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Reactions of Pd β-Diketonate Complexes with Triethylaluminium

L. B. Belykh, T. V. Goremyka, A. V. Rokhin, Yu. Yu. Titova, V. A. Umanets, and F. K. Schmidt

Irkutsk State University, Irkutsk, Russia

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Abstract—Reactions of $Pd(Acac)_2$ and $Pd(Acac)_2PPh_3$ complexes with triethylaluminium in an inert atmosphere are studied by the NMR and IR, electronic microscopy, and X-ray powder diffraction methods. The final products of conversion of the initial Pd(II) complexes are the Pd(0) nanoparticles with the predominant diameter 2–4 nm. The main factors determining the size of Pd(0) particles and the nature of the ligand shell are considered.

The Ziegler systems show the catalytic properties in the many process such as hydration, isomerization, di-, oligo-, and polymerization, carbonylation, etc. Of the principal importance for the catalytic properties of these systems are the nature and the ligand surrounding of a transition metal, the precursor of true catalytically active particles, and the properties of a compound of nontransition metal performing different functions.

The reactions of components of the systems based on β-diketonate or carboxylate complexes of metals of the first transition series with organoaluminium compounds are well studied [1–6]. However, the products of reactions of Pd or Pt bis(acetylacetonates) with trialkylaluminium, which show a high catalytic activity, are studied to a lesser extent [7, 8].

This paper reports the data on the reaction between Pd β-diketonate and triethylaluminium.

EXPERIMENTAL

The solvents were purified following the standard procedures used in the experiments with organometallic compounds [9]. For a deeper purification, benzene and toluene were additionally distilled over $LiAlH_4$ in a rectification column and stored in sealed tubes over 4 Å molecular sieves.

Pd bis(acetylacetonate) was prepared according to the procedure [10]. The ^{1}H NMR (δ, ppm): 5.04 (s, 1H, CH), 1.76 (s, 6H, CH_3).

Bis(acetylacetonato)triphenylphosphinepalladium was synthesized following the procedure described in [11]. The ^{1}H NMR (δ, ppm): 5.19 (s, 1H, CH), 4.03 (d, 1H, CH, $^3J_{PH} = 5.9$ Hz); 1.98 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 2.57 (s, 6H, CH_3); 7.96 (m, CH, Ph); ^{1}P NMR (δ, ppm): 31.

The commercial grade triethylaluminium was distilled in vacuum and a fraction was collected with bp = 48–49°C, 1 mmHg, ^{1}H NMR (δ, ppm): = 1.22 (t, 3H, CH_3), $^1J = 8.24$ Hz), 0.45(q, 2H, CH_2, $^1J = 8.24$ Hz). The reagent was kept in a sealed tube under the argon atmosphere.The solutions of triethylaluminium in benzene were prepared in the Schlenk vessel under the atmosphere of argon.

To prepare diethylaluminium acetylacetonate, a solution of acetylacetone (1 mmol) in benzene was added dropwise to a solution of triethylaluminium in benzene (1.1. mmol). The ^{1}H NMR (δ, ppm): $Acac^-$ 4.95 (s, 1H, CH), 1.61 (s, 6H, CH_3); Et 0.53 (q, 2H, CH_2, $^1J = 8.24$ Hz); 1.54 (t, 3H, CH_3, $^1J = 8.24$ Hz). IR (ν, cm^{-1}): (C=O) + ν(C=C) 1585 and 1525, ν(C=C) + ν(C–CH_3) 1284, 1218, δ(Al–C–H) + ν(C–CH_3) 1187, 1104.

The reaction between Pd bis(acetylacetonate) or bis(acetylacetonato)triphenylphosphinepalladium and triethylaluminium at different reagent ratios was performed under the atmosphere of dry argon purified from oxygen in a temperature-controlled vessel whose design provides the preliminary evacuation and filling with argon.

The reaction course was monitored by IR, NMR, gas-liquid chromatography, and volumetric methods.

IR spectra were recorded on a Specord 75IR spectrometer at 400–4000 cm^{-1} (with the samples prepared in a dry inert atmosphere as suspension in Vaseline oil that was preliminarily heated).

The NMR spectra were recorded on a VXR-500S Varian pulse spectrometer. The chemical shifts **δ** ^{1}H were referenced against tetramethylsilane, δ ^{31}P against 85% H_3PO_4. The positive values of δ correspond to the upfield shift. The ^{31}P spectra were recorded in a solution sealed in a preliminarily evacuated tube filled with argon.

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Table 1. Composition of gases formed in the $Pd(Acac)_2$–$AlEt_3$ system (with $c_{Pd} = 0.025$ mol/l, $T = 30°C$, toluene used as a solvent)

$AlEt_3 : Pd(Acac)_2$	Gas composition, %			Number of gas moles/Pd mol
	ethane	ethylene	butene-1	
2.0	60.1	35.5	4.4	1.9
3.4	52.1	45.5	2.4	2.8
5.0	49.0	45.3	5.7	3.0
10.0	48.5	45.6	5.9	3.3

Analysis of the composition and yield of gaseous products. A solution of $Pd(Acac)_2$ (0.1522 g, 5×10^{-4} mol) in 20 ml of toluene was placed in a temperature-controlled vessel (connected with volumetric system) and some quantity of $AlEt_3$ was introduced by a syringe through the Teflon tube with vigorous stirring. The gas sampling (1 ml) was performed after termination of gas liberation, and the sample was analyzed by the gas-liquid chromatography method on a Chrom-5 chromatograph equipped with a 2.4-m column (filled with CaA phase) and a flame-ionization detector; the column temperature was 100°C, nitrogen was used as a carrier gas. The quantitative analysis of gases dissolved in a liquid phase was performed in terms of the solubility coefficient. The experiments with the $Pd(Acac)_2PPh_3$ complex were performed similarly.

In order to analyze the products of transformations of the Pd complexes at different initial ratios of Al/Pd, the solvent (2/3 of the volume) was distilled off from the reaction system $Pd(Acac)_2$ (or $Pd(Acac)_2PPh_3$)–$nAlEt_3$ after termination of the reaction and pentane was added for precipitation. The obtained brown-black precipitate was washed with pentane in the atmosphere of argon, dried in vacuum (30°C, 1 mmHg), and was stored in sealed tubes under the argon atmosphere.

To perform the elemental analysis for Pd, Al, and P, a weighed sample (~0.01 g) was dissolved in 2 ml of HNO_3 with boiling and then was diluted with water to 50 ml in a measuring flask. The concentration of the Pd and Al ions was determined by the atomic absorption spectroscopy on a 403 Perkin-Elmer spectrometer in a propane–air flame for Pd and acetylene–nitrous oxide for Al; P was analyzed by a photocolorimetric method using the standard procedure [12].

The X-ray powder diffraction analysis was performed on a DRON-3M diffractometer (CuK_α radiation).

The study of the samples by the transmission electronic microscopy was carried out on a BS-300 microscope (Czech). The solution drop was applied on a grid covered with carbon film and dried in the atmosphere of argon. The recording conditions excluded melting and destruction of the analyzed samples under the action of the electron beam.

RESULTS AND DISCUSSION

$Pd(Acac)_2$–$AlEt_3$ system. The addition of $AlEt_3$ to a solution of $Pd(Acac)_2$ in toluene at room temperature is attended by the formation of gaseous substances liberated for 5–10 min and by the change in the solution color from yellow to dark brown.

According to the ^1H NMR data, the reaction between $Pd(Acac)_2$ and $AlEt_3$ gives ethylene ($\delta = 5.35$ ppm) and ethane ($\delta = 0.92$ ppm):

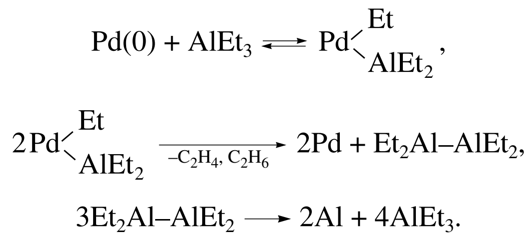
$$Pd(Acac)_2 + 2AlEt_3 \longrightarrow Pd(0)$$
$$+ 2AlEt_2(Acac) + C_2H_6 + C_2H_4.$$

Unlike the systems based on acetylacetonate of Ni [1, 2, 4] and Co [1, 2], which give mainly ethane, the content of ethane and ethylene in the case of $Pd(Acac)_2$ at different ratios of the initial components is close to the equimolar (Table 1). This fact suggests that the destruction of the Pd ethyl complexes formed as a result of the exchange of the Acac ligands, follows the mechanism of the β-hydrate shift.

The predominating amount of ethane as compared to ethylene at Al : Pd = 2 is likely to be due to the partial hydrolysis of $AlEt_3$ with traces of water in a solvent, whose contribution to the change in the composition of the gases formed is more pronounced at low Al : Pd ratios.

As follows from the ^1H NMR data, at Al : Pd = 2 and 3.4, the reaction system does not contain $AlEt_3$ after termination of the reaction, whereas the extent of $Pd(Acac)_2$ conversion was 75% and 97%, respectively. The absence of triethylaluminium from the reaction system suggests that it is spent not only for the reduction of $Pd(Acac)_2$.

The gas evolution data show that at the ratio Al : Pd ≥ 3.4, the relative quantity of primary gases required for the quantitative reduction of Pd(II) exceeds 2 mol per mol of Pd. At high Al : Pd ratios, the yield of gases in the amount exceeding the equimolar amount can be explained by the supplementary decomposition of triethylaluminium in the coordination sphere of Pd according to the following scheme:



$$Pd(0) + AlEt_3 \rightleftharpoons Pd\begin{smallmatrix}\diagup Et\\ \diagdown AlEt_2\end{smallmatrix},$$

$$2Pd\begin{smallmatrix}\diagup Et\\ \diagdown AlEt_2\end{smallmatrix} \xrightarrow[-C_2H_4,\ C_2H_6]{} 2Pd + Et_2Al–AlEt_2,$$

$$3Et_2Al–AlEt_2 \longrightarrow 2Al + 4AlEt_3.$$

The formation of hydrogen in the reaction system $Pd(Acac)_2$–$8AlEt_3$ after the addition of concentrated sodium hydroxide solution can serve an indirect confirmation of the scheme suggested

$$2Al + 2NaOH + 6H_2O = 3H_2 + 2Na[Al(OH)_4].$$

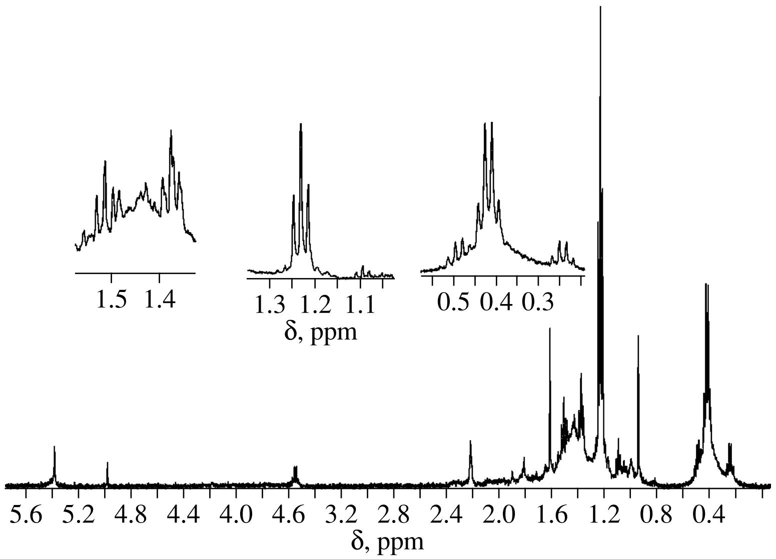
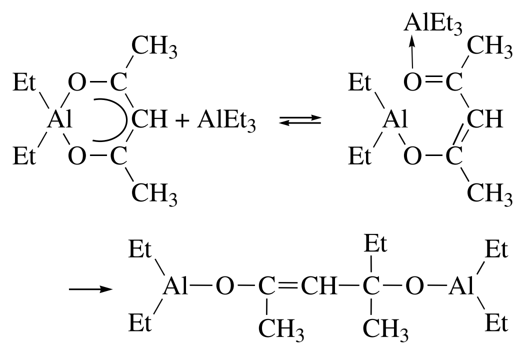


Fig. 1. The ^1H NMR spectrum of the $Pd(Acac)_2$–$5AlEt_3$ system (with toluene-D_8 used as a solvent).

At Al : Pd = 5, the quantitative transformation of $Pd(Acac)_2$ is observed. In addition to $AlEt_2(Acac)$, the reaction system also contains triethylaluminium in a free state. Moreover, the ^1H NMR spectrum contains also broad signals at 1.45 and 0.40 ppm, which do not exhibit hyperfine structure and are typical of the methyl and methylene groups in organoaluminium compounds (Fig. 1). Note that the intensity of the resonance signals from $AlEt_2(Acac)$ and $AlEt_3$ decreases with time, while that of the signals at 1.45 and 0.40 ppm increases. The analogous broad and low-intensity signals were also recorded at the ratio Al : Pd = 3.4.

The broadening of a resonance signal in the ^1H NMR spectrum can be caused by the presence of a radical, by the inter- or intramolecular exchange, or the formation of a microheterogeneous system. The formation of a radical can be excluded in this case, since no other signals in the spectrum are broadened. Therefore, the most probable is the inter- or intramolecular exchange and adsorption of organoaluminium compounds on the surface of the Pd(0) particles.

Trialkylaluminium is known to react with $AlR_2(Acac)$ under mild conditions according to the following equation [13]:



When a solution of diethylaluminium acetylacetonate is added to triethylaluminium, the ^1H NMR spectrum exhibits broadened signals at 1.45 and 0.42 ppm, along with the resonance signals from $AlEt_2(Acac)$. The reaction rate is low, such that even in 1 h, the resonance signals from the reaction product $AlEt_2(C_5H_7O_2)(Et)AlEt_2$ appeared in trace amounts. Hence, the reasons for broadening of the resonance signals are the $AlEt_3$ coordination at the carbonyl group of the Acac ligand and the intramolecular exchange.

At the same time, since the resonance signals from $AlEt_2(Acac)$ in the reaction system $Pd(Acac)_2$–$5AlEt_3$ become less intensive with time and the signals from the reaction product do not appear, we suggest that the signal broadening in the ^1H NMR spectrum occurs not only due to the intramolecular exchange, but also due to adsorption of organoaluminium compounds on the Pd particles.

The reduction of $Pd(Acac)_2$ with triethylaluminium results in the formation of microheterogeneous systems, where the size of the particles in dispersed phase and the nature of the ligand surrounding depend on the ratio Al/Pd. According to the X-ray powder diffraction analysis, the products of $Pd(Acac)_2$ reaction with triethylaluminium are X-ray amorphous compounds, for which the coherent scattering area decreases with the increasing Al : Pd ratio (Table 2).

The highly contrast particles with the predominant diameter of 4.2 nm were detected in the $Pd(Acac)_2$–$3.4AlEt_3$ system by the transmission electron microscopy method (Fig. 2).

It is known [14] that the particle size distribution close to the normal Gauss distribution suggests the particle growth due to adsorption of single atoms on these

Table 2. Products of reactions of the Pd complexes with triethylaluminium

System	The Pd : Al : P ratio in precipitate	CSA according to X-ray powder diffraction data, nm*
$Pd(Acac)_2$–$4AlEt_3$	1 : 1: 0	2.55
$Pd(Acac)_2$–$6AlEt_3$	1 : 1.7 : 0	1.35
$Pd(Acac)_2PPh_3$–$4AlEt_3$	1 : 0.4 : 0.6	1.30
$Pd(Acac)_2PPh_3$–$6AlEt_3$	1 : 1.5 : 0.6	0.94

* CSA is the coherent scattering area (nm) calculated from X-ray picture.

Table 3. Composition of gases formed in the $Pd(Acac)_2PPh_3$–$AlEt_3$ system (with c_{Pd} = 0.025 mol/l, T = 30°C, toluene used as a solvent)

$AlEt_3 : Pd(Acac)_2PPh_3$	Gas composition, %			Number of gas moles/Pd mol
	ethane	ethylene	butene-1	
1.0	60.2	35.4	4.4	0.90
3.4	46.5	50.0	3.5	1.84
5.0	48.6	46.2	5.2	1.95
10	43.2	48.9	7.9	2.68

particles, while the formation of particles as a result of the cluster coagulation is described by the logarithmically normal particle size distribution. The nonspherical shape of the particles and the type of the particle size distribution indicate that the growth of the Pd particles occurs not only due to the adsorption of new Pd atoms on the surface, but also due to the cluster aggregation.

The black precipitate isolated from the $Pd(Acac)_2$–$3.4AlEt_3$ system corresponds, according to the elemental analysis data, to the empirical formula $Pd_1Al_{1.1}C_{9.4}H_{14.6}$. The IR spectrum of a sample exhibits the following absorption bands of $AlEt_2(Acac)$: 1587, 1525, 1284, 1183, 1104 cm^{-1}.

Thus, the reaction between Pd bis(acetylacetonate) and triethylaluminium (Al : Pd = 3.4) in an inert atmosphere results in the formation of Pd nanoparticles stabilized mainly by $AlEt_2(Acac)$. The quantity of the surface atoms in the metal nanoparticles 2.5–3 nm in diameter reaches 45–39% [15]. Taking into account steric factor and capability of $AlEt_2(Acac)$ to form dimers [2], one can suggest that the ligand shell consists of several layers of diethylaluminium acetylacetonate.

The composition of the products of Pd(II) reduction changes when Al : Pd > 3.4. The elemental analysis data show that the ratio between Al and Pd in precipitates increases from 1 at Al : Pd = 2, 3.4 to 1.7 at Al : Pd = 6. The IR spectra of the samples isolated from the system $Pd(Acac)_2$–$nAlEt_3$ (n = 6, 8, 10) exhibit low-intensity absorption bands due to the stretching vibrations ν(C=O) + ν(C=C) (1587 and 1525 cm^{-1}) and ν(C–C) + ν($C–CH_3$) (1284 cm^{-1}) in O,O-chelate-bonded Acac of diethylaluminium acetylacetonate.

The changes observed occur due to the $AlEt_2(Acac)$ interaction with $AlEt_3$ resulting in the formation of an adduct or the addition product. The Pd nanoparticles can be stabilized both by $AlEt_2(Acac)$ and by the products of the reaction of $AlEt_2(Acac)$ with $AlEt_3$.

$Pd(Acac)_2PPh_3$–$AlEt_3$ system. The reaction of $Pd(Acac)_2PPh_3$ with $AlEt_3$ has some distinctions and common features with the reaction with $Pd(Acac)_2$.

The reaction between $Pd(Acac)_2PPh_3$ and triethylaluminium also gives ethane and ethylene in quantities close to the equimolar quantities (Table 3). Note that

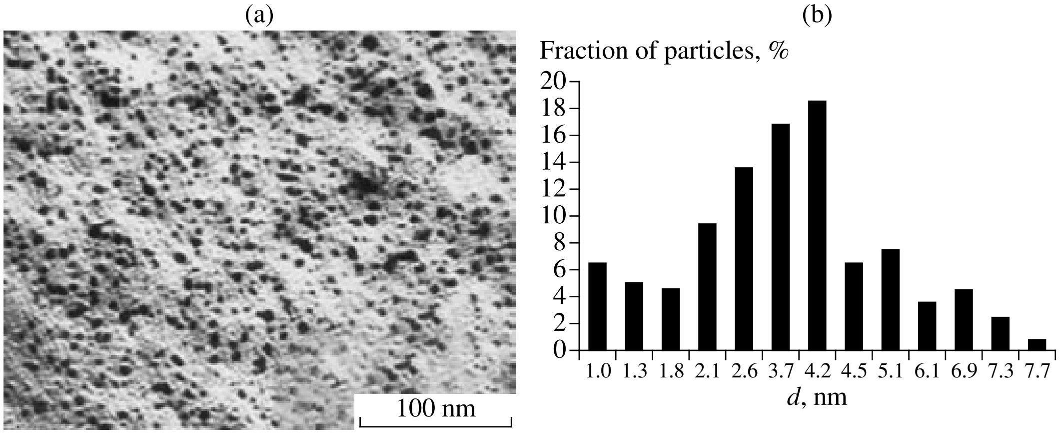


Fig. 2. (a) The electron-microscope picture of the $Pd(Acac)_2$–$3.4AlEt_3$ system; (b) the particle size distribution.

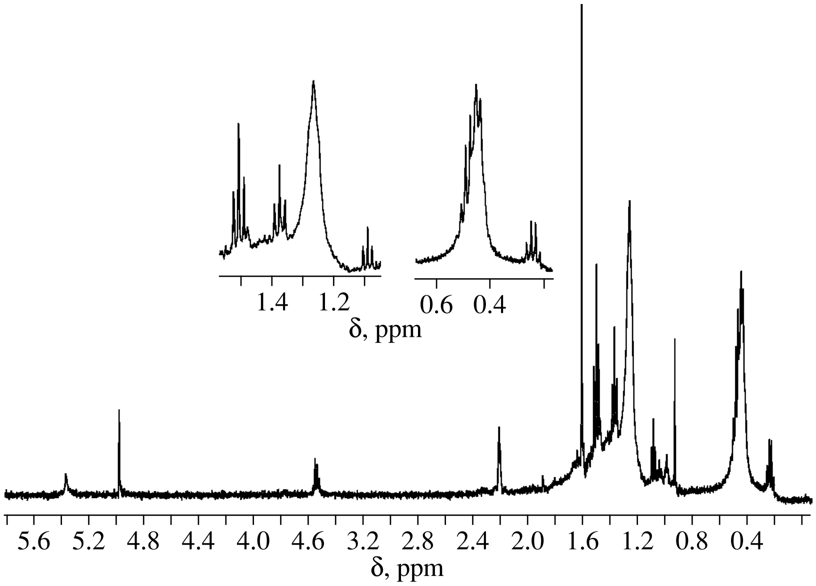


Fig. 3. The ^{1}H NMR spectrum of the Pd(Acac)$_2$PPh$_3$–5AlEt$_3$ system (with toluene-D$_8$ used as a solvent).

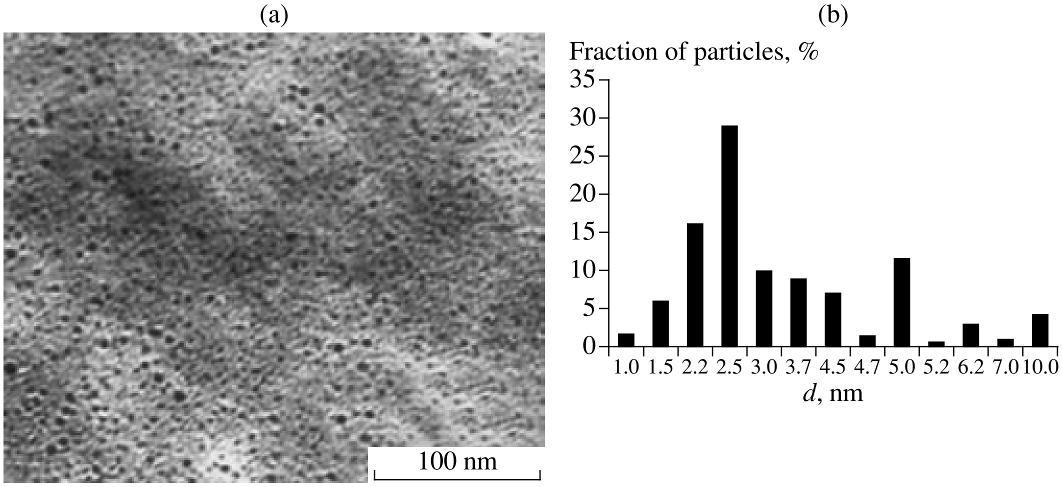


Fig. 4. (a) The electron-microscope picture of the Pd(Acac)$_2$PPh$_3$–3.4AlEt$_3$ system; (b) the particle size distribution.

with the ratio Al : Pd < 10, no additional decomposition of the excess triethylaluminium is observed.

The ^{1}H NMR study revealed that in the reaction of Pd(Acac)$_2$PPh$_3$ with AlEt$_3$ (Al : Pd = 2), the initial Pd complex is spent almost quantitatively. The reaction products recorded in a solution were AlEt$_2$(Acac), ethane, and ethylene. The same situation is observed at Al : Pd = 3.4. The solution does not contain triethylaluminium in a free state. Since the system contains simultaneously an acid and the Lewis base, one can suggest complexation between AlEt$_3$ and PPh$_3$. The model reaction carried out between triphenylphosphine and triethylaluminium showed that the resonance signals from the methyl and methylene groups of the PPh$_3$ · AlEt$_3$ adduct appear in the ^{1}H NMR spectrum at 0.62 ppm (q, CH$_2$, ^1J = 8.24 Hz); 1.58 ppm (t, CH$_3$, ^1J = 8.24 Hz).

The analysis of the ^{1}H NMR spectra of the reaction system Pd(Acac)$_2$PPh$_3$–nAlEt$_3$ confirmed that the adduct of triphenylphosphine and triethylaluminium is not formed in this system. Therefore, the excess AlEt$_3$ is spent in another processes.

When the ratio of the initial reagents (Al : Pd) was increased to 5, the ^{1}H NMR spectrum contained, in addition to the resonance signals from AlEt$_2$(Acac), the broad signals from the methyl and methylene groups at 1.4 and 0.4 ppm and the signals from a free triethylaluminium (Fig. 3). Since no AlEt$_3$ · PPh$_3$ adduct was recorded in the reaction system, the signal broadening is assumed to occur due to the triethylaluminium coordination by Pd or $AlEt_2(Acac)$ contained on the surface of the Pd(0) particles. The $AlEt_2(Acac)$ concentration decreasing with time and the increasing broad signals at 1.4 and 0.4 ppm make the second assumption preferable.

The ^{31}P NMR spectrum of the reaction system $Pd(Acac)_2PPh_3$–$n$$AlEt_3$ recorded at different reagent ratios ($n = 2, 3.4, 6$) exhibits a broad signal at 22 ppm characteristic of PPh_3 coordinated by the Pd atoms in the lowest oxidation states.

A black precipitate isolated from the $Pd(Acac)_2PPh_3$–$3.4AlEt_3$ system is the X-ray amorphous compound with the ratio Pd : Al : P = 1 : 0.4 : 0.6. The IR spectrum of the sample contains the absorption bands due to $AlEt_2(Acac)$ (1587, 1525, 1284 cm^{-1}), and due to off-plane deformation vibrations of the C–H and C–C bonds in monosubstituted benzene ring (706, 676 cm^{-1}).

The electron-microscope picture of the $Pd(Acac)_2PPh_3$–$3.4AlEt_3$ system shows highly contrast particles with the predominant diameter of 2.5 nm (Fig. 4).

The data obtained make it possible to suggest that the reaction of $Pd(Acac)_2PPh_3$ with triethylaluminium (Al : Pd = 3.4) in an inert atmosphere gives Pd(0) nanoparticles, stabilized by both $AlEt_2(Acac)$ and triphenylphosphine.

The study of the reaction of Pd acetylacetonate complexes with triethylaluminium showed that the interaction between the initial components included the exchange of the $Acac^-$ ligands for Et; the subsequent β-hydride shift results in the reduction of Pd(II) to Pd(0) and the formation of the Pd nanoparticles. The ligand surrounding and the size of the Pd nanoparticles are determined by the Al : Pd ratio. Triphenylphosphine stabilizes the Pd complexes and thus prevents coordination of $AlEt_3$ and hampers its further destruction. The introduction of triphenylphosphine favors the formation of a highly dispersed system.

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