis of well-defined molecular compounds possessing vinylsilicon functionality.

Experiments with the use of vinyl-substituted silicon compounds with heteroatom functionalized alkenes (e.g. O, N, B, Si) catalyzed by ruthenium complexes allowed us to draw a general conclusion. While vinylsilanes undergo productive cross-metathesis with allyl-substituted heteroorganic compounds [5,17,18,21] their effective transformation with vinyl-substituted heteroorganic compounds can be achieved only via the silylative coupling [5,15,22,23]. In view of the results of our previous studies, the aim of this paper is to apply the two reactions catalyzed by ruthenium complexes to the efficient and selective synthesis of sulfur substituted vinylsilanes.

## 2. Results and discussion

The experimental data for the reaction of alkyl(phenyl) vinyltrisubstituted silanes with vinyl sulfides catalyzed by Grubbs catalysts [Ru(=CHPh)Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] (**I**) and [Ru(=CHPh)Cl<sub>2</sub>(PCy<sub>3</sub>)(H<sub>2</sub>IMes)] (**II**), and by [RuH(Cl)-



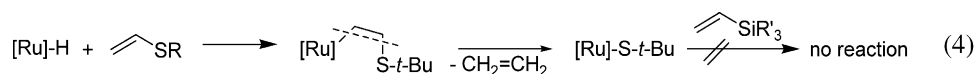
R<sub>3</sub> = (OEt)<sub>3</sub>, Me<sub>3</sub>, Me<sub>2</sub>Ph, R' = *t*-Bu, Et, Ph (3)

The Fischer type ruthenium carbene complex [Ru(=CHSPh)Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] has been recently reported as an effective catalyst in the ring opening/cross-metathesis of norbornene derivatives with vinyl sulfides [24]. This result suggests that vinyl sulfides and consequently S-Fischer carbene complexes can be reactive in cross-metathesis. Nevertheless, Grubbs' catalyst **I**, which immediately transforms into S-Fischer carbene complex during the reaction proved inert in the reaction between vinylsilanes and *t*-butyl vinyl sulfide. Apparently, the well-known decomposition of the first generation Grubbs catalyst (**I**) during the reaction is responsible for this effect [16]. However, the second generation Grubbs catalyst (**II**) appeared very efficient to give β-*t*-butyl vinyltrisubstituted silane.

The reaction catalyzed by **II** proceeds with a strong preference for the formation of *E*-isomer. A five-fold excess of vinylsilane was used to exclude products of self-metathesis of *t*-butyl vinyl sulfide. The open system enabling a removal of ethylene caused a shift to the right of the reversible cross-metathesis equilibrium (see Eq. (2)). The highest yield of the cross-metathesis products (Table 1, entry 6) was obtained in the reaction of vinyltriethoxysilane and *t*-butyl vinyl sulfide. In contrast, trimethylsilyl (entry 11) and dimethylphenylsilyl (entry 12) derivatives did not react with *t*-butyl vinyl sulfide indicating that silyl groups carrying strongly electron-withdrawing substituents at silicon are required for an efficient cross-metathesis [20]. A low transformation of the reaction with volatile trimethylvinylsilane can be explained by performing the process in the closed system.

The catalytic results provide a basis for a synthesis of exemplary silyl derivatives of vinyl sulfides. Selected synthetic procedures are described in Section 3. The products were isolated (*E*-isomer) and characterized by <sup>1</sup>H NMR spectroscopy, GC-MS and elemental analysis.

It was assumed that the reaction of vinylsilanes with vinyl sulfide would occur in the same manner as the reaction with vinyl ethers [15] and vinylpyrrolidinone [23] exhibiting efficient *trans*-silylation and inactive cross-metathesis. However, unexpectedly, the silylation coupling was not observed even at an elevated temperature (110–120 °C). To shed light on the mechanism of the process the insertion of vinyl sulfides into Ru–H (complex **III**) and into Ru–Si bond (complex **IV**) (ratio 3:1, temperature 80 °C, 24 h) were examined (Eq. (4)).



(CO)(PCy<sub>3</sub>)<sub>2</sub>] (**III**) and [Ru(SiMe<sub>3</sub>)(Cl)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (**IV**) are compiled in Table 1. The reaction proceeds according to the following equation.

The <sup>1</sup>H NMR spectrum of a mixture of complex **III** with *t*-butyl vinyl sulfide (after 24 h) indicated a generation of ethylene (singlet at δ = 5.2 ppm) and disappearance of Ru–H. This implies the occurrence of β-sulfide transfer and the formation of sulfide species. The Ru–S was isolated and subsequently

Table 1  
Cross-metathesis vs. silylative coupling of vinyl sulfides with vinyltrisubstituted silanes

Entry	Catalyst	Temperature [°C]	CH <sub>2</sub> =CHSiR <sub>3</sub>	CH <sub>2</sub> =CHSR'	Yield (isolated) %	E/Z
			SiR <sub>3</sub> =	R'=		
1	<b>I</b>	20	Si(OEt) <sub>3</sub>	<i>t</i> -Bu	8	–
2	<b>I</b>	40	Si(OEt) <sub>3</sub>	<i>t</i> -Bu	12	–
3	<b>I</b>	60	Si(OEt) <sub>3</sub>	<i>t</i> -Bu	–	–
4	<b>II</b>	20	Si(OEt) <sub>3</sub>	<i>t</i> -Bu	18	Traces Z
5	<b>II</b>	40	Si(OEt) <sub>3</sub>	<i>t</i> -Bu	67	Traces Z
6	<b>II</b>	60	Si(OEt) <sub>3</sub>	<i>t</i> -Bu	93(80)	10/1
7	<b>II</b>	60	Si(OEt) <sub>3</sub>	Et	47(40)	8/1
8	<b>II</b>	60	Si(OEt) <sub>3</sub>	Ph	41(35)	8/1
9	<b>II</b>	60	Si(OMe) <sub>3</sub>	<i>t</i> -Bu	58	6/1
10	<b>II</b>	60	Si(OSiMe <sub>3</sub> ) <sub>3</sub>	<i>t</i> -Bu	60(52)	Traces Z
11	<b>II</b>	60	SiMe <sub>2</sub> Ph	<i>t</i> -Bu	10	–
12	<b>II</b>	60	SiMe <sub>3</sub>	<i>t</i> -Bu	6	–
13 <sup>a</sup>	<b>III</b>	80	Si(OEt) <sub>3</sub>	<i>t</i> -Bu	Traces	–
14 <sup>a</sup>	<b>IV</b>	80	Si(OEt) <sub>3</sub>	<i>t</i> -Bu	Traces	–

Reaction conditions: argon, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, 24 h. [Ru]:[CH<sub>2</sub>=CHSiR<sub>3</sub>]:[CH<sub>2</sub>=CHSR'] = 2 × 10<sup>-2</sup>:5:1.

<sup>a</sup> argon, toluene, 24 h. [Ru]:[CH<sub>2</sub>=CHSiR<sub>3</sub>]:[CH<sub>2</sub>=CHSR'] = 10<sup>-2</sup>:1:5.

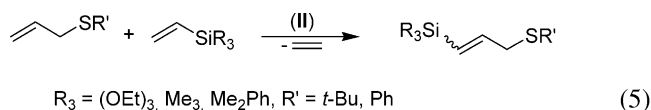
reacted with vinyltrimethylsilane but no insertion of vinylsilane into Ru–S(*t*-Bu) was noticed (see Scheme 2).

On the other hand, the NMR spectra of the products of the complex **IV** containing a Ru–Si bond reaction with *t*-butyl vinyl sulfide indicate the formation of the two products: Me<sub>3</sub>SiCH=CHS(*t*-Bu) and Me<sub>3</sub>SiCH=CH<sub>2</sub>. These products were also identified by GC–MS. The analysis of all products suggests the following processes to proceed (Scheme 2).

In this competitive reaction, complex **IV** reacts with *t*-butyl sulfide to form vinylsilane and complex Ru–S but predominantly to yield silylsulfanylene and an Ru–H complex. Ru–H was not detected (similarly to analogous reactions of the insertion of other olefins into Ru–Si bonds [10–13]) presumably due to a fast reaction of Ru–H with vinyl sulfide.

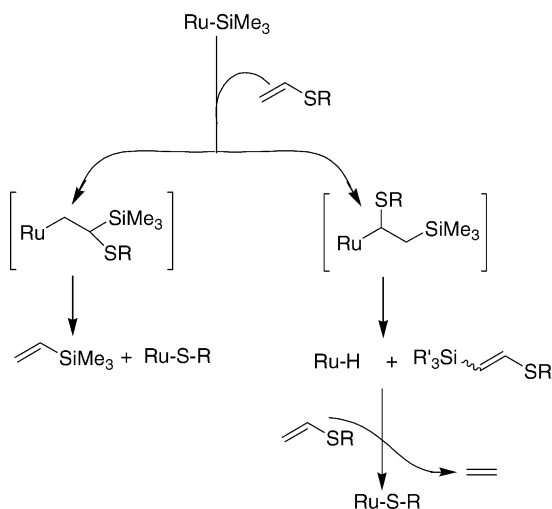
The reactions of vinyltrisubstituted silanes with allyl alkyl sulfides proceed similarly to those with vinyl sulfides giving

in the presence of (**II**) two isomeric products *E* and *Z* 1-silyl-3-sulfanyl propenes according to Eq. (5).



The results of catalytic examinations are compiled in Table 2. Although a five-fold excess of vinylsilane is used the *E* + *Z* products of cross-metathesis are accompanied by traces of products of self-metathesis of allyl sulfides, i.e. RSCH<sub>2</sub>CH=CHCH<sub>2</sub>SR.

Results of examinations of the cross-metathesis of vinylsilanes with allyl sulfides also show that the metathetical conversion significantly decreases when the alkoxy or siloxy substrates in vinylsilanes are replaced by more electron-donating substituents [16–18].



Scheme 2.

Table 2  
Cross-metathesis vs. silylative coupling of allyl *t*-butyl sulfide with vinyltrisubstituted silanes

Entry	Catalyst	Temperature [°C]	CH <sub>2</sub> =CHSiR <sub>3</sub>	Yield (isolated) %	E/Z
			SiR <sub>3</sub> =		
1	<b>I</b>	40	Si(OEt) <sub>3</sub>	14	3/1
2 <sup>a</sup>	<b>II</b>	40	Si(OEt) <sub>3</sub>	55(45)	4.5/1
3	<b>II</b>	40	Si(OEt) <sub>3</sub>	52(42)	4/1
4	<b>II</b>	40	Si(OMe) <sub>3</sub>	32	6/1
5	<b>II</b>	40	Si(OSiMe <sub>3</sub> ) <sub>3</sub>	50	3/1
6	<b>II</b>	40	SiMe <sub>2</sub> Ph	8	–
7 <sup>b</sup>	<b>III<sup>b</sup></b>	80	Si(OEt) <sub>3</sub>	Traces	–
8 <sup>b</sup>	<b>IV<sup>b</sup></b>	80	Si(OEt) <sub>3</sub>	Traces	–

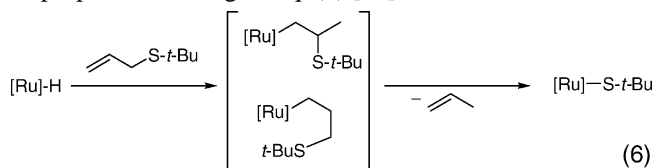
Reaction conditions: argon, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, 24 h. [Ru]:[CH<sub>2</sub>=CHSiR<sub>3</sub>]:[CH<sub>2</sub>=CHCH<sub>2</sub>SR'] = 2 × 10<sup>-2</sup>:5:1.

<sup>a</sup> CH<sub>2</sub>=CHCH<sub>2</sub>SPh was used as a substrate.

<sup>b</sup> argon, toluene, 24 h. [Ru]:[CH<sub>2</sub>=CHSiR<sub>3</sub>]:[CH<sub>2</sub>=CHCH<sub>2</sub>SR'] = 10<sup>-2</sup>:1:5.

The catalytic results enabled us to synthesize silyl derivatives of sulfides. The products were isolated (mostly *E*-isomer) and characterized by  $^1\text{H}$  NMR, GC–MS and elemental analysis.

The inactivity of Ru–H(III) and Ru–Si(IV) complexes in the silylative coupling of allyl *t*-butyl sulfide with vinylsilanes is due to analogous formation of ruthenium sulfides Ru–S–*t*-Bu which was reported previously and involves elimination of propene according to Eq. (6) [25].



As we have already mentioned, vinylsilanes do not undergo the insertion into Ru–S(*t*-Bu) to close the catalytic cycle of the silylative coupling. This is the reason why we have not observed silylative coupling of allyl sulfides with vinylsilanes.

### 3. Experimental

#### 3.1. General methods and chemicals

All syntheses and catalytic tests were carried out under argon.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{29}\text{Si}$  NMR (INEPT) of isolated products were recorded in  $\text{C}_6\text{D}_6$  on a Varian Gemini 300 VT spectrometer (300, 75 and 60 MHz, respectively). 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: vinyltrimethylsilane, vinyldimethylphenylsilane, vinyltriethoxysilane from Gelest; vinyltrimethoxysilane and vinyltris(trimethylsiloxy)silane from ABCR; decane, toluene, dichloromethane, hexane, ethyl acetate, vinyl *t*-butyl vinyl sulfide, ethyl sulfide and vinyl phenyl sulfide from Aldrich; benzene *d*<sub>6</sub> from Dr. A.G. Glaser. Allyl ethyl sulfide [26] and allyl *t*-butyl sulfide [27] were prepared by modified standard methods.  $[\text{Ru}(=\text{CHPh})\text{Cl}_2(\text{PCy}_3)_2]$  (I) and  $[\text{Ru}(=\text{CHPh})\text{Cl}_2(\text{PCy}_3)(\text{H}_2\text{IMes})]$  (II) were obtained from Strem. The ruthenium complexes  $[\text{RuH}(\text{Cl})(\text{CO})(\text{PCy}_3)_2]$  (III) [28] and  $[\text{Ru}(\text{SiMe}_3)(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$  (IV) [29] were prepared by standard procedures.

Prior to use all solvents and chemicals 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 reactions

An oven-dried flask equipped with a condenser was charged under argon with  $\text{C}_2\text{H}_4\text{Cl}_2\text{CH}_2\text{Cl}_2$  (for the olefin

metathesis) and with toluene (for the silylation coupling reaction), dodecane (internal standard), vinylsilane and a respective vinyl or allyl sulfide. The reaction mixture was stirred and heated in a water bath to maintain a desired temperature. Then ruthenium complex was added and the reaction was monitored by GC.

#### 3.3. Representative procedure for synthesis of sulfide substituted vinyl- and propenyl-triethoxysilanes

An oven dried 20 ml flask equipped with a condenser connected with a bubbler was charged with 5 ml dichloromethane, 10.5 mmol of vinylsilane, 2.1 mmol of vinyl(allyl) sulfide and 0.21 mmol of the catalyst  $[\text{Ru}(=\text{CHPh})\text{Cl}_2(\text{PCy}_3)(\text{H}_2\text{IMes})]$  (II). The reaction mixture was stirred and heated at 60 °C (40 °C for allyl sulfides) for 24 h. No standard was added. The product was isolated by removal of all volatiles in vacuum and then the residue was column chromatographed on silica gel (60 mesh) using hexane/ethyl acetate (50/1). Hexane and ethyl acetate were removed in vacuum. The crude product was distilled under vacuum with the use of a microdistillation set.

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

##### 3.4.1. (*E*)-2-(ethylsulfanyl-vinyl)triethoxysilane

Bp 80–85 °C/1 mmHg.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 300 MHz):  $\delta$  1.20 (t, 9H,  $J_{\text{H-H}} = 6.8$  Hz), 1.22 (s, 9H), 2.62 (q, 2H), 3.85 (q, 6H,  $J_{\text{H-H}} = 6.8$  Hz), 6.08 (d, 1H,  $J_{\text{H-H}} = 18.4$  Hz), 7.40 (d, 1H,  $J_{\text{H-H}} = 18.4$  Hz).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 75 MHz):  $\delta$  16.3, 18.5, 26.0, 58.7, 117.0, 144.8.

$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 60 MHz):  $\delta$  –59.2.

EIMS ( $m/z$ ) (rel. int.): 250(5), 235(5), 221(20), 205(15), 188(100), 179(45), 177(64), 175(26), 163(24), 159(22), 149(71), 144(40), 135(32), 133(62), 123(25), 119(29), 107(23), 105(19), 103(15), 79(45), 63(16).

Elem. Anal.: obs. C 48.25; H 8.95, calcd. C 47.96; H 8.85.

##### 3.4.2. (*E*)-2-(*t*-butylsulfanyl-vinyl)triethoxysilane

Bp 92–95 °C/1 mmHg.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 300 MHz):  $\delta$  1.18 (t, 9H,  $J_{\text{H-H}} = 6.9$  Hz), 1.20 (s, 9H), 3.84 (q, 6H,  $J_{\text{H-H}} = 6.9$  Hz), 6.00 (d, 1H,  $J_{\text{H-H}} = 18.4$  Hz), 7.44 (d, 1H,  $J_{\text{H-H}} = 18.4$  Hz).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 75 MHz):  $\delta$  18.5, 31.0, 43.8, 58.7, 117.9, 144.8.

$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 60 MHz):  $\delta$  –59.2.

EIMS ( $m/z$ ) (rel. int.): 278(M<sup>+</sup>), 221(100), 207(12), 193(20), 188(23), 176(63), 167(12), 163(34), 151(19), 147(22), 142(64), 132(25), 119(22), 79(24), 57(33).

Elem. Anal.: obs. C 52.50; H 9.11, calcd. C 51.75; H 9.41.

##### 3.4.3. (*E*)-2-(*t*-butylsulfanyl-vinyl)tris(trimethylsiloxy)silane

Bp 116–119 °C/1 mmHg.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 300 MHz):  $\delta$  0.22 (s, 27H), 1.26 (s, 9H), 6.02 (d, 1H,  $J_{\text{H-H}} = 18.3$  Hz), 7.29 (d, 1H,  $J_{\text{H-H}} = 18.3$  Hz).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 75 MHz):  $\delta$  1.9, 31.1, 39.0, 122.2, 142.0.

$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 60 MHz):  $\delta$  -78.7, 8.8.

EIMS ( $m/z$ ) (rel. int.): 410(M,6), 353(43), 339(100), 297(48), 207(52), 117(16), 73(21), 57(23).

#### 3.4.4. (*E*)-2-(phenylsulfanyl-vinyl)triethoxysilane

Bp 98–102 °C/1 mmHg.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 300 MHz):  $\delta$  1.13 (t, 9H,  $J_{\text{H-H}} = 6.8$  Hz), 3.78 (q, 6H,  $J_{\text{H-H}} = 6.9$  Hz), 5.80 (d, 1H,  $J_{\text{H-H}} = 18.0$  Hz), 6.94–7.34 (m, 5H), 7.39 (d, 1H,  $J_{\text{H-H}} = 18.0$  Hz).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 75 MHz):  $\delta$  18.9, 51.9, 117.6, 126.5, 130.0, 130.6, 133.0, 146.7.

$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 60 MHz):  $\delta$  -59.5.

Elem. Anal.: obs. C 61.98; H 7.33, calcd. C 63.13; H 8.32.

#### 3.4.5. (*E*)-(3-*t*-butylsulfanyl-propenyl)triethoxysilane

Bp 100–105 °C/1 mmHg.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 300 MHz):  $\delta$  1.19 (t, 9H,  $J_{\text{H-H}} = 7.0$  Hz), 1.19 (q, 9H), 3.11(d, 2H), 3.86 (q, 6H,  $J_{\text{H-H}} = 7.0$  Hz), 5.77 (dd, 1H,  $J_{\text{H-H}} = 18.4$  Hz), 6.68 (dt, 1H,  $J_{\text{H-H}} = 18.4$  Hz).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 75 MHz):  $\delta$  18.5, 31.1, 34.7, 42.4, 58.6, 122.5, 149.7.

$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, 60 MHz):  $\delta$  -58.3.

EIMS ( $m/z$ ) (rel. int.): 292(M,-), 237(11), 190(100), 175(6), 163(13), 161(24), 145(10), 119(7), 117(12), 79(6), 57(14).

Elem. Anal.: obs. C 53.48; H 9.35, calcd. C 53.38; H 9.65.

#### 3.4.6. (*E*)-2-(phenylsulfanyl-propenyl)triethoxysilane

Bp 112–115 °C/1 mmHg.

EIMS ( $m/z$ ) (rel. int.): 328(M,-), 283(5), 219(100), 175(25), 163(26), 149(12), 135(7), 131(24), 119(26), 109(11), 107(9), 95(5), 79(11), 69(8).

Elem. Anal.: obs. C 57.39; H 7.58, calcd. C 57.65; H 7.74.

## 4. Conclusions

- Efficient cross-metathesis of trialkoxy- and trisiloxy-substituted vinylsilanes with vinyl- and allyl-substituted sulfides in the presence of  $[\text{Ru}(=\text{CHPh})\text{Cl}_2(\text{PCy}_3)(\text{H}_2\text{IMes})]$  (**II**) catalyst offers a new and very attractive route for syntheses of alkyl (aryl) sulfur-substituted vinylsilanes with high preference for the *E*-isomer which is illustrated by exclusive isolation of this isomer.
- Contrary to the generally observed efficient silylative coupling of heteroatom (O, N, B and Si)-functionalized alkenes with vinylsilanes catalyzed by Ru–H and/or

Ru–Si containing complexes vinyl sulfides do not undergo this transformation. The inactivity is explained by formation of Ru–S intermediate to which no insertion of vinylsilanes (a step necessary in the catalytic cycle of the silylative coupling reactions) is observed.

## Acknowledgements

This work was supported by Grant Nos. K012/T09 and 3T09A 145 26 from the State Committee for Scientific Research (Poland).

## References

- E.W. Colvin, Silicon Reagents in Organic Synthesis, Academic Press, London, 1988 (Chapter 3).
- L. Hevesi, in: A.R. Katritzky, R.J.K. Taylor (Eds.), Comprehensive Organic Functional Group Transformations I (COFGT-I), Elsevier, 1994 (Chapter 2.18).
- T.X. Luk, S.T. Lu, in: Z. Rappaport (Ed.), The Chemistry of Organosilicon Compounds, Wiley, Chichester, 1998 (Chapter 30).
- B. Marciniak, M. Zaidlewicz, C. Pietraszuk, I. Kownacki, in: A.R. Katritzky, R.J.K. Taylor (Eds.), Comprehensive Organic Functional Group Transformations II (COFGT-II), Elsevier, 2004, (Chapter 2.18) in press.
- B. Marciniak, C. Pietraszuk, Curr. Org. Chem. 7 (2003) 691.
- B. Marciniak, C. Pietraszuk, in: R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 2, Wiley/VCH, 2003 (Chapter 2.13).
- B. Marciniak, in: B. Cornils, W.A. Hermann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, 2002 (Chapter 2.6).
- J.A. Reichl, D.H. Berry, Adv. Organomet. Chem. 43 (1998) 203.
- B. Marciniak, Appl. Organomet. Chem. 14 (2000) 527.
- Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, J. Chem. Soc., Chem. Commun. (1999) 703.
- B. Marciniak, C. Pietraszuk, J. Chem. Soc., Chem. Commun. (1995) 2003.
- B. Marciniak, C. Pietraszuk, Organometallics 16 (1997) 4320.
- B. Marciniak, E. Walczuk-Gusciora, C. Pietraszuk, Catal. Lett. 55 (1998) 125.
- B. Marciniak, I. Kownacki, D. Chadyniak, Inorg. Chem. Commun. 2 (1999) 581.
- M. Kujawa-Welten, B. Marciniak, Mol. Catal. A: Chem. 190 (2000) 79.
- C. Pietraszuk, B. Marciniak, H. Fischer, Organometallics 19 (2000) 913.
- C. Pietraszuk, H. Fischer, M. Kujawa, B. Marciniak, Tetrahedron Lett. 42 (2001) 1175.
- M. Kujawa-Welten, C. Pietraszuk, B. Marciniak, Organometallics 21 (2002) 840.
- Y. Itami, B. Marciniak, M. Kubicki, Chem. Eur. J. 10 (2004) 1239.
- C. Pietraszuk, B. Marciniak, H. Fischer, Tetrahedron Lett. 44 (2003) 7121.
- B. Marciniak, in: Y. Imamoglu, L. Bencze (Eds.), Novel Metathesis Chemistry, Kluwer Academic Publishers, 2003, p. 51.
- B. Marciniak, M. Kujawa, C. Pietraszuk, New J. Chem. 24 (2000) 671.

- [23] B. Marciniak, D. Chadyniak, S. Krompiec, *Tetrahedron Lett.* 45 (2004) 4065.
- [24] H. Katayama, M. Nagao, F. Ozawa, *Organometallics* 22 (2003) 586.
- [25] N. Kuznik, S. Krompiec, T. Bieg, S. Baj, K. Skutil, A. Chrobk, *J. Organomet. Chem.* 665 (2003) 167.
- [26] T.P. Dawson, *J. Am. Chem. Soc.* 55 (1933) 2070.
- [27] J.K. Kim, M.C. Caserio, *J. Org. Chem.* 44 (1987) 1897.
- [28] C.S. Yi, D.W. Lee, Y. Chen, *Organometallics* 18 (1999) 2043.
- [29] M.A. Bennett, G. Wilkinson, *Chem. Ind.* (1959) 1516.