COMPLEXES OF $PdCl_2$ WITH PHOSPHORYL- AND THIOPHOSPHORYL-SUBSTITUTED PHOSPHINES AS CATALYSTS FOR THE HYDROCARBOXYLATION OF OLEFINS

M. I. Terekhova, T. E. Kron, N. A. Bondarenko,
É. S. Petrov, and E. N. Tsvetkov

UDC 542.97:547.313.9

The influence of the ligands $Ph_2P(CH_2)_mP(X)Ph_2$ *(L), where* $m = 1, 2$ *and* $X = O, S$*, on the rate and regional selectivity of the hydrocarboxylation of α-olefins has been investigated, catalyzed by* $PdCl_2$*, in a series of organic solvents. A high regional selectivity of the process (>80%) for products with normal structure has been achieved by using L with* $m = 2, X = O$*. The influence of the ligand used and of triphenylphosphine on the properties of the catalytic system in the given reaction has been compared.*

Keywords: *hydrocarboxylation, palladium chloride complexes, bidentate diphosphines, catalysis.*

Complexes of $PdCl_2$ with tertiary phosphines catalyze the hydrocarboxylation of olefins at low CO pressures [1]. However, bidentate diphosphines, for instance $Ph_2PCH_2CH_2PPh_2$ (dppe), deactivate the catalyst at these conditions [2]. Besides this, the replacement in dppe of one Ph_2P group by Ph_2PO gives, on the basis of Rh, a relatively active catalytic system for the hydroformylation of olefins [3]. It is therefore of interest to assess the effect of ligands (L) of the type $Ph_2P(CH_2)_mP(X)Ph_2$ on the hydrocarboxylation of olefins [4], catalyzed by Pd(II) complexes, which is important for the practice.

$$RCH{=}CH_2 + CO + H_2O \xrightarrow{[Pd/L]} \underset{(1)}{RC_2H_4COOH} + \underset{(2)}{RCH(CH_3)COOH} \tag{1}$$

EXPERIMENTAL

The reaction mixture was analyzed by GLC on a Tsvet-110 chromatograph: glass column 200 × 0.3 cm, packed with Chromosorb with 3% H_3PO_4, impregnated with 10% PEGA. The $^{31}P-\{H\}$ NMR spectra were taken on a Bruker WM-250 spectrometer (250 MHz) in the pulsed mode, with 85% H_3PO_4 as the reference. The IR spectra were obtained on a Perkin–Elmer 580 spectrometer in cells with CsI windows. The reaction was carried out in an autoclave, equipped with a magnetic stirrer and a sampling device [2], at 120°C and $P_{CO} = 0.5$-3 MPa. Composition of the reaction mixture: 10 ml solvent, 0.35 g (3.6 mmoles) olefin, 0.16 ml (9 mmoles) H_2O, 0.0065 g (0.036 mmole) $PdCl_2$ (in the run with propylene the olefin pressure was 0.8 MPa, $P_{CO} = 1.6$ MPa). The compounds $Ph_2PCH_2P(O)Ph_2$ and $Ph_2P(CH_2)_2P(O)Ph_2$ were synthesized by the procedures in [5, 6]. The syntheses of $Ph_2P(CH_2)_2P(S)Ph_2$ and $Ph_2P(CH_2)_2P(O)EtPh$ will be described in separate publications. The complex $PdCl_2[Ph_2PCH_2CH_2P(O)Ph_2]_2$ was obtained in EtOH from Na_2PdCl_4 and dppeO by the procedure given in [7]. The decomposition temperature was 250-255°C (methylene chloride–benzene). Found, %: C 61.65; H 4.85; Cl 7.01; P 11.94. $C_{22}H_{48}Cl_2O_2P_4Pd$. Calculated, %: C 62.07; H 4.81; Cl 7.05; P 12.31. ^{31}P NMR spectrum (in $CDCl_3$, δ, ppm): 20.14; 33.09.

L. Ya. Karpov Scientific-Research Physicochemical Institute, Russian Academy of Sciences, 103064 Moscow. Institute of Chemical Reagents and High-Purity Chemicals, 107258 Moscow. Institute of Physiologically Active Substances, Russian Academy of Sciences, 142432 Chernogolovka. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 9, pp. 2003-2007, September, 1992. Original article submitted August 9, 1991.

1063-5211/92/4109-1555$12.50 ©1993 Plenum Publishing Corporation

TABLE 1. Rate and Regional Selectivity of the Hydrocarboxylation of Heptene-1 in Dioxane (catalyst $PdCl_2/n(L)$, 120°C, P_{CO} = 2 MPa)

Test No.	L(*n*) *	r, mmole·liter^{-1}·min^{-1}	*S*, %
1	dppe (3)	Traces	90
2	dppeO (3)	1.75	74
3	dppeO (3)†	1.85	76
4	dppeO (4)	1.60	78
5	dppeO (6)	1.30	87
6	dppmO (3)	0.50	26‡
7	dppeS (3)	Traces	–
8	Ph_3P (6)	2.90	55
9	Ph_3P (6) †	2.80	54
10	Ph_3P (2), dppeO (4)	1.90	83
11	Ph_2PEt (6)	0.45	83

**n* is the L/Pd molar ratio.

†Complex $PdCl_2L_2$ + 1L (test 3) and $PdCl_2(Ph_3P)_2$ + $4Ph_3P$ (test 9).

‡$C_4H_9CH(C_2H_5)COOH$ is also formed (yield 4%), catalyst unstable.

TABLE 2. Influence of Solvent on the Rate and Regional Selectivity of the Hydrocarboxylation of Heptene-1 (catalyst $PdCl_2$/3dppeO, 120°C, P_{CO} = 2 MPa)

Test No.*	Solvent	r, mmole·liter^{-1}·min^{-1}	*S*, %
1	Acetonitrile	0.3	62
2	Dichloromethane	0.8	80
3	Benzene	1.1	81
4	Acetone	0.5	78
5	1,2-Dimethoxymethane	1.4	74
6	Dioxane	8.1	74
7	Benzene–dioxane	2.8	80
8	Dioxane	1.7	88
9	Dioxane	1.1	89

---

*$[H_2P]$ = 0.9 M in tests 1-7, 1.8 M in test 8, and 2.8 M in test 9.

TABLE 3. Influence of the CO Pressure on the Rate (mmole·liter^{-1}·min^{-1}) of Formation of Isomeric Products in Hydrocarboxylation of Heptene-1 (catalyst $PdCl_2$/3dppeO, dioxane, 120°C)

Test No.	P_{CO}	r_1	r_2	*S*, %
1	0.5	0.5	0.05	91
2	1.0	1.0	0.2	83
3	1.5	1.15	0.35	78
4	2.0	1.3	0.45	74
5	2.5	1.15	0.35	77
6	3.0	1.25	0.45	74

RESULTS AND DISCUSSION

Applied to heptene-1, the rate (*r*) and the regional selectivity (*S*) (ratio of the yield of **1** to the summary yield) of the reaction (1) was determined, catalyzed by $PdCl_2$ in the presence of L = $Ph_2P(CH_2)_mP(X)Ph_2$, denoted in the further text by dppmO ($m = 1$, X = O), dppeO ($m = 2$, X = O), and dppeS ($m = 2$, X = S). The results obtained are presented in Tables 1-3. The data in Table 1 show that the best characteristics in reaction (1) are obtained with dppeO. The catalytic activity of the $PdCl_2$ complex with this ligand is much higher than with dppe (tests 1-3), although with respect to *S* the diphosphine surpasses dppeO. It must be pointed out that the method of forming the catalytic system (the addition of three equivalents of L to $PdCl_2$ or of one equivalent to the complex $PdCl_2L_2$ has no effect. The value of *r* decreases somewhat with the increasing excess of dppeO with respect to $PdCl_2$. It is essential that the rate of formation of the acid with normal structure (r_1) is reduced hereby much less than the formation rate of the acid with branched structure (r_2). Thus, when the L/Pd ratio (*n*) is changed from 3 to 6, the value of r_1 decreases by 15% (1.3-1.15 $mmole \cdot liter^{-1} \cdot min^{-1}$), while the value of r_2 decreases by a factor of ~3 (0.46-0.17 $mmole \cdot liter^{-1} \cdot min^{-1}$). As a result of this, *S* increases significantly.

The replacement in the diphenylphosphinyl group of dppeO of one of the Ph radicals by Et has virtually no influence on the effect of the ligand ($r = 1.7$ $mmole \cdot liter^{-1} \cdot min^{-1}$; $S = 70\%$). On the other hand, shortening of the hydrocarbon bridge between the phosphorus atoms leads to a significant decrease of *r* and *S* (tests 2 and 6) and the replacement of the oxygen atom by a sulfur atom in dppeO causes the complete deactivation of the catalyst (test 2 and 7).

It is interesting to compare the influence of dppeO and triphenyl phosphine, the most widely used ligand in homogeneous catalytic systems, based on Pd. The reaction rate in the instance of Ph_3P is significantly higher' however, with respect to the regional selectivity effect this ligand is inferior to dppeO (tests 5 and 8); the partial replacement of Ph_3P by dppeO is also accompanied by an increase in *S* (tests 8 and 10). In the series of monodentate ligands ethyldiphenylphosphine (test 11) gives a high value of *S*; however, *r* decreases significantly. A high value of *S* in the presence of dppeO is observed also in the hydrocarboxylation of some other olefins: propene and decene (70%), and styrene (50%).

The results obtained lead to the assumption that in reaction (1) dppeO acts predominantly as a monodentate ligand, the rigid basic center of which (the O atom) is not capable of such a strong coordination with Pd as the weak coordination center of the tertiary phosphines. This assumption is confirmed by IR and ^{31}P NMR spectroscopic data for the complex of $PdCl_2$ $(dppeO)_2$. The chemical shift for the PO group (33.09 ppm) coincides with its value for the ligand, not bound into a complex; $\nu PO = 1180$ cm^{-1} corresponds to the vibration frequency of the uncoordinated phosphoryl group [8]. Thus, in the instance of dppeO the formation of a stable chelate structure of the complex with the Pd atom, which probably causes the low catalytic activity of the $PdCl_2$ complex with dppe, is not probable.

The effect of dppeO can partly be attributed to its increased basicity in comparison with Ph_3P (*r* usually decreases and *S* increases with increasing basicity of the phosphine [2]). However, this is hardly the only cause of this effect, since with respect to basicity dppeO occupies an intermediate position between Ph_3P and Ph_2PEt, while *S* is the highest for dppeO. One can therefore not eliminate the possibility that between the PO group of dppeO and the Pd atom (the key intermediates of the catalytic cycle) a labile coordination is established, with the formation of weak chelate structures, to which the above-mentioned differences between dppeO and tertiary phosphines are related. The replacement of a strong coordination center by a weaker one (*S* atom) must increase the stability of this kind of complexes and inhibit the reaction (1) from taking place at low CO pressures, which is in fact observed experimentally. The deactivation of the catalyst in the instance of dppeS is not related to its basicity, since the basicity of the phosphine group in dppeS differs only negligibly from its basicity in dppeO.

This assumption is corroborated by the data on the influence of the medium on the catalytic system $PdCl_2/3(dppeO)$ (Table 2). Thus, in acetonitrile *S* is lower than in dichloromethane or benzene (tests 1-3). This can be the result of the fact that the coordinating power of the PO group of dppeO in acetonitrile, which forms complexes with palladium [9], is much weaker than in solvents which are not capable of specific interactions. It must be pointed out in this context that, for moderately basic media (acetone, dioxane, 1,2-dimethoxyethane), intermediate values of *S* have ben obtained (tests 4-6). For triphenyl phosphine, here the values of *S* vary within the limits 55-65% [10], such a correspondence between the nature of the solvent and *S* has not been observed.

The reaction rate apparently does not only depend on the basicity, but also on the polarity of the medium, so that no symbatic relationship exists between the changes of *r* and *S*. The decrease of *r* in benzene, as compared with dioxane (tests 3 and 6), is evidently related to the worse solubility of water in the first solvent. When dioxane is added to benzene the hydrophilic character of the medium increases, r increases to reach a value (test 7) which is higher than in pure dioxane. An increase in the concentration of water in dioxane is accompanied by an increase in S (tests 6, 8, and 9); in distinction from Ph_3P, this makes it possible to carry out the reaction (1) in media with an increased water content.

The increase in P_{CO} usually enhances an increase of r and a drop of S [1]. For $PdCl_2$/3(dppeO) this rule is obeyed only partly (Table 3). First, the formation rates of both products increase with increasing P_{CO} (to 2 MPa, whereby r_2 increases more than r_1) and then remains constant. Thus, at values of $P_{CO} > 2$ MPa, S does not depend on the pressure. The regularities obtained are described satisfactorily by equations of the kind:

$$r=k_1 P_{CO}/(1+k_2P_{CO}), \tag{2}$$

where k_1 and k_2 are equal to 2.6 mmoles/liter^{-1}·min^{-1}·MPa^{-1}; 1.75 MPa^{-1} for r_1 and 0.24 mmole/liter^{-1}·min^{-1}·MPa^{-1}; 0.21 MPa^{-1} for r_2, respectively. An analogous correlation has been applied in [11] to the hydrocarboxylation of cyclohexene.

Thus, all this makes the use of the given phosphine oxide as a component of the homogeneous-catalysis system based on palladium very promising for the synthesis of products with linear structure in the carbonylation of α-olefins.

REFERENCES

1. E. S. Petrov, *Zh. Fiz. Khim.*, **62**, No. 10, 2858 (1988).
2. A. V. Protchenko, T. E. Kron, A.D. Karpyuk, É. S. Petrov, E. N. Tsvetkov, and I. P. Beletskaya, *Zh. Obshch. Khim.*, **56**, No. 1, 90 (1986).
3. US Patent No. 4,687,874; *Ref. Zh. Khim.*, 17N169P (1988).
4. B. R. Serebryakov, T. K. Plaksunov, V. R. Ansheles, and M. A. Dalin, *Higher Olefins. Production and Applications* [in Russian], Khimiya, Leningrad (1984).
5. N. A. Bondarenko, M. V. Rudomino, and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 2180 (1990).
6. N. A. Bondarenko, M. V. Rudomino, and E. N. Tsvetkov, *Synthesis*, No. 2, 125 (1991).
7. S. J. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, No. 6, 770 (1966).
8. S. J. Higgins, R. Taylor, and B. L. Shaw, *J. Organomet. Chem.*, **325**, No. 2, 285 (1987).
9. G. Cavinato and L. Toniolo, *J. Mol. Catal.*, **10**, 161 (1981).
10. A. D. Karpyuk, É. S. Petrov, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR*, **285**, No. 2, 389 (1985).
11. H. Yoshida, N. Sugita, K. Kudo, and J. Takezaki, *Bull. Chem. Soc. Jpn.*, **49**, No. 8, 2245 (1976).