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Catalysis of hydrosilylation

XIX *. Mechanism of hydrosilylation of 1-hexene catalyzed by [RhCl(COD)(phosphine)]

Bogdan Marciniec *, Wojciech Duczmal, Włodzimierz Urbaniak and Elżbieta Śliwińska

Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznań (Poland)

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Abstract

A detailed mechanism of the exemplified hydrosilylation of 1-hexene by triethoxysilane catalyzed by [RhCl(COD)(phosphine)] (**1**), where phosphine is PPh_3 or 1/2 bis(diphenylphosphinoethyl)tetramethyldisiloxane has been presented. The mechanism has been deduced from the results of kinetic studies (by spectrophotometry and GLC) of most of the individual consecutive-competitive steps of the reaction. Individual rate constants have been determined from the reactions of the initial complex **1**, described previously as, and of the isolated intermediates with various substrates and oxidants. It has been concluded that the hydrosilylation consists of two distinct stages, the activation of the rhodium precursor by initiating the active intermediates, followed by a very much faster but usual catalytic cycle of hydrosilylation.

Introduction

Our previous spectrophotometric studies on the reactivity of the complex [RhCl(COD)(phosphine)] (**1**) where phosphine is 1/2 bis(diphenylphosphinoethyl) tetramethyldisiloxane with the hydrosilylation substrates showed that the complex reacts about 4 times faster with 1-hexene than with triethoxysilane [1]. However, careful removal of oxidants by redistillation of the commercial hexene makes the reaction rate drop drastically. A very similar phenomenon was observed in the hydrosilylation of 1-hexene by triethoxysilane catalyzed by Wilkinson complex [2]. Under oxidant-free conditions the replacement of phosphine by 1-hexene in **1**

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* Part XVIII see ref. 8.

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occurs as a two-step reversible reaction by an associative mechanism via a five-coordinated complex [RhCl(COD)(phosphine)(1-hexene)] (**1′**) [3]. If commercial 1-hexene is used and when [oxidant] > [**1**], two distinct reaction steps are observed, (i) oxidation of phosphine to phosphine oxide with generation of [RhCl(COD)] (**2**) and (ii) oxidation of the dimer [{RhCl(COD)}$_2$], that rapidly forms, to the Rh(III) species. Step (ii) is not observed when [oxidant] < [**1**] [4]. The above study on the reactions of **1** with various hydrosilylation substrates is probably the preliminary stage to the whole catalytic process. Here we evaluate the rest of the individual steps of the catalytic cycle examined by spectrophotometry and GLC and propose an overall mechanism for the hydrosilylation.

Results

The initial complex **1** reacts with 1-hexene in benzene solutions at room temperature, regardless of the conditions, to give the complex [RhCl(COD)(1-hexene)] (**2′**),

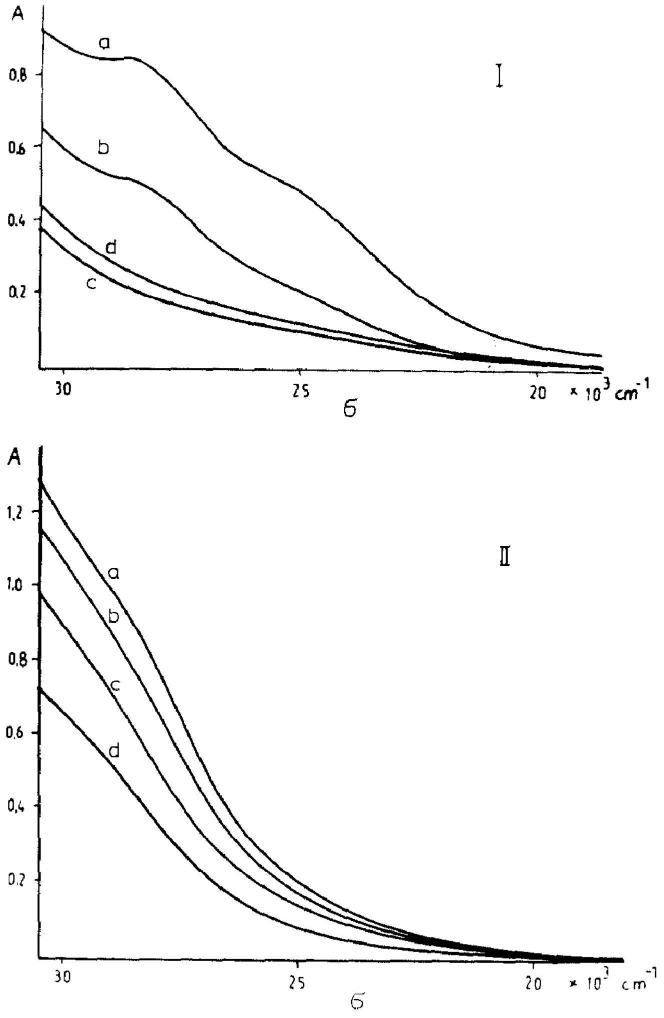


Fig. 1. Spectra of the reactions for the systems **2′** + HSi(OEt)$_3$ (I) and **3** + 1-hexene (II). [Rh] 5.0×10^{-4} *M*; [1-hexene] 0.80 *M*; [HSi≡] 0.53 *M*; *T* 20 ° C; phosphine = 1/2 BPS. Reaction times (h) for I: 0 (a), 10 (b), 36 (c) and 122 (d); and II: 0 (a), 20 (b), 51 (c) and 122 (d).

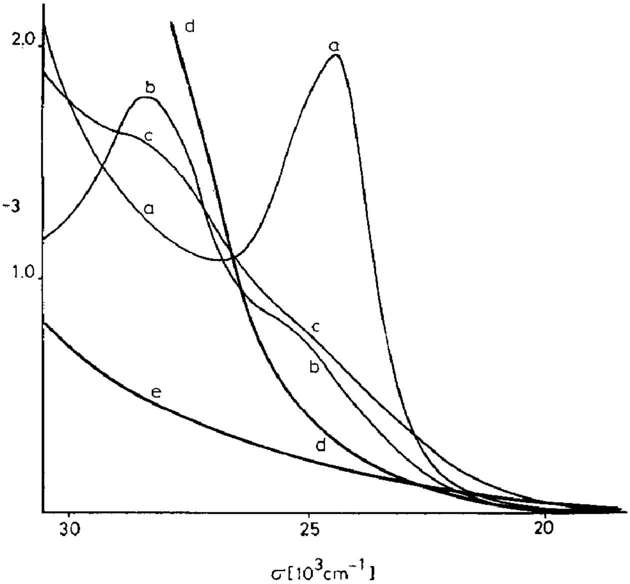


Fig. 2. Electronic spectra of [RhCl(COD)(1/2BPS)] (a), [{RhCl(COD)}$_2$] (b), [RhCl(COD)(1-hexene)] (c), [RhCl(COD)(1/2BPS)H(Si≡)] (d) and of a solution with a maximum concentration of [RhCl(COD)-H(Si≡)(1-hexene)] (e).

and with triethoxysilane to form [RhCl(COD)H(Si≡)(phosphine)] (3) where phosphine = PPh_3 or 1/2 bis(diphenylphosphinoethyl)tetramethyldisiloxane (BPS), but most of experiments involved the latter [1,2,3]. The complexes **2′** and **3** were treated under the same conditions with triethoxysilane and 1-hexene, respectively. The changes in the electronic spectra with time are depicted in Fig. 1.

In both cases, the spectra are very similar and correspond to Rh(III) complexes. Yet, their absorption over the whole region is several times lower than that for the Rh(III) complex, **3**. So we suggest that the complex formed in both systems is [RhCl(COD)H(Si≡)(1-hexene)] (**4**). When the complex **2′** reacts with triethoxysilane in the final stage of the reaction, a slight increase in the absorption is noticed. Thus, in addition to the complexes mentioned, the solution must contain other Rh species that form more slowly, but which absorb more radiation in this region of the spectrum. Consequently, the absorptions by the product **4** cannot be determined from the final spectra. Nevertheless, we assume that of the examined solutions in this system the spectrum having the lowest ϵ value is closest to that of **4**. Figure 2 shows that the molar absorption coefficients for **4** are several times lower than those for other species that can be present in the systems examined.

Thus, a drop in the absorption in the region ca. 26.5×10^3 cm^{-1} (where all the complexes except **4** show similar absorption) can be a measure of the formation of **4**. The observed rate constants, k_{obs}, can be determined from these spectrophotometric data, especially for the initial periods of the reaction. The results given in Table 1 show that the reaction of **2′** with triethoxysilane is several times faster than that of **3** with 1-hexene but both are much slower than those that generate **2″** (in the presence of oxidant) and **3** [1,3].

The reactions in both systems were monitored simultaneously by GLC so that, even at room temperature, the formation of the hydrosilylation product,

Table 1

Kinetic parameters of the reaction of **2′** and **3** with the corresponding substrates of the hydrosilylation. [Rh] 5×10^{-4} *M* [HSi≡] 0.53 *M* [1-hexene] 0.80 *M* *T* 20 °C

System	Phosphine	k_{obs} (s^{-1})	V_0 (mol dm^{-3} s^{-1})	τ (h)
2′ + $HSi(OEt)_3$	BPS	24.7×10^{-6}	1.80×10^{-6}	8
2′ + $HSi(OEt)_3$	PPh_3	26.0×10^{-6}	1.33×10^{-6}	9
3 + 1-hexene	BPS	5.8×10^{-6}	1.30×10^{-6}	23
3 + 1-hexene	PPh_3	2.6×10^{-6}	1.18×10^{-6}	31

hexyltriethoxysilane could be followed. Figure 3 depicts the formation curves of this product (by GLC) and a decrease in the absorptions of the complexes **2′** and **3** (by UV-VIS). The induction period (τ), and the initial rate V_0 of the formation of the hydrosilylation products were determined from Fig. 3. All the kinetic parameters for BPS as phosphine in the initial complex are listed in Tables 1 and 2. For the system **2′** + triethoxysilane, V_0 is achieved at a maximum concentration of **4**, i.e. a minimum in the absorption by solution and differs only slightly from the V_0 of the second system (Fig. 3 and Table 1). The effect of oxidant on the induction period of the reaction of **2′** or **3** with the reagent is given in Table 2. The oxidant has no effect on the k_{obs} and V_0, but its presence shortens the induction period of product formation for the reaction of **3** with 1-hexene.

The reaction of complex **2′** with triethoxysilane and that of **3** with 1-hexene is first order with respect to the reactant (linear dependence of k_{obs} on [HSi≡] or [1-hexene]—Fig. 4). We also observed a considerable decrease in τ with an increase in the concentration of the reagent. On the other hand, V_0 changes slightly with an

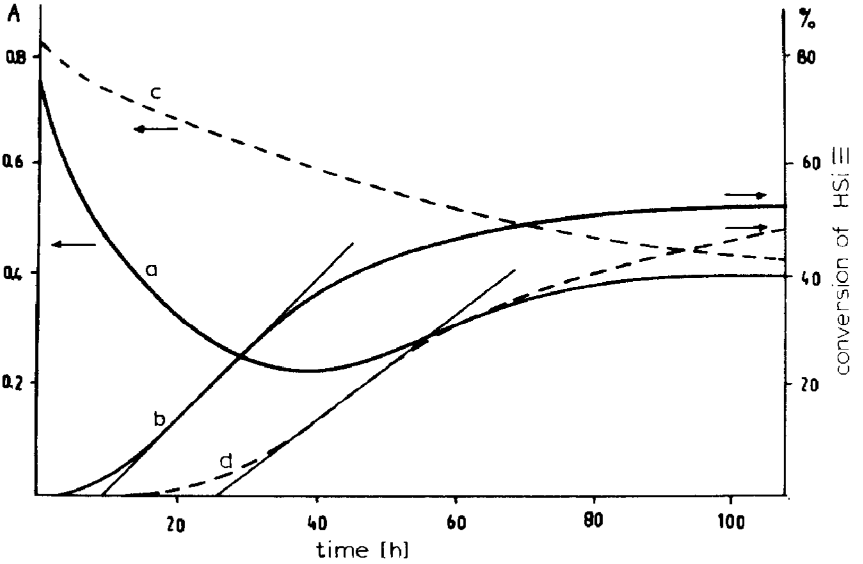


Fig. 3. Changes of absorption of σ 28×10^3 cm^{-1} (a and c) and conversion of $HSi(OEt)_3$ into $C_6H_{13}Si(OEt)_3$ (b and d) in the systems **2′** + $HSi(OEt)_3$ (———) and **3** + 1-hexene (- - - - - -). [Rh] 5.0×10^{-4} *M*; [1-hexene] 0.80 *M*; [HSi≡] 0.53 *M*; *T* 20 °C; phosphine = 1/2BPS. V_0 = slope of tangents in the inflexion point of curves b and d. τ is determined from the intercept of the tangents on the time axis.

Table 2

Kinetic parameters of hydrosilylation in the presence of oxidants ([Rh] 5.0×10^{-4} *M*; [1-hexene] 0.80 *M*; [HSi≡] 0.53 *M*; *T* 30 °C; phosphine = 1/2 BPS)

System	1-Hexene	Atmosphere	k_{obs} (10^{-6} s^{-1})	V_0 (10^{-6} mol dm^{-3} s^{-1})	τ (h)
2′ + $HSi(OEt)_3$	oxidant-free	argon	48.9	4.20	3
2′ + $HSi(OEt)_3$	oxidant-free	air	40.7	4.11	4
2′ + $HSi(OEt)_3$	commercial	argon	45.5	3.98	3.5
3 + 1-hexene	oxidant-free	argon	13.1	2.72	14.5
3 + 1-hexene	oxidant-free	air	14.3	2.95	11
3 + 1-hexene	commercial	argon	20.0	3.01	4

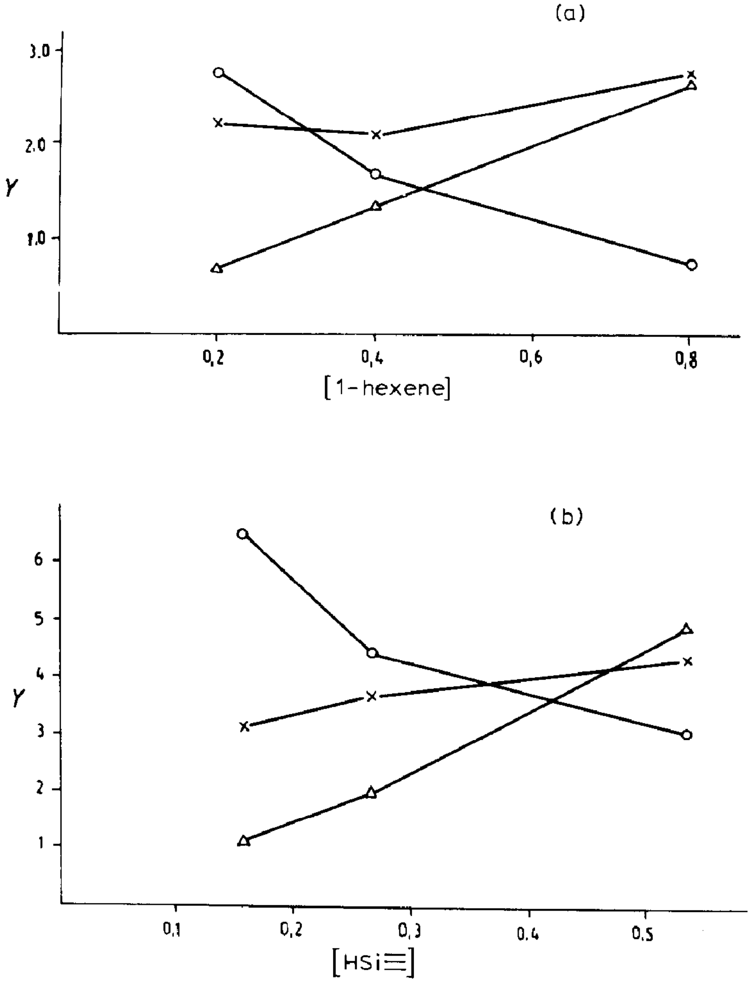


Fig. 4. Kinetic parameters of the reactions in **3** + 1-hexene system (a) and in **2′** + $HSi(OEt)_3$ system (b) for various concentrations of olefin or silane, respectively. [**2′**] 5.0×10^{-4} *M* in 0.80 *M* 1-hexene; [**3**] 5.0×10^{-4} *M* in 0.53 *M* $HSi(OEt)_3$; *T* 30 °C; phosphine = 1/2 BPS. × $Y = V_0$ (10^{-6} mol dm^{-3} s^{-1}), ○ $Y = \tau$ (20 h) for a and τ (h) for b, △ $Y = k_{obs}$ (5×10^{-6} s^{-1}) for a, and k_{obs} (10^{-5} s^{-1}) for b.

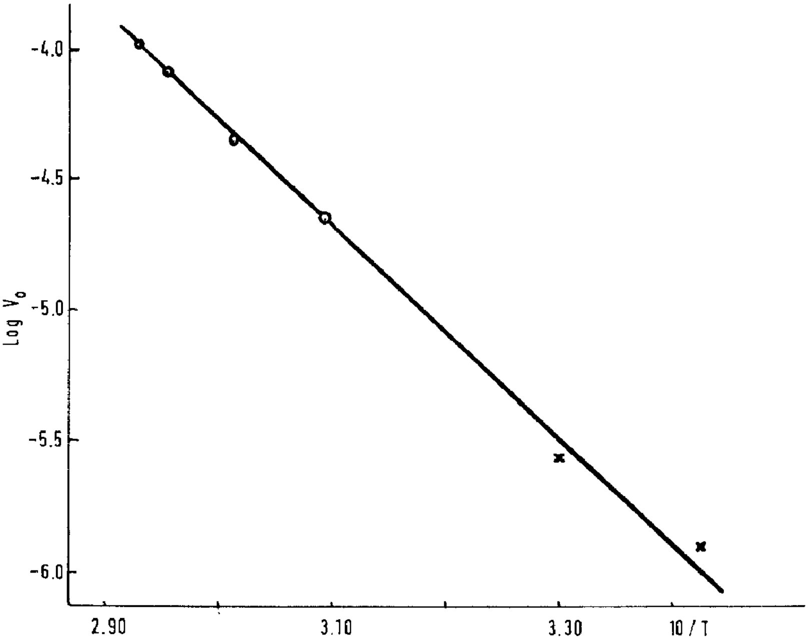


Fig. 5. Arrhenius plot for the reaction of 3 with 1-hexene. Phosphine = 1/2 BPS, ○ from ref. 5, × this work.

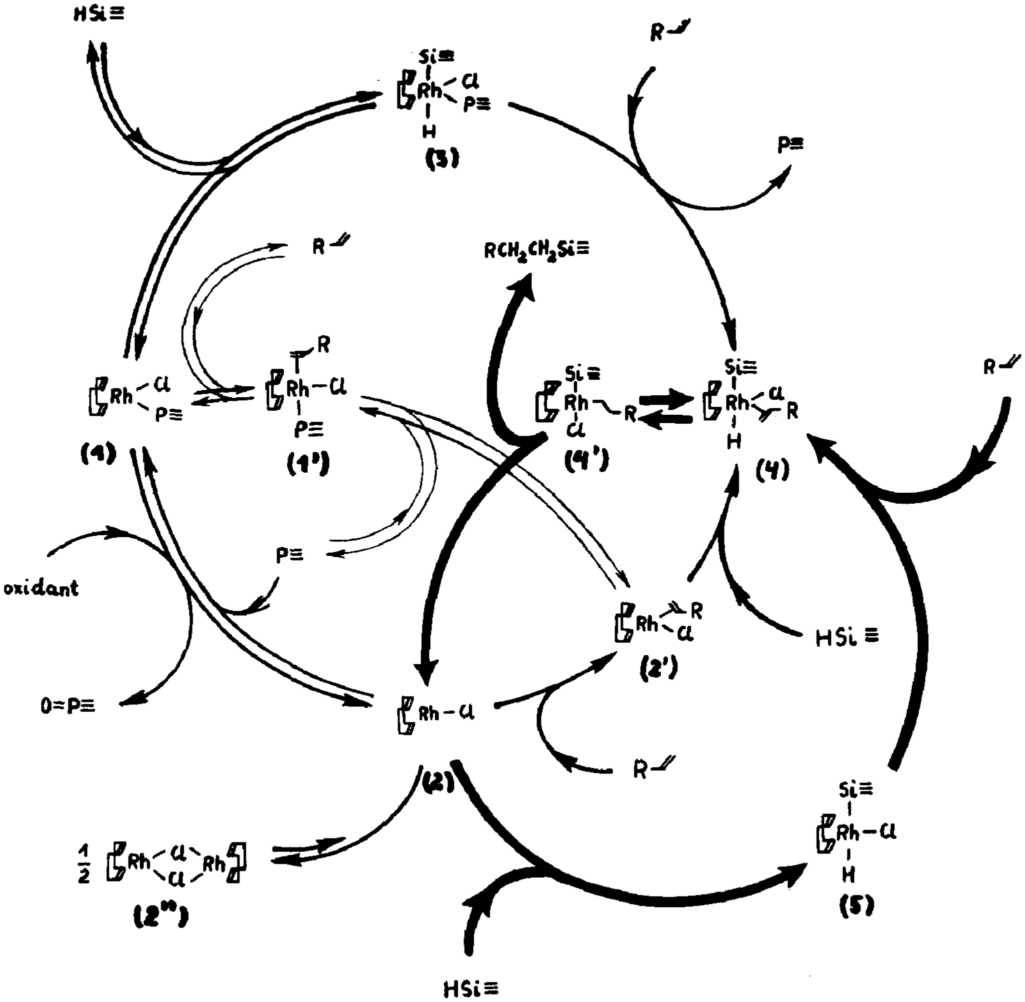
increase of the silane or hexene concentration. Arrhenius plot (Fig. 5) showing previously published data [5] at ambient temperature (50–70 °C) is in a very good agreement with V_0 introduced for the reaction of 3 with 1-hexene at 20 °C and 30 °C at the same concentration of rhodium and the substrates.

Discussion

All the data suggest that the rate of the product formation is controlled by concentration of **4** and its rate of decomposition. However, the values of V_0 are 2–3 orders of magnitude higher than the rate of formation of **4** ($k_{obs} \times [Rh]$); thus, the formation of **4** from **2′** with silane or from **3** with hexene is not involved in the catalytic cycle to give hexyltriethoxysilane. From the kinetic and catalytic data as well as some of the detected and identified of some intermediates, we propose the following scheme of hydrosilylation (Scheme 1).

In Table 3 are listed all the rate constants, equilibrium constants and initial rates for the individual steps of the reaction examined for the phosphines used, viz. PPh_3 and BPS.

The initial complex **1** reacts under oxidant-free conditions to give **2′** or **3**, but another path was found to be faster: In the presence of oxidant a tricoordinated key intermediate is readily formed (being in equilibrium with dimer). These three pathways lead to the complexes **4** and **4′**, which decompose to start in the catalytic cycle of the reaction. The induction period is probably a measure of the level of activation of the initial catalyst i.e. the generation of a key intermediate **2** which favours reaction with triethoxysilane to form complex **5**. The latter (**5**) reacts with 1-hexene to give the hexacoordinated species **4**. The reaction of the π complex to



Scheme 1. Proposed mechanism for the hydrosilylation of 1-hexene by triethoxysilane catalysed by [RhCl(COD)(phosphine)].

give the σ complex (4 → 4′) cannot be detected by the techniques used. Nevertheless, all the routes in the principal cycle are markedly faster than the preliminary stages of complex 4 formation.

Conclusions

1. All the kinetic and analytical measurements have shown that the exemplified catalytic hydrosilylation consists of essentially two stages. The first is an activation of the rhodiummonophosphine precursor to give the active intermediates and 4 → 4′ (Scheme 1), which initiates the usual catalytic hydrosilylation cycle. The rate constants of the individual steps (Table 3) as well as of the observed induction period of the reaction (Tables 1 and 2) indicate that the catalytic cycle occurs at a rate several orders of magnitude greater than that of activation.

2. The proper catalytic cycle proceeds via intermediates without the phosphine ligand. The observed effect of phosphine as well as of the oxidation of phosphine

Table 3

Compilation of the individual rate constants (20 ° C) for the hydrosilylation of 1-hexene by triethoxysilane catalyzed by [RhCl(COD)(phosphine)] (from ref. 3 and 4 or this work).

Step	Constant	For the phosphine	
		PPh_3	1/2 BPS
1 → 1′	k_2	$(1.46 \pm 0.15) \times 10^{-5}$	$(2.11 \pm 0.23) \times 10^{-5}$
1′ → 1	k_1	$(0.93 \pm 0.29) \times 10^{-5}$	$(1.22 \pm 0.36) \times 10^{-5}$
1′ → 2′	k_1	$(1.12 \pm 0.13) \times 10^{-5}$	$(1.57 \pm 0.15) \times 10^{-5}$
2′ → 1′	k_2	$(3.4 \pm 2.6) \times 10^{-4}$	$4.3 \pm 3.2) \times 10^{-4}$
1 → 3	k_2	$(2.44 \pm 0.24) \times 10^{-4}$	$(12.3 \pm 2.4) \times 10^{-4}$
3 → 1	k_1	$(5.4 \pm 1.9) \times 10^{-7}$	$(39 \pm 14) \times 10^{-7}$
1 → 2	k_2	3.2 ± 0.1	4.9 ± 0.4
2 → 1	k_2	–	$> 10^5$
2 → 2′	k_2	–	$< 10^{-8}$
3 → 4 or **4′**	k_2	$(3.2 \pm 1.0) \times 10^{-6}$	$(7.3 \pm 1.3) \times 10^{-6}$
2′ → 4 or **4′**	k_2	$(5.08 \pm 0.61) \times 10^{-5}$	$(4.66 \pm 0.53) \times 10^{-5}$
4 or **4′ → 2**	k_1	$\geqslant 3.3 \times 10^{-3}$	$\geqslant 3.6 \times 10^{-3}$
2 → 5	k_2	–	$\gg 6$
5 → 4	k_2	–	$\gg 6$
2″ ⇄		10^{-8}	

k_1 (s^{-1}) is the first order rate constant
k_2 (dm^3 mol^{-1} s^{-1}) is the second order rate constant
K_d ($mol\ dm^{-3}$) is the dissociation constant

influences only the first activation process (i.e. the induction period) of hydrosilylation whereas the rate of the essential catalytic process remains virtually unchanged. These observations confirm our previous suggestions that for silica- (or silicate-) supported complex catalysts with a ligand structure similar to that of the siloxyphosphine (BPS) used, the anchored complex (via one molecule of phosphine) is released into the solution to catalyze the hydrosilylation homogeneously.

3. The catalytic hydrosilylation studied is one of a few examples which directly and in detail support and develop the general mechanism of the catalysed hydrosilylation proposed by Chalk and Harrod [7].

Experimental

All experiments were carried out under purified and dried argon. Benzene (POCh) and 1-hexene (Fluka AG) were dried and distilled in argon. $HSi(OEt)_3$ was prepared by a published procedure [6] and redistilled under argon before use. [RhCl(COD)(1-hexene)] (**2′**) and [RhCl(COD)H(Si≡)(phosphine)] (**3**) were prepared in benzene solutions from [RhCl(COD)(phosphine)] and 1-hexene (0.80 *M*) or $HSi(Et)_3$ (0.53 *M*). The course of these reactions was monitored spectrophotometrically [1,3]. The preparation of [RhCl(COD)(phosphine)] [5] and its oxidant free reaction with 1-hexene [3] was described previously.

The solutions examined were prepared by the addition of 1-hexene (5 ml) or $HSi(OEt)_3$ (5 ml) to a solution of complex **3** or complex **2′**, respectively, in benzene

(45 ml). Spectrophotometric measurements of the solutions were made by Specord UV-VIS spectrophotometer (Carl Zeiss, Jena) in quartz cells, hermetically sealed with silicon rubber. Gas chromatographic analyses were carried out on a Chrom 5 (Czech.) instrument, equipped with a thermal conductivity detector, in a steel column packed with 10% SE-30 on Chromosorb.

Acknowledgment

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