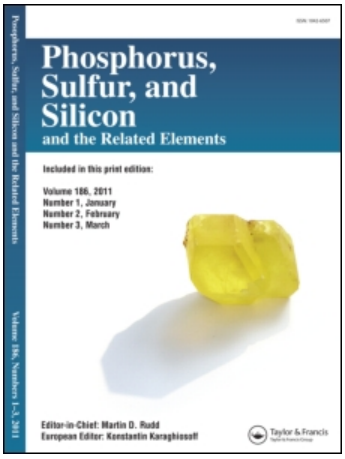

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PROTONATED AMINOPHOSPHINES

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PROTONATED AMINOPHOSPHINES

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The possibility to obtain pure salts of tetrafluoroboric acid with aminophosphines is proved. It is shown by means of NMR spectroscopy and X-ray analysis that the protonation occurs at the phosphorus atom only. All aminophosphonium salts prepared appear not to phosphorylate nucleophiles, whereas phosphorylation occurs when some bases turning the phosphonium salts into H-complexes are added.

Key words: Phosphorylation; nucleophiles; protonation; catalysis; aminophosphines; spectroscopy.

INTRODUCTION

A great number of reactions of aminophosphines with the cleavage of the aminophosphorus bond are known to be catalyzed by amine hydrohalides and other acids.[1] A certain clearity in understanding of this important phenomenon has been achieved recently.[2]

The data obtained by us appears surprising since the acid catalysis of aminophosphine reactions has been previously considered to proceed via formation of quasiphosphonium (or ammonium) salts[3] or formation of halophosphines.[4] In order to clarify this point we have turned to the experimental studies of synthesis and properties of protonated aminophosphines. Some authors dealt with this problem and obtained spectral data on reaction mixtures containing aminophosphines and strong acids[5] but the corresponding salts were not isolated in pure state and their reactivity was not studied. Van der Knaap[6] has managed to prepare a crystalline hydrochloride of a complicated aminophosphine but has not investigated its reactivity and structure.

RESULTS AND DISCUSSION

We have found a simple and convenient route to protonated aminophosphines based on the usage of dry HBF_4, the anion of which presents a very weak nucleophilicity (method a).

The protonation was carried out in ether, the yield of salts **6–10** being 67–93%. This reaction is of wide synthetic use for obtaining salts of aminophosphines **1–5**. Unfortunately, the similar reaction of amidoesters of phosphorous acid with HBF_4

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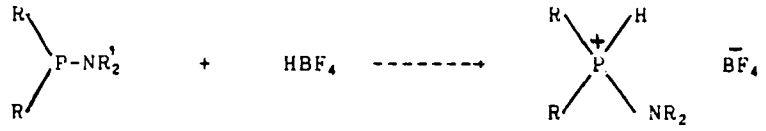


1 - 5 6 - 10

Where: 1, 6: R=NEt_2, R'=Et

2, 7: R=  , NR'_2= 

3, 8: R=i-Pr, R'=Et

4, 9: R=t-Bu, R'=Et

5, 10: R=t-Bu, NR'_2= 

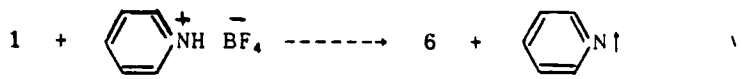
SCHEME 1

results in a complex hardly separatable mixture of products. The salts **6–10** are semiliquid crystals (**6–8**) or crystalline (**9**, **10**) substances. Some of them are hygroscopic (**6–8**) and should be stored in a dry inert atmosphere, others are stable when exposed to air. All of them are soluble in polar non-protondonating solvents such as $CHCl_3$, CH_2Cl_2, MeCN, etc. The isolated salts have been characterized by ^1H (**6**, **9**, **10**) and ^{31}P (**6–10**) NMR spectroscopy (see Experimental). ^1H and ^{31}P NMR spectra of **6**, **9**, **10** show doublet signals ($^1J_{PH}$ = 504–630 Hz, δ ^1H 6.0–7.5, δ ^{31}P = 35–76). A special care should be taken to purification of NMR spectroscopically investigated salts **6–8**. The small quantities of such impurities as excess of aminophosphines, amines, acidic phosphites and others lead to broadening of a double $^1J_{PH}$ and its collapsing at elevated temperatures. For instance the salt **7**, if not washed with hexane, shows at 35°C a broadened singlet in the ^{31}P NMR spectrum ($\Delta\nu_{1/2} \sim 100$ Hz) with the chemical shift varying in dependence on solvent used and concentration between 35 and 47 ppm. When the sample is cooled, this broadened singlet turns into a doublet ($^1J_{PH}$ 632 Hz, CH_2Cl_2, 1 mol·l^{-1}, −70°C) that seems to be caused by slowing of proton exchange processes in the examined system.

Adding bases different in strength to the salts **6–10** made it possible to estimate approximately the aminophosphines' basicity. For example, the aminophosphine **5** appeared to be even a weaker base than DMFA (pKa −1.5). Dissolved in DMFA, salt **10** shows in the ^{31}P NMR spectrum a signal of aminophosphine **5** alone.

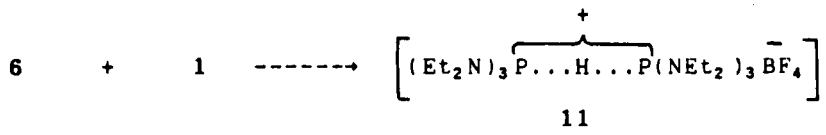
At the same time a base comparable in strength, pyridine, being added to the salts **6** causes a considerable broadening of the ^{31}P NMR signal ($\Delta\nu_{1/2}$ ~320 Hz) with the $^1J_{PH}$ coupling remaining constant.

The fact that pyridine does not deprotonate **6** made it possible to work out a new convenient synthetic route to quasiphosphonium salts. This route involves treatment of aminophosphine with pyridinium tetrafluoroborate followed by the removal of pyridine in the vacuum (method b):



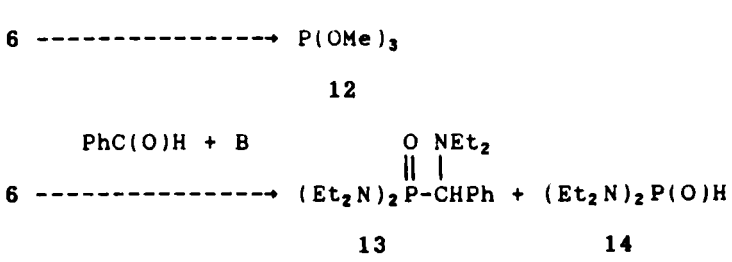
SCHEME 2

Phospho(III)amines were also examined as bases in similar reactions. Thus a reaction of **6** with equimolecular quantity of trisaminophosphine **1** was performed. A broadened singlet in the ^{31}P NMR spectrum ($\Delta\nu_{1/2}$ ~660 Hz) was observed; the formation of complex **11** which presents an exchange of protons between two equivalent phosphorus atoms may be postulated.



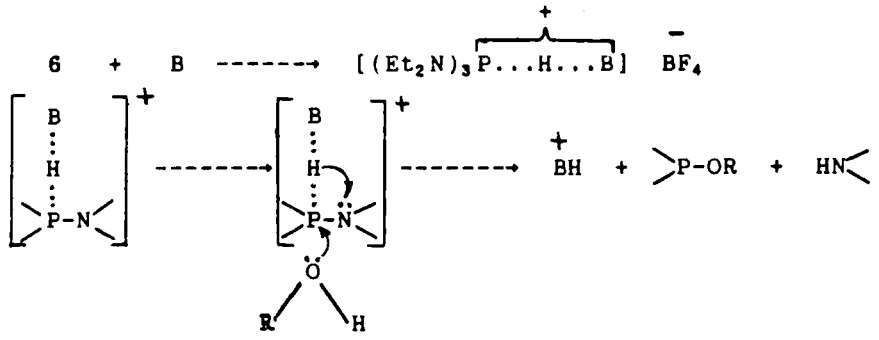
SCHEME 3

6 does not react with alcohols and carbonyl compounds. However, rapid reactions take place if a base B [Et_3N, C_5H_5N, $P(NEt_2)_3$, etc.] is added to the reaction mixture.



SCHEME 4

The process of question is likely to begin with a partial deprotonation of the phosphonium salt with base (B). This leads to H-complexes mentioned above which undergo nucleophilic substitution, such as:



SCHEME 5

There are two roles the hydrogen atom plays in the H-complex. On the one hand it increases the electrophilic ability of phosphorus atom, for instance, in reaction with alcohol. On the other hand it promotes the cleavage of P—N bond by migration from phosphorus to nitrogen. This supposition is proved by the fact that quasiphosphonium salts which are unable to undergo proton exchange [$(Et_2N)_3\overset{+}{P}EtB\bar{F}_4$, **15**, or $(Et_2N)_3\overset{+}{P}Et\bar{B}r$,[7] for instance] do not undergo alcoholysis either under usual conditions or in the presence of Et_3N (see Experimental). Our conclusion turns out to be in agreement with the results of nonempirical quantum chemical calculations of protonated P—N system.[8] However, there are several other viewpoints on the mechanism of aminophosphine protonation reactions[9] which are in disagreement with our experimental data. We have established the structure of aminophosphines **4**, **5**, and their protonated forms **9**, **10** by means of X-ray analysis. They are given in the Figures 1–4. The bond angles and bond lengths are listed in the Tables I–IV and V–VIII, respectively. Protonation shortens the P—N bonds by 0,06(1) Å and 0.078(4) Å and the P—C bonds by an average of 0.04 Å. The phosphorus atom in **9** and **10** has a distorted tetrahedral coordination with a short P—H bond 1.2(1) and 1.29(4) Å.

A number of geometrical features of investigated structures has to be pointed out. The longest P—N bond [1.746(2) Å] was found in pyrrolylphosphine **5**. The length of this bond is more than 1.68–1.71 Å, as it was observed for tripyrrolylphosphine,[10] and turned out to be one of the longest P—N bonds. This bond length is actually equal to the sum of covalent radii of phosphorus and nitrogen atoms on formation of a single bond (0.73 and 1.10 Å[11]) with Schomaker-Stevenson correction[12] for electronegativity difference of these two atoms ($0.73 + 1.10 - 0.09\,|x_N - x_P| = 1.83 - 0.08 = 1.75$ Å). The phosphorus atom in **4** and **5** exhibits distinct pyramidal coordination [the sum of the bond angles is equal to 319.8(8) and 317.4(2)°]

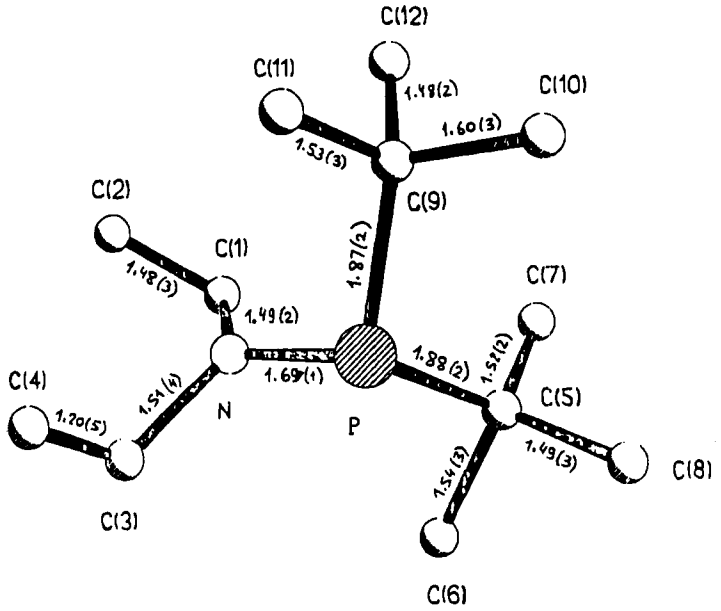


FIGURE 1 X-ray structure of the aminophosphine **4**.

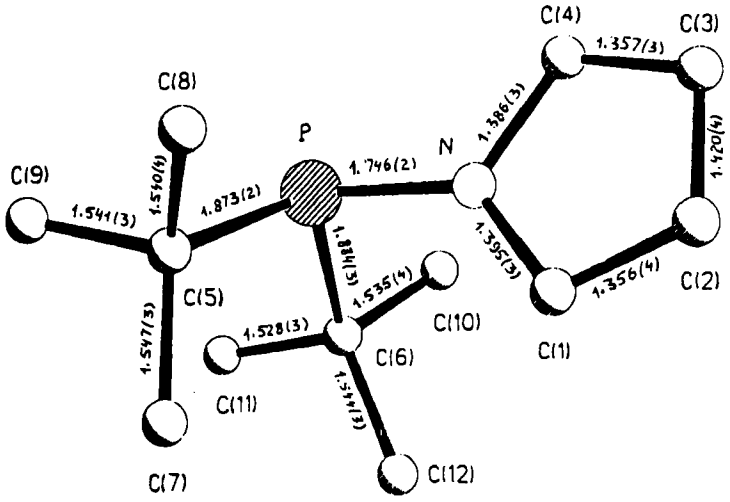


FIGURE 2 X-ray structure of the aminophosphine **5**.

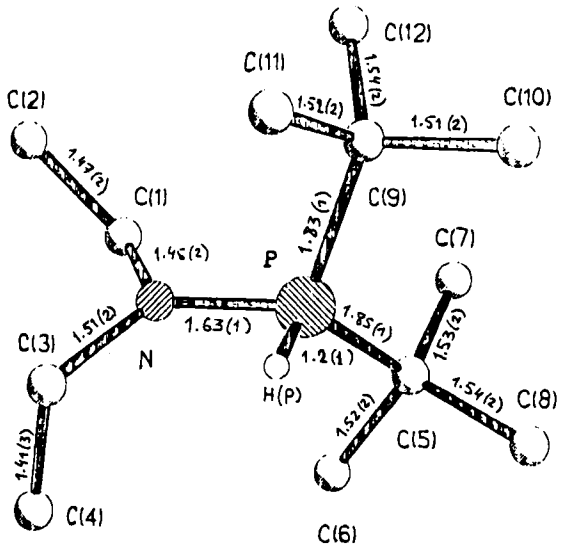


FIGURE 3 X-ray structure of the quasiphosphonium cation **9**.

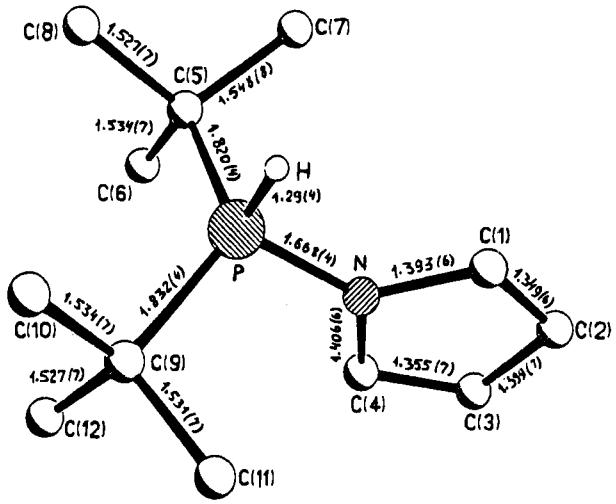


FIGURE 4 X-ray structure of the quasiphosphonium cation **10**.

TABLE I

Bond angles (deg.) of structure **4**

N-P-C(5)	106.8(8)
N-P-C(9)	103.7(8)
C(5)-P-C(9)	109.3(8)
P-C(5)-C(6)	103(1)
P-C(5)-C(7)	118(1)
P-C(5)-C(8)	109(1)
C(6)-C(5)-C(7)	110(2)
C(6)-C(5)-C(8)	107(2)
C(7)-C(5)-C(8)	109(2)
P-C(9)-C(10)	107(2)
P-C(9)-C(11)	104(1)
P-C(9)-C(12)	122(1)
C(10)-C(9)-C(11)	105(1)
C(10)-C(9)-C(12)	111(1)
C(11)-C(9)-C(12)	106(1)
P-N-C(1)	127(1)
P-N-C(3)	116(2)
C(1)-N-C(3)	115(2)
N-C(1)-C(2)	115(1)
N-C(3)-C(4)	126(3)

TABLE II
Bond angles (deg.) in structure **5**

N-P-C(5)	103.3(1)
N-P-C(6)	102.0(1)
C(5)-P-C(6)	112.1(1)
P-N-C(1)	133.1(2)
P-N-C(4)	119.8(2)
C(1)-N-C(4)	107.0(2)
P-C(5)-C(9)	106.3(2)
P-C(5)-C(8)	105.6(2)
C(9)-C(5)-C(8)	107.6(2)
P-C(5)-C(7)	119.3(2)
C(9)-C(5)-C(7)	108.6(2)
C(8)-C(5)-C(7)	108.9(2)
N-C(1)-C(2)	108.7(2)
C(4)-C(3)-C(2)	107.2(2)
P-C(6)-C(10)	103.5(2)
P-C(6)-C(11)	107.9(2)
C(10)-C(6)-C(11)	108.4(2)
P-C(6)-C(12)	118.8(2)
C(10)-C(6)-C(12)	108.0(2)
C(11)-C(6)-C(12)	109.8(2)
N-C(4)-C(3)	109.3(2)
C(1)-C(2)-C(3)	107.8(2)

and is moved out of plane of the neighbouring atoms by 0.68 and 0.71 Å, respectively. On the contrary, coordination of the nitrogen atoms in these compounds is very close to planar trigonal and these atoms are 0.09 and 0.03 Å out of the plane of the nearest atoms in **4** and **5**, respectively. The dihedral angles between two planes NC(5)C(9) and PC(1)C(3), characterizing mutual orientation of phosphorus and nitrogen lone pairs in **4** and **5**, are equal to 91.2 and 84.2°, i.e., their lone pairs are nearly orthogonal. In this regard, it should be emphasized that the phosphorus lone pair in **5** (assuming its partial sp^3 character) is approximately located in the plane of the pyrrolyl heterocycle so the possibility of its conjugation with the π-system of pyrrolyl is excluded.

The shift of the phosphorus atoms out of the plane of non-hydrogen atoms in the protonated cations of **9** and **10** is decreased to 0.43 and 0.44 Å, respectively; moreover, there is no essential change in the orientation of the Et_2N-group and pyrrolyl radical in these cations in comparison with the unprotonated forms. For example, the angle between PC(1)C(3) and NC(5)C(9) planes in **9** is equal to 96.4° (versus 91.2° in **4**). The corresponding angles in **5** and **10** are also similar (88.1 and 94.1°). The planar trigonal coordination of the nitrogen atoms in the cations of **9** and **10** remains unchanged as well.

The torsional angles HPNC(1) and HPNC(3), characterizing orientation of the P—H bond relative to the plane of the amino-group in the cation **9**, are equal to

TABLE III

Bond angles (deg.) in structure **9**

N-P-C(9)	111.9(6)
N-P-C(5)	114.5(6)
C(5)-P-C(9)	116.4(6)
H(P)-P-N	87(6)
H(P)-P-C(5)	124(6)
H(P)-P-C(9)	99(6)
P-N-C(1)	122.9(9)
P-N-C(3)	119.5(9)
C(1)-N-C(3)	117(1)
P-C(9)-C(10)	111.6(9)
P-C(9)-C(11)	105.1(9)
C(10)-C(9)-C(11)	107(1)
P-C(9)-C(12)	113.0(9)
C(10)-C(9)-C(12)	110(1)
C(11)-C(9)-C(12)	111(1)
P-C(5)-C(8)	108.2(9)
P-C(5)-C(7)	114.4(9)
C(8)-C(5)-C(7)	110(1)
P-C(5)-C(6)	105.2(9)
C(8)-C(5)-C(6)	109(1)
C(7)-C(5)-C(6)	110(1)
N-C(1)-C(2)	115(1)
N-C(3)-C(4)	112(2)
F(1)-B-F(2)	111(2)
F(1)-B-F(3)	111(1)
F(1)-B-F(4)	115(2)
F(2)-B-F(3)	105(1)
F(2)-B-F(4)	104(2)
F(3)-B-F(4)	110(1)

17.8 and $-8°$, i.e., the P—H bond is actually in the plane of this group. The analogous values of the torsion angles HPNC(1) and HPNC(4) in **10** are -14 and 173°. Other geometrical parameters of investigated structures have the expected values. There are inter-ion contacts between cations and anions of the type $\overset{+}{P}$—H . . . F—$\bar{B}F_3$ in the crystals **9** and **10** which may be referred to a weak H-bonding. The distance P · · · F(3′)‡ in the structure **9** is equal to 3.65 Å, H · · · *F*(3′) 2.74 Å with angle at H being 134°.

The participation of the F(3′) atom in this H-bond obviously restricts the thermal motion and partial disorder of the anion, and the bond length B—F(3) 1.42(3) Å is close to the expected one contrary to the essentially shortened other B—F distances 1.22–1.26(3) Å, owing to the disorder of anion. The value of the tem-

‡F(3′) atom is related with the basis F(3) atom by transformation $(1/2 - x, 1 - y, 1/2 + z)$.

TABLE IV

Bond angles (deg.) in structure **10**

N-P-C(5)	109.6(2)
C(5)-P-C(9)	122.2(2)
C(5)-P-H	107.2(18)
P-N-C(1)	124.4(3)
C(1)-N-C(4)	107.8(4)
F(1)-B-F(3)	109.1(4)
F(1)-B-F(4)	107.7(4)
F(3)-B-F(4)	107.8(4)
C(1)-C(2)-C(3)	109.0(4)
N-C(4)-C(3)	107.4(4)
P-C(5)-C(7)	104.9(3)
P-C(5)-C(8)	109.1(3)
C(7)-C(5)-C(8)	110.3(4)
P-C(9)-C(11)	105.4(3)
P-C(9)-C(12)	113.1(3)
C(11)-C(9)-C(12)	111.5(4)
N-P-C(9)	110.5(2)
N-P-H	104.9(21)
C(9)-P-H	100.7(19)
P-N-C(4)	127.6(3)
F(1)-B-F(2)	111.2(4)
F(2)-B-F(3)	112.0(4)
F(2)-B-F(4)	108.8(4)
N-C(1)-C(2)	107.6(4)
C(2)-C(3)-C(4)	108.2(4)
P-C(5)-C(6)	113.1(3)
C(6)-C(5)-C(7)	109.3(4)
C(6)-C(5)-C(8)	110.1(4)
P-C(9)-C(10)	106.7(3)
C(10)-C(9)-C(11)	109.9(4)
C(10)-C(9)-C(12)	110.1(4)

TABLE V
Bond lengths (Å) in structure 4

P-N	1.69(1)
N-C(1)	1.49(2)
N-C(3)	1.51(4)
C(1)-C(2)	1.48(3)
C(3)-C(4)	1.20(5)
P-C(5)	1.88(2)
C(5)-C(6)	1.54(3)
C(5)-C(7)	1.52(2)
C(5)-C(8)	1.49(3)
P-C(9)	1.87(2)
C(9)-C(10)	1.60(3)
C(9)-C(11)	1.53(3)
C(9)-C(12)	1.48(2)

TABLE VI
Bond lengths (Å) in structure 5

P-N	1.746(2)
N-C(4)	1.386(3)
N-C(1)	1.395(3)
C(1)-C(2)	1.356(4)
C(2)-C(3)	1.420(4)
C(3)-C(4)	1.357(3)
P-C(5)	1.873(2)
C(5)-C(7)	1.547(3)
C(5)-C(8)	1.540(4)
C(5)-C(9)	1.541(3)
P-C(6)	1.884(3)
C(6)-C(10)	1.535(4)
C(6)-C(11)	1.528(3)
C(6)-C(12)	1.544(3)

TABLE VII
Bond lengths (Å) in structure **9**

P-H	1.2(1)
P-N	1.63(1)
N-C(1)	1.45(2)
N-C(3)	1.51(2)
C(1)-C(2)	1.47(2)
C(3)-C(4)	1.41(3)
P-C(5)	1.85(1)
C(5)-C(6)	1.52(2)
C(5)-C(7)	1.53(2)
C(5)-C(8)	1.54(2)
P-C(9)	1.83(1)
C(9)-C(10)	1.51(2)
C(9)-C(11)	1.52(2)
C(9)-C(12)	1.54(2)
B-F(1)	1.22(2)
B-F(2)	1.24(2)
B-F(3)	1.42(2)
B-F(4)	1.26(2)

TABLE VIII
Bond lengths (Å) in structure **10**

P-H	1.285(42)
P-N	1.668(4)
P-C(9)	1.832(4)
N-C(1)	1.393(6)
C(1)-C(2)	1.349(6)
C(3)-C(4)	1.355(7)
C(5)-C(7)	1.548(8)
C(9)-C(10)	1.534(7)
C(9)-C(12)	1.527(7)
P-C(5)	1.820(4)
N-C(4)	1.406(6)
C(2)-C(3)	1.399(7)
C(5)-C(6)	1.534(7)
C(5)-C(8)	1.527(7)
C(9)-C(11)	1.531(7)
B-F(1)	1.379(6)
B-F(2)	1.377(6)
B-F(3)	1.372(6)
B-F(4)	1.384(5)

perature factor of the F(3) atom is also smaller than that of other F-atoms. The P · · · F(4')§ distance in structure **10** is equal to 3.51 Å, H · · · F(4') 2.28 Å, with the angle of H being 159°. Due to ordering of the anion the B—F bond lengths in **10** are usual and comparable [1.377(6)–1.384(6) Å].

EXPERIMENTAL

All the experiments with compounds of trivalent phosphorus and their salts were performed in an atmosphere of dried argon. ^1H and ^{31}P NMR spectra were obtained on Bruker AM-400 and Bruker WP-80 spectrometers at frequencies of 400 and 32.4 MHz, using TMS and 85% H_3PO_4 standards, respectively.

X-Ray Analysis. Single crystals of **4** and **5** were grown from a melt in the thin-walled sealed glass capillary ($d \sim 0.3$ mm or 0.4 mm) on SYNTEX $P2_1$ diffractometer at $-50°$ or 0°C, respectively, using the procedure described earlier.[13] The monocrystal of **4** was further cooled to -100°C and at this temperature the X-ray experiment was performed. The crystals of **4** are monoclinic at -100°C: a = 13.009(3), b = 9.125(2), c = 12.458(3) Å, β = 91.27(3)°, V = 1478.5(7) Å^3, z = 4, space group $P2_1/c$. Out of the total number of 4533 measured reflections (Mo$K\alpha$-radiation, graphite monochromator, $\theta/2\theta$-scanning, $2\theta \leq 50°$) 700 independent reflections with $|F| \geq 4\sigma$ were used in calculations and refinement. The structure was solved by direct method and refined anisotropically. The coordinates of H-atoms were calculated geometrically and these atoms were taken into account in further calculations with fixed coordinates and U_{iso} = 0.05Å^2. The final refinement was converged to R = 0.098, R_w = 0.089 and GOF = 3.43.

The single crystal of **5** was cooled to -120°C and at this temperature X-ray experiment was performed. The crystals of **5** are monoclinic at -100°C: a = 6.081(2), b = 14.158(3), c = 15.574(3) Å, δ = 99.50(3), V = 1323(1) Å^3, Z = 4, space group $P2_1/c$. Out of the total number 5240 measured reflections (Mo$K\alpha$-radiation, graphite monochromator, $\theta/2\theta$-scanning, $2\theta \leq 56°$) 2657 independent reflections with $|F| \geq 4\sigma$ were used in calculations and refinement. The structure was solved by direct method and refined anisotropically. The coordinates of H-atoms were calculated geometrically and these atoms were used in calculations with fixed coordinates and U_{iso} = 0.08 Å^2. The final refinement was converged to R = 0.054, R_w = 0.049 and GOF = 1.83. The atomic coordinates of non-hydrogen atoms for **4** and **5** are listed in the Tables IX and X.

The single crystals of salts **9**, **10** were obtained as described in the Experimental. An X-ray diffraction study was carried out with an automatic Siemens R3m diffractometer at -90°C. The crystals of salt **9** are ortorhombic at -90°C: a = 8.437(2), b = 12.924(2), c = 15.281(3) Å, V = 1666(1) Å^3, z = 4, the space group $P2_12_12_1$. Out of the total number of 1414 (Mo$K\alpha$-radiation, graphite monochromator, $\theta/2\theta$-scanning, $2\theta \leq 46°$) the 1356 independent reflections with $|F| \geq 4\sigma$ were used in calculations and refinement. The structure was solved by direct method and refined anisotropically. The coordinates of H(P) atoms were found by the difference Fourier-synthesis, positions of the other H-atoms were calculated geometrically, and they were used in calculations with fixed coordinates and U_{iso} = 0.05 Å^2. The refinement was converged to R = 0.115, R_w = 0.121, GOF = 2.23. The coordinates of non-hydrogen atoms for **9** and **10** are listed in the Tables XI and XII. High R-values for structures of **4** and **9** are explained by the poor quality of single crystals and disordering of *t*-Bu- and Et-groups at P and N atoms and BF_4^--anion as well. This disorder manifests in high values of the temperature factors of the corresponding atoms. All calculations were performed with SHELXTL PLUS-PC/AT program.

Aminophosphines **1–3** were synthesized by ordinary methods from corresponding chlorophosphine and equimolecular amounts of the corresponding amine and triethylamine. All the aminophosphines **1–5** were purified additionally by treatment with a solution of butyllithium in hexane according to the recommendations.[14] The solution of 37.2% HBF_4 in diethyl ether was obtained by the reaction of equimolecular amounts of triethyloxonium tetrafluoroborate[15] with ethanol (20°C, 24h). The pyridinium tetrafluoroborate was obtained by treatment of pyridine with equimolecular amount of aqueous HBF_4 followed by evaporation and drying in a vacuum-exsiccator over P_2O_5.

Diethylaminoditertbutylphosphine **4**. Lithium diethylamide[16] (3.16 g, 0.04 mol) in hexane-tetrahydrofurane (1:1) was added to a solution of di(*t*-butyl)chlorophosphine[17] (7.23 g, 0.04 mol). The suspension was stirred at 20°C for 12 h. The solution was filtered, evaporated under reduced pressure and the residue was distilled in the vacuum to give aminophosphine **4**(4.15 g, 47.7% yield), b.p. 74–75°C at 1 mm Hg, n_D^{20} 1.4807. Found, %: C 66.18, H 12.86, N 6.63. Calcd. for $C_{12}H_{28}NP$, %: C 66.32, H 12.99,

§F(4') atom is related with the basis F(4) atom by transformation $(-1/2 - x, 2 - y, 1/2 + z)$.

TABLE IX

Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement coefficients *U*eq ($Å^2 \cdot 10^3$) in structure **4**

Atom	x	y	z	Ueq
P	2518(3)	2440(4)	957(3)	44(1)
N	2656(8)	4160(9)	1440(9)	60(3)
C(1)	2835(12)	4606(15)	2578(10)	71(6)
C(2)	2237(15)	5903(16)	2919(12)	92(8)
C(3)	2844(37)	5335(40)	615(30)	210(20)
C(4)	2197(25)	6002(40)	120(25)	200(35)
C(5)	3614(11)	1332(20)	1542(12)	65(6)
C(6)	4556(12)	2267(22)	1277(15)	118(10)
C(7)	3619(13)	984(25)	2737(11)	108(10)
C(8)	3711(15)	-59(15)	930(15)	100(10)
C(9)	1289(12)	1802(15)	1540(9)	61(5)
C(10)	1124(12)	133(19)	1173(15)	98(8)
C(11)	456(11)	2662(25)	919(13)	99(7)
C(12)	1071(10)	1990(20)	2691(12)	91(8)

TABLE X

Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement coefficients *U*eq ($Å^2 \cdot 10^3$) in structure **5**

Atom	x	y	z	Ueq
P	3256(1)	7987(1)	3089(1)	23(1)
N	1649(3)	8395(1)	2127(1)	27(1)
C(1)	-616(4)	8334(2)	1786(2)	36(1)
C(2)	-966(5)	8727(2)	981(2)	40(1)
C(3)	1120(5)	9055(2)	803(2)	38(1)
C(4)	2675(4)	8838(2)	1505(2)	32(1)
C(5)	2421(4)	6716(2)	3128(2)	26(1)
C(6)	2164(4)	8718(2)	3937(2)	28(1)
C(7)	67(4)	6467(2)	3312(2)	33(1)
C(8)	2704(5)	6297(2)	2240(2)	42(1)
C(9)	4163(4)	6244(2)	3828(20)	37(1)
C(10)	3035(5)	9714(2)	3795(2)	40(1)
C(11)	3285(4)	8370(2)	4832(2)	40(1)
C(12)	-382(4)	8784(2)	3910(2)	45(1)

TABLE XI

Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement coefficients *U*eq ($Å^2 \cdot 10^3$) in structure **9**

Atom	x	y	x	Ueq
P	2141(4)	4884(2)	8842(2)	33(1)
N	3133(12)	5964(8)	8767(7)	74(4)
C(1)	4160(16)	6203(12)	8033(9)	49(5)
C(2)	5793(18)	6460(11)	8277(9)	65(6)
C(3)	2853(21)	6811(9)	9433(14)	79(7)
C(4)	1685(28)	7518(15)	9151(14)	108(10)
C(5)	788(18)	4628(11)	7914(9)	54(5)
C(6)	194(21)	5687(13)	7628(11)	63(7)
C(7)	1562(17)	4075(17)	7139(9)	62(8)
C(8)	-633(17)	3995(15)	8259(9)	62(7)
C(9)	3398(16)	3810(9)	9189(9)	44(5)
C(10)	2450(18)	2830(10)	9316(9)	60(5)
C(11)	4017(19)	4121(13)	10085(9)	57(16)
C(12)	4781(17)	3600(9)	8553(9)	57(5)
B	5980(19)	4881(12)	5906(8)	40(5)
F(1)	6923(20)	4974(12)	6505(12)	229(9)
F(2)	5139(18)	4102(9)	6001(17)	222(13)
F(3)	4900(12)	5725(7)	5883(6)	74(4)
F(4)	6602(19)	4764(14)	5166(9)	224(9)
H(P)	1720(140)	5170(80)	9530(70)	50

N 6.44. ^{1}H NMR ($CDCl_3$): δ = 1.05t (6H, CH_2CH_3), 1.18d [18H, $C(CH_3)_3$, $^3J_{HCCP}$ 12.1 Hz], 3.11 m (4H, CH_2). ^{31}P-{^{1}H} NMR: δ = 100.2.

Pyrrolylditertbutylphosphine **5**. Di(*t*-butyl)chlorophosphine (4.30 g, 0.0238 mmol) was added to a suspension of potassium pyrrolide (2.50 g, 0.0238 mmol) in 10 ml of toluene. The suspension was stirred at 20°C for 12 h. The precipitate was filtered, the solution was evaporated under reduced pressure and the residue was distilled in the vacuum to give aminophosphine **5** (2.30 g, 46.0% yield), b.p. 48°C at 1 mm Hg, n_D^{20} 1.5085. Found, %: C 68.39, H 10.31, N. 6.35. Calcd. for $C_{12}H_{22}NP$, %: C 68.22, H 10.49, N 6.63. ^{1}H NMR (CD_2Cl_2): δ = 1.18d (18H, CH_3, $^3J_{HCCP}$ 12.7 Hz), 6.22 m (2H, NCHCH), 6.94 m (2H, NCH). ^{31}P-{^{1}H} NMR: δ = 91.6.

Preparation of salts **6–10** (*general procedure*). a. A solution of HBF_4 in diethyl ether (1.42 g, 6.02 mmol of HBF_4) was added with stirring to the amines **1–5**. Two layers formed. The heavy layer was washed with hexane (3 × 10 ml) and dried in the vacuum (1 mm Hg) at 20°C for 1h.

Tris(diethylamino)phosphonium tetrafluoroborate **6**. a. Yield 1.35 g (67.0%). ^{1}H NMR (CD_2Cl_2): δ = 1.15–1.29 m (18H, CH_3), 3.08 m (12H, CH_2, $^3J_{HCNP}$ 11.8 Hz), 7.23 d (1H, PH, $^1H_{HP}$ 630 Hz). ^{31}P-{^{1}H} NMR (CD_2Cl_2): δ = 38.3. b. The pyridinium tetrafluoroborate (0.18 g, 1.09 mmol) was added with stirring to a solution of trisaminophosphine **1** (0.27 g, 1.09 mmol) in 0.5 ml of dichloromethane. The reaction mixture was kept at 20°C for 1 h, the solvent was distilled off in the vacuum and the residue was treated as described in a to give salt **6** (0.38 g, 85.0% yield). ^{31}P NMR ($CDCl_3$): δ = 38.8d ($^1J_{PH}$ 630 Hz).

Tripiperidylphosphonium tetrafluoroborate **7**. Yield 1.52 g (68.0%). ^{31}P NMR (CD_2Cl_2): δ = 35.8d ($^1J_{PH}$ 632 Hz).

TABLE XII

Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement coefficients *U*eq ($Å^2 \cdot 10^3$) in structure **10**

Atom	x	y	z	Ueq
P	1823(1)	9862(1)	1714(1)	24(1)
N	2682(4)	10891(3)	1251(3)	28(1)
C(1)	2289(5)	11885(3)	1491(3)	32(1)
C(2)	3116(6)	12508(3)	926(3)	40(1)
C(3)	4046(6)	11923(4)	322(3)	40(2)
C(4)	3774(5)	10931(4)	513(3)	35(1)
C(5)	204(5)	9362(3)	977(3)	30(1)
C(6)	905(6)	8923(5)	102(3)	44(2)
C(7)	-929(7)	10283(5)	761(5)	49(2)
C(8)	-790(6)	8551(4)	1479(4)	40(2)
C(9)	3443(5)	9053(3)	2209(3)	31(1)
C(10)	2595(7)	8441(4)	2957(4)	43(2)
C(11)	4726(6)	9784(5)	2614(4)	51(2)
C(12)	4254(6)	8336(4)	1531(4)	46(2)
B	-4060(5)	9218(4)	-1234(3)	29(1)
F(1)	-3567(4)	8797(3)	-2039(2)	61(1)
F(2)	-3354(4)	8712(3)	-520(2)	63(1)
F(3)	-3665(4)	10231(2)	-1232(2)	59(1)
F(4)	-5785(3)	9134(3)	-1178(2)	57(1)
H(P)	1088(48)	10189(37)	2424(28)	23(10)

Diethylaminodiisopropylphosphonium tetrafluoroborate **8**. Yield 1.14 g (71.0%). ^{31}P NMR ($CDCl_3$): δ = 69.2d ($^1J_{PH}$ 503Hz).

Diethylaminodi(t-butyl)phosphonium tetrafluoroborate **9**. Yield 1.67 g (93.0%). It was additionally purified by precipitation with diethyl ether from a solution in chloroform. Yield 1.44 g (80.0%), m.p. 241–242°C. Found, %: C 48.37, H 7.68, N 4.49. Calcd. for $C_{12}H_{23}BF_4NP$, %: C 48.19, H 7.75, N 4.68. ^1H NMR ($CDCl_3$): δ = 1.21t (6H, CH_2CH_3), 1.45d [18H, $C(CH_3)_3$, $^3J_{HCCP}$ 20 Hz], 3.24 m (4H, CH_2), 6.13d (1H, $^1J_{PH}$ 504 Hz). ^{31}P-{^1H} NMR ($CDCl_3$): δ = 75.7.

Pyrrolyldi(t-butyl)phosphonium tetrafluoroborate **10**. Yield 1.65 g (90.0%), m.p. 194°C (CH_2Cl_2). Found, %: C 47.43, H 9.69, N 4.37. Calcd. for $C_{12}H_{29}BF_4NP$, %: C 47.25, H 9.57, N 4.59. ^1H NMR (CD_3CN): δ = 1.46d (18H, CH_3, $^3J_{HCCP}$ 18 Hz), 6.61s (2H, NCH), 7.21s (2H, NCHCH), 7.48d (1H, PH, $^1J_{PH}$ 516 Hz). ^{31}P-{^1H} NMR (CD_3CN): δ = 70.1.

Tris(diethylamino)ethylphosphonium tetrafluoroborate **15**. Triethyloxonium tetrafluoroborate (1.18 g, 6.2 mmol) was added to a solution of trisaminophosphine **1** in 5 ml of benzene. Two layers formed; the heavy one was separated and washed with hexane (3 × 5 ml) and dried in a vacuum-exsiccator over P_2O_5 to give salt **15** (1.79 g, 85.0% yield) (colorless, semiliquid crystals). ^1H NMR (CD_3OD): δ = 1.21 m (18H, NCH_2CH_3), 1.29t (3H, PCH_2CH_3), 2.47 m (2H, PCH_2), 3.16 m (12H, NCH_2, $^3J_{HCNP}$ 11.0 Hz). ^{31}P-{^1H} NMR (CD_3OD): δ = 60.9.

Reaction of salt **6** *with methanol.* Methanol (0.072 g, 2.247 mmol) was added to a solution of salt **6** in 0.6 ml dichloromethane under stirring. ^{31}P NMR spectrum of the reaction mixture 10 min after mixing at 20°C: δ = 38.3d($^1J_{PH}$ 630 Hz).

Triethylamine (0.0758 g, 0.749 mmol) was added to the obtained reaction mixture with stirring. An

exothermic reaction takes place. ^{31}P NMR spectrum of the reaction mixture 5 min after mixing: δ = 140 s (**12**).

Reaction of salt **6** *with benzaldehyde.* A solution of benzaldehyde (0.09 g, 0.85 mmol) in 0.3 ml of dichloromethane was added with stirring to a solution of salt **6** (0.285 g, 0.85 mmol) in 0.3 ml of dichloromethane. ^{31}P NMR spectrum of the reaction mixture 10 min after mixing: δ = 39.0d ($^1J_{PH}$ 630 Hz).

Triethylamine (0.043 g, 0.425 mmol) was added to the obtained mixture with stirring. ^{31}P NMR spectrum of the reaction mixture 5 min after mixing: δ = 20 (d, $^1J_{PH}$ 570 Hz), 31 (s) 39 (d, $^1J_{PH}$ 630 Hz), corresponding to a mixture of tetraethyldiamide phosphorous acid **14**, tetraethyldiamide α-diethylaminobenzylphosphonic acid **13**, and salt **6** remained in a proportion 2:3:5, 24h later at 20°C for proportion changed to 3:10:0.

For the phosphonate **13** to be identified it was obtained by the procedure described elsewhere[18] and had constants similar to that as reported in the literature. ^1H NMR spectrum of amidophosphonate **13** ($CDCl_3$): δ = 0.7 (t, 6H, $PCNCH_2CH_3$), 1.1 (t, 12H, $PNCH_2CH_3$), 2.7 (m, 4H, $PCNCH_2$, $^4J_{PCNCH}$ 9.6 Hz), 3.2 (m, 8H, $PNCH_2$, $^3J_{PNCH}$ 9.6 Hz), 4.1 (d, 1H, PCH, $^2J_{PCH}$ 19.1 Hz). ^{31}P NMR ($CDCl_3$): δ = 31.

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