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# Competitive-consecutive reaction of vinyltrimethylsilane with triethylsilane catalyzed by ruthenium complexes[†]

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**Summary** – A complex reaction of vinyltrimethylsilane with triethylsilane catalyzed by ruthenium carbonyl and ruthenium phosphine complexes and performed at 80-130°C in air or oxygen-free conditions was followed by GC-MS. Catalytic examinations and identification of the products (**I-X**) allowed us to propose a general scheme for the competitive-consecutive reaction in which the complexes containing Ru-H and Ru-Si bonds play the role of key intermediates.

**ruthenium complex / dehydrogenative silylation / metathesis / vinyltrimethylsilane / triethylsilane**

## Introduction

The catalytic conversion of the mixture of trisubstituted silane and unsaturated organic substrate in the presence of transition metal complexes involves several processes. Although the hydrosilylation reaction usually dominates, especially in the equimolar systems [1, 2], some other processes also occur, namely, silane redistribution, silylation and dehydrogenative silylation, particularly for catalysts based on the Fe, Ru and Os and the Co, Rh and Ir triads (see [3] and references therein).

In the last decade, a few papers have been published on the application of ruthenium complexes (mainly Ru(0) carbonyls) in trisubstituted silane/olefin systems, where high yields of unsaturated silanes (the products of dehydrogenative silylation) were obtained. The products of the silane reactions with alkenes [4-7], their halogen derivatives [8], and alkynes [9], include hydrosilylation adducts, although their presence is not always recorded, *eg*, for the $(C_2H_5)_3SiH$/styrene system [10]. Dehydrogenative silylation offers a new synthesis of alkenylsilanes or bis(silyl)alkenes (in the case when silicon-containing olefins are used as reaction reagents [11, 12]). The bis(silyl)alkenes form a new class of monomers and/or comonomers for polymerization/polycondensation processes.

Our comprehensive study on the hydrosilylation of vinyl-trisubstituted silanes (mostly vinyltrialkoxysilanes) in the presence of ruthenium phosphine complexes [11] indicated that the "regular" hydrosilylation (eq 1a) is accompanied by two different processes, dehydrogenative silylation (eq 1b) and metathesis of vinylsilanes (eq 2), when trialkoxysilanes and Ru(II) phosphine complexes are employed. Moreover, hydrosilanes act as promoters for the ruthenium-catalyzed metathesis (disproportionation) of vinylsilanes [13].

$$\equiv SiH + CH_2{=}CHSi\equiv \xrightarrow{[Ru]} \equiv SiCH_2CH_2Si\equiv \qquad (1a)$$

$$\phantom{\equiv SiH + CH_2{=}CHSi\equiv} \xrightarrow{[Ru]} \equiv SiCH{=}CHSi\equiv + CH_3CH_2Si\equiv \qquad (1b)$$

$$2\ \equiv SiCH{=}CH_2 \xrightarrow{[Ru]} \equiv SiCH{=}CHSi\equiv + CH_2{=}CH_2 \qquad (2)$$

Seki *et al* [12] studied $Ph_3SiH$ and $(C_2H_5)_3SiH$ reaction with vinyltrimethylsilane in the presence of $Ru_3(CO)_{12}$, and they observed only some of the dehydrogenative silylation and the metathesis products $R_3SiCH{=}CHSi(CH_3)_3$ (R = Et, Ph) and $(CH_3)_3SiCH{=}CHSi(CH_3)_3$, respectively. This reaction was carried out at different ratios of the substrate and under mild conditions in an open system under an argon atmosphere. The dehydrogenative silylation of vinyltriethoxysilane by triethylsilane on ruthenium carbonyl clusters was mentioned during a recent conference [6].

In this paper we describe in detail a series of experiments in which ruthenium precursors of different nature and different substrate molar ratios (triethylsilane and vinyltrimethylsilane were the silanes chosen) were applied. We then determine their influence on the selectivity of the products. The aim of this work is to identify all the products observed as well as to explain their origin in view of the proposed scheme for catalysis by ruthenium complexes. A part of this material was already presented in the form of a symposium communication [14].

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[†] Dedicated to Professor Raymond Calas in recognition of his distinguished contribution to organosilicon chemistry.

* Correspondence and reprints

**Table I.** Reaction of vinyltrimethylsilane with triethylsilane catalyzed by ruthenium carbonyl complexes.

| No | Catalyst | Atmosphere | $CH_2{=}CHSi(CH_3)_3$ conversion [%] | $(C_2H_5)_3SiH$ conversion [%] | Product selectivity [%] (GLC) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **I** | **II** | **III** | **IV** | **V** | **VI** | **VII** | **VIII-X** |
| $[(C_2H_5)_3SiH]:[CH_2{=}CHSi(CH_3)_3] = 1{:}10$ | | | | | | | | | | | | |
| 1 | $Ru_3(CO)_{12}$ | air | 65 | 100 | 11 | 11 | 0 | 59 | 8 | 0 | 0 | 11[b] |
| 2 | $Ru_3(CO)_{12}$ | argon | 71 | 100 | 18 | 11 | 0 | 62 | 9 | 0 | 0 | 0 |
| 3 | $[RuCl_2(CO)_3]_2$ | air | 68 | 100 | 10 | 10 | 0 | 64 | 12 | 0 | 0 | 4 |
| $[(C_2H_5)_3SiH]:[CH_2{=}CHSi(CH_3)_3] = 1{:}1$ | | | | | | | | | | | | |
| 4 | $Ru_3(CO)_{12}$ | air | 100 | 90 | 22 | 23 | 4 | 3 | 6 | 28 | 10 | 4 |
| 5 | $Ru_3(CO)_{12}$ | argon | 100 | 75 | 32 | 16 | 1 | 9 | 1 | 25 | 14 | 2 |
| 6 | $Ru_3(CO)_{12}$[a] | argon | 100 | 50 | 43 | 10 | 0 | 3 | 6 | 22 | 16 | 0 |
| 7 | $[RuCl_2(CO)_3]_2$ | air | 100 | 83 | 19 | 26 | 3 | 5 | 2 | 26 | 13 | 6 |

130°C, 6 h, glass ampoules; $[CH_2{=}CHSi(CH_3)_3]:[cat]:[C_6H_6] = 1{:}10^{-2}{:}160$

[a] 80°C, 4 h, $C_6H_6$ reflux; $[(C_2H_5)_3SiH]:[CH_2{=}CHSi(CH_3)_3]:[cat] = 1{:}1{:}2.5 \times 10^{-3}$; [b] **VIII** only.

## Results and discussion

Our interest in this field stems from the preliminary investigation of triethoxysilane/vinyltriethoxysilane/$RuCl_2(PPh_3)_3$ system [11]. It was not previously possible to distinguish between the dehydrogenative silylation and metathesis products because the substituents at both silicon atoms were identical and therefore it was necessary to change the nature of the substrate. The reaction of vinyltrimethylsilane with triethylsilane was studied as a model system at 130°C in air and an oxygen-free atmosphere, in closed systems and in the presence of several Ru complexes (for details, see *Experimental section*). Ruthenium carbonyl and ruthenium phosphine complexes were used as ruthenium precursors, and complexes with Ru-H and/or Ru-Si bonds were also applied, either as well-defined compounds or formed *in situ* when ruthenium chlorophosphine complexes, *eg* $RuCl_2(PPh_3)_3$ and triethylsilane, were present in the reaction mixture [15].

Depending on the ratio of substrates and the nature of the precursor, a certain number of products were observed. Two main competitive processes, dehydrogenative silylation and metathesis, were accompanied by others, such as hydrosilylation and hydrogenation of the C=C bond, migration of silyl groups, and reactions of triethylsilane with ethene. In all cases there were several reactions products (eq 3), which were followed by GC-MS.

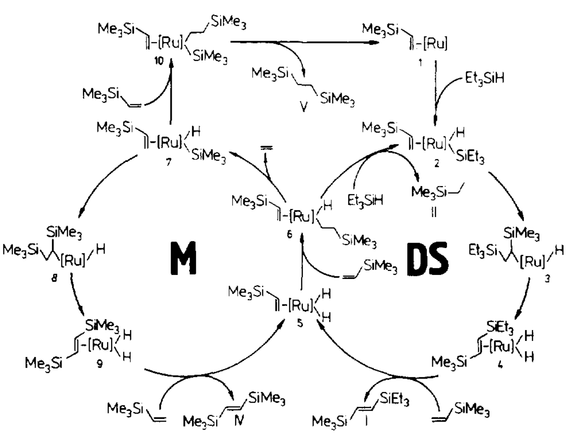
$$\begin{aligned}
&(CH_3)_3SiCH{=}CH_2 + HSi(C_2H_5)_3 \\
&\xrightarrow{[Ru]} \underset{\mathbf{I}}{(CH_3)_3SiCH{=}CHSi(C_2H_5)_3} + \underset{\mathbf{II}}{(CH_3)_3SiC_2H_5} \\
&+ \underset{\mathbf{III}}{(CH_3)_3SiCH_2CH_2Si(C_2H_5)_3} \\
&+ \underset{\mathbf{IV}}{(CH_3)_3SiCH{=}CHSi(CH_3)_3} \\
&+ \underset{\mathbf{V}}{(CH_3)_3SiCH_2CH_2Si(CH_3)_3} + \underset{\mathbf{VI}}{(C_2H_5)_4Si} \\
&+ \underset{\mathbf{VII}}{(C_2H_5)_3SiCH{=}CHSi(C_2H_5)_3} \qquad (3)
\end{aligned}$$

The formation of siloxane by-products $(CH_3)_3SiOSi(CH_3)_3$ **VIII**, $(C_2H_5)_3SiOSi(C_2H_5)_3$ **IX** and $(CH_3)_3SiOSi(C_2H_5)_3$ **X**, which are found in some catalytic systems under oxygen conditions, is due to the presence of oxygen in the reaction mixture. Small amounts of ethane and ethene were present in the reaction mixtures as gaseous products (GC-MS). Additionally, polymeric products were detected in several experiments but at very low yields.

The results of our test reaction performed in the presence of Ru(0) and Ru(II) carbonyls are presented in table I.

Seki *et al* investigated the reaction of vinyltrimethylsilane with triethylsilane in the presence of $Ru_3(CO)_{12}$ [12], but under milder conditions (oxygen-free atmosphere, 70-80°C, 4 h, $C_6H_6$ as a solvent). They reported the formation of only two products, **I** and **IV**, independent of the substrate ratio, but they suggested that two competing reactions occur, namely, dehydrogenative silylation (eq 1b) and disproportionation (metathesis) of vinyltrimethylsilane (eq 2). Surprisingly, no $C_2H_5Si(CH_3)_3$ **II**, a common coproduct of dehydrogenative silylation, was detected. Unfortunately, the authors did not mention any gaseous products, which may have evolved (*eg* ethene and ethane). We performed the above reaction under conditions reported by Seki *et al* [12]. An equimolar reaction occurred yielding several other products (see entry 6 in table I), as well as **I** and **IV**, mentioned by Seki *et al*, we found $Si(C_2H_5)_4$ **VI**, $(CH_3)_3SiC_2H_5$ **II** and $(C_2H_5)_3SiCH{=}CHSi(C_2H_5)_3$ **VII**. Traces of ethene and ethane were also detected in the gas phase.

For the initial ten-fold excess of vinylsilane (see table I), regular metathesis product **IV** dominates, regardless of the ruthenium carbonyl complex used in the reaction conditions applied (130°C, 6 h, air, glass ampoules). As well as equimolar amounts of the products of the dehydrogenative silylation of vinyltrimethylsilane (**I** + **II**), bis(trimethylsilyl)ethane **V** was unexpectedly formed in high yields. The siloxane **VIII** observed for the $Ru_3(CO)_{12}$-catalyzed reactions presumably derives from the oxygenation of $[Ru][Si(CH_3)_3]_2$ species. Formation of all the products formed under the mentioned conditions (exemplary for $Ru_3(CO)_{12}$ catalyst) can be roughly accounted for by the catalytic cycles presented in scheme 1.



**Scheme 1.** 1. Catalytic cycles for the reaction of vinyltrimethylsilane with triethylsilane in the presence of ruthenium complexes. DS : dehydrogenative silylation; M : metathesis (disproportionation).

The model scheme assumes oxidative addition of triethylsilane to Ru(0) carbonyl followed by insertion of vinylsilane into [Ru]-Si≡ bond with elimination of 1-triethylsilyl-2-trimethylsilylethene **I** and addition of [Ru]-H into the next molecule of vinylsilane to release ethyltrimethylsilane **II**, which completes the dehydrogenative silylation (DS) pathway. A competitive metathesis process (M) starts from complex **6** in scheme 1, involving elimination of ethene followed by the insertion of vinylsilane into Ru-Si bond to give finally the metathesis product **IV**. Hydrogenation of ethene by H-Ru-H species leads to ethane, observed in gaseous products. Competitive insertion of vinylsilane into the Ru-H bond (from **7** to **10** in scheme 1) can easily explain the formation of product **V**. The formation of **VIII** is apparently a result of oxygenation of Ru-Si bond in the complex containing two bonded silyl groups and testifies to the presence of such Ru complexes in the catalytic cycle(s).

The promoting role of $HSi(C_2H_5)_3$ in the $Ru_3(CO)_{12}$-catalyzed metathesis of $CH_2{=}CHSi(CH_3)_3$ is well evidenced [16]. The best effect is observed for equimolar ratio of silane and Ru precursor ($Ru_3(CO)_{12}$), *ie* when $[CH_2{=}CHSi(CH_3)_3]:[HSi(C_2H_5)_3] = 10^2$. In the same reaction conditions as applied for other experiments presented in table I 44% conversion of vinylsilane was noted after 6 h, but practically only product **IV** was observed (with selectivity > 90%). Without hydrosilane cocatalysis, only 17% conversion of vinylsilane (mostly toward metathesis product **IV**) was noted. It was also reported previously that $Ru_3(CO)_{12}$ reacts with trialkylsilanes leading to the break up of the trinuclear structure, affording di- and mononuclear derivatives [17]. On the other hand, $[Ru_3(\mu\text{-}H)(CO)_{11}]^-$, which is active in hydrosilylation, reacts with triethylsilane (room temperature, THF) to give the trinuclear derivative $\{Ru_3(\mu\text{-}H)[Si(C_2H_5)_3]_2(CO)_{10}\}^-$, which has two σ-bound $Si(C_2H_5)_3$ ligands [18]. Consequently, $[Ru]\text{-}Si(C_2H_5)_3$ and [Ru]-H species are really responsible for the formation of all the products observed. A direct treatment of $Ru_3(CO)_{12}$ with vinyltrimethylsilane also leads to formation of the $[Ru]\text{-}Si(CH_3)_3$ species [16].

For the initial 1:1 ratio of the substrates (see table I), products other than beside the above-mentioned (**I**, **II**, **IV**, **V** and **VIII**) were formed; **III**, **VI** and **VII** were also found. Compound **III** is a product of regular hydrosilylation :

$$(CH_3)_3SiCH{=}CH_2 + HSi(C_2H_5)_3 \xrightarrow{[Ru]} \underset{\textbf{III}}{(CH_3)_3SiCH_2CH_2Si(C_2H_5)_3} \quad (4)$$

Compound **III** is formed via complex **2** in scheme 1 transformation to $(C_2H_5)_3Si\text{-}Ru\text{-}CH_2CH_2Si(CH_3)_3$ species, followed by elimination of product **III** in the presence of vinylsilane molecule, leading back to the complex **1**. The presented simplified model omitted several pathways, involving the insertion of vinylsilane into the Ru-Si bonds of various $R_3Si\text{-}[Ru]\text{-}SiR_3$ and/or $H\text{-}[Ru]\text{-}SiR_3$ species. Each of these can initiate new cycle, yielding unsaturated and saturated products.

The presence of products **VI** and **VII** can be explained by the following stoichiometric reactions of triethylsilane with ethene evolved during the metathetic conversion of vinylsilanes.

$$HSi(C_2H_5)_3 + CH_2{=}CH_2 \xrightarrow{[Ru]} \underset{\textbf{VI}}{(C_2H_5)_3SiCH_2CH_3} \quad (5)$$

$$HSi(C_2H_5)_3 + 2\,CH_2{=}CH_2 \xrightarrow{[Ru]} \underset{\textbf{XI}}{(C_2H_5)_3SiCH{=}CH_2} + CH_3CH_3 \quad (6)$$

$$2\,(C_2H_5)_3SiCH{=}CH_2 \xrightarrow{[Ru]} \underset{\textbf{VII}}{(C_2H_5)_3SiCH{=}CHSi(C_2H_5)_3} + CH_2{=}CH_2 \quad (7)$$

It can also be noted that some metathetic conversions of both vinylsilanes lead to **I**, producing next ethene molecule :

$$\underset{\textbf{XI}}{(C_2H_5)_3SiCH{=}CH_2} + (CH_3)_3SiCH{=}CH_2 \xrightarrow{[Ru]} \underset{\textbf{I}}{(C_2H_5)_3SiCH{=}CHSi(CH_3)_3} + CH_2{=}CH_2 \quad (8)$$

Therefore, a separate study of the reactions of triethylsilane with ethene in the presence of $Ru_3(CO)_{12}$ (as well as $RuCl_2(PPh_3)_3$) was undertaken to directly confirm the existence of products **VI** and **VII** in the reaction examined. Results of this additional series are presented in table II.

**Table II.** Reaction of triethylsilane with ethene catalyzed by ruthenium complexes.

| No | Catalyst | $(C_2H_5)_3SiH$ conversion [%] | $CH_2{=}CH_2$ pressure | Product selectivity [%] (GLC) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | **VI** | **VII** | **IX** | **XI** | others |
| 1 | $Ru_3(CO)_{12}$ | 63 | - | 0 | 0 | 95 | 0 | 5 |
| 2 | $Ru_3(CO)_{12}$ | 100 | 3 atm | 56 | 8 | 2 | 29 | 5 |
| 3 | $Ru_3(CO)_{12}$ | 100 | 10 atm | 26 | 2 | 2 | 68 | 2 |
| 4 | $RuCl_2(PPh_3)_3$ | 45 | | 0 | 0 | 82 | 0 | 18 |
| 5 | $RuCl_2(PPh_3)_3$ | 100 | 3 atm | 45 | 0 | 5 | 45 | 5 |

130°C, 6 h, air, steel vessel; $[(C_2H_5)_3SiH]:[cat] = 10^2$.

**Table III.** Reaction of vinyltrimethylsilane with triethylsilane catalyzed by ruthenium phosphine complexes.

| No | Catalyst | Atmosphere | $CH_2{=}CHSi(CH_3)_3$ conversion [%] | $(C_2H_5)_3SiH$ conversion [%] | Product selectivity [%] (GLC) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **I** | **II** | **III** | **IV** | **V** | **VI** | **VIII-X** |
| | | | $[(C_2H_5)_3SiH]:[CH_2{=}CHSi(CH_3)_3] = 1{:}10$ | | | | | | | | |
| 1 | $RuCl_2(PPh_3)_3$ | air | 44 | 100 | 10 | 25 | 0 | 24 | 16 | 0 | 25 |
| 2 | $RuCl_2(PPh_3)_3$ | argon | 20 | 100 | 12 | 47 | 0 | trace | 41 | 0 | 0 |
| 3 | $RuH_2(PPh_3)_4$ | air | 35 | 100 | 17 | 33 | 0 | 25 | 25 | 0 | 0 |
| 4 | $RuH_3\{Si{\equiv}\}(PPh_3)_2$[a] | air | 30 | 100 | 18 | 46 | 0 | 18 | 18 | 0 | 0 |
| 5 | Solid A | air | 45 | 100 | 19 | 19 | 0 | 33 | 9 | trace | 20 |
| | | | $[(C_2H_5)_3SiH]:[CH_2{=}CHSi(CH_3)_3] = 1{:}1$ | | | | | | | | |
| 6 | $RuCl_2(PPh_3)_3$ | air | 85 | 68 | 23 | 39 | 4 | 3 | 11 | 11 | 9 |
| 7 | $RuCl_2(PPh_3)_3$ | argon | 60 | 44 | 31 | 43 | 0 | 5 | 12 | 9 | 0 |
| 8 | $RuCl_2(PPh_3)_3$ [b] | argon | < 5 | < 5 | trace | 0 | trace | 0 | 0 | 0 | trace |
| 9 | $RuH_2(PPh_3)_4$ | air | 100 | 75 | 28 | 39 | 4 | 3 | 2 | 11 | 13 |
| 10 | $RuH_3\{Si{\equiv}\}(PPh_3)_2$ | air | 80 | 60 | 16 | 34 | 5 | 6 | 20 | 13 | 6 |
| 11 | Solid A | air | 100 | 65 | 34 | 36 | 7 | 3 | 3 | 8 | 9 |

130°C, 6 h, glass ampoules: $[CH_2{=}CHSi(CH_3)_3]:[cat]:[C_6H_6] = 1{:}10^{-2}{:}160$

[a] $\{Si{\equiv}\} = \{Si(OC_2H_5)_3\}$; [b] 80°C, 4 h, $C_6H_6$ reflux; $[(C_2H_5)_3SiH]:[CH_2{=}CHSi(CH_3)_3]:[cat] = 1{:}1{:}2.5 \times 10^{-3}$.

It is worth emphasizing that under lower ethene pressure (similar to the conditions of the typical reaction of vinylsilane with triethylsilane) more tetraethylsilane **VI** and bis(silyl)ethene **VII** are yielded for $Ru_3(CO)_{12}$ presursor. It was previously reported that $\{Ru_3(\mu\text{-}H)[Si(C_2H_5)_3]_2(CO)_{10}\}^-$ catalyzes triethylsilane addition to ethene (100°C, 15 h) yielding both tetraethylsilane **VI** and vinyltriethylsilane **XI** [19]. The formation of traces of $(C_2H_5)_3SiOSi(C_2H_5)_3$ **IX** is apparently due to the oxygenation of triethylsilane. There is no direct redistribution of triethylsilane (see entry 1 in table II) under the conditions applied: almost all the silane is converted to siloxane **IX**.

In the presence of vinyltrimethylsilane, all the pathways of triethylsilane conversion following the DS and M cycles (scheme 1) include the insertion of ethene evolved during the metathesis into Ru-H and Ru-Si bonds. However, relatively low yields of the metathesis conversion of vinyltrimethylsilane under equimolar conversion of both substrates cannot directly account for the observed high yields of the $(C_2H_5)_4Si$ (see table I).

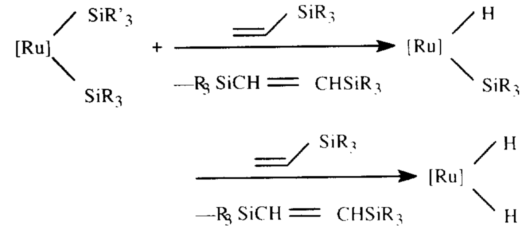
On the other hand, the sum of the unsaturated products **I** and **IV**, which can be formed via the pathways involving $CH_2{=}CH_2$ evolution, only confirms the high yield of **VI** when a different route (beside complex **6** to complex **2**, scheme 1) can be revealed in the formation of $C_2H_5Si(CH_3)_3$ **II**, *ie* via the "hydrogenation" of vinyltrimethylsilane. Such an explanation is particularly important in view of the high yield of **II** detected in the reactions of vinyltrimethylsilane with triethylsilane, catalyzed by ruthenium phosphine complexes (table III) since in this catalytic process practically always [**II**] > [**I**].

Therefore, the DS (see scheme 1) does not provide an adequate explanation for such a high yield of the hydrogenated product **II**.

It is well known that Ru(II) complexes react with hydrosilanes, giving ruthenium products with Ru-H and Ru-Si≡ bonds [20]. Under the same reaction conditions Ru(II) phosphine complexes form hydridosilyl species [21]. $RuCl_2(PPh_3)_3$ reacts with the excess of $(C_2H_5)_3SiH$ producing $RuHCl(PPh_3)_3 \cdot C_6H_6$ in benzene [15] *ie* forming a Ru-H bond. Therefore, well-defined ruthenium hydride and ruthenium hydridosilyl phosphine complexes were used as the precursors for the reaction examined. Additionally, a catalyst that was the product of preliminary treatment of $RuCl_2(PPh_3)_3$ with vinyltrimethylsilane (for details, see *Experimental section*) was placed in table III as solid A. Its spectroscopic analysis shows the presence of ruthenium carbonyl and phosphine species. No Ru-Si≡ species were found. The catalytic activity of this solid is very similar to other Ru carbonyl precursors (compare the yields of **I** and **II**).

Taking into account the promoting effect of the dioxygen in catalysis by ruthenium phosphine complexes [11] (which facilitates dissociation of phosphine ligand by its prior oxygenation), most experiments were carried out in dry air.

Essentially, almost all the results presented in tables I and III indicate a similar course of the reaction catalyzed by ruthenium carbonyl and ruthenium phosphine complexes. In the presence of phosphine complexes, no bis(triethylsilyl)ethene **VII** was yielded; this is easily confirmed by the lack of this product in the direct reaction of $(C_2H_5)_3SiH$ with ethene (see entry 5 in table II). Moreover, as was mentioned above, a high yield of **II** has been observed. This is presumably from the reaction of vinyltrimethylsilane bonded to H-[Ru]-H species. In general, these species can be formed during the vinylsilane molecule insertion into any Ru-Si bond of the complex containing $[Ru](SiR_3)_2$ species ($R = CH_3$ or $C_2H_5$) (in addition to pathways **4** → **5** and **9** → **5** in scheme 1). The presence of disiloxanes **VIII**, **IX** and **X** can be easily accounted for by direct oxygenation of such $[Ru](SiR_3)_2$ species.



(9)

$R = CH_3$, $R' = C_2H_5$

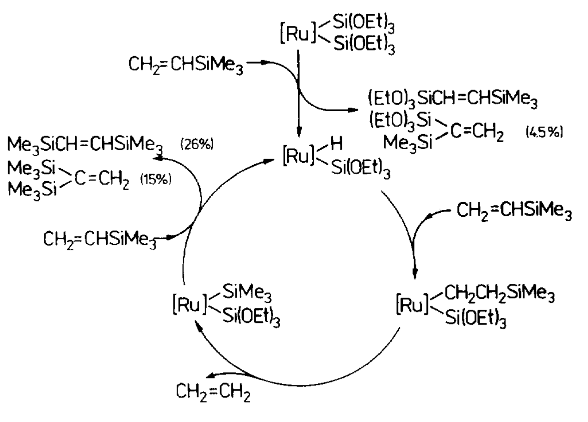
While ethene molecule insertion to Ru-Si≡ bonds has been reported by Wakatsuki [22], we recently reported [23], for the first time, the insertion of vinylsilane molecule into Ru-Si≡ bond, which occurs according to the following equation :

$$[Ru]\text{-}Si(CH_3)_3 + CH_2{=}CHSiR_3 \rightarrow [Ru]\text{-}H + (CH_3)_3SiCH{=}CHSiR_3 \qquad (10)$$

$[Ru] = RuCl(CO)(PPh_3)_2$;
$R_3 = (OC_2H_5)_3$, $(CH_3)_2Ph$, $(CH_3)_3$

We also found that bis(silyl)ruthenium complexes of general formula $[Ru]\text{-}\{Si(OR)_3\}_2$ [21] react with $CH_2{=}CHSi(CH_3)_3$ which can be inserted only to one Ru-Si≡ bond with a low yield (up to 4.5%). This is however sufficiently high to initiate effectively the catalytic metathetis pathway (metathetis product yield is equal to 41%) (see scheme 2). These two experiments strongly support the proposed mechanism (scheme 1).

In the discussion on the role of $HSi(C_2H_5)_3$ for vinyltrimethylsilane metathesis, it should be added that the cocatalytic amounts of $HSi(C_2H_5)_3$, *ie* $[RuCl_2(PPh_3)_3] = [HSi(C_2H_5)_3]$ diminish the inductive period of metathesis process (20% conversion of $CH_2{=}CHSi(CH_3)_3$ towards methathesis products *vs* 2-3% conversion without the cocatalyst; 130°C, 6 h, air). It is interesting to note that beside the typical metathesis product **IV**, another isomer $[(CH_3)_3Si]_2C{=}CH_2$ (**IVa**) was observed. This unusual reaction course testifies to the insertion-elimination mechanism of vinylsilanes metathesis in the presence of ruthenium phosphine complexes [16].



**Scheme 2.** Insertion of vinyltrimethylsilane into Ru-Si≡ bond of ruthenium bis-silyl precursor.

## Conclusions

The reaction of vinyltrimethylsilane with triethylsilane carried out in the presence of ruthenium carbonyl and phosphine catalysts is a complex competitive-consecutive process, consisting of many pathways involving DS, metathesis, hydrogenation and hydrosilylation of vinyltrimethylsilane as well as some other processes such as migration and oxygenation of silyl groups bonded to ruthenium and reactions of triethylsilane with ethene evolved during the metathesis processes.

Catalyst investigations and identification of all products by GC-MS technique allowed us to propose a general scheme indicating a sequence of competitive-consecutive reactions in which ruthenium hydride and ruthenium silyl complexes play the role of key intermediates. Direct evidence for the vinylsilane molecule insertion into Ru-Si≡ bond is discussed.

The proposed mechanism can be effectively applied for the explanation of most of the processes of vinyltrimethylsilane trisubstituted silane system, previously reported and described in this paper, occurring in the presence of ruthenium complexes.

## Experimental section

### *Materials*

$[RuCl_2(CO)_3]_2$, $Ru_3(CO)_{12}$ and $RuH_2(PPh_3)_4$ were purchased from Strem Chemicals. $RuCl_2(PPh_3)_3$ was prepared by standard procedure [24], and $RuH_3[Si(OC_2H_5)_3](PPh_3)_2$ and $Ru[Si(OC_2H_5)_3]_2(PPh_3)_2$ were prepared from $RuCl_2(PPh_3)_3$ reaction with $(C_2H_5O)_3SiH$ [21]. Vinyltrimethylsilane was purchased from ABCR, $HSi(C_2H_5)_3$ from Fluka AG and ethene from Plock Petrochemical Plant (Poland) and were used without additional purification. Benzene was purchased from POCh (Poland), dried and distilled prior to use.

### *General procedure of catalytic tests*

In a typical catalytic test, $2 \times 10^{-5}$ mol of a given solid catalyst was placed in a 20 $cm^3$ glass ampoule containing 0.3 mL benzene under an air atmosphere. Vinyltrimethylsilane (0.3 mL, $2 \times 10^{-3}$ mol) and appropriate amounts of triethylsilane were added, and the sealed glass ampoules were heated at 130°C for 6 h. The reaction mixtures were analysed by the GLC technique. The products of the reaction were identified by GC-MS and NMR methods by comparing their parameters with those of the authentic samples [25].

### General procedure of $(C_2H_5)_3SiH$ reaction with ethene

$Ru_3(CO)_{12}$ or $RuCl_2(PPh_3)_3$ ($6.3 \times 10^{-5}$ mol), 1 mL of dry benzene and 1 mL ($6.3 \times 10^{-3}$ mol) of triethylsilane were placed in 50 $cm^3$ steel pressure reaction vessel under 3 (or 10) atmospheres of ethene and heated at 130°C for 6 h. Some experiments were carried out without ethene. The reaction mixture was analysed by the GLC technique. The products of the reaction were identified by GC-MS and NMR methods by comparing their parameters with those of authentic samples [25].

### Procedure for preparation of solid A

$RuCl_2(PPh_3)_3$, (0.8 g, $8.3 \times 10^{-4}$ mol), 12 mL dry benzene and 6 mL ($4.2 \times 10^{-2}$ mol) of vinyltrimethylsilane were placed in a steel pressure vessel (50 $cm^3$) and heated at 130°C for 48 h. The brown solid was precipitated from solution with dried hexane, washed several times and dried under vacuum. In $^1H$ NMR spectra, neither $Si(CH_3)_3$ nor Ru-H signals were detected.

IR (KBr) [$cm^{-1}$] $\nu_{CH}$ aryl 3 055, $\nu_{CO}$ 1 970.

Elemental analysis [%] C 73.9, H 5.36, P 9.8, Cl 2.3.

### Procedure of insertion test

$Ru[Si(OC_2H_5)_3]_2(PPh_3)_2$ (0.1 g, $1.05 \times 10^{-4}$ mol) was placed in a 10 $cm^3$ glass ampoule containing 0.3 mL benzene under an argon atmosphere. Vinyltrimethylsilane (45.7 $\mu$L, $3.15 \times 10^{-4}$ mol) was added and the sealed glass ampoule was heated at 130°C for 24 h. The reaction mixture was analysed by GLC technique; $(C_2H_5O)_3SiCH{=}CHSi(CH_3)_3$ (3%), $[(C_2H_5O)_3Si][(CH_3)_3Si]C{=}CH_2$ (1.5%), metathesis products of vinyltrimethylsilane (41%) and some siloxanes were detected.

### Analytical measurements

$^1H$ NMR spectra were recorded on a Varian Gemini 300 spectrometer. $C_6D_6$ was used as a solvent. Gas chromatography analysis was carried out with a HP 5890 instrument using 30 m Megabore column HP-1 with TCD. GC-MS analyses were obtained on Varian 3300 GC fitted with a Finnigan Mat ITD 800 GC-MS spectrometer.

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