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Phosphorus Halides Complexes with 4-Dimethylaminopyridine and *N*-Methylimidazole

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Abstract—Formation of complexes between phosphorus halides and 4-dimethylaminopyridine or *N*-methylimidazole was studied. The following phosphorus halides: trichloride, oxychloride, and sulfochloride, were found to form equilibrium mixtures of the complexes containing different numbers of the ligand molecules. Among the studied phosphorus halides only pentachloride and tribromide form stable complexes with a constant composition.

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The ability of phosphorus halides to form complexes with amines has been discovered fairly long ago. In 1954 Trost for the first time postulated formation of complexes in the mixtures of triethylamine with phosphorus halides [1]. More recently the phosphorus trichloride and tribromide complexes with triethylamine [2–4], the phosphorus pentachloride and pentafluoride complexes with pyridine [5–8], the phosphorus trichloride and tribromide and phodphorus pentabromide with 4-dimethylaminopyridine [9, 10] were prepared.

Initially, these complexes were interesting as models of transition state in the reactions of nucleophilic substitution at the phosphorus atom. Further it was found that pyridine and other nitrogen bases manifest catalytic properties in the reactions of phosphorylation that were understandable by assuming formation of the complexes behaving as active electrophilic moieties [11–13].

All the complexes of phosphorus halides with amines are extremely easily hydrolyzable compounds, many of them are partially dissociated in solution, therefore their composition is not constant, that complicates their study and practical application. We carried out a systematic search for more stable complexes among the products of interaction of phosphorus halides with the strongest nucleophiles, 4-dimethylaminopyridine and *N*-methylimidazole.

We studied interaction of phosphorus trichloride (**I**) with 4-dimethylaminopyridine (**II**) at different reagents ratios and concentrations. In all cases in the ^{31}P NMR spectrum of the reaction mixture one strong signal appeared with the position dependent on the ratio and concentration of the components. Fig.1 and Table 1 contain the data obtained for different ratios PCl_3 : 4-dimethylaminopyridine (1:1, 1:2, 1:3, 1:6, 1:10) . Increase in the solution concentration leads to the upfield shift of the signal that returns to initial position at dilution.

The data obtained allow to assume an equilibrium formation fast in the ^{31}P NMR time scale for a series of

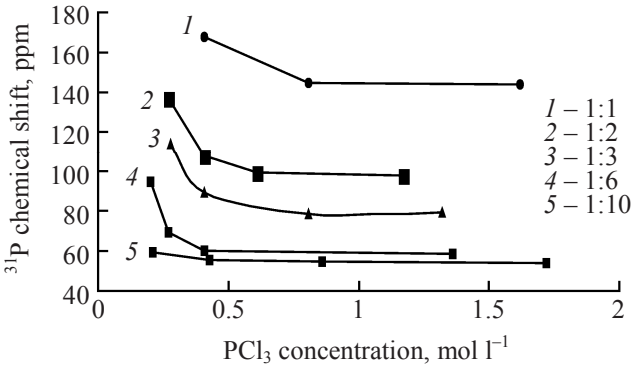


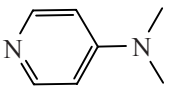
Fig. 1. Plots of ^{31}P chemical shift on the concentration and ratio of reagents in the system PCl_3–4-dimethylaminopyridine.

Table 1. Dependence of ^{31}P chemical shift on the concentration and ratio of the reagents in the system PCl_3–4-dimethylaminopyridine

PCl_3 concentration, mol l^{-1}	^{31}P chemical shift, ppm				
	PCl_3 : 4-dimethylaminopyridine ratio				
	1:1	1:2	1:3	1:6	1:10
0.41	167.7	–	–	–	–
0.81	144.4	–	–	–	–
1.62	144	–	–	–	–
0.27	–	137.1	–	–	–
0.41	–	107.5	–	–	–
0.61	–	99.6	–	–	–
1.17	–	97.6	–	–	–
0.28	–	–	114	–	–
0.41	–	–	89	–	–
0.81	–	–	78.6	–	–
1.32	–	–	79	–	–
0.2	–	–	–	94.5	–
0.27	–	–	–	69.5	–
0.41	–	–	–	59.9	–
1.36	–	–	–	58.6	–
0.21	–	–	–	–	59
0.43	–	–	–	–	55.4
0.86	–	–	–	–	54.6
1.72	–	–	–	–	53.5

phosphorus trichloride complexes with 4-dimethylaminopyridine, with the composition from 1:1 to 1:3 or even higher.

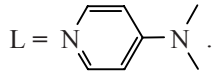
$$\underset{\mathbf{I}}{PCl_3} + \underset{\mathbf{II}}{3L} \rightleftharpoons \underset{\mathbf{III}}{PCl_3 \cdot L} + 2L \rightleftharpoons \underset{\mathbf{IV}}{PCl_3 \cdot 2L} + L \rightleftharpoons \underset{\mathbf{V}}{PCl_3 \cdot 3L}$$

L =  .

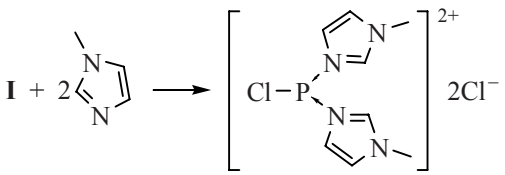
The fast transitions between the complexes lead to the averaging of the NMR signals in the spectra. Neither of the complexes **III–V** is stable enough to be isolated in the individual state. The crystalline products obtained in these syntheses by the effective concentrating of these solution do not have a constant composition that changes depending on the method of their isolation.

Studying the properties of the solutions containing equilibrium mixtures of the 4-dimethylaminopyridine complexes with PCl_3 we for first time found a phenomenon of nucleophilic catalysis in the process of oxidation of phosphorus trichloride with air oxygen. When dry air is blown through the chloroform solution of phosphorus trichloride and 4-dimethylaminopyridine in 1:3 ratio the phosphorus trichloride is readily oxidized to form compound **VI,** the latter is analogous to the phosphorus oxychloride complex with 4-dimethylaminopyridine with composition 1:3. In the absence of 4-dimethylaminopyridine the oxidation does not occur. Similar catalytic effect on the process of oxidation of phosphorus trichloride exhibit triethylamine and tetramethylurea [14].

$$\underset{\mathbf{I}}{} + \underset{\mathbf{II}}{3L} \xrightarrow{O_2} \underset{\mathbf{VI}}{POCl_3 \cdot 3L}$$

L =  .

N-Methylimidazole (**VII**), like 4-dimethylaminopyridine, forms with phosphorus trichloride at the ratio 3:1 an equilibrium mixture of various substances. But unlike the reaction mixture with **II**, the ^{31}P NMR spectrum of this reaction mixture contains three broad signals, at 90, –46 and –112 ppm, indicating that here the ligand exchange proceeds much slower and the complexes formed are stronger. Actually, in this case we succeeded to isolate from the reaction mixture the product **VIII**, whose elemental analysis data were close to that corresponding to the complex of 1:2 composition. In the ^{31}P NMR spectrum of this complex there is a broad signal at 90 ppm. In the reaction of **VIII** with methanol dimethyl hydrogen phosphite **IX** is formed that indicates the retention of the oxidation state in the complex and the absence of the products of C-phosphorylation.



$$\underset{\mathbf{VII}}{} \qquad \underset{\mathbf{VIII}}{}$$

$$\xrightarrow{2\ MeOH} \underset{\mathbf{IX}}{HP(O)(OMe)_2}.$$

Phosphorus tribromide reacts readily with three equivalents of 4-dimethylaminopyridine or *N*-methylimidazole with formation of complexes **XI, XIV**

insoluble in chloroform, with the constant composition 1:3. At the use of a lesser amount of ligands, in both cases formed nonetheless the complex of 1:3 composition while phosphorus tribromide remained in excess. In favor of ionic structure of the complexes attest their high melting points (176°C for **XI**, 183°C for **XIV**) and extremely low solubility. The complexes are poorly soluble in common aprotic solvents and in sulfolane even at heating. The phosphorus chemical shifts in the ^{31}P NMR spectra are 84 ppm (**XI**) and 90 ppm (**XIVa**). These values and results of reactions of these compounds with methanol and diethylamine leading to formation of respective phosphites **XII, XIII**, and **XV** confirm the retention of the phosphorus oxidation state and the absence of the products of C-phosphorylation of the ligands.

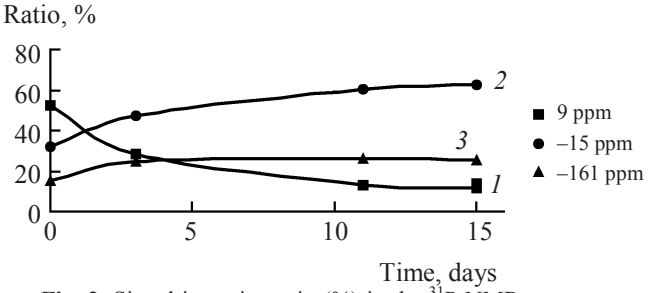
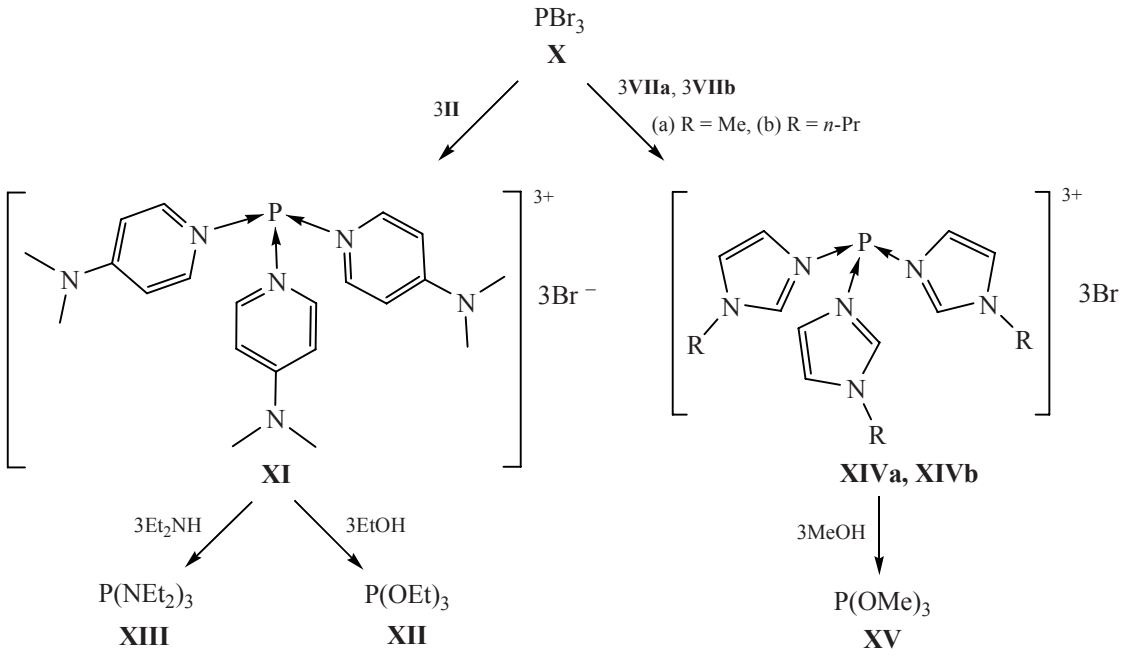


Fig. 2. Signal intensity ratio (%) in the ^{31}P NMR spectrum of reaction mixture of $POCl_3$ with 4-dimethylaminopyridine in chloroform (mole ratio of the reagents 1:3).



Elongation of the chain of imidazole *N*-alkyl group by the replacement of *n*-propyl for methyl group does not increase the complex **XIVb** solubility. Hydrolytic stability of the described complexes **XI, XIVa**, and **XIVb** is low enough. Air moisture hydrolyzed these compounds in a few minutes.

Phosphorus oxychloride with 4-dimethylaminopyridine **II** forms an equilibrium mixture of complexes, but unlike the case of PCl_3 here the exchange and the attainment of the equilibrium proceed much slower. We studied this interaction at different reagent ratios. At the molar halide to ligand ratio 1:3 in the ^{31}P NMR spectrum appear three separate signals (9, –15 and –161 ppm), that obviously correspond to the complexes of different composition (Fig. 2 and Table 2). The equilibrium is achieved slowly, in 10–15 days. At the keeping of the reaction mixture in a sealed ampoule for one year the compounds with the signal at 9 ppm in the ^{31}P NMR spectrum disappeared com-

Table 2. Ratio of signal intensities (%) in the ^{31}P NMR spectrum of the reaction mixture of $POCl_3$ and 4-dimethylaminopyridine in chloroform (mole ratio of the reagents 1:3)

Time, days	Intensity of signal at 9 ppm, %	Intensity of signal at –15 ppm, %	Intensity of signal at –161 ppm, %
0	52.24	32.25	15.48
3	28.64	46.94	24.41
11	13.33	60.61	26.06
15	11.94	62.89	25.16

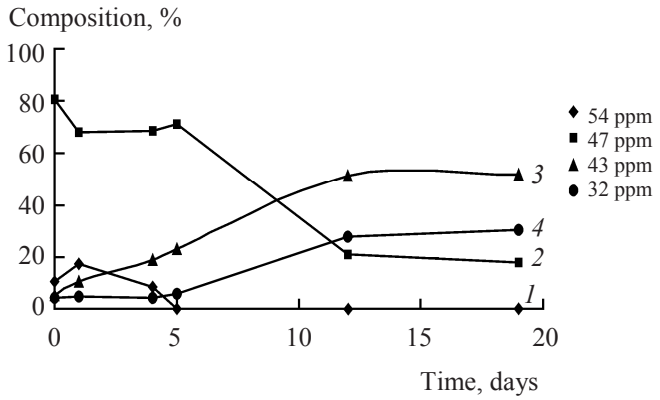


Fig. 3. Signal intensity ratio (%) in the ^{31}P NMR spectrum of reaction mixture of $PSCl_3$ with 4-dimethylaminopyridine in chloroform (mole ratio of the reagents 1:2).

pletely and two other complexes were in the equilibrium.

$$POCl_3 + 3L \rightleftharpoons POCl_3{\bullet}L + 2L$$
XVI **II** **XVII**
9 ppm

$$\rightleftharpoons POCl_3{\bullet}2L + L \rightleftharpoons POCl_3{\bullet}3L,$$
XVIII **XIX**
–161 ppm –15 ppm

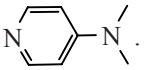
L =  .

Table 3. Ratio of signal intensities (%) in the ^{31}P NMR spectrum of the solution of $PSCl_3$ and 4-dimethylaminopyridine in chloroform (mole ratio of the reagents 1:2)

Time, days	Intensity of signal at 54 ppm, %	Intensity of signal at 47 ppm, %	Intensity of signal at 43 ppm, %	Intensity of signal at 32 ppm, %
0	10.3	80.41	5.15	4.1
1	17.27	68.03	10.34	4.83
4	8.32	68.42	18.9	4.34
5	0	71	23.2	5.8
12	0	21.02	51.28	27.7
19	0	17.7	52.08	30.2
21	0	17.7	52.08	30.2
23	0	21.35	52.08	25
32	0	20	52.63	25.26
52	0	17.64	53.47	26.74

We succeeded to isolate practically pure compounds **XVIII** and **XIX** to which correspond the signals at –161 and –15 ppm. By the data of elemental analysis, compositions of these complexes are 1:2 and 1:3. The structure of the 1:2 complex is confirmed by the spin-spin coupling of the phosphorus nucleus with the pyridine ring α-protons, with the constant 15 Hz.

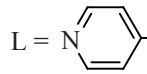
Stability of both these complexes against hydrolysis is much higher than that of the above complexes. According to the ^{31}P NMR spectra the first signals indicating the hydrolysis appear after one hour, and complete hydrolysis proceeds for more than 24 h. Reaction with methanol is even slower. Complex **XVIII** can be dissolved in methanol and react with it with 1-month half-transformation period.

The signal at 9 ppm the most probably corresponds to the intermediate complex of 1:1 composition. At mixing the reagents in 1:1 ratio this signal is the principal one just after mixing, while further its intensity falls with simultaneous increase in intensity of the signals of initial halide (+5.6 ppm) and of the complex of 1:3 composition (–15 ppm).

The sulfochloride **XX** reacts with **II** like the chloride **XVI**, but the mixture contains more different complexes (Fig. 3 and Table 3).

$$PSCl_3 + 3L \rightleftharpoons PSCl_3{\bullet}L + 2L$$
XX **II** **XXI**
32 ppm 47 ppm

$$\rightleftharpoons PSCl_3{\bullet}2L + L \rightleftharpoons PSCl_3{\bullet}3L,$$
XXII **XXIII**
43 ppm

L =  .

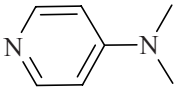
Mixing in 1:1 and 1:3 ratios gives the similar picture.

The signal at 47 ppm in the ^{31}P NMR spectrum is split into a triplet with the constant 15 Hz, the signal at 43 ppm, into a quintet with the same constant. Respective splitting of the signals of pyridine α-protons occurs in ^{1}H NMR spectra. Hence, these ^{31}P signals belong probably to the 1:1 and 1:2 complexes of phosphorus sulfochloride with 4-dimethylaminopyridine respectively. These compounds were not isolated individually. The signal at 54 ppm is very broad, and we failed to assign it to a certain compound. At the ratio **XX**:**II** = 1:6 appears also a signal at 95 ppm split into a quintet.

The course of the process can be understood according to the following scheme: Initially appears a complex of 1:1 composition (47 ppm) that further undergoes disproportion into 1:2 complex (43 ppm) and the free sulfochloride (32 ppm).

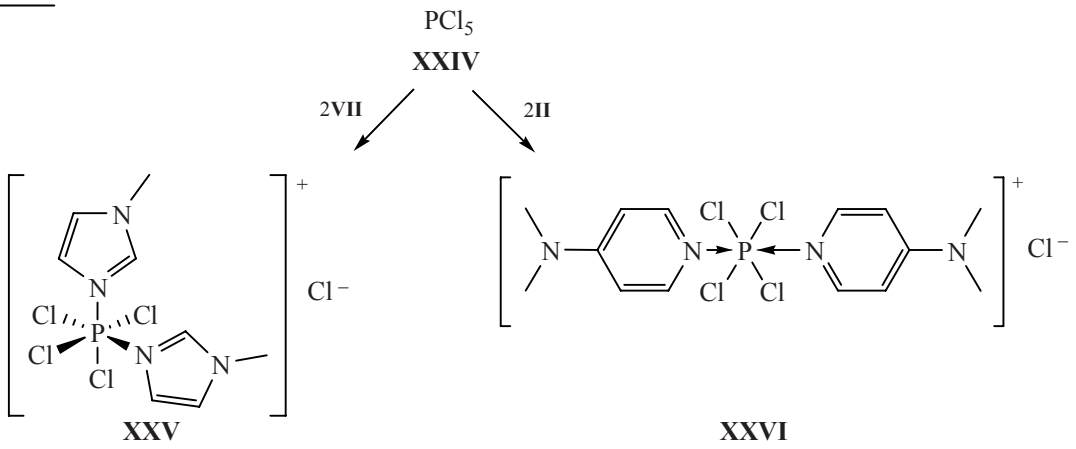
$$PSCl_3 + L \longrightarrow [PSCl_3L]$$

$$2\,[PSCl_3L] \rightleftharpoons PSCl_3 + PSCl_3L_2$$

L =  .

At the interaction of phosphorus pentachloride with 4-dimethylaminopyridine or *N*-methylimidazole in chloroform the crystalline complexes **XXV** and **XXVI** are formed with the compositions 1:2, by the data of elemental analysis.

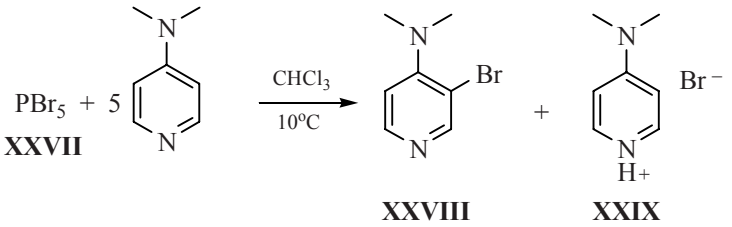
Molecular structure of compound **XXV** was established by X-ray structural analysis. This complex is phosphorus-containing monocation with *cis* arrangement of the ligands.

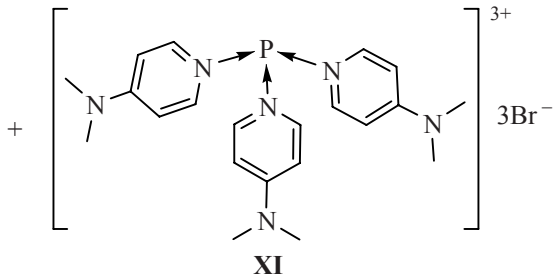


XXV **XXVI**

Structures of complexes **XXV** and **XXVI** and their chemical properties such as hydrolytic stability, reaction with alcohols and diisobutylamine, and their application as condensing agents in the reactions of carboxylic acids with amines we have described in detail [15].

It could be assumed that phosphorus pentabromide **XXVII** will form with **II** the complexes like pentachloride. The data on addition of five 4-dimethylaminopyridine molecules to phosphorus pentabromide with formation of pentacoordinated complex of phosphorus(+5) were published [9], but we showed that these data were erroneous. At mixing the components **XXVII** and **II** in 1:5 ratio even at low temperature bromination of the ligand occurs and then the formation of the complex of phosphorus tribromide **XI** identical to that obtained by us from PBr_3 and 4-dimethylaminopyridine.





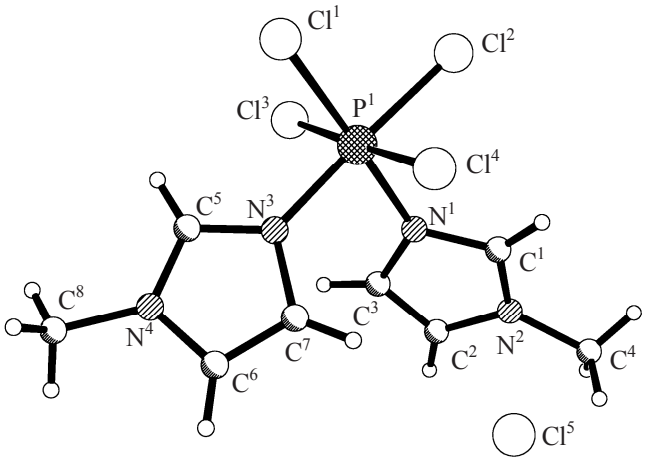


Fig. 4. General view of molecule **XXV**.

Such behavior of phosphorus pentabrmide is understandable, for under the given conditions it dissociates completely (by the data of ^{31}P NMR more than by 95%) into bromine and phosphorus tribromide [16].

Thus, the phosphorus halides: thichloride, oxychloride and sulfochloride, form with 4-dimethylaminopyridine and *N*-methylimidazole the equilibrium mixtures of the complexes of various compositions. The majority of crystalline products isolated from these mixtures have no constant composition and are not individual compounds. Among the studied phosphorus halides only phosphorus pentachloride and phosphorus tribromide form stable complexes with constant composition with 4-dimethylaminopyridine and *N*-methylimidazole.

EXPERIMENTAL

The ^{31}P and ^{1}H NMR spectra of solutions of the studied compounds in $CHCl_3$ (^{31}P) or $CDCl_3$ (^{1}H) were registered on a Varian VXR-300 instrument with operating frequencies 121.42 and 299.95 MHz, respectively. Chemical shifts are given relatively to external reference 85% H_3PO_4 (^{31}P) or internal reference TMS (^{1}H). Reactions were carried out under anhydrous conditions, under the flow of dry argon. The anhydrous solvents were prepared by their distillation over phosphoric anhydride.

Phosphorus trichloride complexation with 4-dimethylaminopyridine. A weighed sample of 4-dimethylaminopyridine of 1, 2, 4, 6, or 10 g was dissolved in 18 ml of chloroform, and to the solution was added a solution of 1.12 g of phosphorus trichloride in 2 ml of chloroform. The reaction was monitored by ^{31}P NMR spectroscopy at dilution and concentration of the reaction mixtures.

Chlorobis(1-methylimidazole)phosphorus(3+) chloride (VIII). To a solution of 3 g of *N*-methylimidazole in 17 ml of chloroform was added dropwise at stirring a solution of 1.67 g of phosphorus trichloride in 3 ml of chloroform. The oil formed crystallized gradually at keeping the reaction mixture for three weeks. The precipitate formed was filtered off, washed with chloroform, and dried in a vacuum. Yield 0.5 g (14 %), mp (decomp.) 155–160°C. The ^{31}P NMR spectrum ($CHCl_3$), δ, ppm: 65–90 br.s. (the signal position depends on the concentration of the solution). The ^{1}H NMR spectrum ($CDCl_3$) was impossible to register because of low solubility of the substance. In DMSO-d_6 occurs reduction of the solvent. Found, %: C 31.65; H 4.30; CI 34.86; N 18.32; P 10.35. $C_8H_{12}Cl_3N_4P$. Calculated, %: C 31.86; H 4.01; Cl 35.27; N 18.58; P 10.27.

Tris(4-dimethylaminopyridine)phosphorus(3+) bromide (XI). To a solution of 3 g of 4-dimethylaminopyridine in 18 ml of chloroform was added dropwise at stirring a solution of 2.21 g of phosphorus tribromide in 2 ml of chloroform. The precipitate formed was filtered off, washed with chloroform, and dried in a vacuum. Yield 4.7 g (90 %), mp (decomp.) 176°C. The ^{31}P NMR spectrum ($CHCl_3$) (concentrated reaction mixture), δ, ppm: 84 s. The ^{1}H NMR spectrum ($CDCl_3$) was not registered due to very low solubility of the substance. In DMSO-d_6 occurs reduction of the solvent. Found, %: C 38.94; H 4.71; Br 37.10; N 12.60; P 4.96. $C_{21}H_{30}Br_3N_6P$. Calculated, %: C 39.58; H 4.75; Br 37.62; N 13.19; P 4.86.

Tris(1-methylimidazole)phosphorus(3+) bromide (XIVa). Synthesized by analogy with **XI** from 3 g of *N*-methylimidazole and 3.15 g of phosphorus tribromide. Yield 5.9 g (98 %), mp (decomp.) 183–185°C. The ^{31}P NMR spectrum($CHCl_3$) (concentrated reaction mixture), δ, ppm: 90 s. The ^{1}H NMR spectrum ($CDCl_3$) was not registered due to very low solubility of the substance. In DMSO-d_6 occurs reduction of the solvent. Found, %: C 27,23; H 4,09; Br 46,30; N 15,81; P 5.97. $C_{12}H_{18}Br_3N_6P$. Calculated, %: C 27,88; H 3,51; Br 46,37; N 16,26; P 5,99.

Tris(1-propylimidazole)phosphorus(3+) bromide (XIVb). Synthesized by analogy with (XI) from 4.39 g of *N*-methylimidazole and 2.97 g of phosphorus

tribromide. Yield 7.05 g (95 %), mp (decomp.) 180°C. The ^{31}P NMR spectrum ($CHCl_3$) (concentrated reaction mixture), δ, ppm: 90 s. Found, %: C 35.35; H 5.15; Br 39.54; N 13.96. $C_{18}H_{30}Br_3N_6P$. Calculated, %: C 35.96; H 5.03; Br 39.88; N 13.98.

Complexation of phosphorus oxychloride with 4-dimethylaminopyridine. A weighed sample of 4-dimethylaminopyridine of 1, 3, or 6 g was dissolved in 18 ml of chloroform, and to the solution was added a solution of 1.12 g of phosphorus oxychloride in 2 ml of chloroform. The reaction was monitored by ^{31}P NMR spectroscopy at dilution and concentration of the reaction mixtures.

For isolation of individual products to a solution of 3 g of 4-dimethylaminopyridine in 18 ml of chloroform was added at stirring a solution of 1.26 g of $POCl_3$ in 2 ml of chloroform. The reaction mixture was concentrated and left standing for 17 days, and then the crystals precipitated were filtered off and dried in a vacuum. The precipitate was identified as complex **XIX**. Yield 2.5 g (59 %). In the ^{31}P NMR spectrum ($CDCl_3$) appeared a signal at δ, ppm: 15.5 s. Some time later in the mixture established an equilibrium of several complexes and appeared signals at δ, ppm (*J*, Hz): –161 quintet, $^3J_{PH}$ 15, corresponding to the complex **XVIII**, and 9 s (complex **XVII**). The ^{1}H NMR spectrum ($CDCl_3$) d, ppm (*J*, Hz): 3.20 s (18H, N–CH_3), 6.79 d (6H arom., $^3J_{HH}$ 7), 8.26 d (6H arom., $^3J_{HH}$ 7). Found, %: C 48.31; H 5.45; Cl 20.31; N 16.62; P 5.97. $C_{21}H_{30}Cl_3N_6OP$. Calculated, % C 48.52; H 5.82; Cl 20.46; N 16.17; P 5.96.

When the filtrate after isolation of complex **XIX** was evaporated an oil formed that crystallized at the addition of acetonitrile. The precipitate was identified as **XVIII** solvate with chloroform molecule. It was filtered off, washed with acetonitrile, and dried in a vacuum. Yield 0.53 g (12%). In the ^{31}P NMR spectrum (DMSO-d_6) appears a signal at δ, ppm:–161 quintet, $^3J_{PH}$ 15. In some time in the mixture an equilibrium was established with other complexes, and the following signals appeared, δ, ppm (*J*, Hz): –15 s, that corresponds to complex **XIX**, and 9 s (complex **XVII**). The ^{1}H NMR spectrum (DMSO-d_6) δ, ppm: 3.19 s (12H, N–CH_3), 6.84 d.d (4H arom., $^3J_{HH}$ 7, $^4J_{PH}$ 2), 8.06 d.d (4H arom., $^3J_{HH}$ 7, $^3J_{PH}$ 15), 8.30 c. (0.8H, $CHCl_3$). Found, %: C 38.87; H 4.83; Cl 34.34; N 12.92; P 6.07. $C_{14.5}H_{20.5}Cl_{4.5}N_4OP$. Calculated, % C 38.08; H 4.52; Cl 34.88; N 12.25; P 6.77. Compounds **XVIII** and **XIX** were not isolated as individual products probably due to their equilibrium in solution. Owing to the absence of individual compounds we were unable to measure accurately their melting points.

Complexation of phosphorus sulfochloride with 4-dimethylaminopyridine. Weighed samples of 4-dimethylaminopyridine of 1, 2, 3, and 6 g were dissolved in 18 ml of chloroform, and to each solution was added a solution of 1.39 g of phosphorus sulfochloride in 2 ml of chloroform. The reaction was monitored by ^{31}P NMR spectroscopy at dilution and concentration of the reaction mixtures.

Complexation of phosphorus pentabromide with 4-dimethylaminopyridine. To a solution of 6.37 g of 4-dimethylaminopyridine in 20 ml of chloroform was added dropwise at stirring a suspension of 3.21 g of phosphorus pentabromide in 10 ml of chloroform. The suspension gradually dissolved. A newly formed precipitate was filtered off, washed with chloroform and dried in a vacuum. Yield 4.1 g (92 %). mp (decomp.) 176°C. Registration of the ^{31}P and ^{1}H NMR spectra failed because the substance formed was insoluble in chloroform and reduced DMSO-d_6. Found, %: C 39.44; H 4.71; Br 37.10; N 12.90; P 4.76. $C_{21}H_{30}Br_3N_6P$. Calculated, % C 39.58; H 4.75; Br 37.62; N 13.19; P 4.86.

By reaction of the obtained complex **XI** with anhydrous methanol we obtained quantitatively trimethylphosphite (by the ^{31}P NMR data). The ^{31}P NMR spectrum (in methanol) δ, ppm (*J*, Hz): 142 m, $^3J_{PH}$ 15.

In the filtrate of this reaction mixture was registered the formation of 3-bromo-4-dimethylaminopyridine as confirmed by the spectrum of the mixed sample with authentic substance.

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