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Formation and Properties of Hydrogenation Catalysts Based on Palladium Complexes with Primary Phosphines

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Abstract—The formation and catalytic properties of hydrogenation catalysts based on palladium(II) complexes with primary phosphines were studied. With the use of IR and UV spectroscopy, XRD analysis and GLC, it was found that the interaction of bis(acetylacetonato)palladium(II) or palladium(II) acetate with primary phosphines in an inert atmosphere resulted in the formation of polynuclear palladium complex associates mainly containing μ^3-PR and a coordinated phosphine. Polynuclear palladium complexes and the palladium phosphide Pd_6P, which is formed from these complexes in an atmosphere of hydrogen, serve as supports for Pd(0) clusters. The effects of the ratio between initial components and the nature of the acido ligand at the palladium atom on the optimum conditions of catalyst formation were considered.

INTRODUCTION

Phosphine complexes of palladium are widely used as catalyst precursors for various organic synthesis reactions, including the reduction of unsaturated hydrocarbons [1–5]. The formation and nature of active species in microheterogeneous hydrogenation catalysts are based on palladium complexes with ternary [1–4] and secondary phosphines [5]. Previously [5], two models of nanosized palladium catalysis were proposed. The first model implies a nucleus formed by palladium atoms and stabilized with phosphine and phosphite ligands. The second model implies a nucleus of the associates of polynuclear palladium complexes with diphenylphosphide and (or) phenylphosphinidene ligands at the surface of which Pd(0) clusters are immobilized. These models correspond to two limiting cases. Nanosized particles of either of the two types can coexist in a real catalytic system because of the degradation of organophosphorus ligands.

Previously, primary phosphines were not used in the formation of complex palladium catalysts for hydrogenation. Interest in these systems is due to the fact that primary phosphines combine the properties of Lewis bases and Brønsted acids. Moreover, they are reducing agents, like other three-coordinated phosphorus-containing compounds.

In this work, the results of a study on the interactions of bis(acetylacetonato)palladium ($Pd(Acac)_2$) and palladium acetate ($Pd(OAc)_2$) with primary phosphines and the formation of microheterogeneous hydrogenation catalysts on this basis are presented.

EXPERIMENTAL

The solvents were purified in accordance with standard procedures used in operations with organometallic compounds [6]. For deeper drying, benzene was additionally distilled from $LiAlH_4$ on a rectification column and kept in sealed ampules in an argon atmosphere. Bis(acetylacetonato)palladium was prepared in accordance with a published procedure [7]. Phenylphosphine was synthesized by the interaction of phenyldichlorophosphine with $LiAlH_4$ [8]. In vacuum distillation, a fraction boiling at 38°C (5 Torr) was collected (^{31}P NMR: $\delta = -122$ ppm; $^1J_{P-H} = 200$ Hz) and kept in a sealed ampule in an argon atmosphere. Octylphosphine was synthesized in accordance with a published procedure [9, 10].

The reactions between palladium salts and primary phosphines at various ratios between the initial components were performed in an oxygen-free dry argon atmosphere in a special vessel, which can be preevacuated and filled with an inert gas. The course of the reaction was monitored using IR, UV, and NMR spectroscopy and gas–liquid chromatography (GLC).

The IR spectra in the region 4000–400 cm^{-1} were measured on a Specord 75 IR spectrometer in cells with KRS windows 0.2 mm in thickness. The concentrations of acetylacetonate ligands bound to palladium and acetylacetone (AcacH) were determined from the intensities of absorption bands at 1580 and 1620 cm^{-1}, respectively. The concentrations of $Pd(OAc)_2$ and CH_3COOH were calculated from the intensities of absorption bands at 1608 and 1712 cm^{-1}, respectively.

The UV spectra were measured on a Specord UV–VIS spectrometer in a welded cell. The concentrations of $Pd(Acac)_2$ and Hacac were calculated from absorption bands at 330 and 290 nm, respectively ($Pd(Acac)_2$

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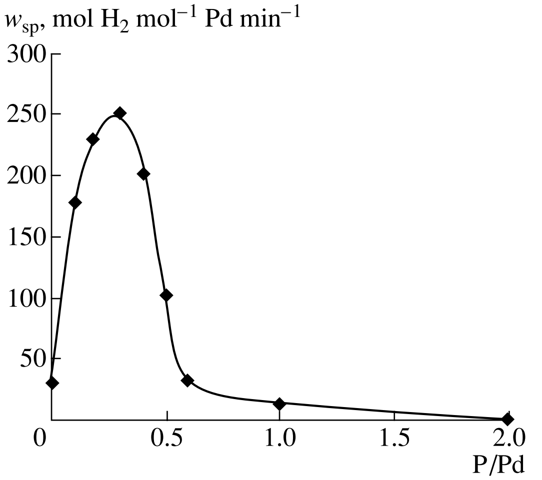


Fig. 1. Styrene hydrogenation in the presence of the $Pd(Acac)_2$ + nPH_2Ph catalytic system. C_{Pd} = 0.9 mmol/l; T = 30°C; P_{H_2} = 1 atm; solvent, DMF; [Substrate]/[Pd] = 870.

ε_{330} = 10 630 l mol^{-1} cm^{-1} and ε_{290} = 3090 l mol^{-1} cm^{-1} for $Pd(Acac)_2$ and ε_{290} = 5000 l mol^{-1} cm^{-1} for AcacH).

After the precondensation of solutions in a vacuum system (20°C; 1 × 10^{-3} Torr), acetylacetone and benzene were determined on a Chrom-5 chromatograph equipped with a 3.6-m packed column (SE-30 as a stationary phase) and a flame-ionization detector. The column temperature was 100°C, and nitrogen was a carrier gas. The error of GLC analysis was no higher than 10%.

The 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. In the analysis of samples by NMR spectroscopy, the test solution was sealed in a preevacuated ampule filled with argon.

The X-ray diffraction (XRD) analysis of catalyst samples was performed on a DRON-3M diffractometer (CuK_α radiation).

Experimental example. A 5-ml portion of a solution of phenylphosphine (1.6 mmol) from a Schlenk vessel was added drop by drop to a solution of 0.4566 g (1.5 mmol) of $Pd(Acac)_2$ in 45 ml of benzene, and the mixture was stirred at room temperature for 24 h. A brick-red precipitate was formed from the solution 2–3 min after the onset of reaction. The filtrate was analyzed at regular intervals by spectroscopic techniques (IR and UV spectroscopy). After completion of the reaction, the resulting precipitate was filtered off in an argon atmosphere, washed with benzene and diethyl ether, and dried in a vacuum (20°C; 1 Torr). Yield: 0.218 g. Found (%): Pd, 30.40; C, 41.90; H, 3.77; P, 14.84.

Experiments at other ratios between phenylphosphine and bis(acetylacetonato)palladium were performed in an analogous manner. The elemental analysis of the precipitate formed in the $Pd(Acac)_2$ + PH_2Ph system (P/Pd = 2) gave the following results (%): Pd, 29.70; C, 42.47; H, 3.78; P, 15.30. Yield: 0.351 g.

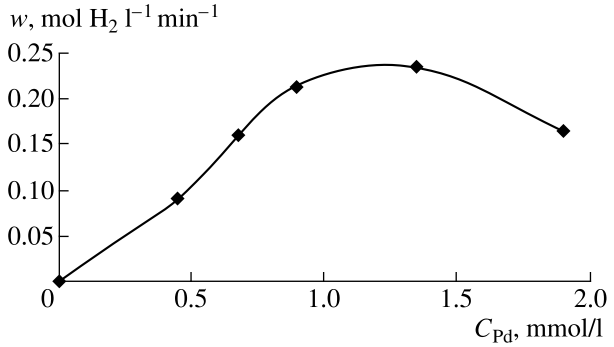


Fig. 2. Dependence of the rate of styrene hydrogenation in the presence of the $Pd(Acac)_2$ + $0.3PH_2Ph$ catalytic system on the concentration of $Pd(Acac)_2$ (C_{Pd}). Solvent, DMF; T = 30°C; P_{H_2} = 1 atm; [Substrate] = 8.7 × 10^{-3} mol.

Preparation of a catalyst based on $Pd(Acac)_2$ and PH_2Ph. A 1-ml portion of a phosphine solution was added to a solution of 0.00304 g (1 × 10^{-5} mol) of $Pd(Acac)_2$ in 9 ml of dimethylformamide (DMF) prepared in a preevacuated long-necked flask filled with hydrogen (P/Pd = 0.1–2). The lemon-yellow reaction mixture was stirred in a hydrogen atmosphere at 80°C for 5 min. The resulting blackish brown “solution” was cooled to 30°C, and a substrate was injected with a syringe. Hydrogenation was performed at an initial hydrogen pressure of 1 atm with intense stirring. The course of the reaction was monitored by volumetry and GLC. The determination procedure for Pd(0) was described elsewhere [11].

RESULTS AND DISCUSSION

The catalytic system based on $Pd(Acac)_2$ and phenylphosphine (P/Pd = 0.3, 1, or 2) was inactive in the hydrogenation of unsaturated substrates without pretreatment with hydrogen. Thus, the hydrogenation of styrene in DMF at 30°C in the presence of these catalysts was characterized by a long induction period (2 h) and a low rate of reaction. A catalyst highly active in hydrogenation (P/Pd = 0.3) was formed after a preliminary reaction with hydrogen in DMF at 80°C for 5–15 min (Fig. 1).

The specific activity remained constant in the hydrogenation of no less than 3000 mol of styrene per mole of Pd; next, the catalyst underwent gradual deactivation accompanied by precipitate formation. The rate of reaction nonlinearly increased as the catalyst concentration was increased to ~1.4 mmol/l and began to decrease at C_{Pd} > 1.4 mmol/l (Fig. 2).

The catalyst exhibited high specific activity and selectivity in the hydrogenation of other substrates (Table 1). In particular, the reduction of benzaldehyde in the presence of Pd/C was usually accompanied by

Table 1. Hydrogenation of organic compounds in the presence of the $Pd(Acac)_2 + 0.3PH_2Ph$ system

Substrate	Specific activity w_{sp}, mol H_2 (mol Pd)$^{-1}$ min^{-1}	Conversion, %	Product composition, %
$PhC{\equiv}CH$	104 (–C≡C–) 112 (–C=C–)	90	Ethylbenzene (85), Oligomers (15)
$PhC{\equiv}CPh$	113 (–C≡C–) 21 (–C=C–)	100	Diphenylethane (69), *cis*-Stilbene (24), *trans*-Stilbene (7)
$PhCH{=}CH_2$	260	100	Ethylbenzene (100)
PhC(O)H*	10	70	Benzyl alcohol (92), Toluene (8)
$PhNO_2^*$	48	97	Aniline (100)

Note: C_{Pd} = 0.9 mmol/l; T = 30°C; P_{H_2} = 1 atm; [Substrate]/[Pd] = 870; solvent, DMF.
* C_{Pd} = 5 mmol/l.

the hydrogenolysis of the C–O bond in the resulting benzyl alcohol, and both of the reactions occurred at comparable rates [12]. The selectivity of the $Pd(Acac)_2 + PH_2Ph$ catalytic system (P/Pd = 0.3) in the hydrogenation of benzaldehyde was as high as 92%. Usually, nitrobenzene was selectively reduced to aniline on palladium catalysts. A high rate of reaction was characteristic of the given catalyst. Its specific activity in the reduction of the nitro group was higher than that of a catalyst containing nanosized palladium particles immobilized on a styrene and divinylbenzene copolymer by a factor of 3.5 [13]; however, it ranked below a palladium catalyst with diphenylphosphine [5].

The nature of the acido ligand at palladium and the primary phosphine affects the optimum conditions of catalyst formation and the properties of the catalyst. In particular, in the systems based on palladium acetate and primary phosphines (PH_2Ph and $PH_2(C_8H_{17})$) in an atmosphere of hydrogen at 30°C, a solution color change from reddish brown to blackish brown was observed in 1–2 min. The specific activity of the resulting catalyst depended on the concentration ratio between initial reactants and reached a maximum value either at P/Pd = 0.5 (for phenylphosphine) or at an equimolar ratio between these components (for octylphosphine) (Fig. 3). The pretreatment of the $Pd(OAc)_2 + nPH_2R$ catalytic system with hydrogen at 80°C for 15 min resulted in a decrease in its activity by more than one order of magnitude.

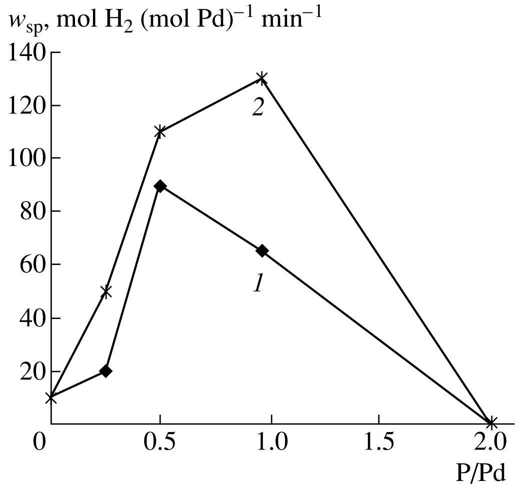


Fig. 3. Styrene hydrogenation in the presence of catalytic systems based on $Pd(OAc)_2$ with (*1*) phenylphosphine and (*2*) octylphosphine. C_{Pd} = 0.9 mmol/l; T = 30°C; P_{H_2} = 1 atm; solvent, DMF; [Substrate]/[Pd] = 870.

To explain the observed phenomena and to obtain information on the nature of hydrogenation-active species, we studied the interactions between palladium(II) compounds and primary phosphines in an inert atmosphere and hydrogen.

The reaction of $Pd(Acac)_2$ with PH_2Ph in benzene, unlike reactions with palladium dichloride [14], occurred at room temperature for 3–5 min, and it was accompanied by the formation of a brick-red precipitate regardless of the ratio between the reactants. According to spectroscopic (IR and UV spectroscopy) and GLC data, the concentration of $Pd(Acac)_2$ in the reaction mixture decreased and AcacH was formed. At a ratio of P/Pd = 0.5–2, about half of the hydrogen atoms of phenylphosphine were consumed for the formation of Hacac (Table 2).

We failed to detect reaction intermediates or products by the ^{31}P NMR monitoring of the $Pd(Acac)_2 + PH_2Ph$ reaction system: the signal of parent phenylphosphine (δ = –120 ppm (t), $^1J_{PH}$ = 200 Hz) disappeared, whereas signals other than those of trace phosphine oxides (δ = 41 ppm (d), $^1J_{PH}$ = 455 Hz; δ = 16 ppm (d), $^1J_{PH}$ = 560 Hz) were not detected.

Two products were isolated from the $Pd(Acac)_2 + PH_2Ph$ reaction system (P/Pd = 1): a precipitate formed in the course of reaction (tentatively denoted as sample 1), the elemental analysis of which corresponds to

Table 2. Interaction of bis(acetylacetonato)palladium with phenylphosphine in benzene

P/Pd	Reaction time	[Pd(Acac)$_2$], %		[AcacH], %		
		IR-spectroscopic data	UV-spectroscopic data	IR-spectroscopic data	UV-spectroscopic data	GLC data
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

Note: Acetylacetone concentration was determined by GLC only after the completion of the reaction.

Table 3. Characterization of the products of the reaction of Pd(Acac)$_2$ with phenylphosphine in argon and hydrogen

P/Pd	IR-spectroscopic data, cm^{-1}			Elemental analysis	XRD coherent-scattering region, nm
	Acac$^-$ (ν(C=O))	ν(P–H)	δ(C–C, C–H) Ph		
1 (Ar)	1583	2280	450, 680, 720	$Pd_1P_{1.7}C_{12}H_{13}$	2.7
2 (Ar)	1580	2283	450, 680, 720	$Pd_1P_{1.8}C_{12}H_{13}$	2.7
0.3 (H_2)	–	–	–	$Pd_8P_1C_1H_1$	2.0
1 (H_2)	–	–	450 br, 680, 700	$Pd_2P_1C_6H_8$	1.5

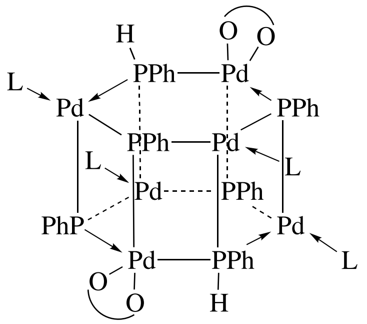
the empirical formula $Pd_1P_{1.7}C_{12}H_{13}$, and unreacted Pd(Acac)$_2$ (30% on a parent basis).

Sample 1 was X-ray amorphous; it was characterized by a diffuse maximum (halo) at *d*/*n* 13.556 Å. The region of coherent scattering was 2.7 nm. The appearance of a halo in the diffraction curve at an initial range of diffraction angles (2θ = 5°–40°) is indicative of a low-ordered structure of the substance, which is typical of oligomeric compounds.

According to IR-spectroscopic data, O,O-chelate acetylacetonate ligands (ν(C=O) = 1583 cm^{-1} and ν(C=C) = 1516 cm^{-1}) and organophosphorus ligands (ν(P–H) = 2280 cm^{-1}, δ(C–H, Ph) = 720 and 680 cm^{-1}, and δ(C–C, Ph) = 450 cm^{-1}) are the constituents of sample 1. The absence of resonance signals from the ^{31}P NMR spectrum of sample 1 dissolved in DMF suggests that the substance occurred in a colloidal dispersed state. The elemental analysis and IR-spectroscopic data did not allow us to answer the question as to which organophosphorus ligands were contained in sample 1: coordinated phenylphosphine, bridging phenylphosphinidene (PPh), or phenylphosphide (PHPh) ligands or a set of the above ligands.

The addition of triphenylphosphine to the Pd(Acac)$_2$ + PH$_2$Ph system (P/Pd = 1) at the onset of reaction resulted in an almost quantitative yield of Hacac. Triphenylphosphine, which is a stronger Lewis base than phenylphosphine, displaced it from the coordination sphere of palladium into solution and hence facilitated a deeper exchange of Acac$^-$ ligands. It is likely that sample 1 mainly consisted of coordinated PH$_2$Ph molecules and phenylphosphinidene ligands. However, the presence of μ^2-phenylphosphide ligands cannot be completely ruled out.

Taking into account IR-spectroscopic, XRD, and elemental analysis data and the capability of phosphinidene ligands to act as not only μ^2- but also μ^3-bridging ligands, we assume that the interaction of PH$_2$Ph with Pd(Acac)$_2$ results in the formation of polynuclear palladium complex associates. They consist of palladium–organophosphorus rings that are joined to each other by the donor–acceptor interaction of μ-PPh ligands with Pd atoms of another ring, for example:



where L is PH$_2$Ph.

It is evident that the product of the reaction of bis(acetylacetonato)palladium with phenylphosphine at a ratio of P/Pd = 2 is of an analogous nature (Table 3). The difference consists in a deeper degree of substitution of organophosphorus ligands for Acac$^-$.

At P/Pd > 2, the Acac$^-$ ligands were quantitatively converted into Hacac, whereas, according to ^{31}P

Table 4. Quantitative characterization of the interaction of palladium(II) compounds with primary phosphines in argon

System	Solvent	P/Pd	PdX_2^*, %	HX*, %
$Pd(Acac)_2 + PH_2Ph$	DMF	0.3	89	3
		0.5	79	24
		1.0	57	43
$Pd(Acac)_2 + PH_2C_8H_{17}$	benzene	1.0	48	50
		2.0	0	101
$Pd(OAc)_2 + PH_2C_8H_{17}$	benzene	0.5	73	36
		1.0	42	47

* X = $Acac^-$ or OAc^-.

NMR-spectroscopic data, an excess of phosphine remained in a free form.

The nature of the primary phosphine (PH_2Ph or $PH_2C_8H_{17}$), the oxygen-containing acido ligand at palladium ($Acac^-$ or OAc^-), and the solvent (benzene or DMF) had an insignificant effect on the interactions of palladium(II) compounds with the primary phosphine and on the composition of products: the reaction was also accompanied by the exchange of acido ligands at palladium for organophosphorus ligands (Table 4). At a ratio of P/Pd < 2, unreacted PdX_2 (X = $Acac^-$ or OAc^-) remained in the system. Note that cherry-red solutions were formed in the interaction of palladium complexes with octylphosphine in benzene and precipitation was not observed. However, the ^{31}P NMR spectra of these systems did not exhibit resonance signals in a region from –300 to +300 ppm; this suggests the formation of colloid solutions.

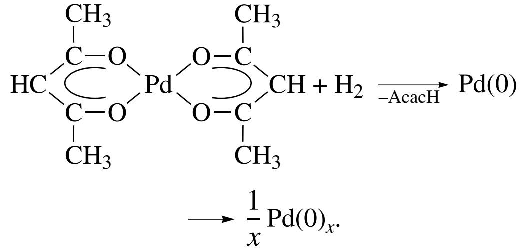
Thus, the interaction of palladium(II) compounds with primary phosphines (P/Pd < 2) in argon resulted in the formation of polynuclear palladium complex associates, and unreacted palladium acetylacetonate (acetate) remained in a free state.

Table 5. Conversion of the $Pd(Acac)_2 + nPH_2Ph$ catalytic system in hydrogen according to UV-spectroscopic and GLC data

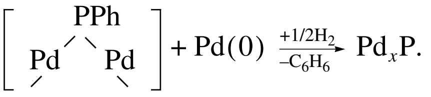
P/Pd	Reaction time, min	$[Pd(Acac)_2]$, %	[AcacH], %	$\frac{[C_6H_6]}{[PH_2Ph]}$
0.3	5	2	99	0.26
0.3	15	0	98	0.50
0.3	40	0	99	0.51
0.5	15	2	87	0.46
0.5	40	0	93	0.45
1.0	15	24	79	0.13
1.0	40	12	83	0.19
1.0	60	–	100	0.20

Note: $T = 80°C$; solvent, DMF; $C_{Pd} = 5$ mmol/l.

The additional treatment of the $Pd(Acac)_2 + nPH_2Ph$ system with hydrogen resulted in the quantitative formation of acetylacetone (Table 5). That is, not only $Pd(Acac)_2$ but also acetylacetonate ligands bound to palladium in polynuclear complexes were subjected to hydrogenolysis. Upon the interaction with H_2, benzene was detected in the products of catalysis along with acetylacetone. The formation of benzene was due to the degradation of organophosphorus ligands. As the P/Pd ratio was decreased, the amount of formed benzene (per mole of phenylphosphine) and the concentration of $Pd(Acac)_2$ increased. The latter compound is readily reduced with hydrogen in DMF at 80°C to Pd(0):



An analogous relationship was obtained with the use of triphenylphosphine [2]. Data on dephenylation are consistent with a previously proposed mechanism according to which the degradation of organophosphorus ligands occurs in the coordination sphere of Pd(0) [5]. Therefore, the formation of benzene in the test system can be represented as described below. Palladium(0) atoms, which result from the hydrogenolysis of $Pd(Acac)_2$, can either combine into clusters or react with the phenylphosphinidene ligands of polynuclear palladium complexes. The oxidative addition of the latter to Pd(0) and the hydrogenolysis of the Pd–C bond results in the formation of benzene and palladium phosphide:



The elemental analysis of a black precipitate (sample 3) isolated from the $Pd(Acac)_2 + 0.3PH_2Ph + H_2$ reaction system corresponds to the empirical formula $Pd_8P_1C_1H_1$. The fraction of Pd(0) in this sample was no higher than 30%, as determined by chemical analysis. According to XRD data, this sample contained palladium in a dispersed state, whose region of coherent scattering was 2 nm, as calculated from the *hkl* line of palladium. Note that an amorphous halo was absent from the diffraction curve in the region of small angles of reflection ($2\theta = 5°–40°$). This suggests the structural degradation of polynuclear palladium complexes, the products of the interaction between the components of the catalytic system in an inert atmosphere [16]. In our opinion, there is no contradiction in XRD data, elemental analysis, and the Pd(0) content. Higher palladium phosphides in an X-ray amorphous state can occur in sample 3; the main diffraction reflections of these compounds can be superimposed on a broadened line of palladium 111. After calcination in argon at 400°C for 4 h, sample 3 transformed to a crystalline state. In this case, along with reflections from crystalline palladium, reflections due to a crystalline phase (*d*/*n* of 2.563, 2.365, 2.255, 2.223, and 2.035 Å) corresponding to the palladium phosphide Pd_6P were detected in the diffraction curve. According to XRD data, the palladium phosphide Pd_6P was the main component of sample 3.

Bakunina *et al.* [16] found that the maximum activity of the $Pd(Acac)_2 + nPPh_3$ system in the hydrogenation of phenylacetylene also corresponded to the ratio of P/Pd = 0.3. The palladium phosphide Pd_3P and crystalline palladium were identified in the reaction system. However, the time of formation of the system with triphenylphosphine was no shorter than a day, whereas it shortened to 5 min with the use of phenylphosphine. It is likely that the promoting effect of phenylphosphine at low P/Pd ratios was related to the fact that the associates of polynuclear palladium complexes with phenylphosphinidene ligands and palladium phosphide produced in the course of the formation of the catalytic system served as a support for palladium(0) clusters.

The catalytic activity of the system dramatically decreased as the ratio was increased to unity. The elemental analysis of a black precipitate (sample 4) isolated from the $Pd(Acac)_2 + PH_2Ph + H_2$ reaction system corresponded to the empirical formula $Pd_2P_1C_6H_8$. The IR spectrum exhibited weak absorption bands characteristic of phenyl fragments. However, an absorption band at 2280 cm^{-1}, which corresponds to the stretching vibrations of the P–H bond, was absent (Table 3). Sample 4 containing 5% Pd(0) was X-ray amorphous. It is our opinion that the dramatic change in the properties of the catalyst at P/Pd = 1 was due to the degradation of organophosphorus ligands with the formation of palladium phosphide. This degradation led to the decomposition of the associates of polynuclear palladium complexes and facilitated the dissociation of coordination PH_2Ph to the solution. As a result of the interaction of $Pd(Acac)_2$ with PH_2Ph, the Pd(0)/Pd(II) ratio decreased.

Thus, the associates of polynuclear palladium complexes with phenylphosphinidene ligands and the palladium phosphide generated from them can serve as supports for Pd(0) clusters. The difference in the conditions of formation of catalytic systems based on $Pd(Acac)_2$ and $Pd(OAc)_2$ is related to the ability of palladium acetate to be reduced with hydrogen under milder conditions.

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