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Steric and Electronic Factors in the Promoting Activity of Diphosphine Ligands in Cyclohexene Hydrocarbomethoxylation Catalyzed by Palladium Acetate

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Abstract—Cyclohexene hydrocarbomethoxylation catalyzed by $Pd(OAc)_2$–*p*-toluenesulfonic acid–diphosphine systems has been investigated for a wide range of diphosphine structures and concentrations. The factors controlling the activity of the palladium-containing catalysts include the hydrocarbon moiety of the ligand and the mutual arrangement of the phosphine groups. A comparison between the promoting effects of monophosphine and diphosphine ligands has demonstrated that bridged *trans*-diphosphines are more efficient in kinetic and concentration terms (TOF and P/Pd ratio, respectively). In particular, the promoting activity of diphosphines is one order of magnitude higher than that of triphenylphosphine, and this effect is attained at 8–65 times lower P/Pd ratios. It is discussed how the catalytic properties of the systems depend on the chelate effect and on the geometric compatibility between the diphosphine structure and the arrangement of vacant *s* and *d* orbitals of the palladium center.

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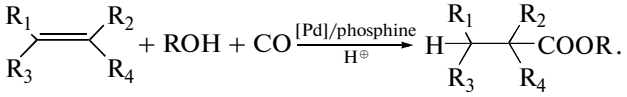
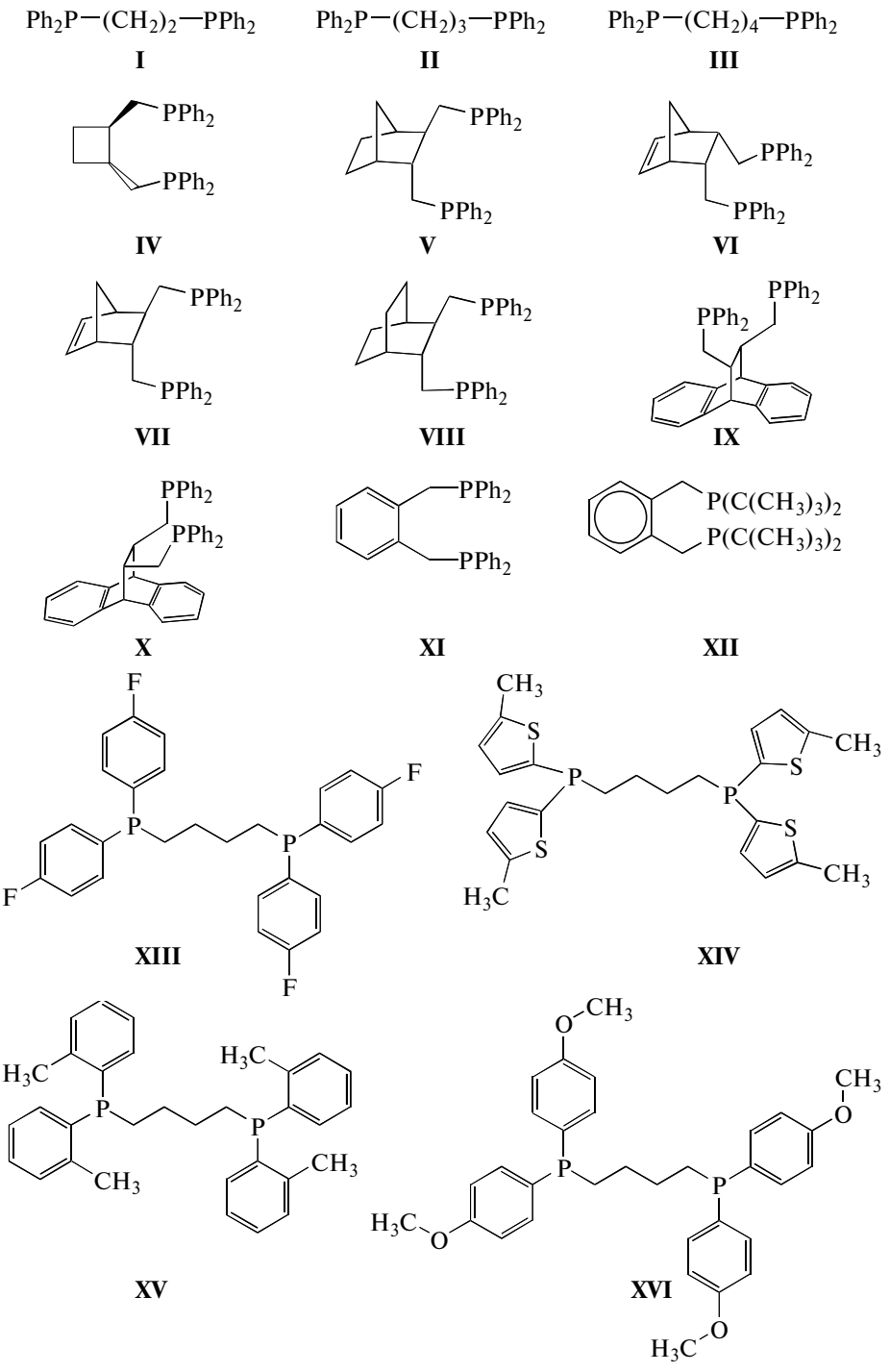
Olefin carbonylation catalyzed by transition metal complexes is a promising way of producing various organic compounds, including pharmaceuticals and agrochemicals [1]. An important carbonylation reaction is alkene hydrocarboalkoxylation in the presence of a palladium complex. This reaction provides means to obtain various esters from readily available alkenes in one step [2]. In 2008, Lucite company commercialized the ethylene hydrocarbomethoxylation process [3]:



Among the catalytic systems employed in alkene hydrocarboalkoxylation, of particular interest are palladium derivatives promoted with strong protonic acids and free phosphines [4–7]. Among the latter, diphosphines are attracting increasing interest, for they act as a chelating agent on the palladium center of the catalyst and form more stable complexes than ordinary phosphines do. This produces a significant effect on the kinetics and regioselectivity of alkene hydroalkoxycarbonylation [3, 8–10].

Although it is obviously essential to understand how the efficiency of palladium complexes in alkene hydrocarboalkoxylation depends on the structure of the diphosphine ligand, there have been no systematic studies in this area. Because of this, we studied the effect of the structure of various diphosphines on the kinetic parameters of cyclohexene hydrocarbomethoxylation as a model reaction. This reaction was chosen for the reason that all reaction sites in cyclohexene are chemically equivalent and the only hydrocarbomethoxylation product is methyl cyclohexanecarboxylate. In addition, we did not expect any considerable extent of copolymerization between cyclohexane and CO, so the run of the reaction was anticipated to characterize the efficiency of the catalytic system as such.

The cyclohexene hydrocarbomethoxylation promoters examined in this study were bis(diphenylphosphino)alkanes **I**–**III**, whose molecules have a two-, three, and four-methylene bridge, respectively, and bisdiphenylphosphines **IV**–**XVI**, which have a four-atom bridge and can form palladium complexes with a bite angle suitable for efficient catalysis of hydrocarbomethoxylation [11]. The structures of synthesized diphosphines are presented below:



EXPERIMENTAL

Diphosphine Synthesis

Some of the diphosphines used in this work were synthesized via standard procedures. These are compounds **I**–**III** [12], **IV** [13], **V** [14, 15], **VI** [14, 15], **VII** [16], **VIII** [17], **IX** [18], **XI** [9], and **XII** [9]. Hitherto unreported *cis*-2,3-bis(diphenylphosphinemethyl)norbornene was obtained in the same way as its *trans* isomer, using the corresponding ditosylate as the starting compound. Aryltetramethylenediphosphines **XIII** and **XIV** were synthesized from the corresponding 1,4-tetrachlorodiphosphinebutane using our original, recently reported procedure [19].

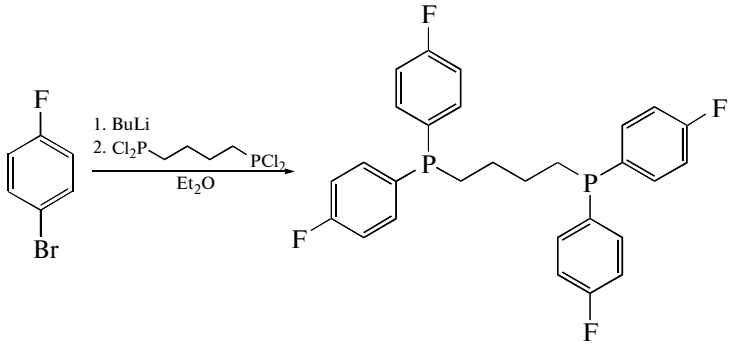
Synthesis of diphosphine VI. Finely divided Li (1 g, 143 mmol) was added to a solution of triphenylphos-

phine (12.45 g, 47.5 mmol) in 70 mL of absolute tetrahydrofuran (THF). The reaction mixture was stirred at room temperature overnight, and a solution of *cis*-2,3-tosyloxymethylnorbornene (12.2 g, 26.4 mmol) obtained via a procedure described by Bricklebank et al. [12], in 30 mL of absolute THF, was then added. The mixture was stirred at room temperature for 20 min and was treated with an aqueous NH_4Cl solution, 10% H_2SO_4, and a saturated NaCl solution. The organic layer was separated and was dried over Na_2SO_4. The solvent was removed in vacuo. The residue was recrystallized from ethanol. Yield: 5 g (42%).

^{31}P NMR ($CDCl_3$), ppm: –17.14.

^{1}H NMR ($CDCl_3$), ppm: 7.54 (m, 10H), 7.38 (m, 10H), 6.14 (s, 2H), 3.06 (s, 2H), 2.41 (s, 4H), 2.28 (s, 2H), 2.20 (m, 2H), 1.43 (d, 1H), 1.17(d, 1H).

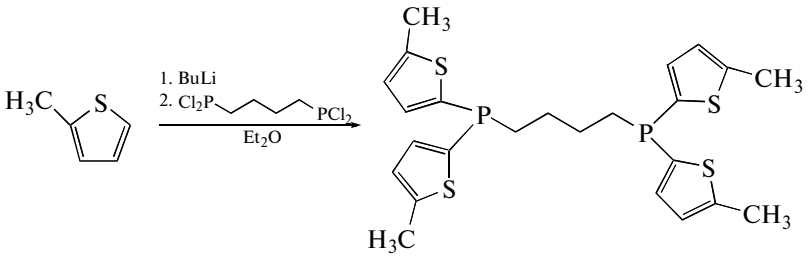
^{13}C NMR ($CDCl_3$), ppm: 139.6 (d), 138.4 (d), 135.5 (s), 133.0 (d), 132.6 (d), 128.5 (d), 128.38 (s), 128.34 (d), 48.6 (s), 47.3 (d), 39.54 (d), 39.4(d), 29.1 (d).



Synthesis of diphosphine XIII. A solution of BuLi (38.5 mmol) in hexane (1.6 N, 24 mL) was added dropwise to 4-fluorobromobenzene (4.2 mL, 38.5 mmol) in 40 mL of absolute diethyl ether under cooling (–40°C). The reaction mixture was warmed to room temperature and was stirred for 4 h. Thereafter, a solution of 1,4-tetrachlorodiphosphinebutane (2 g, 7.7 mmol) in 2 mL of absolute diethyl ether was added dropwise to the reaction mixture under cooling with a water–ice mixture. The reaction mixture was stirred at room temperature overnight. On the next day, it was treated with water (20 mL). The organic layer was separated and was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was dissolved in hot ethanol. The precipitated substance was filtered out and dissolved in benzene, and the solution was filtered through a silica gel bed. Yield: 1.8 g (47%).

^{31}P NMR ($CDCl_3$), ppm: –18.53.

^{1}H NMR ($CDCl_3$), ppm: 7.34 (m, 8H), 7.04 (t, 8H), 1.97 (t, 4H), 1.52 (m, 4H).

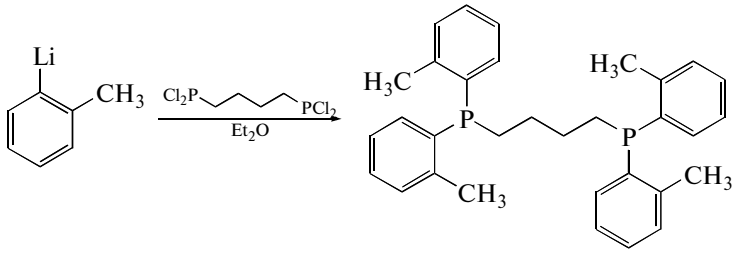


Synthesis of diphosphine XIV. A solution of BuLi (38.5 mmol) in hexane (1.6 N, 24 mL) was added dropwise to 2-methylthiophene (3.9 mL, 40.4 mmol) in 40 mL of absolute diethyl ether under cooling (–40°C). The reaction mixture was warmed to room temperature and was stirred for 4 h. Thereafter, a solution of 1,4-tetrachlorodiphosphinebutane (2 g, 7.7 mmol) in 2 mL of absolute diethyl ether was added dropwise to the reaction mixture under cooling with a water–ice mixture. The reaction mixture was stirred at room temperature overnight. On the next day, it was treated with water (20 mL). The organic layer was separated and was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was dissolved in hot ethanol. The precipitated substance was collected on a filter and vacuum-dried. Yield: 2.8 g (72%).

^{31}P NMR ($CDCl_3$), ppm: –41.21.

^{1}H NMR ($CDCl_3$), ppm: 7.15 (dd, 4H), 6.72 (m, 4H), 2.52 (s, 12H), 2.09 (t, 4H), 1.58 (m, 4H).

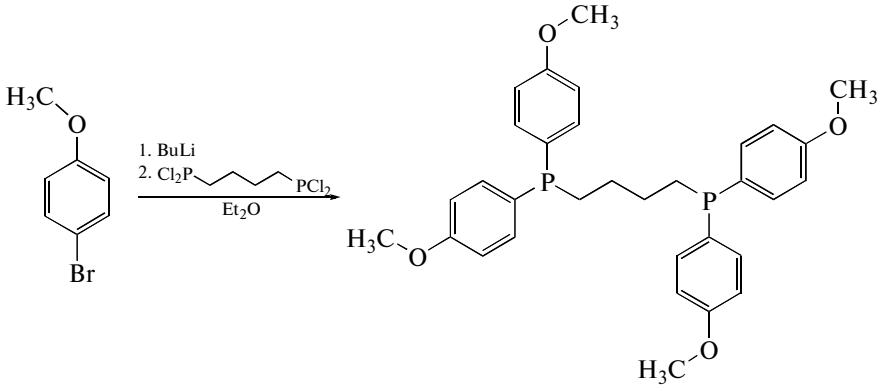
^{13}C NMR ($CDCl_3$), ppm: 145.99, 137.40, 135.24, 126.1, 31.76, 27.37, 15.60.



Synthesis of diphosphine XV [20]. A solution of *o*-bromotoluene (4.6 mL, 38.5 mmol) in 15 mL of absolute diethyl ether was added dropwise to Li (0.53 g, 77 mmol) in 2 mL of absolute diethyl ether. The reaction mixture was boiled for a few hours, and a solution of 1,4-tetrachlorodiphosphinebutane (2 g, 7.7 mmol) in 2 mL of absolute diethyl ether was then added under cooling with a water–ice mixture. The reaction mixture was stirred at room temperature overnight. On the next day, it was treated with water (20 mL). The precipitate was collected on a filter, washed with ethanol (20 mL, two times) and with benzene (20 mL, two times), and vacuum-dried. Yield: 1.5 g (41%).

^{31}P NMR ($CDCl_3$), pp: –38.18.

^{1}H NMR ($CDCl_3$), ppm: 7.16 (m, 16 H), 2.40 (s, 12H), 1.97 (t, 4H), 1.60 (m, 4H).



Synthesis of diphosphine XVI [21]. A solution of BuLi (38.5 mmol) in hexane (1.6 N, 24 mL) was added dropwise to *p*-bromoanisole (7.2 mL, 38.5 mmol) in 40 mL of absolute diethyl ether under cooling (–40°C). Next, the reaction mixture was warmed to room temperature and was stirred for 4 h. Thereafter, a solution of 1,4-tetrachlorodiphosphinebutane (2 g, 7.7 mmol) in 2 mL of absolute diethyl ether was added dropwise to the reaction mixture under cooling with a water–ice mixture. The reaction mixture was stirred at room temperature overnight. On the next day, it was treated with water (20 mL). The organic layer was separated and was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was chromatographed in a SiO_2-packed column (initially in the benzene : petroleum ether = 1 : 1 system and then in benzene). Yield: 1.8 g (43%).

^{31}P NMR ($CDCl_3$), ppm: –27.85.

^{1}H NMR ($CDCl_3$), ppm: 7.10 (m, 16H), 3.84 (s, 6H), 3.74 (s, 6H), 2.00 (m, 4H), 1.78 (m, 4H).

Kinetic Experiments

Cyclohexene hydrocarbomethoxylation was carried out in toluene in a batch reactor [22] at a constant temperature and CO pressure. The constant temperature was maintained by circulating a hot organic medium through the reactor jacket. All experiments were performed at 105°C, a CO pressure of 2.1×10^6 Pa, and the following concentrations (mol/L): $[C_6H_{10}] = 0.1$, $[CH_3OH] = 0.45$, $[(CH_3COO)_2Pd] = 1.0 \times 10^{-3}$, $[TsOH] = 1.2 \times 10^{-2}$. In each series of experiments, we varied the concentration of one of the ligands. At certain intervals, the reaction mass was sampled from the reactor, and the samples were analyzed by GLC on a Tsvet-163 chromatograph (flame-ionization detector, 3000 × 3 mm glass column, Chromosorb W (80/100 mesh) as the support, OV-275 (3%) as the stationary phase, argon as the carrier gas (30 mL/min), injection port temperature of 225°C). The analyses were carried out in the temperature-programmed mode in the temperature range from 75 to 205°C at a heating rate of 8 K/min. Chromatographic calculations were performed using the MultiKhrom program. The reactants and products were identified as their retention times, and the component concentrations were determined by comparing the observed chromatograms with the chromatograms of artificial mixtures with known

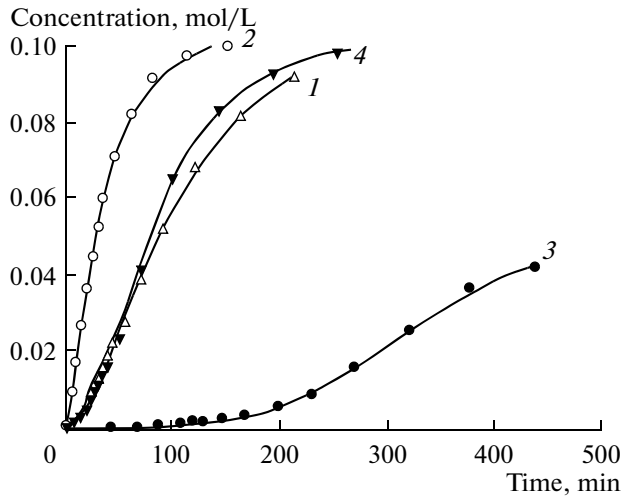


Fig. 1. Methyl cyclohexanecarboxylate accumulation kinetics at a diphosphine concentration of 3.0×10^{-3} mol/L: (*1*) ligand **IV**, (*2*) ligand **V**, (*3*) ligand **VI**, and (*4*) ligand **VIII**.

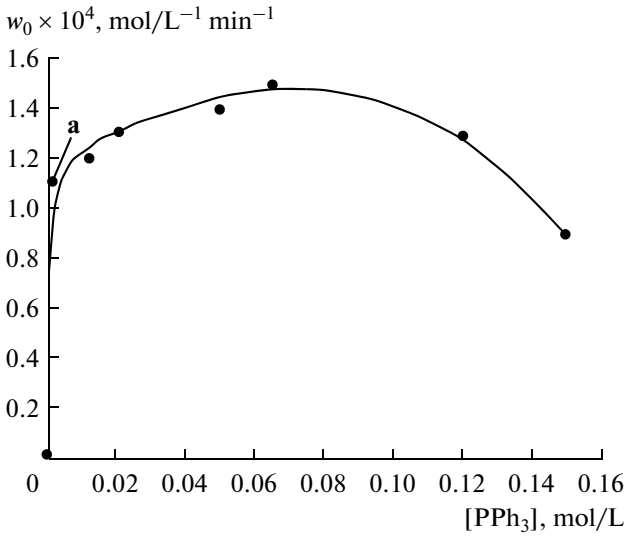


Fig. 2. Effect of the triphenylphosphine concentration on the initial cyclohexene hydrocarbomethoxylation rate.

component concentrations. The internal standard was *o*-xylene.

RESULTS

In order to study the effects of the diphosphine ligand structure and concentration on the cyclohexene hydrocarbomethoxylation rate, we carried out 12 series of experiments in which the catalyst components were $(CH_3COO)_2Pd$, *p*-TsOH, and one of diphosphines **I**–**XII**. For comparing the behaviors of the diphosphine and monophosphine ligands, we performed an additional series of experiments in which triphenylphosphine was used as the ligand.

Figure 1 plots typical dependences of the concentration of the resulting methyl cyclohexanecarboxylate on the reaction time for different catalytic systems. Each concentration versus time curve has an autocatalytic segment indicating the formation of catalytically active complexes during the reaction. With the system involving ligand **V**, there is almost no induction period. Initial reaction rates were derived from the slope of the initial portions of the curves after the end of the autocatalytic period. The kinetic data obtained in this way are presented as plots of the initial hydrocarboalkoxylation rate versus the phosphine ligand concentration (Figs. 2, 3). The curves obtained for ligands **III**–**IX** show an extremum. The systems involving ligands **I**, **II**, and **X**–**XII** are practically inactive throughout the ligand concentration range examined. It is interesting that the reaction rate maximum for the system involving triphenylphosphine corresponds occurs at a much larger P/Pd ratio (~65) than in the case of the systems involving the diphosphine ligands (**III**–**IX**). For diphosphines **III** and **VIII**, the maximum rate is observed at a P/Pd ratio close to 2; for ligands **IV**–**VII** and **IX**, at much larger P/Pd values of ≈ 8. The maximum initial rate w_0 for ligands **III**–**IX** is higher than for PPh_3 (0.150×10^3 mol L^{-1} min^{-1}). It is significant that *trans*-diphosphine **VII** is a 3 times more effective promoter than its *cis* isomer **VI**. Note that the other diphosphine ligands with the *cis* arrangement of phosphine groups (**X**–**XII**) practically do not accelerate cyclohexene hydrocarbomethoxylation. It is noteworthy that the presence of a multiple bond has an effect on the efficiency of the diphosphines. For example, unsaturated diphosphine **VII** is a nearly 2 times less effective promoter than its hydrogenated analogue **V**.

In order to study the effect of the substituents at the phosphorus atoms on the promoting properties of the diphosphine ligands in cyclohexene hydrocarbomethoxylation, we carried out four series of experiments on diphosphines **XIII**–**XVI**, varying their concentrations, with the other conditions fixed (Fig. 4). The increase in electron-donating power in the order **XIII** < **XV** < **XVI** is accompanied, on the qualitative level, by a decreases in the catalytic activity of the system. Unsubstituted diphosphine **III** and methylthiophene-substituted ligand **XIV** are outliers from this order. This is indicated by the turnover frequency (TOF) data referring to the maximum reaction rate for the **TOF** catalytic systems:

Ligand	**I**, **II**, **X**–**XII**	PPh_3	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**XIII**	**XIV**	**XV**	**XVI**
TOF, h^{-1}	0	9.0	21.0	42.0	150.0	15.0	54.0	63.0	57.0	3.0	3.5	1.5	0.9

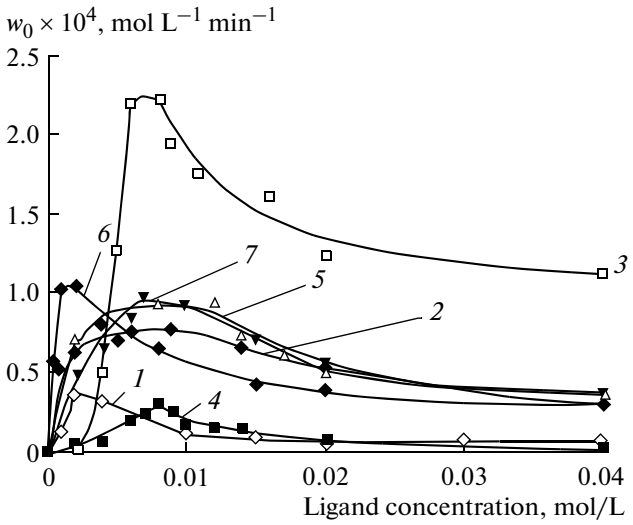


Fig. 3. Effect of the diphosphine ligand concentration on the rate of cyclohexene hydrocarbomethoxylation in the presence of the catalytic systems with the following ligands: (*1*) $Ph_2P–(CH_2)_4–PPh_2$ (**III**), (*2*) $Ph_2P–CH_2–C_4H_6–CH_2–PPh_2$ (**IV**), (*3*) *trans*-**I**), *2* – $Ph_2P–CH_2–C_4H_6–CH_2–PPh_2$ (**IV**), *3* – *транс*-$C_7H_{10}(CH_2PPh_2)_2$ (**V**), (*4*) *cis*-$C_7H_8(CH_2PPh_2)_2$ (**VI**), (*5*) *trans*-$C_7H_8(CH_2PPh_2)_2$ (**VII**), (*6*) $C_8H_{12}(CH_2PPh_2)_2$ (**VIII**), and (*7*) $(C_6H_4CHCHCH_2PPh_2)_2$ (**IX**).

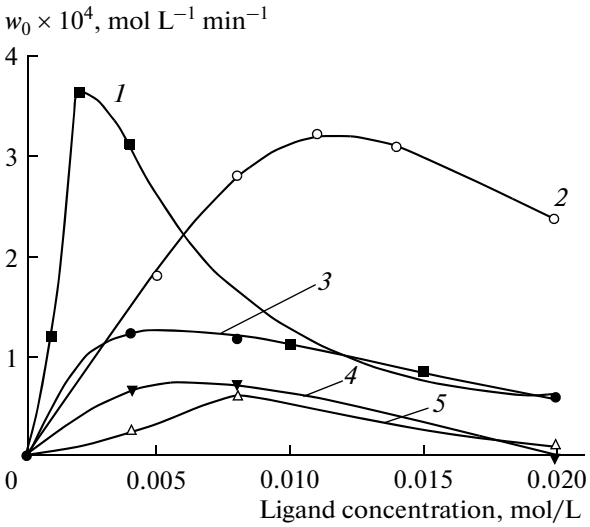


Fig. 4. Effect of the diphosphine ligand concentration on the cyclohexene hydrocarbomethoxylation rate for the following ligands with electron-withdrawing substituents: (*1*) $Ph_2P–(CH_2)_4–PPh_2$ (**III**), (*2*) $(H_3C–C_4H_2S)_2P–(CH_2)_4–P(SC_4H_2–CH_3)_2$ (**XIV**), (*3*) $(FC_6H_4)_2P–(CH_2)_4–P(C_6H_4F)_2$ (**XIII**), (*4*) $(H_3C–C_6H_4)_2P–(CH_2)_4–P(C_6H_4–CH_3)_2$ (**XV**), and (*5*) $(H_3C–O–C_6H_4)_2P–(CH_2)_4–P(C_6H_4–O–CH_3)_2$ (**XVI**).

DISCUSSION

The catalytic activity versus ligand concentration curve for the $Pd(OAc)_2–PPh_3$ system (Fig. 2) differs noticeably in shape from the same curves for the $Pd(OAc)_2$–diphosphine ligand systems, which have an extremum (Fig. 3). The initial segment of the curve presented in Fig. 2 (up to point **a**) indicates a sharp increase in catalytic activity. This is seemingly due to the fact that, in this region, the catalyst component ratio is $[PPh_3]/[Pd(OAc)_2] < 2$, well below the stoichiometric ratio. Under these conditions, the concentration of the resulting active phosphine–palladium complexes—$Pd(PPh_3)_2(TsO)_2$ and $Pd(PPh_3)_2(OAc)_2$ —is limited by the amount of triphenylphosphine introduced into the system. However, as the PPh_3 concentration is further raised, the resulting active complexes are increasingly involved in fast, reversible, ligand-exchange reactions yielding less active complexes. Thus, because of the existence of a complicated equilibrium involving the formation of active complexes and their conversion into low-activity complexes via ligand exchange, the concentration of active complexes as a function of $[PPh_3]$ passes through an extremum and the hydrocarbomethoxylation rate as a function of $[PPh_3]$ has a kink. Even at small $[PPh_3]/[Pd(OAc)_2]$ ratios, the catalytic system remains homogeneous owing to the stabilizing effect of *p*-toluenesulfonic acid and the alkene on palladium [6].

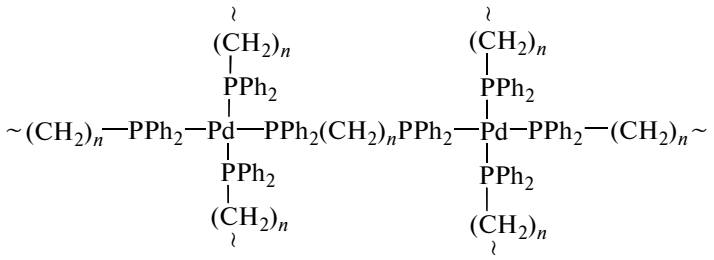
The existence of an extremum in the depeLndence of the reaction rate on the diphosphine concentration suggests that the concentration of active complexes is determined by pure kinetic factors. Apparently, these complexes form under conditions of a nearly irreversible reaction. This is the reason why the ascending portions of the curves plotted in Fig. 3 are highly sloping at low diphosphine concentrations. The fairly sharp decrease in the reaction rate after its passage through the maximum is evidence that the diphosphines are involved in rapid ligand exchange yielding less active complexes.

The high promoting activity of the diphosphine ligands with *trans* phosphine groups at bridging structures might seem paradoxical. All of the *trans*-diphosphines (**IV**, **V**, **VII**–**IX**) are indeed superior in promoting power to the *cis* isomers (**VI**, **X**) and to the nonrigid diphosphines. This is apparently due to the fact that coordination between palladium and a rigid *trans*-diphosphine with a suitable geometry (specifically, a suitable length of the bridge between the phosphorus atoms) allows generation of species displaying the highest catalytic efficiency. This reasoning underlies the concept of a bite angle formulated by van Leenwen et al. [11].

The low activity of ligand **VII**, which has a double bond, as compared to the activity of its hydrogenated analogue **V**, indicates that **VII** possibly forms oligomers whose coordination to the palladium center makes it sterically less accessible to the reactants.

We believe that the almost complete inertness of ligands **I** and **II** in cyclohexene carbomethoxylation and the noticeable promoting effect of ligand **III** can

be explained in terms of the chelate effect, which makes the formation of sterically unstrained metallacycles via coordination between a linear bidentate ligand and a complex-forming metal energetically favorable [24, 25]. Accordingly, for diphosphines **I** and **II**, a more likely process is the competitive formation of inactive polynuclear complexes whose metal atoms are diphosphine-bridged:



Our finding that the promoting power of substituted 1,4-bisdiphenylphosphines increases in the order **XIII** < **XV** < **XVI** is in qualitative agreement with the activating effect of electron-withdrawing substituents in diphosphines on $PdCl_2$-catalyzed styrene hydrocarboalkoxylation [25]. This can be explained in terms of the strengthening of back donation in the formation of Pd–P bonds in the palladium–diphosphine complexes. The higher activity of the base ligand **III** compared to its substituted analogues **XIII**, **XV**, and **XVI** is likely due to the absence of steric hindrance to palladium chelation with **III**. The unexpectedly strong promoting effect of the methylthiophene substituents in **XIV** suggests that this ligand forms more stable complexes owing to its higher denticity. The decrease in TOF on passing to the catalytic systems with ligands **XIII**–**XVI** is due to the sharp decrease in the reaction rate and to the shift of the rate peak to higher diphosphine concentrations.

On the whole, our data point out the necessity of systematically investigating the electronic and steric effects of substituents in diphosphine ligands on the rate and regioselectivity of the reaction.

The marked difference between the P/Pd values maximizing the reaction rate for the diphosphine- and triphenylphosphine-containing systems deserves special attention. We believe that this difference stems from the fact that the chelates are more stable than the complexes with monodentate ligands. This higher stability is due to the synergism of the entropic and energetic factors in chelate formation [24]. As a consequence, a substantially lower concentration of phosphine groups is sufficient for the formation of chelate-type reactive intermediates than for the formation of active complexes with monophosphine ligands [25].

Use of palladium chelates with *trans*-diphosphine ligands as carbonylation catalysts provides opportunity to design high-performance and economically efficient processes for the synthesis of esters and other valuable oxygen-containing products. Owing to their stability, the palladium chelates are anticipated to be multiply reusable in carbonylation processes.

Thus, we have demonstrated that, by varying the bridge structure and the mutual arrangement of the phosphine groups in diphosphine ligands, it is possible to control the activity of the palladium–phosphine catalysts in cyclohexene hydrocarbomethoxylation. The *trans*-diphosphines are much stronger promoters than the *cis*-diphosphines, and the most effective one is **V**.

A comparison between the kinetic behaviors of the monophosphine and diphosphine ligands in cyclohexene hydrocarbomethoxylation demonstrated that the bridged *trans*-diphosphines are more effective and are superior to the other ligands in both kinetic and concentration terms: they afford a higher reaction rate and operate at smaller P/Pd ratios. In particular, the *trans*-diphosphines show a one order of magnitude higher promoting activity than triphenylphosphine and allow the P/Pd ratio to be 8–65 times smaller than in the case of PPh_3.

The role of the chelate effect and of the geometric compatibility between the ligand structure and the positions of vacant *s* and *d* orbitals in the Pd^{2+} cation has been explained.

The palladium chelates with *trans*-diphosphine ligands have been demonstrated to be promising carbonylation catalysts.

ACKNOWLEDGMENTS

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