

# Formation and the Nature of Activity of Ziegler Systems Based on Palladium $\beta$ -Diketonate Complexes in Hydrogenation Catalysis

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**Abstract**—The catalytic properties and nature of Ziegler-type  $\text{Pd}(\text{Acac})_2$  and  $\text{Pd}(\text{Acac})_2\text{PPh}_3$  based catalysts are studied in the hydrogenation of unsaturated compounds. The causes of an extremum appearing in the dependence of the specific activity of the catalyst in styrene and phenylacetylene hydrogenation on the proportions of the starting components are considered. The increase in the specific activity of the  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3$  catalytic system in hydrogenation as a function of the Al/Pd ratio arises from an increase in the degree of dispersion of the microheterogeneous system, an increase in the fraction of reduced palladium, and changes in the nature of the ligand shell. The inhibiting effect is caused by triethylaluminum adsorption on palladium nanoparticles. Palladium nanoparticle models are suggested.

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Ziegler–Natta type catalytic systems, suggested for the polymerization and oligomerization of alkenes [1], are active in various reactions of unsaturated hydrocarbons, including hydrogenation. Most works in this area have been devoted to systems based on  $\beta$ -diketonate, carboxylate, and cyclopentadienyl complexes of metals of the first transition row and on organoaluminum compounds [1–7]. Less attention has been given to the products resulting from the reactions of palladium and platinum bisacetylacetones with trialkylaluminum [8, 9].

The nature and ligand environment of both the transition metal compound (a precursor of the true catalytic species) and the nontransition metal compound, which execute different functions, are of principal significance for the catalytic properties of these systems. Depending on the nature of the transition metal and its ligand environment, mononuclear hydride complexes such as  $(\text{Cp})_2\text{TiH}$  and  $\text{HCo}(\text{PPh}_3)_3$  [4] or reduced metal nanoparticles can result from the interaction between the components of the catalytic systems [1, 4, 6, 7, 9, 10].

Unlike the complexes of metals of the first transition row, the  $\text{Pd}(\text{II})$  complexes are readily reducible with hydrogen under mild conditions. It was shown that microheterogeneous systems result from the reduction of the palladium phosphine complexes with hydrogen or sodium hypophosphite [11, 12]. Use of such a strong reducing agent as triethylaluminum can increase the degree of dispersion of the catalytic system and favors the formation of a more active catalyst. Here, we report the properties and nature of catalytically active species of the systems based on  $\text{Pd}(\text{Acac})_2$  and triethylaluminum, including a system modified by triphenyl-

phosphine, in the hydrogenation of unsaturated compounds.

## EXPERIMENTAL

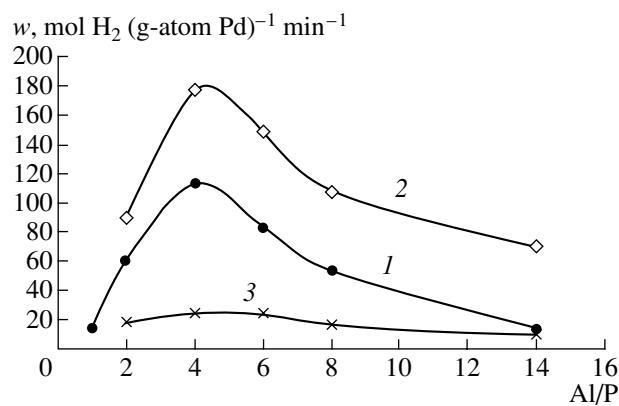
Solvents were purified by standard procedures used in organometallic chemistry [13]. For deeper drying, benzene, toluene, and hexane were additionally distilled from  $\text{LiAlH}_4$  in a distillation column and were stored under argon in sealed ampules above the molecular sieve 4A.

**Palladium biacetylacetone** was synthesized according to a published procedure [14].  $^1\text{H}$  NMR:  $\delta(\text{CH}) = 5.04$  ppm (s, 1 H),  $\delta(\text{CH}_3) = 1.76$  ppm (s, 6 H).

**Bisacetylacetonato(triphenylphosphine)palladium** was synthesized according to a known procedure [15].  $^1\text{H}$  NMR:  $\delta(\text{CH}) = 5.19$  ppm (s, 1 H), 4.03 ppm (d, 1 H,  $^3J_{\text{PH}} = 5.9$  Hz);  $\delta(\text{CH}_3) = 1.98$  ppm (s, 3 H), 1.46 ppm (s, 3 H), 2.57 ppm (s, 6 H);  $\delta(\text{m}, \text{CH, Ph}) = 7.96$  ppm.  $^{31}\text{P}$  NMR:  $\delta = 31$  ppm.

**Triethylaluminum** (commercial) was distilled in vacuo, and the fraction boiling at 48–49°C/1 Torr was collected.  $^1\text{H}$  NMR:  $\delta(\text{CH}_3) = 1.22$  ppm (t, 3 H,  $^1J = 8.24$  Hz),  $\delta(\text{CH}_2) = 0.45$  ppm (q, 2 H,  $^1J = 8.24$  Hz). The distilled substance was stored in a sealed ampule under argon. Solutions of triethylaluminum in hexane were prepared in a Schlenk flask in an argon atmosphere. The concentration of  $\text{AlEt}_3$  was checked volumetrically upon the decomposition of the compound with water and by  $^1\text{H}$  NMR spectroscopy.

**Diethylaluminum acetylacetone** was synthesized by the dropwise addition of a solution of acetylacetone (1 mmol) in benzene to a solution of triethylalu-



**Fig. 1.** Hydrogenation of styrene in the presence of the systems (1)  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3$ , (2)  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + \text{AlEt}_3$ , and (3)  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3 + \text{PPh}_3$  in toluene.  $C_{\text{Pd}} = 5 \text{ mmol/l}$ ,  $T = 30^\circ\text{C}$ ,  $P_{\text{H}_2} = 1 \text{ atm}$ , and  $[\text{St}]/[\text{Pd}] = 174$ .

minimum (1.1 mmol).  $^1\text{H}$  NMR:  $\text{Acac}^-\delta(\text{CH}) = 4.95 \text{ ppm}$  (s, 1 H),  $\delta(\text{CH}_3) = 1.61 \text{ ppm}$  (s, 6 H); Et  $\delta(\text{CH}_2) = 0.53 \text{ ppm}$  (q,  $^1J = 8.24 \text{ Hz}$ , 2 H),  $\delta(\text{CH}_3) = 1.54 \text{ ppm}$  (t,  $^1J = 8.24 \text{ Hz}$ , 3 H). IR:  $\nu(\text{C=O}) + \nu(\text{C=C}) = 1585, 1525 \text{ cm}^{-1}$ ;  $\nu(\text{C=C}) + \nu(\text{C-CH}_3) = 1284, 1218 \text{ cm}^{-1}$ ;  $\delta(\text{Al-C-H}) + \nu(\text{C-CH}_3) = 1187, 1104, 1047, 1010 \text{ cm}^{-1}$ .

**Hydrogenation of unsaturated compounds** was carried out in a thermostated shaking bath under vigorous stirring. A solution of  $\text{AlEt}_3$  in hexane from a Shlenk flask was added dropwise, under flowing hydrogen, to a solution of  $\text{Pd}(\text{Acac})_2$  ( $0.01522 \text{ g}$ ,  $5 \times 10^{-5} \text{ mol}$ ) in toluene in the thermostated shaker, and the mixture was agitated for 5 min. The  $\text{AlEt}_3/\text{Pd}$  ratio was varied between 2 and 16. The total volume of the solution was 10 ml. A substrate was added to the resulting black-brown “solution” and was hydrogenated under vigorous stirring at an initial hydrogen pressure of 1 atm. The reaction was monitored volumetrically and by GLC.

**The reaction between palladium bisacetylacetone (or bisacetylacetonato(triphenylphosphine)palladium) and triethylaluminum** was carried out at different ratios of the starting components in dried and deoxygenated argon in a thermostated vessel allowing preliminary pumping and filling with argon.

**Analysis of the composition and yield of gaseous products.** A certain amount of  $\text{AlEt}_3$  was syringed through a Teflon cork into a solution of  $\text{Pd}(\text{Acac})_2$  ( $0.1522 \text{ g}$ ,  $5 \times 10^{-4} \text{ mol}$ ) in toluene (20 ml) vigorously stirred in a thermostated vessel connected to a volumetric system. After gas evolution stopped, a gas sample (1 ml) was analyzed by GLC. Gases were analyzed on a Chrom-5 chromatograph equipped with a 2.4-m-long CaA-packed column and a flame-ionization detector. The oven temperature was  $100^\circ\text{C}$  and the carrier gas was nitrogen. The quantitative composition of the gases dissolved in the liquid phase was derived from solubility coefficients.

IR spectra were recorded on a Specord 75 IR spectrophotometer in the spectral range  $4000\text{--}400 \text{ cm}^{-1}$  using the KBr glass technique. Samples were prepared as Nujol mulls in a dry inert atmosphere. Nujol was thermally pretreated to remove the traces of water.

NMR spectra were obtained on a VXR-500S Varian pulse spectrometer.  $^1\text{H}$  chemical shifts are relative to tetramethylsilane.  $^{31}\text{P}$  chemical shifts are relative to 85%  $\text{H}_3\text{PO}_4$ . Positive values correspond to a downfield shift. For  $^{31}\text{P}$  NMR experiments, a solution was sealed in an insertion ampule preliminarily pumped and filled with argon.

The X-ray diffraction analysis of catalyst samples was carried out on a DRON-3M diffractometer ( $\text{CuK}_\alpha$  radiation).

TEM studies were carried out on a BS-300 microscope (Czechia). A droplet of a solution was placed on a grid covered with a carbon film and was dried in argon. The measurement conditions ruled out the melting or decomposition of the samples under the action of an electron beam.

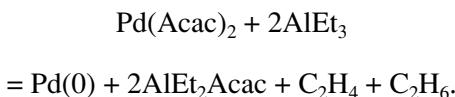
## RESULTS AND DISCUSSION

The specific activity of the system based on  $\text{Pd}(\text{Acac})_2$  and  $\text{AlEt}_3$  in styrene hydrogenation passes through a maximum at  $\text{Al/Pd} = 4$  (Fig. 1).

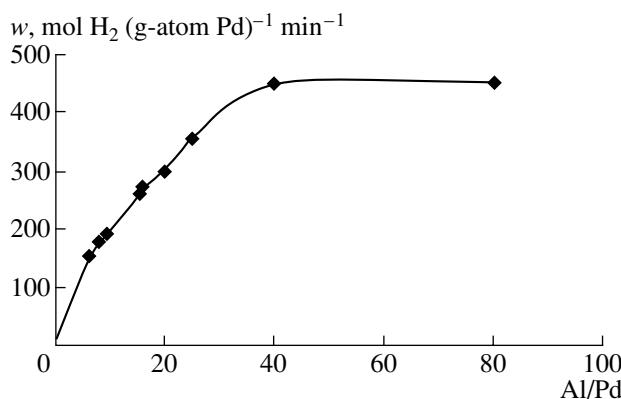
The way the specific activity varies with  $\text{Al/M}$  ( $\text{M} = \text{metal}$ ) in alkene hydrogenation typical of Ziegler catalysts. Such a maximum was previously observed for catalytic systems based on acetylacetones of metals of the first transition row [4]. Note that it appears only when trialkylaluminum is used as the reducing agent and the experiment is conducted under anaerobic and anhydrous conditions. If the solvent contains water, which causes alumoxane formation, or oxygen traces, which oxidize triethylaluminum to diethyl(ethoxy)aluminum, no inhibition of the catalytic system is observed even with an 80-fold excess of the organoaluminum compound (Fig. 2).

The peak of the styrene hydrogenation rate as a function of  $\text{Al/Pd}$  is caused by several factors.

According to  $^1\text{H}$  NMR and GLC data, the reduction of  $\text{Pd}(\text{Acac})_2$  with triethylaluminum yields  $\text{AlEt}_2\text{Acac}$  and nearly equimolar amounts of ethane and ethylene:



According to the stoichiometric equation, a twofold amount of  $\text{AlEt}_3$  is required for the complete reduction of  $\text{Pd}(\text{Acac})_2$ . However, according to  $^1\text{H}$  NMR data, at  $\text{Al/Pd} = 2.0$  and 3.4 the conversion of  $\text{Pd}(\text{Acac})_2$  is 75 and 97%, respectively, and the reaction system contains no triethylaluminum. The increase in the concentration of reduced palladium, which is responsible for hydrogenation catalysis, explains the initial branch of the plot of activity versus  $\text{Al/Pd}$ .



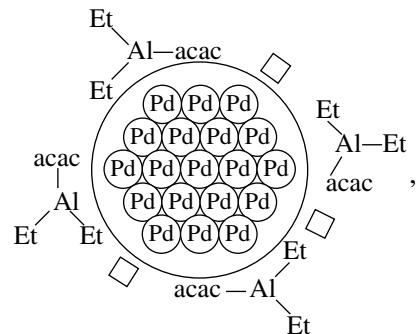
**Fig. 2.** Hydrogenation of styrene in the presence of the system  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3 + 1.5\text{H}_2\text{O}$  in toluene.  $C_{\text{Pd}} = 5 \text{ mmol/l}$ ,  $T = 30^\circ\text{C}$ ,  $P_{\text{H}_2} = 1 \text{ atm}$ , and  $[\text{St}]/[\text{Pd}] = 174$ .

The phase composition of the catalyst should be considered for a deeper understanding of the observed hydrogenation behavior. It was previously shown for Ziegler systems based on cobalt(II) acetylacetone that clusters rather than mononuclear cobalt complexes are active in the hydrogenation [16].

A TEM study of the  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3$  system showed that the reduction of  $\text{Pd}(\text{Acac})_2$  affords a microheterogeneous system. In particular, for  $\text{Al/Pd} = 4$ , Pd particles of diameter 4.2 nm dominate in the system (Fig. 3).

According to elemental analysis data, the black precipitate isolated from the reaction system  $\text{Pd}(\text{Acac})_2 + 4\text{AlEt}_3$  has the formula  $\text{Pd}_{1.0}\text{Al}_{1.1}\text{C}_{9.4}\text{H}_{14.6}$ . The IR spectrum of this substance in Nujol exhibits the absorption bands of  $\text{AlEt}_2\text{Acac}$ : 1587, 1525, 1284, 1183, 1104, 1047, and  $1010 \text{ cm}^{-1}$ . Therefore, the interaction between palladium bisacetylacetone and triethylaluminum ( $\text{Al/Pd} = 4$ ) in an inert atmosphere produces nanosized palladium particles stabilized mainly by  $\text{AlEt}_2\text{Acac}$ . The model of these nanosized palladium

particles can be presented as follows:

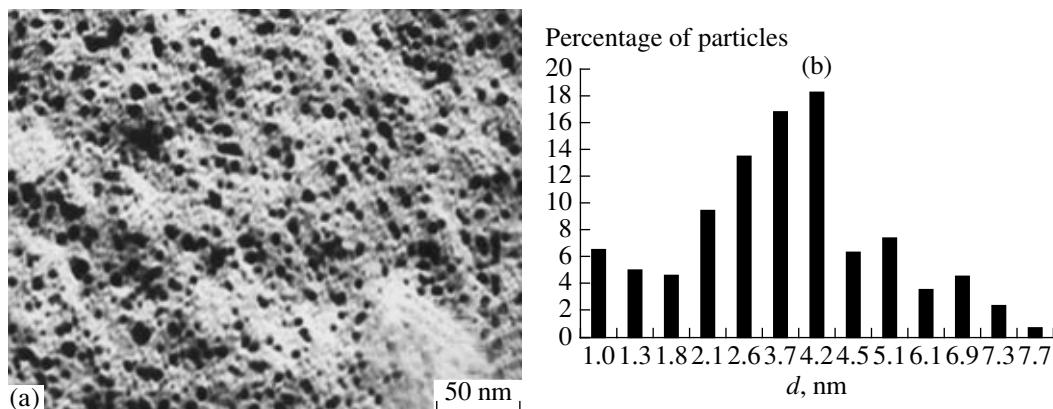


where  $\square$  is a vacant site.

The size of the dispersed particles and the nature of the ligand shell depend on the  $\text{Al/Pd}$  ratio. According to X-ray diffraction data, the catalysts obtained at different  $\text{Al/Pd}$  ratios are amorphous to X-rays and their coherent scattering region (CSR) decreases with an increase in  $\text{Al/Pd}$  (Table 1).

An increase in the degree of dispersion of the system and, accordingly, in the fraction of exposed palladium atoms with an increase in  $\text{Al/Pd}$  must also increase the hydrogenation rate.

In our opinion, the inhibition effect observed at  $\text{Al/Pd} > 4$  is due to a change in the nature of the ligand shell of the palladium nanoparticles. According to  $^1\text{H}$  NMR data, at  $\text{Al/Pd} = 5$ , the reaction system contains unreacted triethylaluminum (Fig. 4). Furthermore, the  $^1\text{H}$  NMR spectrum exhibits broad signals at 1.45 and 0.42 ppm without a hyperfine structure. These signals are characteristic of methyl and methylene groups in organoaluminum compounds. Note that the intensity of the resonance signals from  $\text{AlEt}_2\text{Acac}$  and  $\text{AlEt}_3$  decreases and the intensity of the signals at 1.45 and 0.42 ppm increases with time. Similar broad, low-intensity signals were detected at  $\text{Al/Pd} = 3.4$ . A broadening of a  $^1\text{H}$  NMR signal can be caused by the presence of radicals, intermolecular or intramolecular exchange, and the formation of a microheterogeneous system.

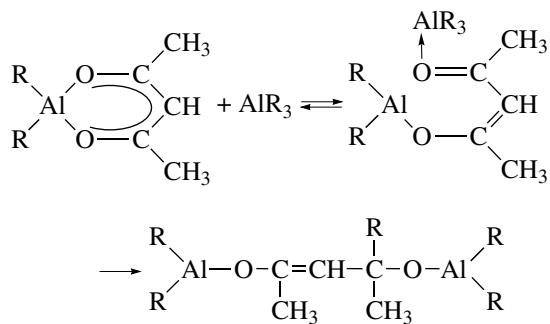


**Fig. 3.** (a) Electron micrograph of the  $\text{Pd}(\text{Acac})_2 + 4\text{AlEt}_3$  system and (b) particle size distribution.

**Table 1.** Products resulting from palladium complexes under the action of triethylaluminum

System	Pd/Al/P in the precipitate	CSR according to X-ray diffraction data, nm
Pd(Acac) <sub>2</sub> + 4AlEt <sub>3</sub>	1 : 1 : 0	2.55
Pd(Acac) <sub>2</sub> + 6AlEt <sub>3</sub>	1 : 1.7 : 0	1.35
Pd(Acac) <sub>2</sub> PPh <sub>3</sub> + 4AlEt <sub>3</sub>	1 : 0.4 : 0.6	1.30
Pd(Acac) <sub>2</sub> PPh <sub>3</sub> + 6AlEt <sub>3</sub>	1 : 1.5 : 0.6	0.94

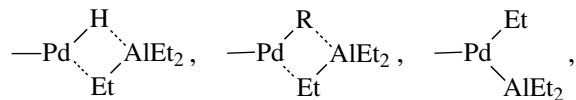
Trimethylaluminum is known to react with AlMe<sub>2</sub>Acac under mild conditions according to the equation [17]



The model reaction between equimolar amounts of AlEt<sub>2</sub>Acac and AlEt<sub>3</sub> at room temperature proceeds slowly, and only trace amounts of the final reaction product are observed even in 1 h. The interaction between AlEt<sub>2</sub>Acac and AlEt<sub>3</sub> terminates mainly at the complex formation stage, as is indicated by broad <sup>1</sup>H NMR signals at  $\delta$  = 1.45 and 0.40 ppm. Since the intensity of the resonance signals from AlEt<sub>2</sub>Acac in the spectrum of the reaction system Pd(Acac)<sub>2</sub> + 5AlEt<sub>3</sub>

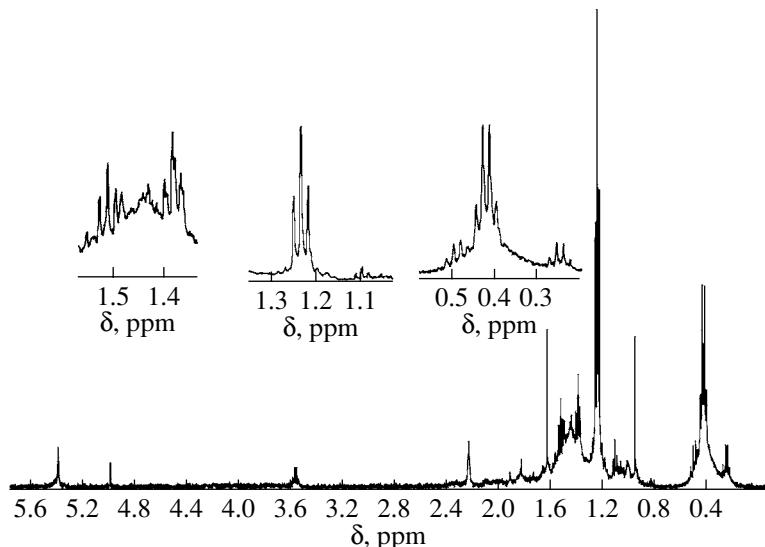
decreases with time and no signals from the product appear, we can assume that the <sup>1</sup>H NMR signals broaden owing to intramolecular exchange and to the adsorption of organoaluminum compounds (AlEt<sub>2</sub>Acac, AlEt<sub>3</sub>) on the palladium particles.

The problem of the nature of the ligand shell of the palladium nanoparticles at large Al/Pd ratios is rather complicated. According to elemental analysis data, the Al-to-Pd ratio in the precipitates increases from 1 at Al/Pd = 2 and 3.4 to 1.7 at Al/Pd = 6 and 10. The IR spectra of samples isolated from the system Pd(Acac)<sub>2</sub> + *n*AlEt<sub>3</sub> (*n* = 6, 8, 10) indicate a decreased intensity of the stretching bands  $\nu$ (C=O) +  $\nu$ (C=C) (1587 and 1525 cm<sup>-1</sup>) and  $\nu$ (C-C) +  $\nu$ (C-CH<sub>3</sub>) (1284 cm<sup>-1</sup>) of the *O,O*-chelating Acac in diethylaluminum acetylacetone. These data suggest that the role of triethylaluminum is not restricted to the reduction of palladium bisacetylacetone. When triethylaluminum enters into the complex formation reaction with AlEt<sub>2</sub>(Acac), it can remove part of this ligand from the coordination sphere of palladium and thus enhance the catalytic activity of the palladium nanoparticles. At the same time, at large Al/Pd ratios, triethylaluminum is likely to react directly with the surface Pd(0) atoms or hydride (alkyl) derivatives. The inhibiting effect of excess triethylaluminum is possibly caused by the formation of surface compounds of the types



of which the oxidative AlEt<sub>3</sub> addition product is believed to be less probable.

Triphenylphosphine oxide was introduced into the reaction system Pd(Acac)<sub>2</sub> + 10AlEt<sub>3</sub> (P(O)Ph<sub>3</sub>/Pd) = 1 during styrene hydrogenation to verify the inhibiting



**Fig. 4.** <sup>1</sup>H NMR spectrum of the Pd(Acac)<sub>2</sub> + 5AlEt<sub>3</sub> system (toluene-d<sub>8</sub> solvent).

effect of triethylaluminum. This effect manifested as a sharp (tenfold) increase in the styrene hydrogenation rate upon the addition of  $\text{P}(\text{O})\text{Ph}_3$ , which formed an adduct with  $\text{AlEt}_3$  and removed it from the coordination sphere of palladium.

The assumption regarding the inhibiting effect of  $\text{AlEt}_3$  agrees well with phenylacetylene hydrogenation data. Specific catalytic activity in phenylacetylene hydrogenation as a function of Al/Pd has a plateau at  $\text{Al/Pd} = 4\text{--}10$  and falls off sharply only at larger Al/Pd ratios (Table 2).

The above distinctions are due to the higher coordinating power of phenylacetylene as compared to styrene and to the capacity of phenylacetylene for competing for a coordination site around palladium. Alumoxanes exert no inhibiting effect. In our opinion, this is due to the fact that their aluminum atoms are coordinatively saturated through donor-acceptor interaction with oxygen during the formation of cyclic or linear oligomeric structures [18].

Modifying the  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3$  system with triphenylphosphine dramatically changes its properties, which appear to depend on the order in which the components were added.

The catalytic system based on the  $\text{Pd}(\text{Acac})_2\text{PPh}_3$  complex and  $\text{AlEt}_3$  manifests a higher activity in styrene hydrogenation than the above-considered system at any Al/Pd ratio (Fig. 1). A specific activity peak is again observed at  $\text{Al/Pd} = 4$ .

A different situation is observed for phenylacetylene hydrogenation (Table 2). In the presence of the  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3$  catalytic system, phenylacetylene is hydrogenated to ethylbenzene and the hydrogenation rates of the triple and double bonds are comparable at  $\text{Al/Pd} = 2\text{--}8$ . The system  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + \text{AlEt}_3$  shows the following distinctions. First, the hydrogenation rates of both the triple and double bonds are lower as compared to those in the phosphine-free system. No hydrogenation takes place at  $\text{Al/Pd} = 10$ . Second, an increase in the Al/Pd ratio changes the ratio between the hydrogenation rates of the triple and double bonds in favor of the latter.

According to X-ray diffraction data (Table 1) and electron microscopy, the particles resulting from the reduction of  $\text{Pd}(\text{Acac})_2\text{PPh}_3$  with triethylaluminum in an inert atmosphere are smaller than in the case of the unmodified palladium complex at the same Al/Pd ratios. For instance, particles with a diameter of 4.2 nm dominate in the  $\text{Pd}(\text{Acac})_2 + 4\text{AlEt}_3$  system, while the reduction of the  $\text{Pd}(\text{Acac})_2\text{PPh}_3$  complex yields particles with a smaller diameter of 2.5 nm (Fig. 5). The difference between the particle sizes determined by X-ray diffraction and electron microscopy arises from the fact that the width of diffraction lines depends not only on the particle size but also on the presence of defects in the nanoparticle structure.

The  $^{31}\text{P}$  NMR spectrum of the reaction system  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + 4\text{AlEt}_3$  contains broad signals at  $\delta =$

**Table 2.** Hydrogenation of phenylacetylene (PA) in the presence of  $\text{Pd}(\text{Acac})_2$ -based systems of the Ziegler type

Catalyst	Al/Pd ratio	$w, \text{ mol H}_2 \text{ (g-atom Pd)}^{-1} \text{ min}^{-1}$	
		$-\text{C}\equiv\text{C}-$	$-\text{C}=\text{C}-$
$\text{Pd}(\text{Acac})_2 + n\text{AlEt}_3$	2	39	34
	4	117	100
	6	121	122
	8	124	124
	10	113	85
	16	24	3
	2	58	67
$\text{Pd}(\text{Acac})_2\text{PPh}_3 + n\text{AlEt}_3$	4	70	79
	6	8*	82
	8	5*	17
	10	0.2*	—
	2	44	13
$\text{Pd}(\text{Acac})_2 + n\text{AlEt}_3 + \text{PPh}_3$	6	150	3
	8	162	2
	10	177	3
	16	24	3

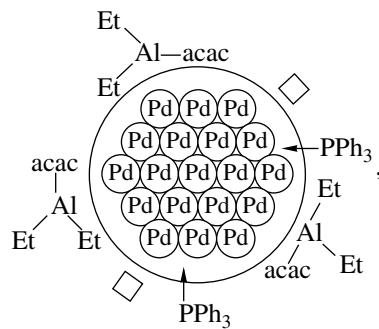
Note:  $C_{\text{Pd}} = 5 \text{ mmol/l}$ ;  $T = 30^\circ\text{C}$ ;  $P_{\text{H}_2} = 1 \text{ atm}$ ;  $[\text{PA}]/[\text{Pd}] = 182$ ; the solvent is toluene.

\* The hydrogenation of PA is accompanied by its oligomerization.

22 and 16.4 ppm (the ratio of their integrated intensities is 10.7 : 1), which are characteristic of the phosphorus nuclei of  $\text{PPh}_3$  coordinated to low-valence palladium atoms.

The IR spectrum of the black precipitate isolated from the  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + 4\text{AlEt}_3$  reaction system (recorded in Nujol) exhibits both the absorption bands of  $\text{AlEt}_2\text{Acac}$  ( $\nu(\text{C=O}) + \nu(\text{C=C}) = 1585$  and  $1525 \text{ cm}^{-1}$ ;  $\nu(\text{C=C}) + \nu(\text{C-CH}_3) = 1284$  and  $1218 \text{ cm}^{-1}$ ;  $\delta(\text{Al-CH-H}) + \nu(\text{C-CH}_3) = 1187, 1104, 1047$ , and  $1010 \text{ cm}^{-1}$ ) and those characteristic of the out-of-plane bending vibrations of the C-H and C-C bonds in the monosubstituted benzene ring ( $706, 676, 450 \text{ cm}^{-1}$ ).

Thus, the nanosized  $\text{Pd}(0)$  particles formed upon the reduction of the  $\text{Pd}(\text{Acac})_2\text{PPh}_3$  complex with triethylaluminum ( $\text{Al/Pd} = 4$ ) are stabilized by both  $\text{AlEt}_2\text{Acac}$  and  $\text{PPh}_3$ . According to elemental analysis data, the  $\text{Pd/Al/P}$  ratio in the precipitate is 1 : 0.4 : 0.6:



where  $\square$  is a vacant site.

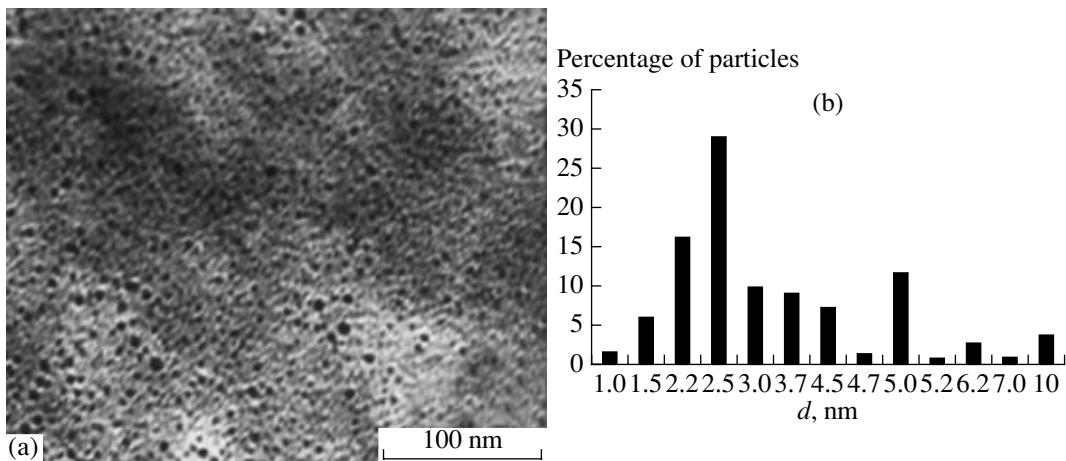


Fig. 5. (a) Electron micrograph of the  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + 4\text{AlEt}_3$  system and (b) particle size distribution (in argon).

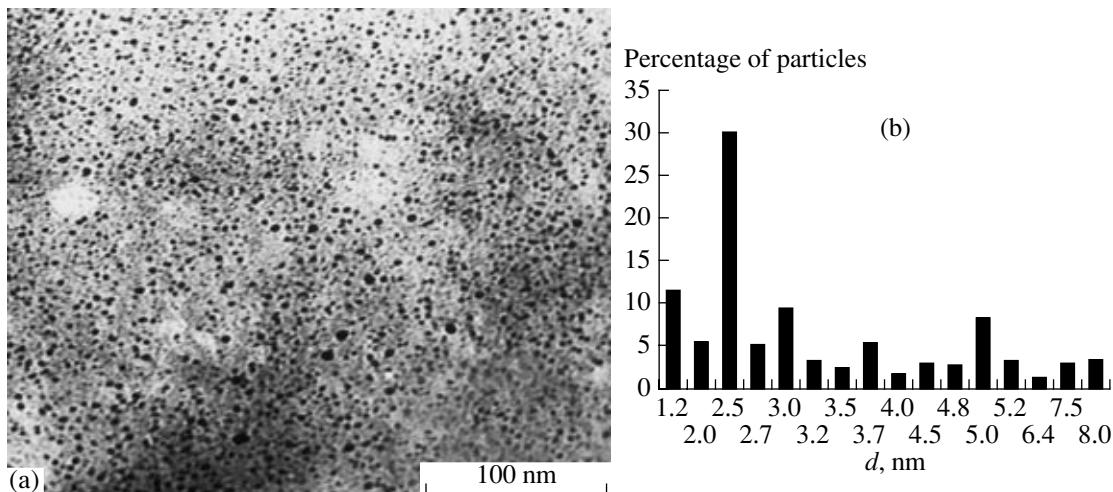


Fig. 6. (a) Electron micrograph of the  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + 4\text{AlEt}_3$  system and (b) particle size distribution (in hydrogen).

These data were obtained for the  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + 4\text{AlEt}_3$  system formed in an argon atmosphere.

The interaction between  $\text{Pd}(\text{Acac})_2$  and  $\text{AlEt}_3$  ( $\text{Al}/\text{Pd} = 4$ ) in a hydrogen atmosphere also produces a microheterogeneous system dominated by particles of diameter 2.5 nm. However, a larger proportion of 1.2-nm particles is observed (Fig. 6).

Unlike the reduction of  $\text{Pd}(\text{Acac})_2\text{PPh}_3$  with triethylaluminum in an inert atmosphere, the same process in hydrogen is accompanied by the decomposition of the phosphine ligands to an extent increasing with the  $\text{Al}/\text{Pd}$  ratio (Table 3).

The decomposition of the phosphine ligands in the palladium complexes under reductive conditions is a well-known fact. An earlier study of the nature of hydrogenation-active species based on  $\text{Pd}(\text{II})$  phosphine complexes [11] demonstrated that the decomposition of the organophosphorus ligands in the coordination

sphere of  $\text{Pd}(0)$  occurs owing to the oxidative addition of  $\text{PR}_3$  to  $\text{Pd}(0)$  followed by  $\text{Pd}-\text{C}$  bond hydrogenolysis. The resulting association species of polynuclear palladium complexes with bridging phosphide and phosphinidene ligands serve as the precursors of  $\text{Pd}(0)$  clusters.

The  $^{31}\text{P}$  NMR spectrum of the  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + 4\text{AlEt}_3 + \text{H}_2$  system contains, along with the broad signals at  $\delta = 22$  and 16.4 ppm, new broad signals at  $\delta = 24.6$  and 28.4 ppm, which can be assigned to both the coordinated triphenylphosphine molecules and bridged diphenylphosphide or phosphinidene palladium complexes without a metal–metal bond [19, 20]. Therefore, the  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + 4\text{AlEt}_3 + \text{H}_2$  system contains both  $\text{Pd}(0)$  particles stabilized by  $\text{PPh}_3$  and the association species of the polynuclear palladium complexes with phosphide and phosphinidene ligands. The proportion

of the latter increases with an increase in the Al/Pd ratio.

The regularities observed for the hydrogenation of styrene and phenylacetylene in the presence of the  $\text{Pd}(\text{Acac})_2\text{PPh}_3 + n\text{AlEt}_3$  system are related, on the one hand, to the formation of finely dispersed systems and, on the other hand, to the formation of polynuclear palladium complexes with organophosphorus ligands, which can serve as Pd(0) cluster precursors. The formation of the finely dispersed systems in the presence of triphenylphosphine explains the promoting effect of the tertiary phosphine in styrene hydrogenation.

The activity of Pd catalysts in the hydrogenation of unsaturated compounds depends on the Pd particle size and, in the case of alkynes and dienes, decreases considerably as the Pd crystallite size decreases below 1 nm [21]. This fact is attributed to either the very strong adsorption of these hydrocarbons on unsaturated sites or the geometric factor related to the small size of the palladium particles. The change in the ratio of the hydrogenation rates of the triple and double bonds indicates that phenylacetylene forms very stable complexes with the active sites. In our opinion, the enhanced bond strength can be due not only to the small size of the Pd(0) particles but also to the changes in the electron density on Pd(0) caused, for example, by the immobilization of the Pd(0) clusters on polynuclear palladium complexes with organophosphorus ligands.

Different hydrogenation properties are manifested by the  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3$  system when triphenylphosphine is introduced 1 min after  $\text{AlEt}_3$ . For styrene hydrogenation, a dramatic decrease in specific activity is observed for any Al/Pd ratio (Fig. 1). Similar data were obtained for hexene-1. Phenylacetylene is hydrogenated to styrene at a high rate in the presence of the system examined (Table 2). The hydrogenation rates of the triple and double bonds differ by a factor greater than 50 at Al/Pd = 6 and 10. A similar dependence was previously observed for the  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3$  system modified with tributylphosphine [22].

The observed differences arise from the fact that triphenylphosphine is added to a partially formed microheterogeneous system. The decomposition of  $\text{PPh}_3$  is insignificant (Table 3), and most of the phosphine remains in the reaction system. Since tertiary phosphines are stronger coordinating ligands than alkenes,  $\text{PPh}_3$  occupies vacant sites in the coordination sphere of palladium and thus prevents styrene hydrogenation. Phenylacetylene can displace triphenylphosphine and stronger ligands, for instance, phosphites, from the coordination sphere of palladium. The method suggested for the preparation of catalytic systems makes it possible to obtain catalysts for selective alkyne hydrogenation.

Thus, the catalytic properties of the Ziegler-type systems based on the palladium acetylacetonate complexes in the hydrogenation of unsaturated compounds depend, to a great extent, on the Al/Pd ratio and the

**Table 3.** Formation of benzene during the formation and functioning of the  $\text{Pd}(\text{Acac})_2 + \text{AlEt}_3$  system modified by triphenylphosphine

$\text{AlEt}_3/\text{Pd}(\text{Acac})_2$ ratio	$\text{C}_6\text{H}_6/\text{PPh}_3$ ratio in the $\text{Pd}(\text{Acac})_2\text{PPh}_3 +$ $\text{AlEt}_3$ system	$\text{C}_6\text{H}_6/\text{PPh}_3$ ratio in the $\text{Pd}(\text{Acac})_2\text{PPh}_3 +$ $\text{AlEt}_3 + \text{PPh}_3$ system
4	0.2*	0.3*
	0.8**	0.4**
	1.3***	0.7***
6	0.9*	0.2*
	1.2**	0.3**
	1.7***	0.4***
8	1.4*	0.04*
	1.5**	0.2**
	1.7***	0.3***

Note:  $C_{\text{Pd}} = 5 \text{ mmol/l}$ ;  $T = 30^\circ\text{C}$ ;  $P_{\text{H}_2} = 1 \text{ atm}$ ;  $[\text{St}]/[\text{Pd}] = 174$ ; the solvent is toluene.

\*1 minute after the introduction of all components.

\*\*After 5 min.

\*\*\*After styrene hydrogenation.

order in which the modifiers are added. The role of triethylaluminum is not restricted to the reduction of the Pd(II) complexes. At high Al/Pd ratios, triethylaluminum inhibits the catalyst through adsorption on the palladium nanoparticles. The mechanism of inhibition of the palladium catalysts by triethylaluminum calls for further investigation.

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