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Effect of Catalyst Structure on the Reaction of α-Methylstyrene with 1,1,3,3-Tetramethyldisiloxane

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Abstract—Reaction of α-methylstyrene with 1,1,3,3-tetramethyldisiloxane in the presence of the complexes of platinum(II), palladium(II) and rhodium(I) is explored. It is established that in the presence of platinum catalyst predominantly occurs hydrosilylation of α-methylstyrene leading to formation of β-adduct, on palladium catalysts proceeds reduction of α-methylstyrene, on rhodium catalysts both the processes take place. In the reaction mixture proceeds disproportion and dehydrocondensation of 1,1,3,3-tetramethyldisiloxane that leads to formation of long chain linear and cyclic siloxanes of general formula $HMe_2Si(OSiMe_2)_nH$ and $(–OSiMe_2–)_m$ (n = 2–6, m = 3–7), respectively. Platinum catalysts promotes formation of linear siloxanes, while both rhodium and palladium catalysts afford linear and cyclic siloxanes as well. Structure of intermediate metallocomplexes is studied.

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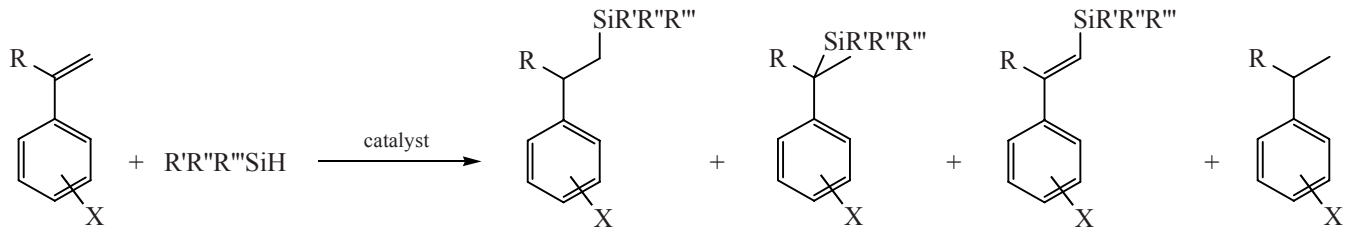
Reaction of catalytic hydrosilylation is the most universal pathway for the synthesis of organosilicon compounds that is applied both in preparative and industrial chemistry. However, the catalysts used in the industry are far from perfection. Therefore seems promising finding the catalytic systems allowing to synthesize the products of a given structure with high chemical yield and selectivity.

Now there are many enough publications on the hydrosilylation of styrene and related compounds with various hydrosilanes in the presence of the complexes of cobalt, nickel, zirconium, palladium, platinum, rhodium and so on [1–8]. The reaction products are respective arylalkylsilanes (Scheme 1).

The more selective hydrosilylating agents compared to hydrosilanes are hydrosiloxanes. The doubtless interesting is application of the siloxanes with two Si–H groups because at hydrosilylation with use of one Si–H group the second one remains intact and can be selectively used for the following hydrosilylation of another substrate that is important for obtaining unsymmetrical siloxanes. An example is the synthesis by hydrosilylation of acetophenone silyl ester [9] followed by hydrosilylation with these compounds of liquid crystal compounds [10].

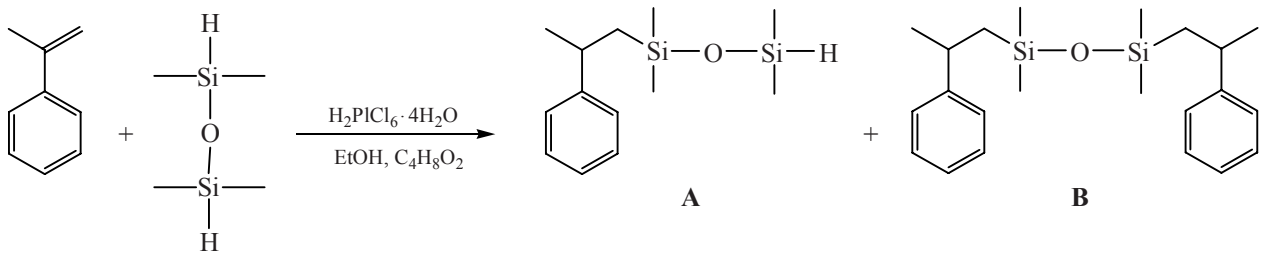
However, there are only a few publication concerning synthesis of styrene derivatrives containing Si–H group. For example, it has been described a reaction of α-methylstyrene with α,ω-bis(trimethylsiloxy)methylhydrosiloxane in anhydrous toluene or tetrahydrofuran resulted in the respective oligomers [11, 12], and addition of 1,1,3,3-tetramethyldisiloxane

Scheme 1.



R = H, CH_3; X = H, Hal, Alk, NO_2, OAlk; R', R", R"' = H, Hal, OAlk, Ph.

Scheme 2.



$[(HMe_2Si)_2O]$ to two mole excess of α-methylstyrene in the presence of solution of platinum hydrochloric acid in a mixture ethanol–dioxane at 110°C [13] (Scheme 2). In the last case the product of disproportion is formed (compound **B**, yield 81%), while the yield of the mono derivative (compound **A**), which is of much greater significance is 3% or less.

For increasing the selectivity of the process of hydrosilylation of styrene homologs with hydrosiloxanes (optimization of the synthesis of adduct **A**) we attempted to study influence of structure of the complexes based on platinum(II), palladium(II) and rhodium(I) on the reaction of α-methylstyrene with tetramethyldisiloxane. Use of α-methylstyrene is defined by the presence of CH_3 group, a convenient moiety for the reaction monitoring with NMR spectroscopy.

As the catalyst we used versatile sulfoxide, triphenylphosphine and cyclooctadiene complexes that have been applied to the hydrosilylation [9, 14–20], as well as pyridine coordination platinum compounds with the catalytic activity suggested either moderate or absent at all [18, 21]. The interest to the latter ones is stipulated additionally by the recently found [22] propensity of the platinum(II) di- and tetrapyridinium complexes to the reactions of substitution of the neutral ligand, that could play a positive role at formation *in situ* of the real catalyst. For the comparison of catalytic activity of platinum catalysts with other metallocomplexes we used coordination compounds of rhodium and palladium with triphenylphosphine and 1-methylcycloocta-1,5-diene (MeCOD) ligands.

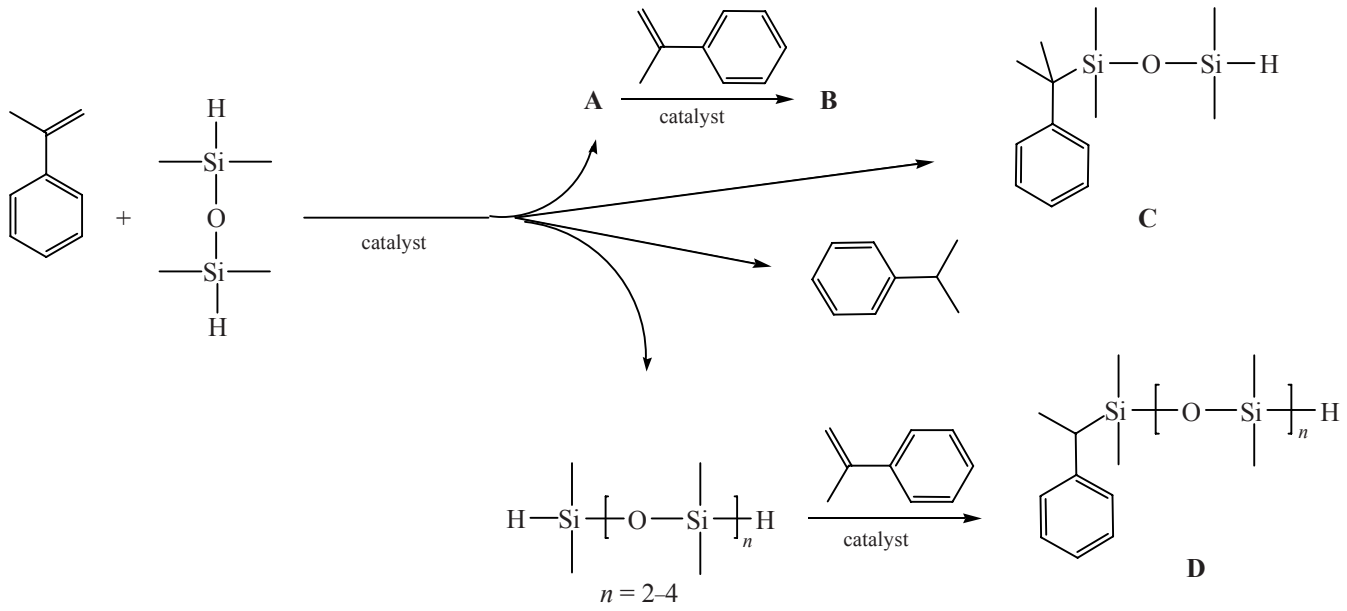
Reaction of α-methylstyrene with $(HMe_2Si)_2O$. The direction of α-methylstyrene reaction with $(HMe_2Si)_2O$ in a great extent depends on the nature of the complex forming atom. With platinum catalysts the main process is hydrosilylation, with palladium ones reduction of α-methylstyrene, rhodium complexes catalyze both these processes (the hydrosilylation some prevails over reduction). The main direction of addition of $(HMe_2Si)_2O$ in the presence of platinum and rhodium catalysts is β-carbon atom of α-methylstyrene (adducts **A** and **B**), in the presence of palladium the hydrosilylation leads to formation of α-adduct (compound **C**). This direction of addition of $(HMe_2Si)_2O$ is well corresponds to the published data on the effect of the metal nature on the direction of addition of hydrosilans to alkens [2, 3, 14, 15], but and exclusion is addition of triethoxysilane to styrene in the presence of C_{60}-fullerenethanolamine platinum complex that yields α-adduct with 100% regioselectivity [23].

The reaction of α-methylstyrene with $(HMe_2Si)_2O$ observed in our case can be described by Scheme 3.

The optimal method of monitoring the process of conversion of reactants is gas-liquid chromatography, but in the case of application of highly selective platinum and palladium catalysts can be applied ^1H NMR spectroscopy. In the ^1H NMR spectrum ($CDCl_3$) at the hydrosilylation of α-methylstyrene appear the characteristic signals of CH_2, CCH_3 and CH groups in 1,1,3,3-tetramethyl-1-(2-phenylpropyl)disiloxane at δ_H 1.01 d.q (2H, *J* 6.7, *J* 7.3 Hz), 1.34 d (3H, *J* 7.5 Hz), 2.96 d.t (1H, *J* 6.5, *J* 7.0 Hz) ppm; while at the reduction of α-methylstyrene the signals of cumene CH_3 and CH groups at δ_H 1.29 d (3H, *J* 7.0 Hz) and 2.93 heptet (1H, *J* 7.0 Hz) ppm.

A typical chromatogram of the reaction mixture contains the peaks related to the initial compounds, α-methylstyrene (retention time 12.6 min) and $(HMe_2Si)_2O$ (retention time 3.4 min); the adducts **A** (retention time 18.7 min), **B** (retention time 27.7 min) and **C** (retention time 17.7 min); cumene (retention time 11.3 min); the products of side transformations of $(HMe_2Si)_2O$: trimethylsilane Me_3SiH (retention time 2.6 min), 1,1,1,3,3-pentamethyldisiloxane $HMe_2SiOSiMe_3$ (retention time 4.0 min), linear dihydrosiloxanes with terminal SiH groups with general structure $HMe_2Si–(–OSiMe_2–)_n–H$ (n = 2–6) and cyclic siloxanes, hexamethylcyclotrisiloxanes (D_3, retention time 8.6 min)

Scheme 3.



and octamethylcyclotetrasiloxane (D_4, retention time 12.4 min) (the D_3 : D_4 ratio is about 1 : 80), and to other products of α-methylstyrene hydrosilylation as well, the hydrosiloxanes are formed as a result of $(HMe_2Si)_2O$ transformation. The main adduct in such side hydrosilylation is 1,1,3,3,5,5-hexamethyl-1-(2-phenylpropyl)trisiloxane (**D**, $n = 2$, retention time 20.8 min). Identification of the above compounds (except adducts) is carried out by the method of chromato-mass spectrometry with use NIST-2005 database.

The mass-spectrum of the products of hydrosilylation contains a peak of the molecular ion with split off hydride (that is characteristic of electron impact) and of a series of low molecular fragments from the styrene and silicon parts of the molecule. For the styrene part are characteristic the peaks of ions with *m/z* 77 $[C_6H_5]^+$, 91 (basic peak), 105 $[C_6H_5CHMe]^+$ and 119 $[C_6H_5CH(Me)CH_2]^+$; for the silicon part 59 $[Me_2SiH$ or $MeSiO]^+$ and 133 $[HSi(Me)_2{\cdot}OSiMe_2]^+$.

The main direction of side pathway of $(HMe_2Si)_2O$ transformations in the presence of the considered metallocomplexes is disproportion of its two molecules into 1,1,3,3,5,5-hexamethyltrisiloxane $HMe_2SiOSi(Me_2)OSiMe_2H$ (retention time 7.9 min) and dimethylsilane Me_2SiH_2 (Scheme 4), as has been reported [9, 24]. Under ambient conditions, Me_2SiH_2 is gaseous [25], therefore the peak corresponding to it does not occur in the chromatogram. The second pathway of formation of $HMe_2SiOSi(Me_2)OSiMe_2H$ which is also possible in our case is disproportion of $(HMe_2Si)_2O$ and $HMe_2SiOSiMe_3$ (Scheme 4). In favor of such direction of join disproportion of siloxanes attests the presence of Me_3SiH in the reaction mixture.

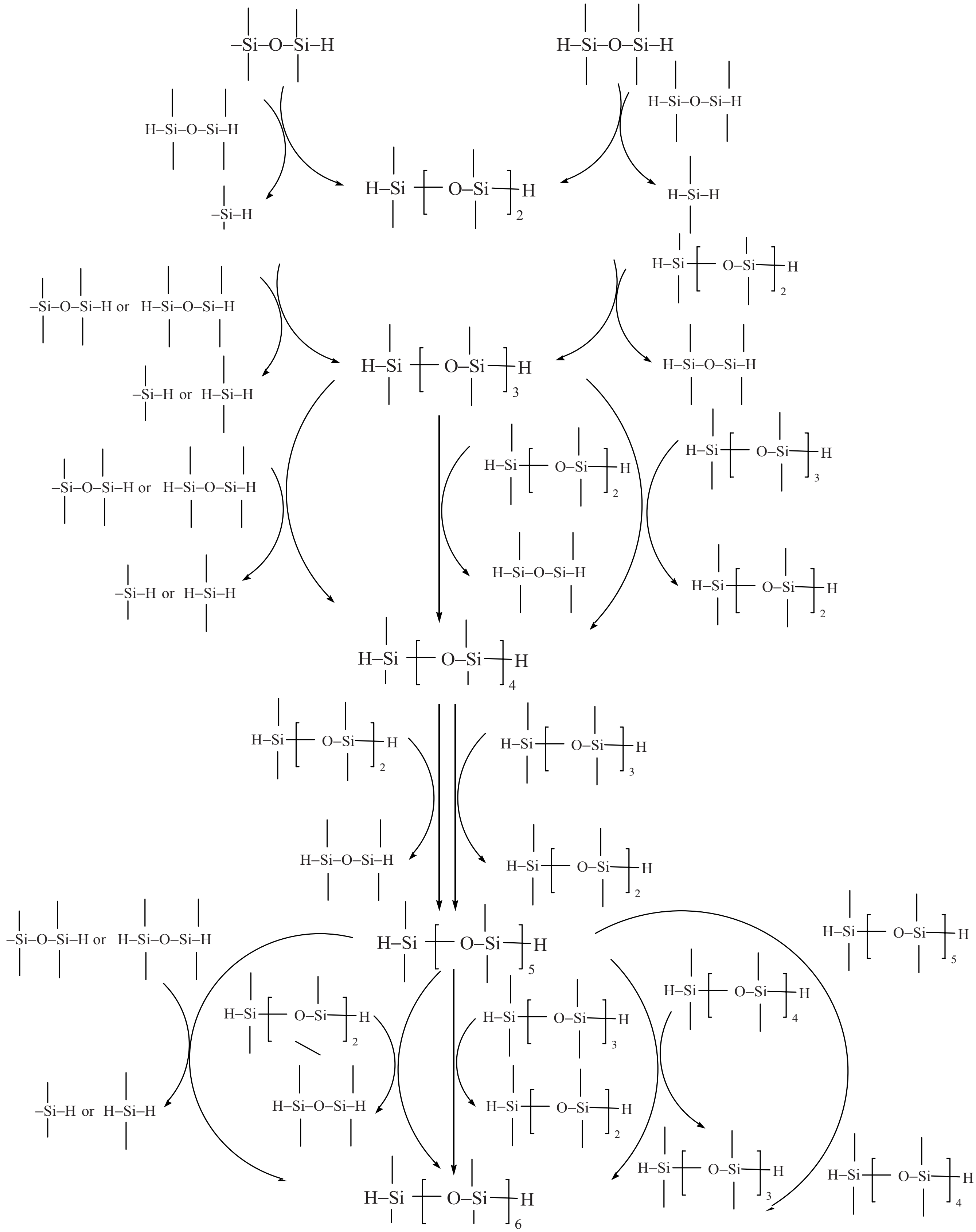
Formation in the reaction mixture of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane $HMe_2SiOSi(Me_2)OSi(Me_2)OSiMe_2H$ (retention time 14.5 min) in turn can be a result of disproportion of two $HMe_2SiOSi(Me_2)OSiMe_2H$ molecules or join disproportion of $(HMe_2Si)_2O$ (or $HMe_2SiOSiMe_3$) with $HMe_2SiOSi(Me_2)OSiMe_2H$ (Scheme 4). The presence in the reaction mixture of other terminal dihydrosiloxanes $HMe_2Si–(–OSiMe_2–)_n–H$ (n = 4–6) in part probably is a result of disproportion of respective siloxanes, in correspondence with Scheme 4. However, the presence in the reaction medium of cyclic siloxanes D_3 and D_4 allows to assume an alternative pathway to dihydrosiloxanes $HMe_2Si–(–OSiMe_2–)_n–H$ (n = 4–6). It is the well known the insertion of cyclosiloxanes to SiOSi bond proceeding in the presence of acids, bases and other promoters [26]. The possible insertion pathways D_3 and D_4 are reflected by the Scheme 5.

One more cause for the appearance of $HMe_2SiOSi(Me_2)OSi(Me_2)OSiMe_2H$ in the reaction mixture is dehydrocondensation of $(HMe_2Si)_2O$ in the presence of water traces [24] according to the reactions:

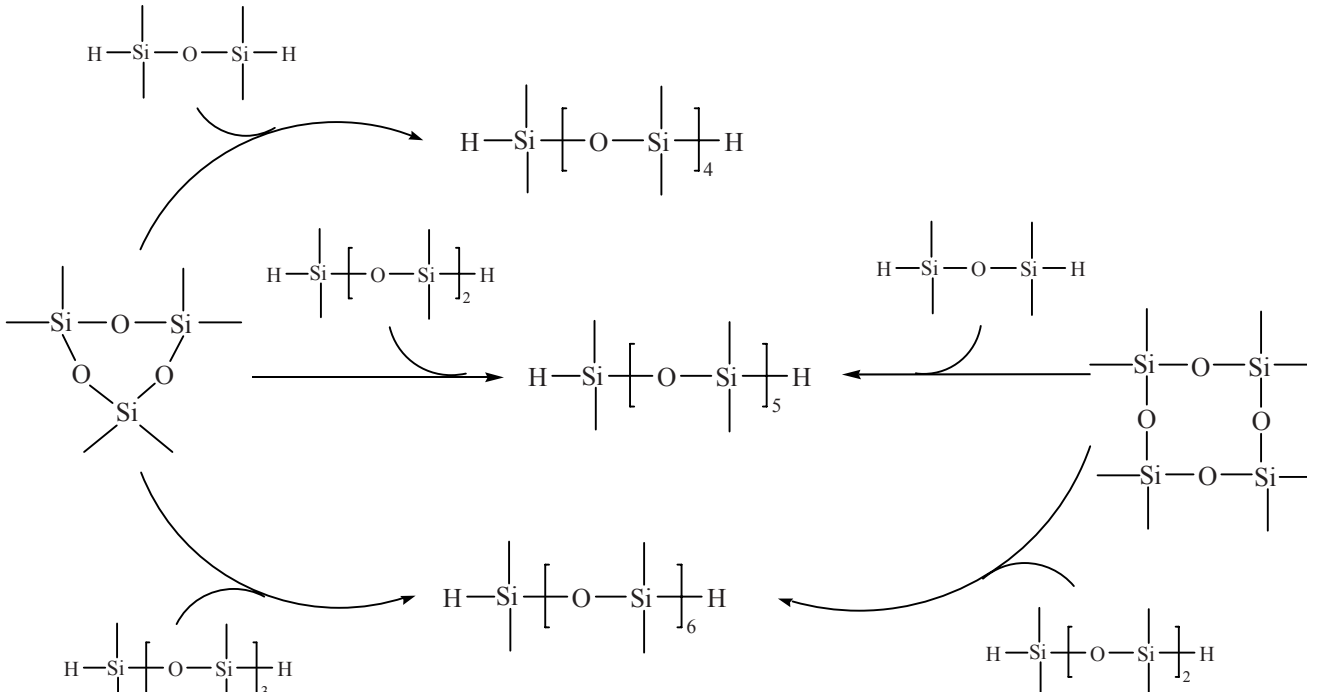
$$(HMe_2Si)_2O + H_2O \rightarrow HMe_2SiOSiMe_2OH + H_2,$$

$$HMe_2SiOSiMe_2OH + (HMe_2Si)_2O \rightarrow HMe_2SiOSi(Me_2)OSi(Me_2)OSiMe_2H + H_2.$$

Scheme 4.



Scheme 5.

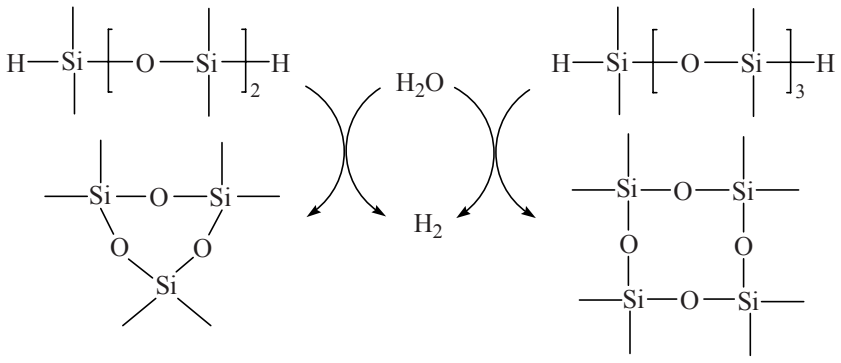


This pathway of $(HMe_2Si)_2O$ transformation is confirmed indirectly by the existence in the reaction mixture of D_3 and D_4, formed, according to publications [26, 27], at the presence of a source of OH groups (e.g., water) from $HMe_2SiOSi(Me_2)OSiMe_2H$ and $HMe_2Si{\cdot}OSi(Me_2)OSi(Me_2)OSiMe_2H$ respectively (Scheme 6).

Effect of platinum complexes. Reaction of α-methylstyrene with $(HMe_2Si)_2O$ in the presence of platinum catalysts leads to predominate formation of β-adducts (compounds **A** and **B**) while cumene, the product of α-methylstyrene reduction, is formed in trace amounts.

Kinetic monitoring of the reaction proceeding of $(HMe_2Si)_2O$ with α-methylstyrene allowed to elucidate the most active catalysts of hydrosilylation (as a measure of activity of a catalyst is taken conversion of α-methylstyrene at the same duration period for all the catalysts). The best are *cis*-dichlorobispyridineplatinum(II) *cis*-$[Pt(Py)_2Cl_2]$ and tetrapyridineplatinum(II) $[Pt(Py)_4]Cl_2$. Conversion of α-methylstyrene at 90°C

Scheme 6.



after 47 h in the presence of *cis*-$[Pt(Py)_2Cl_2]$ was 89%, with $[Pt(Py)_4]Cl_2$ 95% (see the figure). That is, *cis*-$[Pt(Py)_2Cl_2]$ and $[Pt(Py)_4]Cl_2$ are of similar activity. The addition selectivity with both these complexes by the data of chromatography is 99%, the β-adduct : cumene ratio is 380 : 1 and 250 : 1 for $[Pt(Py)_4]Cl_2$ and *cis*-$[Pt(Py)_2Cl_2]$, respectively.

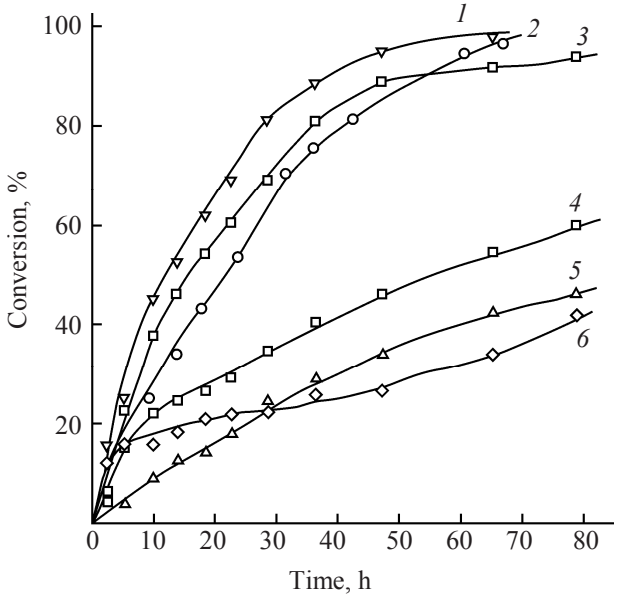
At 80°C *trans*-$[Pt(Py)_2Cl_2]$ displays lower catalytic activity than its *cis*-analog (after 73 h the conversion is 32% against 73% for the *cis*-isomer); increasing the reaction temperature does not changes the observed picture (see the figure). This effect of the metallocomplex configuration on its catalytic properties is well consistent with the published data on the catalysis in the presence of geometric isomers of platinum(II) coordination compounds [3, 14, 18]. However, the fact that di- and tetrapyridine platinum(II) coordination compounds possess catalytic properties is rather unexpected, because earlier has been shown that the presence of one pyridine molecule in the platinum(II) coordination sphere decreases considerably the catalytic activity of the metallo-complex at the hydrosilylation of vinylsiloxanes [18, 20], alkenes [3, 15] and ketones [28], and $[Pt(Py)_2Cl_2]$ does not catalyze this reaction at all [15, 18, 21, 28]. By the chromatographic data, selectivity of addition in the presence of *trans*-$[Pt(Py)_2Cl_2]$ is 99%, the ratio β-adduct : cumene is 248 :1. Thus, the reaction of $(HMe_2Si)_2O$ with α-methylstyrene in the presence of geometric isomers of $[Pt(Py)_2Cl_2]$ proceeds similarly by selectivity.

Diethylsulfoxide substitution for the pyridine ligand in *cis*-$[Pt(Py)_2Cl_2]$ leads to decrease in catalytic activity of the complex: *cis*-$[Pt(Et_2SO)(Py)Cl_2]$ is less active catalyst of α-methylstyrene hydrosilylation than *cis*-$[Pt(Py)_2Cl_2]$ (see the figure). Replacement of the second pyridine ligand by diethylsulfoxide {in going from *cis*-$[Pt(Et_2SO)(Py)Cl_2]$ to *cis*-$[Pt(Et_2SO)_2Cl_2]$} increases the rate of the reaction but the rate remains lower than in the presence of *cis*-$[Pt(Py)_2Cl_2]$ and $[Pt(Py)_4]Cl_2$ {after 10.3 h at 80°C the α-methylstyrene conversion is 25, 36 and 42% in the presence of *cis*-$[Pt(Et_2SO)(Py)Cl_2]$, *cis*-$[Pt(Et_2SO)_2Cl_2]$ and $[Pt(Py)_4]Cl_2$, respectively}. The higher activity of bissulfoxide catalyst as compared with the pyridinesulfoxide one is well consistent with the published data on the hydrosilylation of other unsaturated compounds [3, 18, 20].

The chiral complexes of similar structure, (–)-*cis*-[Pt(Me-*p*-TolSO)(Py)Cl_2] and (–)-*cis*-[Pt(Me-*p*-TolSO)$_2Cl_2$] [the optical activity bears (+)-Me-*p*-TolSO–(+)-methyl-*para*-tolylsulfoxide] show catalytic activity comparable with that of *cis*-$[Pt(Et_2SO)(Py)Cl_2]$ and *cis*-$[Pt(Et_2SO)_2Cl_2]$, respectively, but their application does not lead to asymmetric induction (the data of polarimetry, 18°C, 7 days). Reasons of such behavior of (–)-*cis*-[Pt(Me-*p*-TolSO)(Py)Cl_2] and (–)-*cis*-[Pt(Me-*p*-TolSO)$_2Cl_2$] will be considered below.

Dichloro-η^4-(1-methylcycloocta-1,5-diene)platinum(II) [Pt(MeCOD)Cl_2] that catalyzes successfully the hydrosilylation of siloxane [18] shows lower activity than $[Pt(Py)_4]Cl_2$ and *cis*-$[Pt(Py)_2Cl_2]$ in the earlier steps of the reaction of $(HMe_2Si)_2O$ with α-methylstyrene at 90°C, although the durations for achieving 99% conversion are similar (see figure). But conversion of α-methylstyrene at 80°C after 73 h in the presence of [Pt(MeCOD)Cl_2] is a bit lower (69%) than in the presence of *cis*-$[Pt(Py)_2Cl_2]$ (73%). Selectivity of β-addition in the presence of [Pt(MeCOD)Cl_2] is, by the data of chromatography, 99%, and the ratio β-adduct : cumene is 120:1.

The lowest catalytic activity displays triphenylphosphine complex of platinum(II), that is typical for its catalysis of the reaction of hydrosilylation [2, 3, 29]. However, in the initial steps of this reaction the α-methylstyrene conversion in the presence of *cis*-



Change in time of α-methylstyrene conversion in the reaction with $(HMe_2Si)_2O$ in the presence of catalysts [90°C, C_c 1×10^{-3} mol l^{-1}, α-methylstyrene : $(HMe_2Si)_2O$ = 1:3 mol]: (*1*) $[Pt(Py)_4]Cl_2$; (*2*) [Pt(MeCOD)Cl_2]; (*3*) *cis*-$[Pt(Py)_2Cl_2]$; (*4*) *cis*-$[Pt(Et_2SO)(Py)Cl_2]$; (*5*) *trans*-$[Pt(Py)_2Cl_2]$; and (*6*) *cis*-$[Pt(Ph_3P)_2Cl_2]$.

$[Pt(Ph_3P)_2Cl_2]$ prevails those in the presence of *trans*-$[Pt(Py)_2Cl_2]$ (see figure, curves *5, 6*). A feature distinguishing hydrosilylation of α-methylstyrene from that of other unsarurated compounds [14, 16, 17, 19] in the presence of *cis*-$[Pt(Ph_3P)_2Cl_2]$ is the absence of induction period on the kinetic curve (see figure, curve *6*), that indicates faster formation in the reaction medium of catalytically active moieties. Effect of air oxygen on the hydrosilylation in the presence of phosphine complexes corresponds to that described in literature [19, 30]: the presence of oxygen increases activity of the catalyst (in our case, α-methylstyrene conversion for 100 at 80°C in the presence of oxygen is 43% against 7%).

Thus, the catalysis of α-methylstyrene hydrosilylation with $(HMe_2Si)_2O$ occurs the following order of the effect of neutral ligands on the activity of platinum(II) complexes:

$$Py > MeCOD > Et_2SO > Ph_3P.$$

Influence of palladium and rhodium complexes. Unlike the coordination compounds of platinum(II), the selectivity of reaction of α-methylstyrene with $(HMe_2Si)_2O$ in the presence of rhodium(I) and palladium(II) complexes is not very high.

The hydrosilylation of α-methylstyrene in the presence of triphenylphosphine and methylcyclooctadiene rhodium catalysts {$[Rh(Ph_3P)_3Cl]$ and $[Rh(MeCOD)Cl]_2$ respectively} proceeds with reduction of the substrate in a great extent, while in the presence of triphenylphosphine and methylcyclooctadiene palladium complexes {*cis*-$[Pd(Ph_3P)_2Cl_2]$ and $[Pd(MeCOD)Cl_2]$ respectively} formation of cumene prevails.

Conversion of α-methylstyrene after 50 h at 80°C in the presence of $[Rh(Ph_3P)_3Cl]$ is 7%, with *cis*-$[Pd(Ph_3P)_2Cl_2]$ 1%, while in the presence of *cis*-$[Pt(Ph_3P)_2Cl_2]$ 17%. The β-adduct : cumene ratio in the presence of $[Rh(Ph_3P)_3Cl]$ is about 2:1. After 130 h at 90°C the conversion of α-methylstyrene in the presence of $[Rh(Ph_3P)_3Cl]$ is 41% at the same β-adduct : cumene ratio, while in the presence of *cis*-$[Pd(Ph_3P)_2Cl_2]$ the conversion of α-methylstyrene is not higher than 3%.

The conversion of α-methylstyrene after 73 h at 80°C in the presence of $[Rh(MeCOD)Cl]_2$ and $[Pd(MeCOD)Cl_2]$ is the same (34%), but with both the catalysts is lower than with $[Pt(MeCOD)Cl_2]$ (69%). The β-adduct : cumene ratio in the presence of $[Rh(MeCOD)Cl]_2$ by the data of chromatography is 6:1, while α-adduct : cumene ratio in the presence of $[Pd(MeCOD)Cl_2]$ is 1:160. The such high fraction of the reduction product of α-methylstyrene in the case of $[Pd(MeCOD)Cl_2]$ is a result of fast transformation of the complex into colloidal palladium [at the adding $(HMe_2Si)_2O$ to the reaction mixture it appears as abundant flaky brown precipitate] which does not catalyze hydrosilylation with hydrosiloxanes [18, 31], but by our data is active at reduction of double bonds with the hydrosiloxanes.

The total yield of the products of hydrosilylation with 1,1,3,3-tetramethyldisiloxane in the presence of $[Rh(MeCOD)Cl]_2$ according to the data of chromatography is only 34%, in the presence of $[Rh(Ph_3P)_3Cl]$ 24%; the selectivity of β-addition at the catalysis with $[Rh(MeCOD)Cl]_2$ is 97%, with $[Rh(Ph_3P)_3Cl]$ 87%.

Another feature of the reaction of α-methyl styrene with $(HMe_2Si)_2O$ in the presence of the considered rhodium and palladium catalysts is formation in the reaction mixture of long-chain linear and cyclic siloxanes. By the data of chromato-mas spectrometry, in the reaction mixture besides the mentioned above siloxanes present 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethylheptasiloxane and 1,1,3,3,5,5,7,7,9,9,11,11,-13,13,15,15-hexadecamethyloctasiloxane, decamethylcyclopentasiloxane (D_5), dodecamethylcyclohexasiloxane (D_6) and tetradecamethylcycloheptasiloxane (D_7); the ratio of $D_5 : D_6 : D_7$ is 6 : 4 : 1. Formation of these substances obviously also is a result of disproportion and dehydrocondensation of respective siloxanes, which in this case proceeds along the Schemes 4–6.

Prolonged keeping of reaction solutions containing rhodium and palladium catalysts leads to formation of a gel due to stepwise increase in amount of linear and cyclic high molecular siloxanes, that in the case of, e.g., $[Pd(MeCOD)Cl_2]$ are registered by appearance in ^1H NMR spectrum of three very strong singlet signals of methylsilicon groups protons at δ_H 0.07, 0.08 and 1.00 ppm, and in the ^{13}C NMR spectrum of a broad singlet at δ_C 0.65 ppm.

Reaction of the complexes with the reagents. To reveal why absent the transfer of chirality at the application of optically active platinum(II) complexes containing coordinated (+)-Me-*p*-TolSO, and also for elucidation the mechanism of action of highly active pyridine complexes and low effective phosphine complexes we studied their behavior in the presence of

$(HMe_2Si)_2O$, α-methylstyrene and styrene excess by the method of ^1H and ^{13}C NMR spectroscopy. For the phosphine containing coordination compounds was also used ^{31}P NMR spectroscopy.

At keeping the solution of (–)-*cis*-[Pt(Me-*p*-TolSO)$_2$Cl$_2$] [$CDCl_3$; δ_H, ppm: 2.47 s (3H, Ph-CH_3); 3.48 t ($J_{Pt–H}$ 22.7 Hz, 3H, S–CH_3); 7.41 d (2H, Ph, $J_{H–H}$ 8.2 Hz); 7.95 d (2H, Ph, $J_{H–H}$ 8.3 Hz) in CH_2Cl_2 s $(HMe_2Si)_2O$ [the mole ratio complex : $(HMe_2Si)_2O$ = 1:45.5] at room temperature it initially becomes yellowish-green and then brown. This change in color is explainable by the formation of a platinum–silicon hydride complex that then stepwise is transformed into colloidal platinum [32, 33]. In the ^1H NMR spectrum of the yellowish-green solution occur the signals of free Me-*p*-TolSO [δ_H, ppm: 2.42 s (3H, Ph–CH_3); 2.71 s (3H, S–CH_3); 7.35 d (2H, Ph, $J_{H–H}$ 7.6 Hz); 7.53 d (2H, Ph, $J_{H–H}$ 7.7 Hz)] and of new complex *cis*-[Pt(MeS-*p*-Tol)$_2$Cl$_2$] (MeS-*p*-Tol = methyl-*para*-tolylsulfide) [δ_H, ppm: 2.36 s (3H, Ph–CH_3); 2.66 t (3H, S–CH_3, $J_{Pt–H}$ 40.6 Hz); 7.21 d (2H, Ph, $J_{H–H}$ 8.1 Hz); 7.71 d (2H, Ph, $J_{H–H}$ 8.1 Hz)]. After 15-min keeping at 20°C the parent complex disappears from the reaction mixture and the ratio Me-*p*-TolSO : *cis*-[Pt(MeS-*p*-Tol)$_2$Cl$_2$] becomes equal to 1:3. Heating the reaction mixture to 80°C accelerates the process of reduction. In the ^1H NMR spectrum after 15-min heating occur the signals of *cis*-[Pt(MeS-*p*-Tol)$_2$Cl$_2$] and of free Me-*p*-TolSO and MeS-*p*-Tol [δ_H, ppm: 2.31 s (3H, Ph-CH_3); 2.46 s (3H, S–CH_3); 7.10 d (2H, Ph, $J_{H–H}$ 8.0 Hz); 7.18 d (2H, Ph, $J_{H–H}$ 7.9 Hz)] in 4:1:20 ratio. After 1.5-h heating at 80° C the reaction mixture becomes consisting of *cis*-[Pt (MeS-*p*-Tol)$_2$Cl$_2$] and free sulfide in the ratio 10 : 93. In the case of (–)-*cis*-[Pt(Me-*p*-TolSO)(Py)Cl$_2$] the complex decomposition and formation of free Me-*p*-TolSO and MeS-*p*-Tol proceeds slower, that is defined by known higher stability of platinum(II) pyridine-sulfoxide complexs as compared with bissulfoxide complexes toward their reduction with silcon hydrides [18].

Heating of a mixture of non-coordinated (+)-Me-*p*-TolSO в CH_2Cl_2 and $(HMe_2Si)_2O$ [mole ratio (+)-Me-*p*-TolSO : $(HMe_2Si)_2O$ = 1 : 22.5] also leads to rapid reduction of the sulfoxide into sulfide. By the data of ^1H NMR spectroscopy, after 15 min at 80°C yield of MeS-*p*-Tol is 48% against 80% at the reduction of (+)-Me-*p*-TolSO in the coordination sphere; after 1.5 h 90% against 93%.

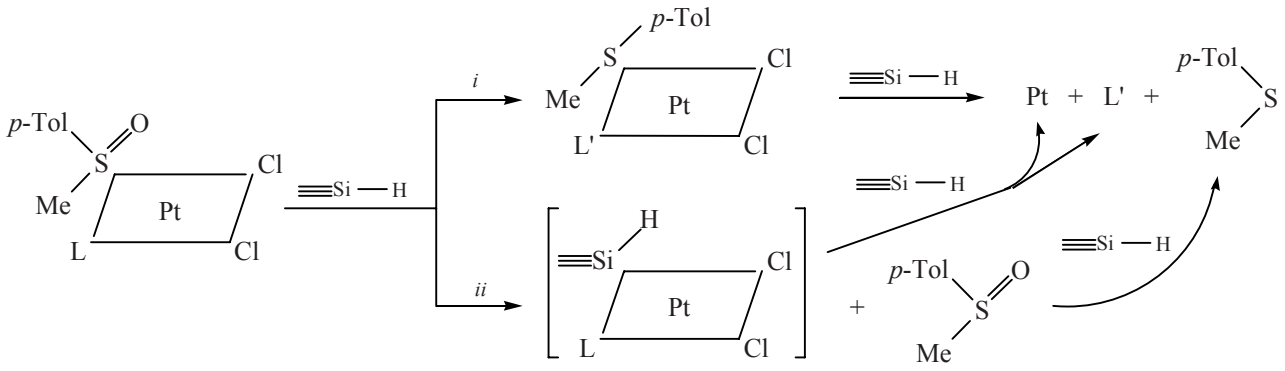
The faster reduction of coordinated (+)-Me-*p*-TolSO as compared with the free sulfoxide is defined by several factors. First, S–O bond in free ligand lies almost in the plane of aromatic ring (as known [34], such configuration is the most advantageous for the sulfoxides with aromatic substituents at the sulfur atom because this assists to partial conjugation of the electrons of rig and S–O bond), while , e.g., in (–)-*cis*-[Pt(Me-*p*-TolSO)$_2$Cl$_2$] the S–O bond of only one sulfoxide ligands is in the plane of the ring (the dihedral angle is 6.8°), while not of the second ligand (the respective dihedral angle is 76°) [35]. Second, at the reduction of coordinated (+)-Me-*p*-TolSO occurs coordination of hydrosiloxane at the platinum atom and hence the Si–H bond becomes activated. At the same time, the fact that coordination of (+)-Me-*p*-TolSO leads to a noticeable shortening of S–O bond {in free (+)-Me-*p*-TolSO, in (–)-*cis*-[Pt(Me-*p*-TolSO)$_2$Cl$_2$] and in (–)-*cis*-[Pt(Me-*p*-TolSO)(Py)Cl$_2$] the S–O bond length is respectively 1.493, 1.482 (in the second sulfoxide 1.473) and 1.469 Å [35–37]} does not affect such considerably the rate of reduction of this bond.

Keeping a solution of (–)-*cis*-[Pt(Me-*p*-TolSO)$_2$Cl$_2$] in CH_2Cl_2 with α-methylstyrene (the complex : α-methylstyrene mole ratio is 1:10) at 20°C leads to changes in the structure of the ^1H NMR spectrum of the solution. After 22 days in the NMR spectrum besides the signals of coordinated and free Me-*p*-TolSO (7:1 ratio) occur singlets at δ_H 2.84, 4.79, 5.14 ppm in the ratio 5:2:2.

In distinct to α-methylstyrene, at keeping a solution of (–)-*cis*-[Pt(Me-*p*-TolSO)$_2$Cl$_2$] in CH_2Cl_2 with styrene (the complex : styrene mole ratio 1:10) at 20°C in the ^1H NMR spectrum appear the signals of free Me-*p*-TolSO, probably due to replacement it in the complex by styrene. After 22 days by the data of NMR the ratio of coordinated Me-*p*-TolSO to free becomes equal to 10:1.

Thus, the absence of asymmetric induction in the presence of platinum(II) complexes with coordinated (+)-Me-*p*-TolSO is due to chirality loss at fast reduction of optically active (+)-Me-*p*-TolSO into achiral sulfide under the action of $(HMe_2Si)_2O$ [in (+)-Me-*p*-TolSO the sulfur(IV) atom is chiral] or at its elimination in the course of catalysis.

The scope of the data obtained and analysis of the published data (other examples of desoxygenation of coordinated sulfoxides are given in [38]) allow to assume the following Scheme of transformation of platinum(II) complexes with (+)-Me-*p*-TolSO in the presence of silicon hydrides:



L = Me-*p*-TolSO, Py; L' = MeS-*p*-Tol, Py.

Reaction of the sulfoxide-containing platinum(II) complexes with silicon hydride proceeds in two directions: (*i*) Reduction by the silicon hydride of Me-*p*-TolSO located in the platinum inner coordination shell into MeS-*p*-Tol and (*ii*) ligand exchange with formation of silicon hydride platinum complex and free sulfoxide. Further transformations of both the metalloxcomplexes and free Me-*p*-TolSO consists in their reduction into colloidal platinum and MeS-*p*-Tol respectively, in the case of (–)-[Pt(Me-*p*-TolSO)(Py)Cl_2] into the colloidal Pt, MeS-*p*-Tol and pyridine.

Reaction of platinum, palladium and rhodium phosphine complexes with silicon hydrides has been studied to the moment in details. It is suggested that in the course of the catalysis are formed both metal–silyl intermediates [16] and metal–hydride complexes [39]. Other authors [19, 40] hold a hypothesis about η^2-coordination of silicon hydrides. However, behavior of phosphine complexes in styrene systems has poorly been studied.

Heating of *cis*-[$Pt(Ph_3P)_2Cl_2$] [δ_P 13.81 t ($J_{Pt–H}$ 3677.4 Hz) ppm] and *cis*-[$Pd(Ph_3P)_2Cl_2$] (δ_P 23.97 ppm) with α-methylstyrene (the complex : α-methylstyrene mole ratio is 1:160) at 90°C for 120 h does not lead to any changes in ^1H, ^{13}C and ^{31}P NMR spectra of the reaction mixture. Heating these complexes with styrene under the same conditions also do not lead to appearance of new signals in ^{31}P NMR spectrum. But appear increase in viscosity of the reaction mixture containing *cis*-[$Pt(Ph_3P)_2Cl_2$], and stepwise polymerization occurs of the reaction mixture containing *cis*-[$Pd(Ph_3P)_2Cl_2$]. In the ^1H NMR spectra of both the mixtures appear broad signals at δ_H 1.47 s, 1.84 s, 6.49 d (*J* 16.9 Hz), 6.59 s and 7.06 d (*J* 17.2 Hz) ppm, in ^{13}C NMR spectrum at δ_C 40.45 s, 44.15 s, 125.64 s, 127.96 s, 145.31 s. These signals by shape and chemical shifts are the same as the signals of extract with chloroform of the polystyrene prepared for this experiment by ionic polymerization of styrene. The polystyrene yield in the presence of *cis*-[$Pd(Ph_3P)_2Cl_2$] by the NMR data is 100% after 23 h, in the presence of *cis*-[$Pt(Ph_3P)_2Cl_2$] 50%.

Heating of [$Rh(Ph_3P)_3Cl$] (δ_P 29.42 ppm) with α-methylstyrene (complex : α-methylstyrene mole ratio is 1:100) at 90°C for 130 h does not lead to changes in ^1H, ^{13}C and ^{31}P NMR spectra of the reaction mixture, while at heating with styrene at the same mole ratio for 130 h in the ^1H and ^{13}C NMR spectra appear the signals of polystyrene. Heating of [$Rh(Ph_3P)_3Cl$] (δ_P 29.41 ppm) with $(HMe_2Si)_2O$ [the complex to $(HMe_2Si)_2O$ mole ratio is 1:100] at 90°C for 31 h damages the complex (the solution becomes dark-brown and in its ^{31}P NMR spectrum occurs only one signal at δ_P 20.68 ppm that responds to triphenylphosphine oxide).

Study of reaction of the platinum pyridine complexes with the reactants applied to hydrosiylation has never been described, therefore we considered this reaction with α-methylstyrene and styrene, and with $(HMe_2Si)_2O$ as well.

Heating of *trans*-[$Pt(Py)_2Cl_2$] with styrene (the complex : styrene mole ratio is 1:10) in $CDCl_3$ at 50°C for 35 h or at 90°C for 46 h leads to appearance in the reaction mixture of polystyrene traces (^1H NMR monitoring), and probably to styrene η^2-coordination [δ_H 7.64 t ($1H^\gamma$, *J* 8.2 Hz), 7.90 d ($2H^\alpha$, *J* 7.8 Hz), the signals of $2H^\beta$ and η^2-CH=CH_2 group are overlapped with the signals of styrene and polystyrene]. By the NMR data the ratio of coordinated pyridine : coordinated styrene is 3 : 1. Heating of *trans*-[$Pt(Py)_2Cl_2$] with α-methylstyrene (the complex : α-methylstyrene mole ratio is 1:10) in $CDCl_3$ at 90°C for 53 h also

leads to appearance in the ^{1}H NMR spectrum of new signals, probably due to α-methylstyrene η^2-coordination [δ_H 7.55 d ($2H^\beta$, *J* 7.1 Hz), 7.79 t ($1H^\gamma$, *J* 7.4 Hz), 7.96 d ($2H^\alpha$, *J* 7.7 Hz)].

Heating of *cis*-$[Pt(Py)_2Cl_2]$ and $[Pt(Py)_4]Cl_2$ with styrene or α-methylstyrene (the complex : reactant mole ratio is 1:10) in $CDCl_3$ at 90°C for 126 h like the case of *trans*-$[Pt(Py)_2Cl_2]$ leads to appearance of signals that we assigned to the traces of coordinated reactant. Also, heating of $[Pt(Py)_4]Cl_2$ with the reactants is accompanied with the pyridine elimination leading to formation of *cis*-$[Pt(Py)_2Cl_2]$. However and idle experiment of heating $[Pt(Py)_4]Cl_2$ in $CDCl_3$ without the reactants at 90°C after 46 h also affords *cis*-$[Pt(Py)_2Cl_2]$ in 90% yield.

Heating of $[Pt(Py)_4]Cl_2$ with styrene taken in a large excess (the complex : styrene mole ratio is 1:100) at 90°C for 7 h induces styrene polymerization and formation of *cis*-$[Pt(Py)_2Cl_2]$, while heating of $[Pt(Py)_4]Cl_2$ with α-methylstyrene under the same conditions eliminates pyridine, the rate of the elimination is only a bit higher than in the idle experiment.

Heating of $[Pt(Py)_4]Cl_2$ with $(HMe_2Si)_2O$ [the complex : $(HMe_2Si)_2O$ mole ratio is 1:10] in $CDCl_3$ at 90°C for 53 h leads to formation of *cis*-$[Pt(Py)_2Cl_2]$. In turn, *cis*-$[Pt(Py)_2Cl_2]$ being heated under the same conditions does not exert any changes while *trans*-$[Pt(Py)_2Cl_2]$ is damaged, as confirmed by the presence in the ^{1}H NMR spectrum of the signals of free pyridine only.

Thus, phosphine and sulfoxide metallocomplexes react more actively with $(HMe_2Si)_2O$, than with α-methylstyrene; in the case of pyridine coordination compounds occurs coordination of α-methylstyrene.

Preliminary activation of complexes. Uncertainty of the data obtained on the reaction of the complex with the reactants inclined us to carry out their preliminary activation with α-methylstyrene or $(HMe_2Si)_2O$ and then estimate the catalytic activity of the resulting substance.

In all cases the preliminary activation of the platinum complexes with tetramethyldisiloxane is accompanied with colorization of the reaction solution to yellow or yellowish-green {e.g., after the treatment of *trans*-$[Pt(Py)_2Cl_2]$, sulfoxide and methylcyclooctadiene complexes the color of solution is green, of pyridinesulfoxide complexes yellowish-green, of $[Pt(Py)_4]Cl_2$ and *cis*-$[Pt(Ph_3P)_2Cl_2]$ light yellow}, and in some cases afford colloidal platinum. Such colorization commonly is suggested to be a result of formation of platinum–hydrosiloxane complexes [32, 33]. Unlike the platinum coordination compounds, after the reaction of rhodium catalysts with $(HMe_2Si)_2O$ the reaction mixture becomes brown.

Analysis of the results listed in the table allows to conclude the following.

The platinum complex with η^4-methylcyclooctadiene or with two sulfoxide ligands being heated in $(HMe_2Si)_2O$ displays a bit higher catalytic activity than the not treated one. On the contrary, the treatment of the complexes with α-methylstyrene led to decrease of α-methylstyrene conversion.

The tendency to decrease in activity of the catalyst after heating it with α-methylstyrene occurs also in the case of pyridinesulfoxide catalyst, and maximal conversion of α-methylstyrene can be achieved without its preliminary treatment.

Dipyridine platinum(II) complex with *cis*-structure in distinct to *cis*-$[Pt(Et_2SO)(Py)Cl_2]$ and *cis*-$[Pt(Et_2SO)_2Cl_2]$ showed a bit higher activity after treatment with α-methylstyrene than untreated complex, while heating with $(HMe_2Si)_2O$ leads to decrease in catalytic properties. At the same time the maximal activity of *trans*-$[Pt(Py)_2Cl_2]$ occurs after its activation with $(HMe_2Si)_2O$: conversion of α-methylstyrene after treatment is 4-fold higher. This can be connected with the difference in the initial steps of the mechanism of action of the geometric isomers of the platinum(II) complexes.

A good sensitivity toward the preliminary treatment showed $[Pt(Py)_4]Cl_2$: its activation with α-methylstyrene is a bit more effective than with $(HMe_2Si)_2O$, while without preliminary heating of the complex with the reactants the α-methylstyrene conversion was twofold lower.

The preliminary keeping of the platinum triphenylphosphine complex with the reactants led to decrease in α-methylstyrene conversion as compared to a not activated system; in the case of $[Rh(Ph_3P)_3Cl]$ the catalyst becomes slightly activated in α-methylstyrene.

The α-methylstyrene conversion in the presence of not treated $[Rh(MeCOD)Cl]_2$ turned to be a bit higher than after its preliminary treatment with α-methylstyrene, while activation of the complex with $(HMe_2Si)_2O$ decreases its catalytic properties considerably.

Thus, in most cases the preliminary treatment of catalysts leads to increase in the reaction rate, but in some cases to decrease, that can be connected with difference in the mechanism of formation of real catalysts.

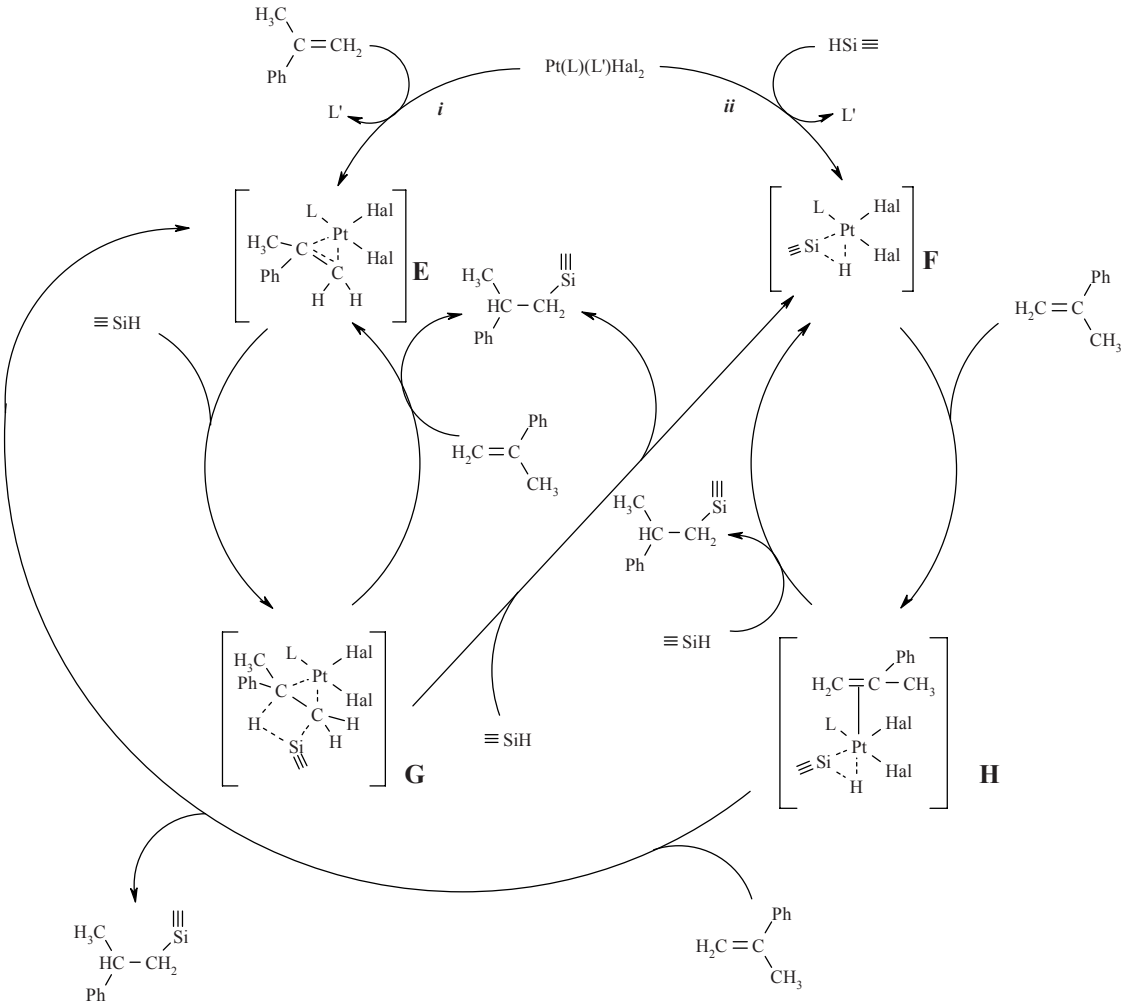
Hydrosilylation mechanism. Current view on the mechanism of catalytic hydrosilylation of C=C bond is based on several Schemes [29, 41–47]. The Scheme of Chalk and Harrod [41] assumes reversible coordination of alkene and oxidative addition of Si–H to the platinum atom and insertion of the coordinated alkene to the metal–hydrogen bond followed by reductive elimination of alkyl and silyl ligand as a key step. Such Scheme explains isotopic exchange between the alkene and Si–D and isomerization of alkene in side process. According to modified Scheme proposed by Chalk and Harrod [42, 43] the insertion proceeds to the metal–silicon bond and then occurs elimination of silyl and hydride ligands. Also, there is another concept of the Si–H bond activation based on the assumption of η^2-coordination of the hydrosilane without complete cleavage of bonds (three-center bonding) [29, 44–47] that has been confirmed by, e.g., of X-ray structural analysis [48, 49]. This Scheme is consistent with the general view on the essence of the catalytic process that assumes only loosening of bonds and formation of unstable intermediate structures that can not be isolated by chemical means.

With the above analysis of behavior of the coordination compounds in the reaction mixtures and assumption of η^2-coordination of the reactants in mind, we propose the following simplified Scheme of the reaction mechanism of hydrosilylation (on an example of formation of β-adduct):

The initial transformation of the platinum(II) complex at the action of reactants is competitive coordination of the reactants for the formation of η^2-styrene (path *i*, complex **E**) or η^2-hydrosiloxane complexes (path *ii*, complex **F**), differ by their catalytic activity. That is, occurs formation of two real catalysts of the process. In the favor of proceeding the (*i*) step attest two facts: the preliminary keeping of $[Pt(Py)_4]Cl_2$ and *cis*-$[Pt(Py)_2Cl_2]$ with α-methylstyrene allows to increase conversion of the latter at its reaction with $(HMe_2Si)_2O$, and appearance in the NMR spectra of the signals of coordinated α-methylstyrene. With sulfoxide and cyclooctadiene catalysts the process is defined by interaction with silicon hydride (path *ii*), as confirmed by the increasing in α-methylstyrene conversion in the reaction with $(HMe_2Si)_2O$ in the presence of the complexses treated preliminary with $(HMe_2Si)_2O$, and this fact is consistent well with the published data on the hydrosilylation mechanism in the presence of sulfoxide and cyclooctadiene catalysts. But we have to note that in the case of $[Pt(MeCOD)Cl_2]$ the paths (*i*) and (*ii*) is differ slightly from the above considered because here after formation of **E** and **F**

Conversion of α-methylstyrene [α-C_9H_{11}] in its reaction with $(HMe_2Si)_2O$ in the presence of preliminary treated and untreated complexes (88°C, 5 h)

Complex	Activation	Conversion, %	Complex	Activation	Conversion, %
$[Pt(MeCOD)Cl_2]$	$(HMe_2Si)_2O$	**29.3**	*cis*-$[Pt(Py)_2Cl_2]$	$(HMe_2Si)_2O$	14.8
	α-C_9H_{11}	5.7		α-C_9H_{11}	**21.5**
	–	10.4		–	19.9
cis-$[Pt(Me_2SO)_2Cl_2]$	$(HMe_2Si)_2O$	**26.2**	$[Rh(Ph_3P)_3Cl]$	$(HMe_2Si)_2O$	Traces
	α-C_9H_{11}	9.8		α-C_9H_{11}	**3.3**
	–	23.3		–	1.9
cis-$[Pt(Et_2SO)_2Cl_2]$	$(HMe_2Si)_2O$	**17.7**	*cis*-$[Pt(Et_2SO)(Py)Cl_2]$	$(HMe_2Si)_2O$	14.5
	α-C_9H_{11}	2.9		α-C_9H_{11}	0.7
	–	7.5		–	**20.8**
trans-$[Pt(Py)_2Cl_2]$	$(HMe_2Si)_2O$	**17.5**	$[Rh(MeCOD)Cl]_2$	$(HMe_2Si)_2O$	3.0
	α-C_9H_{11}	3.7		α-C_9H_{11}	11.2
	–	4.3		–	**14.2**
$[Pt(Py)_4]Cl_2$	$(HMe_2Si)_2O$	18.9	*cis*-$[Pt(Ph_3P)_2Cl_2]$	$(HMe_2Si)_2O$	1.7
	α-C_9H_{11}	**23.8**		α-C_9H_{11}	7.3
	–	9.8		–	**11.2**



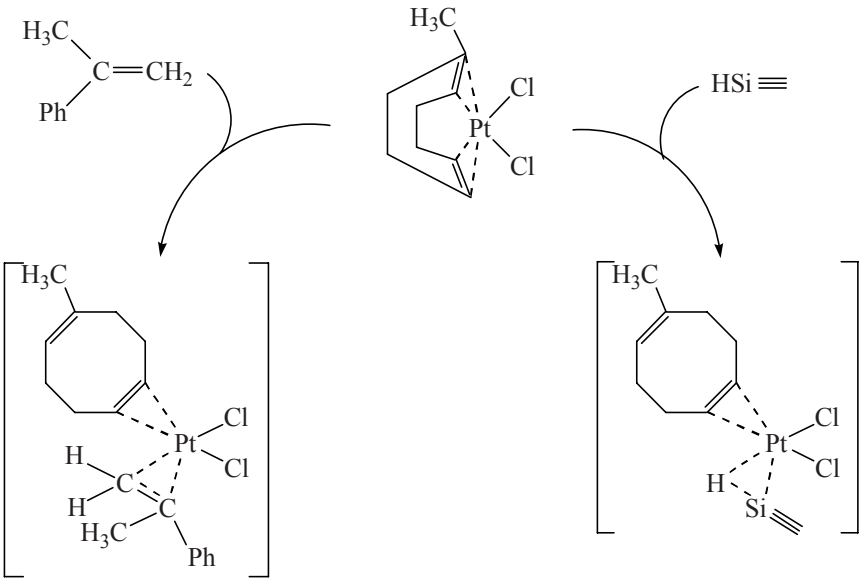
L, L' = sulfox-

complexes the ligand does not leave the coordination sphere remaining η^2-coordinated.

In the next step the formed complexes (**E** and **F**) react with the second reactant. Complex **E** probably affords tetracoordinated transition state **G** that at the action of next α-methylstyrene molecule regenerates the catalyst and affords the final reaction product. In the case of the complex **F** probably occurs coordination of α-methylstyrene at the platinum unoccupied orbital that affords respective platinum–siloxane–styrene intermediate **H**. The latter in turn reacts with next hydrosiloxane molecule affording the final product of the hydrosilylation reaction and regenerating one of the forms of the real catalysts of the process.

The formation of less active form of the catalyst from the more active one in the course of the catalytic process (from active **E** complex the less active **F** or, otherwise, from active **F** less active **E**) can be confirmed at the consideration of kinetic curves of hydrosilylation in the presence of tetrapyridine and methylcyclooctadiene catalysts (see figure, curves *1, 2*; the curves are typical logarithmic ones), that show decrease in the process rate in the final steps, probably due to the above considered reasons.

It is a sophistical problem to decide which form of the real catalyst is formed from *cis*-$[Pt(Ph_3P)_2Cl_2]$ is the most active one. First, the α-methylstyrene conversion in the reaction with $(HMe_2Si)_2O$ in the presence of the complex treated preliminary with the reactants falls compared to the same reaction in the presence of the untreated complex. But conversion of α-methylstyrene at the hydrosilylation in the presence of complex treated with α-methylstyrene turned to be



higher than in the presence of the complex treated with $(HMe_2Si)_2O$. However, e.g. in [28] was reported that induction period of the reaction of hydrosilylation of *para*-substituted styrenes with methyldichlorosilane disappeared when the reaction was carried out in the presence of *cis*-$[Pt(Ph_3P)_2Cl_2]$ treated preliminary with methyldichlorosilane. By our data, keeping of *cis*-$[Pt(Ph_3P)_2Cl_2]$ with $(HMe_2Si)_2O$ is accompanied by partial reduction of the parent complex. In this connection, it is the most probable that the initial transformation of planar-square phosphine complexes of platinum leads to the formation of the real catalysts, the complexes **E** and **F** with comparable catalytic activity, and the Scheme of the catalysis is little differ from the considered above.

The mechanism of interaction of the coordination compounds of palladium with the reactants probably differ from that of platinum catalysts. A feature of the palladium complex is much higher rate of their primary interaction with $(HMe_2Si)_2O$ (path *ii*) than with α-methylstyrene (path *i*). That is, formation of the palladium catalyst with the structure analogous to that of complex **F** prevails. This complex, in turn, predominantly is transformed into metallic palladium at the action of not coordinated $(HMe_2Si)_2O$ molecules rather than react with α-methylstyrene. At the same time when palladium catalyst analogous by structure to the **E** complex is formed, occurs hydrosilylation and reduction of α-methylstyrene. Thus, the real active palladium catalyst is its complex with η^2-α-methylstyrene.

In the case of rhodium catalyst, the first step of the hydrosilylation cycle depends on the structutre of the complex: with mononuclear $[Rh(PPh_3)_3Cl]$ it is the elimination of triphenylphosphine, with binuclear is thermal destruction. In both these cases is formed coordanationally unsaturated center that is instantly occupied by a molecule of solvent–reactant.

Thus, in the reaction of α-methylstyrene with $(HMe_2Si)_2O$ in the presence of the considered complexes occurs formation of two forms of real catalyst (active and little active). Structure and catalytic activity of each form depends not only on the geometry of the parent complex and the nature of the complex forming atom but also on the nature of ligand environment. In a general case, at the decrease in σ-donor and increase in p-acceptor contributions of a neutral ligand (sulfoxide ≈ alkene > Py > phosphine [3, 18]) the real catalyst **E** activity grows and that of the second real catalyst **F** falls.

EXPERIMENTAL

The ^1H, ^{13}C and ^{31}P NMR spectra were registered on Bruker AC-200 and WM-400 spectrometers from samples dissolved in $CDCl_3$ or $(CD_3)_2CO$, at the operating frequencies 200.13 and 400.14 (^1H), 50.33 (^{13}C), 81.01 (^{31}P) MHz. Spectra of samples were registered without additional reference substances, referring to the signal of deuterated solvent.

The IR spectra were taken on Shimadzu FTIR-8400S (4000–400 cm^{-1}) and Hitachi FIS-3 (400–100 cm^{-1}) spectrometers from KBr tablets.

The polarometric investigations were carried out on a Perkin–Elmer 241MC polarimeter in thermostated cells 10 cm length.

Hydrosilylation of α-methylstyrene with three mole excess of 1,1,3,3-tetramethyldisiloxane was carried out in sealed ampoules followed by analysis of the reaction mixture by the method of ^{1}H NMR spectroscopy in a tentative time moment. The complex concentration in the reaction mixture was varied in the range 5×10^{-4}–2×10^{-3} mol l^{-1}.

The catalyst preliminary activation was carried out with α-methylstyrene or $(HMe_2Si)_2O$ in sealed ampoules at 88°C for 5 h. Then the second reactant was added and the mixture was kept 5 h next. For the comparison were taken untreated catalysts and a preliminary prepared mixture of α-methylstyrene and $(HMe_2Si)_2O$. The catalyst concentration in the reaction mixture was 0.85 mmol l^{-1}.

Chromato-mass spectrometric investigation was carried out on an Agilent 6890N chromatograph with mass-selective deterctor Agilent 5973N, EI ionization (70 eV). The column is of quartz capillary DB-5MS (60 m×0.25 mm, phase film thickness 0.25 μm), injector temperature 280°C, interface temperature 290°C, the column temperature was varied from 150°C to 280°C with the rate 10 deg/min; carrier gas helium, flow dividing 1:20; sample value 0.5 μl. For identification of compounds was used NIST-2005 database.

The ratio of the formed products is calculated from their weight yields.

In the experiments were used ethanol, diethyl ether, styrene, α-methylstyrene, $PdCl_2$, $RhCl_3\cdot3H_2O$, MeCOD, and hydrochloric acid of "chemically pure" grade; 1,1,3,3-tetramethyldisiloxane from Acros; *cis*-$[Pt(Et_2SO)_2Cl_2]$, *cis*-$[Pt(Et_2SO)(Py)Cl_2]$, *cis*- and *trans*-$[Pt(Py)_2Cl_2]$, *cis*-$[Pt(Ph_3P)_2Cl_2]$, $[Rh(Ph_3P)_3Cl]$ along the data in [50], $[Pt(MeCOD)Cl_2]$, in [51], (–)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)(Py)Cl_2]$ in [52], *cis*-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$ in [53].

$[Rh(MeCOD)Cl]_2$ was presented courtesy by dr. Uvarov, St. Petersburg Technological Institute.

Dichloro(1,2:5,6-η^4-1-methylcycloocta-1,5-diene) palladium (II). In 1.5 ml of conc. hydrochloric acid was dissolved at heating 303.4 mg of $PdCl_2$. After cooling, to the solution was added 0.54 ml of 1-methylcycloocta-1,5-diene in 40 ml of ethanol. The formed yellow precipitate was kept for 15 min, then filtered off, washed on the filter with 3 ml of ice water and 20 ml of diethyl ether and then dried at room temperature for 24 h. 427 mg of $[Pd(MeCOD)Cl_2]$ was obtained (yield 83.7%). The ^{1}H NMR spectrum ($CDCl_3$; δ_H, ppm): 2.12 s (3H, CH_3), 2.41 m (4H, CH_2, *J* 98 Hz), 3.05 m (4H, CH_2, *J* 94 Hz), 6.28 m (3H, CH, *J* 44 Hz). The ^{13}C NMR spectrum ($CDCl_3$; δ_C, ppm): 28.9 s (1C, CH_3), 29.5 s (1C, CH_2), 30.7 s (1C, CH_2), 31.5 s (1C, CH_2), 36.8 s (1C, CH_2), 96.1 t (1C, CH, J_{Pt-C} 150 Hz), 107.8 s (1C, CH), 113.9 s (1C, CH), 115.9 s (1C, C). The IR spectrum, cm^{-1}: ν(CH) 3390–3350; 2920–2850; ν(C=C) 1515, 1485; δ(CH, Me) 1460, 1405; 1357; 1332; 1305; 1238; 1185; 1165; 1140; 1090; δ(CH, COD) 1010, 987; τ(Me) 960, 920; δ(CH, COD) 880, 862, 843; 807; 782; 725; 543. Far IR spectrum, cm^{-1}: ν(Pd–Cl) 336, 310; 293; 246; δ(Pd–Cl) 197.

Tetrapyridineplatinum(II) chloride. To a mixture of 43.8 mg of *cis*-$[Pt(Py)_2Cl_2]$ and 5 ml of water was added 1.5 ml of pyridine and the mixture was heated on a boiling water bath to formation of transparent solution. The solution was then aerated to dryness and the formed white precipitate was dried in a thermostat at 40°C. 59.7 mg (yield 99.3%) of $[Pt(Py)_4]Cl_2$ was obtained. The ^{1}H NMR spectrum [$(CD_3)_2CO$; δ_H, ppm]: 7.54 t (2Hβ, Py, *J* 6.7 Hz), 8.04 t (1H$^\gamma$, Py, *J* 7.4 Hz); 8.89 d.t (2H$^\alpha$, Py, *J* 5.3, *J* 17.7 Hz); ($CDCl_3$; δ, ppm): 7.53 t (2Hβ, Py, *J* 6.4 Hz); 8.04 t (1H$^\gamma$, Py, *J* 7.3 Hz); 8.90 d.t (2H$^\alpha$, Py, *J* 5.8, *J* 16.8 Hz). The IR spectrum, cm^{-1}: 3117; 3089; ν(CH) 3065, 3028; 3004; 2993; 2979; 2961 sh; 2925; 2847; ν(C=C and C=N) 1610, 1600; ν(C=C and C=N) 1478, 1452; δ(CH) 1222; 1162; 1138; δ(CH) 1084, 1070, 1025; 971, δ(CH) 898, 799, 770, 698. The far IR spectrum, cm^{-1}: ν_s (Pt–N) 305.

1,1,3,3-Tetramethyl-1-(2-phenylpropyl)disiloxane (A). In a sealed ampoule was heated at 85°C for 150 h a mixture of 11 mg of $[Pt(Py)_4]Cl_2$, 2 ml of α-methylstyrene and 8 ml of 1,1,3,3-tetramethyldisiloxane. Then the reaction mixture was distilled in a vacuum, a fraction boiling at 112°C (12 mm Hg). (published bp 80°C at 1 mm Hg. [13]) was selected. Product (2.52 g, yield 53.7%) was obtained. The ^{1}H NMR spectrum ($CDCl_3$, δ_H, ppm): –0.02 s (3H, Si–CH_3), 0.00 s (3H, Si–CH_3), 0.18 s (3H, Si–CH_3), 0.19 s (3H, Si–CH_3), 1.01 d.q (2H, $SiCH_2$, *J* 6.7, *J* 7.3 Hz), 1.34 d (3H, CH_3, *J* 7.5 Hz), 2.96 d.t (1H, CH, *J* 6.5, *J* 7.0 Hz), 4.70 m

(1H, SiH), 7.18 t (1H, Ph, *J* 7.1 Hz), 7.28 m (4H, Ph). The ^{13}C NMR spectrum ($CDCl_3$, δ_C, ppm): 0.54 s (1C, $SiCH_3$), 0.89 s (2C, $SiCH_3$), 0.96 s (1C, $SiCH_3$), 26.03 s (1C, CH_3), 28.30 s (1C, CH_2), 35.64 s (1C, CH), 125.76 s (1C, CH_{arom}), 126.61 s (2C, CH_{arom}), 128.30 s (2C, CH_{arom}), 149.77 s (1C, C_{arom}). The mass-spectrum: *m/z* (relative intensity of the ion,%) 251(1) $[M - H]^+$; 239(5); 208(3); 193(2); 176(3) $[M - H - HSi(CH_3)_2O]^+$ and (or) $[M - H - 5(CH_3)]^+$, and (or) $[M - C_6H_5]^+$; 149(22); 133 (30) $[HSi(CH_3)_2OSi(CH_3)_2]^+$; 119(15) $[C_6H_5CH\cdot(CH_3)CH_2]^+$; 112(9); 105(81) $[C_6H_5CH(CH_3)]^+$; 91(100); 77(11) $[C_6H_5]^+$; 59(4) $[HSi(CH_3)_2]^+$ and/or $[OSiCH_3]^+$; 51(3) $[(CH)_4–H]^+$; 43(3) $[SiCH_3]^+$; 28 4) $[CH_2CH_2]^+$; 18(1).

1,1,3,3-Tetramethyl-1,3-бис(2-phenylpropyl)disiloxane (B). The ^1H NMR spectrum ($CDCl_3$, δ_H, ppm): 1.05 s (12H, Si–CH_3), 0.99 d (2H, $SiCH_2$, *J* 6.9 Hz), 1.00 d (2H, $SiCH_2$, *J* 7.0 Hz), 1.30 d (6H, CH_3, *J* 7.0 Hz), 2.94 q (2H, CH, *J* 6.4, *J* 7.3 Hz), 7.17 t (2H, Ph, *J* 7.5 Hz), 7.24 m (8H, Ph). The ^{13}C NMR spectrum ($CDCl_3$, δ_C, ppm): 0.68 s (1C, $SiCH_3$), 1.05 s (3C, $SiCH_3$), 25.94 s (2C, CH_3), 28.40 s (2C, CH_2), 35.61 s (2C, CH), 125.69 s (2C, CH_{arom}), 126.59 s (4C, CH_{arom}), 128.25 s (4C, CH_{arom}), 149.84 s (2C, C_{arom}).

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