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Effect of the structure and concentration of diphosphine ligands on the rate of hydrocarbomethoxylation of cyclohexene catalyzed by palladium acetate/diphosphine/TsOH system

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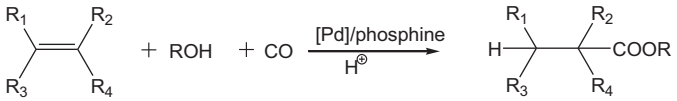
ABSTRACT

Cyclohexene hydrocarbomethoxylation catalyzed by the $Pd(OAc)_2$ – p-toluenesulfonic acid – diphosphine systems with broad variation of diphosphine structure and concentration was studied. It was shown that the hydrocarbon part of the structure and the mutual arrangement of the phosphine groups are the factors that control the activity of palladium-containing catalysts. By comparison of the promoting effects of mono and diphosphine ligands, it is demonstrated that bridging trans-diphosphines show higher efficiency with regard to both the kinetic (TOF) and concentration factors (low P/Pd ratios). In particular, their promoting activity is an order of magnitude higher than that for triphenylphosphine at lower P/Pd ratios (8–65 times). The results were interpreted from the standpoint of chelation effect and the geometric matching of the diphosphine structure to the arrangement of vacant s,d-orbitals of the Pd centre.

1. Introduction

Carbonylation of olefins catalyzed by transition metal complexes is a promising process for the manufacture of various organic compounds, including pharmacological and agrochemical agents [1]. An important carbonylation process is alkene hydrocarboalkoxylation catalyzed by palladium complexes, which represents a one-step route from accessible alkenes to diverse esters [2]. This process has found use in industry. For example, in 2008, Lucite commercialized hydrocarbomethoxylation of ethylene [3] (Scheme 1).



Scheme 1.

Among the catalytic systems used in the hydrocarboalkoxylaton of alkenes, of particular interest are palladium derivatives promoted by strong protic acids and free phosphines [4–7]. In the series of phosphines, diphosphines are used more and more often. While functioning as chelating agents with respect to the catalyst palladium site, they form more stable complexes than usual phosphines, which markedly affects the kinetics and regioselectivity of the hydroalkoxycarbonylation of alkenes [3,8–10]. Despite the obvious topicality of studies dealing with the effect of the diphosphine ligand structure on the efficiency of palladium complexes in the hydrocarboalkoxylation of alkenes, no systematic comparative data on this topic can be found in the literature. Therefore, we undertook a special study to find out how the structure of diverse diphosphines affects the kinetic parameters of the model hydrocarbomethoxylation reaction. As this reaction, we chose hydrocarbomethoxylation of cyclohexene, as all of its reaction sites are chemically equivalent, and methyl cyclohexanecarboxylate is formed as the only hydrocarbomethoxylation product. In addition, for cyclohexene we did not expect a noticeable copolymerization with CO, and, hence, the course of hydrocarbomethoxylation was expected to characterize the efficiency of the chosen catalytic system "as such".

As diphosphines that promote the hydrocarbomethoxylation of cyclohexene, we studied bis-diphenylphosphinoalkanes **1**–**3** containing di-, tri-, and tetramethylene bridges, respectively, and an

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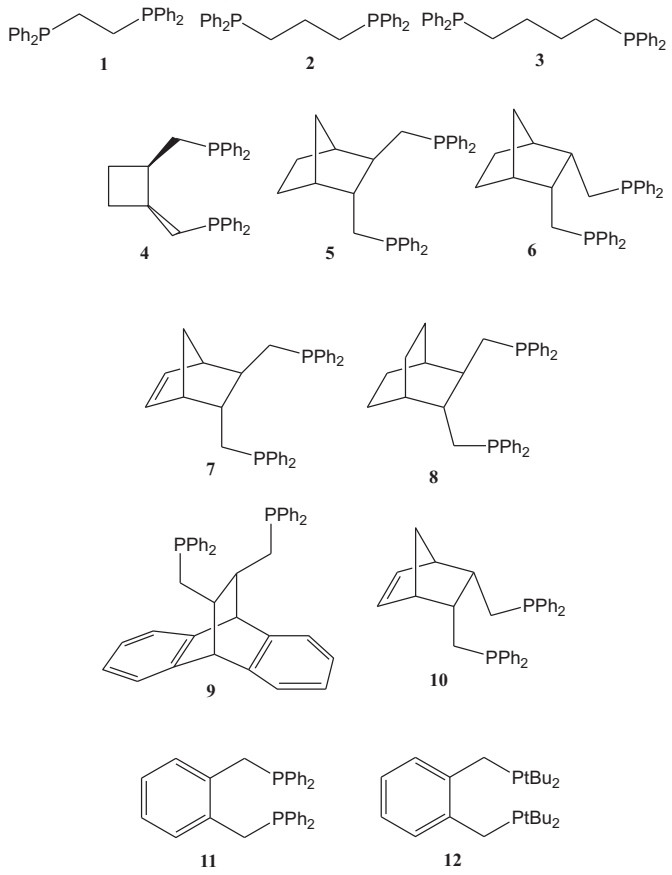
extensive series of bis-diphenylphosphines with a four-membered bridge **4**–**12** able to form bite-angle palladium complexes appropriate for effective catalysis of hydrocarbomethoxylation [11]. Systematic research into the effect of the nature of the substituent at phosphorus is the subject of a separate project and will be reported elsewhere.

The structure of the synthesized diphosphines **1**–**12** is shown below.



2. Experimental

2.1. Synthesis of diphosphines

The diphosphines used in this work were prepared by the reported procedures: **1**, **2**, **3** [12], **4** [13], **5** and **6** [14], **7** [15], **8** [16], **9** [17], **11**–**12** [18].

The previously unknown compounds 10 and 5·Pd(OAc)$_2$ were obtained as follow:

a) *cis*-2,3-Bis-(diphenylphosphinomethyl)-norbornene, 10

Finely divided Li (1 g, 143 mmol) was added to a solution of triphenylphosphine (12.45 g, 47.5 mmol) in 70 mL of anhydrous THF. The reaction mixture was stirred at room temperature overnight. Then a solution of tosylate (12.2 g, 26.4 mmol) obtained as reported [12] in 30 mL of anhydrous THF was added. The reaction mixture was stirred at room temperature for 20 min and then treated with an aqueous solution of NH_4Cl, 10% H_2SO_4, and saturated brine. The organic layer was separated and dried with Na_2SO_4, and the solvent was removed *in vacuo*. The residue was recrystallized from ethanol. Yield 5 g (42%).

^{31}P NMR ($CDCl_3$): −17.14.

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

^{13}C NMR ($CDCl_3$): 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).

b) Adduct of *trans*-2,3-Bis-(diphenylphosphinomethyl)-norbornane and Pd(OAc)$_2$, 5·Pd(OAc)$_2$

trans-2,3-Bis(diphenylphosphinomethyl)norbornane (100 mg, 0.2 mol) prepared by a reported procedure [6] was added to a solution of palladium acetate (50 mg, 0.2 mol) in 2 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h. Then the solvent was removed *in vacuo* and the residue was recrystallized from ether. Yield 100 mg (70%).

^{31}P NMR ($CDCl_3$): 25.7, 20.6.

^{1}H NMR ($CDCl_3$): 7.96 (m, 4H), 7.36 (m, 16H), 2.58 (m, 1H), 2.39 (m, 2H), 2.23 (m, 1H), 2.05 (m, 1H), 1.93 (br.s., 1H), 1.86 (br.s., 1H), 1.38 (m, 10H), 1.22 (d, 2H), 1.08 (m, 1H).

2.2. Procedure of catalytic experiments

The hydrocarbomethoxylation of cyclohexene was studied in the batch reactor described previously [19]. The experiments were carried out in toluene at constant temperature (105 °C) and CO pressure (2.1×10^6 Pa). The invariability of the temperature was ensured by high-temperature organic heat medium circulating through the reactor shell. A mixture of cyclohexene (0.51 mL), methanol (0.91 mL) and o-xylene, the internal standard for chromatography (0.30 mL) in toluene (48.28 mL) was placed in autoclave. A catalytic mixture of $(CH_3COO)_2Pd$ (0.05 mmol), TsOH (0.60 mmol) and one of the ligands (the concentration of one of the ligands being varied within each series from 0 to 7.50 mmol) was placed in special glace "basket" fastened to the autoclave lid. The autoclave was purged three times with 0.6×10^6 Pa of CO and then pressurized to 1.6×10^6 Pa at room temperature. The system was heated to 105 °C and then pressurized to 2.1×10^6 Pa. Then the glace "basket" with catalytic system was immersed in reaction solution. During kinetic experiments, the reaction mixture was sampled at particular time intervals, and the samples were analyzed by gas liquid chromatography on a Tsvet 162 chromatograph with a flame ionization detector. Analysis was carried out using 3000 mm × 3 mm glass columns. The separation was performed with Chromosorb W (80/100 mesh) on the stationary phase OV-275 – 3% at a carrier gas (argon) flow rate of 30 mL/min and evaporator temperature of 225 °C in the temperature programmed mode from 75 to 205 °C at a heating rate of 8 °C/min. Chromatographic calculations were performed using MultiChrom software. The chromatographic peaks of the reactants and product were identified based on the retention times, and the component contents were determined using chromatography of artificial mixtures with known contents of the components.

3. Results and discussion

The influence of the diphosphine ligand structure and concentration on the rate of cyclohexene hydrocarbomethoxylation was studied in 12 series of experiments using $(CH_3COO)_2Pd$, p-TsOH, and diphosphines **1**–**12** as catalyst components. An additional series of experiments with the triphenylphosphine ligand was carried out to compare the behaviors of diphosphine and monophosphine ligands.

Typical results of kinetic experiments are presented in Fig. 1 as dependences of the methyl cyclohexanecarboxylate concentration on the reaction time for catalytic systems. It can be seen that each kinetic curve has an autocatalytic period, which is indicative of the

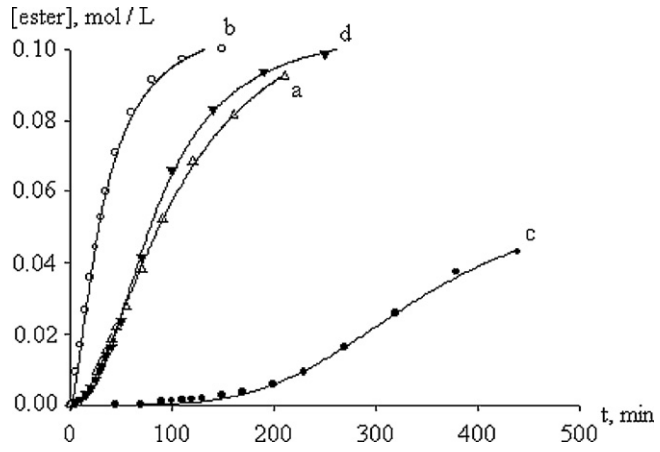


Fig. 1. Kinetic curves for the accumulation of methyl cyclohexanecarboxylate with time at the diphosphine concentration of 3.0×10^{-3} mol/L. (a) ligand **4**, (b) ligand **5**, (c) ligand **6**, and (d) ligand **8**.

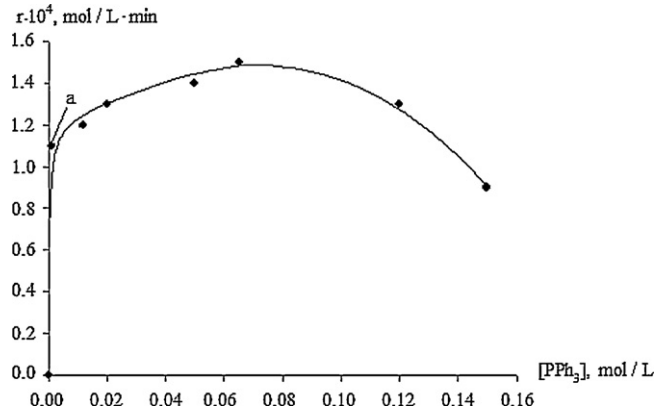


Fig. 2. Effect of the triphenylphosphine concentration on the cyclohexene hydrocarbomethoxylation rate.

formation of active complexes responsible for the catalytic action. Ligand 5 functions almost without an induction period.

The initial reaction rates were determined by differentiating the initial sections of the kinetic curves after completion of the autocatalytic period. The results of determinations are presented in Figs. 2 and 3 as the dependence of the initial hydrocarboalkoxylation rate on the concentration of the phosphine ligands. It can

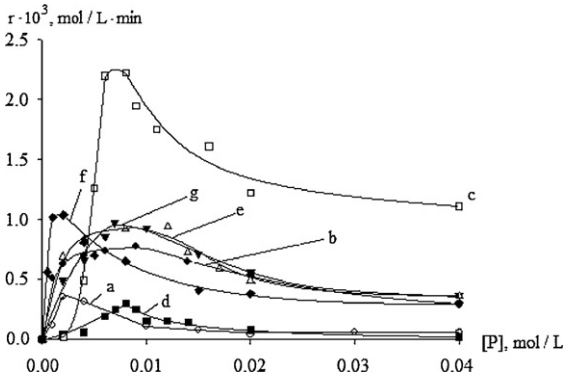


Fig. 3. Effect of the concentration of diphosphine ligands on the cyclohexene hydrocarbomethoxylation rate. (a) $Ph_2P–(CH_2)_4–PPh_2$ (ligand **3**), (b) trans-$Ph_2P–CH_2–C_4H_6–CH_2–PPh_2$ (ligand **4**), (c) trans-$C_7H_{10}(CH_2PPh_2)_2$ (ligand **5**), (d) cis-$C_7H_{10}(CH_2PPh_2)_2$ (ligand **6**), (e) trans-$C_7H_8(CH_2PPh_2)_2$ (ligand **7**), (f) $C_8H_{12}(CH_2PPh_2)_2$ (ligand **8**), and (g) $(C_6H_4CHCHCH_2PPh_2)_2$ (ligand **9**).

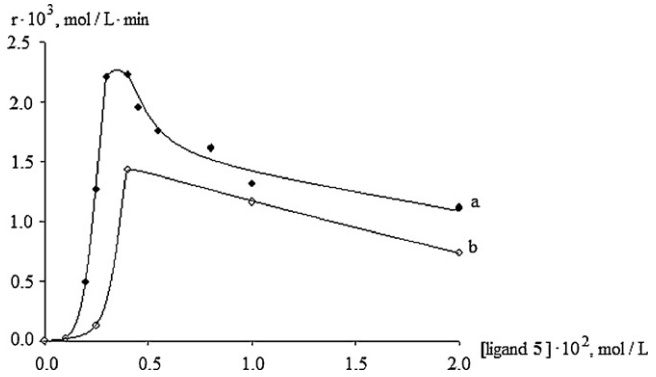


Fig. 4. Effect of the concentration of ligand **5** on the cyclohexene hydrocarbomethoxylation rate. (a) Reaction rate vs. concentration of free ligand **5** in the presence of $(CH_3COO)_2Pd$ (1.0×10^{-3} mol/L). (b) Reaction rate vs. the total concentration of ligand **5** in the presence of the complex [$(CH_3COO)_2Pd$·ligand **5**] (1.0×10^{-3} mol/L).

be seen that for ligands **3**–**9** all of the presented dependences pass through extrema. Meanwhile, the catalytic systems with ligands **1**, **2**, and **10**–**12** were virtually inert over the whole concentration range of the latter. It is of interest that the position of the maximum rate for triphenylphosphine corresponds to much higher P/Pd ratio (~65) than that for diphosphine ligands (**1**–**8**). Moreover, diphosphines **3** and **8** demonstrate the P/Pd maximum close to 1, and compounds **4**–**7** and **9** exhibit the maximum activity at much higher P/Pd ratio (~8). The values of the maximum rate ($r^0 \times 10^3$, mol/L) were higher for ligands **3**–**9** than for PPh_3 (0.150). It is significant that trans-diphosphine **5** proved to be an order of magnitude more effective promoter than the cis-isomer **6**. In this respect, it is noteworthy that all other diphosphine ligands with cis- or "cis-like"-arranged phosphine groups (**10**–**12**) had almost no accelerating effect on the hydrocarbomethoxylation of cyclohexene. On the other hand, attention is attracted by the fact that a double bond influences the efficiency of diphosphines. Indeed, unsaturated diphosphine **7** was a twice less efficient promoter than the hydrogenated analog **5**.

In order to study the lability of palladium phosphine catalysts, we compared hydrocarbomethoxylation of cyclohexene catalyzed by the $Pd(OAc)_2$ – **5** – TsOH system and by the pre-synthesized adduct **5**·$Pd(OAc)_2$. The results of these experiments are presented in Fig. 4. It can be seen that the $Pd(OAc)_2$ – **5** catalytic system has a higher catalytic activity than the complex **5**·$Pd(OAc)_2$ over the whole range of variation of the ligand **5** concentration. This fact prompts the idea that the active intermediates of the reaction using $Pd(OAc)_2$ and **5** do not involve the adduct **5**·$Pd(OAc)_2$, but the reaction follows an alternative route.

The obtained data can be summarized as the turnover frequency (TOF) for $Pd(OAc)_2$ – p-TsOH–diphosphine (monophosphine) systems at the maximum rate (Table 1).

The curve of the catalytic activity of the $Pd(OAc)_2$–PPh_3 system presented in Fig. 2 differs markedly from the plots for the $Pd(OAc)_2$–diphosphine ligand systems, which pass through a maximum (Fig. 3). Two sections can be distinguished in this curve. One characterizes a steep increase in the activity from 0 to 1.1×10^{-4} mol/(L min) in the range of PPh_3 concentrations from 0 to 8.0×10^{-4} mol/L and the other one shows a slightly sloping dependence of the activity on the PPh_3 concentration that passes through a maximum in the concentration range of 8.0×10^{-4} to 0.15 mol/L. It is easy to see that the hydrocarbomethoxylation rate of 1.1×10^{-4} mol/(L min) attained in the first section differs little from the rate at the extremum (1.5×10^{-4} mol/(L min)). This indicates, in our opinion, that the formation of the palladium phosphine complexes responsible for the catalysis is a reversible reaction. At

Table 1
Turnover frequency values for $Pd(OAc)_2$–p-TsOH–diphosphine (monophosphine) systems at the maximum rate of hydrocarbomethoxylation.

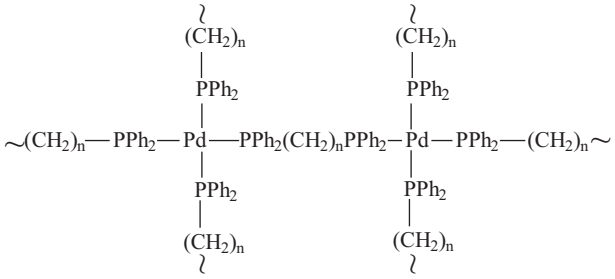
Ligand No.	**1**, **2**, **10**–**12**	PPh_3	**3**	**4**	**5**	**6**	**7**	**8**	**9**
TOF (h^{-1})	0	9.0	21.0	42.0	150.0	15.0	54.0	63.0	57.0

point *a*, this reaction is not far from equilibrium, which results in sharp retardation of the formation of the complexes after this point has been passed. In the second section, as the triphenylphosphine concentration increases, the fraction of ligand exchange reactions with its participation, resulting in the formation of less active complexes, starts to grow. Finally, gradual retardation of the reversible formation of active complexes and acceleration of ligand exchange reactions with their participation leads to a kink in the dependence of the hydrocarbomethoxylation rate on the PPh_3 concentration and to the observed maximum.

The pattern of the extreme curves of the reaction rate vs. the diphosphine concentration attests rather to purely kinetic control of the concentration of active complexes. Apparently, the reaction of their formation proceeds under conditions where it is nearly irreversible. This accounts for the high slope of the ascending part of the curves shown in Fig. 3 in the region of low concentrations of diphosphines until the maximum is reached. In addition, the fairly steep decline after the maximum in these curves attests to a high rate of ligand exchange involving diphosphines, resulting in the formation of less active complexes.

High promoting activity of diphosphine ligands with trans-phosphine groups at bridging structures prompts the idea of a favorable spatial arrangement of these groups with respect to vacant s,d-orbitals of palladium. This is in line with the reported fact that linear diphosphine ligands are bound in the 1,3-position in the square plane configuration of palladium complexes [20]. Correspondingly, the bridging bidentate ligands with cis-phosphine groups have either low promoting activity (ligand **6**) or no such activity at all (ligand **10**). Similarly, the lack of activity of ligands **11**, **12** attests to an unfavorable positions of their phosphine groups relative to the Pd vacant s,d-orbitals. The relatively low activity of ligand **7** containing a double bond compared with the hydrogenated analog **5** implies that **7** may form oligomers, which are coordinated to the palladium site, thus making it spatially less accessible for reagents.

The virtually inert behavior of ligands **1** and **2** in the carbomethoxylation of cyclohexene and the noticeable promoting effect of ligand **3** reflect, in our opinion, the role of the chelation effect where the formation of sterically non-strained metal rings upon the coordination of a linear bidentate ligand to the complexing metal is energetically favorable [21,22]. In this case, the competing formation of inactive polynuclear complexes in which the metal atoms are linked by diphosphine bridges is more probable for diphosphines **1** and **2**.



The considerable difference of the P/Pd ratios at the maximum observed for diphosphines and triphenylphosphine deserves special attention. In our opinion, this is due to high stability of chelates compared with the complexes containing monodentate ligands. This stability was found to be caused by the concerted action of the entropy and energy factors upon the chelate formation [21]. As a consequence, the formation of chelate type active intermediates requires much lower concentrations of phosphine groups than the formation of active complexes with monophosphine ligands [22].

Thus, the use of palladium chelates based on trans-diphosphine ligands as catalysts in the carbonylation opens up prospects for the development of highly efficient processes economical as regards the cost of the catalyst for the manufacture of esters and other valuable oxygenate products. Owing to the stability of chelate complexes, the possibility of their multiple use in carbonylation is predicted.

4. Conclusions

It was shown that variation of the structure of the bridge and mutual arrangement of the phosphine groups in diphosphine ligands is a factor of control over the activity of palladium phosphine catalysts in the hydrocarbomethoxylation of cyclohexene. trans-Diphosphines are much superior over cis-diphosphines as regards the promoting activity. Ligand **5** is most efficient among the studied diphosphines.

A comparison of the kinetic behavior of mono- and di-phosphine ligands in the hydrocarbomethoxylation of cyclohexene showed that bridging trans-diphosphines are more efficient as regards both the kinetic (high reaction rates) and concentration factors (low P/Pd ratios). In particular, the promoting activity of trans-diphosphines is an order of magnitude higher than this value for triphenylphosphine at P/Pd ratios 8–65 times lower than required when the latter ligand is used.

The obtained results were interpreted from the standpoint of chelation effect and the geometric matching of the ligand structure to the arrangement of vacant s,d-orbitals of the Pd centre.

It is concluded that palladium chelates with trans-diphosphines would be useful as catalysts of carbonylation.

Acknowledgments

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