840 *Organometallics* **2002,** *21,* 840−845

Cross-Metathesis of Vinylsilanes with Allyl Alkyl Ethers Catalyzed by Ruthenium−Carbene Complexes

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Received August 3, 2001

The cross-metathesis of vinyltrialkoxy- and vinyltrisiloxysilanes as well as divinyltetraethoxydisiloxane with various allyl alkyl ethers catalyzed by $Cl_2(PCy_3)_2Ru({=}CHPh)$ **(I)** is presented. The reaction is accompanied by self-metathesis of allyl alkyl ethers. The catalytic examination presented in this paper has allowed us to develop optimum conditions for selective synthesis of 1-silyl-3-alkoxy-propenes $(R'O)_3SiCH{=}CHOR$ (where R = Et, *n*-Bu, Cy, Ph, $PhCH_2$, Gly, Me_3Si, R′ = Me, Et, $SiMe_3$) with high preference of the *E*-isomers (*E*/*Z* > 7:1). This allowed the selective isolation of the *E*-isomer. A stoichiometric study of **I** with substrates has been carried out. The results are discussed on the basis of a metallacarbene mechanism.

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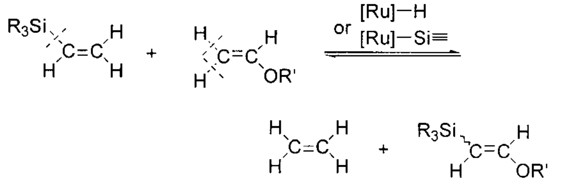
Introduction

Alkenylsilanes, especially vinyl- and allylsilanes, have become a commonly used class of organosilicon reagents in organic synthesis.[1] However, the study of their transformation by olefin metathesis has been limited. Vinylsilanes (mainly trimethylsilyl derivatives) were prepared using traditional methods, i.e., hydroboration of silylalkyne derivatives followed by alcoholysis of the B−C bond,[2] hydrogenation of silylalkynes using palladium catalysts,[1c] and silylation of terminal alkenes with halogenotrimethylsilane in the presence of organomagnesium[3a] and organolithium[3b] compounds. In the past decade the silylative coupling of vinyltrisubstituted silanes with a variety of olefins, catalyzed by ruthenium and rhodium complexes, was developed. Novel and well-known silicon-containing olefins were prepared by this procedure.[4] Silylative coupling of vinyl alkyl ethers with vinylsilanes catalyzed by ruthenium complexes involving or generating Ru−H/and Ru−Si bonds has proved to be an effective method for synthesis of l-silyl-2-(alkoxy)ethenes.[5] The reaction, catalyzed initially by a Ru−carbene complex (Grubbs' catalyst), also gives such products but according to the nonmetallacarbene mechanism, i.e., via an intermediately generated Ru−H bond.[6]



(1)

where: $SiR_3 = SiMe_3$, $SiMe_2Ph$, R′ = alkyl, aryl

On the other hand, recent reports on the activity of well-defined functional group tolerant molybdenum carbene complexes in the ring-opening cross-metathesis (AROM/CM) of norbornene[7] or ruthenium carbenes in RCM of acyclic silyl ether dienes,[8] the cross-metathesis of vinyl-substituted silsesquioxanes with alkenes,[9] and above all highly efficient cross-metathesis of vinyltrialkoxy- and vinyltrisiloxysilanes with styrene,[10] *p*-substituted styrenes, l-alkenes, allyl derivatives,[11] 5-hexen-l-yl acetate[12] and degradation of 1,4-polybutadienes[13] have opened new opportunities for the wide application of the olefin metathesis in organosilicon chemistry.

Well-defined ruthenium carbenes have been reported recently as efficient catalysts of ring-closing metathesis of dienes and for cross-metathesis involving functionalized olefins[14] (e.g., functionalized unsaturated alcohols,[14e,f] sulfones,[14g] phosphonates,[14h] fluorinated olefins[14i]). Therefore, the aim of this work was to develop a synthetic method for l-silyl-3-(alkoxy)propenes using cross-metathesis of vinyl-substituted silanes with allyl

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Publication on Web 02/07/2002

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Table 1. Effect of Alkyl Substituent of Allyl Alkyl Ether $ROCH_2CH{=}CH_2$ in Its Cross-Metathesis with Vinyltriethoxysilane Catalyzed by $Cl_2(PCy_3)_2Ru({=}CHPh)$ (I) on the Yield and Selectivity of the Products[i]

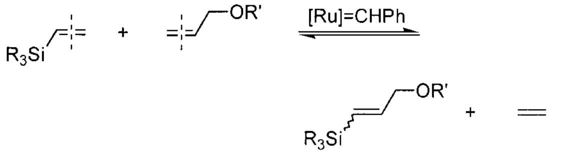
R	conversion of $ROCH_2CH{=}CH_2$ [%]	yield (isolated yield) of (E+Z) $ROCH_2CH{=}CHSi(OEt)_3$ [%]	E/Z	yield of $ROCH_2CH{=}CHCH_2OR$ [%]
ethyl	81	74 (73)	6/1	7
n-butyl	85	75 (75)	7/1	10
	91[a]	86	7/1	5
	88[b]	86	7/1	traces
	100[c]	95	6/1	5
	78[d]	67	6/1	11
	63[e]	52	7/1	11
	50[f]	38	10/1	12
	30[g]	22	11/1	8
	100[h]	91	3/1	9
cyclohexyl	80	50	5/1	30
phenyl	80	72 (70)	5/1	8
benzyl	100	86[16]	12/1	14
glycydyl	70	50 (45)	8/1	20
trimethylsilyl	85	65[17]	9/1	20

[a] $[H_2C{=}CHSi(OEt)_3]$:[ether] = 10:1. [b] $[H_2C{=}CHSi(OEt)_3]$:[ether] = 15:1. [c] $[H_2C{=}CHSi(OEt)_3]$:[ether] = 3:1 (allyl ether added in portions during first 2 h). [d] $[Cl_2(PCy_3)_2Ru({=}CHPh)]$:[ether] = 2×10^{-2}:5:1. [e] $[Cl_2(PCy_3)_2Ru({=}CHPh)]$:[ether] = 1×10^{-2}:5:1. [f] Room temperature. [g] Closed system. [h] $[Cl_2(PCy_3)$(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)$Ru({=}CHPh)$ **(II)**]. [i] Reaction conditions: $[Cl_2(PCy_3)_2Ru({=}CHPh)]$:$[H_2C{=}CHSi(OEt)_3]$:[ether] = 5×10^{-2}:5:1, CH_2Cl_2, reflux, 3 h, argon.

alkyl ethers in the presence of ruthenium−carbene complexes (mainly Grubbs' catalyst $Cl_2(PCy_3)_2Ru({=}CHPh)$ **(I)**). The reaction of vinyltriethoxysilane with allyl phenyl ether was reported previously as an example of the cross-metathesis of vinylsilanes with olefins.[11]

Results and Discussion

Catalytic Examinations. The reactions of vinyltrisubstituted silanes with allyl alkyl ethers proceed in the presence of ruthenium alkylidene complex according to eq 2, giving two isomeric products, (E/Z)-1-silyl-3-(alkoxy)propenes and ethylene. The yield of the products (two isomers, E+Z) is essentially equal to the percent conversion of the allyl alkyl ether used.



(2)

where: $SiR_3 = Si(OEt)_3$, $Si(OMe)_3$, $Si(OSiMe_3)_3$,
R' = alkyl, aryl $Si(OEt)_2[OSi(OEt)_2(CH{=}CH_2)]$

The results of reactions of vinyltriethoxysilane with various allyl alkyl ethers carried out in the presence of the Grubbs' catalyst $Cl_2(PCy_3)_2Ru({=}CHPh)$ are compiled in Table 1. Although a 5-fold excess of vinylsilane is used, the products (two isomers, E+Z) of cross-metathesis are accompanied by products of self-metathesis of ethers, i.e., $R'OCH_2CH{=}CHCH_2OR'$. However, when a 15-fold excess of vinylsilane is used and the ethylene is removed from an open reaction system by a gentle flow of argon, a high conversion of the allyl alkyl ether and almost quantitative selectivity to silyl(alkoxy)propene were observed. When the metathesis was carried at room temperature (in an open system), a 50% conversion of allyl *n*-butyl ether was observed with E/Z = 10:1, but when in the closed system, the same reaction gave only 30% conversion of the allyl ether.

A decrease in the initial concentration of the Ru−carbene catalyst in the range 5×10^{-2} to 1×10^{-2} diminished the yield of the products, but an increase of the catalyst concentration (5×10^{-2}) during a 3 h reaction time gave a slight enhancement of the final conversion (from 82% to 88%) of the allyl *n*-butyl ether and of the selectivity (from 75% to 80%) of the E+Z product. Apparently, the well-known decomposition of the ruthenium−carbene catalyst during the reaction is responsible for this effect.

In contrast to silylative cross-coupling of vinylsilanes with allyl compounds[5,6] and other transformations of the latter, no products of allyl−vinyl isomerization were observed in the present work since the isomerization of allyl derivatives in the presence of ruthenium complexes occurs predominantly above 60 °C. Therefore, the cross-metathesis of allyl alkyl ethers with vinylsilanes carried out at ≤40 °C exclude such a side process.

The conclusion that removal of ethylene and the excess of vinylsilane causes a shift to the right of the reversible cross-metathesis with allyl alkyl ethers agrees with earlier observations made by Grubbs[8,12] and those in our work.[10,11] A replacement of the Ru−benzylidene **(I)** by the more active $Cl_2(PCy_3)$(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)$Ru{=}CHPh$ (**II**) increases the conversion of the allyl ether but does not change the final selectivity of the silyl(alkoxy)propenes.

The catalytic results provide a basis for a synthesis of silyl derivatives of ethers. Selected synthetic procedures are described in the Experimental Section. The products were isolated (E isomer) and characterized by ^1H NMR spectroscopy, GS−MS, and elemental analysis. Results of the examinations of the cross-metathesis of vinyl-substituted silanes with alkenes obtained to date have revealed that the metathetical conversion significantly decreases when the alkoxy or siloxy substitutents

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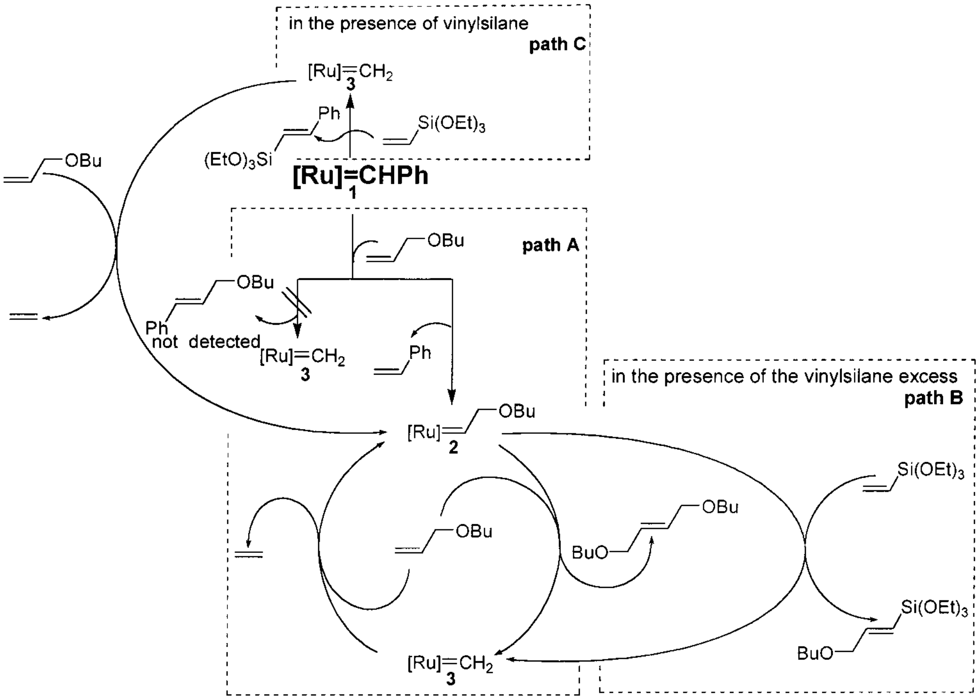
Table 2. Cross-Metathesis of Allyl *n*-Butyl Ether and Allyl Phenyl Ether with Selected Vinyltrisubstituted Silanes[a]

	allyl *n*-butyl ether		allyl phenyl ether	
$H_2C{=}CHSiR_3$ SiR$_3$	yield of (isolated yield of) (E+Z) $BuOCH_2CH{=}CHSiR_3$ [%]	E/Z	yield of (E+Z) $PhOCH_2CH{=}CHSiR_3$ [%]	E/Z
$Si(OMe)_3$	86[b] (80)	5/1	69[b]	5/1
$Si(OSiMe_3)_3$	80 (76)	9/1	81	4/1
$Si(OEt)_2[OSi(OEt)_2CH{=}CH_2]$	75[c] (75)	16/1		

[a] Reaction conditions: $[Cl_2(PCy_3)_2Ru({=}CHPh)]:[H_2C{=}CHSi(OR)_3]:[ether] = 5 \times 10^{-2}:5:1$, CH_2Cl_2, reflux, 3 h, argon. [b] 1 h. [c] $[H_2C{=}CHSi(OEt)_2OSi(OEt)_2CH{=}CH_2]:[ether] = 2:1$.

Scheme 1



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in vinyltri(alkoxy) or vinyltri(siloxy)silanes are replaced by other groups.[10,11]

Stoichiometric reactions of the Grubbs' carbene complex with vinylmethyl-substituted silanes provided the first evidence for β-silyl migration in a metallacyclobutane followed by reductive elimination of an allylsilane. This constitutes a terminating step in the Ru–carbene-catalyzed cross-metathesis of olefins with methyl-substituted vinylsilanes.[15] According to the above experiment, we have essentially limited the cross-metathesis with allyl alkyl ethers to vinylsilanes with other oxygen-containing substituents at silicon, to eliminate the possibility of β-SiR$_3$ transfer. The results are compiled in Table 2.

Divinyltetraethoxydisiloxane was tested in the process according to the general procedure, i.e., using a 2-fold excess of this compound relative to allyl ether to yield finally E+Z products of only one vinyl group at silicon with allyl *n*-butyl ether, $BuOCH_2CH{=}CHSi(OEt)_2OSi(OEt)_2CH{=}CH_2$.

Stoichiometric Study. To shed light on the mechanism of the process and, in particular, to obtain information about the individual steps of the catalytic cycle, the stoichiometric reactions of **1** with allyl *n*-butyl ether in molar ratio 1:1, with allyl *n*-butyl ether and vinylsilane in molar ratio 1:1:1, and with allyl *n*-butyl ether and vinylsilane in molar ratio 1:2:10 were examined.

The reaction of the Grubbs' catalyst with allyl *n*-butyl ether resulted in formation of styrene and 3-(alkoxy)-propylidene complex **2**. This process is accompanied by a series of subsequent reactions as illustrated in Scheme 1 (path A).

The composition of selected components of the reaction mixture system is presented in Figure 1. Changes in the concentrations of allyl *n*-butyl ether and its homometathesis products were omitted for clarity.

Styrene and propylidene complex **2** were detected after 5 min. Ethylene and the self-metathesis product also were detected at the very first stages of the reaction. The study of the system containing the Grubbs' complex, allyl *n*-butyl ether, and vinyltriethoxysilane using a molar ratio of 1:1:1 revealed that the Grubbs' catalyst reacts with both the allyl ether (Scheme 1, path A) and the vinylsilane (path C) with the formation of styrene and a styrylsilane, respectively. A series of reactions occurring in such a system is also illustrated in Scheme 1. The stoichiometric reaction of **1** with vinylsilanes was reported previously;[10] it occurs as presented at the top of Scheme 1. Also, in this case, the

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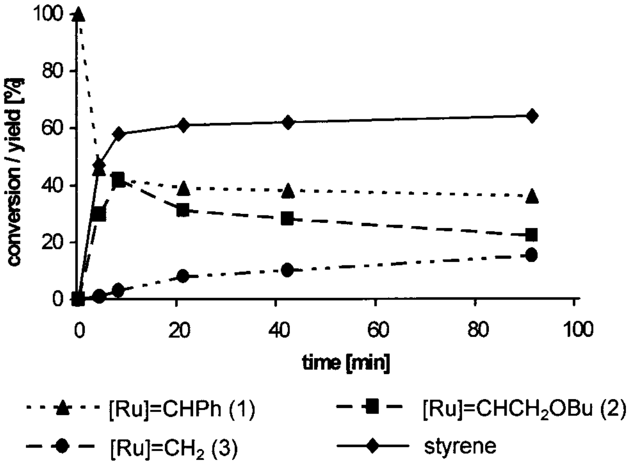

Figure 1. Composition of initial substrates and products of the equimolar reaction of **I** with allyl *n*-butyl ether with time.

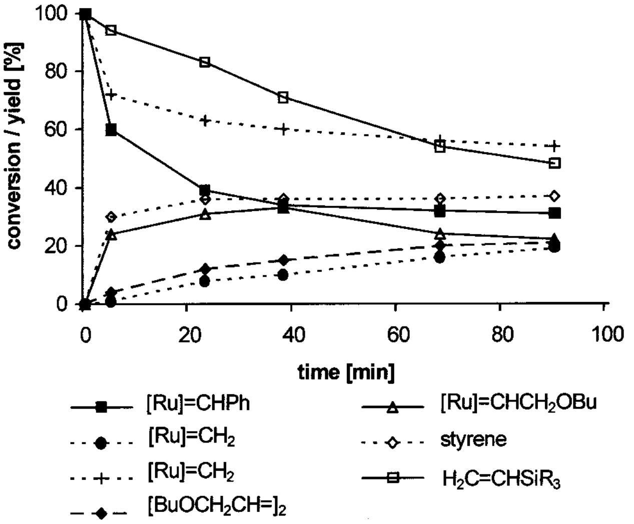

Figure 2. Composition of initial substrates and products of the examined reaction of **I** with allyl *n*-butyl ether and vinyltriethoxysilane with time.

formation of ethylene and the product of self-metathesis of allyl *n*-butyl ether were observed after 5 min. After 1 h reaction time only traces of the product of the cross-metathesis of vinylsilane with allyl *n*-butyl ether (path B) were observed, which indicates a much higher reactivity of the ruthenium butoxypropylidene complex with allyl *n*-butyl ether than with the vinylsilane. The composition of selected components of the reaction mixture is given in Figure 2. Changes of concentrations of the silylstyrene were omitted for clarity.

As the catalytic process must be carried out using an excess of vinylsilane in order to avoid formation of allyl ether homo-metathesis product, another experiment was performed in which the progress of a reaction of a system containing Grubbs' complex (**I**), allyl *n*-butyl ether, and the vinylsilane in molar ratio 1:2:10 was followed by ^{1}H NMR spectroscopy. The distribution of ruthenium between carbene complexes **1**, **2**, and **3** and noncarbene (unidentified) complexes vs reaction time is presented in Figure 3.

Analysis of this relationship reveals a few implications important from the catalytic point of view. The initiator ([Ru]=CHPh) is not completely consumed in the system (path A and/or C, Scheme 1), even in the presence of an excess of the reactants. After 2.5 h some amount of **1** is still present in the reaction mixture. Effective decomposition of carbene complexes takes place in the reaction system. After 1.5 h only 60% of the initial total carbene concentration was detected. As the reaction progressed, the concentration of methylidene complex **3** as well as of its content in the total carbene concentration in the system increased. After 1.5 h **3** constituted 60 mol % of the overall carbene content.

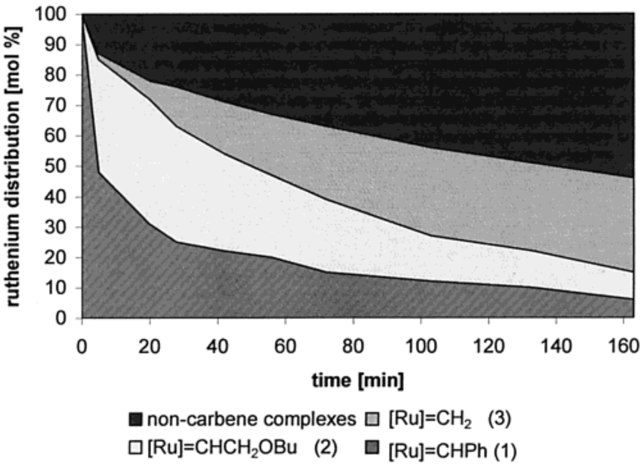

Figure 3. Distribution of ruthenium complexes with time of the reaction of **I** with allyl *n*-butyl ether and vinyltriethoxysilane in the ratio 1:2:10.

The most important catalytic conclusions that follow from the series of stoichiometric reactions are that ruthenium methylidene **3** is the predominant carbene complex formed in the reaction mixture and that the concentration of the real catalyst is much lower than can be expected from the amount of the initiator used. The excess of the vinylsilane, necessary in catalytic examinations to avoid the formation of the homometathesis product, contributes to the effective formation of the [Ru]=CH$_2$ complex, which, unfortunately, readily undergoes nonmetathetical decomposition. In view of the above, an important conclusion is that an addition of some amounts of the allyl ether during the reaction would enhance the final yield of the cross-metathesis product. This observation was confirmed experimentally (see Table 1).

Mechanistic Implications. The results of the catalytic studies and stoichiometric reactions of the substrates with **I** as well as previously reported results on the cross-metathesis of vinylsilanes with styrene[10] and other olefins[11] have led us to propose a reasonable mechanism for the catalytic reaction of vinylsilanes with allyl alkyl ethers occurring in the presence of Grubbs' complex (see Scheme 1).

As we have previously stated,[10] dissociation of PCy$_3$ from the initial complex **I** generates a coordinatively unsaturated and catalytically active complex **1**. The stoichiometric study has definitively shown that both substrates react competitively with **1** (to yield **2**) when an equimolar ratio of substrates is used and with **3** in 5−15-fold excess of vinylsilane.

According to the general metathetical mechanism, both reactions occur via the respective ruthenacycles (omitted in Scheme 2 for clarity), which are converted immediately to give ruthenium carbenes **2** and **3**. The

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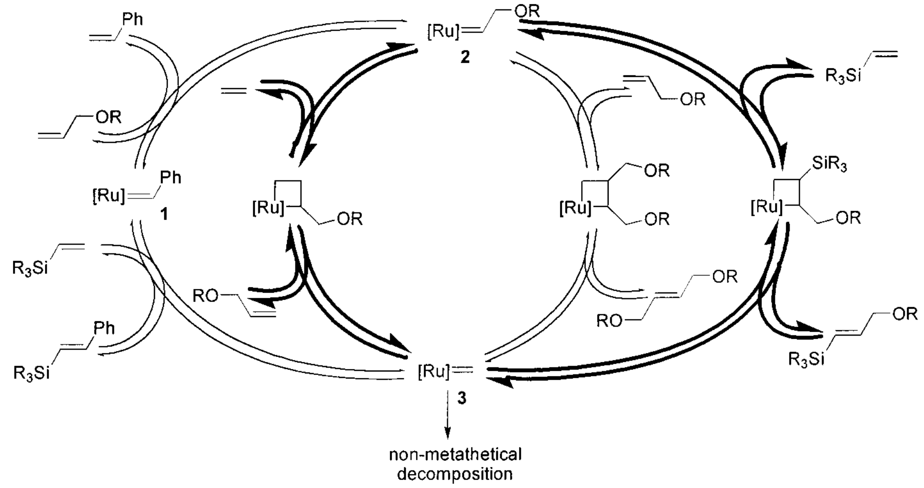
Scheme 2



two products of the above-discussed elementary pathways. i.e., styrene and silylstyrene, have also been confirmed in the stoichiometric studies. When equimolar amounts of the substrates are used, **2** and **3** react more readily with allyl ethers to yield the products of their self-metathesis. However, the catalytic as well as stoichiometric reactions performed using an excess of the vinylsilanes favor the cross-metathesis, e.g., the highest, 15-fold, excess of vinyltriethoxysilane over allyl *n*-butyl ether gives exclusively silyl(alkoxy)ethene. Thus the reaction of **2** with vinylsilane to yield ruthenium methylidene **3** is the crucial step in the catalytic cycle, ensuring high selectivity of the cross-metathesis process. Similarly as in the previously reported systems, the substrate-independent decomposition of **3** is the factor reducing the concentration of the catalytically active species. A more active next generation Grubbs' catalyst, containing more sterically hindered ligands (see catalyst **II**, Table 1), might improve the catalytic activity of $[Ru]{=}CH_2$ and simultaneously reduce its decomposition. It is necessary to mention that the competitive reaction of **3** with vinyltrialkoxysilanes, reported previously,[10] leads to exchange of the methylidene unit but does not produce the silylcarbene complex. An isomerization of allyl alkyl ethers was not observed when the starting ether was used alone, nor in products of the cross-metathesis, which confirms that [Ru]−H complexes are not generated in situ under the conditions ($T \leq 40$ °C) tested.

It can be finally concluded that ruthenium−carbenes (Grubbs' complex (**I**)) catalyze effectively the cross-metathesis of vinyltrialkoxy- and vinyltrisiloxysilanes (also divinyltetraethoxydisiloxane) to give, under optimum conditions (10−15-fold excess of the vinylsilane), 1-silyl-3-(alkoxy)propenes with high preference for the *E*-isomer, as illustrated by the exclusive isolation of the *E*-isomer. Detailed stoichiometric studies and the results of catalytic experiments enable us to propose a reasonable catalytic cycle for the cross-metathesis involving also self-metathesis of allyl alkyl ethers, which, however, can be eliminated by using an excess of the vinylsilane.

Experimental Section

General Experimental Procedures. All syntheses and catalytic tests were carried out under argon. ^1H NMR spectra of isolated products were recorded in C_6D_6 on a Varian Gemini 300 VT spectrometer (300 and 75 MHz, respectively). When necessary for a correct signal assignment, COSY (^1H, ^1H) 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 ethyl ether, allyloxytrimethylsilane, and allyl glycydyl ether from Aldrich, allyl *n*-butyl ether from Fluka, vinylsilanes (vinylsiloxane) from ABCR, benzene-d_6 from Dr. Glaser A.G., $Cl_2(PCy_3)_2Ru({=}CHPh)$ (**I**) and $Cl_2(PCy_3)$(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)Ru=CHPh (**II**) d from Strem Chemicals, dodecane from Aldrich, and dichloromethane from POCh (Poland).

Prior to use all solvents were dried and distilled over CaH_2 in argon. All liquid reagents were distilled, dried with molecular sieves, and degassed by repeated freeze−pump−thaw cycles.

Catalytic Reactions. In the typical procedure, an oven-dried flask equipped with a condenser and a magnetic stirrer bar was charged under argon with CH_2Cl_2, dodecane (internal standard), the vinylsilane (vinyldisiloxane), and the respective allyl alkyl ether. The reaction mixture was stirred and heated to maintain a gentle reflux. The ruthenium benzylidene complex **I** was added, and the progress of the reaction was monitored by GC before and 3 h after addition of the complex. The conversion of the substrates was calculated using the internal standard method.

Stoichiometric Reactions. In an NMR tube 0.01 g (1.21×10^{-5} mol) of **I**, 0.001 g of anthracene (internal standard), and 0.7 mL of C_6D_6 were placed under argon and an ^1H NMR spectrum was recorded. Then 1.8 μL (1.21×10^{-5} mol) of allyl *n*-butyl ether was added, and the reaction was monitored by ^1H NMR sepctroscopy at room temperature.

Similar experiments were performed in systems containing the Grubbs' complex, allyl *n*-butyl ether, and vinyltriethoxysilane in molar ratios [Ru]:[ether]:[vinylsilane] = 1:1:1 and [Ru]:[ether]:[vinylsilane] = 1:2:10. In these experiments the mixture of ether and vinylsilane was added to the C_6D_6 solution of **I**.

Representative Procedure for the Synthesis of New Products of Cross-Metathesis. The syntheses were performed under argon using **I** as the catalyst and dry and deoxygenated reagents and solvents. An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under argon with CH_2Cl_2 (5 mL), the vinylsilane (37.86 mmol), and the allyl ether (2.55 mmol). The reaction mixture was stirred and heated to maintain a gentle reflux.

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Published on February 7, 2002 on http://pubs.acs.org | doi: 10.1021/om0107035

The ruthenium benzylidene complex **I** (0.13 mmol) was added, and the reaction was carried out for 3 h. In all cases the *E*-isomer was isolated. No standard was added. The solvent was removed under atmospheric pressure. The product was isolated by distillation in a vacuum.

Analytical Data of New Products. (*E*)-1-Triethoxysilyl-3-ethoxypropene, (*E*)-EtOCH$_2$CH=CHSi(OEt)$_3$. ^{1}H NMR (C_6D_6, ppm, coupling constants in Hz): δ 6.64 (dt, J = 18.8, 4.3; 1H) (=CH); 5.98 (dt, J = 18.8, 1.8; 1H) (=CHSi); 3.78−3.96(m, 8H) (OCH$_2$; =CH*CH$_2$*O); 3.58 (q, J = 7.0; 2H) (OCH$_2$); 1.18(t; J = 7.0; 9H) (CH$_3$); 1.09 (t, J = 7.0; 3H) (CH$_3$). MS, *m*/*z* (%): 249 (M, 2), 203 (13), 175 (49), 163 (77), 131 (36), 119 (100), 79 (33). Anal. Calcd for $C_{11}H_{24}O_4Si$: C, 53.23; H, 9.68. Found: C, 52.94; H, 9.54. Bp: 78 °C/1 mmHg.

(*E*)-1-Triethoxysilyl-3-*n*-butoxypropene, (*E*)-*n*-BuOCH$_2$-CH=CHSi(OEt)$_3$. ^{1}H NMR (C_6D_6, ppm, coupling constants in Hz): δ 6.64 (dt, J = 18.9, 4.2; 1H) (=CH); 5.98 (dt, J = 18.8, 1.8; 1H) (=CHSi); 3.80−3.90 (m, 8H) (OCH$_2$; =CH*CH$_2$*O); 3.27 (q, J = 7.0; 2H) (=CHC*H$_2$*O); 1.30−1.60 (m, 4H) (CH$_2$); 1.19 (t; J = 7.0; 9H) (CH$_3$); 0.87 (t, J = 7.0; 3H) (CH$_3$). MS, *m*/*z* (%): 275 (M,1), 231 (10), 219 (35), 175 (78), 163 (100), 131 (45), 119 (91). Anal. Calcd for $C_{13}H_{28}O_4Si$: C, 56.52; H, 10.14. Found: C, 56.86; H, 10.36. Bp: 80 °C/1 mmHg.

(*E*)-1-Triethoxysilyl-3-phenyloxypropene, (*E*)-PhOCH$_2$-CH=CHSi(OEt)$_3$. ^{1}H NMR (C_6D_6, ppm, coupling constants in Hz): δ 7.08−7.18 (m, 3H) (Ph); 6.73−6.95 (m, 2H) (Ph); 6.64 (dt, J = 18.8, 4.3; 1H) (=CH); 6.00 (dt, J = 18.8, 1.2; 1H) (=CHSi); 4.23 (m, 2H) (=CHC*H$_2$*O); 3.82 (q, J = 7.1, 6H) (OCH$_2$); 1.18 (t; J = 7.1; 9H) (CH$_3$). MS, *m*/*z* (%): 295 (M, 23), 267 (44), 252 (87), 223 (40), 163 (100), 159 (48), 119 (96). Bp: 122 °C/1 mmHg.

(*E*)-1-Triethoxysilyl-3-glicydyloxypropene, (*E*)-GlyOCH$_2$-CH=CHSi(OEt)$_3$. ^{1}H NMR (C_6D_6, ppm, coupling constants in Hz): δ 6.62 (dt, J = 18.2, 4.2; 1H) (=CH); 5.98 (dt, J = 18.2, 1.2; 1H) (=CHSi); 3.78−4.07 (m, 8H) (OCH$_2$; =CH*CH$_2$*O); 3.50 (dd, J = 11.5, 3.0, 1H) (CH$_2$); 3.14 (dd, J = 11.5, 5.8) (CH$_2$); 2.91 (m, 1H) (CH); 2.55 (dd, J = 5.0, 4.1, 1H) (CH$_2$, *epoxy*); 2.35 (dd, J = 5.2, 2.5; 1H) (CH$_2$, *epoxy*); 1.09 (t, J = 7.0, 9H) (CH$_3$). MS, *m*/*z* (%): 275 (M, 2), 231 (29), 175 (45), 163 (83), 135 (43), 119 (100), 79 (40). Bp: 115 °C/1 mmHg.

(*E*)-1-(Vinyltetraethoxydisiloxanyl)-3-butoxypropene, (*E*)-*n*-BuOCH$_2$CH=CHSi(OEt)$_2$OSi(OEt)$_2$CH=CH$_2$. ^{1}H NMR (C_6D_6, ppm, coupling constants in Hz): δ 6.70 (dt, J = 18.8, 4.2; 1H) (=CH); 5.96−6.21 (m, 4H) (*H$_2$*C=C*H*Si; =C*H*Si); 3.82−3.96 (m, 10H) (OCH$_2$; =CH*CH$_2$*O); 3.25 (t, J = 7.0; 2H) (OCH$_2$); 1.20 (t; J = 7.0; 12H) (CH$_3$); 0.83 (t, J = 7.3; 3H) (CH$_3$). MS, *m*/*z* (%): 392 (M,1), 346 (15), 279 (100), 273 (79). Anal. Calcd for $C_{19}H_{40}O_8Si_3$: C, 47; H, 8.33. Found: C, 47.76; H, 8.68. Bp: 96 °C/mmHg.

(*E*)-1-Triethoxysilyl-3-cyclohexoxypropene, (*E*)-CyOCH$_2$-CH=CHSi(OEt)$_3$. MS, *m*/*z* (%): 301 (M, 1), 191 (73), 174 (100), 159 (33), 135(26), 119 (60), 79 (28).

(*E*)-1-Triethoxysilyl-3-benzyloxypropene, (*E*)-PhOCH$_2$-CH=CHSi(OEt)$_3$. MS, *m*/*z* (%): 309 (M, 3), 189 (26), 175 (34), 163 (76), 131 (77), 119 (57), 91 (100).

(*E*)-1-Triethoxysilyl-3-(trimethylsiloxy)propene, (*E*)-Me$_3$SiOCH$_2$CH=CHSi(OEt)$_3$. MS, *m*/*z* (%): 292 (M, 2), 279 (100), 235 (80), 207 (31), 163 (55), 119 (47), 79 (22).

(*E*)-1-Trimethoxysilyl-3-*n*-butoxypropene, (*E*)-*n*-BuOCH$_2$-CH=CHSi(OMe)$_3$. ^{1}H NMR (C_6D_6, ppm, coupling constants in Hz): δ 6.62 (dt, J = 18.9, J = 4.2; 1H) (=CH); 5.94 (dt, J = 18.9, J = 1.5; 1H) (=C*H*Si); 3.83 (dd, J = 4.0, J = 1.5; 2H) (CH$_2$O*CH$_2$*CH=); 3.24 (t, J = 6.3; 2H) (*CH$_2$*OCH$_2$CH); 1.45−1.52 (m;2H) (CH$_2$); 1.29−1.39 (m; 2H) (CH$_2$); 0.86 (t, J = 4.8; 3H) (CH$_3$). MS, *m*/*z* (%): 234 (M, 3), 203 (23), 177 (49), 145 (55), 121 (100), 115 (26), 91 (66).

(*E*)-1-Trimethoxysilyl-3-phenoxypropene, (*E*)-PhOCH$_2$-CH=CHSi(OMe)$_3$. MS, *m*/*z* (%): 253 (M, 17), 222 (30), 131 (31), 121 (100), 107 (15), 91 (78), 59 (19).

(*E*)-1-Tris(trimethylsiloxanyl)silyl-3-*n*-butoxypropene, (*E*)-*n*-BuOCH$_2$CH=CHSi(OSiMe$_3$)$_3$. ^{1}H NMR (C_6D_6, ppm, coupling constants in Hz): δ 6.49 (dt, J = 18.9, J = 4.2; 1H) (=CH); 5.96 (dt, J = 18.9, J = 1.8; 1H) (=CHSi); 3.87 (dd, J = 4.2; J = 1.8; 2H) (CH$_2$O*CH$_2$*CH=); 3.29 (t, J = 6.3, 2H) (*CH$_2$*OCH$_2$CH=); 1.41−1.57 (m, 2H) (CH$_2$); 1.24−1.39 (m, 2H) (CH$_2$); 0.86 (t, J = 4.5; 3H) (CH$_3$); 0.23 (s; 27H) (CH$_3$). MS, *m*/*z* (%): 407 (M, 1), 351 (100), 335 (31), 321 (24), 281 (68), 207 (17), 73 (22).

(*E*)-1-Tris(trimethylsiloxanyl)silyl-3-phenoxypropene, (*E*)-PhOCH$_2$CH=CHSi(OSiMe$_3$)$_3$. MS, *m*/*z* (%): 428 (M, 43), 323 (30), 295 (15), 207 (100), 191 (41), 163 (3), 73 (59).

Acknowledgment. This work was supported by Grants No. 1649/T09/2000/19 and PBZ-KBN 15/T09/99/01g from The State Committee for Scientific Research (Poland). The authors thank Dr. S. Krompiec for sending allyl cyclohexyl ether, allyl phenyl ether, and allyl benzyl ether.

OM0107035