

ORGANOSILICON COMPOUNDS. LXXVIII.*

THE EFFECT OF STRUCTURE
OF SILYL HYDRIDES
ON HYDROSILYLATION OF OLEFINS

M. ČAPKA, P. SVOBODA, V. BAŽANT and V. CHVALOVSKÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague-Suchdol*

Received September 1st, 1970

The relative rate constants (k_{re1}) of the addition of ethylchlorosilanes of the type $(C_2H_5)_3-nCl_nSiH$ ($n = 0-3$) to 1-heptene and of propylethoxysilanes of the type $(n-C_3H_7)_3-n(OC_2H_5)_nSiH$ ($n = 0-3$) to 1-hexene catalyzed with H_2PtCl_6 were determined. Also were measured k_{re1} of the addition of phenyldimethylsilane, *p*-chlorophenyldimethylsilane, and *p*-methoxyphenyldimethylsilane to ethylene catalyzed with H_2PtCl_6 , $Co_2(CO)_8$ and $RhCl[(C_6H_5)_3P]_3$. It was found that the reactivity of a silane increases with decreasing hydridic character of its Si—H bond. The addition of *p*-substituted phenyldimethylsilanes to ethylene catalyzed with H_2PtCl_6 and $RhCl[(C_6H_5)_3P]_3$ is first order in ethylene. The mechanism of the reaction and the effect of structure of the silanes on their reactivity in hydrosilylation reaction are discussed.

Due to undefined induction period and poor reproducibility of the reaction^{1,2}, the study of the effect of the structure of silanes on the rate of their addition to olefins could not be supported by sufficiently reliable kinetic measurements.

Although some attempts have been made to determine the reactivity of silicon hydrides in the hydrosilylation of olefins, these studies unfortunately suffer mostly from methodical imperfections (*e.g.* the rate constants of the addition of alkylsilanes of the type $RSiH_3$ were determined from the overall loss of the Si—H bond³, the calculation of the rate constants was based on the yields of products isolated by distillation of small quantities of the compounds⁴, the comparison of the reactivity of silanes was made using inconsistent⁵ or undefined⁶ reaction conditions) and thus they do not make it possible to draw conclusions concerning the mechanism of the reaction.

For the hydrosilylation of olefins catalyzed with dicobaltoctacarbonyl, Chalk^{7,8}, on the basis of the analysis of the reaction products, presumed the effective catalyst to be hydridocobalt-tetracarbonyl, formed by the reaction of dicobalt octacarbonyl with a silane, to which an olefin is coordinated. The subsequent attack of the silicon hydride on this alkylcobalt complex leads to the formation of an alkylsilane and the catalyst hydridocobalt tetracarbonyl.

Mac Diarmid⁹ examined the reaction of hydridocobalttetracarbonyl with ethylene and found that certain reaction proceeds both in the gas and liquid phase, he has been however unsuccessful

* Part LXXVII: This Journal 36, 2174 (1971). Also Part II of the series „Catalysis by Metal Complexes“. Part I: Chemický průmysl 21, 324 (1971).

in neither proving nor disproving that the product of the reaction is ethylcobalttetracarbonyl. The product did not react with silicon hydride and thus the mechanism proposed by Chalk could be accepted only on condition that the presumed ethylcobalt tetracarbonyl was completely decomposed within 85 seconds at 25°C (the time needed for the addition of the silane). It seems that the mechanism of the reaction is more complex.

On the other hand, the ease with which bis(triphenylphosphine)trichlorosilylrhodium chloride¹⁰ is formed indicates that in this case a coordination of the silane to the transition metal complex may precede the attack of the olefin. Another mechanism was proposed for the hydrosilylation catalyzed with olefin-platinum and -rhodium complexes, presuming¹¹ the formation of an intermediate complex having both olefin and silyl group bonded to the transition metal. Recently, a series of hydrogenation catalysts was employed¹² in the hydrosilylation of olefins, which stresses the similarity of mechanism of both reactions.

Attempting to elucidate still unclear mechanism of hydrosilylation, we tried both to ascertain the effect of the structure of silanes on the rate of their addition to olefins and to investigate the kinetics of the reaction. We believed that comparison of the effect of the structure of silanes in their additions catalyzed with the three, most important catalysts — hexachloroplatinic acid, tris(triphenylphosphine)rhodium chloride, and dicobaltoctacarbonyl — would enable us to find similarities in general mechanism.

EXPERIMENTAL

Compounds Used

Ethylene, 1-hexene, 1-heptene, and hexachloroplatinic acid were commercial products used without further purification. The following compounds were prepared in the usual manner: tripropylsilane¹³, dipropylethoxysilane¹⁴, propyldiethoxysilane¹⁴, triethoxysilane¹⁴, tris(triphenylphosphine)rhodium chloride¹⁵. Dicobalt octacarbonyl was kindly provided by Dr Sedlmayer (Institute of Chemical Technology, Pardubice).

Ethylchlorosilane was obtained by rectification of the mixture of ethylchlorosilanes obtained by direct synthesis (Research Institute of Organic Syntheses, Pardubice-Rybitvi), diethylchlorosilane was prepared by ethylation of ethylchlorosilane with ethylmagnesium bromide.

Phenyldimethylsilane, *p*-chlorophenyldimethylsilane, and *p*-methoxyphenyldimethylsilane were prepared by reduction of appropriate chlorosilanes with sodium bis(2-methoxyethoxy)aluminium hydride¹⁶.

Physical constants of all starting silanes and olefins were identical with those reported.

Hydrosilylation Products

Heptyltrichlorosilane was prepared in the usual manner¹⁷. Heptyltriethylsilane, heptylethylchlorosilane and heptyldiethylchlorosilane were prepared by the reaction of 1 ml (7.1 mmol) of 1-heptene with 1 ml of the appropriate silane catalyzed with 0.1 ml of 0.02M solution of hexachloroplatinic acid in tetrahydrofuran in a sealed ampule. The ampule was heated to 100°C for 4 hours. The products of the reaction were isolated by gas chromatography.

Hexyltripropylsilane, hexyldipropylethoxysilane, hexylpropyldiethoxysilane, and hexyltriethoxysilane were prepared in a similar fashion. These were isolated by distillation.

p-Methoxyphenyldimethylethylsilane. A stainless steel autoclave was charged with 2 ml of *p*-methoxyphenyldimethylsilane and 0.3 ml of freshly prepared 0.01M solution of hexachloroplatinic

acid in tetrahydrofuran. The autoclave was flushed twice with ethylene at the pressure 10 atm and then pressurized by ethylene to 25 atm. Within 10 minutes the pressure dropped to 15 atm. After warming up to 100°C and re-filling of the autoclave by ethylene to the pressure of 25 atm, the pressure kept constant. After cooling, the reaction mixture was distilled under reduced pressure. Chromatographic analysis showed that the obtained *p*-methoxyphenyldimethylethylsilane contained approx. 3% of a higher boiling compound (presumably telomer). Phenyldimethylethylsilane and *p*-chlorophenyldimethylethylsilane were obtained similarly.

Physical constants and elemental analyses of the hydrosilylation products are presented in Table I.

Kinetic Measurements

Competition additions of the ethylchlorosilanes to 1-heptene and of the propylethoxysilanes to 1-hexene were carried out in sealed glass ampoules. To weighed amounts of the ethylchloro-

TABLE I

Physical Constants of the Products of the Addition of Silicon Hydrides to Olefins

Compound	n_D^{20}	Formula (Mol. weight)	Calculated/Found	
			% C	% H
$C_7H_{15}SiCl_3$	1.4461 ^a	$SiC_7H_{15}Cl_3$ ^b (233.658)	—	—
$C_7H_{15}Si(C_2H_5)Cl_2$	1.4468	$SiC_9H_{20}Cl_2$ (227.3)	47.89 47.57	8.88 8.87
$C_7H_{15}Si(C_2H_5)_2Cl$	1.4449	$SiC_{11}H_{25}$ ^c (220.9)	—	—
$C_7H_{15}Si(C_2H_5)_3$	1.4415 ^d	$SiC_{13}H_{30}$ (214.5)	73.07 72.80	13.99 14.10
$C_6H_{13}Si(OC_2H_5)_3$	1.4112 ^e	$SiC_{12}H_{28}O_3$ (248.4)	58.13 58.01	11.29 11.36
$C_6H_{13}Si(C_3H_7)(OC_2H_5)_2$	1.4217	$SiC_{13}H_{30}O_2$ (246.5)	63.37 63.31	12.13 12.27
$C_6H_{13}Si(C_3H_7)_2(OC_2H_5)$	1.4412	$SiC_{14}H_{32}O$ (244.5)	68.95 68.78	13.01 13.19
$C_6H_{13}Si(C_3H_7)_3$	1.4439	$SiC_{15}H_{34}$ (242.5)	—	—
$C_6H_5Si(CH_3)_2(C_2H_5)$	1.4943 ^f	$SiC_{10}H_{16}$ ^g (164.3)	72.97 73.09	9.80 9.81
<i>p</i> -ClC ₆ H ₄ Si(CH ₃) ₂ (C ₂ H ₅)	1.5117	$SiC_{10}H_{15}Cl$ ^h (198.8)	60.26 60.42	7.50 7.61
<i>p</i> -(CH ₃ O)C ₆ H ₄ Si(CH ₃) ₂ (C ₂ H ₅)	1.5068	$SiC_{11}H_{18}O$ ⁱ (194.4)	68.05 67.98	9.15 9.34

^a Ref.¹⁷ n_D^{20} 1.4462. ^b B.p. 210°C/760 Torr; reported²⁰ 210.7°C/760 Torr. ^c Calculated: 16.05% Cl; found: 16.18% Cl. ^d Reported²¹ n_D^{20} 1.4422; ^e n_D^{20} 1.4100 (ref.²²). ^f n_D^{20} 1.4938 (ref.¹⁹). ^g B.p. 76°C/15 Torr, ref.¹⁸ gives 198°C/759 Torr. ^h B.p. 110°C/15 Torr. ⁱ B.p. 115°C/15 Torr.

silanes and propylethoxysilanes placed in the ampule was added 0.10–0.15 ml of 1-heptene and 1-hexene, respectively, by means of calibrated pipette and 0.1 ml of 0.02M solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in tetrahydrofurane. After sealing, the ampule was immersed into thermostated oil bath kept at 120°C for the period of 4 hours. Each 15 minutes, the content of the ampule was shaken. Then the ampule was cooled and the reaction mixture analysed by gas chromatography. The weighted amounts were chosen so that the conversion of olefins would not exceed 10 mol. %.

The addition of ethylene to the phenyldimethylsilanes and of trimethylsilane to 1-decene were carried out in an apparatus enabling to work at constant pressure of a gaseous component and to follow the time-dependence of the consumption of the gas by a volumetric method (Fig. 1).

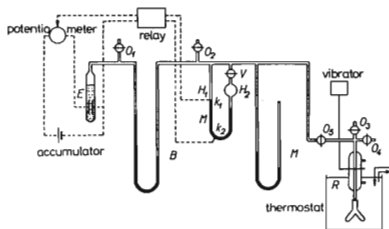


FIG. 1

Apparatus for Kinetic Following of the Reactions at Constant Pressure of One Reactant
For description see Experimental.

The reaction vessel *R* is connected with the 50 ml gas burette *B*, the initial pressure (measured by the manometer *M* as the overpressure, relative to the atmospheric pressure) is set up by turning out the valve *V* in the reference arm H_2 of the manometer *M*. If the pressure drops after the mixing of reaction components, the level of mercury in the arm H_1 of the manometer *M* rises until it touches the point contact K_1 and thus makes the relay circuit. By this signal the relay makes the circuit from the accumulator (via potentiometer) to the electrolyser *E*, which produces the mixture hydrogen–oxygen till the pressures in the reaction vessel and in the arm H_2 are not equalized. The consumed amount of the gas can be then directly read on the gas burette. The measuring

TABLE II

Relative Rates of the Addition of the Ethylchlorosilanes to 1-Heptene Catalyzed with Hexachloroplatinic Acid

Compound	$(\text{C}_2\text{H}_5)_3\text{SiH}$	$(\text{C}_2\text{H}_5)_2\text{SiHCl}$	$\text{C}_2\text{H}_5\text{SiHCl}_2$	SiHCl_3
k_{rel}	1	1.94	2.64	3.00

part of the apparatus was placed in a thermostated box made of poly(methacrylate) and the reaction vessel was immersed into a thermostat bath and its external circuit was warmed up to the same temperature. The reaction vessel was fixed by means of a clamp to a vibrator, the vibrations of which as well as the rate of the evolution of the gases in the electrolyser were chosen so that the physical factors would not be the rate-determining ones.

The air-outlet valves are designated as O_1 and O_4 , the valve O_5 separates the apparatus from the reaction vessel. Prior to the reaction the valve O_3 is connected with a vacuum pump and the valve O_4 is connected with the gas reservoir, and after multiple flushing the apparatus this is filled by the gas to the required pressure. The second hydrosilylation component was placed in one arm of the vessel, while the other arm was charged with catalyst.

Analysis of the Reaction Mixture and the Calculation of the Rate Constants

The relative rate constants of competition hydrosilylations, k_{rel} , were calculated in the usual way²³. During the competition additions of the silanes to ethylene, the conversion of the reaction was followed with the aid of the above apparatus and the reaction was stopped when 10% conversion of the olefin was reached.

In the case of single reactions the rate constants were calculated from the first order kinetic equation

$$kt = 2.3 \log \frac{V_{\infty} - V_0}{V_{\infty} - V_T},$$

where V_0 , V_T , V_{∞} are the volumes read on the gas burette in the beginning of the reaction, in time T , and after the completion of the reaction, respectively.

The analyses of the reaction mixtures from the competition addition of the silanes to 1-heptene were carried out on a chromatograph (Instrument Development Laboratories of Czechoslovak Academy of Sciences, Prague) equipped with a catharometer, using the column filled with 5% Silicone Elastomer E 301 fixed on grounded unglazed tiles "Pórovina" (oven temperature 165°C); the reaction mixtures from the additions to ethylene and 1-hexene were analyzed on a Chrom III instrument (Laboratorní přístroje, Prague) equipped with a flame-ionization detector using the column packed with 4% poly(ethylene glycol adipate) on the grounded unglazed tiles ("Pórovina"), except for those containing *p*-methoxyphenyldimethylsilane, the analyses of which were carried out using the column filled with 4% Apiezon L on the ground unglazed tiles.

RESULTS AND DISCUSSION

Recently²⁴ we found that the relative reactivity of olefins in the addition of trichlorosilane catalyzed with hexachloroplatinic acid is determined above all by the electron density of their C=C bonds. In some cases also steric effects play a role.

In the present paper we were interested in the effect of the structure of silicon hydrides. From data given in Table II it is evident that the reactivity of silane towards 1-heptene significantly and systematically increases in the order $(C_2H_5)_3SiH < (C_2H_5)_2ClSiH < (C_2H_5)Cl_2SiH < Cl_3SiH$, following the order of the decreasing electron density of the siliconhydrogen bond caused by successive replacement of ethyl groups by more electronegative chlorine atoms. The increase in the relative reactivity is not however additive in nature and also the correlations with Taft σ^*

constants for the ethyl and chloro substituents are not satisfactory. The change in the reactivity cannot be thus ascribed to the operation of the inductive effects of the groups only.

The increase in the reactivity observed with the ethylchlorosilanes studied is not compatible with the mechanism proposed by Speier²⁵, who explained the formation of *n*-heptylsilanes during the addition of silicon hydrides to 3-heptene by the addition of the hydride anion to the olefin, which precedes the transfer of the negative charge to the terminal carbon atom, which is followed by nucleophilic attack of the formed carbanion on the silicon.

We have thus studied the effect of the structure of silicon hydrides with the series of nearly isosteric propylethoxysilanes of the type $(C_3H_7)_3-n(OC_2H_5)_nSiH$ ($n = 0-3$), (Table III). The reactivity again increases from tripropylsilane to propyldiethoxysilane, in harmony with the decreasing electron density of the silicon-hydrogen bond. However, triethoxysilane exhibits surprisingly lower reactivity, relative to propyldiethoxysilane. Similar order of the reactivity was already found by us¹⁴ during base-catalyzed solvolysis of the Si—H bonds of the same series of silanes. In this reaction structure effects are even more pronounced (Fig. 2), which may be caused by the fact that in the nucleophilic substitution the reaction proceeds on the central silicon atom whilst in the hydrosilylation rather the hydrogen atom of the hydride is expected to be the reaction center.

Unexpectedly lower reactivity of triethoxysilane in its base-catalyzed solvolysis has not been unambiguously accounted for¹⁴. Several factors, such as the increased solvation of this hydride or increasing field effect of the three negatively charged oxygen atoms, which undoubtedly may effectively repulse the negative nucleophilic particle, were offered as possible explanation. It was also pointed out that the precise steric arrangement of the last two members of this series is not known.

With regard to the fact that the differences between the Si—H stretching frequencies, which in first approximation may be regarded as the measure of the polarity of the Si—H bond, are roughly constant in this series of silanes (Fig. 2) the lower reactivity of triethoxysilane can be hardly accounted for by electronic effects (in particular by the competition between the $-I$ effect of the alkoxy group and the back-

TABLE III

Relative Rates of the Addition of the Propylethoxysilanes to 1-Hexene Catalyzed with Hexachloroplatinic Acid

Compound	$(n-C_3H_7)_3SiH$	$(n-C_3H_7)_2SiH(OC_2H_5)$	$n-C_3H_7SiH(OC_2H_5)_2$	$SiH(OC_2H_5)_3$
k_{rel}	1	4.33	15.26	11.25

donating effect of the ($p \rightarrow d$) π interaction). We believe that the steric similarity between the *n*-propyl and ethoxy groups is not sufficient, particularly when these are bonded to silicon: while the Si—C—C bond angle preserves its value 109° , this Si—O—C angle may be increased, due to the effect of back-donation of the unshared electron pairs of the oxygen to the empty *d*-orbitals of silicon.

In order to ascertain the influence of electronic effects of substituents on the course of hydrosilylation without necessity of allowing for possible change in the geometry of transition state, we have chosen a series of *p*-substituted phenyldimethylsilanes as model compounds. In view of the fact that the kinetics of the reaction had not been so far well established, we tried to determine the order of the reaction in individual components and the corresponding rate constants.

To simplify the kinetic equations, we carried out the hydrosilylation at a constant concentration of one component, here at constant pressure of ethylene. The sufficiently low boiling point of this olefin excluded the distortion of data by its condensation. Under efficient stirring and at constant temperature the amount of dissolved ethylene, too, is reasonably constant.

In all cases the reaction was found to be first order in ethylene. The rate constant was not so reproducible as to allow the separation of the influence of temperature and of catalyst concentration.

Kinetic relationships are qualitatively illustrated by data given in Table IV. The

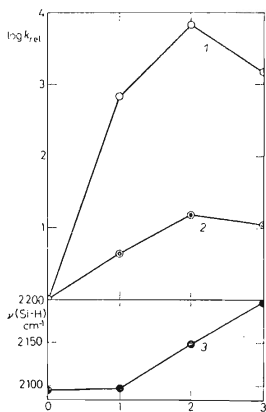


FIG. 2

The Effect of Structure of the Propylethoxysilanes

$(C_2H_5O)_n(C_3H_7)_{3-n}SiH$ ($n = 0-3$) on the Relative Rate of Their Ethanolysis Catalyzed with Sodium Ethanolate ○, on the Relative Rate of Their Hydrosilylation Addition to 1-Hexene Catalyzed with Hexachloroplatinic Acid ○, and on Si—H Stretching Frequencies, $\nu(Si-H)$, ●.

cause of wide-spread kinetic data cannot be seen in the kinetic procedure used, but rather in the influence of trace amounts of impurities, of the age of the catalyst, and its preparation. These factors may influence the concentration and life-time of the intermediate complex.

As to the reaction order, the obtained data convincingly show the first order in silicon hydrides both for hexachloroplatinic acid and for tris(triphenylphosphine)-rhodium chloride. The plot of $\log(V_\infty - V_0)/(V_\infty - V_T)$ vs. time t is linear at least over two half-times of the reaction. The reaction catalyzed with dicobaltoctacarbonyl was not so fast to investigate it kinetically.

When in turn in the addition to 1-decene the pressure of trimethylsilane (b.p. 9°C) was kept constant, the influence of its condensation and of the solubility of its vapours could not be excluded. As we were unable to determine the relative reactivity of silanes from the rate constants, we have employed the method of competition reactions. We compared the effect of structure of the silanes using the three, most frequently used homogeneous catalysts. In all cases (Table V) *p*-chloro substituent increased the reactivity of the silane, relative to unsubstituted one, while the *p*-metho-

TABLE IV

First Order Rate Constants of the Addition of *p*-Substituted Phenyltrimethylsilanes to Ethylene Catalyzed with H_2PtCl_6 or $RhCl(P(C_6H_5)_3)_3$

The reaction was carried out under constant pressure of ethylene (1017 Torr), the initial amounts of the silanes were 2 mmol.

Silane	Catalyst	R^a	Temperature °C	$k \cdot 10^2$ min ⁻¹
Phenyltrimethylsilane	H_2PtCl_6 in C_4H_8O	$3 \cdot 10^{-7}$	30	9.2
		$1.2 \cdot 10^{-6}$	30	7
		$7 \cdot 10^{-7}$	15	4.6
	$RhCl(P(C_6H_5)_3)_3$ in CH_2Cl_2	$3 \cdot 10^{-4}$	60	8
		$1.2 \cdot 10^{-4}$	60	12
		$3 \cdot 10^{-5}$	60	3
<i>p</i> -Chlorophenyltrimethylsilane	H_2PtCl_6 in C_4H_8O	$4 \cdot 10^{-6}$	15	3
		$2 \cdot 10^{-6}$	15	15
		$7 \cdot 10^{-7}$	30	0.1
<i>p</i> -Methoxyphenyltrimethylsilane	H_2PtCl_6 in C_4H_8O $RhCl(P(C_6H_5)_3)_3$ in CH_2Cl_2	$2.3 \cdot 10^{-6}$	15	4
		$6 \cdot 10^{-5}$	15	2

^a The molar ratio of the catalyst to the silane.

xy group had the opposite effect. The decrease in the polarity of the Si—H bond thus brings about the increase in the reactivity of the hydride.

The observed effect is however very small. At variation 0.5 in Hammett σ constants the difference in $\log k_{rel}$ amounts to 0.238 for $RhCl/P(C_6H_5)_3/3$, the dependence on substitution being even less pronounced in the case of H_2PtCl_6 and $Co_2(CO)_8$ as catalysts. The search of a correlation of the reactivity with structure for the whole series of substituents was thus meaningless.

The higher sensitivity to substituent effects in the case of the hydrosilylation catalyzed with tris(triphenylphosphine) rhodium chloride (compared to the other catalysts used) can be explained by the assumption that here the pre-coordinated ethylene is more tightly bonded. In all cases the transition state is only slightly polar.

From the fact that the increase in electron density of the C=C bond brings about the increase in the reactivity of the olefins in hydrosilylation¹⁸, and that the lower electron density of the Si—H bond increases the reactivity of silicon hydrides, it cannot be decided which of the two reactants (olefin or silane) is coordinated as the first one.

In view of the fact that hydrosilylation products contain the silyl group bonded to terminal carbon of the alkyl, it can be concluded that in hydrosilylation catalyzed

TABLE V

Relative Rate Constants of the Addition of *p*-Substituted Phenyl dimethylsilanes to Ethylene Catalysed with Hexachloroplatinic Acid, Tris(triphenylphosphine) rhodium Chloride and Dicobalt Octacarbonyl

The reaction was carried out at 5°C under the pressure of ethylene 1017 Torr. 1 mol of the investigated and the reference silane was used in the measurements; k_{rel} for phenyl dimethylsilane = 1.

Substituent	k_{rel} (the catalyst used)		
	25 mg of $2 \cdot 10^{-4}M$ - H_2PtCl_6 in tetrahydrofurane	25 mg of $5 \cdot 10^{-3}M$ - $RhCl(P(C_6H_5)_3)_3$ in dichloromethane	100 mg of $0.1M$ - $Co_2(CO)_8$ in hexane
<i>p</i> -CH ₃ O	0.85	0.78	0.88
H	1	1	1
<i>p</i> -Cl	1.06	1.35	1.01
<i>p</i> -Cl : <i>p</i> -CH ₃ O ^a	1.24	1.73	1.11
<i>p</i> -Cl : <i>p</i> -CH ₃ O ^b	1.17	1.72	1.04

^a Calculated from the values obtained by competition reaction with unsubstituted silane as the reference compound. ^b Determined by the competition reaction of *p*-chloro- with *p*-methoxyphenyl dimethylsilane.

with transition metal complexes the olefin is coordinated at first as a π -complex, which is converted into a σ -complex bonded to the metal atom by the terminal carbon. The metal-carbon bond (with the $M^{\delta+}-C^{\delta-}$ polarity²⁶) is then attacked by silicon hydride. The kind of the coordination of the silicon hydride and the mechanism of its attack on the olefin σ -complex cannot be deduced from the obtained results.

REFERENCES

1. Chalk A. J., Harrod J. F.: *J. Am. Chem. Soc.* **87**, 16 (1965).
2. Meals R. N.: *Internat. Symposium on Organosilicon Chemistry, Prague 1965*, p. 141. Butterworths, London 1966.
3. Koroleva G. N., Rejchsfeld V. O.: *Ž. Obšč. Chim.* **37**, 2768, 2774 (1967).
4. Ponomarenko V. A., Čerkaev V. G., Zadorožnyj N. A.: *Izv. Akad. Nauk SSSR* **1960**, 1616.
5. Odabashyan G. V., Romaškin I. V., Rogačevskij V. L., Kiričenko L. J.: *Ž. Obšč. Chim.* **38**, 2331 (1968).
6. Kagan E. G.: *Ž. Obšč. Chim.* **37**, 1692 (1967).
7. Chalk J. A., Harrod J. F.: *J. Am. Chem. Soc.* **87**, 1133 (1965).
8. Chalk J. A., Harrod J. F.: *J. Am. Chem. Soc.* **89**, 1640 (1967).
9. Baay Y. L., Mac Diarmid A. G.: *Inorg. Chem.* **8**, 986 (1969).
10. de Charentanay, Osborn J. A., Wilkinson G.: *J. Chem. Soc. A* **1968**, 787.
11. Chalk A. J., Harrod J. F.: *J. Am. Chem. Soc.* **87**, 16 (1963).
12. Chalk A. J.: *J. Organometal. Chem.* **21**, 207 (1970).
13. Dolgov B. N., Charitonov N. P., Voronkov M. G.: *Ž. Obšč. Chim.* **24**, 1178 (1954).
14. Hetflejš J., Mareš F., Chvalovský V.: *This Journal* **31**, 586 (1966).
15. Osborn J. A., Jardine F. M., Young J. F., Wilkinson G.: *J. Chem. Soc. A* **1966**, 1711.
16. Čapka M., Chvalovský V.: *This Journal* **34**, 2782 (1969).
17. Kolesova V. A., Voronkov M. G.: *Chem. listy* **51**, 686 (1957).
18. Bygdén A.: *Chem. Ber.* **45**, 707 (1912).
19. Benkeser R. A., Schroeder W., Thomas O. H.: *J. Am. Chem. Soc.* **80**, 2283 (1958).
20. Voronkov M. G., Romanova N. G., Smirnova L. G.: *Chem. listy* **52**, 640 (1958).
21. Whitmore E. G., Sommer L. H., DiGiorgio P. A., Strong W. A., van Strien R. E., Bailey D. H., Hall H. K., Pietrusza E. W., Kerr G. T.: *J. Am. Chem. Soc.* **68**, 475 (1946).
22. Larsson E.: *Kgl. Fysiograf. Sällskap. Lund, För.* **12**, 63 (1952); *Chem. Abstr.* **48**, 10545 (1954).
23. Čapka M., Chvalovský V.: *This Journal* **33**, 2872 (1968).
24. Čapka M., Svoboda P., Chvalovský V.: *Chem. průmysl*, in press.
25. Saam J. C., Speier J. L.: *J. Am. Chem. Soc.* **80**, 4104 (1958).
26. Ugo R.: *La Chimica e l'Industria* **51**, 1319 (1969).

Translated by J. Hetflejš.