

Highly active and selective catalysts of hydrogenation based on palladium bis-acetylacetonate and phenylphosphine

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Abstract

Catalytic properties of the hydrogenation system based on palladium bis-acetylacetonate and phenylphosphine have been studied. Promoting effect of phenylphosphine with low ratio P/Pd has been found. Interaction between phenylphosphine and Pd(acac)₂ in hydrogen atmosphere leads to the formation of Pd₆P and associates of palladium polynuclear complexes with organophosphorous ligand, on which Pd(0) clusters are immobilized.

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1. Introduction

Unique capability of transition metals to catalyze the hydrogenation of unsaturated organic molecule by hydrogen is useful in many industrial processes [1,2]. Among VIII group of transition metals the palladium-based catalysts for hydrogenation are of special interest [1–17]. The modification of palladium by nitrogen-containing bases (quinoline, ethylenediamine, pyridine), as well as alkaloids allows preparing of highly selective catalysts for alkyne and conjugated diene hydrogenation [1–3], chemoselective hydrogenation of unsaturated aldehydes and ketones [7,8], enantioselective hydrogenation of α,β -unsaturated acid derivatives, etc. [2,3,9,10]. Along with studies of the Pd supported heterogeneous catalysts as well as developing chemistry of Pd nanoclusters [5,6,11,12], determination of mechanistic formation and activity nature of Pd complex catalysts with phosphine ligands is in progress [13–17]. The nanoscale particle formation has been found to be under reductive catalysis conditions. The nanoscale particle nature depends on P/Pd ratio, a reductant, and a solvent [13,16]. While the modifying effect of

the tertiary [13–17] and secondary phosphines [16] on the properties of palladium complex catalysts in hydrogenation has been examined in details, the primary phosphines are not used in this process up to now. However, these systems are quite interesting due to their ability to be both Lewis bases and Brønsted acids. Besides, they possess reductive properties like other tricoordinative phosphatic compounds. In the presented work, we report on the promoting effect of phenylphosphine in the course of formation of microheterogeneous hydrogenation catalysts on the base of Pd(acac)₂.

2. Experimental

2.1. Materials

All solvents and reagents were of analytical or chemical grades. Benzene, DMF and unsaturated substrates were purified by standard methods [18]. A procedure [19] has been used for preparation of palladium bis-acetylacetonate. Phenylphosphine synthesis was performed by interaction of phenylchlorinephosphine with LiAlH₄ [20]. A fraction with 38 °C/5 mmHg, was collected during vacuum distillation (³¹P NMR: $\delta = -122$ ppm, $J_{P-H} = 200$ Hz). It was preserved in a soldered ampoule under argon atmosphere.

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2.2. Interaction of palladium bis-acetylacetonate with phenylphosphine

A reaction between $\text{Pd}(\text{acac})_2$ and PH_2Ph at different reagent ratios was carried out in the atmosphere of a dry and oxygen-free argon in a special finger-shape vessel whose construction makes it possible to evacuate and then fill it with argon. A solution of PH_2Ph (5 ml, 1.6 mmol) was added by drops from a Schlenk vessel to a solution of $\text{Pd}(\text{acac})_2$ (0.4566 g, 1.5 mmol) in 45 ml of benzene, and the mixture was stirred at room temperature for a daytime. In 2–3 min after the reaction began, the brick-red precipitate was formed. A filtrate was analyzed in definite time intervals by IR and UV spectroscopy. When the reaction ended, the precipitate was filtered off using Schott filter in the atmosphere of argon, washed with benzene, ether, and dried in vacuum (20 °C/1 mmHg). The product yield was 0.218 g. Found (%): Pd, 30.40; C, 41.90; H, 3.77; P, 14.84.

2.3. Catalyst preparation

Five milliliters phosphine solution (P/Pd=0.3) was added to the solution of 0.6088 g (2×10^{-3} mol) $\text{Pd}(\text{acac})_2$ in 80 ml DMF in a glass thermostatically controlled vessel filled by hydrogen. A yellow–citrine reaction mixture was stirred under hydrogen pressure 1 atm at 80 °C during 15 min. After 1–2 min a change of color to black-brown occurred. After the completion of reaction (15 min) a black suspension was cooled to room temperature, solvent was distilled off (2/3 from volume) and ether was added to form a residue. The residue was washed by ether under an argon atmosphere and dried up in vacuum (50 °C/1 mmHg). The product yield was 0.147 g (62%). Elemental analysis of black deposit: Pd, 89.83%; P, 3.23%; C, 2.31%; H, 0.35%. The similar procedures were performed at other P/Pd.

Monitoring over catalyst forming process was performed by UV spectroscopy and GLC. For this purpose the samples have been taken at fixed intervals. The $\text{Pd}(\text{acac})_2$ concentration was calculated relative to 330 nm absorption band ($\epsilon_{330} = 10,630 \text{ l cm}^{-1} \text{ mol}^{-1}$), acetylacetonate—relative to 290 nm (for HAcac $\epsilon = 5000 \text{ l cm}^{-1} \text{ mol}^{-1}$, for $\text{Pd}(\text{acac})_2$ $\epsilon = 3090 \text{ l cm}^{-1} \text{ mol}^{-1}$). Acetylacetonate and benzene were analyzed by GLC after a precursory recondensation of the solution using a vacuum setup (20 °C/1 $\times 10^{-3}$ mmHg). Gas-liquid chromatograms were recorded by “Chrom-5” chromatograph (column 3.6 m, packing phase, SE-30, DIP flame ionization detector, 100 °C, nitrogen as a carrier gas). The error of acetylacetonate and benzene determination was not more than 10%.

2.4. Instruments

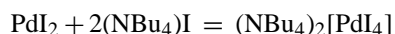
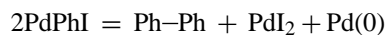
IR spectra were recorded by Specord 75IR spectrometer (the spectra of sample solutions in benzene were recorded in

KRS cell (0.2 mm thickness)) that was preliminarily blown through with argon (with essential oil mulls). UV spectra were recorded by Specord UV–Vis spectrometer in a sealed cell. NMR spectra were measured on a VXR-500S Varian impulse spectrometer. The ^{31}P chemical shifts were referenced to 85% H_3PO_4 . The positive values correspond to the downfield shift. Before analyzing the samples by NMR spectroscopy, a solution was placed and sealed in a tube that was preliminarily evacuated and filled with argon. Analysis of the catalyst samples by X-ray powder diffraction was performed on a DRON-3M diffractometer ($\text{Cu K}\alpha$ radiation).

Transmission electron microscopic (TEM) studies of the catalysts were performed on BS-300 electron microscopes (Czech Republic). A drop of the solution was poured on a grid holder covered with the carbon film followed by drying in an argon atmosphere. TEM studies of catalysts were performed under minimal current of the electron beam to minimize specimen heating (accelerating voltage 80 kV).

2.5. Procedure of Pd(0) analysis [21]

A solution containing 2×10^{-5} mol Pd in 10 ml DMF was placed in a preliminarily evacuated flask filled with argon and kept at a constant temperature and 0.1477 g (0.4 mmol) NBu_4I and 0.109 ml (1 mmol) of iodobenzene were added. The reaction mixture was stirred with a magnetic stirrer at 80 °C until the constant concentration of PdI_2^{2-} -anion formed in the following reactions:



The concentration of PdI_4^{2-} was measured by spectrophotometry on a Specord UV–Vis spectrometer using an absorption band at 340 nm ($\epsilon_{340} = 23,750 \text{ l cm}^{-1} \text{ mol}^{-1}$) in an all-soldered quartz cell with the 0.1 cm thickness.

2.6. General hydrogenation procedure

Reactions were carried out at 30 °C and 1 atm hydrogen pressure with intensive stirring in a glass vessel in the presence of catalytic system formed in situ. One milliliter phosphine solution (P/Pd=0.1–2) was added to the solution of 0.0034 g (0.01 mmol) $\text{Pd}(\text{acac})_2$ in 9 ml DMF, prepared in a special glass vessel vacuum-treated and filled by hydrogen. A yellow–citrine reaction system was stirred in hydrogen atmosphere at 80 °C during 5–15 min. Obtained black-brown-colored “solution” was cooled to 30 °C, a substrate was injected by a syringe, and hydrogenized with intensive stirring to exclude reaction progression in diffusive region. The monitoring was performed by GLC and volumetrically.

Table 1
Styrene hydrogenation in the presence of Pd-black formed from Pd(acac)₂ (solvent = DMF, T = 30 °C, P_{H₂} = 1 atm, [substrate] = 8.7 × 10⁻³ mol)

Concentration of Pd(acac) ₂ ^a (× 10 ³ mol/l)	Specific activity, W (mol H ₂ /(mol Pd min) ⁻¹)		Styrene conversion (%)	
0.45	2	11 ^b	3	29 ^b
0.90	6	19 ^b	25	61 ^b
2.27	12	16 ^b	62	100 ^b
4.54	9	12 ^b	100	100 ^b

^a Pd(acac)₂ hydrogenation was performed at 80 °C.

^b Pd(acac)₂ reduction was performed with water addition (1%) to solvent.

3. Results and discussions

3.1. Catalytic hydrogenation

As shown earlier, palladium bis-acetylacetonate as well as palladium acetate [22] is not reduced by hydrogen in aprotic solvents (benzene, toluene) at a temperature below 80 °C in a nonaqueous medium. The role of water was found to destroy the oligomeric [Pd(acac)₂]_n structure, preserved on dissolving in benzene and to promote heterolytic splitting of hydrogen molecule. The hydrogenolysis of Pd(acac)₂ in DMF proceeds under milder conditions; however at 30 °C the reaction is over in 40 min, while at 80 °C the reduction time decreases to 5–15 min, depending on concentration.

The maximal specific activity of Pd black is no more than 19 mol styrene mol Pd min. Fast deactivation of the catalyst in the hydrogenation is observed at the low initial Pd(acac)₂ concentration (Table 1). On addition of water to the system the Pd black activity increases as well as a degree of styrene conversion. TEM shows the presence of Pd particles with a diameter in the 7–30 nm range which are aggregating to give chainlike structures (Fig. 1).

To obtain more effective catalytic system phenylphosphine was used as a modifier. The catalytic hydrogenation of styrene in the presence of a system based on Pd(acac)₂ + nPH₂Ph (P/Pd = 0.3; 1; 2) at 30 °C in DMF is characterized by a long inductive period (40 min) and a low reaction rate. The most active hydrogenation catalyst is formed after precursory interplay of the components of Pd(acac)₂ + nPH₂Ph system with hydrogen in DMF at 80 °C during 5–15 min. The effect of phenylphosphine is ultimate when P:Pd = 0.3 (Fig. 2).

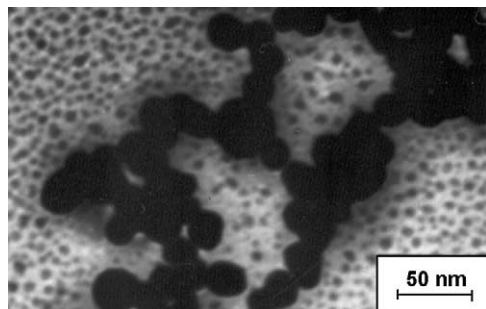


Fig. 1. TEM image of the Pd-black.

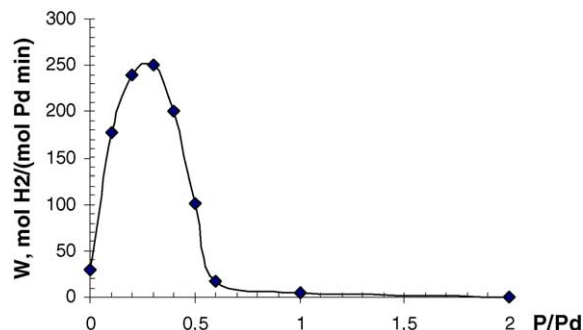


Fig. 2. Hydrogenation of styrene in the presence of Pd(acac)₂ + nPH₂Ph catalytic system: C_{Pd} = 0.9 × 10⁻³ mol/l, solvent = DMF, T = 30 °C, P_{H₂} = 1 atm, [substrate]/[Pd] = 870.

The specific activity of Pd(acac)₂ + 0.3PH₂Ph remains unchanged during hydrogenation of not less than 3000 mol styrene per mole of Pd, then catalyst deactivation occurs gradually, accompanied with precipitation. The reaction rate depends nonlinearly on catalyst concentration over the range from 0.5 to 2.0 mmol/l and attains plateau when C_{Pd} = 1 mmol/l (Fig. 3).

The high specific activity and selectivity of the system is observed in hydrogenation of other unsaturated hydrocarbons, carbonyl and nitro groups (Table 2).

Benzaldehyde reduction in the presence of Pd catalysts (Pd/C) is usually accompanied with hydrogenolysis of C=O bond in formed benzyl alcohol, and rates of the two reactions are comparable with one another [2], while the selectivity of the Pd(acac)₂ + 0.3PH₂Ph system in benzaldehyde hydrogenation attains 95%. Nitrobenzene is usually selectively reduced to aniline over the Pd/C catalyst. The advantage of our catalyst is connected with a high reaction rate. The specific activity of this catalyst in nitro group reduction exceeds that of nanoscale particles immobilized on the styrene and divinylbenzene copolymer by a factor of 3.5 [23]. But, this catalyst activity is second to earlier studied palladium catalyst with diphenylphosphine [16]. Activity of Pd(acac)₂ + 0.3PH₂Ph-based catalyst can be increased when it is formed in the presence of an activated carbon (“Sibunite”, with specific surface 450 m²/g). Productivity of (Pd(acac)₂ + 0.3PH₂Ph)/C system in styrene hydrogenation attains 11,300 mol substrate per mol

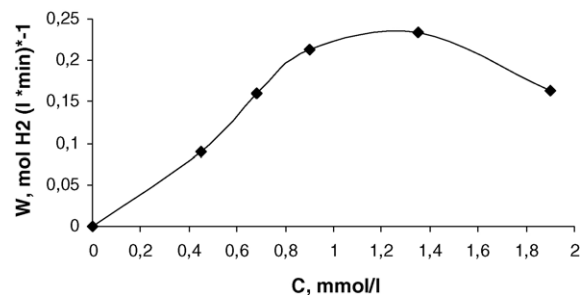


Fig. 3. Rate of styrene hydrogenation vs. Pd(acac)₂ concentration in the presence of Pd(acac)₂ + 0.3PH₂Ph catalytic system: solvent = DMF, T = 30 °C, P_{H₂} = 1 atm, [substrate] = 8.70 × 10⁻³ mol.

Table 2

Hydrogenation in the presence of Pd(acac)₂ + 0.3PH₂Ph system C_{Pd} = 0.9 × 10⁻³ mol/l, solvent = DMF, T = 30 °C, P_{H₂} = 1 atm, [substrate]/[Pd] = 870

Substrate	Specific activity, W (mol H ₂ (mol Pd min) ⁻¹)	Conversion (%)	Products (%)
PhC≡CH	104 (–C≡C–), 112 (–C=C–)	100	Ethyl benzene (85), styrene (15)
PhC≡CPh	113 (–C≡C–), 21 (–C=C–)	100	Diphenyl ethane (69), <i>cis</i> -stilbene (24), <i>trans</i> -stilbene (7)
PhCH=CH ₂	260	100	Ethyl benzene (100)
PhC(O)H [*]	10	70	Benzyl alcohol (92), toluene (8)
PhNO ₂ [*]	48	97	Aniline (100)

^{*}C_{Pd} = 5 × 10⁻³ mol/l. The prime effectiveness of benzaldehyde and nitrobenzene hydrogenation catalytic system has been observed at 5 × 10⁻³ mol/l concentration.

Pd (Fig. 4). The catalytic specific activity does not change during hydrogenation of 5200 mol styrene.

3.2. Formation of hydrogenation catalyst

Pd(acac)₂ + nPH₂Ph

To obtain information on the nature of the Pd active forms the interaction between Pd(acac)₂ and phenylphosphine in both the inert atmosphere and hydrogen has been studied.

On addition of phenylphosphine to Pd(acac)₂ in benzene (P/Pd = 0.5, 1, 1.5, 2.0) the yellow color of the solution changes to orange and the solution muddiness is observed. IR spectra of the Pd(acac)₂ + nPH₂Ph exhibits absorption bands at 1560 and 1516 cm⁻¹ with lower intensities; the appearance and an increase of absorption band intensity at 1620 and 1706 cm⁻¹ are also observed. The absorption bands at 1560 and 1516 cm⁻¹ correspond to the stretching vibrations of ν(C=O) and ν(C=C) in O,O-chelate acetylacetonate ligands; absorption bands at 1620 and 1706 cm⁻¹ correspond to the stretching vibrations of ν(C=O) of the enol and keto form of acetylacetonate, respectively [24].

UV spectrum of the Pd(acac)₂ + nPH₂Ph system exhibits the reduction of the band intensity at 330 nm (due to electron transitions in palladium complexes with O,O-chelated acac⁻ ligands). IR and UV spectroscopy data indicate that reaction between Pd(acac)₂ and phenylphosphine at room temperature is over in 3–5 min (Table 3).

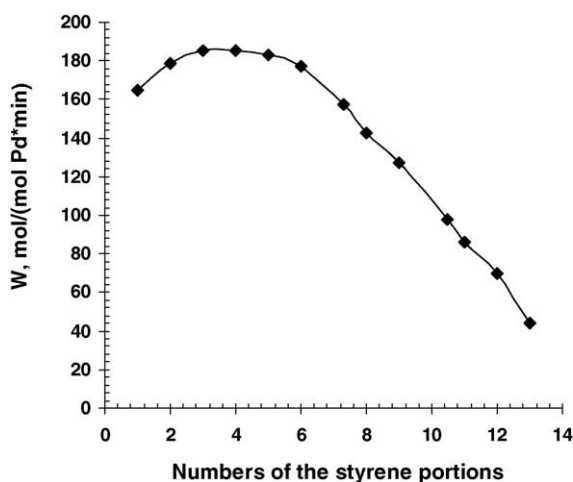
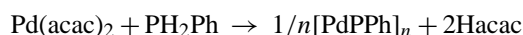


Fig. 4. Hydrogenation of styrene in the presence of Pd(acac)₂ + 0.3PH₂Ph/C catalytic system: C_{Pd} = 0.9 × 10⁻³ mol/l, solvent = DMF, T = 30 °C, P_{H₂} = 1 atm. In one styrene portion is 8.70 × 10⁻³ mol.

It is known that primary phosphines exhibit both alkaline and acidic properties [4]. The acidic properties of phosphine are amplified by a coordination to metal ion that makes possible a proton elimination from phosphine. At first sight one might assume that a quantitative exchange of acidoligands for PPh occurs due to interplay between equimolecular quantities of Pd and PH₂Ph:



However, quantitative analysis of IR and UV spectra of the solutions and GLC data indicate that at PH₂Ph/Pd(acac)₂ = 0.5:1, from 20 to 25% of the acac⁻ ligands are converted to acetylacetonate (see Table 3). With equimolar reagent ratio, one half the acac-ligands is converted to acetylacetonate, while the second half remains as the chelated acetylacetonate ligands.

The ³¹P NMR monitoring of the reaction system Pd(acac)₂ + nPH₂Ph in benzene does not reveal intermediates and reaction products, except the small quantities of phosphine oxide (δ = 16 ppm (d) ¹J_{P–H} = 560 Hz); a signal from starting phenylphosphine (δ = –122 ppm (t), ¹J_{P–H} = 200 Hz) is not detected as well. This fact is indicative of palladium complexes with organophosphorous ligands are in colloido-dispersion state.

The analogical quantitative trends were obtained when process of the interaction was performed in DMF (Table 4).

Two of substances were isolated from the Pd(acac)₂ + nPH₂Ph (P:Pd = 1) system, i.e. unreacted Pd(acac)₂ (30% of the starting reagent) and reaction product (the precipitate of brick-orange color), marked “sample I”. The presence of

Table 3

Quantitative parameter of reaction between Pd(acac)₂ and PH₂Ph in benzene (IR, UV, and GLC data)

PH ₂ Ph/ Pd(acac) ₂	Reaction time	Concentration of Pd(acac) ₂ (%)		Concentration of Hacac (%)		
		IR ^a	UV ^a	IR ^a	UV ^a	GLC ^b
0.5	5 min	74	77	25	20	
0.5	1 h	76	77	21	23	
0.5	24 h	76	80	22	28	19
1	5 min	43	48	52	54	
1	24 h	42	49	55	52	56
2	5 min	–	–	94	96	
2	24 h	–	–	94	95	102

^a The determination error is 10%.

^b The acetylacetonate concentration was determined by GLC for every reagent ratio only after the reaction was over and after preliminary distillation in vacuum.

Table 4
Quantitative parameter of reaction between Pd(acac)₂ and PH₂Ph in DMF

PH ₂ Ph/ Pd(acac) ₂	Reaction time (min)	Concentration of Pd(acac) ₂ (%)	Concentration of Hacac (%)
0.3	5	89	8
0.5	5	79	24
1.0	5	57	43

unreacted palladium bis-acetylacetonate points to the fact that the intermediate complexes are more reactive than the starting Pd(acac)₂ and more rapidly react with phenylphosphine.

IR spectrum (in vaseline oil) of sample I contains the absorption band at 2280 cm⁻¹ due to the stretching vibrations of the P–H bond [25], the bands at 1583 and 1516 cm⁻¹ produced by the stretching vibrations of ν(C=O) and ν(C=C) in the O,O-chelated acetylacetonate ligand, the absorption bands at 720, 680, and 450 cm⁻¹ from off-plane deformation vibrations of the C–H and C–C bonds in a monosubstituted benzene ring.

The sample I is X-ray amorphous substance with a diffuse maximum (halo) at d/n 13.556 Å; the coherent scattering range being equal to ≈2.7 nm. The appearance of halo on the diffraction curve in the initial range of the diffraction angles (2θ = 5–40°) is evidence for a low-ordered structure and the formation of oligomers. On dissolving of the sample I in DMF, a colloidal solution is formed, in which the average particle size of dispersive phase is 3 nm (TEM data) (Fig. 5). The elemental analysis gives the empirical formula Pd₁P_{1.7}C₁₂H₁₃.

IR and elemental analysis data show that the sample I contains the O,O-chelated acetylacetonate and organophosphorous ligands. It is unknown, which are these organophosphorous ligands: either coordinated PH₂Ph and the bridging phenylphosphinidene (PPh) ligands, or phenylphosphide ligands (PHPh) or their combination.

To answer this question the following experiment was performed. Triphenylphosphine was added into the Pd(acac)₂ solution before introduction of phenylphosphine (PPh₃/Pd(acac)₂ = 0.75, PH₂Ph/Pd(acac)₂ = 1). In this case, the amount of acetylacetonate formed increases and reaches 100%. Triphenylphosphine is the Lewis base that is more

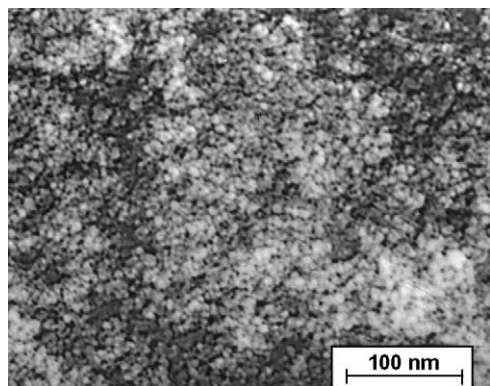
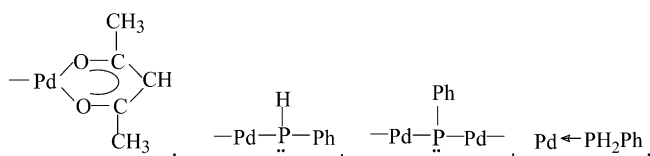


Fig. 5. TEM image of the system Pd(acac)₂ + PH₂Ph (sample I).

stronger than phenylphosphine and must be able to replace acetylacetonate from the coordination sphere of palladium in the intermediates or reaction products. This favors more profound exchange of the acac⁻ ligands.

After a sufficiently long build up time (12 h), the ³¹P NMR spectrum of system Pd(acac)₂ + PPh₃ + PH₂Ph shows a broad resonance signal in the range from 0 to 45 ppm that can be assigned to both PPh₃ coordinated to different palladium atoms and the bridging organophosphorous ligands in the complexes containing no metal–metal bond (Fig. 6) [26].

The results obtained give indirect evidence that the sample I contains molecules of the coordinated phenylphosphine. So, the associates of palladium polynuclear complexes are formed as a result of the interaction between phenylphosphine and Pd(acac)₂. According to the elemental data, three Pd atoms fall on something like one acac⁻ and five organophosphorous ligands. Thus, the sample I includes following types of fragments:



which are bound by the covalent and donor–acceptor bonds between Pd and PPh, PHPh ligands.

In our opinion, the change of P/Pd basically influences the relationship between unreacted Pd(acac)₂ and associates of palladium polynuclear complexes, which are present in the system at P/Pd < 2. At the ratio PH₂Ph/Pd(acac)₂ > 2 the quantitative conversion of acac⁻ ligands into Hacac is attained; ³¹P NMR reveals a free phenylphosphine along with Pd polynuclear complexes in the reaction system.

When catalytic system Pd(acac)₂ + nPH₂Ph is formed under the hydrogen atmosphere (T = 80 °C, P_{H₂} = 1 atm) the orange color of the solution changes to black-brown within 5 min after the reaction beginning. UV spectroscopy and GLC data show additional formation of acetylacetonate, the total amount of which has reached near 100% (Table 5). It indicates that both Pd(acac)₂ and acetylacetonate Pd-bonded ligands in the polynuclear complexes undergo hydrogenolysis to afford Hacac. In the interaction with hydrogen, benzene was found along with acetylacetonate by GLC. The amount of

Table 5
Transformation of the system Pd(acac)₂ + nPH₂Ph in hydrogen T = 80 °C, solvent = DMF, C_{Pd} = 5 × 10⁻³ mol/l

PH ₂ Ph/ Pd(acac) ₂	Reaction time (min)	Concentration of Pd(acac) ₂ (%)	Concentration of Hacac (%)	C ₆ H ₆ /P H ₂ Ph
0.3	5	2	99	0.26
0.3	15	0	98	0.50
0.3	40	0	99	0.51
0.5	15	12	87	0.46
0.5	40	0	93	0.45
1.0	15	24	79	0.13
1.0	40	12	83	0.19
1.0	60	—	113	0.20

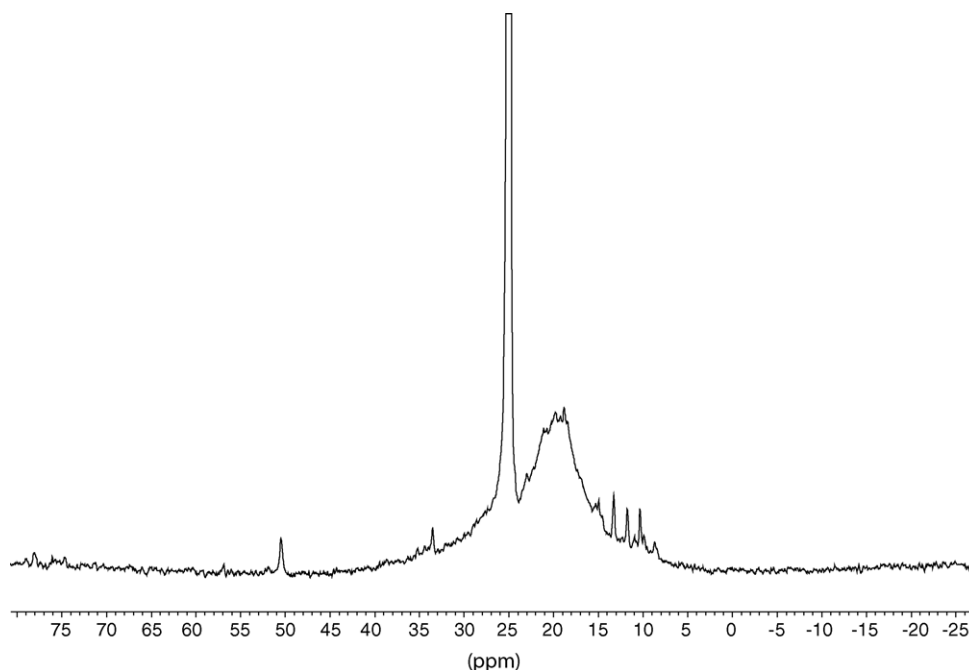


Fig. 6. The ^{31}P NMR spectrum of the system $\text{Pd}(\text{acac})_2 + 0.75\text{PPh}_3 + \text{PH}_2\text{Ph}$ in benzene (with $\text{P}(\text{O})\text{Ph}_3$ as the external standard, $\delta = 25$ ppm).

benzene formed per phosphine mole was increasing as ratio P/Pd decreased (Table 5). Similar dependence was observed with triphenylphosphine [27]. The benzene formation was associated with dephenylation of the organophosphorous ligands, destruction of which was found earlier under reductive conditions [13–16].

As the most effective catalytic system was found to be when P/Pd = 0.3, all further experiments were carried out with this ratio.

The TEM data point to the presence of highly contrast particles in black-brown solution formed after a hydrogen treatment of $\text{Pd}(\text{acac})_2 + 0.3\text{PH}_2\text{Ph}$ system (Fig. 7). The average diameter of these particles is 5 nm. The black residue (marked sample 2) has been isolated from the reaction system; elemental analysis of the sample 2 corresponds to the gross formula $\text{Pd}_8\text{P}_1\text{C}_3\text{H}_5$; a content of Pd(0) determined by chemical method does not exceed 30%. X-ray diffraction analysis exhibits more broad diffraction maximum on diffrac-

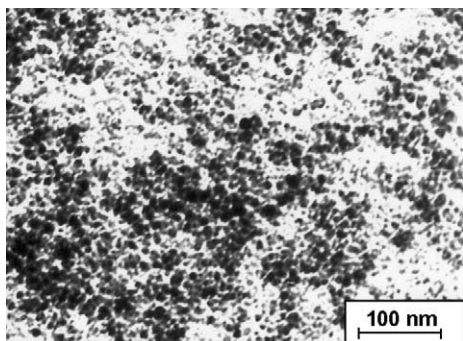


Fig. 7. TEM image of the system $\text{Pd}(\text{acac})_2 + 0.3\text{PH}_2\text{Ph} + \text{H}_2$.

tion curve (d/n 2.249, 1.941, 1.378 Å) which can be pertained to highly dispersive Pd. A coherent scattering range calculated with respect to Pd line hkl 1 1 1, using Scherrer formula, is 2 nm. The absence of amorphous halo on the diffraction curve of the sample 2 in the starting range of diffraction angles ($2\theta = 5\text{--}40^\circ$) testifies that the destruction of Pd polynuclear complexes after a hydrogen treatment of the catalytic system occurs.

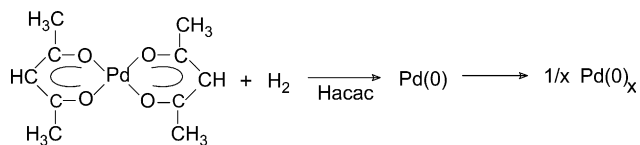
Further heating of the sample 2 at 400°C under an argon atmosphere during 4 h leads to catalyst transformation into crystalline state. Along with low-power reflexes from crystalline Pd, reflexes at d/n 2.563, 2.365, 2.255, 2.223, 2.035 Å pertained to palladium phosphide (Pd_6P) were registered.

The represented data allow a conclusion that sample 2 is not an individual substance but an indivisible mixture which consists of Pd(0), Pd_6P and palladium phosphinidene complexes. It is known, that PR ligand is able to form bonds with two, three and even four metal atoms [28]. Taking into account this fact the averaged composition of sample 2 can be given by different hypothetical formulae: $[\{\text{Pd}(\text{O})\}_4\{\text{Pd}_6\text{P}\}_{0.5}\{\text{Pd}_2\text{PPh}\}_{0.5}]$ (I), $[\{\text{Pd}(\text{O})\}_{3.5}\{\text{Pd}_6\text{P}\}_{0.5}\{\text{Pd}_3\text{PPh}\}_{0.5}]$ (II); $[\{\text{Pd}(\text{O})\}_3\{\text{Pd}_6\text{P}\}_{0.5}\{\text{Pd}_4\text{PPh}\}_{0.5}]$ (III). The formula III corresponds best to both elemental analysis of sample 2 and to the Pd(0) content in it. Noteworthy, that a Pd part in the formal zeroth oxidation extent and connected with organophosphorous ligands is not probably determined by this method. The hydrogen excess in the sample 2 might be present due to hemisorption of hydrogen by Pd.

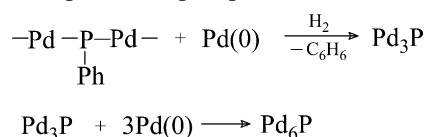
The data above allow us to conceive the formation of catalytic system as follows.

The interaction of bis-acetylacetonate with phenylphosphine leads to the change of acac^- ligands for PPh and

PHPh fragments to give associates of palladium polynuclear complexes. The part of Pd(acac)₂ remains in solution when P/Pd < 2. Unreacted Pd(acac)₂ is reduced by hydrogen at 80 °C in DMF to Pd(0):



Taking into account the fact established earlier that destruction of organophosphorous ligands proceeds in Pd(0) coordinative sphere [16], one can assume two ways of palladium atom conversion: aggregation to one another to afford palladium clusters; interaction with palladium polynuclear complexes. Oxidative addition of PPh ligands to Pd(0) followed by hydrogenolysis of Pd–C bond lead to the formation of benzene and palladium phosphides:



The associates of palladium polynuclear complexes and palladium phosphide act as a carrier for a Pd(0) cluster. Redistribution between Pd(0) and Pd complexes with containing phosphorus ligands in favor of the latter occurs, when P/Pd ratio is higher; it gives rise to lowering of the catalytic system activity.

4. Conclusions

A new highly active catalyst for hydrogenation of unsaturated bonds, carbonyl and nitro groups based on Pd bis-acetylacetonate and phenylphosphine has been suggested. The conversion of Pd(acac)₂ + nPH₂Ph in hydrogen leads to the formation of nanoscale particles containing Pd(0), Pd phosphide and Pd phosphinidene complexes. The associates of Pd phosphinidene complexes and Pd phosphide act as the carrier for a Pd cluster.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molcata.2004.12.023](https://doi.org/10.1016/j.molcata.2004.12.023).

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