Catalytic activity of silyloxy-rhodium(I) complexes in hydrosilylation of alkenes [1]

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Abstract

Silyloxy-rhodium(I) complexes of the general formula $[\{(\text{diene})\text{Rh}(\mu\text{-OSiMe}_3)\}_2]$ (**I**) where diene = cod, nbd, showed much higher catalytic activity in the hydrosilylation of 1-hexene by triethoxysilane than respective chloro-rhodium(I) complexes, $[\{(\text{diene})\text{Rh}(\mu\text{-Cl})\}_2]$ (**II**). Kinetic dependence of the rate on the initial concentration of [Rh] and stoichiometric reactions of Rh-complexes with triethoxysilane and 1-hexene allow a distinction between the catalytic cycles of the reactions occurring in the presence of silyloxy-rhodium vs. chloro-rhodium complexes. Direct reaction of triethoxysilane with (**I**) was followed by next elementary steps, in particular reductive elimination of disiloxane $(\text{EtO})_3\text{SiOSiMe}_3$ which generates hydridorhodium(I) complex suggested as an intermediate for the catalysis of the hydrosilylation by silyloxy-rhodium complexes. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Molecular complexes incorporating M–O–Si bonds (where M = transition metal) are good models for metal complexes supported on silica and silicate surface, commonly used in catalysis (e.g., Refs. [1–4]). Due to high catalytic activity of rhodium complexes in many organic reactions a synthesis, X-ray structure and characterization of complexes containing Rh–O–Si bond have recently been the subject of intense investigation [5–9]. Unfortunately, the catalytic activity of these molecular well-defined catalysts has been illustrated in only a few exemplary reactions [3,10,11].

The results of our comprehensive study on the synthesis and X-ray structure of the rhodium-(I) complexes of the general formula $[\{(\text{diene})\text{-Rh}(\mu\text{-OSiMe}_3)\}_2]$ (where diene = cod (**Ia**) and nbd (**Ib**)), as well as their reactivity with phosphines and triethylsilane [7–9] prompted us to investigate the scope of their catalytic activity in olefin hydrosilylation.

On the other hand, the study on the hydrosilylation of the 1-hexene catalyzed by [RhCl(cod)-(1-hexene)] [12] and [RhCl(cod)PPh$_3$] [13] reveals possible formation pathways for the com-

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plex $[RhCl(cod)(1-hexene)(H)(SiR_3)]$ which is an active intermediate in associative mechanism of the process. Moreover, the proper catalytic cycle proceeds via intermediates not-involving the phosphine ligands. The observed effect of phosphine as well as phosphine oxidation affects only the first activation process (i.e., occurring during the induction period) of the hydrosilylation, whereas the rate of the essential catalytic cycle remains virtually unchanged [13].

In view of these results silyloxy-rhodium complexes (**Ia**) and (**Ib**) not containing phosphine ligands have been used in the hydrosilylation of 1-hexene, in order to compare directly the role of the silyloxy ligand with chloro analogues in the catalytic process.

2. Results

2.1. Catalytic and kinetic examination

Two silyloxy-rhodium complexes of the general formula $[\{(diene)Rh(\mu-OSiMe_3)\}_2]$ (where diene = cod (**Ia**) and nbd (**Ib**)), as well as two respective chloro-rhodium complexes $[\{(diene)-Rh(\mu-Cl)\}_2]$ (where diene = cod (**IIa**) and nbd-(**IIb**)) were tested in the hydrosilylation of 1-

hexene by triethoxysilane according to the Eq. (1)

$$(EtO)_3SiH \ + \ \diagup\!\!\!\diagup^{C_4H_9} \ \xrightarrow{[Rh]} \ (EtO)_3Si\diagup\!\!\!\diagup^{C_4H_9} \tag{1}$$
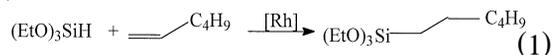
When the two substrates were used at the equimolar ratio, a parallel isomerization of 1-hexene to 2-hexene and next to 3-hexene causes a lower yield of the hydrosilylation products, while at the excess of the alkene, almost quantitative conversion of triethoxysilane is observed under the same conditions. Hexyltriethoxysilane is the exclusive product of the reaction and no hexenyltriethoxysilane is detected as a possible product of the dehydrogenative silylation observed when some other rhodium complexes are used as catalysts (e.g., Ref. [14]).

In order to eliminate the side reactions of 1-hexene isomerization, kinetic measurements were performed for the ratio [silane]:[1-hexene] = 1:10 or 1:5. Thus, the reaction is the first-order with respect to silane. Selected kinetic curves of the hydrosilylation course in the presence of the two types of the catalysts used are shown in Fig. 1. They also illustrate a determination of the kinetic parameters k_{obs} and induction period τ. The kinetic parameters were calculated by fitting experimental data of relative
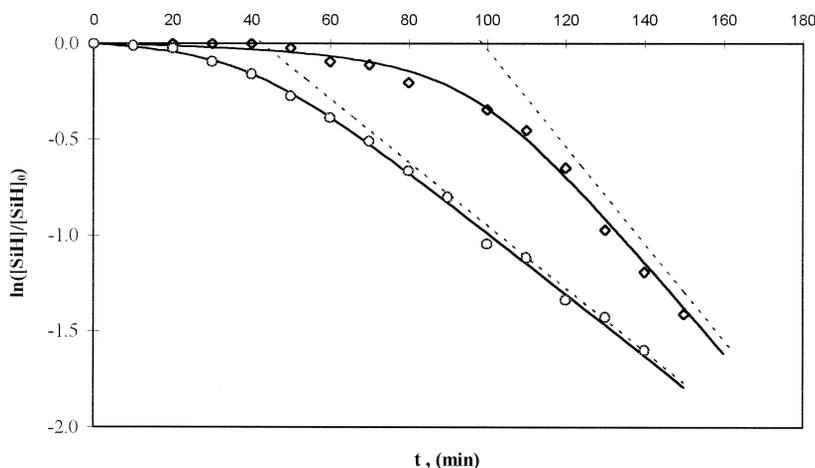
Fig. 1. Exemplary plot of the $\ln([SiH]/[SiH]_0)$ vs. time of the hydrosilylation catalyzed by (**Ia**) ([Rh] = 0.0872×10^{-3} mol/l; $[SiH]_0 = 0.436$ mol/l, [1-hexene]$_0$ = 4.40 mol/l) ($\bigcirc$) and (**IIa**) ([Rh] = 3.488×10^{-3} mol/l; $[SiH]_0 = 0.436$ mol/l, [1-hexene]$_0$ = 4.40 mol/l) ($\diamondsuit$) at 35°C.

silane concentration $[SiH]/[SiH]_0$ vs. time (t) to a exponential function with hyperbolical exponent using nonlinear least square procedure. The slope of asymptote of hyperbole is equal to pseudo first-order rate constant k_{obs} and the abscissa of intersection of asymptote with t axis can be recognized as an induction period τ.

The effect of the catalyst concentration on the above mentioned parameters is compiled in Table 1, and the relationship between k_{obs} and

the initial concentration of a rhodium catalyst is illustrated in Figs. 2 and 3.

The reaction catalyzed by silyloxy-rhodium complexes (**Ia**) and (**Ib**) is of the first order with respect to the rhodium complex (Fig. 2). No difference was found between the catalytic activity of (**Ia**) and (**Ib**), i.e., the kind of diene did not change the rate.

On the other hand, the dependence of the k_{obs} of the hydrosilylation catalyzed by [{(cod)Rh(μ-

Table 1
Effect of catalyst concentration on the kinetic parameters at 35°C

[Rh] (10^{-3} mol/l)	$[SiH]_0$ (mol/l)	10^3 [Rh]/$[SiH]_0$	k_{obs} (1/min)	τ (min)	$r^{2\,a}$
[{(cod)Rh(μ-OSiMe$_3$)}$_2$] (**Ia**)					
0.0218	0.436	0.05	0.0056	109.2	0.9944
0.0436	0.436	0.1	0.0095	103.5	0.9760
0.0436	0.436	0.1	0.0112	104.2	0.9969
0.0872	0.872	0.1	0.0140	110.6	0.9949
0.0872	0.436	0.2	0.0186	56.4	0.9888
0.0872	0.436	0.2	0.0165	42.6	0.9988
0.1308	0.436	0.3	0.0267	46.8	0.9912
0.1308	0.436	0.3	0.0223	33.8	0.9829
0.1526	0.436	0.35	0.0349	10.9	0.9951
0.1526	0.436	0.35	0.0322	10.4	0.9545
0.1744	0.436	0.4	0.0380	7.4	0.9795
0.1744	0.436	0.4	0.0415	9.3	0.9958
0.1744	0.872	0.2	0.0348	43.1	0.9987
0.3488	0.872	0.4	0.0661	3.1	0.9972
[{(nbd)Rh(μ-OSiMe$_3$)}$_2$] (**Ib**)					
0.0872	0.872	0.1	0.0149	111.1	0.9891
0.1744	0.872	0.2	0.0332	58.7	0.9964
0.3488	0.872	0.4	0.0693	27.2	0.9600
[{(cod)Rh(μ-Cl)}$_2$] (**IIa**)					
1.744	0.436	4	0.0186	156.0	0.9866
2.616	0.436	6	0.0203	123.2	0.9722
3.488	0.436	8	0.0252	98.7	0.9927
3.488	0.436	8	0.0254	89.2	0.9952
4.36	0.436	10	0.0254	76.4	0.9688
4.36	0.436	10	0.0301	73.0	0.9757
6.976	0.872	8	0.0353	99.6	0.9601
8.72	0.436	20	0.0335	69.3	0.9940
8.72	0.436	20	0.0368	60.7	0.9879
13.08	0.436	30	0.0483	45.8	0.9904
13.08	0.436	30	0.0455	48.8	0.9938
13.08	0.436	30	0.0440	49.7	0.9879
[{(nbd)Rh(μ-Cl)}$_2$] (**IIb**)					
0.1744	0.872	0.2	0.0040	380.0	0.9845
1.744	0.872	2	0.0123	118.0	0.9889
21.8	0.872	25	0.0471	34.0	0.9989

[1-hexene] = 4.40 mol/l. [a] Square of correlation coefficient.
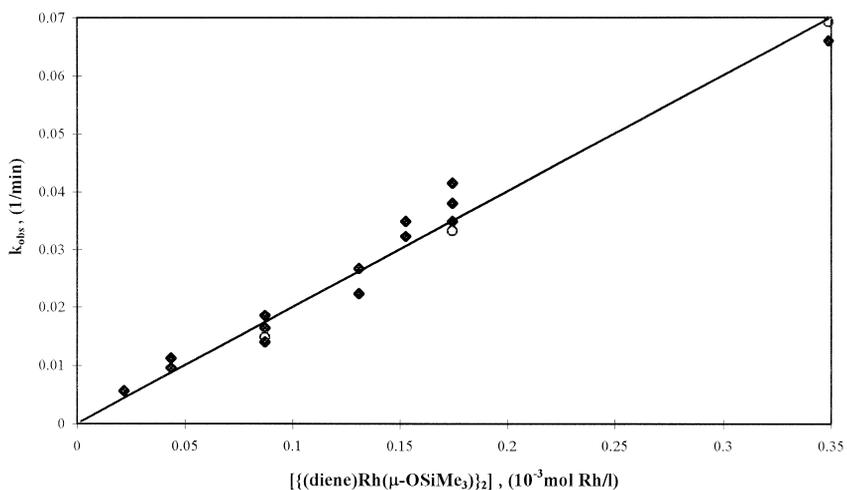
Fig. 2. Pseudo first-order rate constants k_{obs} vs. the initial concentration of (**Ia**) (♦) and (**Ib**) (○).
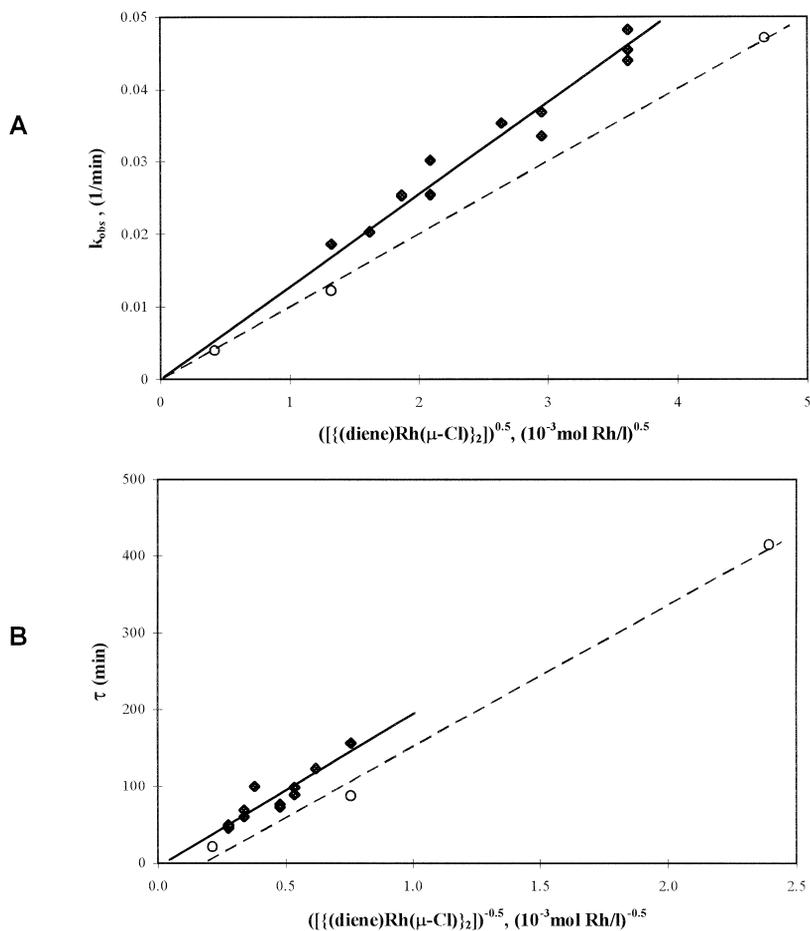
Fig. 3. Pseudo first-order rate constants k_{obs} (A) and the induction period τ (B) vs. square root (A) and the reciprocal of the square root (B) of the initial concentration (**IIa**) (♦) and (**IIb**) (○), respectively.

Cl)}$_2$]complex (**IIa**) on the catalyst concentration is nonlinear with downward deviation as concentration of rhodium increases. However, the linear dependence of k_{obs} on the [{(cod)-Rh(μ-Cl)}$_2$]$^{1/2}$ (Fig. 3A) is the evidence supporting the mechanism of the hydrosilylation catalyzed by rhodium-chloride complexes in which the equilibrium of dissociation of chloro-rhodium dimer is a rate controlling step.

$$[Rh]_d \overset{K_1}{\rightleftharpoons} [Rh]_m + [Rh]_m$$
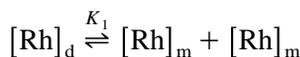
$$[Rh]_m = K_1^{1/2}[Rh]_d^{1/2}$$

The concentration of monomeric chloro-rhodium complex is proportional to square root of the initial concentration of the dimer (**IIa**). It is also worthy to say that the same linear dependence of the induction period τ on reciprocal of the square root of the initial concentration of the rhodium complex (Fig. 3B) supports the idea that the rate determining step of the [Rh] formation proceeds in the activation process for which the induction period can be regarded as a measure.

2.2. Stoichiometric reactions of [(diene)Rh(μ-OSiMe$_3$)]$_2$ (Ia, IIa) with triethoxysilane

^{1}H NMR study on the reaction of [(cod)Rh(OSiMe$_3$)]$_2$ dimer (**Ia**) with triethoxysilane was performed in C$_6$D$_6$. A direct reaction of (**Ia**) with HSi(OEt)$_3$ occurs as in Scheme 1.

The ^{1}H NMR spectra allow a determination of the chemical shifts and the coupling constant of Rh–H for individual complexes. When HSi(OEt)$_3$ was used in excess the spectra revealed the presence of four doublets. Two of them are more intensive, i.e., $\delta = -13.27$ ppm (d, $J_{Rh-H} = 43.8$ Hz) and $\delta = -13.26$ ppm (d, $J_{Rh-H} = 43.8$ Hz) and the other two less intensive $\delta = -13.24$ ppm (d, $J_{Rh-H} = 43.2$ Hz) and $\delta = -13.25$ ppm (d, $J_{Rh-H} = 43.2$ Hz). Slight differences in the chemical shifts and coupling constants suggest isomeric complexes to be
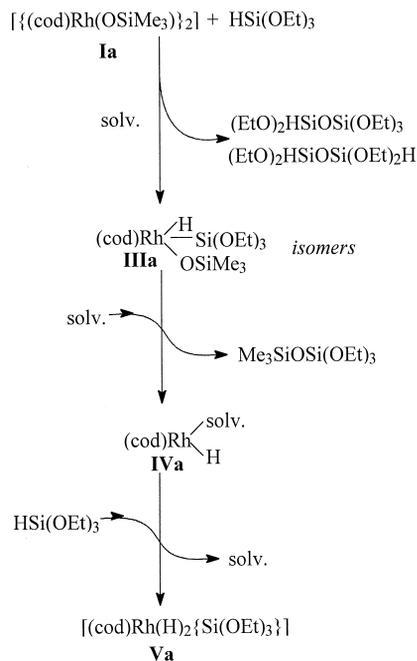
Scheme 1.

formed in the mixture of the pentacovalent rhodium complexes. Unfortunately, this method of study does not distinguish isomers of (**IIIa**) and/or (**Va**) (see Scheme 1). Rh(III) pentacovalent complexes containing Rh–H bonds are recorded in a high field ($\sim 13-\sim 18$ ppm) [15], e.g., (Ph$_3$P)$_2$RhHCl[Si(OEt)$_3$] $\delta = -14.85$ ppm [16]; [(Ph$_3$P)$_2$RhH$_2$Cl]$_2$ $\delta = -14.6$ ppm [16]; (η^5-C$_5$Me$_5$)RhH[Si(OEt)$_3$](C$_2$H$_4$) $\delta = -13.61$ ppm ($J_{Rh-H} = 35.5$ Hz) [17]; (η^5-C$_5$-H$_5$)RhH[Si(iso-Pr)$_3$](C$_2$H$_4$) $\delta = -14.85$ ppm (d, $J_{Rh-H} = 31.6$ Hz) [18]; (η^5-Me$_3$Si-C$_5$H$_4$)RhH$_2$(SiMe$_3$)$_2$ $\delta = -13.90$ ppm (d, $J_{Rh-H} = 39.2$ Hz) [19]. The formation of hydride rhodium complexes in the reaction examined is supported by the IR spectra of the reaction mixtures which show the disappearance of the band attributed to the Si–H bond ($\nu = 2200$ cm^{-1}) and appearance of the bands due to Rh–H bonds $\nu = 2129$ cm^{-1} (w). Contrary to the respective reaction of (**Ia**) with HSiEt$_3$ there is no resonance observed due to the [{(cod)-RhH}$_4$] cluster formation (quartet $\delta = -11.85$ $J_{Rh-H} = 14.4$ Hz) [7].

A rapid elimination of disiloxane $(EtO)_3SiOSiMe_3$ in the reaction mixture detected by GC–MS techniques can be regarded as direct evidence for reductive elimination of (**IIIa**) (Scheme 1). This is a key step for generating Rh(I) hydride intermediate active in the hydrosilylation and other reactions. Although (**IVa**) is not distinguished in the NMR spectra as an intermediate as it was in the reaction of (**Ia**) with Et_3SiH [7], the fast consecutive oxidative addition $(EtO)_3SiH$ has to yield (**Va**). Four pentacoordinated rhodium complexes observed in ^1H NMR spectra probably make a mixture of (**IIIa**) and (**Va**) isomers.

The siloxane $(EtO)_3SiOSiMe_3$ being the product of reductive elimination of (**IIIa**) is accompanied by two other disiloxanes detected in similar amounts. GC–MS analysis allows their identification as products of redistribution (condensation) of triethoxysilane proceeding according to the following equations:

$$2\ HSi(OEt)_3 \begin{cases} \xrightarrow{-EtOH} (EtO)_3SiOSiH(OEt)_2 \\ \xrightarrow{-EtOEt} (EtO)_2HSiOSiH(OEt)_2 \end{cases} \quad (2)$$
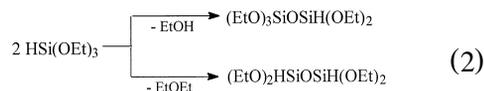
The two above are the side reactions characteristic of all alkoxysilanes transformations [20].

Analogous NMR measurements of the reaction products of $[(nbd)Rh(OSiMe_3)]_2$ (**Ib**) with triethoxysilane have also shown a doublet $\delta = -13.39$ ppm ($J_{Rh-H} = 43.5$ Hz) at the equimolar ratio of substrates and another two doublets $\delta = -13.37$ ppm ($J_{Rh-H} = 43.8$ Hz) and $\delta = -13.40$ ($J_{Rh-H} = 43.8$ Hz)—recorded at the excess of triethoxysilane. Besides, also the same three disiloxanes were detected by the GC–MS method.

Similar ^1H NMR study of the stoichiometric amounts of chloro-rhodium complexes (**IIa**, **IIb**) with triethoxysilane did not reveal any products of the oxidative addition (particularly a chemical shift in negative part of the spectrum attributable to the Rh–H bond). The reaction of Rh complexes with 1-hexene was followed by Vis-spectroscopy. The initial complex (**Ia**) and

(**IIa**) reacts with the olefin in benzene solution at room temperature. Electronic spectra of (**Ia**) show strong absorption bands at 28.0×10^3 cm^{-1} and (**IIa**) 28.4×10^3 cm^{-1} both attributable to the metal-cod transfer band ($d_z2-\pi^*$) [21]. Seventy-two hours treatment of (**Ia**) with 1-hexene causes the disappearance of the band at 28.0×10^3 and the appearance of a new band at 28.5×10^3 cm^{-1}. It can be accounted for by the following equation [21–23].

$$(3)$$
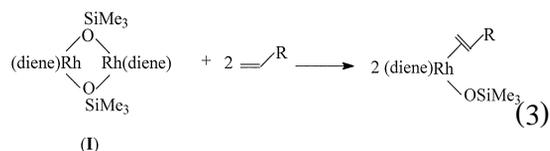
3. Discussion

Results of the kinetic and catalytic measurements of the 1-hexene hydrosilylation as well as of the stoichiometric reactions of Rh-complexes with the substrates ($HSi(OEt)_3$ and 1-hexene) suggest essential differences in the mechanistic pathways and particularly in the rate-controlling steps.

The linear dependence of k_{obs} of the process on the $([Rh])^{1/2}$ (**IIa**, **IIb**) concentration is a convincing evidence that the pathway $(1) \rightarrow (1a)$ (Scheme 2) is a rate-determining step of the whole consecutive process occurring in the presence of chloro-rhodium catalysts. The proper catalytic cycle occurs according to associative mechanism of Chalk and Harrod [24]. In excess of 1-hexene $(1a) \rightarrow (2)$ occurs readily and it is followed by fast oxidative addition of $HSi(OEt)_3$ $(2) \rightarrow (3)$ and $\pi \rightarrow \sigma$ rearrangement of the rhodium–olefin complexes to yield finally product and recover the active complex (**2**).

Silyloxy-rhodium complexes ((**Ia**), (**Ib**)) lead the catalytic process via a direct reaction of the dimer with triethoxysilane (which is supported by the stoichiometric study of this step), giving complexes (**5**) and (**1a**). The latter is yielded
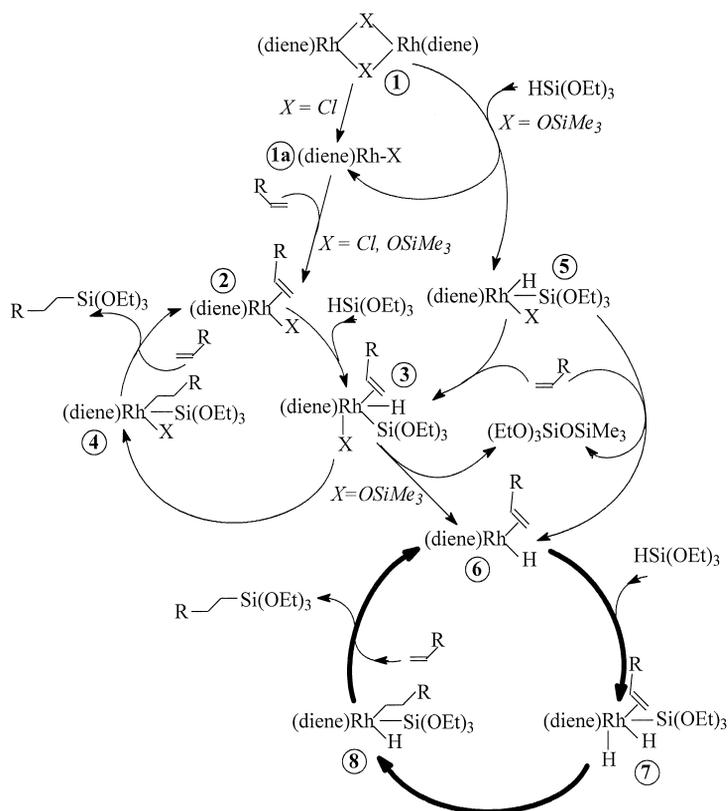
Scheme 2.

omitting the initial equilibrium—[dimer (**1**)] ↔ [monomer (**1a**)]. Thus, this pathway is followed by (**1a**) → (**2**) → (**3**). However, the main pathway for the transformation with silyloxy-rhodium complexes starts from complex (**5**) which after reductive elimination of $(EtO)_3SiOSiMe_3$ and coordination of 1-hexene (succession of these two pathways cannot be established, i.e., (**5**) → (**3**) → (**6**), and/or (**5**) → (**6**) by the methods used) the hydride-rhodium(I) complex (**6**) is generated.

(**6**) opens a separate catalytic cycle of the hydrosilylation (also proceeding via Chalk–Harrod mechanism [17], which is responsible for much higher catalytic activity of (**Ia**) and (**Ib**) as compared to (**IIa**) and (**IIb**), respectively. A formation in situ of the 16e hydride-rhodium(I) intermediate (as a consequence of the fast reductive elimination of disiloxane followed by

the olefin coordination) is a crucial step of the silyloxy-rhodium complex transformation, of great importance in molecular catalysis.

The variant of Chalk and Harrod mechanism involving the insertion of alkene into Rh–Si of the complexes (**3**) and (**7**) [24] is omitted in the scheme proposed, since no unsaturated product of the dehydrogenative silylation in the excess of the olefin was found.

4. Conclusions

(1) Catalytic and kinetic measurements of the hydrosilylation of the exemplary olefin—1-hexene have shown a much higher catalytic activity of the silyloxy-rhodium complexes (**Ia**, **Ib**) than chloro-rhodium analogues (**IIa**, **IIb**).

(2) Stoichiometric reaction of silyloxy-rhodium complexes with triethoxysilane and 1-hexene and chloro-rhodium complexes with 1-hexene as well as different dependencies of the k_{obs} of the hydrosilylation on the initial catalyst concentration have made grounds for the different mechanisms proposed (Scheme 2) for catalysis by Rh^I-O-$SiMe_3$ and Rh^ICl-complexes.

(3) 16e hydride-rhodium(I) complex—[(diene)RhH(alkene)] generated in an excess of alkene in situ after reductive elimination of trimethyltriethoxysiloxane seems to be a key intermediate in the catalytic transformations with silyloxy-rhodium complexes.

5. Experimental

5.1. Materials, equipment and analytical measurements

All manipulations were carried out under argon using standard Schlenck techniques and a glove-box. All solvents (POCh, Merck) were freshly distilled under argon and dried prior to use, C_6D_6 (Dr. Glaser) and 1-hexene (Fluka) were distilled under argon and kept over 4A molecular sieves. Triethoxysilane was prepared by alcoholysis of trichlorosilane and redistilled under argon before use. [{(cod)Rh(μ-OSiMe_3$)}_2$] and [{(nbd)Rh(μ-OSiMe_3$)}_2$] were prepared according to the method reported earlier [7]. $RhCl_3 \times nH_2O$ was purchased (Merck). [{(cod)-Rh(μ-Cl)}_2$] [25] and [{(nbd)Rh($\mu$-Cl)}_2$] [26] were prepared according to the literature procedure. ^{1}H NMR spectra were recorded on a Varian 300 MHz instrument using 5 mm Wilmed tubes with silicon septa. Visible spectra were recorded using a Specord UV–Visible spectrometer (Carl Zeiss Jena) in quartz cells of 1 cm thickness sealed with silicon rubber. IR spectra were recorded in nujol kept over molecular sieves, using Fourier transform IR Brucker JFS-119 vs. GC–MS analyses were carried out with a Varian 3300 chromatograph (equipped

with a DB-1, 30 m, capillary column) connected to a Finningan Mat 700 mass detector.

Catalytic experiments were carried out in sealed glass ampoules under argon. Kinetic measurements were also carried out under argon at 35°C in a thermostated vessel of 20 ml capacity. Solutions for kinetic studies were prepared by mixing the required aliquots of the rhodium complex solution in benzene and 1-hexene followed by addition of the silane. The course of the hydrosilylation was monitored by GC analysis (consumption of triethoxysilane) on a Varian 3300 with a Megabore column DB-1, 30 m and TCD as detector.

5.2. Reaction of [{(cod)Rh(μ-OSiMe_3$)}_2$] with triethoxysilane

[{(cod)Rh(μ-OSiMe_3$)}_2$] (0.043 g, 0.012 mmol) was put into an NMR tube and C_6D_6 (0.6 cm^3) was injected. Then 35.6 μl of $HSi(OEt)_3$—0.19 mmol was added step by step by a Hamilton chromatography syringe. The solution changed colour from orange–yellow into deep cherry after less than 20 min.

^{1}H NMR after 24 h (C_6D_6) $\delta = 3.73$ ppm (quart, $J_{H-H} \sim 7$ Hz). ^{1}H NMR δ: -13.27 ppm (d, $J_{Rh-H} = 43.8$ Hz), -13.26 ppm (d, $J_{Rh-H} = 43.8$ Hz), -13.24 ppm (d, $J_{Rh-H} = 43.2$ Hz) and -13.25 ppm (d, $J_{Rh-H} = 43.2$ Hz).

After the next portion of microliters of $HSi(OEt)_3$ was added the spectrum showed change at the negative range. ^{1}H NMR δ: -13.26 ppm (d, $J_{Rh-H} = 43.2$ Hz) and -13.27 ppm (d, $J_{Rh-H} = 43.2$ Hz), -13.24 ppm (d, $J_{Rh-H} = 43.2$ Hz), -13.24 ppm (d, $J_{Rh-H} = 43.5$ Hz) and -13.25 ppm (d, $J_{Rh-H} = 43.5$ Hz).

GC–MS chromatography of C_6D_6 solutions indicated the presence of three disiloxanes: $m/z = M^+ - H$ 297, $M^+ - C_2H_4$ 269, $M^+ - EtO$ 253 $(EtO)_2HSiOSi(OEt)_3$; $m/z = 253, 207, 162$ $(EtO)_2HSiOSiH(OEt)_2$; and $m/z = 252$ $(EtO)_3SiOSiMe_3$.

Acknowledgements

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