Silyloxy-rhodium(I) complex catalyzed disproportionation of vinylsilanes and vinylsiloxanes

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Abstract

Effective disproportionation of vinyltrisubstituted silanes and vinyltris(methyl, trimethylsiloxy)silanes as well as intermolecular condensation of divinyltetramethyldisiloxane proceed in the presence of $[\{(cod)Rh(\mu\text{-}OSiMe_3)\}_2]$ (**I**) to yield 1,2-bis(silyl)ethenes accompanied by 1,1-bis(silyl)ethenes as well as cyclic and linear bis(siloxy)ethenes, respectively. The silyloxy-rhodium(I) complex (**I**) shows much higher catalytic activity than the respective chloro-rhodium(I) complex $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$ (**II**). Mechanistic implications based on catalytic data and very recent evidence reported by Brookhart on hydrovinylation of Rh complex by vinyltrimethylsilane enabled us to suggest the involvement of Rh–H and Rh–Si intermediates as responsible for the catalytic reactions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Vinylsilanes; Vinylsiloxanes; Silyloxy-rhodium complexes; Disproportionation

1. Introduction

Transition metal–silyloxy complexes are of a great interest particularly as models for metal complexes immobilized on silica and silicated surfaces [1–5]. Due to the high catalytic efficiency of rhodium complexes, the synthesis of those of them which contain a silyloxy ligand has recently been the subject of an intensive study [6–11]. Lately, the first X-ray crystal structures of $[\{(cod)Rh(\mu\text{-}OSiPh_3)\}_2]$ [8], $[\{(CO)_2Rh(\mu\text{-}OSiPh_3)\}_2]$ [8] as well as

$[\{(diene)Rh(\mu\text{-}OSiMe_3)\}_2]$ where diene = 1,5-cyclooctadiene (cod) [10], and 2,5-norbornadiene (nbd) [11] were reported.

However, the catalytic activity of these well-defined molecular catalysts has been illustrated only in few exemplary reactions [4,12,13].

On the other hand, rhodium–hydride complexes, e.g. $[RhH(CO)(PPh_3)_3]$ (similarly to ruthenium–hydride complexes), appeared to be very effective catalysts for disproportionation of vinylsilanes and their co-disproportionation with styrene [14]. The reaction referred to as metathesis of vinylsilanes does not involve a process of C=C bond cleavage, which is formally characteristic of the olefin metathesis, but instead a new type of olefin conversion has been revealed, called silylative coupling of

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olefins by vinylsilanes (Eq. (1)) for Ru–H and Ru–Si complexes [15–18]. The insertion of vinylsilane (or bis(silyl)ethene) into the Rh–H bond followed by β-silyl transfer to form a Rh−Si bond and elimination of ethylene (and vinylsilane, respectively), in view of the kind of product (determined by MS) of styrene-d_8 with vinylsilane, have accounted for a non-metalla-carbene mechanism of a new rhodium complex catalyzed silylation of olefins with vinylsilanes [14].


M = Ru, Rh

$$(1)$$
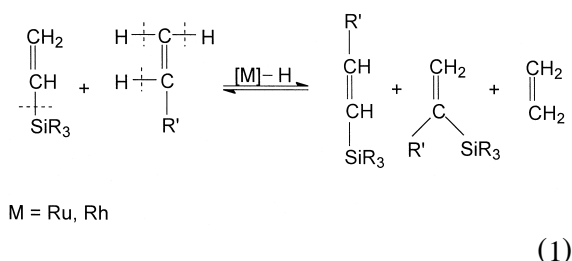
Spectroscopic study of the dimer [{(cod)Rh-(μ-OSiMe$_3$)}$_2$] (**I**) with alkenes suggest a formation of π-complexes of monomeric Rh(I)-[(diene)Rh(OSiMe$_3$)(alkene)] [13]. The latter, as a 16e rhodium(I) complex already containing

the coordinated olefin molecule, seems to be a good catalyst for disproportionation of vinylsilanes. The aim of this work is to test (**I**) as a precursor of the reaction discussed and to make an attempt at explanation of its mechanistic pathways.

2. Results and discussion

2.1. Catalytic examinations

The disproportionation of vinyltrisubstituted silanes occurs in the presence of (**I**) in a wide temperature range (60–130°C) according to Eq. (2).

$$(2)$$
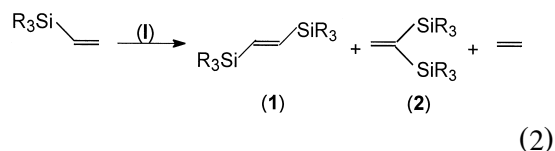
Catalytic examinations, whose results are given in Table 1, show that complex (**I**) appeared to be a very effective catalyst in the

Table 1

The effect of substituents and temperature on the disproportionation of vinyltrisubstituted silanes catalyzed by (**I**)

Reaction conditions: [Rh]:[CH$_2$ = CHSiR$_3$]:[benzene] = 10^{-2}:1:1.5, glass ampoules, argon, 24 h.

R_3	Conversion of vinylsilane [%]	Yield of bis(silyl)ethenes [%]	(**1**)/(**2**)
130°C			
Me$_3$	75 (53)[a]	75 (53)[a]	1.2 (1.3)[a]
Me$_2$Ph	59	56	2.2
(OEt)$_3$	19	9	3.0
Me(OEt)$_2$	66	62	1.0
(OCH$_2$CH$_2$OCH$_3$)$_3$	73 (58)[a]	73 (58)[a]	2.5 (1.2)[a]
Ph$_2$(OEt)	78 (68)[a]	70 (61)[a]	5.8 (4.2)[a]
Ph(OEt)$_2$	70	70	1.1
60°C			
Me$_3$	71 (0)[a]	71 (0)[a]	1.2
Me$_2$Ph	64	61	2.4
(OEt)$_3$	17	15	1.1
Me(OEt)$_2$	75	60	2.0
(OCH$_2$CH$_2$OCH$_3$)$_3$	64 (23)[a]	64 (23)[a]	1.1 (3.0)[a]
r.t.			
Me$_2$Ph	13	13	10

[a] In parentheses: 2 h.

Table 2
The effect of substituents on the disproportionation of vinyltrisubstituted silanes catalyzed by (**II**)
Reaction conditions: $[Rh]:[CH_2 = CHSiR_3]:[benzene] = 10^{-2}:1:1.5$, glass ampoules, argon, 24 h, 130°C.

R_3	Conversion of vinylsilane [%]	Yield of bis(silyl)ethenes [%]	(**1**)/(**2**)
Me$_3$	5	5	10
Me$_2$Ph	20	18	2.2
Me(OEt)$_2$	26	21	5.6

reactions of the most vinyltriorganosilanes used and yielded two isomers: E-1,2-bis(silyl)ethene (**1**) and 1,1-bis(silyl)ethene (**2**). Both types of isomers were previously prepared in ruthenium catalyzed reactions [16] and fully characterized by NMR spectroscopy for the majority of triorganosilyl derivatives.

The yields of the majority of reactions presented correspond to the total conversion of vinylsilanes used, except for those with some alkoxysubstituted silanes in case of which disiloxanes were found as by-products.

It is worth emphasizing that contrary to ruthenium complexes involving Ru−H and Ru−Si bonds which are effective at 80–130°C [17,18], the reaction proceeds efficiently under

milder conditions (60°C). The efficiency of (**I**) was compared to analogous chloro-rhodium complex $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$(**II**). The selected data for (**II**) are summarized in Table 2 showing much less catalytic effectiveness.

Since the disproportionation of vinylsiloxanes can be a good model for cross-linking of polydimethylsiloxanes containing internal vinyl-substituents at silicon [19], the reaction was also tested for catalytic properties of (**I**). The results are compiled in Table 3.

Although catalyst (**I**) is less effective in the disproportionation of vinyltris(trimethyl-siloxy) silane than $[RuCl_2(PPh_3)_3]$ and $[RuHCl(CO)(PPh_3)_3]$, the yields of bis-(methyl,siloxy)ethenes are similar to those reported for ruthenium catalyzed reactions [19], but can occur effectively at milder conditions (at 90°C instead 130°C). The fact that the transformation of vinylme-thyldi(trimethylsiloxy)silane gives almost exclusively E-isomer ((**3**)/(**4**) = 11) can be a valuable information to establish real conditions for cross-linking of poly(methy,vinyl) siloxanes via the catalytic disproportionation.

Chloro-rhodium complex (**II**) was previously used in catalytic polycondensation of divinylte-tramethyldisiloxane (DVTMDS) (130°C, glass
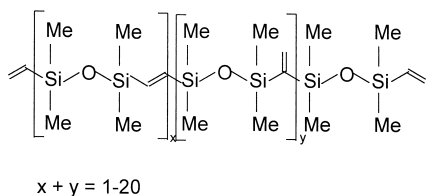
Table 3
The effect of substituents on the disproportionation of vinylsiloxanes catalyzed by (**I**)
Reaction conditions: $[Rh]:[CH_2 = CHSiR_3]:[benzene] = 10^{-2}:1:1.5$, glass ampoules, argon, 24 h, 90°C.
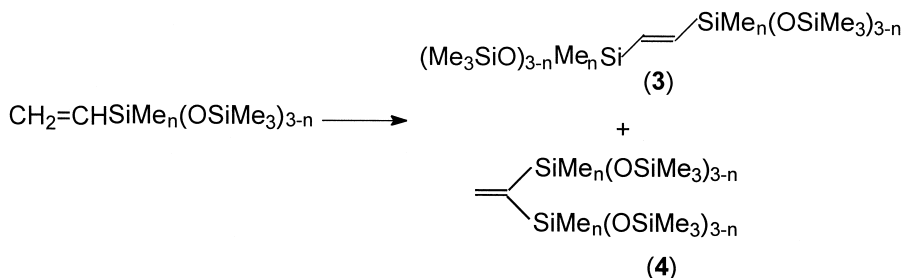

n	Conversion of vinylsiloxane [%]	Yield of bis(siloxy)ethenes [%]	(**3**)/(**4**)
0	5	5	only E-isomer
1	50	50	11.3
2	44	44	1.6

ampoules, $[\text{DVTMDS}]:[(\textbf{II})] = 1:5 \times 10^{-3})$ to yield finally the isolated linear polymer ($M_n = 1815$, $M_w/M_n = 1.16$ and $DP \approx 10$) of the structure below [20]:

Me   Me │ Me   Me │ Me   Me
Si — O — Si — Si — O — Si — Si — O — Si
Me   Me │ Me   Me │ Me   Me

x + y = 1-20

However, rhodium catalyst (**II**) favours cyclization of DVTMDS to yield 30% of (**5**) [22] under the optimum conditions (130°C, 3 weeks) in the synthetic procedure [21,22].

Therefore, silyloxy-rhodium complex (**I**) was also tested in condensation of divinyltetramethyldisiloxane to get, under the optimum conditions (80°C, 5 days, glass ampoule), a mixture of three dimeric products (**5**, **6**, **7**) (the yield 31%, selectivity of (**5**) 60%, (**6**) −30%, (**7**) −10%).

(3)

(5)

(6)

(7)
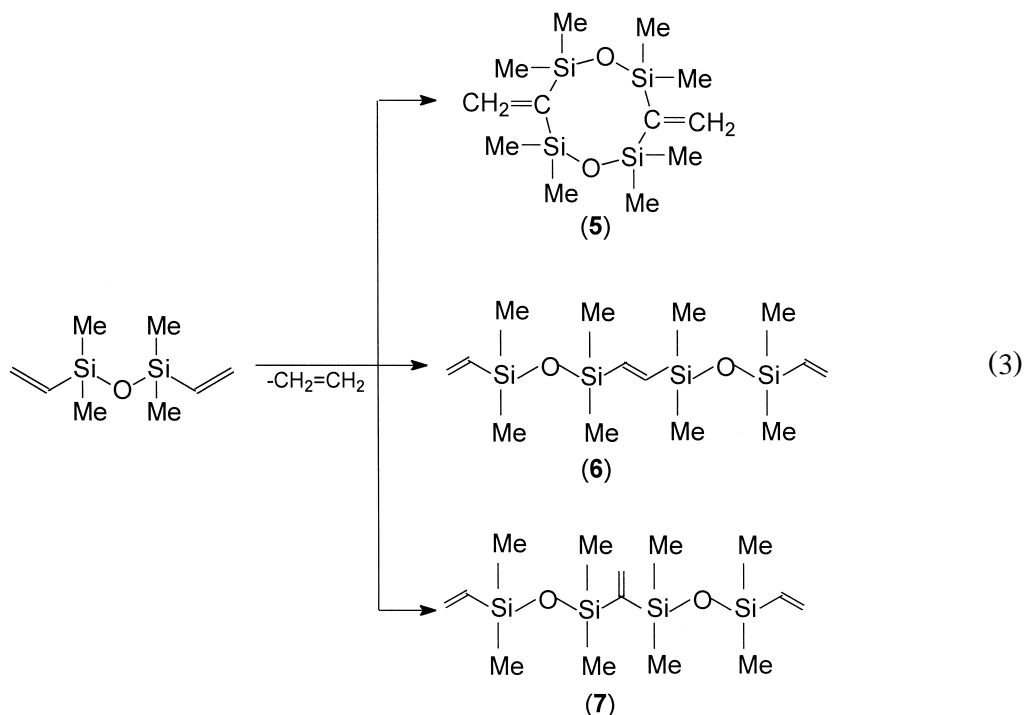
The conversion of DVTMDS was high (98%), but the dimeric products are accompanied by oligomeric ones formed according to the scheme given previously [20–22].

2.2. Mechanistic implications

All examinations of the application of (**I**) as a catalyst in disproportionation of vinyltrisubsti-

tuted silanes and vinyltris(methyl,siloxy)silane as well as condensation of divinyltetramethyldisiloxane suggest the same mechanism of the process yielding mostly two products: 1,2-bis(silyl,siloxy)ethene (E-isomer) and 1,1-bis(silyl,siloxy) ethene with the preference of E-isomer.

Inactivity of ruthenium–carbene complexes (e.g. Grubbs catalysts) [19] and high effective-

ness of the complexes containing initially Ru−H, Ru−Si [18] as well as Rh−H and Rh−Si [14] bonds in the above mentioned processes imply that silyloxy-rhodium (as well as chlororhodium) complexes catalyze these processes according to the mechanism involving Rh−H and Rh−Si intermediates. Many rhodium (I) complexes have been well-known to readily form complexes with vinylsilanes, e.g. [(acac)-

Rh(CH_2 = CHSiR$_3$)$_2$] [23] and very recently [C_5Me_5Rh(CH_2 = CHSiMe$_3$)$_2$] (**III**) [24]. The latter complex was the subject of a very stimulating experiment which has been done by Brookhart group [24] under thermolysis conditions (140°C, cyclohexane-d$_{12}$ as a solvent, 10th excess of CH_2=CHSiMe$_3$) and controlled by ^{1}H NMR to show the occurrence of the following process:

$$(4)$$
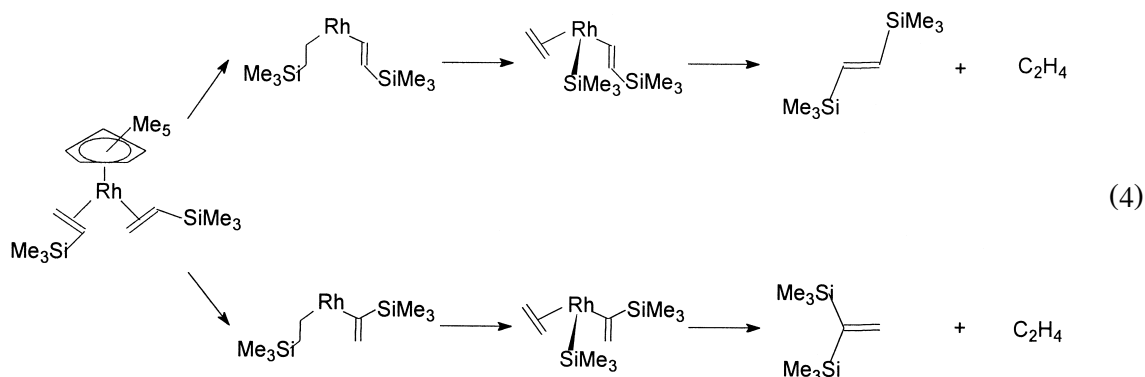
After 1 week of continuous heating at 140°C, 80% conversion of vinyltrimethylsilane was observed, leading to 72% of E-isomer (1,2-bis-(tri-

methylsilyl)ethene) and 28% of 1,1-bis(trimethylsilyl)ethene. Thus, the experiment provides the convincing evidence for hydrovinyla-
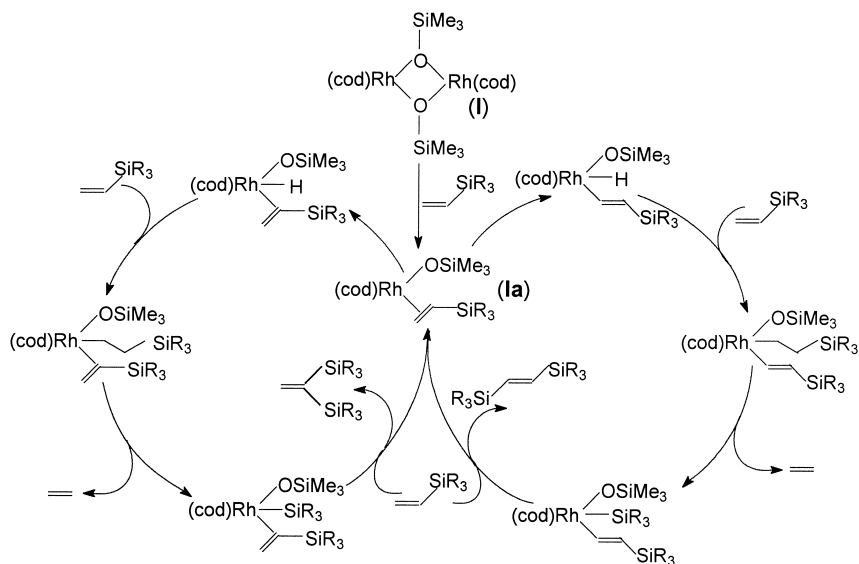
R$_3$ = Me$_3$, Me$_2$Ph, (OEt)$_3$, (OCH$_2$CH$_2$OCH$_3$)$_3$, Ph$_2$(OEt), Ph(OEt)$_2$, Me$_2$(OSiMe$_3$), Me(OSiMe$_3$)$_2$, (OSiMe$_3$)$_3$

Scheme 1. Disproportionation of vinylsilanes catalyzed by (**I**).

tion of one of the coordinated molecule of vinylsilane followed by the insertion of the second molecule of vinylsilane into the generated Rh–H bond and subsequent elimination of ethylene and reductive elimination of the two types of bis(silyl)ethenes.

On the basis of Brookhart measurements and our catalytic data, the following catalytic scheme for disproportionation of vinylsilanes occurring in the presence of (**I**) (Scheme 1) can be proposed.

The process proceeds via preliminary coordination of one molecule of vinylsilane generating 16e monomeric rhodium complex (**Ia**), which readily (under much milder conditions that in case of Brookhart complex (**III**)) undergoes hydrovinylation (also in two modes — see Scheme 1) followed by the insertion of the second vinylsilane coordinated subsequently to the rhodium center. The evidence proving the insertion of vinylsilane into Ru–Si [18] and Rh–Si [14] bonds of the key intermediates of this process was reported previously.

After elimination of ethylene (β-Si transfer), Rh–Si intermediate is generated, from which (according to the dissociative mechanism) in the reductive elimination step, we obtained two types of bis(silyl)ethenes as products. This mechanism also can work in the case of polycondensation of DVTMDS.

Our previous study on a comparison of silyloxy-rhodium complex (**I**) and chloro-rhodium complex (**II**) in the hydrosilylation of 1-hexene [13] suggests that in the absence of hydrosilane (like in this disproportionation reaction) the extremely high effectiveness of (**I**) over (**II**) is due to a much more facile cleavage of dimeric complex (**I**) than (**II**), as a result of the coordination of vinylsilane to form complex (**Ia**).

3. Experimental

3.1. General methods and chemicals

All synthesis and manipulations were carried out using standard Schlenk and high-vacuum techniques otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 VT spectrometer in C_6D_6 at 300 and 75 MHz, respectively.

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 a ITD 800 Finnigan MAT (ion trap detector)). GC analysis were carried out on a Varian 3300 gas chromatograph with a Megabore column DB-1, 30 m and TCD as a detector.

Chemicals were obtained from the following sources: vinylsilanes and vinylsiloxanes from ABCR, benzene from OBR PR Plock (Poland), benzene-d$_6$ from Dr. Glaser, Basel. All solvents, vinylsilanes and vinylsiloxanes were dried and distilled under dry argon atmosphere prior to use. $[\{(cod)Rh(\mu\text{-Cl})\}_2]$ [25] and $[\{(cod)Rh(\mu\text{-OSiMe}_3)\}_2]$ [9] were prepared according to the previously reported methods.

3.2. General procedure for catalytic examinations

The rhodium complex, benzene, toluene (internal standard), vinyltrisubstituted silane or vinyltrisubstituted siloxane were placed in the evacuated and filled with argon glass ampoule at the ratio $[Rh]:[CH_2=CHSiR_3]:[benzene] = 10^{-2}:1:1.5$. The sealed ampoule was heated in the required conditions. The composition of the reaction mixture was analyzed by GC. The conversion, yield and selectivity were calculated by GC using the internal standard method.

The majority of the products mentioned in Tables 1–3 were previously prepared in the ruthenium catalyzed reactions [16,19,26]. Products of DVTMDS conversion were also previously prepared and identified [21,22].

4. Conclusions

1. Silyloxy-rhodium dimeric complex (**I**) appeared to be a very effective catalyst for

disproportionation of vinyltrisubstituted silanes and vinyltris(methyl,siloxy)silanes as well as intermolecular cyclization of divinyl-tetramethyldisiloxane mostly occurring at milder conditions and more effectively than previously reported Ru and Rh complexes containing M−H and M−Si bonds.

2. All the reactions occur via the mechanism involving Rh−H and Rh−Si intermediates, generated in situ via preliminary hydroviny-lation of vinylsilane coordinated to rhodium atom.

Acknowledgements

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