POLYPHOSPHORUS LIGANDS, CONTAINING P(III) AND P(V) IN THE MOLECULE, AND THEIR COMPLEXES WITH PALLADIUM

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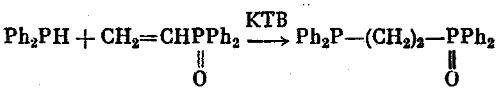
Coordination potentialities of compounds containing both atoms of trivalent and pentavalent phosphorus, i.e., including fragments of phosphine and phosphine oxide, are practically not investigated. Some compounds of this type are synthesized, and their reactions with palladium are investigated in the present work.

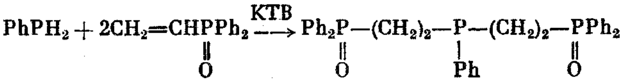
Tetraphenylethylenediphosphine monoxide (L^1) is obtained by the addition of diphenylphosphine to vinyldiphenylphosphine oxide in the presence of catalytic amounts of potassium tert-butylate (KTB):



$$Ph_2PH + CH_2{=}CH\underset{\substack{\|\\ O}}{P}Ph_2 \xrightarrow{KTB} Ph_2P{-}(CH_2)_2{-}\underset{\substack{\|\\ O}}{P}Ph_2$$

(L^1)

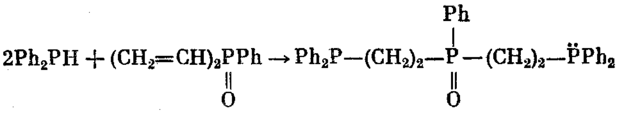
Phenylbis(β-diphenylphosphorylethyl) phosphine (L^2) is synthesized by the reaction of phenylphosphine and 2 moles of vinyldiphenylphosphine oxide in the presence of KTB:



$$PhPH_2 + 2CH_2{=}CH\underset{\substack{\|\\ O}}{P}Ph_2 \xrightarrow{KTB} Ph_2\underset{\substack{\|\\ O}}{P}{-}(CH_2)_2{-}\underset{\substack{|\\ Ph}}{P}{-}(CH_2)_2{-}\underset{\substack{\|\\ O}}{P}Ph_2$$

(L^2)

Phenylbis(β-diphenylphosphinoethyl)phosphine oxide (L^3) is obtained by the addition of two molecules of diphenylphosphine to divinylphenylphosphine oxide:



$$2Ph_2PH + (CH_2{=}CH)_2\underset{\substack{\|\\ O}}{P}Ph \rightarrow Ph_2P{-}(CH_2)_2{-}\overset{\substack{Ph\\ |}}{\underset{\substack{\|\\ O}}{P}}{-}(CH_2)_2{-}\ddot{P}Ph_2$$

(L^3)

The compounds obtained, recrystallized from alcohol or benzene, are colorless crystalline substances, readily soluble in $CHCl_3$ (not less than $5\cdot10^{-2}$ mole/liter), poorly soluble in alcohols and DMFA, and insoluble in acetone, benzene, and CCl_4.

The acid–base properties of compounds L^1 and L^3 are studied by means of the potentiometric titration with $HClO_4$ in a nitromethane medium [1]; L^2 was not studied because of its low solubility in nitromethane. The investigated compounds contain two centers which are capable of protonation: $P^V{=}O$ and $\overset{\diagdown}{\underset{\diagup}{-}}P$. For triphenylphosphine and triphenylphosphine oxide, $pK_a(CH_3NO_2) = 5.3$ [2]* and 2.8 [3]. There is one break in potential at the point of 100% neutralization on the potentiometric titration curve of L^1, which corresponds to the protonation of the P(III) atom: $pK_a(CH_3NO_2) = 7.70$. Further addition of $HClO_4$ does not lead to protonation of the P = O group, the basicity of which evidently was appreciably decreased because of the influence of the phosphonium group.

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*Revised in conformity with [1].

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TABLE 1. UV and ^{31}P NMR Spectra of Compounds L^1, L^2, and L^3, and Their Complexes with Pd(II)

Compound	λ_{max}, nm	$\delta^{31}P$, ppm (−30°C)	J_{PP}, Hz
L^1	257	δ_1 −13,20 δ_2 34,68	50,0
$PdL_2{}^1Cl_2\cdot 2H_2O$	257, 380	$\delta_1=\delta_2=34{,}45$	
$PdL_4{}^1Cl_2\cdot 8H_2O$	257, 340	$\delta_1=\delta_2=34{,}45$	
L^2	267	δ_1 −16,96 δ_2 34,32	43,5
$PdL_2{}^2Cl_2\cdot 5H_2O$	267, 335	δ_1 18,83; δ_1' 18,16 δ_2'' 33,10; δ_2''' 34,38	26,8
L^3	268	δ_1 −13,10 δ_2 42,76	46,0
$PdL^3Cl_2\cdot 2H_2O$	268, 340	δ_1 19,60; δ_1' 18,73 δ_2'' 43,09; δ_2''' 43,83	56,0

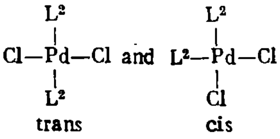
Similar results, especially of the participation in protonation of the P =O group and P(III) atom, should also be expected for L^3. Compound L^3 has one break in potential at the point of 200% neutralization on the titration curve, which indicates the simultaneous protonation of both P(III) centers. This is evidently caused by their mutual remoteness, since in tetraphenylethylenediphosphine (L^4) $Ph_2P{-}(CH_2)_2{-}PPh_2$, obtained according to [4], P(III) atoms are protonated separately, giving two breaks in potential on the titration curve: pK_1 7.46 and pK_2 5.03. The values of pK_1 and pK_2, calculated according to the method of Noyes [5], for L^3 are 7.38 and 6.08.

Compounds L^1, L^2, and L^3 easily react with $PdCl_2$ forming colored complexes which are soluble in a $DMFA{-}CH_2Cl_2$ medium. Upon addition of water and ether to the solutions, complex compounds of Pd(II) with L^1, L^2, and L^3 precipitate in the form of fine crystals. As is seen from Table 1, Pd(II) forms two compounds with ligand L^1: $PdL_2{}^1Cl_2\cdot 2H_2O$ (I) and $PdL_4{}^1Cl_2\cdot 8H_2O$ (II). Ligands L^2 and L^3 form compounds only of the composition $PdL_2{}^2Cl_2\cdot 5H_2O$ and $PdL^3Cl_2\cdot 2H_2O$ with Pd(II).

Bands in the UV range of absorption spectra of the complex compounds evidently belong to bands of the transfer of charge from metal to ligand, which is characteristic for complexes containing ligands of the π-acceptor type, which possess stable low-energy orbitals [6]. In the case under consideration charge transfer is accomplished on free orbitals of P(III).

In the $^{31}P{-}\{^1H\}$ NMR spectrum of the free L^1 ligand the nuclei of two nonequivalent P atoms appears as an AX quadruplet with chemical shifts of −13.20 and 34.68 ppm (new ^{31}P NMR δ scale) ($J_{PP} \approx 50.0$ Hz). Narrow singlet signals at 34.45 ppm (see Table 1) are observed in spectra of $PdL_2{}^1Cl_2\cdot 2H_2O$ and $PdL_4{}^1Cl_2\cdot 8H_2O$ complexes in contrast to the spectrum of the free ligand. The signal of the P(III) atom in spectra of the complexes is shifted to 47.65 ppm downfield with reference to the corresponding signal of the free ligand. The positions of the signal of the P(V) atom in spectra of the complex and of the free ligand are practically coincidental ($\Delta\delta = 0.23$ ppm, see Table 1). This indicates the participation of only P(III) atoms in complex formation with Pd(II). Equalization of shielding on both P atoms during coordination of L^1 with Pd(II) leads to degeneration of the spectrum of the double-spin system to a narrow singlet.

A doublet signal of the nuclei of two P(V) atoms at 34.32 ppm and a triplet signal of the nucleus of a P(III) atom at −16.96 ppm ($J_{PP} \approx 43.5$ Hz) are observed in the $^{31}P{-}\{^1H\}$ NMR spectrum of ligand L^2. Only the P(III) signal is substantially shifted (to ~35.5 ppm) downfield in the $^{31}P{-}\{^1H\}$ NMR spectrum of the $PdL_2{}^2Cl_2\cdot 5H_2O$ complex. It is of interest to note that the multiplicity of all signals is doubled, possibly owing to the existence of cis and trans isomers, in the spectrum of this complex in contrast to the spectrum of the free ligand.



$$\underset{\text{trans}}{Cl{-}\overset{L^2}{\underset{L^2}{Pd}}{-}Cl} \quad \text{and} \quad \underset{\text{cis}}{L^2{-}\overset{L^2}{\underset{Cl}{Pd}}{-}Cl}$$

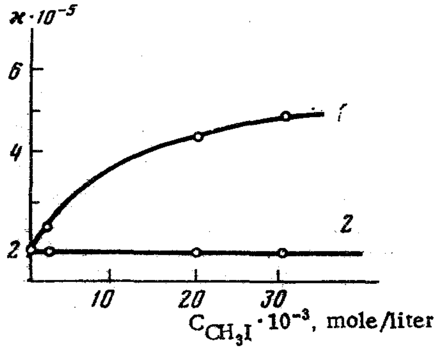
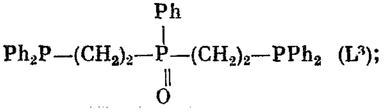


Fig. 1. Change of specific conductance of nitromethane solutions upon the addition of CH_3I: 1)



$$Ph_2P{-}(CH_2)_2{-}\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}{-}(CH_2)_2{-}PPh_2 \quad (L^3);$$

2) $PdL^3Cl_2 \cdot 2H_2O$.

A triplet signal of a P(V) atom at 42.76 ppm and a doublet signal of two P(III) atoms −13.10 ppm (J_{PP} = 46.0 Hz) are observed in the $^{31}P{-}\{^1H\}$ NMR spectrum of ligand L^3. The signal of the two P(III) atoms is substantially shifted downfield ($\Delta\delta \approx 32$ ppm) in the spectrum of the $PdL^3Cl_2 \cdot 2H_2O$ complex; the position of the signal of the P(V) atom in the spectrum of the complex was changed insignificantly compared to the signal of the free ligand, clearly indicating the simultaneous coordination of both P(III) atoms of the L^3 ligand in the $PdL^3Cl_2 \cdot 2H_2O$ complex. The multiplicity of all signals is also doubled in the spectrum of the complex in contrast to the spectrum of the free ligand L^3, evidently because of the formation of cis and trans isomers. It is possible that in this case dimeric particles of the composition $Pd_2L_2{}^3Cl_4 \cdot 4H_2O$ are formed owing to the general tendency of $PdCl_2$ to dimerize in solution [7].

The participation in complex formation of both P(III) atoms of the L^3 ligand is also shown by the titration with CH_3I of solutions of the $PdL^3Cl_2 \cdot 2H_2O$ complex and the free L^3 ligand in a solution of CH_3NO_2. The reaction of CH_3I with an uncoordinated molecule of phosphine proceeds in nitromethane according to the equation $R_3\ddot{P} + CH_3I \rightarrow R_3PCH_3^+ + I^-$, leading to the increase in the conductance of the solution [8]. Upon the addition of CH_3I to a solution of the ligand the conductance increases, but the conductance of a solution of the complex in an analogous experiment is practically unchanged (Fig. 1). This indicates that all P(III) atoms in the complex are connected to the metal.

All of the isolated compounds of Pd(II) with L^1, L^2, and L^3 include from two to eight molecules of water (see Table 1). The water content is calculated from data of elemental analysis and are determined thermogravimetrically. Evidently the water molecules are bonded by H bonds with oxygen of the phosphoryl groups of the ligands, and also penetrate the crystal lattice. Water is not part of the composition of the isolated complex, according to the method is [9], of Pd(II) with tetraphenylethylenediphosphine (L^4), which contains only P(III) atoms, since H-bond formation is excluded because of the absence of phosphoryl groups. In this case the complex compound PdL^4Cl_2 is formed.

Comparison of IR spectra of the compounds L^1, L^2, and L^3 and their complexes with palladium with the IR spectrum of tetraphenylethylenediphosphine (L^4) [10] and its complex with Pd(II), and also the literature data, concerning spectral developments of the formation of complexes of the type $(Ph_3P)_2MHal_2$, where M = Zn, Cd, Hg; Hal = Cl, Br, I [11], allowed one to separate a series of bands of IR absorption of compounds L^1, L^2, and L^3, which are susceptible to complex formation with $PdCl_2$.

It is shown in [11] that the reaction of Ph_3P with metals leads to a change of frequencies and intensities of the bands, pertaining to the so-called X-sensitive vibration (q, r, t, and y modes), i.e., to those which include in themselves motion of atom X of the group $X(C_6H_5)$ and therefore sensitive to its condition (in the case in question X = P, n = 2).

TABLE 2. Bands of IR Absorption of Compounds L^1, L^2, L^3, and L^4 and Their Complexes with Pd(II)

Compound	X-sensitive modes			$\nu P=O$, cm^{-1}
	q	r	y	
Ph_3P [10]	1089	698 692	499 497 489	
$(Ph_3P)_2ZnCl_2$ [10]	1100	714	489 506 512	–
L^1	1110 m 1128 s	712 m 730 s 743 m 750 sh 760 sh	475 w 510 m 515 m 540 m	1188 s
$PdL_2{}^1Cl_2\cdot 2H_2O$	1110 s 1128 s	735 vs	490 m 512 m 535 m 545 m	1180 s, br
$PdL_4{}^1Cl_2\cdot 8H_2O$	1110 m 1128 s	737 s 740 s 765 sh	515 s 535 s	1180 s 1190 s
L^2	1110 m 1128 s	735 sh 743 s, br 760 sh	498 m 512 m 548 m	1180 s 1192 sh
$PdL_2{}^2Cl_2\cdot 5H_2O$	1110 m 1122 s	740 s, br	498 m 520 m 548 m	1180 s, br
L^3	1110 sh 1122 s	705 sh 720 sh 735 s 750 sh	500 sh 515 m 543 s	1180 s 1192 sh
$PdL^3Cl_2\cdot 2H_2O$	1110 s 1122 s	725 sh 735 s 740 s	485 w 513 s 520 s 542 s	1180 s
L^4	1103 m	705 m 730 s 742 m 753 m	480 m 508 m 515 sh	–
PdL^4Cl_2	1110 s	707 s 720 s 748 m 750 m 755 m	488 m 535 m	–

The intensity of the q band in the 1100-1110 cm^{-1} range is sharply increased in the IR spectra of ligands L^1, L^2, and L^3 upon complex formation, shifting somewhat to high frequencies. So, bands of medium intensity at 1110 cm^{-1} for L^1, L^2, and L^3 and at 1103 cm^{-1} for L^4 are observed in spectra of the free ligands, and a very intense band at 1110 cm^{-1} is contained in spectra of complexes of $PdL_2{}^1 2H_2O$, $PdL^3Cl_2\cdot 2H_2O$, and PdL^4Cl_2, which indicates the participation of a P(III) atom in coordination [11]. The intensity of the q band is not increased in the spectra of $PdL_4{}^1Cl_2\cdot 8H_2O$ and $PdL_2{}^2Cl_2\cdot 5H_2O$. The other X-sensitive vibrations, r, t, y [10, 11], are changed simultaneously, but they are less characteristic (Table 2).

Upon formation of complexes of the type $(Ph_3P=O)_2\cdot ZnHal_2$ (Hal = Cl, Br, I) the X-sensitive vibrations are insignificantly changed and the basic characteristic of coordination at the $P^V=O$ group is the reduction of the frequency of its valence vibration ν P=O [11]. The band ν P=O is significantly broadened and shifted to lower frequencies in the $PdL_2{}^1Cl_2\cdot 2H_2O$ spectrum in comparison with the band of the free L^1 ligand. One can conjecture that this shifting is determined by the coordination of $P^V=O$ with water, which, as was found, is contained in the crystalline sample.

EXPERIMENTAL

For compound $PdL_2{}^1\cdot 2H_2O$, 3.7% H_2O was found and 3.5% calculated; for $PdL_4{}^1Cl_2\cdot 8H_2O$, 7.2% H_2O was found and 7.3% calculated; for $PdL_2{}^2Cl_2\cdot 5H_2O$, 6.4% H_2O was found and 6.4% calculated. The water content in the remaining cases was calculated on the basis of the data from the elemental analysis.

Electronic absorption spectra of chloroform solutions of ligands and their complexes with Pd(II) were taken on an SF-4A spectrophotometer. ^{31}P NMR spectra were taken at −30°C in $CHCl_3$ on a Bruker HX-90 spectrometer, IR spectra were taken on a UR-20 spectrometer in KBr pellets. The conductance of nitromethane solutions was measured in a vessel with Pt electrodes at 25°C.

Water was determined on a F. Paulik—J. Paulik—L. Erdey derivatograph system.

Tetraphenylethylenediphosphine Monoxide (L^1). A mixture of 3.3 g (0.0143 mole) of vinyldiphenylphosphine oxide and 0.27 g (0.0024 mole) KTB was added to a solution of 2.7 g (0.0143 mole) of diphenylphosphine in 20 ml of abs. xylene; the temperature was increased to 30°C. Then the mixture was heated for 6 h at 100°C. The completely congealed mixture was recrystallized twice from alcohol. A yield of 5.3 g (89%) was obtained with a mp of 194°C. Found: C 75.3; H 5.7; P 14.9%. $C_{26}H_{24}P_2O$. Calculated: C 75.4; H 5.8; P 15.0%.

Phenylbis(β-diphenylphosphorylethyl)phosphine (L^2). A mixture of 0.8 g (0.0075 mole) of phenylphosphine and 0.5 g (0.005 mole) KTB was added to a solution of 3.4 g (0.015 mole) of vinyldiphenylphosphine oxide in 20 ml of abs. benzene. After boiling (4 h), the solid portion was filtered and recrystallized from alcohol. A yield of 7.6 g (90%) was obtained with a mp of 258-260°C. Found: P 16.3%. $C_{34}H_{33}P_3O_2$. Calculated: P 16.4%.

Phenylbis(β-diphenylphosphinoethyl)phosphine oxide (L^3). An amount of 6.4 g (0.034 mole) of diphenylphosphine was added to 3.1 g (0.017 mole) of divinylphenylphosphine oxide in 30 ml of abs. benzene and the mixture was heated for 2 h at 100°C and for 2 h at 130°C. The solid product was recrystallized twice from benzene. A yield of 7.6 g (72.5%) was obtained with a mp of 235-238°C. Found: C 74.1; H 6.0; P 16.5%. $C_{34}H_{33}P_3O$. Calculated: C 74.2; H 6.0; P 16.9%.

$PdL_2^1Cl_2\cdot 2H_2O$. A solution of 0.4637 g ($1.12\cdot 10^{-3}$ mole) of L^1 in 1 ml of CH_2Cl_2 was added to a solution of 0.1 g ($5.6\cdot 10^{-4}$ mole) of $PdCl_2$ in 2 ml of DMFA. The mixture was heated for 20 min at 80-90°C and was diluted with a large amount of water. The oily substance which separates was triturated in ether, during which a yellow precipitate formed. The precipitate was dissolved in a minimum amount of DMFA, then the substance was precipitated by a large amount of water and ether, mp of 146-148°C (with decomposition). Found: C 59.2; H 4.7%. $C_{52}H_{52}P_4O_4Cl_2Pd$. Calculated: C 59.9; H 5.0%.

$PdL_4^1Cl_2\cdot 8H_2O$. A solution of 0.0142 g ($3.44\cdot 10^{-5}$ mole) of L^1 in 10 ml of alcohol was added to a solution of 0.0015 g ($8.6\cdot 10^{-6}$ mole) of $PdCl_2$ in 10 ml of 1 M HCl. After heating for 20 min at 100°C, the compound which formed was extracted with 10 ml of $CHCl_3$. The $CHCl_3$ was evaporated and the remaining mass was triturated in ether. The residue was dissolved in a minimum amount of DMFA and the complex was precipitated by a large amount of water and ether, mp >250°C. Found: C 62.1; H 5.3; P 12.6%. $C_{104}H_{112}O_{12}P_8Cl_2Pd$. Calculated: C 63.1; H 5.7; P 12.5%.

$PdL_2^2Cl_2\cdot 5H_2O$. A solution of 0.232 g ($4.1\cdot 10^{-4}$ mole) of L^2 in 10 ml of CH_2Cl_2 was added to 0.037 g ($2.05\cdot 10^{-4}$ mole) of $PdCl_2$ in 20 ml of DMFA. The mixture was heated for 20 min at 80-90°C, then the complex was precipitated by water and ether. The separating yellow precipitate was dissolved in a minimum amount of DMFA and was precipitated once more; mp >250°C (with decomposition). Found: C 59.0; H 5.3; P 13.7%. $C_{68}H_{76}P_6O_9Cl_2Pd$. Calculated: C 58.3; H 5.4; P 13.3%.

$PdL^3Cl_2\cdot 2H_2O$. A solution of 0.154 g ($2.8\cdot 10^{-4}$ mole) of L^3 in 3 ml of CH_2Cl_2 was added to a solution of 0.05 g ($2.5\cdot 10^{-4}$ mole) of $PdCl_2$ in 3 ml of DMFA. The mixture was heated until a change of color, then a large amount of water was added. The yellow precipitate was filtered and washed with ether. Found: C 53.7; H 4.4; P 11.8%. $C_{34}H_{37}P_3O_3Cl_2Pd$. Calculated: C 53.4; H 4.9; P 12%.

PdL^4Cl_2. The complex was obtained according to [8].

CONCLUSIONS

New polyphosphorus compounds are synthesized which contain atoms of P(III)and P(V): tetraphenylethylenediphosphine monoxide, phenylbis(β-diphenylphosphorylethyl)phosphine, and phenylbis(β-diphenylphosphinoethyl)phosphine oxide. Their acid—base properties and their complex formation with Pd(II) were studied.

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