

# Cross-metathesis *vs.* silylative coupling of vinyl alkyl ethers with vinylsilanes catalyzed by a ruthenium–carbene complex (Grubbs catalyst)

Bogdan Marciniec,\* Małgorzata Kujawa and Cezary Pietraszuk

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland. E-mail: marcinb@main.amu.edu.pl

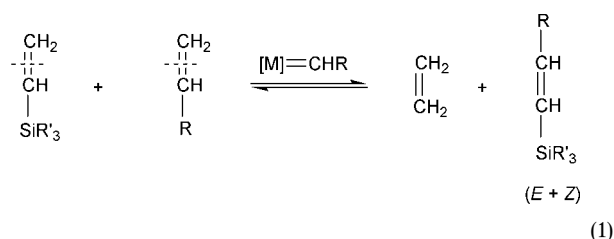
Received (in Strasbourg, France) 26th April 2000, Accepted 30th June 2000

Published on the Web 17th August 2000

Grubbs complex,  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (**I**) is a very effective catalyst of the cross-disproportionation of vinyl-trisubstituted silanes  $\text{H}_2\text{C}=\text{CHSiR}_3$  [where  $\text{R}_3 = \text{Me}_3, \text{PhMe}_2, (\text{OEt})_3$ ] with vinyl alkyl ethers  $\text{H}_2\text{C}=\text{CHOR}'$  [where  $\text{R}' = \text{ethyl, propyl, butyl, } t\text{-butyl, } t\text{-pentyl, 2-(ethyl)hexyl, cyclohexyl, trimethylsilyl}$ ] to yield a mixture of (*E* + *Z*) 1-silyl-2-alkoxyethenes. The reaction occurs quantitatively under milder conditions (60 °C) than the analogous one catalyzed by  $\text{Ru-H}$  and/or  $\text{Ru-Si}$  complexes reported previously (80 °C).<sup>7</sup> The stoichiometric reaction of (**I**) and  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}_2$  (**III**) with vinyl ethyl ether leads to the formation of  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}(\text{OEt})$  (**II**), inactive in the stoichiometric reaction with vinylsilanes but very active in the catalytic process. Experiments with the use of deuterated vinylsilanes indicate the non-metallacarbene mechanism of the reaction and provide evidence for the initiation of  $\text{Ru-H}$  bond formation *via* the hydrovinylation with vinylsilanes.

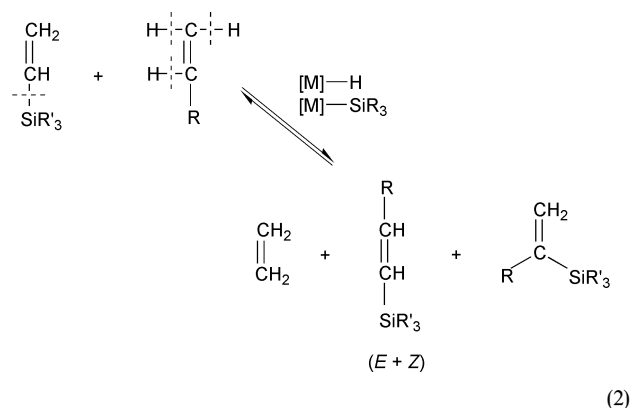
Many metallacarbenes ( $\text{Mo}$ ,  $\text{W}$  and  $\text{Ru}$ ) catalyze the metathetical conversion of silicon-containing olefins.<sup>1</sup> However, the effective self-metathesis as well as acyclic diene metathesis (ADMET) polymerization of vinyl-substituted organosilicon olefins and dienes (*e.g.*, vinylsilanes and divinyl-diorganosilanes), even in the presence of well-defined  $\text{Mo}$ ,  $\text{W}$ ,  $\text{Ru}$  complexes, has not been reported yet. The inactivity of metallacarbene initiators in productive homometathesis of vinylsilanes is accounted for by steric effects and the relative stability of the silyl-substituted carbenes bonded to the metal.<sup>2</sup>

However, reports on ruthenium–carbene-complex catalyzed cross-metathesis of vinyl-substituted silsesquioxanes with alkenes<sup>3</sup> and ADMET copolymerization of divinyl-dimethylsilane with dienes,<sup>4</sup> as well as our recent successful experiments on the cross-metathesis of vinyltrialkoxysilanes and vinyl-trisiloxysilanes with styrene,<sup>5</sup> show the potential utility of metathetical conversion of vinylsilanes and contribute to better understanding of the process. Cross-metathesis of vinylsilanes with olefins can be depicted by the following general scheme [eqn. (1)] and proceeds according to the metallacarbene mechanism.



On the other hand, recent reports on the disproportionation of vinyl-substituted silicon compounds and their co-disproportionation (trans-silylation) with olefins<sup>6</sup> catalyzed by ruthenium, rhodium and cobalt complexes containing (or generating)  $\text{M-H}$  and  $\text{M-Si}$  bonds have shown that the reactions occur through the cleavage of the  $=\text{C-Si}$  bond of vinyl-

silane and the  $=\text{C-H}$  bond of the olefin (also vinylsilane in the self-disproportionation) according to the following equation:

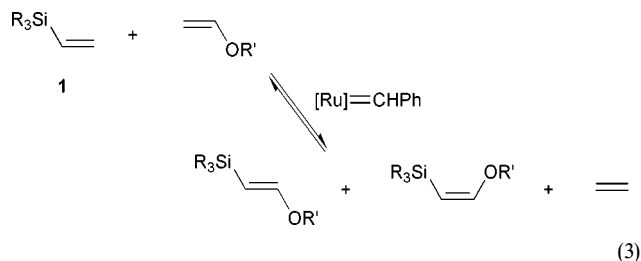


The mechanism of the latter type of silylolefin conversion was evidenced by stoichiometric reactions including an insertion of ethylene,<sup>6a</sup> styrene<sup>6c</sup> and vinylsilane<sup>6b</sup> into  $\text{Ru-Si}$  bonds. Our recent synthetic examinations confirm the non-metallacarbene mechanism for  $\text{Ru-H}$  and/or  $\text{Ru-Si}$  complexes catalyzing the reaction of vinyl alkyl ethers with vinyl-trisubstituted silanes, yielding a mixture of (*E* + *Z*) 1-silyl-2-alkoxyethenes.<sup>7</sup> Interestingly 1-silyl-1-alkoxyethene was not found among the products.

In view of the above the aim of this work is to check the catalytic activity of ruthenium–carbene complexes (*e.g.*, Grubbs catalyst) in the cross-metathesis of vinyl alkyl ethers with vinylsilanes.

## Results and discussion

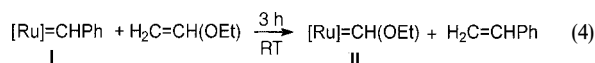
The reaction of vinyl-trisubstituted silanes with vinyl alkyl ethers proceeds in the presence of the Grubbs catalyst,  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ , at 60 °C according to eqn (3)



where  $\text{SiR}_3 = \text{SiMe}_3$  (**1a**),  $\text{SiMe}_2\text{Ph}$  (**1b**) and  $\text{Si(OEt)}_3$  (**1c**), giving two isomeric products (*E* and *Z*)-1-silyl-2-alkoxyethenes and ethylene. The same products were found in an analogous process catalyzed by Ru–H and Ru–Si complexes.<sup>7</sup> Interestingly, in both reactions 1-silyl-1-alkoxyethene was not formed.

The catalytic data on the reaction of vinyltrimethylsilane (**1a**) with various vinyl alkyl ethers are presented in Table 1. The yield of the products (two isomers *E* + *Z*) is predominantly close or equal to the conversion of the vinylsilane used. Vinyl ethyl ether and vinyl cyclohexyl ether were selected for the catalytic reaction with two other vinyl-trisubstituted silanes, vinyl dimethylphenylsilane (**1b**) and vinyl triethoxysilane (**1c**). The obtained results are collected in Table 2.

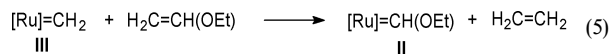
In order to study the mechanism of the process, the stoichiometric reaction of the Grubbs catalyst (**I**) with vinyl ethyl ether was performed. The reaction occurs readily at room temperature and yields quantitatively the ruthenium complex with ethoxy-substituted carbene ligand (**II**).



Complex **II** was found to also exhibit high catalytic activity in an exemplary reaction (Table 1).

Ruthenium methyldiene complex  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}_2$  (**III**) reacts efficiently only with an excess of vinyl ethyl ether, giving

the ethoxycarbene complex (**II**) and ethene. The reaction of **III** with a 100-fold excess of ether results, after 3 h at room temperature, in the formation of **II** in 40% yield and by 60% conversion of the methyldiene complex.



However, contrary to catalytic effects, an independent stoichiometric study on the reactivity of **II** with the vinylsilanes  $\text{CH}_2=\text{CHSiR}_3$  (where  $\text{R} = \text{Me, OEt}$ ) at room temperature and at 60 °C showed no expected products of cross-disproportionation (cross-metathesis). Only unidentified products of decomposition of **II** were detected.

The results of all catalytic and stoichiometric studies of the system  $\text{R}_3\text{SiCH}=\text{CH}_2 + \text{R'OCH}=\text{CH}_2 + \text{Ru-H}$  (Ru–Si) lead apparently to ambiguous conclusions.<sup>7</sup> Direct insertion of the ether molecule into Ru–Si as well as catalytic examinations of  $\text{CDH}=\text{CDSiMe}_3$  with vinyl ethyl ether provide evidence for the non-metallacarbene mechanism of the reaction.<sup>7</sup> On the other hand, the similar ratios of *E/Z* isomeric products in processes catalyzed by both types of ruthenium complexes (*i.e.*, Ru–H or Ru–Si and Ru=CHR) as well as the only slightly milder experimental conditions (shorter time and lower temperature for the efficient synthetic procedure) required for the reactions catalyzed by the ruthenium carbene complex **I** suggest that in all cases it is actually the cross-disproportionation of vinyl-trisubstituted silanes with vinyl alkyl ethers that occurs *via* the same intermediates.

Stoichiometric metathesis of transition metal carbenes with vinyl ethers was reviewed by Grubbs *et al.*<sup>8</sup> Complexes of the type  $(\text{PPh}_3)_2(\text{X})_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  can undergo stoichiometric metathesis with both terminal and internal vinyl ethers, leading to formation of ethoxy-substituted carbene species  $(\text{PPh}_3)_2(\text{X})_2\text{Ru}=\text{CH(OR)}$ . The complexes generated in such a way are catalytically inactive in the metathesis polymerization (ROMP) of norbornene.<sup>8</sup>

However, <sup>1</sup>H NMR experiments showed, at room temperature, a slow decomposition of  $(\text{TFA})_2(\text{PPh}_3)_2\text{RuCH(OR)}$  ( $\text{R} = \text{Et, CH}_2\text{Ph}$ ) accompanied by the formation of a hydride complex (resonance at –17.5 ppm in <sup>1</sup>H NMR spectrum),<sup>8</sup> which also slowly disappeared after several days. In our system  $[\text{CH}_2=\text{CHSiMe}_3 \text{ or } \text{CH}_2=\text{CHSi(OEt)}_3 + \text{II}]$  studied at 60 °C, a disappearance of the carbene resonance is observed but there is no Ru–H intermediate detected by <sup>1</sup>H NMR and IR spectroscopy, although the peak at  $\nu = 1993\text{ cm}^{-1}$  observed in the IR spectrum can be attributed to carbonyl coordinated to ruthenium.

Grubbs' *et al.* proposed two possible decomposition pathways consistent with their observations to yield either Ru–CO or Ru–H complexes.<sup>8</sup> Regardless of the type of complex finally formed, both can be the initiators of the insertion–elimination process for cross-disproportionation of vinyl alkyl ethers with vinylsilanes. Although  $\text{Ru(CO)}_3(\text{PPh}_3)_2$  contain an Ru–H bond, it appeared to also be a good catalyst for the cross-coupling of vinylsilanes with vinyl alkyl ethers, presumably due to ortho-metallation of the ruthenium triphenylphosphine complex to generate a Ru–H bond.<sup>7</sup> The respective cyclohexylphosphine complex (obtained from **I**) can react in the same way as the triphenylphosphine complex.<sup>9</sup> The previously observed silylative coupling of olefins with vinylsilanes and vinylsiloxanes catalyzed by  $\text{RuCl}_2(\text{CO})_3$ ,<sup>6d,10</sup>  $\text{Ru}_3(\text{CO})_{12}$ ,<sup>11</sup>  $\text{Cp}^*\text{Rh}(\text{H}_2\text{C}=\text{CHSiMe}_3)_2$ <sup>12</sup> and  $[(\text{cod})\text{Rh}(\mu\text{-OSiMe}_3)_2]_2$ ,<sup>13</sup> supported by some stoichiometric experiments,<sup>12</sup> suggests that hydrovinylation involving oxidative addition of the vinylsilane (or styrene) to the metal can also be regarded as an initiating step for Ru–H bond formation.

In order to check the role of **I** and **II** in generating Ru–H complexes experiments with deuterium-labelled vinylsilane  $\text{D}_2\text{C}=\text{CDSiMe}_3$  were performed. In the first experiment the

**Table 1** The effect of the alkyl substituent of vinyl alkyl ether  $\text{ROCH}=\text{CH}_2$  in its reaction with vinyltrimethylsilane catalyzed by  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (**I**) on the yield and selectivity of the products<sup>a</sup>

R	Yield (%)	<i>E/Z</i>
Ethyl	99	4
Propyl	96 (90 <sup>b</sup> ) (3 <sup>c</sup> ) (90 <sup>d</sup> )	2.5 (2 <sup>b</sup> ) (3 <sup>d</sup> )
Butyl	100	4
<i>t</i> -Butyl	100	1
<i>t</i> -Pentyl	93	1
2-(Ethyl)hexyl	98	4
Cyclohexyl	100	1.5
Trimethylsilyl	70	1

<sup>a</sup> Reaction conditions: 60 °C, 24 h, argon, sealed glass ampoules,  $[\text{H}_2\text{C}=\text{CHSiMe}_3] : [\text{ether}] : [\text{catalyst}] = 1 : 5 : 1 \times 10^{-2}$ , except for <sup>b</sup> (1 : 5 :  $5 \times 10^{-3}$ ) and <sup>c</sup> (1 : 5 :  $2 \times 10^{-3}$ ). <sup>d</sup>  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH(OEt)}$  (**II**) was used as a catalyst.

**Table 2** Cross-disproportionation of vinyl dimethylphenylsilane (**1b**) and vinyl triethoxysilane (**1c**) with selected vinyl alkyl ethers catalyzed by **I**<sup>a</sup>

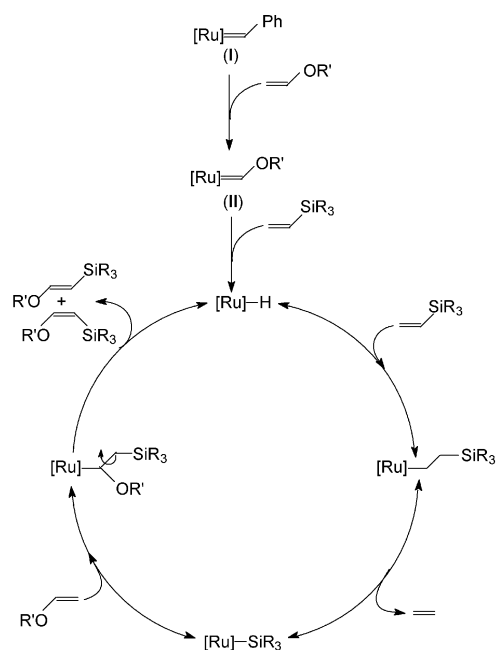
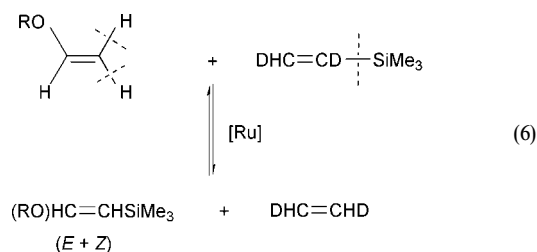
	<b>1b</b>		<b>1c</b>	
	Yield (%)	<i>E/Z</i>	Yield (%)	<i>E/Z</i>
Vinyl ethyl ether	97	6	94	1
	11 <sup>b</sup>	3	6 <sup>b</sup>	4
Vinyl cyclohexyl ether	99	4	98	1

<sup>a</sup> Reaction conditions: 60 °C, 24 h, sealed glass ampoules, argon,  $[\text{H}_2\text{C}=\text{CHSi(OEt)}_3] : [\text{ether}] : [\text{catalyst}] = 1 : 5 : 1 \times 10^{-2}$ . <sup>b</sup> RT, 24 h.

stoichiometric reaction of the ethoxycarbene complex **II** with vinylsilane- $d_3$  was studied by  $^1\text{H}$  NMR (60 °C, 6 h,  $\text{C}_6\text{D}_6$ ). No H/D exchange in the vinyl group of the vinylsilanes was detected after the reaction, which proves that generation of the Ru–H bond *via* ortho-metallation (or by decomposition of ruthenium carbene) did not take place. In another experiment, the stoichiometric reaction of **II** with a mixture of  $\text{H}_2\text{C}=\text{CHSiMe}_3$  and  $\text{D}_2\text{C}=\text{CDSiMe}_3$  (60 °C, 24 h) leads to H/D isotopic exchange in all positions of the vinyl groups (and homocoupling products as well; observed by  $^1\text{H}$  NMR spectroscopy), under the same conditions in which **II** is decomposed to Ru-carbonyl products. The hydrovinylation with  $=\text{C}-\text{H}$  ( $=\text{C}-\text{D}$ ) of vinylsilane seems to be a key step for the generation of the ruthenium–hydrogen intermediates that initiate the process of the silylative coupling of olefins with this vinylsilane.

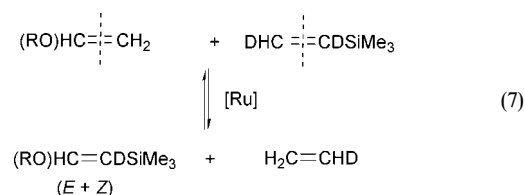
Moreover, contrary to the very effective cross-coupling of vinyltrimethylsilane with vinyl propyl ether (see Table 1), a separate study on the catalysis of homocoupling of vinylsilanes by **II** showed only slight conversion (15%, *E* product). Apparently, the role of vinylsilane, especially under the catalytic conditions (100-fold excess of vinylsilane over the catalyst) is just to generate Ru–H and subsequently Ru–Si bonds but a key step of this process is the insertion of the olefin into the Ru–Si bond. The latter proceeds more readily with vinyl propyl ether than with vinylsilane.

As in previous studies,<sup>6c,e,7</sup> the experiment with deuterium-labelled olefin was performed to distinguish between the two mechanisms. The reaction of  $\text{HDC}=\text{CDSiMe}_3$  with vinyl ethyl ether catalyzed by **I** was studied by GC/MS. If the reaction proceeds according to the non-metallacarbene mechanism [eqn. (6)] the silylalkoxyethene product formed in the first stage of the reaction would contain no deuterium atom:



**Scheme 1** Cross-metathesis *vs.* silylative coupling of vinyl alkyl ethers with vinylsilanes catalyzed by ruthenium–carbene complex (Grubbs catalyst)

However, if the reaction occurs according to the metallacarbene mechanism, the cross-metathesis process shown in eqn. (7) would take place, leading to exclusive formation of 1-trimethylsilyl-2-ethoxyethene- $d_1$ :



When the reaction is run for a prolonged time, a mixture of  $d_0$ ,  $d_1$  and  $d_2$  products is expected, because H/D exchange in the vinyl group of ether takes place when Ru–H (Ru–D) complexes are present in the system.

A GC-MS analysis of the reaction mixture after 6 h showed the formation of 1-trimethylsilyl-2-ethoxyethene- $d_0$  accompanied by traces of  $d_1$  and  $d_2$  products. This strongly confirms the non-metallacarbene mechanism of the process.

Results of this study have proven the high catalytic activity of Grubbs' complex for the reaction of vinylsilanes with vinyl ethers. The ruthenium ethoxycarbene complex that is formed in the reaction of benzylidene or methylenide complexes with vinyl ethyl ether does not form any organosilicon products in the stoichiometric reaction with vinylsilanes but reveals high catalytic activity for the reaction examined. The results of stoichiometric and catalytic experiments with the use of deuterium-labelled vinylsilanes provide convincing evidence that instead of cross-metathesis the silylative coupling (silylation) of vinyl alkyl ethers with vinylsilanes takes place. On the basis on the previously reported mechanism of the catalysis by well-defined Ru–H and Ru–Si complexes,<sup>7</sup> we can conclude that the reaction occurs *via* an insertion–elimination mechanism initiated by a Ru–H complex generated *in situ* from complexes **I** or **II** or their decomposition products *via* hydrovinylation with vinylsilane. The simplified catalytic scheme is presented in Scheme 1.

## Experimental

All manipulations were carried out in argon using standard Schlenk techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{C}_6\text{D}_6$  on a Varian Gemini 300VT spectrometer (300 and 75 MHz, respectively). Infrared spectra (KBr plates) were recorded using an FT-IR Bruker IFS-113v. The mass spectra of the products and substrates were determined by GC-MS analysis (Varian 3300 gas chromatograph equipped with a DB-1, 30 m capillary column and ITD 800 Finnigan MAT). GC-analyses were performed on Hewlett–Packard HP 5890 series II with a HP-1, 30 m megabore column and TCD.

Chemical reagents were received from the following sources: vinyl alkyl ethers from Aldrich, benzene from Lachema (Czech Republic), toluene from R&D Center of Petrochemie Płock (Poland), benzene- $d_6$  from Dr. Glaser, A.G. Basel,  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  was purchased from Strem Chemicals.  $\text{HDC}=\text{CDSiMe}_3$  and  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}_2$  were prepared according to described methods.<sup>7,14</sup> Prior to use all solvents were dried and distilled over  $\text{CaH}_2$  in argon.

## Catalytic studies

In a typical catalytic test a benzene solution of the ruthenium catalyst was placed in glass ampoules under argon. Then the reagents (usually used in the ratio

$[\text{H}_2\text{C}=\text{CHSiR}_3] : [\text{ether}] : [\text{Ru}] = 1 : 5 : 1 \times 10^{-2}$ ) and toluene as an internal standard were added. The sealed ampoules were heated at the required conditions. The composition of the reaction mixture was analyzed by GC. The yield was calculated by GC using the internal standard method. The reaction products were identified using authentic samples synthesized by catalytic reaction in the presence of  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  and/or  $\text{RuCl}(\text{SiMe}_3)(\text{CO})(\text{PPh}_3)_2$ , as described previously.<sup>7</sup>

### Labelling experiments

**Reaction of  $\text{HDC}=\text{CDSiMe}_3$  with  $\text{H}_2\text{C}=\text{CHOEt}$  catalyzed by  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ .**  $(\text{PCy}_3)_2\text{Cl}_2\text{R}=\text{CHPh}$  (0.001 g,  $1.22 \times 10^{-6}$  mol), benzene (0.3 ml),  $\text{HDC}=\text{CDSiMe}_3$  (0.012 g,  $1.17 \times 10^{-4}$  mol) and  $\text{H}_2\text{C}=\text{CHOEt}$  (0.044 g,  $6.11 \times 10^{-4}$  mol) were placed in a 2 ml glass ampoule, which was heated at 60 °C for 6 h. The reaction mixture was analyzed by GC-MS. Two isomers of  $(\text{EtO})\text{HC}=\text{CHSiMe}_3$ , accompanied by traces of  $\text{d}_1$  and  $\text{d}_2$  products, were identified.

**Stoichiometric reaction of  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}(\text{OEt})$  with  $\text{D}_2\text{C}=\text{CDSiMe}_3$ .**  $(\text{PCy}_3)_2\text{Cl}_2\text{R}=\text{CH}(\text{OEt})$  (0.005 g,  $6.32 \times 10^{-6}$  mol) was dissolved in 0.3 ml  $\text{C}_6\text{D}_6$  in a 2 ml glass ampoule. Then  $\text{D}_2\text{C}=\text{CDSiMe}_3$  ( $6.5 \times 10^{-4}$  g,  $6.30 \times 10^{-6}$  mol) was added with a syringe. The ampoule was sealed and heated at 60 °C for 24 h. The reaction mixture was analyzed by  $^1\text{H}$  NMR. No signals indicating H/D coupling in the vinyl group or in any region of the spectrum were observed after reaction.

**Reaction of  $\text{D}_2\text{C}=\text{CDSiMe}_3$  with  $\text{H}_2\text{C}=\text{CHSiMe}_3$  in the presence of  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}(\text{OEt})$ .**  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}(\text{OEt})$  (0.001 g,  $1.26 \times 10^{-6}$  mol) was dissolved in 0.3 ml  $\text{C}_6\text{D}_6$  in a 2 ml glass ampoule. Then  $\text{D}_2\text{C}=\text{CDSiMe}_3$  ( $1.3 \times 10^{-4}$  g,  $1.26 \times 10^{-6}$  mol) and  $\text{H}_2\text{C}=\text{CHSiMe}_3$  ( $1.3 \times 10^{-4}$  g,  $1.30 \times 10^{-6}$  mol) were added. The ampoule was sealed and heated at 60 °C for 24 h.  $^1\text{H}$  NMR analysis of the reaction mixture shows that all resonances assigned to vinylic protons of  $\text{H}_2\text{C}=\text{CHSiMe}_3$  are accompanied by new multiplets of similar chemical shifts.

### Stoichiometric reactions

$(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (**I**, 0.010 g,  $1.22 \times 10^{-5}$  mol) and 0.001 g anthracene (internal standard) were dissolved in 0.6 ml of  $\text{C}_6\text{D}_6$  in a NMR tube. Then vinyl ethyl ether ( $1.2 \mu\text{l}$ ,  $1.25 \times 10^{-5}$  mol) was added. The reaction was carried out in a closed NMR tube at room temperature and monitored by  $^1\text{H}$  NMR. Quantitative reaction was observed after 3 h.

$(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}_2$  (**III**, 0.005 g,  $6.69 \times 10^{-6}$  mol) and 0.0005 g anthracene (internal standard) were dissolved in 0.6 ml of  $\text{C}_6\text{D}_6$  in an NMR tube. Then vinyl ethyl ether ( $0.64 \mu\text{l}$ ,  $6.69 \times 10^{-6}$  mol) was added. The reaction was carried out in a closed NMR tube at room temperature or at 60 °C and controlled by  $^1\text{H}$  NMR. In another reaction a 100-fold excess of vinyl ethyl ether was used.

$(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}(\text{OEt})$  (**II**, 0.003 g,  $3.79 \times 10^{-6}$  mol) and 0.0003 g anthracene (internal standard) were dissolved in 0.6 ml of  $\text{C}_6\text{D}_6$  in an NMR tube. Then an equimolar amount of  $\text{CH}_2=\text{CHSiMe}_3$  or  $\text{CH}_2=\text{CHSi}(\text{OEt})_3$  were added. The reaction was carried out in an NMR tube at room temperature (or at 60 °C) and monitored by  $^1\text{H}$  NMR. No expected metathesis products were observed. The decomposition of ethoxycarbene complex **II**, leading to unidentified products was the only change observed in the system. IR spectra show the presence of  $\text{Ru}(\text{CO})$  ( $\nu = 1933 \text{ cm}^{-1}$ ) and the absence of  $\text{Ru}-\text{H}$  bonds in the decomposed complex **II**.

### Synthesis of $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}(\text{OEt})$

$(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (0.050 g,  $6.07 \times 10^{-5}$  mol) was dissolved in benzene in a Schlenk tube. Then vinyl ethyl ether

( $5.8 \mu\text{l}$ ,  $6.06 \times 10^{-5}$  mol) was added. The mixture was stirred for 3 h at room temperature. The contents were evaporated in vacuum to dryness, followed by work up with 5 ml of methanol. The reddish solid was filtered off, washed 3 times with 5 ml of methanol and dried in vacuum. Yield 0.021 g (44%) based on Ru carbene complex used.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ : 1.05 (t, 3H)  $\text{CH}_3$ ; 1.10–2.30 (m, 66H)  $\text{PCy}_3$ ; 3.82 (q, 2H)  $\text{OCH}_2$ ; 14.76 (s, 1H)  $=\text{CH}$ .  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  34.99.

### Representative procedure for the synthesis of $(Z,E)$ -1-trimethylsilyl-2-alkoxyethene

$(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (0.0287 g,  $3.49 \times 10^{-5}$  mol), benzene (0.5 ml), vinyltrimethylsilane (0.35 g,  $3.45 \times 10^{-3}$  mol) and vinyl propyl ether (1.48 g,  $17.2 \times 10^{-3}$  mol) were placed in a 20 ml glass ampoule under argon. The ampoule was sealed and heated at 60 °C for 24 h. The reaction mixture was distilled to yield  $(Z/E)$ -1-trimethylsilyl-2-propoxyethene (bp 110–120 °C, 0.45 g, 82%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.12 (s, 9H)  $\text{SiMe}_3$  (E); 0.29 (s, 9H)  $\text{SiMe}_3$  (Z); 0.83 (t, 3H)  $\text{CH}_3$  (E), 0.77 (t, 3H)  $\text{CH}_3$  (Z); 1.51 (m, 2H)  $\text{CH}_2$  (E); 1.34 (m, 2H)  $\text{CH}_2$  (Z); 3.42 (t, 2H)  $\text{OCH}_2$  (E); 3.31 (t, 2H)  $\text{OCH}_2$  (Z); 4.52 (d, 1H,  $J = 15.0$  Hz)  $\text{CHSi}$  (E); 4.29 (d, 1H,  $J = 8.4$  Hz)  $\text{CHSi}$  (Z); 6.53 (d, 1H,  $J = 15.0$  Hz)  $\text{CHO}$  (E); 6.38 (d, 1H,  $J = 8.4$  Hz)  $\text{CHO}$  (Z).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{H}_6$ ): 0.24  $\text{SiMe}_3$  (E); 0.63  $\text{SiMe}_3$  (Z); 11.16  $\text{CH}_3$  (E); 10.94  $\text{CH}_3$  (Z); 23.17  $\text{CH}_2$  (E); 23.89  $\text{CH}_2$  (Z); 69.56  $\text{OCH}_2$  (E); 74.11  $\text{OCH}_2$  (Z); 95.44  $\text{CHSi}$  (E); 100.36  $\text{CHSi}$  (Z); 157.04  $\text{CHO}$  (E); 159.32  $\text{CHO}$  (Z). MS [ $m/z$  (rel. int.)]: 158 (M, 11) (E); 158 (M, 8) (Z); 143 (23) (E); 143 (21) (Z); 118 (17) (E); 118 (14) (Z); 117 (100) (E); 117 (100) (Z); 75 (18) (E); 75 (14) (Z). Anal. calcd. for  $\text{C}_8\text{H}_{18}\text{OSi}$ : C, 60.69; H, 11.46; Found: C, 60.01; H, 11.50.

### Acknowledgement

This work was supported by Grant No 13 T09A 074 from the State Committee for Scientific Research (Poland).

### References

- For recent reviews on metathesis of silicon-containing olefins see: (a) K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, London, 1997; E. Finkel'shtein and B. Marciniak, in *Progress in Organosilicon Chemistry*, eds. B. Marciniak and J. Chojnowski, Gordon and Breach, Langhorne, 1995, p. 443.
- R. R. Schrock, R. T. DePue, J. Feldman, K. B. Yap, D. C. Yag, W. M. Davis, L. Park, M. DiMare, M. Schofield, J. Anhaus, E. Walborsky, E. Evitt, C. Kruger and P. Betz, *Organometallics*, 1990, **9**, 2262.
- F. J. Feher, D. Soulivong, A. G. Eklund and K. Wyndham, *Chem. Commun.*, 1997, 1185.
- K. B. Wagener and D. W. Smith, *Macromolecules*, 1991, **24**, 6073.
- C. Pietraszuk, B. Marciniak and H. Fischer, *Organometallics*, 2000, **19**, 913.
- (a) Y. Wakatsuki, Y. Yamazaki, M. Nakano and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1991, 703; (b) B. Marciniak and C. Pietraszuk, *J. Chem. Soc., Chem. Commun.*, 1995, 2003; (c) B. Marciniak and C. Pietraszuk, *Organometallics*, 1997, **16**, 4320; (d) B. Marciniak and M. Lewandowski, *Tetrahedron Lett.*, 1997, **38**, 3777; (e) B. Marciniak, E. Walczuk-Gusciora and C. Pietraszuk, *Catal. Lett.*, 1998, **55**, 125; (f) T. Mise, Y. Takaguchi, T. Umemiya, S. Shimizu and Y. Wakatsuki, *Chem. Commun.*, 1998, 699; (g) B. Marciniak, C. Pietraszuk and M. Kujawa, *J. Mol. Catal.*, 1998, **133**, 41; (h) B. Marciniak, *New J. Chem.*, 1997, **21**, 815; (i) B. Marciniak and J. Guliński, *J. Organomet. Chem.*, 1984, **266**, C19; (j) B. Marciniak, C. Pietraszuk and Z. Foltynowicz, *J. Organomet. Chem.*, 1994, **474**, 83; (k) F. Kakiuchi, A. Yamada, N. Chatani, S. Murai, N. Furukawa and Y. Seki, *Organometallics*, 1999, **18**, 2033.
- B. Marciniak, M. Kujawa and C. Pietraszuk, *Organometallics*, 2000, **19**, 1677.

- 8 Z. Wu, S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1995, **117**, 5503.
- 9 B. Chaudret and R. Poilblanc, *Organometallics*, 1985, **4**, 1722.
- 10 B. Marciniak, Z. Foltynowicz, C. Pietraszuk, J. Guliński and H. Maciejewski, *J. Mol. Catal.*, 1994, **90**, 213.
- 11 B. Marciniak, C. Pietraszuk and Z. Foltynowicz, *J. Mol. Catal.*, 1992, **76**, 307.
- 12 C. P. Lenges, P. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 1999, **121**, 4385.
- 13 B. Marciniak, E. Walczuk-Gusciora and P. Blaziejewska-Chadyniak, *J. Mol. Catal.*, in press.
- 14 P. Schwab, M. B. France, J. W. Ziegler and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2039.