

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

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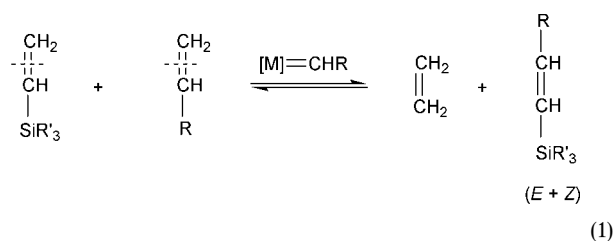
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Grubbs complex, $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ (**I**) is a very effective catalyst of the cross-disproportionation of vinyl-trisubstituted silanes $\text{H}_2\text{C}=\text{CHSiR}_3$ [where $\text{R}_3 = \text{Me}_3, \text{PhMe}_2, (\text{OEt})_3$] with vinyl alkyl ethers $\text{H}_2\text{C}=\text{CHOR}'$ [where $\text{R}' = \text{ethyl, propyl, butyl, } t\text{-butyl, } t\text{-pentyl, } 2\text{-(ethyl)hexyl, cyclohexyl, trimethylsilyl}$] 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 Ru-H and/or Ru-Si complexes reported previously (80°C).⁷ 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 Ru-H bond formation *via* the hydrovinylation with vinylsilanes.

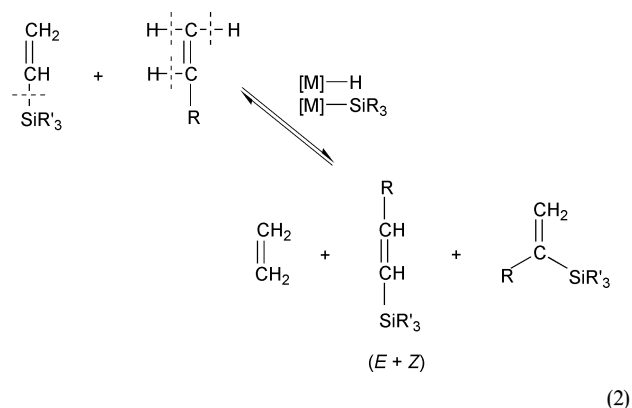
Many metallocarbenes (Mo, W and Ru) catalyze the metathetical conversion of silicon-containing olefins.¹ However, the effective self-metathesis as well as acyclic diene metathesis (ADMET) polymerization of vinyl-substituted organosilicon olefins and dienes (*e.g.*, vinylsilanes and divinyl-diorganosilanes), even in the presence of well-defined Mo, W, Ru complexes, has not been reported yet. The inactivity of metallocarbene 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.²

However, reports on ruthenium–carbene-complex catalyzed cross-metathesis of vinyl-substituted silsesquioxanes with alkenes³ and ADMET copolymerization of divinyl-dimethylsilane with dienes,⁴ as well as our recent successful experiments on the cross-metathesis of vinyltrialkoxysilanes and vinyl-trisiloxysilanes with styrene,⁵ 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 metallocarbene mechanism.



On the other hand, recent reports on the disproportionation of vinyl-substituted silicon compounds and their co-disproportionation (trans-silylation) with olefins⁶ catalyzed by ruthenium, rhodium and cobalt complexes containing (or generating) M-H and 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:

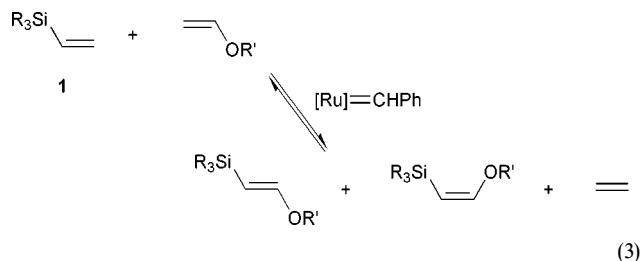


The mechanism of the latter type of silylolefin conversion was evidenced by stoichiometric reactions including an insertion of ethylene,^{6a} styrene^{6c} and vinylsilane^{6b} into Ru-Si bonds. Our recent synthetic examinations confirm the non-metallacarbene mechanism for Ru-H and/or Ru-Si complexes catalyzing the reaction of vinyl alkyl ethers with vinyl-trisubstituted silanes, yielding a mixture of (*E* + *Z*) 1-silyl-2-alkoxyethenes.⁷ 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

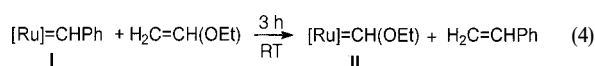
The reaction of vinyl-trisubstituted silanes with vinyl alkyl ethers proceeds in the presence of the Grubbs catalyst, $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$, at 60°C according to eqn (3)



where $\text{SiR}_3 = \text{SiMe}_3$ (**1a**), SiMe_2Ph (**1b**) and 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.⁷ 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 methylenide 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

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^a

R	Yield (%)	<i>E/Z</i>
Ethyl	99	4
Propyl	96 (90 ^b) (3 ^c) (90 ^d)	2.5 (2 ^b) (3 ^d)
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

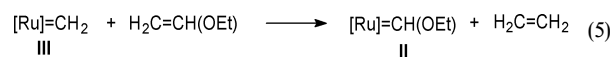
^a Reaction conditions: 60 °C, 24 h, argon, sealed glass ampoules, $[\text{H}_2\text{C}=\text{CHSiMe}_3] : [\text{ether}] : [\text{catalyst}] = 1 : 5 : 1 \times 10^{-2}$, except for ^b (1 : 5 : 5×10^{-3}) and ^c (1 : 5 : 2×10^{-3}). ^d $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH(OEt)}$ (**II**) was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

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

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

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

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 methylenide 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 R = 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 $\text{R}_3\text{SiCH}=\text{CH}_2 + \text{R}'\text{OCH}=\text{CH}_2 + \text{Ru}-\text{H}$ (Ru–Si) lead apparently to ambiguous conclusions.⁷ 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.⁷ 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.*⁸ 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.⁸

However, ¹H NMR experiments showed, at room temperature, a slow decomposition of $(\text{TFA})_2(\text{PPh}_3)_2\text{RuCH(OR)}$ (R = Et, CH_2Ph) accompanied by the formation of a hydride complex (resonance at –17.5 ppm in ¹H NMR spectrum),⁸ which also slowly disappeared after several days. In our system $[\text{CH}_2=\text{CHSiMe}_3$ 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 ¹H 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.⁸ 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 $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ 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.⁷ The respective cyclohexylphosphine complex (obtained from **I**) can react in the same way as the triphenylphosphine complex.⁹ The previously observed silylative coupling of olefins with vinylsilanes and vinylsiloxanes catalyzed by $\text{RuCl}_2(\text{CO})_3$,^{6d,10} $\text{Ru}_3(\text{CO})_{12}$,¹¹ $\text{Cp}^*\text{Rh}(\text{H}_2\text{C}=\text{CHSiMe}_3)_2$ ¹² and $[(\text{cod})\text{Rh}(\mu\text{-OSiMe}_3)]_2$,¹³ supported by some stoichiometric experiments,¹² 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

$[\text{H}_2\text{C}=\text{CHSiR}_3] : [\text{ether}] : [\text{Ru}] = 1 : 5 : 1 \times 10^{-2}$) 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.⁷

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, 1.22×10^{-6} mol), benzene (0.3 ml), $\text{HDC}=\text{CDSiMe}_3$ (0.012 g, 1.17×10^{-4} mol) and $\text{H}_2\text{C}=\text{CHOEt}$ (0.044 g, 6.11×10^{-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 d_1 and 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, 6.32×10^{-6} mol) was dissolved in 0.3 ml C_6D_6 in a 2 ml glass ampoule. Then $\text{D}_2\text{C}=\text{CDSiMe}_3$ (6.5×10^{-4} g, 6.30×10^{-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 ^1H 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 $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}(\text{OEt})$. $(\text{PCy}_3)_2\text{Cl}_2\text{R}=\text{CH}(\text{OEt})$ (0.001 g, 1.26×10^{-6} mol) was dissolved in 0.3 ml C_6D_6 in a 2 ml glass ampoule. Then $\text{D}_2\text{C}=\text{CDSiMe}_3$ (1.3×10^{-4} g, 1.26×10^{-6} mol) and $\text{H}_2\text{C}=\text{CHSiMe}_3$ (1.3×10^{-4} g, 1.30×10^{-6} mol) were added. The ampoule was sealed and heated at 60 °C for 24 h. ^1H 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, 1.22×10^{-5} mol) and 0.001 g anthracene (internal standard) were dissolved in 0.6 ml of C_6D_6 in a NMR tube. Then vinyl ethyl ether ($1.2 \mu\text{l}$, 1.25×10^{-5} mol) was added. The reaction was carried out in a closed NMR tube at room temperature and monitored by ^1H NMR. Quantitative reaction was observed after 3 h.

$(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CH}_2$ (**III**, 0.005 g, 6.69×10^{-6} mol) and 0.0005 g anthracene (internal standard) were dissolved in 0.6 ml of C_6D_6 in an NMR tube. Then vinyl ethyl ether ($0.64 \mu\text{l}$, 6.69×10^{-6} mol) was added. The reaction was carried out in a closed NMR tube at room temperature or at 60 °C and controlled by ^1H 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, 3.79×10^{-6} mol) and 0.0003 g anthracene (internal standard) were dissolved in 0.6 ml of C_6D_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 ^1H 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, 6.07×10^{-5} mol) was dissolved in benzene in a Schlenk tube. Then vinyl ethyl ether

($5.8 \mu\text{l}$, 6.06×10^{-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. ^1H NMR (C_6D_6) δ : 1.05 (t, 3H) CH_3 ; 1.10–2.30 (m, 66H) PCy_3 ; 3.82 (q, 2H) OCH_2 ; 14.76 (s, 1H) $=\text{CH}$. ^{31}P NMR (C_6D_6) δ 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, 3.49×10^{-5} mol), benzene (0.5 ml), vinyltrimethylsilane (0.35 g, 3.45×10^{-3} mol) and vinyl propyl ether (1.48 g, 17.2×10^{-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%). ^1H NMR (C_6D_6) δ 0.12 (s, 9H) SiMe_3 (E); 0.29 (s, 9H) SiMe_3 (Z); 0.83 (t, 3H) CH_3 (E), 0.77 (t, 3H) CH_3 (Z); 1.51 (m, 2H) CH_2 (E); 1.34 (m, 2H) CH_2 (Z); 3.42 (t, 2H) OCH_2 (E); 3.31 (t, 2H) OCH_2 (Z); 4.52 (d, 1H, $J = 15.0$ Hz) CHSi (E); 4.29 (d, 1H, $J = 8.4$ Hz) CHSi (Z); 6.53 (d, 1H, $J = 15.0$ Hz) CHO (E); 6.38 (d, 1H, $J = 8.4$ Hz) CHO (Z). ^{13}C NMR (C_6H_6): 0.24 SiMe_3 (E); 0.63 SiMe_3 (Z); 11.16 CH_3 (E); 10.94 CH_3 (Z); 23.17 CH_2 (E); 23.89 CH_2 (Z); 69.56 OCH_2 (E); 74.11 OCH_2 (Z); 95.44 CHSi (E); 100.36 CHSi (Z); 157.04 CHO (E); 159.32 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.

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