

# Selective Dimerization of Styrene to 1,3-Diphenylbutene-1 in the Presence of [(acac)Pd(PAr<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>/BF<sub>3</sub>OEt<sub>2</sub> Catalytic Systems

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**Abstract**—Selective dimerization of styrene to 1,3-diphenylbutene-1 in the presence of [(acac)Pd(PAr<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> + BF<sub>3</sub>OEt<sub>2</sub> catalytic systems, where R = C<sub>6</sub>H<sub>5</sub>, o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, or o-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, has been studied. Under the optimal conditions (B/Pd = 8, T = 75°C, R = C<sub>6</sub>H<sub>5</sub>), the conversion of styrene to the products exceeds the conversion for the known analogs and reaches 1.5 tons of styrene/g-atom of palladium with amounts of dimers and trimers of 91 and 9%, respectively. The dimers consist of up to 100% 1,3-diphenylbutene-1 with a trans/cis isomer ratio of 95/5.

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Dimerization of alkenes in the presence of metal complex catalysts is an effective method for the production of olefins of a higher molecular weight, which are used as intermediates in the chemical industry, or directly as the desired products [1, 2]. In particular, dimers of styrene are in demand as feedstock for organic synthesis, in the production of synthetic rubber, insulating oil, as solvents for polystyrene and heat-transfer agents, as well as the trimers [3].

Among a large number of catalysts based on transition metal compounds capable of dimerizing styrene [4–15], the catalysts based on Pd complexes are characterized not only by traditionally high selectivity of styrene conversion to dimers, but also a high conversion of styrene into the products.

In a series of efficient palladium catalysts for the selective dimerization of styrene, catalytic systems based on palladium bis-acetylacetone and boron trifluoride etherate are active also in the processes of di- and oligomerization of ethylene and propylene [16, 17], telomerization of diene hydrocarbons with secondary amines [18], and additive polymerization of norbornene and alkynnorbornenes [19, 20].

This paper presents the results of experiments on the effect of various factors, including the ratio of components of highly organized catalytic systems of the [(acac)Pd(PAr<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>/BF<sub>3</sub>OEt<sub>2</sub> composition, the nature of tertiary phosphines, temperature, and the conditions for the formation of an activated complex (AC) on the conversion of styrene to dimers. The aim was to increase the efficiency of catalytic systems formed on the basis of Pd(acac)<sub>2</sub> and BF<sub>3</sub>OEt<sub>2</sub> in the processes of the selective dimerization of styrene to 1,3-diphenylbutene-1, as well as to obtain additional information on the nature of the catalytic action of such systems, which are potentially active in the pro-

cesses of conversion of diene hydrocarbons, norbornene, and its derivatives.

## EXPERIMENTAL

**Styrene dimerization reaction** was carried out in a thermostatted glass vessel under argon. After charging the reactor with styrene and the components of the catalytic system, the reaction mixture was stirred over 0.5 h at room temperature to form the catalyst and then the temperature of the experiment was set up. The reaction rate was monitored by measuring the consumption of styrene; at the end of the experiment, styrene and the reaction products were distilled off, and the yield was determined by weighing the substances. The styrene conversion was monitored by GLC with a TSVET-100M instrument, a 2.7-m packed column with the SE-30 stationary phase, a column oven temperature of 100°C, nitrogen as the carrier gas, and a pressure at the column inlet of 0.8 atm.

Dimers were separated by vacuum distillation and analyzed by gas chromatography–mass spectrometry (MAT-212 instrument, T = 100–200°C, length of the capillary column 20 m, SE-30 phase), GLC (Chrom-5 instrument, column length 3.7 m, SE-30 phase, nitrogen carrier gas, T = 140°C), IR (a Perkin Elmer device, registration range 200–4000 cm<sup>-1</sup>), and <sup>1</sup>H NMR spectroscopy (a Varian-500S instrument, TMS standard).

**Styrene** was purified by shaking it with a 5% alkali solution until a portion of alkali became colorless. After that it was washed with distilled water, dried over anhydrous calcium chloride, and distilled in a vacuum. **Argon** was treated for the removal of moisture and oxygen by successively passing it through columns filled with phosphorus pentoxide, granular alkali,

molecular sieves 5 Å, and copper powder heated to 250°C. *Boron trifluoride etherate* (Acros) was distilled before use under argon over calcium hydride.

**Synthesis of [(acac)Pd(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>** was conducted in an argon atmosphere. Boron trifluoride etherate (0.41 ml, 3.282 mmol) was added dropwise to a solution of Pd(acac)<sub>2</sub> (0.5000 g, 1.641 mmol) and PPh<sub>3</sub> (0.8611 g, 3.282 mmol) in 40 ml of benzene. The lemon-yellow precipitate was filtered on a Schott funnel, washed with benzene and dried in a vacuum. 91% yield. Mp 174–176°C.

<sup>1</sup>H NMR (acetone-*d*<sub>6</sub>), δ 1.5 (singlet, 6H, –CH<sub>3</sub> of acac), 5.6 (singlet, 1H, –CH of acac), 7.2–7.8 (multiplet, 30H, –PPh<sub>3</sub>); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>), δ 27.5 [–CH<sub>3</sub> of acac], 102.3 (–CH of acac), 128–136 (–PPh<sub>3</sub>), 188.4 (–C=O); <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>C<sub>12</sub>) δ –153.51 (singlet, 1F), –153.56 (singlet, 4F) (BF<sub>4</sub>), the ratio of integrals of the signals of 1 : 4 corresponds to the natural abundance of <sup>10</sup>B/<sup>11</sup>B isotopes = 19.4%/80.6%); <sup>11</sup>B NMR (acetone-*d*<sub>6</sub>) δ –0.56 [BF<sub>4</sub>, quintet, 1 : 4 : 6 : 4 : 1, J<sub>B-F</sub> = 1.1 Hz]; <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>) δ 36.0 [–PPh<sub>3</sub>]).

IR (cm<sup>–1</sup>) 1523, 1565 (C=C and C=O bonds of acac group), 1590 (C=C bonds in benzene ring); 1465, 1478 (CH<sub>3</sub> of acac); 1020–1150 (BF<sub>4</sub>); 730, 750, 960, 980 (C–H bonds of benzene ring); 511, 522, 543 (bending vibrations of the P–C bonds and benzene ring).

Elemental analysis, calculated for C<sub>41</sub>H<sub>37</sub>BF<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Pd, %: Pd 13.0; C 60.3; H 4.5; P 7.6; B 1.35; F 9.3. Found, %: Pd 12.8; C 61.2; H 4.3; P 7.1; B 1.1; F 8.25.

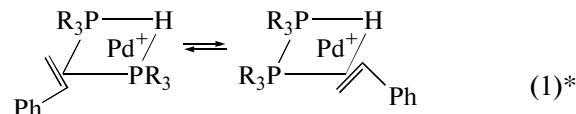
**Synthesis of [(acac)Pd(P(*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>, [(acac)Pd(P(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>, and [(acac)Pd(P(*o*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>** was carried out similarly to [(acac)Pd(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>.

## RESULTS AND DISCUSSION

For the Pd(acac)<sub>2</sub>/BF<sub>3</sub>OEt<sub>2</sub> and Pd(acac)<sub>2</sub>/PR<sub>3</sub>/BF<sub>3</sub>OEt<sub>2</sub> (R = Ph, *n*-Bu) catalytic systems, the concepts of the composition of the activated complexes (**AC**) as palladium hydrides of the HPd(L, L')<sub>n</sub>BF<sub>4</sub> type (L is unsaturated hydrocarbon, L = L' or PR<sub>3</sub>, *n* = 1, 2) were experimentally substantiated. In this case, the structural fragment BF<sub>4</sub> in the AC may be linked to Pd in charge-transfer complexes: HPd(L<sub>2</sub>–<sub>n</sub>L'<sub>n</sub>)F·BF<sub>3</sub> (*n* = 0, 1), or in the ion pair form [HPd(L, L')]<sup>+</sup>BF<sub>4</sub><sup>–</sup> (L' = PR<sub>3</sub>) [21]. General principles for the quite sophisticated mechanism of the formation of such an activated complex suggest two stages. At the first stage, the formation of the structural fragment BF<sub>4</sub> directly involves the first acetylacetone ligand at Pd, BF<sub>3</sub>OEt<sub>2</sub>, and trace amounts of H<sub>2</sub>O in an aromatic solvent. The second stage suggests the formation of the Pd–H bond with the participation of the second

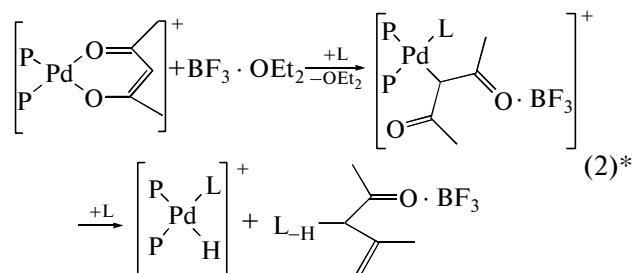
acetylacetone ligand at Pd, BF<sub>3</sub>OEt<sub>2</sub>, and an unsaturated hydrocarbon.

Among the investigated catalysts based on Pd(acac)<sub>2</sub> and BF<sub>3</sub>OEt<sub>2</sub>, the Pd(acac)<sub>2</sub> + 2PPh<sub>3</sub> + 7BF<sub>3</sub>OEt<sub>2</sub> system is the most efficient in the styrene dimerization process. In the presence of the system, the conversion of styrene to the desired products reaches 75 000 moles per g-atom of palladium with the selectivity for dimers represented by 1,3-diphenylbutene-1 up to 93% [22]. Using such a system as an example, Tkach et al. [23] also found that trans–cis rearrangement between the preactivated and activated complexes precedes the formation of the [H(L)Pd(PAr<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>–</sup> AC (Eq. 1). With the optimized parameters of the process, the catalyst conditioning time determined by the trans–cis rearrangement can reach more than 120 min [22]

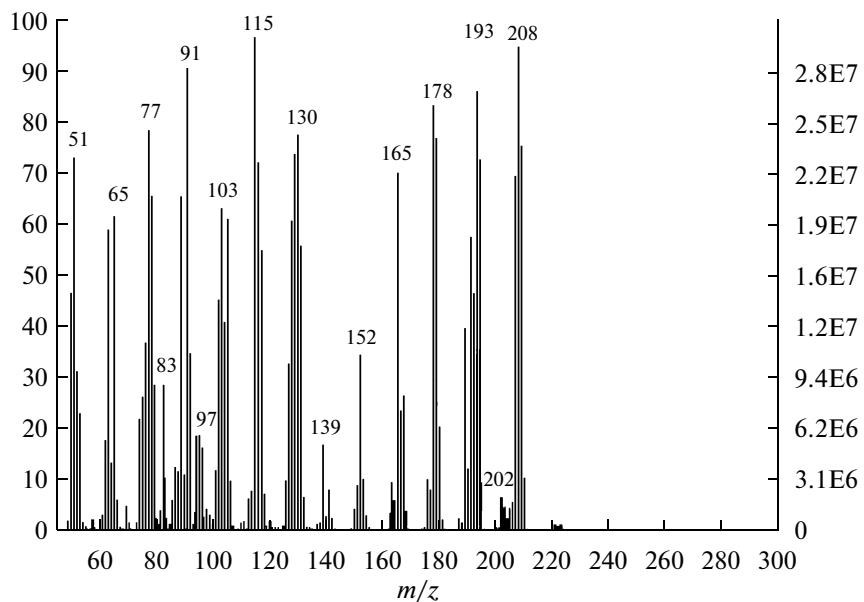


\*In the equation, BF<sub>4</sub><sup>–</sup> anion is omitted for clarity.

Based on the analysis of the array of data set on the mechanism of the formation of complexes active in the conversion of unsaturated hydrocarbons for the systems in question, we suggest a new strategy for the task-oriented design of the [H(L)Pd(PAr<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>–</sup> activated complex. The solution to this problem is based on the previous development of an efficient method for the synthesis of the cationic palladium complexes [(acac)Pd(PAr<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> [24]. These complexes are highly organized structures and, in essence, they imitate the composition of the preactivated complexes formed at the first stage of the interaction between the components of the Pd(acac)<sub>2</sub> + 2PAr<sub>3</sub> + 7BF<sub>3</sub>OEt<sub>2</sub> system. The determining difference of the [(acac)Pd(PAr<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> complexes as preactivated ones is that the organophosphorus ligands are in the cis-position to each other in the square-planar complex cation [25]. In this case, the transformation of the complexes to the AC with the participation of an unsaturated hydrocarbon and boron trifluoride excludes the preliminary trans–cis rearrangement



\*For clarity, P = PAr<sub>3</sub>, L = styrene molecule, and the BF<sub>4</sub><sup>–</sup> anion is omitted in the equatio .



**Fig. 1.** Mass spectrum of 1,3-diphenylbutene-1.

By IR, NMR, and mass spectrometry, it was shown that the product of styrene dimerization in the presence of  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4/\text{BF}_3\text{OEt}_2$  based systems is exceptionally 1,3-diphenylbutene-1. According to the GLC data, the *cis/trans* ratio of 1,3-diphenylbutene-1 isomers is 5/95. The presence of the *trans*- and *cis*-isomers is also confirmed by the appearance in the IR spectra of absorption bands at 965 and 910  $\text{cm}^{-1}$ , respectively, assigned to  $\delta_{\text{C}-\text{H}}$  vibrations at the double bond [26].

The molecular weight of 1,3-diphenylbutene-1, which is  $M = 208$ , was confirmed by mass spectrometry (Fig. 1).

Figure 2 shows the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1,3-diphenylbutene-1. In the  $^1\text{H}$  NMR spectrum, the methyl protons in the 4-position of 1,3-diphenylbutene-1 appear as a signal at 1.98 ppm. The resonance signal at 4.12 ppm characterizes the methine proton in the 3-position. Signals of vinyl protons in the 1- and 2-positions appear in the region of 6.92 ppm. In this case, the value of the constant of spin–spin coupling of protons  $\text{H}^1$  and  $\text{H}^2$  is  $^2\text{J} = 15/27 \text{ Hz}$ . This value is very close to that of spin–spin interaction between the  $\text{H}^1$  and  $\text{H}^2$  protons described in [9], indicating the *trans* double bond. The aromatic protons are characterized by a signal of 7.76 ppm.

In the  $^{13}\text{C}$  NMR spectrum, there are 6 groups of signals in the range from 20 to 150 ppm. The resonance signal at 21.76 ppm refers to the methyl carbon ( $\text{C}^4$ ). Methine carbon  $\text{C}^3$  shows a signal at 43.00 ppm. The resonance signal at 135.65 ppm characterizes  $\text{C}^1$  carbon. The signal of the second vinyl carbon  $\text{C}^2$  appears at 138.10 ppm. The signal at 146.63 ppm is attributed to the aromatic carbon bonded to  $\text{C}^3$  atom.

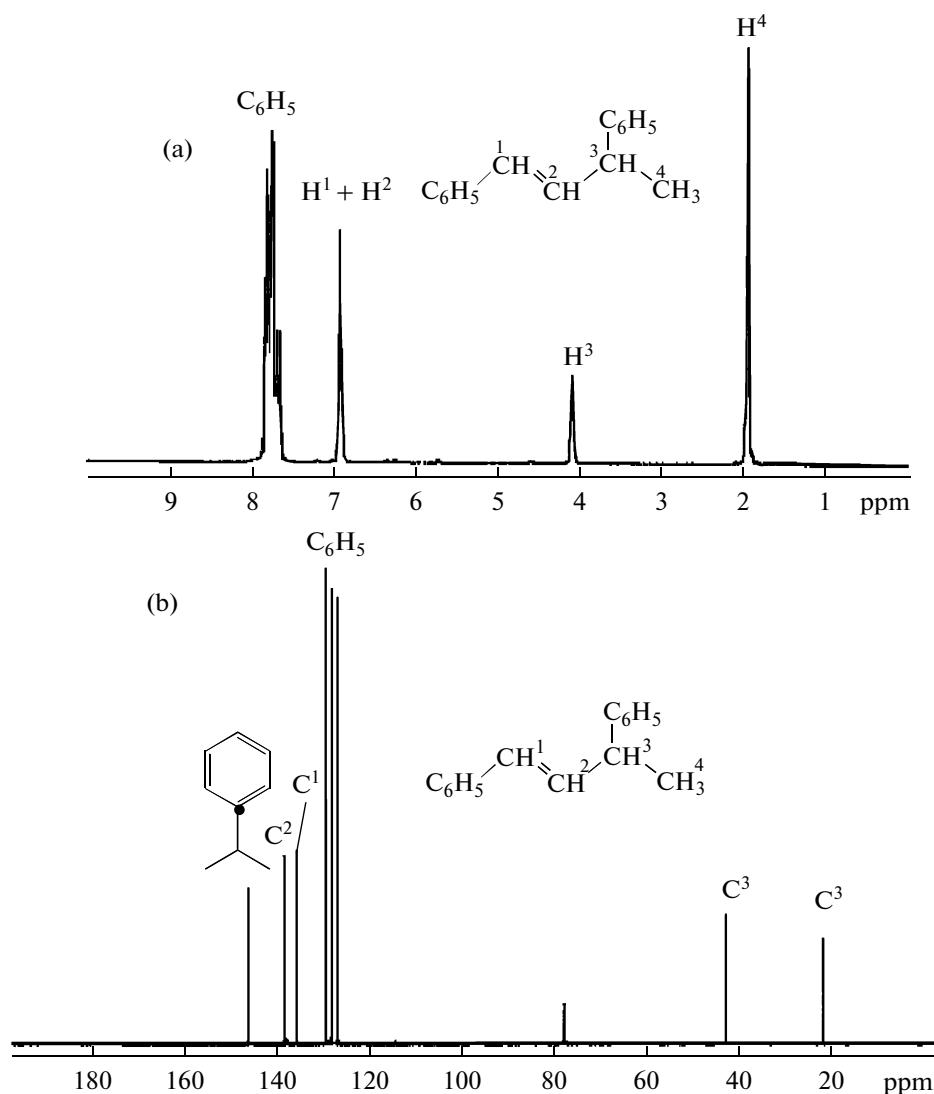
Signals of other aromatic carbons appear in the range from 126.65 to 129.23 ppm.

At the first stage of the study of the selective dimerization of styrene in the presence of two-component catalyst systems of the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4/\text{BF}_3\text{OEt}_2$  composition, we separately tested both the palladium complexes and  $\text{BF}_3\text{OEt}_2$  at 45°C. The palladium complexes per se did not show activity in the conversion of styrene. In the experiment with  $\text{BF}_3\text{OEt}_2$  (2.63 mol of styrene,  $1.25 \times 10^{-3}$  mol of  $\text{BF}_3\text{OEt}_2$ ), the complete conversion of styrene to a polymer ( $M_n = 31\,500$ ) was observed. An analysis of the polymer by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy showed that the product is atactic polystyrene typical of cationic initiators similar to those described in [27].

The data on the effect of the B/Pd ratio on the selectivity and conversion of styrene to the target products in the presence of the reference catalyst system  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + n\text{BF}_3\text{OEt}_2$  are presented in Table 1.

Table 1 shows that as the B/Pd ratio increases from 2 to 8, the selectivity for styrene dimers remains within 89–93% at a yield of trimers of 7 to 11%. At relatively large B/Pd ratios, processes of cationic polymerization of styrene begin to occur along with the main process of selective oligomerization of styrene to dimers. So, at a B/Pd ratio of 12, the amount of heavy products presented mainly by polymers of styrene reaches 28%. At a B/Pd ratio of 25, the complete conversion of styrene to polymers was observed in the standard experiment.

Note a substantial effect of the B/Pd ratio in the range from 2 to 8 on the product yield, which, in particular, increases roughly 3.5 times. Consequently, for the process of selective dimerization of styrene, the



**Fig. 2.** NMR spectra of 1,3-diphenylbutene-1 in  $\text{CDCl}_3$ : (a)  $^1\text{H}$  NMR, and (b)  $^{13}\text{C}$  NMR.

B/Pd ratio of 5–8 can be recommended as optimal for achieving a high conversion of the reactant to the desired products.

**Table 1.** The effect of the B/Pd ratio on the conversion of styrene to oligomers (catalytic system,  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + n\text{BF}_3\text{OEt}_2$ ;  $T = 70^\circ\text{C}$ ; reaction time, 6 h; styrene/Pd = 120000; quantity of Pd,  $3.7 \times 10^{-6}$  mol)

B/Pd	Yield, mol of styrene/g-at of Pd	Product composition, wt %	
		dimers	oligomers
2	26733	93	7
3	56765	93	7
5	66225	92	8
8	92242	89	11
12	111164	72	28

The typical shape of kinetic curves for styrene dimerization occurring over the  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 / 5\text{BF}_3\text{OEt}_2$  catalyst system in the range of  $50$ – $80^\circ\text{C}$  is shown in Fig. 3. It was found that the selective dimerization of styrene in the presence of the  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 / 5\text{BF}_3\text{OEt}_2$  system is first-order in catalyst and zero-order in substrate and is described by the general rate equation of the type  $W = k_{\text{obs}} \times [\text{Pd}]$  (prior to deactivation). On the basis of the data, it can be concluded that the stationary portions of the rate curves observed in the first stage within a certain time (from 50 min to 5 h) are caused by a constant concentration of the AC.

At the next step, the experiments were carried out at  $70^\circ\text{C}$  as the optimum temperature for the  $\text{Pd}(\text{acac})_2/\text{PAr}_3/\text{BF}_3\text{OEt}_2$  catalysts of the previous generation [22].

Experimental results on the dimerization of styrene in the presence of catalytic systems of the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4 + 5\text{BF}_3\text{OEt}_2$  type that are presented in Table 2 make it possible to analyze the effect of the nature of trivalent phosphorus compounds as ligands on the process in question. According to Tolman [28], the quantitative characteristics of the electronic and steric effects of phosphine ligands in the transition metal complexes are expressed by the frequency of  $\text{A}_1$  carbonyl vibrations ( $\nu$ )— $(\text{Ni}(\text{CO})_3\text{L})$  complexes were used as an example—and a cone angle in a three-dimensional model ( $\theta$ ), respectively. An analysis of the data in Table 2 shows that the decrease in the yield on passing from  $\text{PPh}_3$  to  $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$  and  $\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_3$  is caused by an increase in both the basicity of the organophosphorus ligand in the series  $\text{PPh}_3 < \text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_3 \approx \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$  and steric effects. In this case, the organophosphorus ligands  $\text{PPh}_3$  and  $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$  are characterized by the same cone angles ( $\theta = 145^\circ$ ), but differ in basicity, in contrast to  $\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_3$  and  $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ , for which the values of the cone angles vary considerably (from  $\theta = 145^\circ$  to  $\theta = 194^\circ$ ) at a relatively close basicity.

In a series of the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4/\text{BF}_3\text{OEt}_2$  systems studied as catalysts for the selective dimerization of styrene (Table 2), the composition modified by  $\text{P}(o\text{-CH}_3\text{OC}_6\text{H}_4)_3$  turned out to be substantially inactive. The observed effect is presumably due to the fact that  $\text{P}(o\text{-CH}_3\text{OC}_6\text{H}_4)_3$ , which is a monodentate organophosphorus ligand in nature, behaves as a bidentate ligand under the experimental conditions during the formation of the AC and blocks coordination sites free for the coordination of substrate molecules to Pd. This feature can be effectuated upon the coordination to palladium in preactivated complexes of organophosphorus ligands of this type not only by the phosphorus atom, but also by the oxygen atom of the methoxy group of the aryl substituent.

The effect of the temperature on the dimerization of styrene in the presence of the reference catalyst system  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + 5\text{BF}_3\text{OEt}_2$  was studied in the range from 50 to 80°C (Table 3). From the analysis of the data it follows that at the experimental conditions the maximum yield reached a value of 114500 mol of styrene per g-atom of Pd with a selectivity of 92% at 75°C. With increasing temperature of

Turnover frequency, mol of styrene/g-at of Pd × h

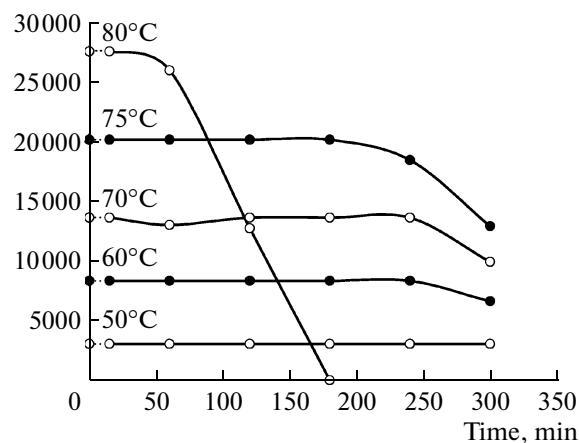


Fig. 3. The typical shape of styrene dimerization rate curves; the experiments at different temperatures  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + 5\text{BF}_3\text{OEt}_2$ ; styrene/Pd = 120000; quantity of Pd,  $3.7 \times 10^{-6}$  mol).

the experiments up to 80°C, the yield decreases sharply to 61150 mol of styrene per g-atom of Pd because of thermal deactivation of the AC.

Under the optimal conditions characterized by the use of the  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + 8\text{BF}_3\text{OEt}_2$  system and  $T = 75^\circ\text{C}$ , the yield reaches 153 000 mol of styrene per g-atom of Pd, which exceeds that for all known analogs. In particular, for the  $\text{Pd}(\text{acac})_2 + 2\text{PPh}_3 + 7\text{BF}_3\text{OEt}_2$  system, which is similar in the nature of action, the maximum yield (75 000 moles of styrene per g-atom of Pd) was obtained at 70°C. By increasing the temperature to 75°C, the yield for such a system is substantially reduced to 59 000 moles of styrene per g-atom of Pd.

The  $\text{Pd}(\text{acac})_2/\text{PAr}_3/\text{BF}_3\text{OEt}_2$  and  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4 / \text{BF}_3\text{OEt}_2$  systems, which are active in the processes of converting unsaturated hydrocarbons, have the same nature of catalytic activity due to the identity of the  $[\text{H}(\text{L})\text{Pd}(\text{PAr}_3)_2]^+ \text{BF}_4^-$  AC. A substantial difference in the performance of such systems may be caused by the different AC formation routes. This conclusion is clearly illustrated by the rate curves for the transformation of styrene in the pres-

Table 2. The effect of the nature of tertiary phosphines on the conversion of styrene to oligomers (catalytic system,  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4 + 5\text{BF}_3\text{OEt}_2$ ;  $T = 70^\circ\text{C}$ ; reaction time, 6 h; styrene/Pd = 120 000; quantity of Pd,  $3.7 \times 10^{-6}$  mol)

B/Pd	Yield, mol of styrene/g-at of Pd	Product composition, wt %		$\nu, \text{cm}^{-1}$	$\theta, \text{deg}$
		dimers	oligomers		
Ph	66225	93	7	2068.9	145
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	62690	93	7	2066.7	145
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	55670	93	7	2066.3	194
<i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	—	traces	—	2058.6	194

**Table 3.** The effect of the temperature on the conversion of styrene to oligomers (catalytic system,  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + 5\text{BF}_3\text{OEt}_2$ ; reaction time, 7 h; styrene/Pd = 120 000; quantity of Pd,  $3.7 \times 10^{-6}$  mol)

$T, ^\circ\text{C}$	Yield, mol of styrene/g-at of Pd	Product composition, wt %	
		dimers	oligomers
50	18100	95	5
60	48250	93	7
70	71100	93	7
75	114530	92	8
75*	153000	91	9
80	61150	88	12

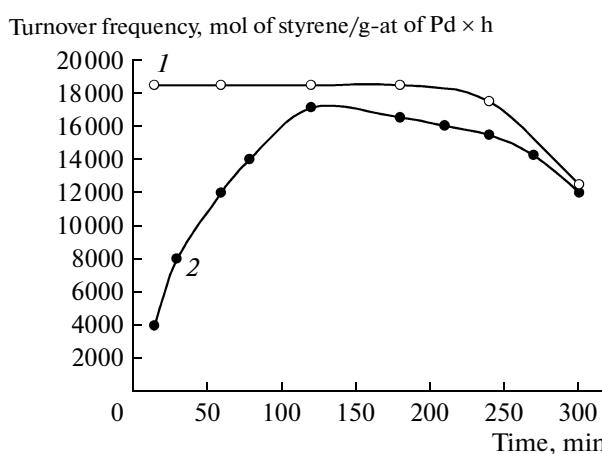
\* In the experiment, B/Pd = 8; styrene/Pd = 160 000.

ence of the  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + 8\text{BF}_3\text{OEt}_2$  and  $\text{Pd}(\text{acac})_2 + 2\text{PPh}_3 + 7\text{BF}_3\text{OEt}_2$  systems (Fig. 4). Figure 4 shows that a substantial increase in the conversion of styrene to dimers for the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4/\text{BF}_3\text{OEt}_2$  system (curve 1) even at the same temperature ( $70^\circ\text{C}$ ) is caused primarily by the absence of the catalyst formation period, which is typical of the  $\text{Pd}(\text{acac})_2/2\text{PAr}_3/n\text{BF}_3\text{OEt}_2$  catalysts of the preceding generation (curve 2).

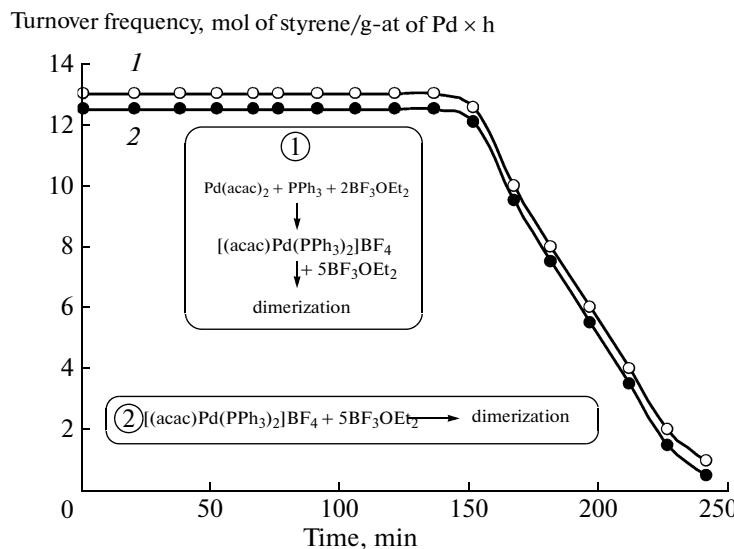
In the next stage of the study, we examined the feasibility of the in situ formation of the AC with a prescribed composition and structure in the substrate medium (without prior synthesis of cationic palladium

complexes) by charging a reactor with the components of the  $\text{Pd}(\text{acac})_2/\text{PPh}_3/\text{BF}_3\text{OEt}_2$  catalytic system in strict proportion and sequence. In the experiment, the cationic complex  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4$  was obtained directly in the styrene medium at room temperature by the reaction:  $\text{Pd}(\text{acac})_2 + 2\text{PPh}_3 + 2\text{BF}_3\text{OEt}_2 \rightarrow [(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + \text{acacBF}_2 + 2\text{OEt}_2$ . Then,  $5\text{BF}_3\text{OEt}_2$  was added to the mixture and the temperature was raised to  $70^\circ\text{C}$ . In the case of this experimental procedure, the rate curve was identical to that for the system directly using the palladium complex  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4$  (Fig. 5, curves 1, 2). A distinctive feature of the experiments on the in situ formation of active catalysts is a low reproducibility of results under optimized conditions; the feature is associated not only with an increase in the temperature to  $75^\circ\text{C}$  and the B/Pd ratio up to 8, but, above all, with a high styrene/Pd ratio, up to 160 000. The data presented are a clear illustration of the conclusion that the potentially high efficiency of the AC generated by the interaction of components of the  $\text{Pd}(\text{acac})_2/\text{PPh}_3/\text{BF}_3\text{OEt}_2$  system at high styrene/Pd ratios substantially decreases as compared with the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4/\text{BF}_3\text{OEt}_2$  system. This may be due to the relative increase in the amount of uncontrolled impurities in the substrate and, consequently, to the development of side processes at the stage preceding the formation of the AC as an ionic entity. Thus, to obtain high yields of styrene dimers, the direct use of palladium complexes of the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4$  type is preferred; the synthesis of the complexes is relatively simple and is characterized by high yields (90% or more).

Thus, it was found that the catalytic systems of the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4/\text{BF}_3\text{OEt}_2$  composition are highly efficient catalysts for the selective dimerization of styrene to 1,3-diphenylbutene-1. Under the optimum conditions (B/Pd = 8,  $T = 75^\circ\text{C}$ , Ar = Ph), the conversion of styrene to products reaches 1.5 t per g-atom of Pd, giving dimers 91 and 9% trimers; with the dimers containing up to 100% of *trans*- and *cis*-1,3-diphenylbutene-1 in the 95/5 ratio. It was shown that the decrease in the activity and conversion of styrene into the target products on the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4/\text{BF}_3\text{OEt}_2$  catalyst system when changing the nature of the organophosphorus ligands in the series  $\text{PPh}_3 < \text{P}(\text{o}-\text{CH}_3\text{C}_6\text{H}_4)_3 \approx \text{P}(\text{p}-\text{CH}_3\text{C}_6\text{H}_4)_3$  is caused by both an increase in their basicity and steric properties. The possibility of obtaining activated complexes of a given composition and structure in the substrate medium in situ (without prior synthesis of the cationic Pd complexes) by charging the reactor with the components of the  $\text{Pd}(\text{acac})_2/\text{PPh}_3/\text{BF}_3\text{OEt}_2$  catalytic system was studied. It was shown that the direct use of complexes of the  $[(\text{acac})\text{Pd}(\text{PAr}_3)_2]\text{BF}_4$  type is preferred to obtain high yields of styrene dimers.



**Fig. 4.** The dependence of the activity on the reaction time for catalyst systems: (1)  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + 8\text{BF}_3\text{OEt}_2$ ; styrene/Pd = 120 000,  $T = 70^\circ\text{C}$ ; (2)  $\text{Pd}(\text{acac})_2 + 2\text{PPh}_3 + 7\text{BF}_3\text{OEt}_2$  (styrene/Pd = 105 000,  $T = 70^\circ\text{C}$ ).



**Fig. 5.** Comparison of systems, in which complex  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4$  is formed *in situ* by the interaction of  $\text{Pd}(\text{acac})_2 + 2\text{PPh}_3 + 2\text{BF}_3\text{OEt}_2$ , with the  $[(\text{acac})\text{Pd}(\text{PPh}_3)_2]\text{BF}_4 + 5\text{BF}_3\text{OEt}_2$  system ( $T = 70^\circ\text{C}$ , styrene/Pd = 50 000).

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