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INTERMEDIATES IN HYDROSILYLATION OF VINYLTRICHLOROSILANE CATALYZED BY PALLADIUM PHOSPHINE COMPLEXES*

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Summary

Hydrosilylation of vinyltrichlorosilane by trichlorosilane in the presence of Pd(0) and Pd(II) phosphine complexes at 120 °C leads to quantitative formation of 1,1-bis(trichlorosilyl)ethane (α-adduct), whereas this reaction with vinyltri(methyl, chloro)silanes gives β-adducts [2].

Treatment of $PdCl_2(PPh_3)_2$ with trichlorosilane (vinyltrichlorosilane) at 120 °C allowed generation of intermediates which appeared to be active at 45 °C (at 80 °C) in the hydrosilylation of vinyltrichlorosilane by trichlorosilane. Spectroscopic and other analytical examinations of the isolated intermediates, as well as their catalytic activities determined on the basis of kinetic measurements, have led to the proposal of an improved scheme for hydrosilylation of vinyltrichlorosilane by palladium phosphine complexes given earlier [3]. The nature of the palladium–silicon–hydrogen bonds in the intermediates isolated presumably plays a crucial role in mechanistic considerations in the hydrosilylation of vinyltrichlorosilane by trichlorosilane. Kinetic evidence was also found for catalysis by dimeric palladium species.

Introduction

A study of the hydrosilylation of vinyltri(chloro, methyl)silanes by tri(chloro, methyl)silanes in the presence of palladium phosphine complexes showed the reaction to proceed effectively, giving predominantly 1,2-bis(silyl)ethanes (β-adducts), except in the case of all chloro substituents at both silicon atoms of the substrates [3]. The latter reaction was reported earlier [2] to give almost quantitatively 1,1-bis(trichlorosilyl)ethane (α-adduct). Consequently, the above-mentioned reaction occurs according to the following scheme:

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*Part XVII in the series *Catalysis of Hydrosilylation;* for Part XVI see [1].

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$$\begin{array}{l} \mathrm{Cl}_n(\mathrm{CH}_3)_{3-n}\mathrm{SiH} \\ \quad + \mathrm{CH}_2{=}\mathrm{CHSi}(\mathrm{CH}_3)_m\mathrm{Cl}_{3-m} \end{array} \left\{ \begin{array}{l} \rightarrow \mathrm{Cl}_n(\mathrm{CH}_3)_{3-n}\mathrm{SiCH}(\mathrm{CH}_3)\mathrm{Si}(\mathrm{CH}_3)_m\mathrm{Cl}_{3-m} \\ \qquad\qquad (\alpha\text{-adduct})\ n = 3;\ m = 0 \\ \\ \rightarrow \mathrm{Cl}_n(\mathrm{CH}_3)_{3-n}\mathrm{SiCH}_2\mathrm{CH}_2\mathrm{Si}(\mathrm{CH}_3)_m\mathrm{Cl}_{3-m} \\ \quad n = 1 - 3;\ m = 0 - 3;\ \text{except}\ n = 3;\ m = 0 \\ \quad (\beta\text{-adduct}) \end{array} \right. \qquad (1)$$

Detailed examinations have shown almost identical efficiency of two triphenylphosphine complexes of palladium used as precursors, *i.e.* $\mathrm{Pd(PPh_3)_4}$ and $\mathrm{PdCl_2(PPh_3)_2}$, regardless of the oxidation state of the metal and conditions of metal complex preparation. Preliminary treatment of the Pd(0) and Pd(II) precursors prior to use by trichlorosilane or vinyltrichlorosilane has no effect on the high yield of the α-adduct observed under the conditions examined (120 °C, 6 h) [3]. However, formation of the palladium complexes with silanes and their high catalytic activity in the hydrosilylation under milder conditions could be evidence for the presence of active intermediates. Therefore, the aim of our present studies is to find, possibly isolate, and evaluate palladium intermediates responsible for the rate and unusual regioselectivity of the reaction under study.

Experimental

Materials

Trichlorosilane and vinyltrichlorosilane as well as all solvents used were commercial products distilled prior to use. $\mathrm{Pd(PPh_3)_4}$ and $\mathrm{PdCl_2(PPh_3)_2}$ were prepared by the methods described earlier [4, 5].

Synthesis of Pd complexes with silanes

Palladium complexes with silanes were prepared by treating $\mathrm{Pd(PPh_3)_4}$ or $\mathrm{PdCl_2(PPh_3)_2}$ with trichlorosilane and vinyltrichlorosilane as substrates of the hydrosilylation, and are denoted as given in Table 1. A typical procedure for the synthesis of complexes is as follows: 5×10^{-5} mole of the precursors ($\mathrm{PdCl_2(PPh_3)_2}$ or $\mathrm{Pd(PPh_3)_4}$) and 5×10^{-3} mole of the trichlorosilane (complexes A, B, C, D and E) or vinyltrichlorosilane (B′, C′, D′) were placed in a glass ampoule and sealed in an atmosphere of dry air (complexes A, B, B′, D and D′) or argon (C, C′ and E) and heated at 120 °C for 6 h (all complexes except A) or at room temperature for 24 h (A). Soluble (except A) complexes at 120 °C were cooled at 20 °C. The brown (B, C, D, E), yellow (B′, C′) or orange (D′) solids were filtered, washed with hexane and dried *in vacuo*.

Analytical measurements

Elemental C, H, P and Cl analyses were carried out with a Perkin-Elmer microanalyzer. Palladium was analyzed spectrophotometrically [6]

TABLE 1

Designation of intermediates isolated from the reaction of precursors $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ with silane substrates

Symbol	Silane	Conditions
$PdCl_2(PPh_3)_2$		
A	$HSiCl_3$	20 °C, 48 h, air
B	$HSiCl_3$	120 °C, 6 h, air
B′	$CH_2=CHSiCl_3$	120 °C, 6 h, air
C	$HSiCl_3$	120 °C, 6 h, argon
C′	$CH_2=CHSiCl_3$	120 °C, 6 h, argon
$Pd(PPh_3)_4$		
D	$HSiCl_3$	120 °C, 6 h, air
D′	$CH_2=CHSiCl_3$	120 °C, 6 h, air
E	$HSiCl_3$	120 °C, 6 h, argon

TABLE 2

The ratios of gram-atoms in intermediates and precursors based on elemental analysis

Compound	C	H	P	Cl	Si	Pd
$PdCl_2(PPh_3)_2$	38	33	2.1	2.1	—	1.0
B	38	34	1.7	2.3	0.83	1.0
B′	42	42	2.2	2.5	0.73	1.0
C	47	41	2.4	2.9	0.87	1.0
C′	43	45	2.2	3.5	0.73	1.0
$Pd(PPh_3)_4$	73	60	4.0	—	—	1.0
D	52	50	2.6	2.0	0.60	1.0
D′	48	49	2.6	1.2	0.46	1.0
E	61	50	3.0	2.0	0.62	1.0

and silicon gravimetrically, by a commonly used method. Complexes based on $PdCl_2(PPh_3)_2$ (m.p. = 270 °C) are decomposed above 100 °C, whereas the complexes based on $Pd(PPh_3)_4$ (m.p. = 105 °C) precursor are decomposed above 80 °C. Analytical data of the intermediates are summarized in Table 2.

The IR spectra were recorded (in the range 4000 - 200 cm^{-1}) on a Perkin-Elmer Model 180 spectrophotometer, as KBr and CsBr pellets). ^1H NMR spectra of only partially soluble intermediates in $CDCl_3$ and/or C_6D_6 solutions were measured using a JEOL FX 900 spectrometer with TMS as an internal standard. Spectroscopic data are presented in Table 3.

Gas chromatographic analyses were carried out on a GCHF 18.3 Chromatron (GDR) instrument using a steel column packed with 10% SE-30 on Chromosorb P-AW-DMCS with a thermal conductivity detector.

TABLE 3

Spectroscopic data of intermediates B - E

Compound	B	C	D	E
	IR[a] *(ν in cm^{-1})*			
Pd—H	2260	2260	2260	2260
Si—H	340	340	340	340
Pd—Cl	360	365	360	360
Si—Cl	470	460	460	460
O—O	880	—	880	—
Si—O—Si	1050 - 1150	—	1050 - 1150	—
	^{1}H NMR[b] *(δ in ppm)*			
Si—H	4.46	4.46	4.46	4.46
Pd—H	—	−13.2	—	—

[a] ν(SiH) (in $HSiCl_3$) = 2270 cm^{-1}.

[b] δ (SiH) (in $HSiCl_3$) = 6.09 ppm.

Hydrosilylation tests

Most experiments were carried out in sealed glass ampoules under dry air or argon, unless indicated otherwise. In a typical run, a glass ampoule containing vinylsilane (0.005 mol), hydrosilane (0.005 mole) and a catalyst (2×10^{-4} mol/mole vinylsilane) was heated without solvent at a given temperature for a given time. 1,1-Bis(trichlorosilyl)ethane, a product of hydrosilylation, was identified by GLC technique.

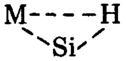
Kinetic measurements

Kinetic experiments were carried out in a thermostatted vessel of 20 ml capacity equipped with a stopcock. In a typical individual run, 5 ml of homogeneous toluene solution of the catalyst (B or D) and a given amount of vinyltrichlorosilane was placed in a thermostatted reaction vessel for 10 min with magnetic stirring. Subsequently, an equimolar amount of trichlorosilane was injected into the reaction vessel; samples of the reaction mixture were collected with a syringe at specified time intervals (usually 5 - 10 min) and analyzed by GLC technique, using n-dodecane as a reference.

Results

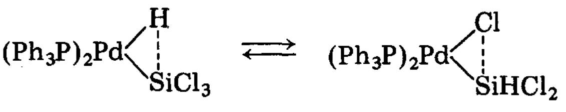
Treatment of palladium complexes with trichlorosilane at 120 °C results in a formation of palladium–silyl complex mixtures B and C. IR spectra of complexes B, C exhibit absorption bands at 2260 ± 10 cm^{-1} that could be attributed to the Pd—H [7, 8] and/or Si—H [9] bond, although broad signals in this region indicate a predominance of silicon-bonded hydrogen over Pd—H, particularly under dioxygen conditions. Chemical shifts of hydrogen in Pd—H species were detected and measured in some complexes, especially in those treated under oxygen-free conditions. On the otner hand, the chemical shift δ 4.46 ppm, which presumably corresponds to silicon-attached hydrogen, is observed for most palladium complexes treated by hydrosilanes at 120 °C (B, C, D and E) regardless of the atmosphere used for preparation. The chemical shift of the silicon-bonded hydrogen in Pd—Si complex mixtures is shifted upfield in comparison with the corresponding ^{1}H chemical shift of free trichlorosilane (δ 6.09 ppm). However, it should be noted that the measured chemical shifts characterise only the soluble parts of the intermediate mixtures, since they were not totally soluble in C_6D_6 and $CDCl_3$ at room temperature. On the other hand, preliminary examinations of the complexes from $PdCl_2(PPh_3)_2$ with methyldichlorosilane (under analogous conditions as B and C) showed no Si—H absorption in the IR spectra, and benzene solutions indicated no ^{1}H chemical shift in the region corresponding to the hydrogen of Si—H bond.

H/Cl exchange at silicon occurring via the transition metal center is a well-known redistribution reaction of organosilicon and silicon compounds [10], *e.g.* with the nickel complex $NiCl_2(PPh_3)_2$ [11]. Therefore, most hydrosilylation processes of the compounds particularly involving chloro and alkoxy substituents at the silicon are accompanied by H/Cl or H/OR redistribution, which is markedly facilitated by olefins [12]. Nevertheless, in the absence of olefins, both types of palladium–silyl complexes can be formed with the H—Pd—Si predominating. But recent NMR studies by Colomer *et al.* [13] on silicon manganese hydrides show the possibility of bond interaction between silicon and hydrogen at the metal center. This bond can be actually expressed as the following three-centered bond representing a structural tautomer (2):



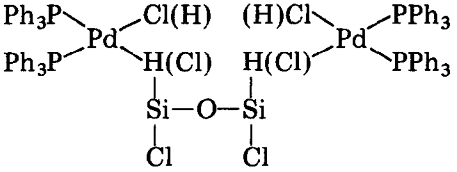
$$M\text{---}H \;\; \overset{}{\underset{Si}{}} \qquad (2)$$

Both reported phenomena, H/Cl exchange and silicon–hydrogen affinity at a metal center, as well as the spectroscopic analysis of the complexes B and C, allow us to propose the existence of the following equilibrium:



$$(Ph_3P)_2Pd\langle^{H}_{SiCl_3} \rightleftharpoons (Ph_3P)_2Pd\langle^{Cl}_{SiHCl_2} \qquad (3)$$

Treatment of palladium complexes by silanes in the presence of dioxygen can also lead to the formation of $(Ph_3P)_2PdO_2$ in the cooled mixture. IR spectra of the complexes obtained under such conditions show a strong band assigned to the O—O bond (870 - 890 cm^{-1}) of $(PPh_3)_2PdO_2$ species [8]. The spectra also showed a slight broad band at 1000 - 1200 cm^{-1} attributable to Si—O—Si. This may correspond to the formation of a Pd complex with siloxanes formed in the presence of a mixture in which hydrogen can be attached to palladium or silicon:



(4)

A treatment of the precursors by trichlorosilane in air (complexes B and D) reduces markedly the content of chlorine and phosphorus in the isolated complex mixtures, presumably due to the hydrolysis of the Si—Cl bond by the introduced moisture, followed by condensation of silanol groups to siloxanes, and release of the phosphine ligands by their oxygenation to phosphine oxide [14], respectively. All analytical and spectroscopic data indicate that the complexes B and C consist of mixtures of monomeric palladium–silyl complexes $PdH(SiCl_3)(PPh_3)_2$ and/or $PdCl(SiHCl_2)(PPh_3)_2$, as well as dimeric complexes (4) with siloxy ligand and monomeric $Pd(PPh_3)_2O_2$ or $PdO(PPh_3)_2$ or oligomers $[Pd(PPh_3)_2]_n$, although species of the composition $P:Pd > 2$ (under oxygen-free conditions) cannot be ruled out. It is also worth considering the formation of dimers bridged by PPh_2 [12] Cl, O or perhaps $SiCl_2$. All analytical results confirm that complexes isolated from the treatment of $Pd(PPh_3)_4$ precursor with trichlorosilane (D and E) contain the same type of intermediates proposed for complexes B and C obtained under given conditions.

Reaction of $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ with vinyltrichlorosilane leads to intermediates involving presumably coordinatively bound vinylsilanes of the general formula $PdCl_x(PPh_3)_n(CH_2{=}CHSiCl_3)$ where $x = 0$ and 1, but the respective complexes with divinylsiloxane must also be considered under moisture conditions. No $Pd(O_2)$ stretching band was observed in the complexes obtained under oxygen conditions. The above considerations of the Pd complex formulas are based only on the elemental analysis and well-known ability of palladium phosphine complexes to form such adducts with π-donors [16], since IR and ^1H NMR spectroscopic analysis has shown no characteristic bonding, besides Pd—Cl (340, 360 cm^{-1}) and Si—O—Si (1050 - 1150 cm^{-1}), in the intermediates isolated. A reduction of Pd(II) to Pd(O) possibly occurs during the treatment of vinylsilanes. However, no detailed study has yet been carried out, since no effective activation of precursors by vinylsilanes below 95 °C was found.

The complexes A - E as well as the precursors $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were tested in the addition reaction of trichlorosilane with vinyltrichlorosilane. The yields of 1,1-bis(trichlorosilyl)ethane (α-adduct) obtained under given conditions are summarized in Table 4. The results show much higher catalytic activity of all intermediates obtained by treating the precursors with trichlorosilane at 120 °C (determined over the entire range of temperatures 45 - 120 °C) and vinyltrichlorosilane (only above 80 °C) as compared to those of the precursors and the intermediates obtained at room temperature (A).

TABLE 4

Yield of 1,1-bis(trichlorosilyl)ethane (α-adduct) in % in the reaction of trichlorosilane with vinyltrichlorosilane catalyzed by palladium complexes[a]

Complex	% Yield (time)				
	45 °C	60 °C	80 °C	95 °C	120 °C
$PdCl_2(PPh_3)_2$	0	0	0	0	62 (2 h) 96 (6 h)
A	0	0	0	0	70 (6 h)
B	60 (2 h) 90 (4 h)	95 (4 h)	95 (1 h)	85 (15 min)	94 (5 min)
B′	traces (12 h)	traces (12 h)	5 (1 h)	92 (60 min)	94 (5 min)
C	traces (12 h)	90 (4 h)	65 (1 h)	88 (35 min)	95 (5 min)
C′	traces (12 h)	traces (12 h)	5 (1 h)	92 (60 min)	94 (5 min)
$Pd(PPh_3)_4$	0	0	20 (1 h)	—	70 (2 h)
D	40 (2 h) 52 (4 h) 95 (12 h)	90 (1 h)	94 (1 h)	90 (15 min)	93 (5 min)
D′	0 (12 h)	traces (1 h)	10 (1 h)	—	96 (55 min)
E	80 (12 h)	93 (1 h)	94 (1 h)	90 (15 min)	93 (5 min)

[a] $[\equiv SiH]_0:[CH_2{=}CHSi{\equiv}]_0:[cat]_0 = 1:1:2 \times 10^{-4}$.

The most active, B, D and E, effectively catalyze the reaction even at 45 °C. Therefore, catalysts B and D were tested in kinetic measurements for the effects of temperature, concentrations of catalyst and substrates on the initial rate (V_0) or the reaction examined, with the aim to express quantitatively the catalytic activity of the intermediates isolated. This dynamic parameter was determined graphically from the initial course of the kinetic curves of autocatalytic shape. A reaction of trichlorosilane with vinyltrichlorosilane was studied within the temperature range 90 - 105 °C. Our experiments essentially show the first order of the reaction with respect to hydrosilane and vinyltrichlorosilane, but an unusual second-order of the reaction with respect to the catalyst (B and D) (Fig. 1).

An Arrhenius plot of the initial rate V_0 *vs.* $1/T$ permits evaluation of the energy of activation, which is identical for both catalysts studied. Error limits are standard deviations obtained by least-squares regression treatment of the linear form of the respective equations (Table 5).

Discussion

The previously proposed scheme for generation of active intermediates of the reaction examined [3] must be improved, since the data obtained in this work (Scheme 1), *i.e.* much higher activity of the intermediates B and D, suggests that they contain active intermediates. Fitton *et al.* [17]

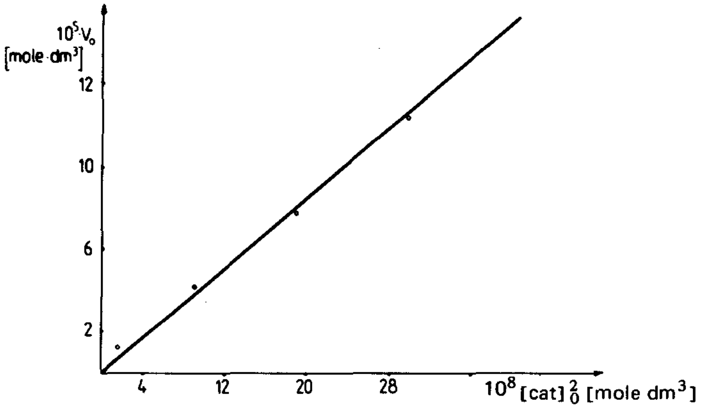


Fig. 1. Plot of the initial rate of the hydrosilylation reaction *vs.* the square of the concentration of catalyst used.

TABLE 5

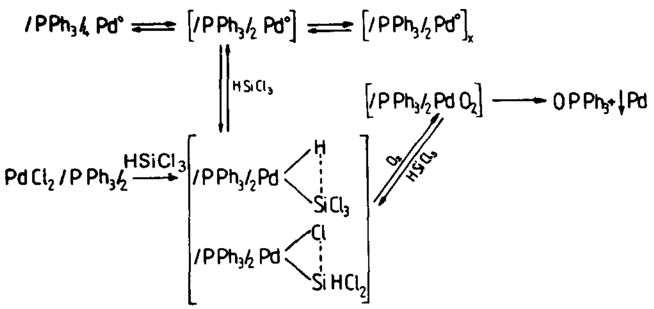
Kinetic measurements of the hydrosilylation of vinyltrichlorosilane by trichlorosilane[a]

Catalyst	B		D	
$[CH_2{=}CHSi{\equiv}]_0$ / $[HSi{\equiv}]_0$	1:1	1:2	1:1	1:2
Temp. (°C)	10^5 V_0 (M s^{-1})			
90	7.05	7.3	4.7	5.4
95	8.4	11.1	5.5	8.4
100	16.2	16.4	11.2	14.4
105	24.0	27.8	15.8	18.0
E_a (kcal mol^{-1})	22.2 ± 0.6	21.8 ± 0.3	21.6 ± 0.4	22.0 ± 0.3

[a] $[HSi{\equiv}]_0 = 5 \times 10^{-3}$ and 10^{-2} M, $[CH_2{=}CHSi{\equiv}]_0 = 5 \times 10^{-3}$ M, $[CH_2{=}CHSi{\equiv}]_0$: $[\text{cat.}]_0$ = 2.10^{-4}; air, toluene.

and Tsuji *et al.* [4] proposed an oligomeric complex $[(PPh_3)_2Pd]_n$ as an intermediate in catalytic reactions involving trichlorosilane. Scheme 1 shows a path creating the palladium–silyl complexes from both precursors used in the activation process occurring during preparation of the complexes B and D.

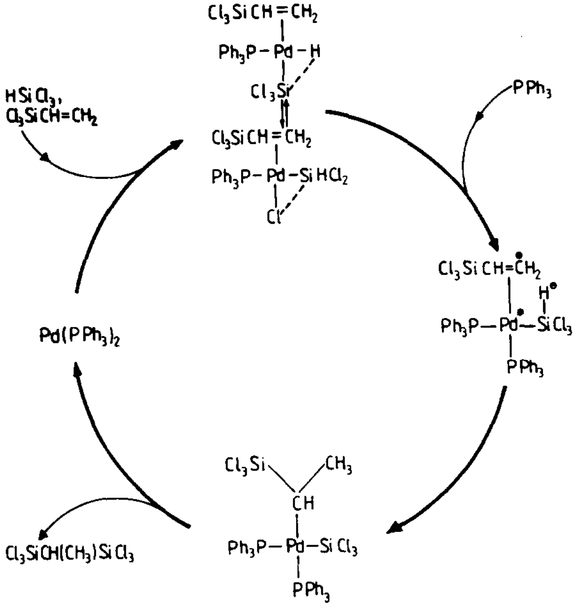
Formation of these complexes proceeds via an oxidative addition of hydrosilane (and elimination of $SiCl_4$ and HCl, or H_2) in which the metal oscillates presumably between the oxidation states of 0 and II or, perhaps, II and IV. In the presence of vinylsilane, metal coordination to the complexes (eqn. (3)) takes place possibly by replacing the phosphine ligand; during the hydrosilylation cycle (according to the general mechanisms [18,



Scheme 1. Mechanism of palladium–silyl intermediate formation.

19]) addition of Pd—H to C=C bond coordinated to the metal is followed by σ-alkyl(silyl)–metal complex formation, leading finally to an α-adduct, as was shown earlier in detail [3]. However, different regioselectivities of the hydrosilylation of vinyltrichlorosilane by trichlorosilane (α-adduct) and by tri(chloro, methyl)silane (β-adducts) cannot be fully accounted for by those mechanistic considerations.

All analytical data confirm the idea of the hydrogen bonded to silicon rather than palladium in the intermediate. Therefore, we propose Scheme 2 for possible reactions of the complexes (Scheme 1) with vinyltrichlorosilane (π-complex → σ-complex)



Scheme 2. Mechanism of the palladium–silyl intermediate interaction with vinyltrichlorosilane.

Interactions of H—Pd—Si and Cl—Pd—Si in the two (I and II) palladium-silyl complexes with a coordinating molecule of vinylsilane are assumed to involve a five-covalent silicon, bonded to a palladium(III) center, with hydridic hydrogen, favouring hydride transfer from the silicon atom to the β-carbon of the vinylsilane molecule. Replacement of the chlorine by a methyl group, markedly decreasing the electron-withdrawing effect of the substituents at silicon, reduces the possibilities of palladium–silicon(V) intermediate formation and simultaneously the reaction path via such intermediates. The above considerations do not rule out a catalytic role of the Pd—H bond in the hydrosilylation. Actually, the nature of the H—Pd—Si bond, which depends on other substituents at silicon and on the ligands at the palladium atom, seems to be crucial in determining the unusual regioselectivity of the reaction examined.

Kinetic measurements have revealed a favourable catalysis of this reaction by palladium dimer(s) (a second-order reaction with respect to the catalyst observed) which can react with one molecule of hydrosilane (or vinyltrichlorosilane) in the rate-determining step. Such a phenomenon was also found for ruthenium phosphine complex-catalyzed hydrosilylation of vinyltriethoxysilane by triethoxysilane, but only at low concentrations of catalysts [20].

In the case of the examined palladium complexes, such dimers can be bridged by diphenylphosphine species according to the literature data [15], as well as by silicon-containing species *e.g.* $SiCl_2$. The latter can form in the reaction of the Pd center with dichlorosilane, detected experimentally in the redistribution of trichlorosilane occurring in the presence of the palladium complexes examined. Such dimers optimally explain the kinetic data and favour the reaction mechanism involving π-complex → σ-complex (see also Scheme 2). Efforts toward the isolation and identification of all intermediates in the palladium phosphine complex-catalyzed hydrosilylation are continuing.

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