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Formation and Nature of Microheterogeneous Catalysts Based on Palladium Complexes[1]

F. K. Shmidt, L. B. Belykh, and T. V. Cherenkova
Irkutsk State University, Irkutsk, 664033 Russia

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Abstract—The mechanism of the formation and the nature of microheterogeneous catalysts for hydrogenation are discussed using acetylacetonate complexes of palladium with phosphine ligands as an example. Polynuclear palladium complexes with phosphide and phosphinidene ligands are obtained, and their role in the formation of hydrogenation catalysts is found. As distinct from phosphide complexes, amide complexes of palladium are unstable in a hydrogen atmosphere and undergo reduction to form highly dispersed palladium black.

INTRODUCTION

Phosphine complexes of palladium(II) are the precursors of catalysts for various processes of organic synthesis. The nature and the mechanism of the formation of catalytically active complexes are one of the most important problems in catalysis. In this work, the results of a study on the transformations of β-diketonate phosphine complexes of palladium under the action of various reducing agents are presented. The aim of this study was to reveal the nature of microheterogeneous hydrogenation catalysts and to develop new methods for the synthesis of active and selective catalytic systems.

EXPERIMENTAL

Solvents were purified according to conventional procedures used in operations with organometallic compounds [1]. The $Pd(acac)_2PPh_3$ complex was synthesized according to [2]. For this complex the data of elemental analysis are: Anal. calcd. (%): Pd, 18.72; C, 59.32; H, 5.12; P, 5.64. Found (%): Pd, 17.59; C, 61.15; H, 5.23; P, 4.95.

Trioctylphosphine was synthesized according to the procedure described in [3]; T_b = 210°C/5 torr (^{31}P NMR: $\delta = -41$ ppm). Diphenylphosphine was prepared according to [4]; T_b = 152°C/13 torr (^{31}P NMR: $\delta = -41$ ppm; $J_{P-H} = 210$ Hz).

Synthesis of catalysts based on the $Pd(acac)_2 + nPPh_3$ system. A 0.9740-g portion of $Pd(acac)_2$ (3.2 mmol) and 0.2112 g (0.8 mmol) of triphenylphosphine were placed into a thermostatically controlled vessel connected to a volumetric system; the vessel was evacuated and then filled with hydrogen. A 20-ml portion of toluene (or DMF) was added in a hydrogen flow. The resulting solution was stirred in a hydrogen atmosphere at a gauge pressure of 1 atm and a temperature of 80°C for 24 h until the quantitative formation of acetylacetone. After reaction completion, the solution became colorless, and a black precipitate was formed. The precipitate was decanted, washed several times with diethyl ether, and dried in a vacuum. Experiments at other $PPh_3/Pd(acac)_2$ ratios were performed in a similar manner.

Acetylacetone and benzene in the catalyzate were determined by GLC after preliminary recondensation from the liquid phase on a vacuum setup (20°C/1×10^{-3} torr) to prevent the formation of these substances from the catalyzate in a chromatographic column during analysis. A Chrom-5 chromatograph with a 3.6-m column packed with SE-30 and a flame-ionization detector was used; the analysis temperature was 120°C, and nitrogen was a carrier gas. Errors in the determination of acetylacetone and benzene were at most 10%.

NMR spectra were measured on a VXR-500S pulse spectrometer (Varian). The chemical shifts of ^{31}P are given with reference to 85% phosphoric acid. Positive values correspond to downfield shifts. The IR spectra of samples in mineral oil were measured in the region 4000–400 cm^{-1} on a Specord IR-75 instrument.

Analysis of catalyst samples by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) was performed using BS-300 and BS-540 microscopes (Czech Republic). The samples were preliminarily dispersed in hexane for 1 min using a UZDN-A ultrasonic processor (power input of 100 W). A drop of the resulting suspension was applied to a supporting net coated with a carbon film and dried in an argon atmosphere. The conditions of measurements prevented the test samples from melting and decomposing under exposure to an electron beam.

The X-ray diffraction analysis of catalyst samples was performed using a DRON-3 diffractometer with CoK_α radiation.

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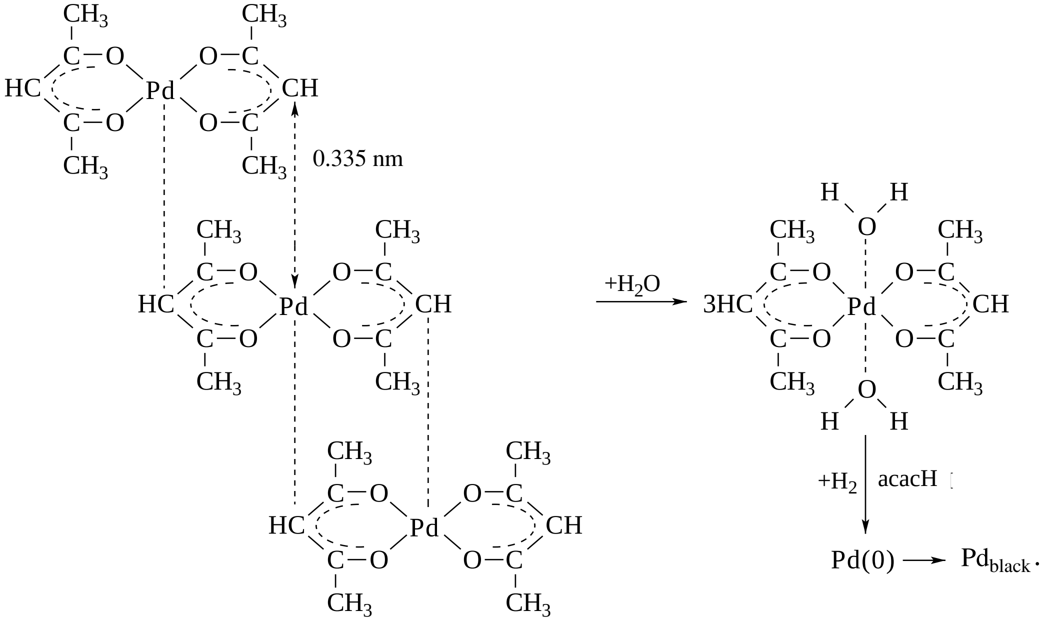
RESULTS AND DISCUSSION

The formation of hydrogenation catalysts by the reduction of β-diketonate complexes of palladium was examined using molecular hydrogen or sodium hypophosphite as a reducing agent.

In contrast to carboxylate complexes [5], acetylacetonate complexes of palladium are reduced by hydrogen in aprotic solvents under more severe conditions ($T = 80°C$). In this case, it was found [6] that bis(acetylacetonato)palladium, the oligomeric structure of which is also retained upon dissolving in benzene, is not reduced by hydrogen in aprotic solvents in the absence of water. Similar behavior was also found for palladium acetate. The role of water is that it degrades the oligomeric structures $[Pd(acac)_2]_n$ and facilitates the heterolytic cleavage of a hydrogen molecule. For example, at $n = 3$:



The activity of Pd black formed by reduction is low in the hydrogenation of unsaturated hydrocarbons: ~0.2 mol phenylacetylene (mol Pd)$^{-1}$ min^{-1}. The addition of a tertiary phosphine in even a small amount to the reaction system before the treatment with hydrogen resulted in a dramatic increase in the specific activity [7, 8]. Figure 1 indicates that this activity reached a maximum at P/Pd ~ 0.4 and then decreased.

This fact motivated our study of the modifying effect of a tertiary phosphine on the formation of hydrogenation catalysts in the system $Pd(acac)_2 + nPPh_3 + H_2$ ($n = 0.25, 0.5, 0.75$, and 1.0).

Nature of Microheterogeneous Catalysts Based on $Pd(acac)_2 + nPPh_3 + H_2$

The reaction between equimolar amounts of a tertiary phosphine PR_3 (triphenylphosphine, tributylphosphine, or trioctylphosphine) and $Pd(acac)_2$ affects the nature of a bond in an acetylacetonate ligand. A chelate coordination bond is transformed into a covalent C–Pd bond to form a complex of the composition $Pd(acac)_2PR_3$ [9, 10]. At P/Pd < 1, a mixture of $Pd(acac)_2$ and $Pd(acac)_2PR_3$ occurs in the reaction system. Note that a tertiary phosphine in the presence of water can exhibit reducing properties to form a $Pd(PR_3)_4$ complex with a low hydrogenation activity and $P(O)R_3$ [11] according to the reaction

$$Pd(acac)_2 + 5PR_3 + H_2O$$

$$\longrightarrow Pd(PR_3)_4 + P(O)R_3 + 2acacH.$$

Therefore, the dryness of solvents is of particular importance.

First, let us consider the reactions of the individual complex $Pd(acac)_2PPh_3$ under exposure to hydrogen in a toluene or DMF medium.

The interaction of $Pd(acac)_2PPh_3$ with hydrogen is characterized by an induction period, the duration of which is 40 or 5–10 min in toluene or DMF, respectively [7, 8]. The *S*-shaped curve of hydrogen absorption indicates the autocatalytic reaction. Acetylacetone is formed at the beginning of the interaction of $Pd(acac)_2PPh_3$ with hydrogen, and benzene is formed thereafter (Fig. 2).

According to NMR- and IR-spectroscopic data, the hydrogenolysis of the C-bonded acetylacetonate ligand takes place at this stage to form the unstable intermediate $[Pd(acac)PPh_3]_2$ (**I**) as follows:

$$2Pd(acac)PPh_2 + H_2 \longrightarrow [Pd(acac)(PPh_3)]_2 + 2acacH.$$

The subsequent transformation of **I** results in the mixed-ligand binuclear complex $[Pd(acac)PPh_2]_2$ (**II**):

$$[Pd(acac)(PPh_3)]_2 + H_2 \longrightarrow [Pd(acac)PPh_2]_2 + 2C_6H_6.$$

The trinuclear palladium complex $[Pd_3(PPh_2)_3(PPh_3)_3]^+acac^-$ (**III**) was also detected by NMR spectroscopy. It is well known [12] that analogous complexes result from a reaction between $Pd(PPh_3)_4$ and $[PdCl_2(PPh_2)_2(PHPh_2)_2]$ in a hydrogen atmosphere. We did not detect the direct formation of a Pd(0) complex under these conditions. However, it was found earlier [13] that the extremely unstable complex $[Pd(PPh_3)]_2$ was formed in the reaction between $Pd(acac)_2PPh_3$ and formic acid in equimolar amounts. In excess formic acid (HCOOH/Pd > 1), the complex $[Pd(PPh_3)Pd(PPh_2)]$ was formed. These results suggest the formation of $[Pd(PPh_3)]_2$ as an intermediate in the reaction of $Pd(acac)_2PPh_3$ with hydrogen. Thus, the formation of **III** can be expressed by the equation

$$2[Pd((PPh_3)]_2 + [Pd(acac)PPh_2]_2 + H_2$$

$$= [Pd_3(PPh_2)_3(PPh_3)_3]^+acac^- + 3Pd + C_6H_6 + acacH.$$

The mechanism of $Pd(acac)_2PPh_3$ reduction by hydrogen in toluene or DMF is analogous [7, 14].

When the process was performed in DMF, a dark brown precipitate poorly soluble in DMF was formed in the reaction system after the quantitative formation of acetylacetone. The empirical formula of this precipitate is $Pd_5P_4C_{36}H_{31}$. The precipitate is X-ray amorphous; it is characterized by a halo with a maximum at 2.231 Å. The coherent-scattering region calculated by the Selyakov–Scherrer equation [15] is ~10 Å.

The IR spectrum of the precipitate exhibits inadequately resolved absorption bands in the region 690–750 cm^{-1}, which are related to out-of-plane deformational C–H vibrations in monosubstituted benzene rings. The ^{31}P NMR spectrum of a DMF solution of the sample exhibits a number of signals from –20 to 40 ppm, which can be attributed to both diphenylphosphine ligands in polynuclear palladium complexes and triphenylphosphine phosphorus nuclei coordinated to palladium atoms. A portion of triphenylphosphine is oxidized and the rest of it remains as PPh_3 ligands; the yield of benzene is approximately 0.8–0.9 mol per 1 mol of palladium. Consequently, more than one Ph group undergoes dephenylation, and the precipitate consists of a set of palladium compounds with organophosphorus ligands, which can generally be described as $[Pd_5(PPh_2)_2(PPh)_2]$ or $[Pd_5(PPh)_3PPh_3]$.

According to TEM data, the precipitate consists of regularly shaped spherical globules 0.2–1.2 μm in diameter. The high contrast, which points to a high level of interactions between the globules and an electron beam, is indicative of a high palladium concentration in the globules. Palladium is uniformly distributed over the entire volume (Fig. 3).

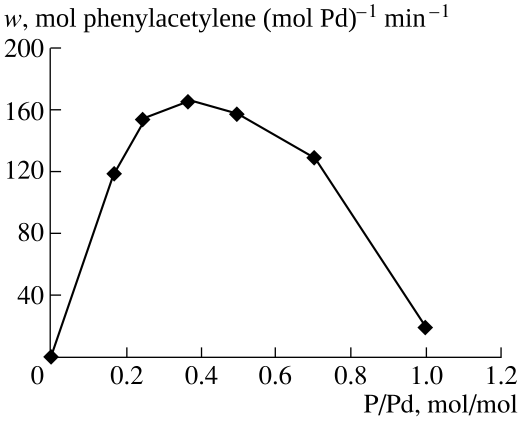


Fig. 1. Specific rate of phenylacetylene hydrogenation in the presence of the catalytic system $Pd(C_5H_7O_2)_2$ + $nPPh_3$ as a function of the molar ratio P/Pd (T = 80°C; solvent, DMF; P_{H_2} = 1 atm; at P/Pd = 0, w = 0.2 mol phenylacetylene (mol Pd)$^{-1}$ min^{-1}.

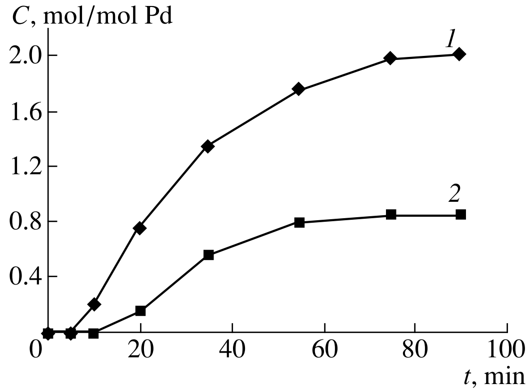


Fig. 2. Relative concentrations (C) of (*1*) acetylacetone and (*2*) benzene as functions of time in the reduction of $Pd(acac)_2PPh_3$ by hydrogen in DMF at 80°C and m_{Pd} = 6 mmol.

According to SEM data, the precipitate also consists of regularly shaped spherical microglobules, mostly 0.5–1.0 μm in diameter. The formation of spherical particles at a level of 1 μm is possible only under the conditions of phase separation in the system. The agglomeration of globules primarily occurs by the coalescence of finer particles from 0.1–0.2 μm and above. This mechanism is supported by the broad statistical particle-size distribution. The shape of globules (regular sphere) and the mechanism of growth (coalescence) indicate that a nascent phase enriched in palladium exhibits a low viscosity close to that of coacervate systems (coacervation is the separation of a newly formed phase as droplets enriched in solute). Coacervate systems are most typical of high-molecular compounds with low molecular weights or of the polymer–solvent system enriched in solvent [16]. Taking into account a low thermodynamic affinity of the precipitate to solvent, which manifests itself in the low solubility, we believe that this type of phase separation results from a

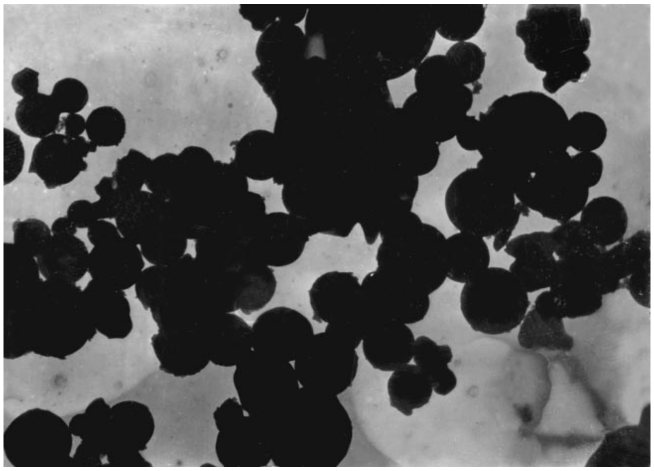
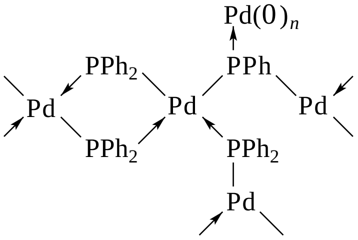


Fig. 3. Electron micrograph of a precipitate isolated from the system $Pd(acac)_2PPh_3 + H_2$ (TEM data; 1 cm in the micrograph corresponds to 1.43 μm).

low molecular weight of the reaction product (at a level of oligomers). The subsequent reaction of the formed polymeric phase with hydrogen and deeper dephenylation of organophosphorus ligands result in polymer structuring and transition to a solid state of aggregation.

The above data suggest that the precipitate formed in the $Pd(acac)_2PPh_3 + H_2$ system is the following palladium-containing organophosphorus polymer, which consists of polynuclear palladium complexes with bridging diphenylphosphide and phenylphosphinidene ligands linked to each other by donor–acceptor interactions:



On the other hand, dissolving this precipitate in DMF followed by centrifuging the solution did not result in precipitate formation. These results indicate that, on dissolving the sample, the constituent globules underwent degradation to form finer particles with a largest size of 3 nm. This data interpretation can associate an increase in the catalytic activity upon diluting the solution with the dissociation of oligomeric structures by coordinating a solvent (DMF) [8].

Complexes **I**, **II**, and **III** exhibit no catalytic activity in hydrogenation, whereas the activity of a microheterogeneous catalyst of the empirical formula $Pd_5P_4Ph_6$ is approximately equal to 40 mol phenylacetylene (mol Pd)$^{-1}$ min^{-1}.

Let us consider the nature of reaction products in the $Pd(acac)_2 + nPPh_3$ system at P/Pd < 1. As well as at $n = 1$, the reaction in the $Pd(acac)_2 + nPPh_3$ system was performed until the quantitative formation of acetylacetone. Note that a change in the P/Pd ratio affects the degree of degradation of organophosphorus ligands (Table 1). This behavior was observed in the reduction of the $Pd(acac)_2 + nPPh_3$ system by hydrogen in both toluene and DMF.

A decrease in the P/Pd ratio results in an increase in the benzene content of the reaction system on a tertiary phosphine basis. These data indicate that the ratio between starting reactants rather than the nature of an aprotic solvent is a key factor affecting the degradation of a tertiary phosphine and, as a consequence, the nature of reaction products in the catalytic system $Pd(acac)_2 + nPPh_3$. Therefore, experiments performed in toluene are described below.

At the ratio P/Pd = 0.25, the formation of benzene was almost quantitative on a triphenylphosphine basis. The black precipitate isolated from the reaction system is described by the empirical formula $Pd_{3.46}PC_{2.36}H_{2.12}$. According to X-ray diffraction data, it contains palladium in a crystalline form (*d*/*n* 2.246, 1.945, 1.376, and 1.174 Å) and a substance amorphous to X-rays. The amount of palladium metal in different samples can vary from 5 to 25% depending on the degree of removal from coarse palladium metal particles. The molecular formula of the reaction product minus Pd black has the form $[(Pd_{3.26}P)_{0.61}\{Pd_2(PPh)\}_{0.39}]$. Previously [7], the interatomic distances in analogous samples were found by EXAFS to be equal to 2.54, 3.14 (Pd–Pd), and 2.18 Å (Pd–P) and were attributed to the palladium phosphide Pd_3P; the solid-state NMR spectrum exhibited two signals due to phosphorus nuclei in different states. A set of experimental and published data suggests that the reaction products in the $Pd(acac)_2 + 0.25PPh_3 + H_2$ system consist of a mixture of palladium phosphides of the predominant composition Pd_3P and palladium compounds with phenylphosphinidene.

The composition of the reaction products was changed as the ratio P/Pd was increased to 0.5. According to X-ray diffraction data, the black precipitate isolated from the reaction system contains an amorphous substance characterized by a diffuse maximum (halo) at 2.250 Å and a crystalline phase with reflections of medium intensities on the diffuse halo profile. The crystalline phases correspond to palladium phosphides of the compositions $Pd_{4.8}P$ (*d*/*n* 2.414, 2.326, 2.260, 2.252, 2.225, 2.158, 2.116, 2.027, 1.993, and 1.878 Å) and Pd_6P (*d*/*n* 2.715, 2.564, 2.359, 2.254, 2.222, 2.107, 2.011, 1.924, and 1.862 Å). The lines at 3.145 and 1.512 Å were unidentified.

According to IR-spectroscopic data, monosubstituted benzene units (δCH = 690–730 cm^{-1}) were present in the precipitate, whereas triphenylphosphine oxide was absent (no phosphoryl group absorption bands at νP=O 1120 and 1200 cm^{-1}). Elemental analysis (empirical formula $Pd_2PC_{4.7}H_{4.6}$), IR-spectroscopic, and X-ray diffraction data suggest that the precipitate contains polynuclear palladium complexes with PPh_2 and (or) PPh ligands along with phosphides. The sample cannot be identified by ^{31}P NMR spectroscopy because of its low solubility.

According to IR-spectroscopic data, the precipitate isolated from the reaction system $Pd(acac)_2 + 0.75PPh_3$ also contains phenyl groups ($\delta CH = 690–750\ cm^{-1}$). It is described by the empirical formula $Pd_6P_5Ph_{11.5}$. Because $Pd(acac)_2$ is reduced by hydrogen more rapidly than the $Pd(acac)_2PPh_3$ complex, Pd(0) particles can occur in the precipitate. Taking into account that $Ph/P > 2$, we believe that the precipitate contains PPh_3 ligands along with other ligands.

According to X-ray diffraction data, the precipitate is a mixture of compounds in amorphous and crystalline states. The amorphous phase is characterized by a diffuse maximum at 2.241 Å, the coherent-scattering region of which is ~13 Å. The diffraction pattern of the crystalline phase exhibits reflections only at small diffraction angles ($2\theta = 10°–30°$); this fact suggests the presence of weakly ordered structures. The reflections of the crystalline phase (*d*/*n* 7.424, 6.758, 5.809, 5.302, 4.670, 4.443, 4.063, and 3.768 Å) are consistent with the reflections of the crystalline phase in catalyst samples based on $Pd(acac)_2PPh_3 + NaH_2PO_2$, which were ascribed to polynuclear complexes like $[Pd(PPh_2)]_n$ [17].

According to SEM data, the test precipitate has a globule as an independent structural unit; this unit repeated many times leads to various types of supramolecular structures. The globule size is 0.2–1.0 μm. The ability of globular polymers to form structures that are more complex, in which globules play a role of elementary units, is limited. If a polymer is monodispersed with respect to molecular weight, the globules can be arranged to form structures with the closest packing of spheres. In this case, the inconsistency between the sizes of individual globules dramatically restricts the possibilities of forming microcrystallinity zones. External manifestations of crystallinity are packs of globules. The following types of supramolecular structures were found in the given sample: floccular, unstructured amorphous, spicular, and clustered structures. Note that the mutual arrangement of discrete portions of a chain macromolecule in a globule is usually disordered, and almost any polymer transferred to a globular form occurs in an amorphous state [16]. For this reason, the crystallinity of globular polymers exhibits a well defined topographical expression, which is detected by electron microscopy.

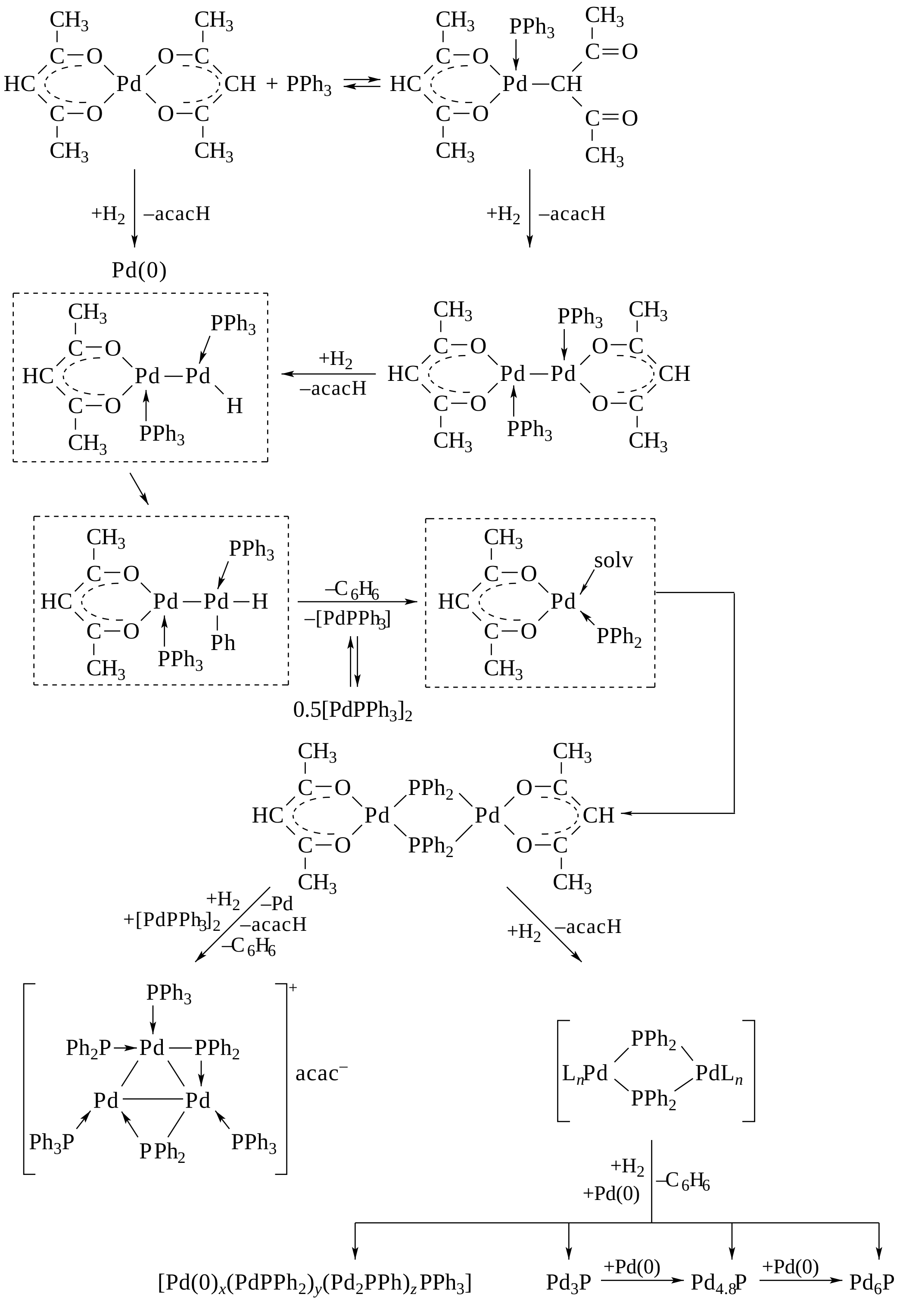
The elemental analysis, IR-spectroscopic, X-ray diffraction, and electron-microscopic data suggest that the product of reduction of the system $Pd(acac)_2 + 0.75PPh_3$ by hydrogen is also a palladium-containing organophosphorus polymer. It is likely that this polymer contains amorphous reduced palladium particles and polynuclear palladium complexes with organophosphorus ligands with different numbers of phenyl groups. The composition of the precipitate can be expressed by the molecular formula $[Pd(0)_3PdPPh_2Pd(PPh_2)_2(PPh_3)_2]$ or $[Pd(0)_3PdPPh_2Pd_2(PPh)(PPh_3)_3]$.

Thus, an excess of bis(acetylacetonato)palladium in the formation of a catalyst in the presence of triphenylphosphine facilitates the degradation of organophosphorus ligands to result in phosphides of different compositions at low P/Pd ratios. At first glance, contradictory data were obtained in this case: at the ratio $P/Pd = 0.25$, a palladium phosphide of the composition Pd_3P was formed, whereas the phosphides $Pd_{4.8}P$ and Pd_6P enriched in palladium were formed at the ratio $P/Pd = 0.50$. These findings can be interpreted as follows. The reduction of $Pd(acac)_2$ by hydrogen leads to the formation of Pd(0), which can both undergo aggregation to form crystalline palladium and react with intermediates of the main process to facilitate the degradation of organophosphorus ligands with the formation of palladium phosphides. The formation of crystalline palladium results in a decrease in the Pd/P ratio, compared with the initial value, and in the formation of palladium phosphides of the predominant composition Pd_3P. Note that the reduction of $Pd(OAc)_2 + 0.25PPh_3$ by hydrogen in DMF under analogous conditions on the addition of nickel acetate resulted in the formation of nickel metal and the palladium phosphide Pd_6P.

Table 1. Reduction products in the $Pd(acac)_2$–$n$$PPh_3$ system

$\frac{PPh_3}{Pd(acac)_2}$, mol/mol	C_6H_6/PPh_3, mol/mol		Empirical formula	X-ray diffraction data
	solvent			
	toluene	DMF		
0.25	2.60	2.90	$Pd_{3.46}PC_{2.36}H_{2.12}$	Crystalline Pd; substance amorphous to X-rays
0.50	1.68	2.16	$Pd_2PC_{4.7}H_{4.6}$	$Pd_{4.8}P$; Pd_6P; substance amorphous to X-rays
0.75	1.02	1.17	$Pd_6P_5Ph_{11.5}$	$Pd(PPh_2)_2$; substance amorphous to X-rays
1.00	0.90	0.83	$Pd_5P_4C_{36}H_{31}$	Substance amorphous to X-rays

Taking the above data into account, the formation of a hydrogenation catalyst can be represented as follows (hypothetical intermediates are outlined by dashed frames):



Below, we consider the results of studies on the catalytic properties of the samples in the hydrogenation of unsaturated compounds (Table 2).

The specific activity of catalyst samples in the hydrogenation of a model compound (styrene) decreased with a decrease in the P/Pd ratio in the starting catalytic system. As mentioned above, the degree of the degradation of organophosphorus ligands in the formation of catalysts increased in the above direction. Atomic absorption analysis data (Table 2) provide evidence that deeper degradation of organophosphorus ligands results in a decrease in the solubility of catalyst samples and, as a consequence, in a decrease in the concentration of active complexes in solution. Note that, unlike olefins, α-acetylene hydrocarbons (phenylacetylene and 1-hexyne), which exhibit a high coordination ability, increase the solubility of catalyst samples by degrading palladium-containing organophosphorus polymers on coordination. Polynuclear palladium complexes with organophosphorus ligands pass into the solution (the ^{31}P NMR spectrum exhibits resonance signals in the region from –10 to 30 ppm and upfield signals with $\delta = -210$ ppm). The soluble complexes have an order of magnitude higher hydrogenation activity than the insoluble portion of catalysts (palladium phosphides and palladium metal).

The activity of the catalytic system considerably decreased with an increase in the ratio P/Pd > 1. A decrease in the activity depends on the nature of tertiary phosphine; for example, at P/Pd = 2, the activity in olefin hydrogenation decreased to zero in the case of tributylphosphine.

Taking into account the microheterogeneous character of catalyst samples, it was suggested that the use of alkylphosphines (tributylphosphine and trioctylphosphine) leads to an increase in the solubility of palladium-complex catalysts, which occur in a colloidal disperse state, and the activity in hydrogenation, leaving the catalyst formation mechanism unchanged [18]. For example, in contrast to all of the above catalyst samples with triphenylphosphine, the system $Pd(acac)_2P(C_8H_{17})_3 + H_2$ formed under the same conditions (80°C; $P_{H_2} = 1$ atm) was found to be completely soluble even in toluene. The activity of this system in the hydrogenation of α-olefin and bisubstituted acetylene hydrocarbons and conjugated dienes is several times higher than that of the catalyst samples with triphenylphosphine (Table 3).

Thus, the data on the formation of a hydrogenation catalyst based on $Pd(acac)_2PR_3$ complexes under the action of hydrogen allowed us to propose the following catalyst model: this is a palladium-containing organophosphorus polymer or palladium phosphides at P/Pd ≤ 0.5, on which clusters containing Pd(0) are immobilized. A decrease in the P/Pd ratio results in the formation of insoluble palladium phosphides and in a decrease in the fraction of reduced Pd(0), because of which the catalytic activity of the systems in hydrogenation decreases.

Table 2. Catalytic properties of catalyst samples isolated from the system $Pd(acac)_2 + nPPh_3 + H_2^*$ in the hydrogenation of styrene (St)

$\frac{PPh_3}{Pd(acac)_2}$, mol/mol	w, mol (mol Pd)$^{-1}$ min^{-1}	Fraction of dissolved palladium, %	
		with no substrate	with phenylacetylene
0.25 (toluene)**	5.8	0.5	3.0
0.50 (toluene)	30.0	12.5	23.3
0.75 (toluene)	78.0	95.0	95.5
0.25 (DMF)	0.3	–	–
0.50 (DMF)	43.7	21.1	47.3
1.00 (precipitate) (DMF)	58.7	53.5	95.0

* Reaction conditions: $m_{Pd} = 0.02$ mmol; solvent, DMF; $T = 30$°C; St/Pd = 450 mol/mol; $P_{H_2} = 1$ atm.

** The solvent in which the catalyst sample was synthesized is indicated in parentheses.

Microheterogeneous Hydrogenation Catalyst Based on $Pd(acac)_2PPh_3 + NaH_2PO_2$

Previously [17, 19], microheterogeneous catalysts of a similar nature were found using sodium hypophosphite as a reducing agent. The reduction of the complex $Pd(acac)_2PPh_3$ with sodium hypophosphite proceeds via a number of steps including the exchange of a carbon-bonded acetylacetonate ligand for the hypophosphite anion, the subsequent hydrolysis of the mixed-ligand complex, and a step of the reductive elimination from the complex $[Pd(acac)(H_2PO_2)(PPh_3)(solv)]$:

$$Pd(acac)_2PPh_3 + NaH_2PO_2$$

$$\xrightarrow[-acacNa]{} Pd(acac)PPh_3(H_2PO_2)$$

$$\xrightarrow{+H_2O,\ -acacH} Pd(OH)(PPh_3)(H_2PO_2)$$

$$\xrightarrow[-H_3PO_3]{} \{Pd(PPh_3)\}.$$

The reaction is complicated by the catalytic oxidation of the hypophosphite anion with the liberation of hydrogen into the reaction system. Triphenylphosphine ligands undergo dephenylation under the action of hydrogen to form polynuclear palladium complexes different in structure and composition. The degradation of phosphine ligands in the coordination sphere of palladium and the partial oxidation of triphenylphosphine by trace oxygen lead to the formation of a microheterogeneous palladium complex catalyst.

According to SEM data, the precipitate isolated from the reaction system $Pd(acac)_2PPh_3 + NaH_2PO_2$ contains the following three types of supramolecular forms: a homogeneous unstructured material, crystalline fibrillar structures similar in shape to a leaf (close to dendrites), and fibrillar plate-type crystals immersed

Table 3. Hydrogenation of unsaturated hydrocarbons in the presence of the $Pd(acac)_2P(C_8H_{17})_3 + H_2$* catalytic system

Substrate	w, mol H_2 (mol Pd)$^{-1}$ min^{-1}		Products**
	–C≡C–	–C=C–	
Phenylacetylene	68	27	Styrene (50), ethylbenzene (24), and oligomers (25)
1-Hexyne	60	39 0***	Hexane (34), *cis*-2-hexene (20), and *trans*-2-hexene (32)
Tolan	325	11	*cis*-Diphenylethylene (44), *trans*-diphenylethylene (traces), and 1,2-diphenylethane (66)
Styrene	–	376	Ethylbenzene (100)
1-Hexene	–	232 5***	Hexane (44), *cis*-2-hexene (12), and *trans*-2-hexene (44)
Stilbene	–	3	1,2-Diphenylethane (14)
1,3-Pentadiene	–	600	1-Pentene (10) and 2-pentene (40)

* Reaction conditions: $m_{Pd} = 5 \times 10^{-3}$ mmol; substrate/Pd = 1800 mol/mol; $T = 30$°C; $P_{H_2} = 2$ atm; $V_{toluene} = 10$ ml.

** The product yield (%) is given in parentheses.

*** Hydrogenation of *cis*-2-hexene.

in an amorphous phase. These crystal structures are typical of polymer materials.

According to TEM data, the precipitate is a low-contrast substance (globules around 0.25 μm in diameter) in which dark spherical particles with a characteristic diameter of 2.5–7.5 nm (predominantly 5 nm) are uniformly distributed. An increased electron contrast of the dark spherical particles is indicative of a high concentration of a contrasting substance (palladium) in them, and the particle size suggests the microheterogeneous nature of the catalyst. The precipitate was examined by X-ray diffraction analysis in order to answer the question of whether the high-contrast particles are nanosized palladium particles or organopalladium clusters.

According to X-ray diffraction data, the precipitate is a combination of amorphous and crystalline phases. A phase of palladium metal was not detected in the diffraction pattern. It is well known that an increase in the dispersity of a sample results in line broadening in the X-ray diffraction pattern. This is typical of particles with sizes of 100 to 2 nm. A sample with a particle size smaller than 2 nm is amorphous to X-rays [15]. Additionally measured X-ray diffraction patterns of various palladium blacks with particle sizes of 2–5 nm exhibited narrow lines ascribed to a palladium metal phase. Based on TEM and X-ray diffraction data, we believe that the high-contrast particles are palladium clusters with organophosphorus ligands like $Pd_x(PPh_2)_y(PPh_3)_z$, where $x > y + z$.

The diffraction pattern of the crystalline phase exhibits reflections at small diffraction angles ($2\theta = 10°–30°$). This fact is consistent with the idea of the formation of polymer compounds in the system. Because the structure of fibrous materials is much less ordered than the structure of an ordinary crystal, the intensities of reflections rapidly decrease as the scattering angle increases, and the diffraction pattern exhibits reflections only in the initial region of diffraction angles [15]. As such compounds, we can suggest polynuclear complexes like $[Pd(PPh_2)]_n$ formed in the reactions

$$Pd(PPh_3) = Pd(Ph)(PPh_2),$$

$$nPd(Ph)(PPh_2) + 0.5nH_2 = [Pd(PPh_2)]_n + nC_6H_6.$$

Thus, the microheterogeneous catalyst obtained in an inert atmosphere (this catalyst exhibits low hydrogenation activity) consists of a polymer matrix like $[Pd(PPh_2)]_n$ in which the palladium clusters with organophosphorus ligands $Pd_x(PPh_2)_y(PPh_3)_z$, where $x > y + z$, are uniformly distributed.

The effect of catalyst activation was observed in the hydrogenation of unsaturated hydrocarbons. This effect increased the catalyst activity by more than one order of magnitude and improved the catalyst selectivity [19]. Catalyst activation and deactivation in the course of the hydrogenation of unsaturated hydrocarbons are associated with a deeper dephenylation of PPh_2 ligands in a hydrogen atmosphere. According to TEM data, deeper dephenylation resulted in the diffusion of high-contrast particles from the bulk of a globule to the surface and farther to the bulk of the reaction system followed by aggregation to a particle size of 10–25 nm.

The observed behavior can be explained as follows. The subsequent hydrogenolysis of PPh_2 ligands results in the formation of phosphinidene ligands (PPh), for which six types of bonding are known. It is likely that the ability of a PPh ligand to form bonds with three or even four metal atoms is responsible for the subsequent aggregation of palladium particles in the catalytic system and a rearrangement of this system. The absence of reflections due to a palladium metal phase from the diffraction pattern indicates that high-contrast particles also consist of palladium clusters with phosphorus-containing (phenylphosphinidene and diphenylphosphide) ligands. It is likely that a mixture of both an organopalladium polymer and an ordinary organophosphorus polymer serves as a polymer matrix.

This microheterogeneous catalyst exhibits high activity in the hydrogenation of various unsaturated compounds. Its maximum specific activity is approximately 180–200 mol of a substrate (mol Pd)$^{-1}$ min^{-1} at 30°C and a hydrogen pressure of 1 atm. Note that the fraction of active centers, which was determined by poisoning them with thriphenylphosphite, was no higher than 15% provided that 1 mol of $P(OPh)_3$ was consumed per mole of palladium [20].

Thus, the formation of hydrogenation catalysts based on palladium phosphine complexes results in microheterogeneous catalysts containing organophosphorus ligands with different degrees of substitution. In this case, it is believed that polynuclear palladium complexes with bridging diphenylphosphide and phenylphosphinidene ligands serve as a support for reduced palladium particles. In support of the hypothesis on the role of polynuclear phosphide and phosphinidene complexes of palladium, an independent synthesis of such complexes was performed by the exchange reactions of bis(acetylacetonato)palladium with corresponding alkali metal phosphides.

Catalytic Systems Based on Phosphide and Phosphinidene Complexes of Palladium

Polynuclear palladium complexes of the composition $[\{Pd(PPh_2)_3\}_n^{n-}\, n\mathrm{Na}^+]$, which were prepared by the reaction [21]

$$\mathrm{Pd(acac)_2 + NaPPh_2 \xrightarrow[-Na(acac)]{} [Pd(acac)PPh_2]_2}$$

$$\mathrm{\xrightarrow[-Na(acac)]{+NaPPh_2} [Pd(PPh_2)_2]_2}$$

$$\mathrm{\xrightarrow{+NaPPh_2} 1/\mathit{n}[\{Pd(PPh_2)_3\}_{\mathit{n}}^{\mathit{n}-}\ \mathit{n}Na^+],}$$

are inactive in the hydrogenation reaction and do not undergo dephenylation under exposure to hydrogen. Similar properties were also observed in polynuclear palladium complexes with diphenylphosphide ligands of the composition PdP_4Ph_6, prepared by the interaction of $Pd(acac)_2$ with diphenylphosphine. Note that, in contrast to tertiary phosphines, the reactions of secondary phosphines with Pd(II) compounds do not stop at the step of complexation. The ligand exchange of acetylacetonate for diphenylphosphide takes place with the formation of acetylacetone and polynuclear palladium complexes. The systems under discussion exhibited catalytic activity only after the addition of palladium acetate followed by treatment with hydrogen at 80°C in a DMF medium. In this case, at the instant palladium acetate was reduced, along with the formation of acetic acid, benzene was liberated in an equimolar amount with respect to the palladium acetate added (as detected by GLC).

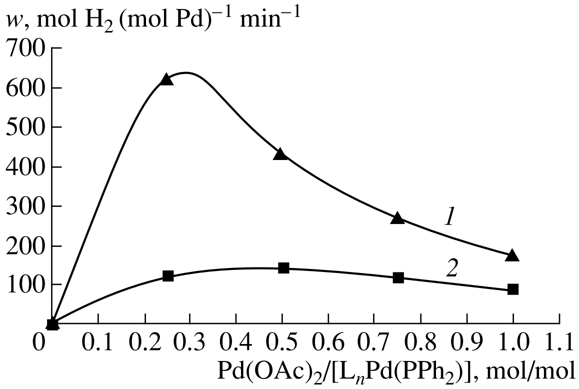


Fig. 4. Specific rate of styrene (St) hydrogenation in the presence of the catalytic system $[L_nPd(PPh_2)] + xPd(OAc)_2$ as a function of the ratio between initial components: (*1*) *w* on a $Pd(OAc)_2$ basis and (*2*) *w* on a total Pd basis. $C_{[L_nPd(PPh_2)]}$ = 1 mmol/l; T = 30°C; P_{H_2} = 2 atm; m_{St} = 9 mmol; solvent, DMF.

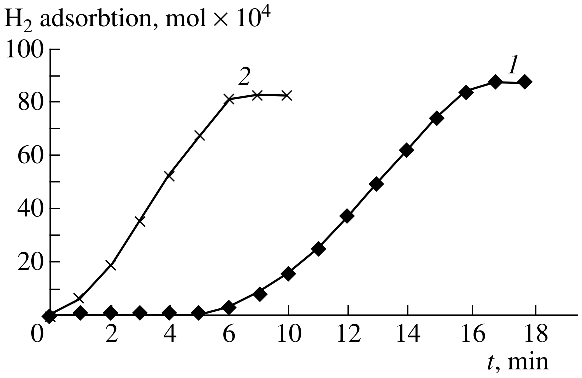
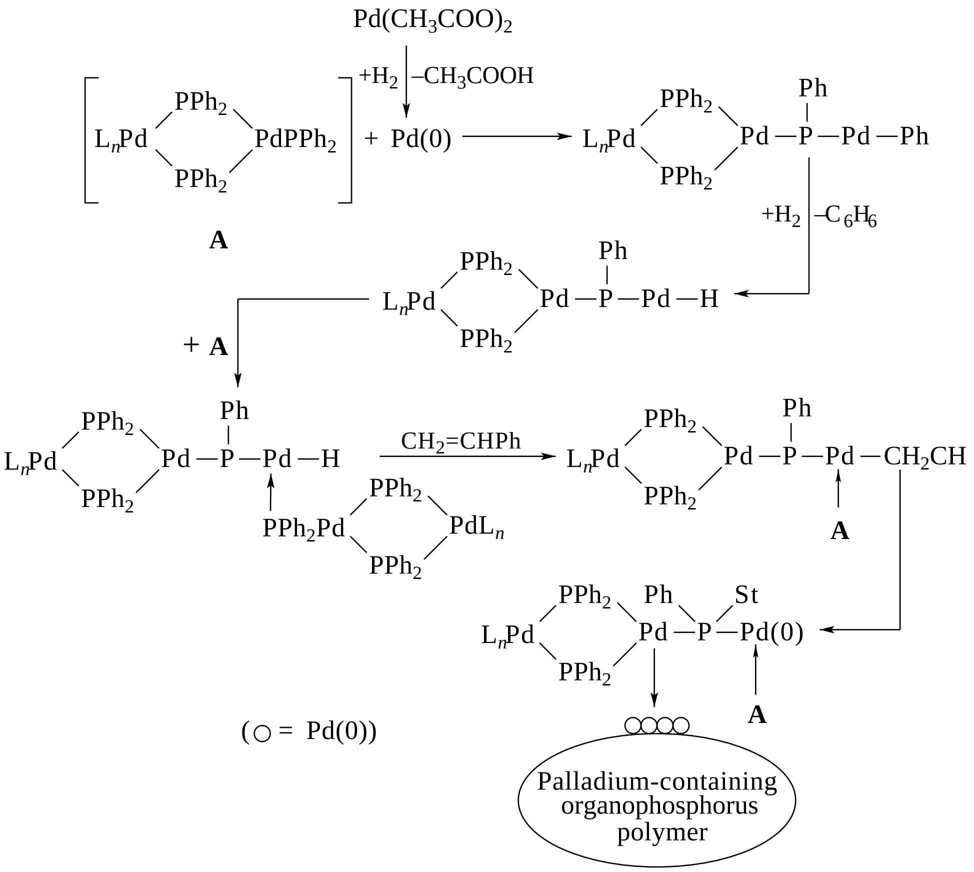


Fig. 5. Kinetic curves of styrene hydrogenation in the catalytic system $[L_nPd(PPh_2)] + xPd(OAc)_2$ at the following ratios $Pd(OAc)_2/[L_nPd(PPh_2)]$ between the initial components: (*1*) 0.25 and (*2*) 1.0. $C_{[L_nPd(PPh_2)]}$ = 1 mmol/l; T = 30°C; P_{H_2} = 2 atm; m_{St} = 9 mmol; solvent, DMF.

Polynuclear palladium complexes are completely inactive in catalytic hydrogenation, and the activity of palladium black prepared by the reduction of palladium acetate by hydrogen under identical conditions is at most 15 mol H_2 (mol Pd)$^{-1}$ min^{-1}, whereas a $Pd(OAc)_2$-modified catalytic system is more than 40 times more active than the parent components in the hydrogenation of unsaturated bonds. The maximum activity was 622 mol H_2 (mol Pd)$^{-1}$ min^{-1} at the ratio $Pd(OAc)_2/[L_nPd(PPh_2)]$ = 0.25 ($[L_nPd(PPh_2)]$ is the symbolic notation for polynuclear palladium complexes) (Fig. 4).

The hydrogenation of styrene was accompanied by an induction period, which shortened as the ratio $Pd(OAc)_2/[L_nPd(PPh_2)]$ was increased (Fig. 5).

The induction period and the absence of the degradation of organophosphorus ligands during this period indicate that the catalytic activity appears only after the reaction of the catalyst with the styrene substrate. Because palladium is transformed from a reduced form to an oxidized species in the course of dephenylation, we believe that the induction period is associated with palladium reduction. It is well known that, in hydrophosphorylation catalyzed by platinum and palladium complexes, a coordinated olefin is inserted into M–P (for Pt and Pd) and M–H (for Pd) bonds [22]. The subsequent step of reductive elimination leads to hydrophosphorylation products and the regeneration of M(0). Based on the available data, we suggest the following mechanism for the formation of hydrogenation catalysts:



According to the above scheme, either single Pd(0) atoms can be active in hydrogenation or an active center containing an ensemble of palladium atoms $[Pd(0)]_n$ can be formed in the course of catalyst generation. The possibility of forming hydride clusters containing palladium hydrides $[Pd_xH_y]_n$ under conditions of catalytic hydrogenation should not be ruled out.

To obtain comprehensive information on the role of various palladium complexes in hydrogenation, phosphinidene complexes of palladium were prepared by the reaction of $Pd(acac)_2$ with Li_2PPh [21]. A black precipitate amorphous to X-rays, which was formed by the interaction between the initial components, corresponds to the molecular formula $[Pd_4(PPh)_3]_n$. A higher palladium content can be due to the reduction of a portion of $Pd(acac)_2$ by intermediates formed in the reaction system in the course of the main reaction that affords phosphinidene complexes. It is likely that phosphines formed in the reaction of Li_2PPh with water, which is present as an impurity, play the role of a reducing agent.

Thus, in this case, reduced palladium particles are formed at the stage of the synthesis of phosphinidene complexes. This precipitate is characterized by low solubility even in polar solvents (DMF and DMSO). A nonlinear increase in the rate of the hydrogenation of unsaturated hydrocarbons with catalyst concentration is indirect evidence for the association of complexes. Table 4 summarizes data on the specific activity at an optimum concentration of the catalyst.

In contrast to phosphide and phosphinidene complexes of palladium, imide and amide complexes of palladium prepared by the interaction of $Pd(acac)_2$ with LiNHPh (Li_2NPh) are unstable in a hydrogen atmo-

Table 4. Catalytic activity of the complex $[Pd_4(PPh)_3]_n$ in the hydrogenation of unsaturated bonds*

Substrate	Turnover frequency, min^{-1}		Product** (product yield, %)
	–C≡C–	–C=C–	
Phenylacetylene	144	82	Ethylbenzene (100)
Tolan	129	36	*cis*-Stilbene (47.2); *trans*-stilbene (9.04); and diphenylethane (43.56)
Styrene	–	260	Ethylbenzene (100)
1-Hexene	–	228	Hexane (92.50) and
		31**	*trans*-2-hexene (6.80)
		8***	
Ethyl *p*-nitrobenzoate		1.8****	Ethyl *p*-aminobenzoate

* Reaction conditions: $C_{Pd} = 1.5 \times 10^{-4}$ mol/l; solvent, DMF; P_{H_2} = 1 atm; T = 30°C.

** Hydrogenation of *cis*-2-hexene.

*** Hydrogenation of *trans*-2-hexene.

**** Reduction of the nitro group.

sphere and undergo reduction to form palladium black. According to X-ray diffraction data, the coherent-scattering region for the palladium black particles is 53 Å.

The results of this study suggest that the palladium atom (or palladium hydride) ensembles immobilized on palladium-containing organophosphorus polymers are responsible for the catalytic activity in the microheterogeneous catalysts under consideration.

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