The hydrosilylation reaction, i.e. the reaction between unsaturated compounds and silicon hydrides, was first mentioned in 1947 as an example of the reaction of trichlorosilane and 1-octene in the presence of acetyl peroxide [1]. In 1957 Speier et al. [2] discovered one of the most efficient homogeneous metal complex catalysts of this reaction, viz. chloroplatinic acid, which was given the name the Speier’s catalyst. Since then hydrosilylation has been actively studied. Initially researchers’ effort has been focused on the synthesis and application of new organosilicon compounds and later on the search and development of new catalysts for this reaction. As a result, organosiloxanes with different structures and properties have been synthesized, and also new efficient catalysts, such as the Karstedt [vinylsiloxane complexes of Pt(0)] [3] and Wilkinson catalysts [rhodium(I) tris(triphenylphosphine) chloride] [4], as well as colloidal catalysts have been discovered [5–12]. Hydrosilylation of unsaturated compounds has been the subject of monographs, reviews, and books [13–23], but, however, insufficient attention has still been paid to hydrosilylation in siloxane systems.

The reaction of vinyl- and hydrosiloxanes is a particular case of the hydride addition reaction and conforms to the general regularities for such reactions [14–16]. Siloxanes, like most unsaturated compounds, are hydrosilylated to form α- or β-adducts, i.e. the reaction either follows Markovnikov’s rule (the first case) or occurs against this rule (Farmer’s rule, the second case).

The overwhelming part of early research on hydrosilylation in siloxane systems was based on the catalysis either with chloroplatinic acid and its modifications or with vinylsiloxane complexes of Pt(0). Therewith, the greatest contribution into the synthesis of new organosilicon compounds was made by the research group of Acad. K.A. Andrianov. Other works were focused on modeling the curing process and research on the influence of the structure of metal complex catalysts on reaction conversion and selectivity. Certain researchers compared their proposed catalysts with the Speier’s or Karstedt’s catalysts; siloxane activity studies were also reported. Zhdanov et al. [24] synthesized branched polyorganocyclosiloxanes by the addition of tetravinylcyclotetrasiloxane (H(CH₂=CH)SiO)₄ and tetraphenylcyclosiloxane [H(C₆H₅)SiO]₄ to trimethylvinylcyclotrisiloxane \([\text{CH}_3\text{Si=CHSiO}]_3\), tetralkyltetravinylcyclotetrasiloxane \([\text{CH}_n\text{Si=CHSiO}]_4\), and tetravinylcyclotetrasiloxane \([\text{C}_6\text{H}_5\text{Si=CHSiO}]_4\), in ampules in the presence of H₂PtCl₆·6H₂O (100–105°C, (0.7–1.0)−10⁻³ g/g mixture as a 0.01 N THF solution) [24]. The reaction products were optically transparent glassy substances. To prepare network polyorganocarbosiloxanes, the polymer, after the gel point had been reached, was heated at 100–105°C for an additional 100 h.

Andrianov et al. [25] proposed to perform hydrosilylation of 1-vinyl-1,3,3,5,5,7,7-heptamethylyclosiloxane with hydrosiloxanes of the general formula H(CH₃)ₙSi(OSi(CH₃)₂)₃, \((n = 0–2)\) by the ampule method at 20, 50, and 90°C in the presence of Speier’s catalyst. The activity of hydrosiloxanes, measured by the relative rate constants of competitive reactions, was found to be the higher the less the number of bulky trimethylsiloxy groups at the silicon atom linked to hydrogen. Consequently, according to the authors of [25], the...
activity is primarily controlled by steric factors, rather than the presence of the silicon atom of =Si substituents which facilitate dissociation of the Si−H bond. Gas chromatography revealed, along with adducts, by-products whose fraction increased as the reaction temperature increased and the activity of the hydrosiloxane decreased in the order [25] 

\[ \text{H}(\text{CH}_3)_2\text{SiOSi(CH}_3)_2\text{Si}(\text{OSi(CH}_3)_2\text{)}_2 > > \text{H}_2\text{Si}[\text{OSi(CH}_3)_3\text{]}_3 \]

Polyaddition of dihydromethylsiloxanes to divinylmethyldisiloxanes with terminated trimethylsiloxy groups in the presence of Speier’s catalyst gives rise to liquid β-adducts (1H NMR data) with MW < 2000 [26]. Comparison of the hydrosilylation rates of divinylsiloxane polymerization allows us to synthesize organocyclotrisiloxanes in which the silicon atom is surrounded by the dimethylsiloxane chains with terminated methylsiloxanyl groups [29]. In the presence of catalytic amounts of chloroplatinic acid, the reaction occurs by the β-carbon atom of the vinyl group (IR and 1H NMR data) 

\[ \text{R} = \text{CH}_3, \text{C}_6\text{H}_5; \text{R} = \text{C}_6\text{H}_5, \text{R'} = \text{CH}_3; \text{R} = \text{R'} = \text{C}_6\text{H}_5 \]

The hydrosilylation reaction was used to synthesize organocyclotetrasiloxanes in which the silicon atom is surrounded by the dimethylsiloxane chains with terminated trimethylsiloxy groups [29]. In the presence of catalytic amounts of chloroplatinic acid, the reaction occurs by the β-carbon atom of the vinyl group (IR and 1H NMR data) 

\[ \text{R} = \text{CH}_3, \text{R'} = \text{C}_6\text{H}_5; \text{R} = \text{C}_6\text{H}_5, \text{R'} = \text{CH}_3; \text{R} = \text{R'} = \text{C}_6\text{H}_5 \]

The reaction of hydrosiloxanes of the general formula 

\[ \text{H}_2\text{Si}[\text{OSi(CH}_3)_3\text{]}_3 \]

with vinylorganocyclotrisiloxanes in the presence of Speier’s catalyst gives rise to organocyclotetrasiloxanes which are β-adducts having methylsiloxanyl ethyl groups at the silicon atom (IR data) [30, 31]
The nature of the R and R' substituents in the ring does not affect the reaction initiation temperature, and it tends to increase with increasing number of substituents n in the hydrosiloxane (70ºC at n = 0; 90ºC at n = 1, and 130ºC at n = 2). The activity order for hydrosiloxanes with terminated Si−H groups is the following [30]:

\[ \text{HS(CH}_3)_2 > \text{H(CH}_2)_3\text{SiOSi(CH}_3)_2 > \text{H(CH}_2)_5\text{SiOSi(CH}_3)_2 \]

Further cross-linking of the above oligomers, which occurs in the presence of tetramethylammonium polydime-

\[
\begin{align*}
\text{H}_2\text{C} & \equiv \text{C} - \text{H} & \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{H} \\
\text{Si} & \equiv \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{H} \\
\text{H}_2\text{C} & \equiv \text{C} - \text{H} & \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{H}
\end{align*}
\]

The reaction was performed in CCl\(_4\) at 50–85ºC in the presence of H\(_2\)PtCl\(_6\)·6H\(_2\)O ([1.4–4.2] × 10\(^{-4}\) M) [33]. The products were exclusively \(\beta\)-adducts (IR and \(^1\)H NMR data). Kinetic studies of this reaction showed that it is first-order in catalyst and second-order in monomer and involves intermediate formation of a monomer−catalyst compound. The activation energy at the catalyst concentration 1.4 × 10\(^{-4}\) M is 71.23 kJ/mol [33].

The result of the polyaddition of 3-vinyl-, 3-allyl, and 3-(4-vinylphenyl)-1,1,3,3-tetramethylsiloxanes and 7-vinyl-1,1,3,3,5,5,7,7-octamethyldisiloxane depends on the type of the catalyst and gives rise to oligomers with molecular weights varying from 1600 to 5600 [34].

The polyaddition of \(\alpha\)-\(\omega\)-dihydromethylsiloxanes to 1,5-divinyl-1,3,3,5,7,7-hexamethyldicyclosiloxane under argon at an equimolar reagent ratio (100–110ºC, 50–160 h, solvent toluene or none) in the presence of H\(_2\)PtCl\(_6\)·6H\(_2\)O [(1−1.5) × 10\(^{-5}\) g/g initial mixture as a 0.01 N solution in THF; part of the catalyst was added before reaction, and the rest in 25–140 h] gives viscous liquids with molecular weights varying from 75000 to 471000, depending on the molecular weight of the starting dihydrosiloxane [36].

\[ \text{H(CH}_3)_2\text{SiOSi(CH}_3)_2\text{R}(\text{R'}\text{SiOSi(CH}_3)_2\text{R})\text{R} \quad (n = 2, R = \text{CH}_3, R' = \text{CH}_2\text{CH}_3, R'' = \text{C}_6\text{H}_5; R = \text{CH}_3, R' = \text{CH}_2\text{CH}_3, R'' = \text{C}_6\text{H}_5; n = 4, R = \text{R} = \text{CH}_3) \]

1. Dimitry Andreevich de Vekki, PhD (Chem.), Associate Professor, Department of Chemical Technology of Rubber, e-mail: hydrosilation@newmail.ru
2. Nikolai Konstantinovich Skvortsov, Dr. Sci. (Chem.), Professor, Department of Chemical Technology of Rubber, e-mail: skvorn@mail.ru
To prevent reduction of viscosity of polymers obtained by the catalytic hydrosilylation reaction, it should be performed with H₂PtCl₆ ⋅ 6H₂O dissolved in THF rather than isopropanol [36]. Based on the IR spectra and experiments on prolonged heating of a mixture of the starting divinylhexamethylcyclotetrasiloxane isomers, Zhdanov et al. [36] drew a conclusion that the polyaddition occurs with retention of the structure of the starting compounds and involves no polymerization of divinylhexamethylcyclotetrasiloxanes; polymerization can be induced by heating of hydrosilylation products in the presence of an anionic polymerization catalyst (0.001–0.1%).

The synthesis of polyorganosiloxanes containing both linear and cyclic fragments in the chain was described in [37].

The reaction of 1,7-dimethyl-3,5,9,11-tetraphenyl-1,7-divinyltricyclohexasiloxane with α,ω-dihydromethylphenylsiloxanes was performed in toluene in the presence of H₂PtCl₆ in THF [(0.16−2.1) ⋅ 10⁻³ mol/mol active hydrogen]. The reaction was followed by monitoring the content of active hydrogen in the reaction mixture; gradual increase of the specific density of toluene solutions was observed. The reaction rate and depth was found to change as the chain length in the starting α,ω-dihydrosiloxane changes in the order:

\[ H(CH₃)₂Si(OSi(CH₃)₂)ₙSi(CH₃)₂H > H(CH₃)₂Si(OSi(CH₃)₂)ₙ₋₁OSi(CH₃)₂H > H(CH₃)₂Si(OSi(CH₃)₂)ₙ₋₂OSi(CH₃)₂H > \]

The hydrosilylation of tetramethylcyclotetrasiloxane with tetramethylcyclotetrasiloxane in the presence of H₂PtCl₆ (60−200 °C, 1 ⋅ 10⁻⁸ mol/g hydrosiloxane) was used to synthesize 3D polymers [38], and with α,ω-dihydromethylsiloxanes H(CH₃)₂Si(OSi(CH₃)₂)ₙSi(CH₃)₂H (n = 0−200) in the presence of H₂PtCl₆⋅6H₂O (100−110°C, (1−1.5) ⋅ 10⁻⁸ g/g mixture as a 0.01 N solution in THF), regular network polycarbodiorganosiloxanes were obtained [39]. It was shown that the aggregation state of final products depends on the starting reagent ratio. The reaction of the above dihydrosiloxane (n = 20, 30, 60, 130) with 1,3,5-trimethyl-1,3,5-trivinylcyclosiloxane and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane in the presence of H₂PtCl₆⋅6H₂O (100°C) produces network tri- and tetrafunctional polymers [40].

Network carborane-siloxane polymers can be obtained by reactions of carborane-siloxane monomers containing terminal vinyl and ethynyl groups with linear and branched hydrosiloxanes (unsaturated substrate-to-branched hydrosiloxane ratio is 1:0.5 or 1:1; the unsaturated substrate-to-linear hydrosiloxane ratio is 1:1.04, 1:0.53, or 1:0.27) in the presence of Speier’s [41] and Karstedt’s catalysis in hexane [42].

The addition of a linear polymethylhydrosiloxane to vinylcarborane-siloxane involves the β-carbon atom and gives colorless plastic polymer networks with a high cross-linking degree [41, 42].
Vinyl- and acetylcarborane-siloxanes are hydrosilylated by tetrakis(dimethylsiloxyl)-, methyltris(dimethylsiloxyl)-, and phenyltris(dimethylsiloxyl)silanes are hydrosilylated by Farmer’s rule to form network polymers, and, therewith, at the acetylcarborane-silane : hydrosiloxane ratio 2:1, the acetyl fragment takes up only one hydrosiloxane molecule, whereas at the 1:1 ratio, already two (IR data).

Kolel-Veetil and Keller [42] noted that Karstedt’s catalyst (2.1−2.4 % of Pt in xylene) is compares in activity with Speier’s catalyst (2.1−2.4 % of Pt in THF); in the absence of hexane in the reaction medium, the reaction occurs momentarily and involves strong heat release. The resulting polymers exhibit a high thermo-oxidative stability which depends on the structure of the hydrosiloxane.

The polyaddition of polyhydroorganosiloxanes to polyvinylorganosiloxanes in the presence of $\text{H}_2\text{PtCl}_6$ (150°C, acid concentration $1 \times 10^{-3}$ mol/mol vinyl groups, 5–6 h) gave cross-linked polymers [45, 46]. It was found that replacement of methyls by phenyls on the silicon atoms linked to reacting groups of the starting polyorganosiloxanes results in a reduction of the curing degree of the products for steric reasons. Moreover, replacement of the hydroxyl by trimethylsilyl groups in branched siloxane polymers adversely affects their thermal stability, unlike what is observed in linear polymers [46].

Hydrosilylation of pentamethylyvinylcyclotrisiloxane and heptamethylyvinylcycloterasiloxane with dihydrosiloxanes in the presence of $\text{H}_2\text{PtCl}_6$ ($1 \times 10^{-5}$ g/g vinylsiloxane) at 50−100°C was described in [47].
Analysis of the IR, $^1$H NMR, and GLC data showed that the reaction is primarily involves the vinyl $\beta$-carbon atom, and its selectivity is virtually temperature-independent. The reaction of dihydrosiloxanes with vinylcyclosiloxane at a 1:2 molar ratio involves initial formation of monooadducts, and, only after 50% of dihydrosiloxane has reacted, the second hydrogen starts to react. The hydrosilylation rate decreases as the siloxane chain length increases in the order:

$$[\text{H(CH}_3\text{)}_2\text{Si}_2\text{O}] > \text{H}[(\text{CH}_3\text{)}_2\text{Si}]_3\text{Si(CH}_3\text{)}_2\text{H} >> \text{H}[(\text{CH}_3\text{)}_2\text{Si}]_4\text{Si(CH}_3\text{)}_2\text{H}$$

Petrov and Volovin [48] described the $\text{H}_2\text{PtCl}_6$-catalyzed reaction of 1,3-dienyl-1,3-dimethyldisiloxane with 1,3-dienyl-1,3-dimethyldisiloxane and 1,3-dienyl-1,1,3,3-tetramethyldisiloxanes to form a polymer with the molecular weight 800–900 and various ratios of the number of Si–C bridges and the number of siloxane groups ($n = 0, 1$):

$$2\text{H}_2\text{PtCl}_6 \text{Si} \rightarrow \text{Pt} \rightarrow \text{Si} \rightarrow \text{H}_2\text{PtCl}_6$$

Meladze et al. [56] have described the reaction of vinylcyclosiloxanes with hydromethylsiloxanes in the presence of $\text{H}_2\text{PtCl}_6$ (however, complete conversion of Si–H groups could not be achieved)

$$\text{CH}_3\text{Si}+(\text{CH}_3\text{)}_2\text{Si} \rightarrow \text{CH}_3\text{Si}+(\text{CH}_3\text{)}_2\text{Si} \rightarrow \text{CH}_3\text{Si}+(\text{CH}_3\text{)}_2\text{Si} \rightarrow \text{CH}_3\text{Si}+(\text{CH}_3\text{)}_2\text{Si}$$

The reaction of a linear vinylsiloxane and a silicon monomer having active Si–H groups (0.8–3 SiH/alkene radical) in the presence of $\text{H}_2\text{PtCl}_6$ at 150°C was considered in [54]. The curing of linear polyorganosiloxanes having vinylsiloxy units in the chain members in the presence of structuring agents (organohydrosiloxanes) at 50–100°C leads to disiloxane groups which then act as cross-linking moieties to form linear diorganosiloxane macromolecules [55].

Meladze et al. [56] have described the reaction of vinylcyclosiloxanes with hydromethylsiloxanes in the presence of $\text{H}_2\text{PtCl}_6$ (however, complete conversion of Si–H groups could not be achieved)

$$\text{CH}_3\text{Si}+(\text{CH}_3\text{)}_2\text{Si} \rightarrow \text{CH}_3\text{Si}+(\text{CH}_3\text{)}_2\text{Si} \rightarrow \text{CH}_3\text{Si}+(\text{CH}_3\text{)}_2\text{Si} \rightarrow \text{CH}_3\text{Si}+(\text{CH}_3\text{)}_2\text{Si}$$

$\text{R} = \text{Me}, \text{Ph}$
Silicone rubbers were proposed to be obtained by hydrosilylation in the presence of metal oxides (for example, ZnO) as fillers [57]. The reaction mixture, along with polydimethylsiloxanes with terminated vinyl and methyl groups (viscosity 15 and 17 MPa at 25°C, respectively), hydro- methylpolysiloxane, and the Pt catalyst, contained octa-tetramethylcyclosiloxane and polydimethylsiloxane with terminated OH groups. Patents have been granted for hydrosilylation of siloxanes with unsaturated groups (≥ 2) or organopolysiloxanes (SiO(CH3)2)x(Si(CH3)2)(R)SiOCH3, [where R is a substituted or an unsubstituted hydrocarbon group (other than alkene), a, b, and c fulfill the following conditions: 0.2 ≤ a/(a + b + c) ≤ 0.6 and 0.001 ≤ b/(a + b + c) ≤ 0.2], siloxanes with Si–H groups (≥ 2) in the presence of platinum catalysts [58, 59]; hydrosilylation siloxanes with hydroxyl groups or polysiloxanes with Si–H groups or polysiloxanes with unsaturated and Si–H groups, as well as thermo stable fillers and a dialkyl platinum catalyst [61].

Compositions with a low linear distribution coefficient and high shock resistance, hardness, strength, and refractive index can be obtained from phenyl-containing polyorganosiloxanes (C6H5)xR1SiO1/2, [R = unsaturated substituent; R1 = alkyl group], or a (a + b + c) = 25–95 %; b/(a + b + c) = 5–75 %; a/(a + b + c) = 0.10 %; a + b + c = 1.0–1.9, per siloxane, a linear polyorganosiloxane with alkene (≥ 2), phenyl, and methyl groups, siloxanes with Si–H (≥ 3) and Si–CH3 groups, a platinum vinylsiloxane complex [62].

Organosilicon compositions comprising a mixture of polyorganosiloxanes with terminated vinyl groups (CH2=CH)x(R)SiO1/2, (R = Si(CH3)3 or a mixture of (Si(CH3)3SiO1/2)x(R)SiOCH3, x = 1–100; viscosity 10–100 mPa·s), poluorganosiloxanes with terminating internal Si–H groups [(H)CH2)x(R)SiO1/2, (R = Si(CH3)3 or (Si(CH3)3SiO1/2)x(H)SiOCH3, (x = 1–100; viscosity 10–100 mPa·s), (CH3)2O(CH2)xSiO1/2,(R)SiOCH3, x = 1–100; viscosity 10–100 mPa·s), a platinum-containing catalyst, and an alkene-containing reaction modifier show improved strength and flexibility [63]. Organosilicon compositions containing highly viscous polyorganosiloxanes with terminated (viscosity 5000–100000 mPa·s) and side-chain vinyl groups (viscosity ≥ 200000 mPa·s), a Si–H-containing filler, and a platinum complex show a high breaking extension [64].

The composition comprising organopolysiloxanes with sili-con–alkene groups (≥ 2), polysiloxanes (R2H)xSiO1/2, (R = Si(CH3)3 or a mixture of (Si(CH3)3SiO1/2)x(H)SiOCH3, x = 30–200; n = 10–100; p = 0–10; q = 1; k + r = 1–10; 0.5 ≤ (k + m)/[k + r + m + n + p + q] ≤ 1; viscosity 5–1000 mPa·s) and Karstedt’s catalyst deposited on a polyethylene-coated paper, was proposed for manufacturing antiadhesive paper [65]. A mixture of methylhydrosiloxanes, divinyldimethylsiloxanes, and a platinum catalyst was proposed as a component of hair shampoos [66].

Multicomponent silicone rubbers are synthesized from a mixture of organopolysiloxanes containing ≥ 2 unsaturated groups (viscosity ≥ 1000 mPa·s), organopolysiloxanes having ≥ 2 hydroxy groups or other hydrolysable groups, or their mixture (average polymerization degree ≥ 250), a filler with a hydrophilic surface, organopolysiloxanes containing Si–H bonds (≥ 2 Si–H bonds per 1 mol of siloxane with a viscosity of 10 mPa·s) and a hydrosilylation catalyst, which are fed to the reaction zone from different feeders [67]. The reactions of 1,1,3,3-tetramethylsiloxane, oligohydrodimethylsiloxane – (CH3)3SiO{H(CH3)SiO}30Si(CH3)3, dihydridoligomethylsiloxane (viscosity 1·10−9 mPa·s), and oligomethylhydrodimethylsiloxane (viscosity 3·4·10−9 mPa·s) with αω-divinyloligosiloxane (CH2=CH)x(CH3)3SiO(CH2)xSi(CH3)3, 1- vinyl-1,1,3,3-pentamethyldisiloxane, and 3-vinyl-1,1,3,5,5-heptamethyldisiloxane can be accomplished in the presence of the platinum complexes ([CH2=CH]x(CH3)3SiO)2PtCl2, (EtOCp)2Pt(OEt)2, [Pt(Cp)2Cl2], and Pt(cod)Fe(CO)5S2 at 50–80°C [68]. Therewith, the reaction rate depends on the structure of the starting reagents and the catalyst. For example, in the presence of [(EtOCp)2Pt(OEt)2] hydrolylation occurs faster in the system oligomethylhydrodimethylsiloxane – [(CH3)3SiO]2Si(CH2)xCH=CH2, in the presence of Pt(cod)Fe(CO)5S2, in the system oligomethylhydrodimethylsiloxane – (CH2)xSiO(OSi(CH3)x)2Si(CH3)xCH=CH2, whereas in the presence of [Pt(Cp)2Cl2] the reactions in both the above-mentioned systems occur at almost the same rates. The authors of [68] note that the reactivity of hydrosilanes follows common laws, whereas the reactivity of vinylsiloxanes primarily depends on the structure of the platinum catalyst: in the presence of [(EtOCp)2Pt(OEt)2], more active are vinylsiloxanes with an internal vinyl group, in the presence of Pt(cod)Fe(CO)5S2, with a terminated vinyl group, whereas with [Pt(Cp)2Cl2] both groups of vinylsiloxanes compare with each other in reactivity. The observed regularities were explained by different formation – dissociation rates of transient metal complexes. The activity of the studied complexes decreases in the order:

\[
\{(CH2)x=CH(CH3)3SiO)xPtCl2\rangle > (ETOCp)2Pt(OEt)2 > Pt(cod)Fe(CO)5S2
\]

Simpson et al. [69, 70] performed a kinetic study of hydrolylation of the divinyldimethylsiloxane (CH2=CH)x(CH3)3Si(OSi(CH3)x)2Si(CH3)xCH=CH2 with an equimolar amount or a 3.2-fold molar excess of the polysiloxane (CH3)3Si(OSi(CH3)x)2Si(CH3)xCH=CH2 in the presence of a platinum catalyst and 1-ethynylcyclohexanol (catalysis inhibitor) at 25–120°C. The hydrosilylation kinetics were measured in 1.5–27-µm thin films deposited by spin coating freshly prepared reaction mixtures on silicon wafers. It was shown that the total reaction time linearly decreases with increasing film thickness. The reaction was found to be accompanied by side processes: hydrolysis of Si–H groups and reactions of newly formed Si–OH groups with each other or with Si–H groups to form new siloxane bonds.

Platinum and palladium complexes with silylpropoxynitrile ligands were studied as catalysts in the reaction of 1-vinyl-1,1,3,3,3-pentamethyldisiloxane and 1,1,3,3,3-pentamethyldisiloxane at 80°C [71]. It was found that palladium complexes are inactive in this reaction, whereas all platinum catalysts give β-adducts in 94–95% yields. However, the selective of the addition in their presence is lower than in the presence of Karstedt’s catalyst.
dihydropermethyloligosiloxanes and studied hydrosilylation of 1-vinyl-1,1,3,3,3-pentamethyldisiloxane with excess 1,1,3,3,3-pentamethyldisiloxane in the presence of Karstedt’s catalyst in a xylene solution [73]. The resulting copolymers are stable up to 400°C under nitrogen and up to 300°C in air; at higher temperatures, Si–C bond cleavage or depolymerization occur.

Podoba et al. [74] in their study on the reactions of dimethylvinylsilicone rubber (brand SKTV-1) and dimethylsilicone rubber (brand SKT) with oligoethylhydrosiloxane and oligomethylhydrodimethylsiloxane in the presence of Speier’s catalyst obtained evidence showing that curing of rubbers by the hydrosilylation reaction is accompanied by side reactions. The authors suggested that the major side reaction is dehydrocondensation of hydrosiloxanes, which involves Si–H consumption (IR data) for forming Si–O–Si bonds and plays an important role in building a 3D network structure during the silicone rubber curing process. Oligoethylhydrosiloxane was found to be more reactive in the hydrosilylation reaction than silicone rubber curing process. Oligoethylhydrosiloxane was important role in building a 3D network structure during the curing process of Pt(II) complexes involves the following reactions [75]:

\[ \text{Formation of Si–Si bonds is observed with cyclooctadiene, bis-sulfoxide, and sulfide catalysts, but the contribution of Si–Si compounds into side reactions associated with hydrosilylation processes is no more than 1% (NMR data). In terms of the rate effect on side reactions associated with hydrosilylation, the above-considered ligands in platinum catalysts can be ranked as follows:} \]

\[ \text{phosphine < pyridine sulfoxide < sulfide ≈} \]

\[ \text{sulfoxide < cyclooctadiene.} \]

\[ \text{The mechanism of disproportionation of hydrosiloxanes depends on the type of the catalyst and, according to [75], involves inner-sphere transformations of coordinated hydrosiloxanes; for example, the reaction with (HMe}_2\text{Si})_2\text{O involves formation of a n}^\text{tetrhydrosiloxane complex.} \]

\[ \text{The disproportionation of vinylsiloxanes (CH}_2\text{=CH})\text{Me}_2\text{Si(OSiMe}_3\text{)}_2, (n = 0, 1, 2) in the presence of [Rh(cod)\text{([μ-OSiMe}_3\text{])}_2]} \]

\[ \text{leads to geometric isomers of silylethylene [76]} \]

\[ \text{The disproportionation of vinylsiloxanes (CH}_2\text{=CH})\text{Me}_2\text{Si(OSiMe}_3\text{)}_2, (n = 0, 1, 2) in the presence of [Rh(cod)\text{([μ-OSiMe}_3\text{])}_2]} \]

\[ \text{leads to geometric isomers of silylethylene [76]} \]

\[ \text{The disproportionation of vinylsiloxanes (CH}_2\text{=CH})\text{Me}_2\text{Si(OSiMe}_3\text{)}_2, (n = 0, 1, 2) in the presence of [Rh(cod)\text{([μ-OSiMe}_3\text{])}_2]} \]

\[ \text{leads to geometric isomers of silylethylene [76]} \]

\[ \text{The disproportionation of vinylsiloxanes (CH}_2\text{=CH})\text{Me}_2\text{Si(OSiMe}_3\text{)}_2, (n = 0, 1, 2) in the presence of [Rh(cod)\text{([μ-OSiMe}_3\text{])}_2]} \]

\[ \text{leads to geometric isomers of silylethylene [76]} \]

\[ \text{The disproportionation of vinylsiloxanes (CH}_2\text{=CH})\text{Me}_2\text{Si(OSiMe}_3\text{)}_2, (n = 0, 1, 2) in the presence of [Rh(cod)\text{([μ-OSiMe}_3\text{])}_2]} \]
Hydrosilylation of poly(methylvinylsiloxane) with poly(methylhydrosiloxanes) in the presence of immobilized rhodium phosphate complexes [Rh(cod)(μ-OSiMe3)]2, [Rh(cod)(μ-OSiMe3)(CH2=CH2)]2, and [Rh(cod)(PR3)(μ-OSiR’3)]2 (R = Cy or Ph; R’ = Me or i-Pr) [77]. The advantage of these catalysts is that they are inactive at room temperature.

Marciniec et al. [78] proposed to perform hydrosilylation of 1,1,5,5-tetramethyl-3-trimethylsiloxy-3-vinyltrisiloxane with 1,1,3,5,5,5-heptamethyltrisiloxane in the presence of rhodium siloxide complexes [Rh(cod)(μ-OSiMe3)]2, [Rh(cod)(μ-OSiMe3)(CH2=CH2)]2, and [Rh(cod)(PR3)(μ-OSiR’3)]2 (R = Cy or Ph; R’ = Me or i-Pr) [77]. The advantage of these catalysts is that they are inactive at room temperature.

Kownacki et al. [82] suggest that a dissociation of M–P bond via oxygenation of tertiary phosphine ligand is the crucial step for generation of Ir(cod)H(vinylsiloxane) species, which is a key intermediate of hydrosilylation in the presence of iridium siloxide complexes. At the same time, the curing process of polysiloxanes catalyzed by [Ir(cod)(PCy3)(OSiMe3)] and [Ir(μ-OSiMe3)(PCy3)(OSiMe3)] occurs at a higher temperature (about 200°C) than the same system catalyzed by Karstedt-diallylmaleate system (130°C), and does not require an inhibitor to maintain low viscosity of the reaction mixture at room temperature for several days.

Brand et al. [83] performed a detailed kinetic study of the reaction between low-molecular hydro- and vinylsiloxanes...
Vinyl-1,1,3,3-tetramethylsiloxane with 1,1,3,3-drosilanes [15, 18, 84].

The reaction order increases to 2 is explained by decelerated formation of an olefin complex and redox addition of dihydrosiloxane. However, the mechanism proposed Brand et al. [83] is valid only for hydrosilylation in the presence of vinylsiloxane Pt(0) complexes, as, according to published data, square-planar Pt(II) complexes initially react with dihydrosiloxanes [15, 18, 84].

Dvornic et al. [85–87] have described the reaction of 3-vinyl-1,1,3,3-tetramethyloxilane with 1,1,3,3-tetramethylsiloxane in the presence of Karstedt's catalyst (3–10^{-5} mol Pt/mol of CH=CH₂ and a reaction temperature of about 50°C). It was shown that the reactivity increases as the number of the (CH₃)₃SiO groups increases in the order:

\[
(\text{CH₃})₃\text{SiO(CH₃)₂ > (CH₃)₃\text{SiO(Si(CH₃)₃)₂ > (CH₃)₃\text{SiO(Si(OH)Si(CH₃)₂) > (CH₃)₃\text{SiO(Si(OH)₂Si(CH₃)₂ > (CH₃)₃\text{SiO(Si(OH)₃Si(CH₃)₂)}}}
\]

Kinetic studies of this reaction showed typical first order for the product formation [87]. The activation energy of hydrosilylation is 78.2 KJ/mol. Rate of hydrosilylation increases with increasing concentration of catalyst and temperature of reaction, and depends on the equilibrium between binuclear Karstedt's catalyst and these activated mononuclear Pt-complexes.

Comparative experiments on the addition of dihydrosiloxanes to vinylsiloxanes in the presence of catalysts, assessed by the conversion 1,1,3,3,5,5,5-heptamethytrisiloxane was found to be characteristic of the rhodium acetylacetonate complex. The activity of the catalysts, assessed by the conversion 1,1,3,3,5,5,5-heptamethytrisiloxane decreases in the order [Р(НС₂Н₄Н)₃С] > [Р(НС₂Н₄Н)₃С] > [Р(В₃Н₃)₃С] > [Н₂С₆Н₄].

In the system 1,1,3,3,3-pentamethyldisiloxane – vinylcyclosiloxane, the following catalyst activity order was obtained [Р(В₃Н₃)₃С] > [Р(НС₂Н₄Н)₃С] > [Р(НС₂Н₄Н)₃С] > [Н₂С₆Н₄].

The work of Gorschov and co-workers [92] who explored the behavior of silicon hydrides, as well as polyfunctional hydro- and vinylsiloxanes in the presence of PtCl₆·6H₂O and tetracoordinatedammonium salts of the general formula [(С₂Н₅)₃Н]X[Pt(II)] (X = NO₂, n = 4, R = С₅Н₁₁, p-OC₆H₄С₂Н₅, С₂Н₅С₂Н₅; С₂Н₅С₂Н₅; С₂Н₅С₂Н₅; С₂Н₅С₂Н₅) showed that the reactivity of cyclic vinylsiloxanes...
steric hindrance of the newly formed \( \text{CH}_2\text{CH}_2\text{Si(OEt)}_3 \) groups, Si–H groups strongly decelerated hydrosilylation at conver-}


ging reaction pathway was \( \beta \)-addition. It was also found that
tetraorganylammonium salts are slightly less active than chloro-
platinic acid. The greatest difference was observed in the system
tetramethyldisiloxane molecule is added, largely by Farmer’s
preparation was thus extended to higher conversion. The prevai-
ning reaction by a factor 1.2. The least selective addition was observed in
the presence of \( \text{H}_2\text{PtCl}_6 \). The lowest \( \beta \) was with
presence of \( \text{H}_2\text{PtCl}_6 \), and it is the slowest (>10 h) in the
presence of \( \text{H}_2\text{PtCl}_6 \). The selectivity of catalysis involves the formation of a platinum hydride complex as the main stage

\[
\begin{align*}
\text{R}^+\text{HC=CHR}^- & \rightarrow \text{R}^+\text{HC=CHR}^+ \\
\text{R}^+\text{HC}=\text{CHR}^+ & \rightarrow \text{R}^+\text{HC}=\text{CHR}^+ \\
\text{R}^+\text{HC}=\text{CHR}^+ & \rightarrow \text{R}^+\text{HC}=\text{CHR}^+ \\
\end{align*}
\]

We performed a comparative study of the catalytic activity
of bornyl, methyl, and triethylammonium platinates
(\( \text{Am}=\text{(+)}\text{-BornylNH}_3, \text{(-)}\text{-MenthylNH}_3, \text{Et}_3\text{NH} \)), and
(\( \text{(+)}\text{-BornylNH}_3\))\[\text{PtCl}_x\] using the bifunctional siloxanes
1,1,3,3-tetraethyldisiloxane and 1,3-divinyl-1,1,3,3-
tetramethyldisiloxane at a 1:1 molar ratio [94]. Hydrosilylation
involves both one and two active groups (Si–H or Si–
H = CH) leading to \( \alpha, \beta, \) and diadducts (NMR, IR, GCMS,
and GLC data) which fact transform into higher molecular
adducts (viscosity > 0.34 Pa·s). Initially, one 1,1,3,3-
tetramethyldisiloxane molecule is added, largely by Farmer’s
rule:

\[
\begin{align*}
\text{CH}_2\text{CH} = \text{CH}_2 & \rightarrow \text{CH}_2\text{CH} = \text{CH}_2 \\
\text{CH}_2\text{CH} = \text{CH}_2 & \rightarrow \text{CH}_2\text{CH} = \text{CH}_2 \\
\text{CH}_2\text{CH} = \text{CH}_2 & \rightarrow \text{CH}_2\text{CH} = \text{CH}_2 \\
\end{align*}
\]

The resulting monoadducts then fast transform into into
\( \beta, \beta \)-adducts (major products) and
\( \alpha, \alpha \)- and \( \alpha, \beta \)-adducts (minor products). The activity of the
catalyst, as measured by the time required for
[\( \text{CH}_2\text{H} = \text{CH}_2\text{Me}_{5}\text{Si} \)], 0 to reach 50% conversion decreases in
the following order:

\[
\text{Me}_3\text{SiO}([\text{CH}_2\text{H} = \text{CH}_2\text{Me}_{5}\text{Si}])_2 \rightarrow \text{Et}_2\text{SiO}([\text{CH}_2\text{H} = \text{CH}_2\text{Me}_{5}\text{Si}])_2
\]

The full conversion of 1,3-divinyl-1,1,3,3-
tetramethyldisiloxane is the most rapid (470 min) in the presence
of \( \text{Et}_2\text{NH} \)\[\text{PtCl}_x\], and it is the slowest (>10 h) in the presence of \( \text{(+)}\text{-BornylNH}_3\))\[\text{PtCl}_x\]. The selectivity of \( \beta \)-addition (\( \text{H} \) NMR data) varies in the following order:

\[
\begin{align*}
\text{(+)}\text{-BornylNH}_3 \text{PtCl}_x (95\%) & \rightarrow \text{(+)}\text{-BornylNH}_3 \text{PtCl}_x (95\%) \\
\text{Et}_2\text{NH} \text{PtCl}_x (92\%) & \rightarrow \text{Et}_2\text{NH} \text{PtCl}_x (92\%) \\
\end{align*}
\]

The above siloxanes were also hydrosilylated in the presence
of Pt(II) and Pt(IV) complexes of the general formulas

\[
\begin{align*}
\text{CH}_2\text{H} = \text{CH}_2\text{Me}_{5}\text{Si} & \rightarrow \text{CH}_2\text{H} = \text{CH}_2\text{Me}_{5}\text{Si} \\
\text{CH}_2\text{H} = \text{CH}_2\text{Me}_{5}\text{Si} & \rightarrow \text{CH}_2\text{H} = \text{CH}_2\text{Me}_{5}\text{Si} \\
\end{align*}
\]
The reaction in a bifunctional siloxane medium (two Si–H groups) involves either one or both active hydrogen atoms, and this further decreases the activity of bis-sulfoxide Pt(II) complexes. The most catalytically active in aprotic solvents can form a good alternative for Pt(IV) complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

The hydrosilylation of vinyl-[CH2=CHMe]3SiOSiMe3, 3-vinyl-1,1,3,3,5,5-heptamethylytrisiloxane, 1,3-divinyl-1,1,3,3,5,5,5-heptamethylytrisiloxane, and 1,1,3,3,5,5,7,7-octamethyltrisiloxane in the presence of square-planar platinum complexes [Pt(LL′)X2] (L = RR’SiH; R = Me, Et; R′ = Me, Et, p-Tol; L′ = RR’Si Py, α-Pic, α-aminoypyridine (α-NH2Py), CH2=CH2, Ph3PS; LL′ = cod, 1-methylcycloocta-1,5-diene (MeCOD); X = Cl, Br, NO3; X2 = C6H3Cl2) yields β-and α-adducts whose ratio depends on the structure of the reagents and the thermodynamics of the process, as well as on the type of the catalyst [84].

The catalytic activity of octahedral and square-planar platinum complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

By the reaction of the Pt(II) complexes with inner sphere sulfoxide ligands, the reactivity of vinyl- and hydrosiloxanes is much dependent on the electronic and steric characteristics of the substituents on the silicon atom. In the presence of sulfoxide Pt(II) complexes, the reactivity of hydrosiloxanes is decreased in the following order [84]:

\[
Na^+ > H^+ > Et3NH^+ > NH4^+ > K^+ > \text{other} > Cl^->Br^->I^->NO3^- > OH^-
\]

The reaction of hydrosiloxanes in a double bond (two Si–H groups) involves either one or both active hydrogen atoms, and this further decreases the activity of bis-sulfoxide Pt(II) complexes. The most catalytically active in aprotic solvents can form a good alternative for Pt(IV) complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

The catalytic activity of octahedral and square-planar platinum complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

The catalytic activity of octahedral and square-planar platinum complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

By the reaction of the Pt(II) complexes with inner sphere sulfoxide ligands, the reactivity of vinyl- and hydrosiloxanes is much dependent on the electronic and steric characteristics of the substituents on the silicon atom. In the presence of sulfoxide Pt(II) complexes, the reactivity of hydrosiloxanes is decreased in the following order [84]:

\[
Na^+ > H^+ > Et3NH^+ > NH4^+ > K^+ > \text{other} > Cl^->Br^->I^->NO3^- > OH^-
\]

The reaction of hydrosiloxanes in a double bond (two Si–H groups) involves either one or both active hydrogen atoms, and this further decreases the activity of bis-sulfoxide Pt(II) complexes. The most catalytically active in aprotic solvents can form a good alternative for Pt(IV) complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

The catalytic activity of octahedral and square-planar platinum complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

The catalytic activity of octahedral and square-planar platinum complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

The catalytic activity of octahedral and square-planar platinum complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

The catalytic activity of octahedral and square-planar platinum complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

By the reaction of the Pt(II) complexes with inner sphere sulfoxide ligands, the reactivity of vinyl- and hydrosiloxanes is much dependent on the electronic and steric characteristics of the substituents on the silicon atom. In the presence of sulfoxide Pt(II) complexes, the reactivity of hydrosiloxanes is decreased in the following order [84]:

\[
Na^+ > H^+ > Et3NH^+ > NH4^+ > K^+ > \text{other} > Cl^->Br^->I^->NO3^- > OH^-
\]

The reaction of hydrosiloxanes in a double bond (two Si–H groups) involves either one or both active hydrogen atoms, and this further decreases the activity of bis-sulfoxide Pt(II) complexes. The most catalytically active in aprotic solvents can form a good alternative for Pt(IV) complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].

The catalytic activity of octahedral and square-planar platinum complexes with inner-sphere ligands has some special features. The rate of hydrosilylation in the presence of Pt(IV) complexes with inner sphere sulfido ligands is higher compared to similar Pt(II) complexes. At the same time, bis-sulfoxide platinum(IV) complexes are less efficient hydrosilylation complexes than their square-planar analogs. Therewith, the nature of the acidic ligand has almost no effect on the activity and selectivity of the catalysts [95].
The activity of vinylsiloxanes in their reaction with siloxanes in the presence of the same platinum colloid depends on the electronic environment of the silicon atom attached to the vinyl group, decreasing in the order: 

\[ \text{Me}_2\text{SiO}	ext{SiMe}_2\text{CH}_2 > \text{Me}_2\text{SiOSiMe}_2\text{CH}_2 > \text{Me}_2\text{SiOSiMe}_3\text{CH}_2 \]

than siloxanes with one Si–H bond [12]

\[ \text{(Me}_2\text{SiO)}_3\text{SiH} \text{Me}_2 \text{OSiMe}_3 \text{HMe} \text{SiOSiMe}_3 \text{H} \]

Faltynek [97] proposed zero-valent nickel complexes of the general formula NiXG (X = bidentate cyclic alkenes C_10H_16, G = mono- and bidentate phosphorus-containing groups containing hydride bonds; substituted or unsubstituted hydrocarbon radicals or phosphorus-containing groups with different atoms attached to phosphorus) as catalysts of hydrosilylation of polysiloxane systems. Such complexes successfully catalyze this reaction, and it occurs already at room temperature to give organosilicon elastomers.

Meuser and Mignani [98] described the synthesis of catalysts for hydrosilylation of siloxanes, specifically platinum complexes \( (n = 1, 2; R, R', R'' = \text{alkyl and/or acyl radicals, for instance, CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7; R'' = \text{alkyl and/or acyl radicals}) \) and photoinduction. Photoassistance involves continuous irradiation of a precatalyst (a real catalyst is considered to be formed directly in the reaction medium) for maintaining its catalytic activity.

A typical example of the photoinductive effect of light is the reductive photodissociation of the ligand in a Pt(II) acetate complex (50 ppm) on exposure to visible light, forming a highly active 14-electron platinum center, which was studied on an example of gel formation (84 s) in a mixture of 37.5 parts of polymethylsiloxane with vinyl terminated groups and 2.5 parts of polymethylhydrosiloxane with trimethylsilyl terminated groups [102].

Another interesting example of photoactivation of metal complexes, related to the photoinductive effect of light, is the near-UV irradiation of \( \left( \eta^8\text{-cyclopentadienyl}\right)\text{trialkylplatinum(II)} \) in the presence of polyaromatic sensitzers absorbing visible light, leading to formation of colloidal platinum which exhibits a high catalytic activity in the reaction of hydrosiloxanes \( \text{R}_2\text{Si}(\text{OSiR}_3)_2\text{R} \) (\( \text{R} = \text{H, cycloalkyl, Ph}) \), much enhanced by air oxygen due to oxidation of the dissociated phosphine into a weakly coordinating phosphine oxide.

An example of the photoinductive effect of light on catalysts is provided by the hydrosilylation of \(-\text{1,3-divinyl-1,1,3,3-tetramethyldisiloxane and hept-1-ene with 1,1,3,3-tetramethyldisiloxane and heptamethylcyclohexasiloxane in the presence of photoactivated rhodium(I) complexes, primarily [Rh(PPh_3)_2Cl] (light with } \lambda = 300–450 \text{ nm}) \) [105]. It was found that hydrosilylation is appreciably accelerated compared to the dark process and the irradiation efficiency is much enhanced by air oxygen due to oxidation of the dissociated phosphine into a weakly coordinating phosphine oxide.

The \( \text{[Rh(Ph}_3\text{P)}_2\text{Cl(SiMe}_2\text{Cl)]} \) complex proved to be the most efficient among the rhodium catalysts studied, and its efficiency did not depend on temperature (25–70°C) and irradiation and compared with the efficiency of irradiated Wilkinson’s catalyst (70°C) [105]. The reaction catalyzed by \( \text{[Rh(Ph}_3\text{P)}_2\text{Cl]} \) was suggested to occur via a mononuclear oxo complex \( \text{[Rh(Ph}_3\text{P)}_2\text{Cl)}_2\text{OCH}_2\text{Cl]} \) rather than a dimeric oxo complex \( \text{[Rh(Ph}_3\text{P)}_2\text{Cl)}_2\text{OCH}_2\text{Cl]} \), as even though in the latter case the key stage of catalyst generation, specifically phosphine dissociation, is more facile. Therewith, after completion...
of irradiation, air oxygen oxidized phosphine into phosphine oxide, thereby preventing the reverse reaction and providing a high concentration of the rhodium catalyst. The reduced efficiency of this catalyst in the subsequent dark process was associated with the formation of a silicon–rhodium complex.

We performed a GLC and $^1$H NMR study of the reaction of 1,1,1,3,5,5,5-heptamethyltrisiloxane and 1,1,3,3-tetramethyldisiloxane with 3-vinyl-1,1,1,3,5,5,5-heptamethyltrisiloxane and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane in the presence of the rhodium(I) complexes $[\text{Rh}(\text{Ph}_2\text{PCH=CH}_2)\text{Cl}]$ and $[\text{Rh}(\text{PPh}_3)\text{Cl}]$ and thermo- and photoactivated platinum(II) complexes $[\text{Pt}(\text{R}_2\text{R'}\text{X})\text{Cl}_2] \ (X = \text{P, R} = \text{Me, R'} = \text{Ph}; X = \text{P, As, Sb, R} = \text{R'} = \text{Ph or Bu})$ [106]. The effect of neutral ligands on the activity of Pt(II) catalysts in the thermally induced hydrosilylation in low-molecular siloxane systems decreases in the following order:

$$\text{SbPh}_3 > \text{AsPh}_3 > \text{PPh}_3 > \text{PPhMe}_2 > \text{PBu}_3$$

The hydrosilylation rate changes inconsiderably but slightly decreases in the following order of complexes [106]:

$$\text{cis-}[\text{Pt}(\text{PMe}_2\text{Ph})\text{Cl}_2] > \text{cis-}[\text{Pt}(\text{PPh}_3)\text{Cl}_2] > \text{cis-}[\text{Pt}(\text{PBu}_3)\text{Cl}_2]$$

The addition rate in the presence of $\text{cis-}[\text{Pt}(\text{PPh}_3)(\text{Py})\text{Cl}_2]$ is lower than in the presence of $\text{cis-}[\text{Pt}(\text{PPh}_3)\text{Cl}_2]$; the least active was Wilkinson’s catalyst. The activation energy of the reaction of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with a triple molar excess of 1,1,3,3-tetramethyldisiloxane in the presence of $\text{cis-}[\text{Pt}(\text{PPh}_3)\text{Cl}_2]$ in the fast hydrosilylation region was $10.2 \pm 0.8 \text{ kJ/mol} \ (\ln k_0 = 0.89)$.

The photoinduced addition of hydrosilanes to vinylsiloxanes in the presence of bis-phosphine Pt(II)-complexes (wide-band light, Pyrex filter) occurs at a slightly higher rate compared to the dark process and has an appreciably shorter induction period [106]. Detailed study of hydrosilylation in the presence of a photoactivated complex $\text{cis-}[\text{Pt}(\text{PPh}_3)\text{Cl}_2]$ showed that 1 min irradiation is the most favorable in terms of the hydrosilylation rate.

Phosphine ligands quite differently affect the efficiency of photoactivated catalysts in siloxane systems compared to the dark process; for example, the induction period decreases in the following order of phosphine ligands

$$\text{PPh}_3 > \text{PBu}_3 >> \text{PMe}_2\text{Ph}$$

This order parallels the order of the ability of organosilicon compounds to reduce the phosphine complexes

$$\text{HMe}_2\text{SiOSiMe}_3 > (\text{HMe}_2\text{Si})_2\text{O} >> \text{MeSiHCl}_2 >> [\left((\text{CH}_2=\text{CH})\text{Me}_2\text{Si}\right)_2\text{O}]$$

The mechanism of hydrosilylation in the presence of phosphine Pt(II) complexes suggests an attack of the hydrosiloxane on the $\text{cis}$-complex, which results in expulsion of the neutral ligand from the inner coordination sphere of Pt(II) to form a $\eta^2$-silicon hydride complex. Subsequently, coordination of the vinylsiloxane takes place and reaction with a further hydrosilane molecule to give reaction products and regenerate the catalyst.
The mechanism of hydrosilylation in the presence of photoactivated catalysts involves initial photodissociation of the ligand, leading to formation of a coordinately unsaturated platinum center, and the latter then reacts with the hydrosiloxane. Further conversions of the η²-hydrosiloxane complex occur, according to [106], like those shown in the dark hydrosilylation scheme.

One more example of the inductive effect of light is provided by the hydrosilylation of divinyltetramethyldisiloxane with pentamethyl- and tetramethyldisiloxane in the presence of photoactivated alkene- and sulfoxide-containing Pt(II) complexes [Pt(MeCOD)Cl₂], (–)-cis-[Pt(Me-p-TolSO₂)Cl₂], and (–)-trans-[Pt(Me-p-TolSO₃)(C₆H₅CH=CH₂)Cl₂] [107]. Detailed study of the effect of photoactivation time on the rate and selectivity of hydrosilylation showed that hydrosilylation selectivity is almost independent of photoactivation time, whereas the rate of β,β-adduct formation is directly related to photoactivation time. The strongest effect of irradiation was observed with the bis-sulfoxide complexes in view of their higher sensitivity to light quanta. Photolysis of these complexes results in the dissociation of the neutral ligand to form a coordinately unsaturated center which, in their turn, immediately reacts with siloxanes, yielding new hydrosilylation catalysts. At the same time, photoactivation of trans-complexes was unsuccessful, which is associated with their inability for photodissociation [106].

The strongest effect of the rate of photoinduced hydrosilylation is observed in the case of the bis-sulfoxide complexes containing the second photosensitive center (the oxalate ligand). The effect of the anionic ligand environment of the activity of photoactivated bis-sulfoxide catalysts decreases in the order [107] $\text{C}_2\text{O}_4^{2–} > \text{NO}_3^{–} > \text{Cl}– > \text{Br}^{–}$.

The practical application of photoactivation in hydrosilylation has been recently reported. For example, Mistele [108] has patented a hermetic with improved adhesion to plastic, containing a silicon fluid, Si–H and vinyl-containing polysiloxanes, and a hydrosilylation photocatalyst.

Thus, the catalytic hydrosilylation considered in the present review is a convenient synthetic approach to a great variety of siloxanes, including high-molecular siloxanes, which are attracting permanent interest. The reactivity of hydrosiloxane. Further conversions of the η²-hydrosiloxane complex occur, according to [106], like those shown in the dark hydrosilylation scheme.
and vinylsiloxane vs controlled by three main factors: molecular weight, steric effect, and electron-donor power of the substituent on the silicon atom (their increase have a negative reactivity impact); the reactivity of linear vinylsiloxanes is higher compared to cyclic vinylsiloxanes, and, moreover, it is dependent on the structure of the catalyst. The contribution of side reactions associated with hydroisilylation, i.e. disproportionation of hydro- and vinylsiloxanes and dehydrocondensation of hydroisoxanes, depends on the activity and structure of the catalyst (the lower activity the less side reactions), but sometimes side reactions play a great role in the formation of the 3D network of the resulting siloxane oligomers and polymers.

Most researchers prefer to experiment with commercial Speier’s and Karstedt’s catalysts. However, such approach has certain drawbacks associated with difficulty controlled reaction rate and a long induction period of hydroisilylation reactions in the presence of those catalysts. The alternative efficient catalysts for hydroisilylation in siloxane systems are alkene-, phosphorus-, and sulfur-containing platinum complexes which allow the curing regime of siloxane compositions to be varied over a wide range and enhance the addition selectivity in most cases. Rhodium(I), nickel, cobalt and iron complexes are less efficient in siloxane systems, whereas palladium complexes are almost inactive. Of undeniable interest is hydroisilylation in the presence of photoactivated metal complexes; however, this catalyst activation technology has not yet been commercialized, probably, because of the complicated instrumentation and lack of commercial efficiency. At the same time, the works concerning the mechanism of hydroisilylation in siloxane systems are few in number, and their results are controversial. However, over the past years a certain tendency of researchers is observed to agree that the key stage stage of hydroisilylation is the coordination of hydroisoxane, leading to formation of a real catalyst of the process.

In any case, hydroisilylation in siloxane systems is far form being understood, and the potential of possible catalysts is far from being exhausted. The most promising approach seems to consist in the search for new platinum catalysts with ligands capable of coordinating silicon hydrogens.

The work was financially supported by the Russian Foundation for Basic Research (project nos. 13-03-00890a).

References