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Formation of Palladium Phosphides in the Reaction of Bis(dibenzylideneacetone)palladium(0) with White Phosphorus

N. I. Skripov, L. B. Belykh, L. N. Belonogova, A. V. Rokhin, T. P. Stepanova, and F. K. Shmidt

Irkutsk State University, ul. K. Marksa 1, Irkutsk, 664003 Russia,
email: belykh@chem.isu.ru

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Abstract—The reaction of bis(dibenzylideneacetone)palladium(0) with white phosphorus was studied using the methods of NMR, UV spectroscopy, and X-ray powder diffraction. The products of the reaction are shown to be palladium phosphides, their composition depending on the ratio of the reagents. The mechanism of the formation of the palladium-enriched phosphides is suggested, which includes the formation of palladium diphosphide PdP_2 that subsequently reacts with the excess of bis(dibenzylideneacetone)palladium(0) leading to palladium phosphides Pd_5P_2, $Pd_3P_{0.8}$, $Pd_{4.8}P$, and free dibenzylideneacetone.

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In recent 10–15 years a qualitative jump occurred in the chemistry of elemental phosphorus. On the one hand, the methods of activation of white phosphorus in the coordination sphere of the transition metal complexes were substantially developed, namely, the coordination chemistry of white phosphorus [1–6]. The structure of the formed phosphorus fragment is strongly influenced by the nature of the ligands in the coordination sphere of the transition metal. Transition metal complexes having the molecule of P_4 as a η^1-ligand are stable only in the presence of bulky ligands in the coordination sphere of the metal [6], otherwise the splitting of the P–P bond occurs with subsequent recombination of small fragments into binuclear complexes or polyatomic aggregates [1–4], or hydrolytic oxidation in the presence of water [3, 6]. The transition metal plays a role of a stabilizer of all phosphorus intermediates from the simplest phosphide anion to complex phosphorus oligomers P_n with up to 14 phosphorus atoms.

On the other hand, a field is developed connected with the use of white phosphorus as a modifier for preparation of nanoparticles highly effective in hydrogenation. In particular, we have first shown that introduction of white phosphorus into the reaction system prior to the stage of reduction of palladium bis(acetylacetonate) [$Pd(acac)_2$] with hydrogen allows to increase the turnover number and turnover frequency in hydrogenation of alkenes almost by the order of magnitude [7, 8]. The main reason of the promoting effect of white phosphorus on the catalytic properties of the system $Pd(acac)_2$–P_4–H_2 is the increase in the dispersity and stability of the formed nanoparticles [8]. The modifying effect of elemental phosphorus on the catalytic properties of palladium catalysts depends on a number of factors: the nature of the acidoligand in the precursor, reducer, concentration and the ratio of the reagents [9]. We believe that one of the reasons of the effect of the nature of the acidoligand on the properties of nanosized palladium catalysts modified with elemental phosphorus is the difference in the rates of reduction of Pd(II) to Pd(0), subsequent reaction of Pd(0) with elemental phosphorus, and clusterization of Pd(0). For the active in hydrogenation palladium catalysts modified with elemental phosphorus the following model was suggested: the core of the nanoparticle consists of palladium phosphides, mainly Pd_6P, and its surface, of the active in the hydrogenation Pd(0) clusters.

It is known that palladium phosphides can be obtained by various methods: the high temperature synthesis from the elements [10], thermal decomposition of organometallic precursors, in particular, phosphine complexes formed *in situ* from the metal salt and trioctylphosphine [11], decomposition of tertiary, secondary and primary phosphines in the coordination sphere of Pd(0) in hydrogen atmosphere [12, 13], reaction of metal nanoparticles with trioctylphosphine at 280–300°C [14]. For chemical simulation of separate stages of formation of palladium catalysts modified with elemental phosphorus for hydrogenation carried out under mild conditions and for elaboration of new approaches to the synthesis of nanoparticles effective in hydrogenation, we have studied the reaction of bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] with white phosphorus at room temperature. The $Pd(dba)_2$ complex was chosen due to the fact that dibenzylideneacetone is a relatively labile ligand and is not subjected to destructive transformations in the palladium coordination sphere.

Dibenzylideneacetone (dba) forms with the platinum group metals several types of complexes in which it acts as a monodentate alkene with electron-withdrawing substituent, $M(dba)_3$ (M = Pd, Pt) or as a bridging ligand in binuclear complexes of platinum and palladium, $M_2(dba)_3 \cdot Solv$ (Solv = $CHCl_3$, CH_2Cl_2, C_6H_6) [15]. Bis(dibenzylideneacetone)palladium(0) $Pd(dba)_2$ used by us as a precursor belongs to binuclear complexes $M_2(dba)_3 \cdot (dba)$ (M = Pd, Pt) with three bridging dibenzylideneacetone ligands in the s-*cis*, s-*trans*–conformation, where the molecule of dibenzylideneacetone is captured during crystallization instead of the molecule of the solvent. The binuclear structure of the $Pd(dba)_2$ complex is retained in the solution [15].

$$Pd_2(dba)_3(dba) + Solv \rightleftarrows Pd_2(dba)_3(Solv) + dba$$

Hereinafter we will use the traditional designation for bis(dibenzylideneacetone)palladium [$Pd(dba)_2$].

Since the dibenzylideneacetone ligand is one of the most labile from the known π-ligands, the relative kinetic stability of the $Pd(dba)_2$ complex in solution may depend on the nature of the solvent. As showed the UV spectroscopy, the intensity of the 525 nm absorption band of complex $Pd(dba)_2$ ($d \rightarrow d^*$ transition, $\varepsilon_{525} = 6400$ l mol^{-1} cm^{-1}) in an inert atmosphere in benzene remained unchanged during 20 days for the concentration of 3 mM. At the same time, when $Pd(dba)_2$ was dissolved in DMF, the intensity of the absorption band at 525 nm in the UV spectrum at 30°C decreased. After 3 h, complex $Pd(dba)_2$ in DMF was completely destroyed and the solution contained free dibenzylideneacetone whose concentration calculated from the absorption band at 325 nm ($n \rightarrow \pi^*$ transition, $\varepsilon_{525} = 33540$ l mol^{-1} cm^{-1}) was ca. 2 mM (see the table).

Transformation of complex $Pd(dba)_2$ in DMF in inert atmosphere: $c_0[Pd(dba)_2]$ 1 mM, *T* 30°C

Time, min	Concentration of $Pd(dba)_2$		Concentration of dba, mM
	c, mM	%	
20	0.711	71.1	0.59
60	0.570	57.0	0.90
90	0.313	31.2	1.36
120	0.164	16.4	1.74
150	0.095	9.5	1.93
180	0	0	2.06

The decrease in the concentration of complex $Pd(dba)_2$ in DMF is due to the substitution of the coordinated dibenzylideneacetone by the DMF solvent molecules, which are unable to stabilize Pd(0) complexes. Taking into account the composition of the $Pd(dba)_2$ complex in the solution, the process can be represented by the following stoichiometric equations.

$$Pd_2(dba)_3(Solv) + xSolv \rightleftarrows 2Pd(0)\{Solv\}_{x+1} + 3dba,$$

$$Pd(0)\{Solv\}_{x+1} \rightarrow 1/nPd_n + (x + 1)Solv.$$

Here, Solv is DMF, $x \leq 3$.

The formed palladium nanoclusters of the average size, according to the transmission electron microscopy, of ~3 nm are aggregatively unstable and interact with the formation of branched chains (Fig. 1).

Since DMF is in excess, the decomposition of the $Pd(dba)_2$ complex in DMF at 30°C obeys the kinetic equation of the pseudo-first order.

$$r = k_I c[Pd(dba)_2].$$

Here, *r* is the reaction rate, k_1 is the rate constant (min^{-1}), *c* is the current concentration.

The numerical value of the rate constant k_1 calculated from the equation $k_I = 1/t \ln c_0/c$ is equal to 1.28×10^{-2} min^{-1}, (c_0 is the initial concentration, *t* is the time of the reaction).

Considering the results on the kinetic stability of bis(dibenzylideneacetone)palladium(0) in the solution, the experiments on the reaction of $Pd(dba)_2$ with elemental phosphorus were carried out in benzene. The reaction in an inert atmosphere proceeds smoothly at room temperature. Addition of the solution of white

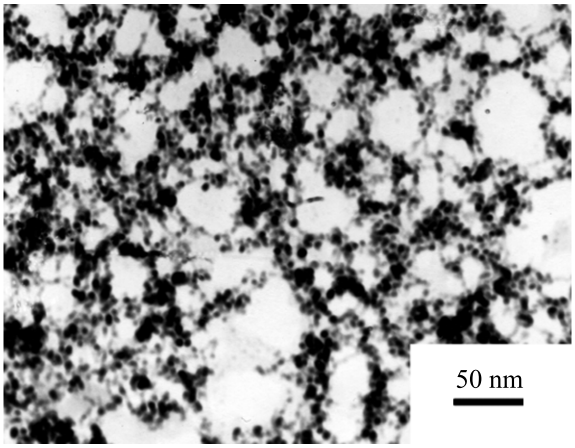


Fig. 1. TEM image of palladium nanoclusters formed from complex $Pd(dba)_2$ in DMF: c_{Pd} 1 mM, T 30°C.

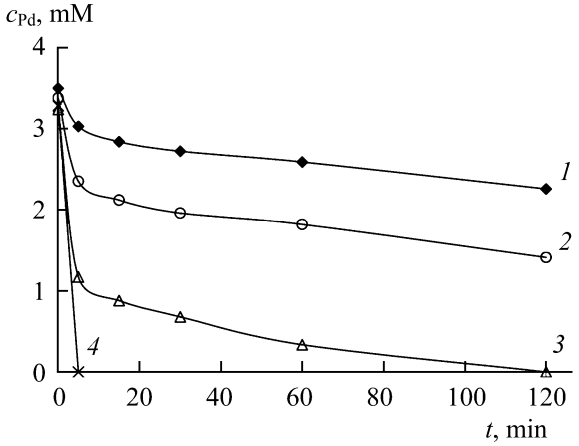


Fig. 2. Kinetic curves of transformation of $Pd(dba)_2$ for the reaction of white phosphorus in benzene at various molar ratios of the reagents: $[P_4]:[Pd(dba)_2]$ = (*1*) 0.05, (*2*) 0.1, (*3*) 0.25, and (*4*) 0.5. $c_{Pd(dba)2}$ 3.3 mM, T 20°C.

phosphorus to the solution of complex $Pd(dba)_2$ in benzene with the ratio $[P_4]:[Pd] = 0.5$ or $[P]:[Pd] = 2.0$ (to one phosphorus atom) results in a change in the color from wine red to yellow in 10–20 s from the beginning of the reaction and in the formation of a black precipitate. In the UV spectrum of the reaction system $Pd(dba)_2$–0.5 P_4 $\{c_0[Pd(dba)_2]$ 3.280 mM$\}$ the absorption band at 525 nm is absent suggesting the complete transformation of the $Pd(dba)_2$ complex. The concentration of dibenzylideneacetone is 5.864 mM, consequently, all dibenzylideneacetone from its complex $Pd(dba)_2$ remains in the solution. In the ^{31}P NMR spectrum of the system $Pd(dba)_2$–$0.5P_4$ taken after 10 min from the beginning of the reaction the signal of white phosphorus (δ_P –522 ppm) is lacking, and no other signals are registered in the region of 500 to –550 ppm.

The black precipitate isolated from the reaction system $Pd(dba)_2$–$0.5P_4$ (sample 1) is X-ray amorphous and so highly disperse that even an amorphous halo cannot be registered on the X-ray diffractogram. After calcination of sample 1 for 4 h at 400°C, on the diffraction curve broadened reflections of crystalline phases were registered belonging to palladium phosphides PdP_2 and Pd_5P_2, the former predominant. Hence, the reaction of $Pd(dba)_2$ with white phosphorus in benzene at the ratio $[P_4]:[Pd] = 0.5$ leads predominantly to the formation of the phosphide PdP_2 most enriched with phosphorus, whose formation, taking into account the composition of the $Pd(dba)_2$ complex in the solution, can be represented by the following stoichiometric equation.

$$Pd_2(dba)_3Solv + P_4 \rightleftarrows 2PdP_2 + 3dba + Solv,$$

where Solv is benzene.

We have found that the reaction between $Pd(dba)_2$ and elemental phosphorus at room temperature does not stop at the stage of the phosphide PdP_2 formation. For the ratio $[P_4]:[Pd] < 0.5$ ($[P_4]:[Pd] = 0.1$; 0.25) in the system $Pd(dba)_2$–nP_4 the transformation of the complex $Pd(dba)_2$ is also close to quantitative although the time of the reaction, according to the UV spectral data, increases from 10–20 s for $[P_4]:[Pd] = 0.5$ to 3 h for $[P_4]:[Pd] = 0.25$; 24 h ($[P_4]:[Pd] = 0.1$, conversion 90%). For the ratio $[P_4]:[Pd] = 0.05$ the conversion of $Pd(dba)_2$ after 6 days is ~70%.

On the kinetic curves of the dependence of concentration of $Pd(dba)_2$ on time of the reaction with white phosphorus two parts can be distinguished (Fig. 2). In the first (initial) part the rate of the reaction varies depending on concentration of white phosphorus from 1.10×10^{-4} ($[P_4]:[Pd] = 0.05$) to 2.04×10^{-4} ($[P_4]:[Pd] = 0.1$) and $4.54\cdot10^{-4}$ ($[P_4]:[Pd] = 0.25$) mol l^{-1} min^{-1}, that corresponds to the first order with respect to phosphorus. In the second part of the kinetic curve the rate diminishes 15–40 times. Such a sharp decrease in the reaction rate in the solution can be caused by inhibition by the reaction products or by changing the type of the reaction from homogeneous to heterogeneous. It is noteworthy that in the ^{31}P NMR spectrum of the system $Pd(dba)_2$–nP_4 (n = 0.05; 0.25) taken after 10 min from the beginning of the reaction the signal of white phosphorus disappears and no other signals are registered in the region of 500 to –550 ppm both in the starting period and after one day.

In total, the spectral and kinetic data allow an assumption that at various ratios of the reagents in the first stage $Pd(dba)_2$ reacts with white phosphorus with the formation of palladium phosphide PdP_2. Further transformations of $Pd(dba)_2$ are caused by its reaction with PdP_2. Since PdP_2 is poorly soluble, the reaction of $Pd(dba)_2$ should proceed on the surface of palladium nanophosphide. Transition from homogeneous to heterogeneous reaction in this case would give rise to a sharp decrease in the reaction rate.

To establish the nature of the intermediates and the final products of transformation the black precipitate formed in the reaction system $Pd(dba)_2$–$0.05P_4$ was isolated (sample 2). Taking into account that the conversion of $Pd(dba)_2$ was about 70%, and the solution, as showed the NMR spectroscopy data, did not contain phosphorus or the products of its transformations, the ratio P/Pd in the precipitate should be equal to ~1:3.

From the diffraction pattern analysis, sample 2 is a combination of crystalline and amorphous phases. On the diffraction curve of sample 2 on the profile of the amorphous halo for the reflection angles $2\theta = 30°–75°$ the reflections of crystalline phases were registered, which belong to palladium phosphides PdP_2; $Pd_3P_{0.8}$, and $Pd_{4.8}P$; an admixture of highly disperse palladium metal is also possible. Palladium phosphide $Pd_3P_{0.8}$ is known to crystallize in the cementite type (Fe_3C), and its difference from the ideal composition in the phosphide Pd_3P (Pd/P = 3:1) is due to random vacancies of phosphorus [16]. We failed to identify some reflections of the crystalline phases in the range of small reflection angles $2\theta = 6°–30°$.

The results of analysis of sample 2 of palladium phosphide PdP_2 are consistent with the aforementioned hypothesis that, irrespective of the ratio of the reagents, the reaction of $Pd(dba)_2$ with white phosphorus proceeds via the formation of palladium phosphide, whose further slow reaction with Pd(0) results in the palladium-enriched phosphides.

$$Pd_2(dba)_3Solv + P_4 = 2PdP_2 + 3dba + Solv,$$

$$PdP_2 + 2Pd_2(dba)_3 = Pd_5P_2 + 6dba,$$

$$2Pd_5P_2 + Pd_2(dba)_3 = 4Pd_3P + 3dba,$$

$$0.93Pd_3P + Pd_2(dba)_3 = Pd_{4.8}P + 3dba.$$

Additional experiments have shown that palladium phosphide PdP_2 does react with $Pd(dba)_2$ at room temperature with the initial rate of 7×10^{-7} mol l^{-1} min^{-1} $\{c_0[Pd(dba)_2]$ 3.550 mM, $Pd(dba)_2:PdP_2 = 11\}$.

Quantitative phase analysis of sample 2 was impossible. Taking into account that the ratio $[P_4]:[Pd] = 0.05$ (or $[P]:[Pd] = 0.20$ to one phosphorus atom), no more than 10% of PdP_2 calculated on $Pd(dba)_2$ can be formed in the first stage. This is consistent with the experimental data. Since the conversion of $Pd(dba)_2$ is 70% and the ratio P/Pd in the precipitate ~0.3, it can be shown that 80% of PdP_2 and 52% of $Pd(dba)_2$ will be consumed for $Pd_3P_{0.8}$ formation; 3.5% of $Pd(dba)_2$ will react with 4.4% $Pd_3P_{0.8}$ to give $Pd_{4.8}P$ (3.5%). Thus, sample 2 contains mainly phosphide $Pd_3P_{0.8}$ (89.8%) and small amounts of PdP_2 (3.7%) and $Pd_{4.8}P$ (6.5%).

Therefore, it was proved experimentally that the reaction of $Pd(dba)_2$ with white phosphorus at room temperature affords palladium phosphides, their composition depending on the initial ratio of the reagents. The formation of the palladium-enriched phosphides proceeds via a series of subsequent steps including the formation of palladium diphosphide, which further reacts with the excess of $Pd(dba)_2$ giving rise to palladium phosphides Pd_5P_2, $Pd_3P_{0.8}$, $Pd_{4.8}P$.

EXPERIMENTAL

UV spectra were registered on a SF-2000 spectrophotometer in quartz cell 0.01 cm thick. NMR spectra were registered on a VXR-500S Varian pulse spectrometer. ^{31}P chemical shifts are given relative to 85% phosphoric acid. Positive values correspond to downfield shifts. ^{1}H and ^{13}C chemical shifts are given relative to tetramethylsilane.

Diffraction pattern analysis of the catalysts samples was performed on a DRON-3M diffractometer, CuK_α radiation. Analysis of the samples by transmission electron microscopy was performed on a Philips EM-410 microscope. A drop of the *in situ* formed catalyst solution was put on a grid covered with carbon film and dried in argon atmosphere. The conditions of the experiment excluded melting and decomposition of the studied samples under the action of the electron beam.

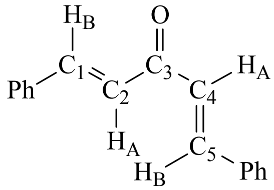
Solvents (benzene, DMF) were purified by standard procedures used in the work with organometallic compounds [17]. DMF was additionally stored over dry copper sulfate to remove water and amines till the formation of green solution and was twice distilled in a vacuum (8 Torr) at the temperature no higher than 42°C. Benzene was finally dried by distillation over $LiAlH_4$

and stored in an argon atmosphere in sealed ampules over molecular sieves 4A. The concentration of water in benzene determined by the Fisher method [18] was 1.1×10^{-3} M, in DMF, 0.8 M.

White phosphorus was purified mechanically from the surface products of oxidation and washed with dry benzene. The solution of white phosphorus in benzene was prepared and stored in an inert atmosphere in a finger type vessel, whose design allowed us to evacuate it and fill with argon. ^{31}P NMR spectrum: δ_P –522 ppm.

Dibenzylideneacetone was synthesized by the reaction of benzaldehyde with acetone [19] and crystallized from ethanol. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ coincide with the literature data [20].

Bis(dibenzylideneacetone)palladium(0) was prepared by reduction of $PdCl_2$ with methanol in the presence of sodium acetate and dibenzylideneacetone using the procedure described in [21, 22], as dark-violet precipitate with mp 152°C (150°C [23]). Taking into account that $Pd(dba)_2$ exists in solution in the dimeric form $Pd_2(dba)_3Solv$ [15], the following designations were used for description of the ^{1}H NMR spectra of $Pd(dba)_2$. Three bridging bidentate dibenzylideneacetone ligands in the *s-cis-s-trans*-conformation were designated as dba(1), dba(2), dba(3), the alkene fragment of dibenzylideneacetone in the *cis*-position to the carbonyl group, as *cis*-alkene, in the *trans*-position, as *trans*-alkene. The signals were assigned according to [24].



^{1}H NMR ($CDCl_3$, δ, ppm) dba (1): *cis*-alkene 6.65 d (1H, CH_A, $^3J_{HH}$ 13.4 Hz), 6.77 d (1H, CH_B, $^3J_{HH}$ 13.4 Hz); *trans*-alkene: 4.99 d (1H, CH_A, $^3J_{HH}$ 13.4 Hz), 5.94 d (1H, CH_B, $^3J_{HH}$ 13.4 Hz);. dba (2): *cis*-alkene 6.37 d (1H, CH_A, $^3J_{HH}$ 13.4 Hz), 6.47 d (1H, CH_B, $^3J_{HH}$ 13.4 Hz); *trans*-alkene: 4.96 d (1H, CH_A, $^3J_{HH}$ 13.4 Hz), 5.89 d (1H, CH_B, $^3J_{HH}$ 13.4 Hz); dba (3): *cis*-alkene 5.13 d (1H, CH_A, $^3J_{HH}$ 13.4 Hz), 5.34 d (1H, CH_B, $^3J_{HH}$ 13.4 Hz); *trans*-alkene: 6.16 d (1H, CH_A, $^3J_{HH}$ 12.2 Hz), 6.81 d (1H, CH_B, $^3J_{HH}$ 12.2 Hz); dba (free): 7.76 d (2H, $2CH_A$, $^3J_{HH}$ 16 Hz), 7.11 d (2H, $2CH_B$, $^3J_{HH}$ 16 Hz). The signals with δ 4.96 and 4.99 ppm are overlapped [24]. The presence of three dibenzylideneacetone ligands in the palladium complex and of free dibenzylideneacetone is proved by the presence of four singlets in the region of 180–190 ppm with δ_C 189.4, 184.9, 182.2, 181.1 ppm.

The reaction of bis(dibenzylideneacetone)palladium(0) and white phosphorus with different ratio of the reagents was performed in dry oxygen-free argon atmosphere in a finger type vessel in benzene solution.

a. To the wine-red solution of 0.5 g (9.4×10^{-4} mol) of $Pd(dba)_2$ in 210 ml of benzene 9.4 ml (4.7×10^{-4} mol) of the solution of white phosphorus in benzene was added. At mixing, the solution rapidly changes the color from wine red to black; after 10–20 s from the beginning of the reaction a black precipitate was formed and the solution turned yellow. The filtrate was analyzed by the methods of ^{31}P NMR and UV spectroscopy. When the reaction was completed the solution was decanted from the precipitate, the precipitate was washed thrice with benzene (10 ml) and dried in a vacuum (30°C, 1 Torr). Yield 0.16 g. The sample is X-ray amorphous. To make it crystalline, it was kept in a sealed tube at 400°C in inert atmosphere for 4 h and cooled slowly. The diffraction pattern analysis of sample 1 after heating showed the following reflections on the diffraction curve, *d/n, A* (I/I_0): 4.004(46) (not identified), 3.340(15) (Pd_5P_2), 2.998(31) (not identified), 2.930(65) (PdP_2), 2.878(94) (PdP_2), 2.722(100) (Pd_5P_2, PdP_2), 2.515(29) (Pd_5P_2, PdP_2), 2.448(15) (Pd_5P_2), 2.284(32) (Pd_5P_2), 2.122(31) (Pd_5P_2), 2.111(37) (Pd_5P_2), 2.080(38) (Pd_5P_2), 2.052 (38) (PdP_2), 2.002(35) (PdP_2), 1.982(15) (Pd_5P_2), 1.900 (23) (PdP_2), 1.838(33) (Pd_5P_2), 1.795(31), 1.735(23) (Pd_5P_2), 1.689(20) (PdP_2), 1.489(15) (not identified), 1.470(25) (Pd_5P_2, PdP_2) 1.367(15) (Pd_5P_2), 1.349(11) (Pd_5P_2), 1.308(11) (Pd_5P_2). The reflections were assigned according to the known X-ray characteristics of PdP_2 [10] and Pd_5P_2 (PDF 19-887) [25].

b. To the wine-red solution of 0.69 g (1.2×10^{-3} mol) of $Pd(dba)_2$ in 260 ml of benzene 4 ml (6.0×10^{-5} mol) of the solution of white phosphorus in benzene was added. A black precipitate is immediately formed although the solution remains wine-red. The mixture was treated as above. The filtrate was analyzed by the methods of ^{31}P NMR and UV spectroscopy. After 6 days the solution was decanted from the precipitate, the precipitate (sample 2) was washed thrice with benzene (10 ml) and dried in vacuum (30°C, 1 Torr). Yield 0.15 g. Sample 2 is a combination of crystalline and amorphous phases. The diffraction pattern analysis of sample 2 showed the following reflections on the crystalline phase in the range of reflection angles $2\theta = 30^\circ$–75° and on the profile of amorphous halo at 2θ 35°–45°, *d*/*n*, *A* (I/I_0): 2.910(8) (PdP_2), 2.871(24) (PdP_2), 2.796(6) ($Pd_{4.8}P$), 2.739(17) (PdP_2), 2.667(5) ($Pd_{12}P_{3.2}$), 2.623(15) ($Pd_{4.8}P$), 2.548(7) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 2.505(28) (PdP_2, $Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 2.473(15), 2.420(18) ($Pd_{4.8}P$), 2.362 (28) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 2.320(34) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 2.288(40) ($Pd_{12}P_{3.2}$), 2.247(53) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 2.222 (47) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 2.188(35), 2.168(27) ($Pd_{4.8}P$), 2.118(24) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 2.100(22) ($Pd_{12}P_{3.2}$), 2.075 (20) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 2.068(20) ($Pd_{4.8}P$), 2.044(16) (PdP_2), 2.022(12) ($Pd_{4.8}P$), 1.987(11) (PdP_2, $Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 1.958(11) ($Pd_{4.8}P$), 1.933(11) ($Pd_{4.8}P$), 1.920 (11), 1.902(10) (PdP_2, $Pd_{4.8}P$), 1.882(6) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 1.880(4) ($Pd_{12}P_{3.2}$, $Pd_{4.8}P$), 1.837(7) ($Pd_{12}P_{3.2}$), 1.802(4) ($Pd_{4.8}P$), 1.779(4) ($Pd_{12}P_{3.2}$), 1.767(4) ($Pd_{12}P_{3.2}$), 1.749(4) ($Pd_{12}P_{3.2}$), 1.714(2) (PdP_2), 1.680 (2) ($Pd_{12}P_{3.2}$), 1.595(2) ($Pd_{12}P_{3.2}$), 1.519(2) ($Pd_{12}P_{3.2}$), 1.454(1) (PdP_2, $Pd_{12}P_{3.2}$), 1.374(4) ($Pd_{12}P_{3.2}$), 1.366(4) (PdP_2), 1.318(7) (PdP_2). The reflections were assigned according to to the known X-ray diffraction data for PdP_2 [10], $Pd_{12}P_{3.2}$ (PDF 42-0922) and $Pd_{4.8}P$ (PDF 19-0890) [23]. Palladium phosphide $Pd_{12}P_{3.2}$ is also denoted as $Pd_3P_{0.8}$. The presence of admixture of palladium metal is possible: *d*/*n* (I/I_0): 2.247, 1.958, 1.374. Some lines at small reflection angles was not identified; 1.318(7) (PdP_2).

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