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PALLADIUM COMPLEXES OF PHOSPHORUS ACID DISUBSTITUTED ETHERS. SYNTHESIS, STRUCTURE, CATALYSIS

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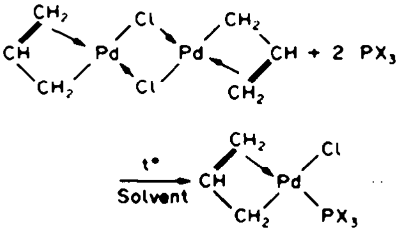
Abstract—Complexes of the type of [$Pd_2Cl_2L_4$] have been prepared by the reaction of bis-(π-allylpalladiumchloride) with phosphorous acid disubstituted ethers; their structure has been studied by IR- and NMR-spectroscopy and X-ray analysis. The complexes have a dimeric centro-symmetric structure which is usual for bivalent palladium compounds with a slightly distorted flat-square coordination of the central atom. These compounds are active catalysts for hydrogenation of unsaturated compounds. Complexes of biphosphites of sugars can impart asymmetry in hydrogenation of prochiral substrates.

The study of complexes of transition metals with trivalent phosphorus derivatives is of interest due to their structure, reactivity and catalytic properties in numerous reactions.[1] Complexes of transition metals with hydrophosphorylic compounds containing trivalent phosphorus in one of their tautomeric forms are much less studied.[2,3] It was the object of our paper to study the synthesis, structure and catalytic properties of palladium complexes with the most popular hydrophosphoryl compounds-disubstituted esters of phosphorous acid.



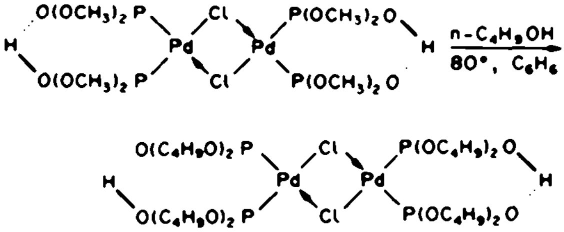
(1)

(I)

The starting compound for the preparation of the complexes is bis-(π-allylpalladiumchloride) which has been used by many authors in syntheses of asymmetric complexes containing amine, arsine and stibine ligands.[4] Also described are examples of the utilization of bis-(π-allylpalladiumchloride) in the synthesis of complexes I with various compounds of trivalent phosphorus of the PX_3 type.[5] Palladium complexes of a new type have been obtained with yields 85–90% by reaction of bis-(π-allylpalladiumchloride) with dialkyl or diaryl phosphites. In this case the reaction changes its direction obviously due to the presence of a mobile hydrogen atom in phosphite. This atom ensures elimination of π-allyl from the complex sphere in the form of propene which has been identified by GLC. In this version of the reaction the palladium system retains chlorine bridges:

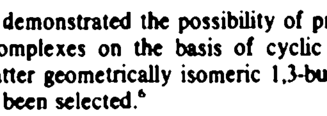
Complexes with dialkyl or diaryl phosphites have been prepared by reaction of ligands with bis-(π-allylpalladiumchloride) at a molar ratio of the reagents of 4:1 in absolute benzene.

The synthesis of binuclear complexes such as II can be also effected by transesterification of the ligand inside the coordination sphere of the complexes. The reaction proceeds under mild conditions with substantially quantitative yield of the final product. For example:

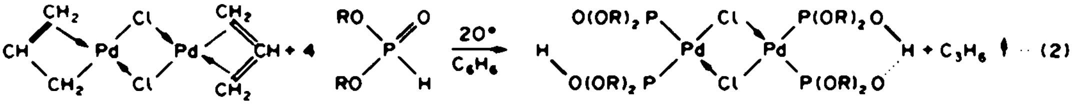


We have also demonstrated the possibility of producing palladium complexes on the basis of cyclic phosphites. As the latter geometrically isomeric 1,3-butylene phosphites have been selected.[6]

Taking into consideration a considerable conformation stability, one could assume that upon the reaction of *cis*- and *trans*-1,3-butylene phosphites with bis-(π-allylpalladiumchloride) stereoisomerically nonequivalent complexes would be formed. The complex with phosphite *cis*-isomer should have axial orientation of the metal, while the complex with *trans*-isomer-equatorial:



This assumption has been proven experimentally. Both complexes have been prepared by reacting *cis*- and *trans*-butylenephosphites with bis-(π-allylpalladium-



(2)

R = CH_3, C_2H_5, iC_3H_7, iC_4H_9, C_6H_5

(II)

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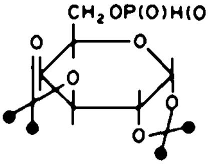
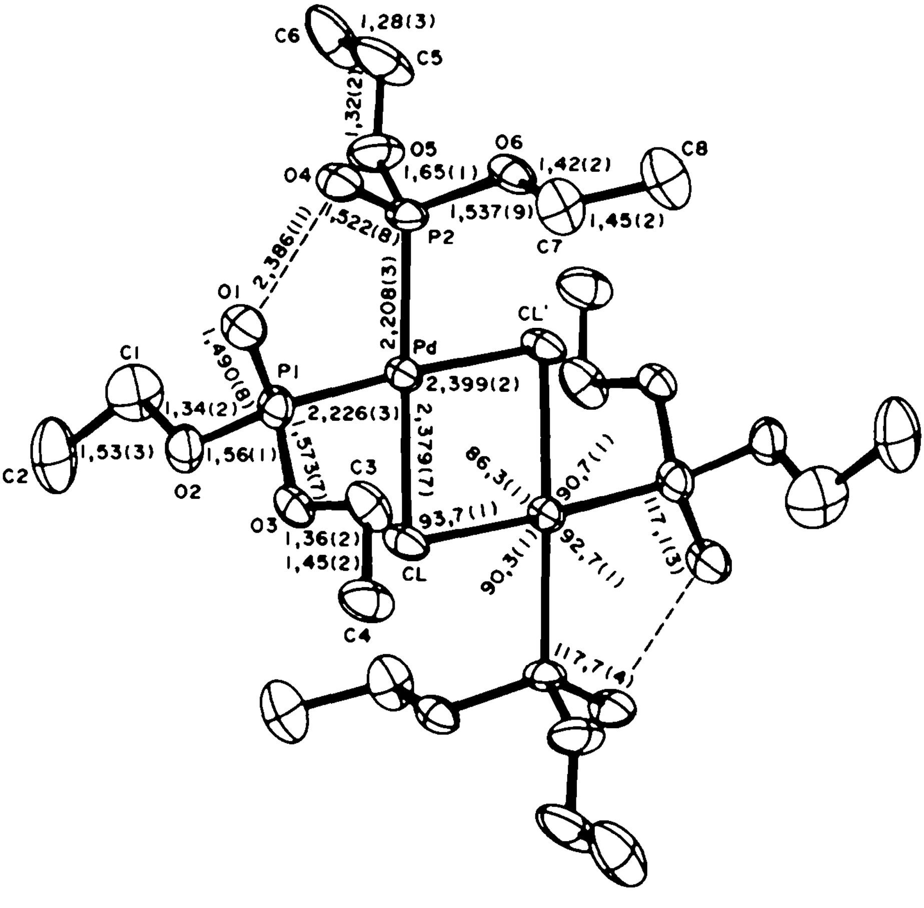
†This is a full account of the two preliminary communications (i) (*Dokl. Acad. Nauk USSR* **233**, 870 (1977) and (ii) (*Dokl. Acad Nauk USSR* **253**, 1389 (1980).

chloride) at a molar ratio of the reagents of 4:1 and isolated as two individual compounds differing by their physico-chemical properties.

Extending our studies onto P-H compounds derived from sugars we have obtained crystalline complexes of type II by reacting bis-(π-allylpalladiumchloride) with alkylglycophosphites.†



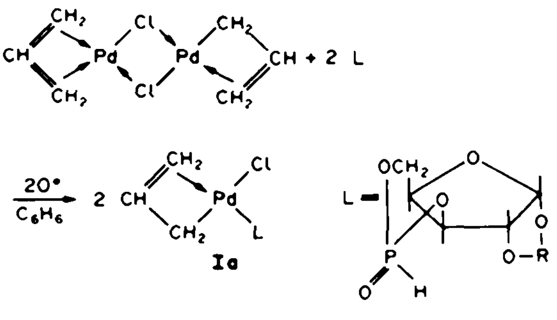


Physico-chemical characteristics of complexes of type II are given in Table 1. The identity of the resulting compounds was proven by TLC and NMR ^{31}P methods. Their structure has been established on the basis of spectral investigations, elemental analysis and cryoscopy. NMR ^{31}P spectra of the products are singlets with the chemical shift of 68–76 ppm. This points to the absence of a P-H bond and equivalence of both organophosphorus ligands. The complex formation is accompanied by a shift of the signal towards a lower field, i.e. by deshielding of the nucleus of the phosphorus on account of a strong δ-bonding with the palladium atom.

From the data of IR-spectroscopy it follows that absorption bands at 465,445 cm^{-1} corresponding to a π-allyl group are absent in the spectra of the complexes. Also absent are absorption maxima corresponding to a P-H bond (2430; 970 cm^{-1}).

The presence of a wide band at 3440 cm^{-1} corresponds to the stetching modes of the associated OH group. On the other hand, the presence of an absorption band at 275 cm^{-1} points to the presence of a palladium-chlorine bond.[8]

While continuing the study of palladium complexes with phosphorylated sugars, we have studied palladium compounds (Ia) with individual cyclobiphosphites of carbohydrates. By reaction of bis-(π-allylpalladiumchloride) with 3,5-cyclophosphites of 1,2-isopropylidene(cyclohexylidene)-α-D-xylofuranose‡ yellow crystalline compounds soluble in benzene, dioxane, chloroform and DMFA have been obtained.



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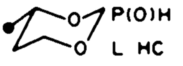
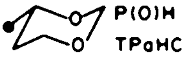
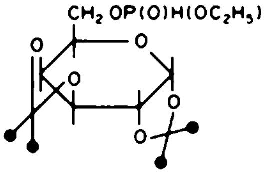
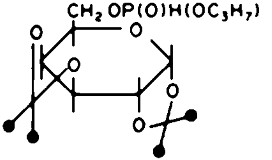
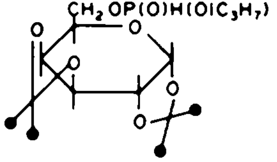
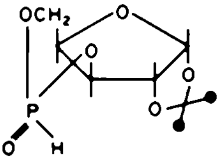
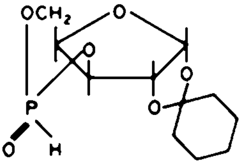
† We have prepared alkylglycophosphites by transesterification of the simplest dialkylphosphites with carbohydrate derivatives.[7]

‡ The synthesis is disclosed in 20.

Table 1.

Ligand	Compound	m.p. (°C)	M	$\delta^{31}P$ (ppm)	$[\alpha]^{17}_D$
$(CH_3O)_2POH$	1	127	660	75.4	
$(C_2H_5O)_2POH$	2	90	780	71.9	
$(iC_3H_7O)_2POH$	3	113	890	72.8	
$(iC_4H_9O)_2POH$	4	124	1011	69.2	
$(C_6H_5O)_2POH$	5	182	1160	88.9	
 L HC	6	166	810	68.3	
 TPaHC	7	198	778	71.9	
	8	68	1700	73.3	−23.39 (C = 2.51, C_2H_5OH)
	9	74	1730	75.6	+24.13 (C = 2.60, C_2H_5OH)
	10	78	1720	76.2	−24.28 (C = 2.43, C_2H_5OH)
	11	142	430	103.0	+54.36 (C = 2.06, C_2H_5OH)
	12	153	462	105.2	+51.81 (C = 2.41, C_2H_5OH)

The isolated complexes are individual compounds having NMR ^{31}P spectra comprising singlets with chemical shifts of 103 and 105 ppm. It should be noted, that this points to a known structural distinction of the compounds under consideration from previously described ones (Table 1). In IR-spectra of complexes 1a there are absorption bands characteristic of the bond Pd–Cl (275 cm^{-1}) and π-allyl group (512, 403, 370 cm^{-1}). Therefore, the reaction between bis-(π-allylpalladiumchloride) and cyclic phosphites of sugars results in the formation of products of the type I which is apparently due to steric factors. The values of molecular mass and elemental analysis justify the suggested structure of mononuclear complexes (Table 1).

X-ray analysis

An X-ray analysis of a diethylphosphite derivative $Pd_2Cl_2\{[(EtO)_2PO]_2H\}_2$ 2 (see Table 1) has been carried out to prove the structure of complexes of type II. Unfortunately, it has been impossible to reveal the hydrogen atoms in different syntheses of electron density due to a strong disorder of the ethoxy groups which is manifested in high values of their anisotropic temperature factors. This disorder results in considerably lowered values of the bonds lengths of the terminal ordinary C–C bonds in ethoxy groups (e.g. the length of C(5)–C(6) bond is reduced to 1.28(3) Å) and increased values of the bond angles P(2)O(5) C(5) and O(5)C(5)C(6) respectively 137(2) and 118(2)° (bond angles in the three other ethoxy groups are as usual). The attempts to carry out a diffraction experiment at a low temperature have proved to be unsuccessful, since the crystals cracked even with slow cooling which might be either due to a phase transition with a change of a cell, or due to ordering of ethoxy groups causing the breakdown of a single crystal.

The coordinates of the non-hydrogen atoms of the complex **2** are given in Table 2, values of the bond angles are given in Table 3. Shown in the diagram are the general view of the complex studied bond lengths and some bond angles. All calculations are made on a "Eclipse S/200" computer using modified† EXTL programmes.

The complex studied **2** has a dimeric centro-symmetric structure, which is a characteristic of bivalent palladium compounds with a slightly distorted flat-square coordination of the central atom. Atoms of P(1), P(2), Cl and Cl are coplanar with an accuracy of ±0.03 Å and the Pd atom is substantially within their plane (extending from their plane by 0.016 Å). Due to the central symmetry of the complex the cycle Pd_2Cl_2 is planar, bond lengths Pd–Cl (2.379(2) and 2.399(2) Å) fall within the range of values characteristic for the structurally investigated dimeric π-complexes of palladium, (2.366–2.527 Å)[9,10] and slightly surpass the value 2.32 Å found in dianion $Pd_2Cl_6^{2-}$.[11]

The structural data on palladium complexes of the type II with phosphite ligands are rather scarce. In Table 4 geometric parameters of (II) are compared with the similar characteristics of the dimeric complex $Pd_2(SCN)_2[(Ph_2PO)_2H]_2$ **2b**[12] and monomeric Pd (μ_2–S_2PMe_2)[$(Ph_2PO)_2H$] **2c**.[13] Also known is the structure of a similar dimeric ruthenium complex $[P(OMe)Ph_2]_2[P(OH)Ph_2]RuCl_3Ru[P(OH)Ph_2]_2(Ph_2PO)$.[14] In all these complexes there is a very strong intramolecular hydrogen bond O–H . . . O between two *cis*-positioned phosphite ligands at the same metal atom which have substantially the same geometric parameters.

In **2** the difference in bonds lengths P(1)–O(1) 1.490(8) Å and P(2)–O(4) 1.522(8) Å is not high (0.0032 Å, i.e. 4σ) so that a longer bond Pd–P(1) corresponds to a shorter distance P(1)–O(1) (Pd–P(1) 2.226(3) Å, Pd–P(2) 2.208(3) Å). The bond length P(1)–O(1) is close to distances P–O in the phosphiteanion $[HOC(Me)_2C(me)_2O–P(H)O_2]$ in the structure of the hydrate of the potassium salt of 2-hydroxy-2,3,3-trimethylpropanephosphorous acid (1.483(3) Å)[15] where the negative change is delocalized on both groups of the P–O anion similarly to that observed in the salts of the carboxylic acids.

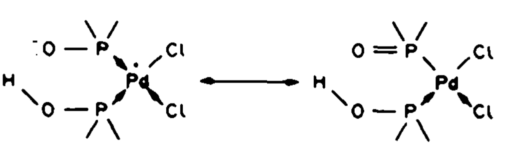
Table 2. Coordinates of non-hydrogen atoms ($\times 10^4$, for Pd $\times 10^5$)

Atom	x	y	z
Pd	7371(7)	92608(3)	94667(6)
Cl	742(4)	9865(1)	11561(2)
P(1)	2095(3)	8473(1)	10530(3)
P(2)	733(4)	8766(1)	7444(3)
O(1)	2365(9)	7876(3)	9717(8)
O(2)	3686(10)	8734(4)	11158(9)
O(3)	1383(8)	8287(3)	11945(6)
O(4)	1349(11)	8077(4)	7417(8)
O(5)	1766(13)	9235(5)	6452(9)
O(6)	−884(10)	8761(3)	6681(7)
C(1)	4816(29)	8968(10)	10383(21)
C(2)	6161(19)	9235(10)	11309(25)
C(3)	−40(17)	7995(7)	11910(16)
C(4)	−395(18)	7817(9)	13314(16)
C(5)	1954(24)	9316(12)	5120(16)
C(6)	3097(22)	9661(14)	4732(21)
C(7)	−2072(16)	8357(7)	7197(16)
C(8)	−3554(20)	8540(8)	6516(17)

Table 3. Bond angles ω (deg.)

Angle	ω	Angle	ω
ClPdCl'	86.3(1)	O(4)P(2)Pd	117.7(4)
P(1)PdCl	90.7(1)	O(4)P(2)O(5)	110.3(5)
P(2)PdCl	176.0(1)	O(4)P(2)O(6)	106.9(5)
P(1)PdCl'	176.9(1)	O(5)P(2)Pd	105.2(4)
P(2)PdCl'	90.3(1)	O(5)P(2)O(6)	102.7(5)
P(1)PdP(2)	92.7(1)	O(6)P(2)Pd	113.1(3)
PdClPd'	93.7(1)	P(1)O(2)C(1)	123(1)
O(1)P(1)Pd	117.1(3)	P(1)O(3)C(3)	118(1)
O(1)P(1)O(2)	109.8(5)	P(2)O(5)C(5)	137(1)
O(1)P(1)O(3)	109.3(4)	P(2)O(6)C(7)	118(1)
O(2)P(1)Pd	110.8(4)	O(2)C(1)C(2)	110(2)
O(2)P(1)O(3)	96.4(4)	O(3)C(3)C(4)	108(1)
O(3)P(1)Pd	111.6(3)	O(5)C(5)C(6)	118(2)
		O(6)C(7)C(8)	108(1)

It is seen from Table 4 that the P–O distances in **2** are essentially shorter than those found in **2b** and **2c** and close to the lengths of the P=O double bonds in compounds with phosphoryl groups forming strong hydrogen bonds.[16] Along with the data of [31]P NMR on chemical shifts demonstrating the predominant δ-character of Pd–P bonds in **2**, this also points to a possible contribution of not only the form **A** to the structure of **2**, but of the "phosphoryl" form **B** as well:



A **B**

In accordance with the above it should be also noted that the distances Pd–P in **2** are slightly shorter than those detected in some phosphine complexes of Pd(2+) (e.g. 2.326(7)–2.333(7) Å in $PdI_2(PMe_2Ph)_2$,[17] 2.234(1)–2.282(1) Å in $PdCl_2[Ph_2P(CH_2)_nPPh_2]$, wherein n = 1, 2, 3).[18]

Short distances O . . . O in structures of type II indicate that hydrogen bonds in these compounds should be close to the symmetric ones of the type O . . . H . . . O, having one-hole potential and, hence, bonds P–O should be equivalent. Frequently the observed slight asymmetry of similar strong H-bonds residing either in a non-central position of the hydrogen atom,‡ or, as observed in **2a–c**, different P–O distances, is apparently due to different surroundings of the oxygen atoms in P–O groups in the crystal. A similar asymmetry of strong one-minimum hydrogen bonds "induced" by the crystal field has also been noticed earlier for compounds with phosphoryl groups, for example in the structure of $Ph_3PO \ldots H \ldots OPPh_3{}^+ClO_4^-$.[16] It should also be noted that symmetry of the strong hydrogen bond in the anion $Ph_2PO \ldots H \ldots OPPh_2^-$ in complexes of type II has been proven by IR-spectral investigation using isotope-substituents.[12,19]

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†The programme modification is effected in X-ray analysis Laboratory of INEOS AN USSR by A. I. Yanovsky and R. G. Gerr.

‡Except for **2b**, no hydrogen atoms in O . . . H . . . O bridges have been revealed in the structures under consideration.

Table 4. Comparison of some geometric parameters of palladium complexes with phosphite ligands

No.	Compound	O…O, Å	P–O, Å	Pd–P, Å	Literature
2a	$Pd_2Cl_2\{[(C_2H_5O)_2PO]_2H\}_2$	2.386(11)	1.490(8) 1.522(8)	2.226(3) 2.208(3)	this paper
2b	$Pd_2(SCN)_2[(Ph_2PO)_2H]_2$	2.421(7)	1.536(6) 1.549(6)	—	4
2c	$Pd(\mu_2\text{–}S_2PMe_2)[(Ph_2PO)_2H]$	2.414(20)	1.545(14)	2.264(4)	5

Catalytic properties

Compounds of palladium with organophosphorus ligands, during recent years, have been shown to be stable and selective hydrogenation catalysts.[21]

Complexes of type II are active catalysts for hydrogenation of nitrobenzene and unsaturated organic compounds after treatment with sodium borohydride in an atmosphere of air or oxygen. It has been shown that olefines with a terminal double bond are hydrogenated slowly, while olefines with the double bond in an inner position, as well as cyclic olefines are not reduced. Acetylene hydrocarbons are hydrogenated at high rates. The products of hydrogenation of acetylenes with the inner position of the triple bond are the corresponding olefines. Diene hydrocarbons add one mole of hydrogen at a high rate. Hydrogenation proceeds selectively: only olefines are detected in the products (Table 5). It should be noted that the size of the hydrocarbon radical in ligands only slightly affects the efficiency of catalysts—with increasing size of the radical the mean rate of hydrogenation steadily decreases. It is also of interest that the ligand stereochemistry has an effect on the catalytic activity of palladium complexes: complexes based on isomeric 1,3-butylene phosphites have different catalytic activity.

During recent years complexes with chiral ligands, mainly phosphine ones,[22] have been used in catalysis of hydrogenation of prochiral substrates. Complexes based on alkylglycophosphites catalyze hydrogenation of such substrates as dimethylitaconate itaconic acid, etc., but the optical yield of these reactions does not exceed 1%. Regarding the presence of equal amounts of two diastereomers in alkylglycophosphites as the reason for the low optical yield, we have decided to obtain a catalytic system based on compounds formed in the interaction of diastereomeric phosphites and optically active α-phenylethylamine:

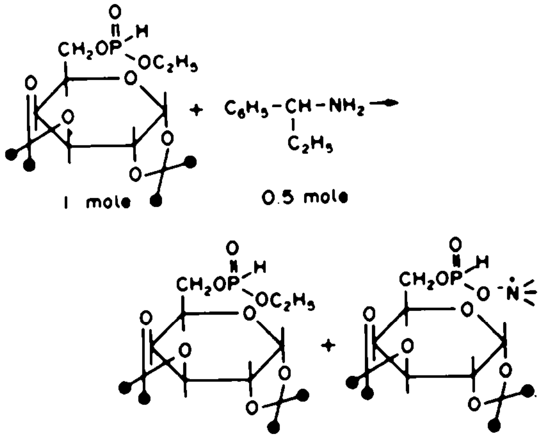

Table 5. Catalytic properties of complex 2 (see Table 1) Hydrogenation conditions: 20°, solvent–ethanol

Substrate	Catalytic properties		Reaction products	Catalyzate composition (%)
	V_{max} (ml/min)	time (min)		
Hexene-1	1.5	45	hexane	6.5
			hexene-1	41.4
			hexene-2	52.1
		105	hexane	9.4
			hexene-1	36.0
			hexene-2	54.6
Hexyne-1	19	4	hexene-1	40.0
			hexene-2	60.0
		64	hexane	7.0
			hexene-1	35.0
			hexene-2	58.0
Nonyne-4	26	3	nonene-4	100
Isoprene	29	4	3-methylbutene-1	27.0
			2-methylbutene-1	33.0
			2-methylbutene-2	40.0
		64	isopentane	4.3
			3-methylbutene-1	21.5
			2-methylbutene-1	27.9
			2-methylbutene-2	46.3
Nitrobenzene	43	5	aniline	100

Table 6. Asymmetry-producing effect of palladium complexes with sugar biphosphites (see Table 1)

Complex	Substrate	Hydrogenation product	Optical yield (%)	Catalytic properties	
				V_{max} (ml/min)	time (min)
8	dimethylitaconate	dimethyl-2-methyl-succinate	23	10	12
	itaconic acid	2-methylsuccinic acid	15.4	13	15
	citraconic acid	2-methylsuccinic acid	10.5	11	15
	α-acotylamino-cinnamic acid	α-acetylphenyl-alanine	1.1	2	1200
11	itaconic acid	2-methylsuccinic acid	27.0	5	26
12	itaconic acid	2-methylsuccinic acid	10.0	3	40

The system (III) has been used in hydrogenation of prochiral compounds (Table 6). The best results are obtained in the case of using individual stereoisomers of cyclophosphites of 1,2-alkylidenexylofuranoses (L). In these compounds the phosphorus fragment is just as asymmetric as the sugar one which offers advantages over the above-mentioned non-cyclic phosphites. Palladium complexes based on these compounds showed a good asymmetry-inducing capacity in hydrogenation of prochiral substrates (Table 6). It should be noted that the nature of the 1,2-alkylidene fragment provides a marked influence on the optical yield. Thus, in hydrogenation of itaconic acid on the 1,2-isopropylidene derivative of cyclophosphite the optical yield is 27%, while on the 1,2-cyclohexylidene derivative it is equal to 10%. The fact that we have noted can probably be explained by different selectivity of the precatalytic adsorption of the substrate on the catalyst.

EXPERIMENTAL

NMR ^{31}P spectra were recorded on a HX-90 E "Bruker" instrument relative to 85% phosphoric acid. IR-spectra were taken on a UR-20 instrument in a thin layer, tablets or vaseline oil within the range of 3600–250 cm $^{-1}$. Specific rotation were determined on a spectropolarimeter "Spectropol-1" in cuvettes of 0.1 dm. Gas-liquid chromatographic analysis were carried out on instruments "Carlo Erba" and LChM-8MD, detector-katharometer, carrier-gas–helium, 80–40 ml/min.

The lattice parameters and intensities of 3944 independent reflections were measured on an automatic 4-circle diffractometer "Syntex $P2_1$" (MoK_α-radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta < 58°$) at room temperature. Crystals of 2 are monoclinic, at 22°C $a = 8.556(2)$, $b = 20.715(3)$, $c = 9.666(1)$ Å, $\beta = 92.64(1)°$, $d_{calc} = 1.619$ g/cm^3, $V = 1711.5$ Å^3, $z = 2$, space groupe $P2_1/a$. The structure was solved by the heavy-atom method and refined in the anisotropic full-matrix least squares approximation to $R = 0.063$ and $R_w = 0.065$.

Synthesis of palladium complexes with dialkyl (or aryl) phosphites

1. To a solution of 0.4 g of bis-(π-allylpalladium-chloride) in 10 ml of absolute benzene 0.48 g of dimethylphosphite is added at 20°C. After 30 min the solution changed its colour from bright yellow to colourless. After distilling off benzene *in vacuo* a white powder is formed which is recrystallized from ethanol. The yield is 0.63 g (88%), m.p. 127–128°, $\delta^{31}P$ 75.4 ppm. Found: C 15.0 H 3.8 P 18.6 Pd 31.8 Cl 10.5 ($C_8H_{26}O_8P_4Pd_2Cl_2$). Calc for C 14.6 H 3.9 P 18.8 Pd 31.8 Cl 10.3.

In a similar manner the following compounds have been obtained.

2. Yield 0.73 g (87%), m.p. 90–91° $\delta^{31}P$ 71.9 ppm. Found: C 25.4 H 5.0 P 16.3 Pd 26.9 Cl 9.5 ($C_{16}H_{42}O_8P_4Pd_2Cl_2$). Calc for C 24.9 H 5.4 P 16.1 Pd 27.5 Cl 9.2.

3. Yield 0.81 g (85%), m.p. 113–115°, $\delta^{31}P$ 72.8 ppm. Found: C 33.4 H 6.4 P 14.2 Pd 23.8 Cl 8.1 ($C_{24}H_{58}O_8P_4Pd_2Cl_2$). Calc for C 32.6 H 6.5 P 14.0 Pd 24.0 Cl 8.0.

4. Yield 0.9 g (85%), m.p. 124–126°, $\delta^{31}P$ 69.2 ppm. Found: C 40.0 H 7.9 P 12.3 Pd 20.9 Cl 7.4 ($C_{32}H_{74}O_4$ Pd_2Cl_2). Calc for C 38.6 H 7.4 P 12.4 Pd 21.3 Cl 7.1.

5. Yield 1.1 (90%), m.p. 182–184°, $\delta^{31}P$ 88.9 ppm. Found: C 51.1 H 3.5 P 10.9 Pd 17.8 Cl 7.0 ($C_{48}H_{42}O_4P_4Pd_2Cl_2$). Calc for C 49.9 H 3.6 P 10.7 Pd 18.3 Cl 6.1.

Synthesis of palladium complexes by transesterification of biphosphite inside the coordination sphere of complexes of type II

To a solution of 0.4 g of complex 1 in benzene 0.18 g of *n*-butanol is added at 80° in an inert atmosphere. The reaction mixture is stirred for 6 h, the reaction progress is controlled chromatographically. The solvent is evaporated *in vacuo*, the resulting white powder is recrystallized from ethanol. The yield is 0.52 g (92%), m.p. 160–162°, $\delta^{31}P$ 71.0 ppm. Found: C 40.3 H 8.0 P 12.7 Pd 21.1 Cl 7.5 ($C_{32}H_{74}O_4P_4Pd_2(Cl_2)$. Calc for C 38.6 H 7.4 P 12.4 Pd 21.3 Cl 7.1.

Synthesis of palladium complexes with isomeric 1,3-butylenephosphites

6. To a solution of 0.4 g of bis-(π-allylpalladium chloride) in 10 ml of absolute benzene 0.6 g of *cis*-1,3-butylene phosphite is added at 20°. After 30–40 min the solution turns light-yellow and precipitation of colourless crystals starts. Within 3 h the solution becomes colourless and precipitation stops, the crystals are filtered and recrystallized from ethanol. The yield is 0.83 g (93%) m.p. 166–168°, $\delta^{31}P$ 68.3 ppm. Found: C 24.0 H 4.2 P 15.3 Pd 26.0 Cl 8.3 ($C_{16}H_{34}O_{12}P_4Pd_2Cl_2$). Calc for C 23.2 H 4.1 P 15.0 Pd 25.6 Cl 8.6.

In a similar manner there is obtained a complex with *trans*-1,3-butylenephosphite.

7. Yield 0.85 g (95%), m.p. 198–200°, δ^{31} P 71.8 ppm. Found: C 24.3 H 4.5 P 14.9 Pd 26.1 Cl 8.2 ($C_{16}H_{34}O_{12}P_4Pd_2Cl_2$). Calc for C 23.2 H 4.1 P 15.0 Pd 25.6 Cl 8.6.

Synthesis of palladium complexes with phosphorylated sugars

8. To a solution of 0.2 g of bis-(π-allylpalladiumchloride) in 20 ml of absolute benzene 0.8 g of 6-*O*-ethylphosphite of 1,2,3,4-diisopropylidenegalactopyranose is added at 20°. After 12 h the solution turns pale-yellow from bright-yellow and colourless crystals partly precipitate. After distilling-off the solvent in vacuum the resulting viscous syrup is rubbed with hexane. The white powder formed is recrystallized from ethanol. Yield 0.65 g (73%), m.p. 68–70°, $\delta^{31}P$ 73.3 ppm, $[\alpha]_D^{17}$ − 23.9 (C = 2.5 C_2H_5OH). Found: C 41.0 H 5.5 P 7.8 Pd 13.0 Cl 4.1 ($C_{46}H_{80}O_{32}P_4Pd_2Cl_2$). Calc for C 39.7 H 5.8 P 7.3 Pd 12.5 Cl 4.2.

In a similar manner all other compounds described below have been prepared.

9. Yield 0.57 g (64%), m.p. 74–75°, δ^{31}P 73.8 ppm, $[\alpha]_D^{17}$ + 22.4 (C = 2.3, C_2H_5OH). Found: C 41.9 H 6.5 P 7.0 Pd 11.9 Cl 4.4 ($C_{60}H_{106}O_{32}P_4Pd_2Cl_2$). Calc for C 41.3 H 6.1 P 7.1 Pd 12.1 Cl 4.1.

10. Yield 0.51 g (57%), m.p. 78–80°, δ^{31}P 73.6 ppm, $[\alpha]_D^{17}$ + 24.4 (C = 2.6, C_2H_5OH). Found: C 42.0 H 5.9 P 7.5 Pd 12.6 Cl 3.8 ($C_{60}H_{106}O_{32}$ $P_4Pd_2Cl_2$). Calc for C 41.3 H 6.1 P 7.1 Pd 12.1 Cl 4.1.

11. Yield 0.11 g (51%), m.p. 142–143°, δ^{31}P 103 ppm, $[\alpha]_D^{17}$ + 54.36 (C = 2.06, C_2H_5OH). Found: C 32.4 H 4.5 P 7.1 Pd 26.0 Cl 8.1 ($C_{11}H_{18}O_6P$ Pd Cl). Calc for C 31.5 H 4.3 P 7.4 Pd 25.3 Cl 8.4.

12. Yield 0.12 g (49%), m.p. 153–155°, δ^{31}P 105 ppm, $[\alpha]_D^{17}$ + 51.8 (C = 2.30, C_2H_5OH). Found: C 37.1 H 4.5 P 6.8 Pd 22.2 Cl 7.5 ($C_{14}H_{22}O_6P$ Pd Cl). Calc for C 36.7 H 4.8 P 6.7 Pd 22.9 Cl 7.7.

REFERENCES

[1] B. James, In *Homogeneous Hydrogenation*. MIR, Moscow, (1976).

[2] E. E. Nifat'ev, *Uspekhi Khimii* **47**, 1565 (1978).

[3] D. M. Roundhill, R. P. Sperline and W. B. Beauleu, *Coord. Chem. Rev.* **26**, 263 (1978).

[4] *Methods of Organoelemental Chemistry*, Book 2, (Edited by A. N. Nesmeyanov and K. A. Kocheshkov). Nauka, Moscow (1975).

[5] A. T. Teleshev, Cand. thesis, MGPI nmd. V. I. Lenin, Moscow (1979).

[6] E. E. Nifant'ev and A. A. Borisenko, *Tetrahedron Letters* 309 (1972).

[7] E. E. Nifant'ev and T. S. Kukhareva, *J. Gen. Chem.* **49**, 757 (1979).

[8] M. P. Michael In *The Organic Chemistry of Palladium*, Vol. 1, p. 89. Academic Press, New York (1971).

[9] N. C. Baenziger, C. V. Goebel, B. A. Foster and J. R. Doyle, *Acta Crystallogr.* **B34**, 1681 (1978).

[10] F. Dahan, *Acta Crystallogr.* **B32**, 1941 (1976).

[11] E. A. Kelly, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc. Chem. Comm.* 289 (1977).

[12] D. V. Naik, G. J. Palenik, S. Jacobson and A. J. Carty, *J. Am. Chem. Soc.* **96**, 2286 (1974).

[13] M. C. Cornock, R. O. Gould, C. L. Jones and T. A. Stephenson, *J. Chem. Soc. Dalton Trans.* 1307 (1977).

[14] R. O. Gould, C. L. Jones, W. J. Sime and T. A. Stephenson, *Ibid.* 669 (1977).

[15] M. Yu. Antipin, A. E. Kalinin, Yu. T. Struchkov, A. A. Kryuchkov, E. I. Matrosov and M. I. Kabachnik, *J. Struct. Chem.* **21**, 168 (1980).

[16] M. Yu. Antipin, A. E. Kalinin, Yu. T. Struchkov, E. I. Matrosov and M. I. Kabachnik, *Kristallographia* **25**, 514 (1980).

[17] N. A. Bailey and R. Mason, *J. Chem. Soc. A* 2594 (1968).

[18] W. L. Steffen and G. J. Palenik, *Inorg. Chem.* **15**, 2432 (1976).

[19] A. J. Carty, S. T. Jacobson, R. T. Simpson and N. J. Taglor, *J. Am. Chem. Soc.* **97**, 7254 (1975).

[20] E. E. Nifant'ev, M. P. Koroteev, N. M. Pugashova, T. S. Kukhareva and A. A. Borisenko, *J. Gen. Chem.* **51**, 1900 (1981).

[21] C. A. Tolman, *Chem. Rev.* **77**, 313 (1977).

[22] T. Jawame, T. Yoshida, M. Sato, *J. Chem. Soc. Japan* 1652 (1976).