

EFFECT OF DENTATE NUMBER OF ANCHORED PHOSPHINE  
LIGANDS ON THE COMPOSITION  
AND CATALYTIC PROPERTIES OF THEIR  
PALLADIUM COMPLEXES

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Mono-, di- and triphosphine ligands anchored by a Si-C bond to the surface of silica have been synthesized. Complexes of Pd(II) and Pd(0) with these ligands have been obtained. On the basis of elemental analysis and UV spectroscopy, structures of the complexes formed are suggested. The catalytic properties of the above complexes in the selective hydrogenation of cyclopentadiene are compared.

Проведён синтез моно-, ди- и трифосфиновых лигандов, закреплённых связью Si-C с поверхностью силикагеля. Получены комплексные соединения Pd(II) и Pd(0) с этими лигандами. На основании данных элементного анализа и УФ-спектроскопии предложены структуры образующихся комплексов. Сопоставлены каталитические свойства полученных комплексов в реакции селективного гидрирования циклопентадиена.

The structure and catalytic properties of anchored transition metal complexes are affected by various factors, one of them being the nature of the surface ligand ( $L_s$ ) binding a transition metal ion to the carrier surface /1, 2/. The nature of  $L_s$  is determined among others by its dentate number.

In this communication, we report on the effect of dentate number of the anchored phosphine ligand on the composition and catalytic properties of their palladium complexes.

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## EXPERIMENTAL

Phosphine ligands were anchored via treatment of silica ( $S = 60 \text{ m}^2/\text{g}$ , heated at  $600^\circ\text{C}$  at a residual pressure of 0.01 Torr) with phosphorus-containing ethoxysilane at  $150^\circ\text{C}$  for 20 hrs. Depending on the silane used, the following modified carriers were obtained:  $\text{Si}-\text{CH}_2\text{CH}_2\text{PPh}_2$  ( $\text{P}_1$ );  $\text{Si}-(\text{CH}_2\text{CH}_2\text{PPh}_2)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{PPh}_2$  ( $\text{P}_2$ );  $\text{Si}-(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  ( $\text{P}_3$ ) where  $\text{Si}$  is the silica surface.

Palladium complexes were bonded to phosphine-containing silica either from an acetate solution of  $(\text{PhCN})_2\text{PdCl}_2$  or from a benzene solution of  $\text{Pd}(\text{DBA})_2$  (where DBA is disteryl ketone). All operations were performed in a sealed vacuum apparatus.

$(\text{PhCN})_2\text{PdCl}_2$ ,  $(\text{PPh}_3)_2\text{PdCl}_2$ ,  $\text{Pd}(\text{DBA})_2$ ,  $\text{Pd}(\text{PPh}_3)_3$  and  $(\text{EtO})_3\text{SiC}_2\text{H}_4\text{PPh}_2$  were synthesized as described /3-7/.

Preparation of  $(\text{EtO})_2\text{Si}(\text{C}_2\text{H}_4\text{PPh}_2)\text{C}_2\text{H}_4\text{PPh}_2$

To a solution of 0.2 mol  $\text{Cl}_3\text{SiCH}=\text{CH}_2 + 200 \text{ ml}$  ether was added under stirring 400 ml  $\text{ClMgCH}_2\text{C}(\text{CH}_3)\text{CH}_2$  (0.2 mol) in ether solution. 10 hrs later the solution was separated from the precipitate and 0.6 mol ethanol was added. The solvent was removed in a flow of  $\text{N}_2$  and the residue was fractionated. To the fraction boiling at 84-114/50 Torr (9 g), was added with 17 g  $\text{HPPH}_2$  and the mixture irradiated by UV light for 50 hrs. The reaction mixture was distilled and the fraction boiling at 170-180/0.05 Torr was separated. Elemental analysis and the  $^1\text{H-NMR}$  spectrum are in agreement with the formula mentioned.

Preparation of  $\text{EtOSi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{P-Ph})_3$

To a solution of 0.3 mol  $\text{ClMgC}_3\text{H}_5 + 750 \text{ ml}$  ether, 0.1 mol  $(\text{EtO})_4\text{Si}$  and 50 ml xylene were added. Ether was removed and the reaction mixture kept for 5 hrs at  $100^\circ\text{C}$ . The reaction product was separated from the solid residue by

vacuum rectification. After the second rectification, 16 g of product was obtained (b. p. 85.5–86.5/10 Torr, yield = 82%). According to the NMR spectrum, the product was triallylethoxysilane.

To 0.02 mol  $\text{EtOSi}(\text{C}_3\text{H}_5)_3$  was added 0.07 mol  $\text{HPPH}_2$  and the mixture irradiated by UV light for 200 hrs. Under vacuum at 120 °C, 0.01 mol  $\text{HPPH}_2$  was separated from the reaction mixture. According to the NMR spectrum, the residue was  $\text{EtOSi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ .

Methods of analysis. The elemental composition of catalysts (P and Pd) was determined by the procedure described in Refs /8,9/. Electronic spectra were recorded on a Specord UV-VIS instrument.  $\text{SiO}_2$  with anchored complexes was pressed to plates of 5–10 mg  $\text{SiO}_2/\text{cm}^2$ , then impregnated with benzene and placed into the instrument /10/.

The products of hydrogenation were analyzed chromatographically in a column containing cobalt phthalocyanins on graphitized soot.

## RESULTS AND DISCUSSION

1. Structure of anchored complexes. Data of elemental analysis, the absorption bands and the catalytic properties of the compounds prepared are given in Table 1. The data (compare I with IV; 2,3 with III) permit to conclude that Pd(0) forms mononuclear anchored complexes regardless of the dentate number of the phosphine ligand. When Pd(II) is bonded to  $\text{P}_1$  and  $\text{P}_2$ , complexes with one palladium atom coordinated to an anchored ligand are mainly formed (compare 4 with II; 5 with I). The formation of complexes of such a composition for  $\text{P}_1$  was shown in Ref. /10/. The weak absorption bands at 34000 and 25500  $\text{cm}^{-1}$  for complex 3 indicate the presence of small quantities of a species with one palladium atom bonded to one phosphorus atom. The binding of Pd(II) on  $\text{P}_3$  leads, according to the data of Table 1, to the formation of complexes with P to Pd atomic ratios of 2:1 and 1:1. The most probable structures of the anchored complexes prepared are listed in Table 1.

Table 1

Data on anchored palladium complexes (elements in  $10^{-4}$  g-at/g  $\text{SiO}_2$ ).

Pd min. Hydrogenation conditions:

No.	Complex	Data of analysis					
		P	Pd	P/Pd	Absorption bands ( $10^3 \text{ cm}^{-1}$ )		
1	$\text{P}_1 + \text{Pd}(0)$	1.10	0.50	2.20	34.0(w)	30.0(s)	19.0(w)
2	$\text{P}_2 + \text{Pd}(0)$	1.10	0.53	1.90		27.0(s)	
3	$\text{P}_3 + \text{Pd}(0)$	1.60	0.51	3.15		29.5(s)	
4	$\text{P}_1 + \text{Pd(II)}$	1.10	0.67	1.65	34.0(s)		25.5(s)
5	$\text{P}_2 + \text{Pd(II)}$	1.10	0.60	1.85	34.0(w)	29.0(s)	25.5(w)
6	$\text{P}_3 + \text{Pd(II)}$	1.60	1.10	1.45	34.0(w)	29.0(w)	25.5(w)
7	$\text{Pd}^* / \text{SiO}_2$		1.00				

Absorption bands of individual complexes ( $10^3 \text{ cm}^{-1}$ ): I-( $\text{PPh}_3$ )<sub>2</sub>PdCl<sub>2</sub> 29.0(s);II-( $\text{PPh}_3$ )<sub>2</sub>Pd<sub>2</sub>Cl<sub>4</sub> 34.0(s), 25.5(s); III-( $\text{PPh}_3$ )<sub>3</sub>Pd 29.5(s); IV-Pd(DBA)<sub>2</sub>

34.0(w), 30.5(s), 19.0(w).

\* Alternative structure in parentheses

2. Catalytic properties. The highest catalytic activity is shown by the monophosphine complexes. The complex of zerovalent palladium(0), No. 1, slightly exceeds the activity of Pd/SiO<sub>2</sub> (dispersity 0.3). The complex of Pd(0) with P<sub>2</sub> is inactive and the low catalytic activity of catalyst 3 is due to the admixture of monophosphine complexes. The selectivity of the hydrogenation of cyclopentadiene (CPDE) to

Hydrogenation activity for CPDE (A) and CP (B) in mol CPDE (CP)/g-at.

T = 30 °C, 25 ml ethanol, 0.5 ml CPDE

Catalytic properties			Supposed structure
A	B	A/B	
109.6	52.2	2.1	
0.0	0.0	-	
6.5	3.8	1.7	
32.7	17.9	1.9	
5.7	1.7	3.4	
4.7	0.8	5.9	
86.0	35.5	2.4	

cyclopentene (CPE) and cyclopentane (CP) at full conversion of CPDE was 96–98% for all the catalysts listed in Table 1.

The analysis of the correlation between structure and the ratio of rates A/B, an interesting conclusion can be drawn. All bonded mononuclear palladium complexes have A/B ratios close to that on metallic palladium (Nos. 1, 4). A/B for complex 6 is significantly higher than that for complex 4, probably owing to the polynuclear structure of complex 6. In this case the admixtures of binuclear complexes in catalyst 5 are responsible for the increased value of A/B as compared with mononuclear complex 4.

REFERENCES

1. Yu.I. Yermakov; in Theoretical problems of catalysis, p. 147. Institut Kataliza, Novosibirsk 1977.
2. V.A. Semikolenov, V.A. Likholobov, Yu.I. Yermakov: Kinet. Katal., 18, 1294 (1977).
3. M. S. Kharash, R. S. Seiler, F.R. Mayo: J. Amer. Chem. Soc., 60, 882 (1938).
4. J. Chatt, L.M. Venanzi: J. Chem. Soc., 2351 (1957).
5. T. Ukai, H. Rawazura, Y. Ishii: J. Organomet. Chem., 65, 253 (1974).
6. E. O. Greaves, C.J. Lock, P.M. Maitlis: Can. J. Chem., 46, 3879 (1968).
7. H. Niebergall: Makromolek. Chem., 52, 218 (1962).
8. E. V. Arinushkina: Manual on chemical analysis of soils (in Russian). Lomonosov University, Moskva 1970.
9. S. I. Ginsburg: Analytical chemistry of platinum metals (in Russian). Nauka, Moskva 1972.
10. V.L. Kuznetsov: Thesis, Institut Kataliza, Novosibirsk 1977.