Synthesis of *N*-aryl-substituted iminophosphoranes and NMR spectroscopic investigation of their acid–base properties in acetonitrile

Toomas Rodima,[a] Vahur Mäemets[b] and Ilmar Koppel *[a]

[a] *Institute of Chemical Physics, University of Tartu, Jakobi 2, Tartu, Estonia, 51014. Tel.: +372-7375263; Fax: +372-7375264; E-mail: ilmar@chem.ut.ee*
[b] *Centre of Scientific Competence, University of Tartu, Jakobi 2, Tartu, Estonia, 51014*

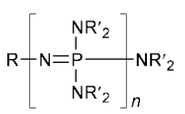
Received (in Cambridge, UK) 4th May 2000, Accepted 15th June 2000
Published on the Web 26th July 2000

A series of $RN{=}P(Pyrr)_3$ iminophosphoranes (P_1 phosphazenes), where R is amino-, α-naphthyl- or substituted phenyl group, is prepared by the Kirsanov reaction and characterized by FT NMR and other properties. The ΔpK_a-values of the 12 different synthesized phosphazenes and $C_6H_5N{=}P(NMe_2)_3$ are determined in acetonitrile relative to the reference bases using ^{13}C NMR spectroscopy. The obtained pK_a-values are compared with the corresponding values of RNH_2 amines. The pK_a-values of the synthesized phosphazenes in acetonitrile range from 14.6 to 26.8 pK_a units.

Introduction

The alkylphosphazenes (**A**) and some other classes of novel

A



B

$R{-}N{=}P(Pyrr)_3$

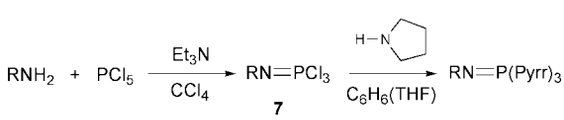
Pyrr denotes the pyrrolidin-1-yl (pyrrolidino) radical

non-ionic bases are known to be very strong uncharged bases.[1,2] The basicity of $MeN{=}P(NMe_2)_3$, which is a rather weak base, is comparable with or even higher than the basicity of cyclic or acyclic alkylated amidine and guanidine bases like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,1,3,3-tetramethylguanidine (TMG), pentamethylguanidine (PMG), *etc*. The relatively high basicity of the latter type of compounds as compared with the alkylamines arises primarily from the very extensive delocalization of the cationic charge in their protonated forms. This is contributed to by the resonance interactions and in several cases is also due to the intramolecular chelation between protonation site and neighboring lone-pair-carrying groups.[3] In acetonitrile, for most of the alkylphosphazenes the pK_a is within the range 26–47 pK_a-units.[1,2a] At the same time, in acetonitrile the basicity range from 18 to 26 pK_a units is relatively scarcely covered by the basicity ladder (except for the substituted 1,1,3,3-tetramethyl-2-phenylguanidines measured by Leffek *et al.*[3d] which partially cover that region). The analogous problem exists in the case of DMSO solutions where the corresponding basicity interval between aliphatic amines ($pK_a < 11$) and phosphazenes ($pK_a > 15$) is not tightly covered.[4] To extend the basicity scale of phosphazenes in acetonitrile towards the lower pK_a-values in the present work we synthesized α-naphthyl- and a series of substituted [2,4-$(NO_2)_2$-, 4-Cl-2-NO_2-, 2,6-Cl_2-, 2,5-Cl_2-, 2-Cl-, 4-Br-, H-, 4-MeO- and 4-Me_2N-substituted phenyl]tripyrrolidinophosphazenes (**B**) and determined their ΔpK_a-values in acetonitrile by ^{13}C NMR spectroscopic methods using reference compounds with suitable pK_a-values. Also, $C_6H_5N{=}P(NMe_2)_3$ and $H_2NN{=}P(Pyrr)_3$ were synthesized and their pK_a-values were determined.

Results and discussion

Syntheses

There are two general methods for direct preparation of *N*-substituted iminophosphoranes. These are the Staudinger reaction of alkyl or aryl azides with tertiary phosphines and the route based on the Kirsanov reaction between phosphorus chlorides and amines.[5] In the present work we synthesized the (monomeric) phosphazenes (P_1) by the Kirsanov reaction according to Schemes 1 and 2.



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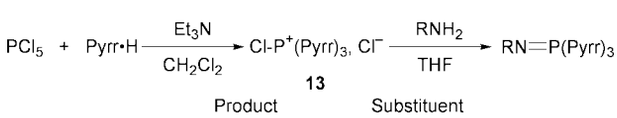
Product	Substituent
1	R = 2,4-$(NO_2)_2C_6H_3$
2	R = 4-Cl-2-$NO_2C_6H_3$
3	R = 2,6-$Cl_2C_6H_3$
4	R = 2,5-$Cl_2C_6H_3$
5	R = 2-ClC_6H_4
6	R = α-Naphthyl

Scheme 1



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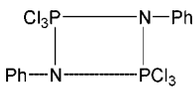
Product	Substituent
8	R = 4-BrC_6H_4
9	R = C_6H_5
10	R = 4-$MeOC_6H_4$
11	R = 4-$NMe_2C_6H_4$
12	R = NH_2

Scheme 2

The Cl atoms in intermediate **7** are reactive and can be readily replaced by such nucleophiles as C_6H_5MgBr, H_2O, C_6H_5ONa, amines, *etc*. Usually the aryl-substituted compounds **7** are crystalline dimeric compounds such as the diazadiphos-

phetidines **14**. According to Zhmurova and Kirsanov[6] the conversion of **14** to the monomer occurs at room temperature in 1,4-dioxane and in polar solvents. This is not the case in benzene solution. However, both forms **7** and **14** can be used



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for the preparation of other phosphazenes by replacing the chlorine atoms with *e.g.*, with amino groups. The process of substitution of Cl atoms of the chlorophosphazenes is mainly controlled by the properties of its imino substituents and by the amine used for the substitution reaction. For example, if R is a sterically hindered alkyl group[1] then dimethylamine, isopropylamine and pyrrolidine are capable of replacing all three chlorine atoms in **7**. In the case of $C_6H_5SO_2$ as the R-group, Me_2NH permits complete substitution (the mono- and di-substituted products were not formed), Et_2NH replaces only two chlorine atoms and $Me_2NCH_2NMe_2$ **15** introduces two dimethylamino groups.[7,8] At the same time, reaction of **15** with **14** leads to replacement of only one chlorine atom of the PCl_3 group with -NMe_2. Attempted isolation of di- and tri-substituted compounds was not successful.[8]

In the present study we found that pyrrolidine reacts readily with intermediates **7** according to Scheme 1 if the R-group is *α*-naphthyl or a phenyl which carries electron-withdrawing substituents. Exploiting this fact we obtained compounds **1**–**6** as free bases with moderate yields. The attempt to obtain compounds **9**–**11** by an analogous method failed as efforts to isolate them from the reaction mixture were unsuccessful. So, it seems that in intermediates **7** the electrophilicity of the phosphorus atom with an electron-donating group such as C_6H_5-, 4-MeO-C_6H_4- and 4-$Me_2NC_6H_4$ is not sufficient for the substitution of the attached chlorine atoms by pyrrolidine. Compounds **8**–**12** were readily synthesized according to Scheme 2, but in the course of the preparation (except for **12**) the solvent was changed from CH_2Cl_2 to THF.

For the pK_a measurements of the phosphazenes in acetonitrile the HPF_6 (or $HClO_4$) salts of compounds **1**–**6**, **8**–**12** and $C_6H_5N{=}P(NMe_2)_3$ **16** were prepared. Details of all synthetic and analytical procedures alongside other measured parameters can be found in the Experimental.

NMR spectra of phosphazenes

The complete list of ^{13}C NMR chemical shifts (δ_C) and ^1H chemical shifts (δ_H) for phosphazenes and their salts is presented in the Experimental. The most important values from a viewpoint of ΔpK_a calculations are collected in Table 1. As one can see, the difference in chemical shifts for the C^1 carbon of phosphazene and its HPF_6 or $HClO_4$ salt ranges from 11 to 18 ppm and for the C^4 carbon from 6 to 13 ppm. This is quite remarkable and reduces the error introduced into the ΔpK_a calculations by the specific effects of the NMR method. These are the local microscopic magnetic fields, which are dependent on the molecule's structure and its adjacent neighbors, thereby manipulating the observable chemical-shift value of atoms used in ΔpK_a calculations as well as the overall inaccuracy of the chemical-shift-determination procedure. The large difference in the δ_C-values for phosphazene and its salt allows one to perform the ΔpK_a calculations with acceptable results at phosphazene-indicator pK_a differences up to one pK_a unit. Comparison of the δ_C-values for phenyl-substituted phosphazenes and α-naphthylphosphazene shows that the transformation of the phosphazene from neutral base to HPF_6 or $HClO_4$ salt causes a decrease of the C^1 chemical shift and an increase of the C^4 chemical shift for the aromatic ring. This phenomenon is analogous to that for the anilines where the transformation of aniline to its salt causes similar effects for the aniline C^1 and C^4 carbons.[9] This indicates that the center of basicity is the imino group of the phosphazene molecule. Another observation is that usually the P–C, P–H as well as the H–H spin–spin coupling constants are larger for phosphazenes than for their salts. In pairs of a phosphazene base and its HPF_6 or $HClO_4$ salt the δ_H-values of aromatic protons are larger for phosphazenes. The δ_C- and δ_H-values of the pyrrolidines were relatively insensitive to variations in the R-group. For pyrrolidines some increase in the δ_H-values and a small but systematic change in the δ_C-values (for >N-*C*H_2-CH_2- an increase, for >N-CH_2-*C*H_2- a decrease) accompanied the transformation from neutral phosphazene to the phosphazene HPF_6 or $HClO_4$ salt.

Table 1 The δ_C-values of the C^1 (δ_{C1}) and C^4 (δ_{C4}) carbons of the phosphazene phenyl substituent and their differences [$\delta_{C(b)} - \delta_{C(s)}$] for the free phosphazene bases and their HPF_6 or $HClO_4$ salts in acetonitrile

Compound	δ_{C1}	δ_{C4}
1	153.7	134.8
1·HPF_6	141.6	143.0
$\delta_{C(b)} - \delta_{C(s)}$	12.1	−8.2
2	146.2	117.6
2·HPF_6	134.9	128.9
$\delta_{C(b)} - \delta_{C(s)}$	11.3	−11.3
3	146.3	117.8
3·HPF_6	132.6	130.8
$\delta_{C(b)} - \delta_{C(s)}$	13.7	−13.0
4	151.0	116.2
4·HPF_6	136.4	127.2
$\delta_{C(b)} - \delta_{C(s)}$	14.6	−11.0
5	149.7	116.9
5·HPF_6	135.0	127.6
$\delta_{C(b)} - \delta_{C(s)}$	14.7	−10.7
6	150.0	115.5
6·HPF_6	135.6	126.7
$\delta_{C(b)} - \delta_{C(s)}$	14.4	−11.2
8	153.1	107.2
8·HPF_6	138.5	117.0
$\delta_{C(b)} - \delta_{C(s)}$	14.6	−9.8
9	153.4	116.4
9·HPF_6	138.9	125.0
$\delta_{C(b)} - \delta_{C(s)}$	14.5	−8.6
10	147.0	151.8
10·HPF_6	130.8	158.3
$\delta_{C(b)} - \delta_{C(s)}$	16.2	−6.5
11	145.0	143.8
11·$HClO_4$	127.0	149.6
$\delta_{C(b)} - \delta_{C(s)}$	18.0	−5.8
16	153.0	116.8
16·HPF_6	138.8	125.5
$\delta_{C(b)} - \delta_{C(s)}$	14.2	−8.7

pK_a determination

The equilibrium acidity measurements for the determination of pK_as of various classes of compounds in different solvents are used widely and a large number of these values are collected into reviews.[4,10]

However, there are very few data available for *N*-phenyl-substituted iminophosphoranes. Yurchenko has measured by potentiometric titration the pK_a of **16** and some other analogous imino(amino)phosphazenes in nitromethane.[11] Using the indicator bases with known pK_a-values as reference compounds the ΔpK_a-values of phosphazenes were calculated from ^{13}C (^1H) NMR spectral data of mixtures of the phosphazene with indicator base in acetonitrile. Depending on the type of indicator base and its pK_a relative to that of the measured phosphazene the mixture of two compounds was made where the phosphazene was in the base form and the indicator in the acid form, or *vice versa*.

Table 2 The calculated ΔpK_a- and pK_a-values for phosphazenes in acetonitrile

Phosphazene (R substituent)	Indicator	pK_a of indicator[11]	ΔpK_a of phosphazene	pK_a of phosphazene	Average pK_a of phosphazene
1 [2,4$(NO_2)_2C_6H_3$]	Lutidine	13.99	0.67	14.7	14.5
	Collidine	14.38	0.05	14.4	
2 (4-Cl-2-$NO_2C_6H_3$)	EA	17.53	−0.06	17.5	17.5
3 (2,6-$Cl_2C_6H_3$)	TEA	18.45	−0.32	18.1	18.0
	EA	17.53	0.29	17.8	
4 (2,5-$Cl_2C_6H_3$)	TEA	18.45	−0.58	17.9	17.9
	EA	17.53	0.45	18.0	
5 (2-ClC_6H_4)	Pyrrolidine	19.58	0.18	19.8	19.8
	MMS[a]	21.6; 20.3[b]	−0.33	21.3; 20.0[b]	
	DAB	20.12	−0.22	19.9	
6 (α-Naphthyl)	MMS[a]	21.6; 20.3[b]	0.37	22.0; 20.7[b]	20.7[b]
8 (4-BrC_6H_4)	PhTMG	20.6	0.35	21.0	21.0
	$C_6H_5CO_2H$[a]	20.7	0.68	21.4	
9 (C_6H_5)	TMG	23.3	−0.68	22.6	22.6
10 (4-$MeOC_6H_4$)	TMG	23.3	0.01	23.3	23.4
	DBU	24.3	−0.87	23.5	
11 (4-$Me_2NC_6H_4$)	TMG	23.3	0.64	23.9	23.9
	DBU	24.3	−0.44	23.9	
12 (H_2N)	TBD	25.97	0.86	26.8	26.8
16 $C_6H_5N{=}P(NMe_2)_3$	DAB	20.12	0.78	20.9	20.9
	MMS[a]	21.6; 20.3[a]	0.47	22.1; 20.8[a]	
	$C_6H_5CO_2H$[a]	20.7	0.36	21.1	

[a] Carboxylic acids which tend to form strong hydrogen bonds and various associates. The pK_a-values obtained on the basis of those indicators are excluded from the calculation of the average pK_a-value for phosphazene. [b] The pK_a-value for MMS obtained in the present work using pyrrolidine as the reference base and the pK_a of the phosphazene calculated on the basis of it.

The indicators (Ind) used were of different types. TBD, DBU, TMG, 1,1,3,3-tetramethyl-2-phenylguanidine (PhTMG), 1,4-diaminobutane (DAB), triethylamine (TEA), pyrrolidine, 2-aminoethanol (EA), 2,6-dimethylpyridine (lutidine) and 2,4,6-trimethylpyridine (collidine) as neutral bases were added to the phosphazene HPF_6 salt solution to give the equilibrium (1).

$$P_1H^+\cdot PF_6^- + \text{Ind} \rightleftharpoons P_1 + \text{IndH}^+\cdot PF_6^- \qquad (1)$$

Monomethyl succinate (methyl hydrogen succinate) (MMS) and benzoic acid ($C_6H_5CO_2H$) as neutral weak protonic acids were added to the phosphazene solution to give the equilibrium (2).

$$P_1 + \text{IndH} \rightleftharpoons P_1H^+ + \text{Ind}^- \qquad (2)$$

The calculation of the ΔpK_a-value of the phosphazene relative to the used indicator compound pK_a was performed on the basis of equations (3) and/or (4). In the case of phosphazene HPF_6 salts ($P_1\cdot HPF_6$) and TBD, DBU, DAB, TMG, PhTMG, TEA, lutidine, pyrrolidine, collidine or EA (Ind), equation (3) holds.

$$\Delta pK_a = \lg([P_1\cdot HPF_6][\text{Ind}]/[\text{Ind}\cdot HPF_6][P_1]) \qquad (3)$$

In the case of a neutral phosphazene and MMS or $C_6H_5CO_2H$ (IndH), then equation (4) applies.

$$\Delta pK_a = -\lg([P_1][\text{IndH}]/[P_1H^+]\,[\text{Ind}^-]) \qquad (4)$$

In these equations, P_1 denotes phosphazene. As could be seen, in calculations of the ΔpK_a the concentrations rather than activities are used. This approach is based on the assumption that the activity coefficient ratios for P_1, Ind, IndH and their respective protonated or deprotonated forms are constants. For determination of the ΔpK_a the solutions of phosphazenes and their protonated forms (HPF_6 or $HClO_4$ salts), and indicators and their protonated or deprotonated forms, in acetonitrile were prepared and the corresponding ^1H and ^{13}C NMR spectra were recorded. These spectra were used for the determination of chemical shifts of the individual species contributing to the observable average chemical-shift values in phosphazene–indicator mixtures. Obtained chemical shifts were used for determination of the $[P_1\cdot HPF_6]/[P_1]$ and $[\text{Ind}]/[\text{Ind}\cdot HPF_6]$, *etc.*, quotients. The investigated phosphazenes were mainly phenyl-substituted ones where the δ_C- as well the δ_H-values of the phenylic substituent atoms in the base and salt forms are significantly different. The chemical shifts of C^1 and C^4 of the aromatic ring, as the most sensitive carbon atoms to the phosphazene protonation, were used for the ΔpK_a calculation. Both these shifts give approximately identical ΔpK_a-values for the phosphazene. Only in some cases was the difference up to the 0.1 pK_a units. Although the primary data used for the ΔpK_a calculations were δ_C-values of phosphazene and indicator, in some cases the δ_H-values of the indicator compounds and phosphazene aromatic substituent were used as additional data in calculations. That was done if the usage or evaluation of the indicator δ_C shifts was impossible when they were not sufficiently sensitive to the protonation–deprotonation process, or when the scatter of ΔpK_a-values obtained using δ_C shifts was relatively large. On the NMR time-scale, there is a fast exchange and/or conversion between different species in any phosphazene–indicator mixture and the spectral lines of the individual species shown in equations (1) and (2) are not directly observable. However, the well defined and identifiable lines at the weighted average chemical shifts for mixtures of phosphazene base with its salt form and for indicator base form with its protonated form are observable. Therefore, knowing the chemical shifts of individual species, their concentrations in equations (3) and (4) can be calculated on the basis of equations (5) and (6). For the phosphazene the calculation was performed according to equation (5). P_{1s} denotes the

$$[P_1]/[P_{1s}] = |\delta - \delta_{P1s}|/|\delta_{P1} - \delta| \qquad (5)$$

phosphazene salt form and $[P_1] + [P_{1s}]$ is equal to the total amount of the phosphazene in solution. For the indicator the calculation was performed according to equation (6).

$$[\text{Ind}]/[\text{IndH}] = |\delta - \delta_{\text{Ind}}|/|\delta_{\text{IndH}} - \delta| \qquad (6)$$

Chemical shifts of the species were obtained from the corresponding ^{13}C NMR spectra. Obtained ΔpK_a-values and pK_a-values of the indicators used are presented in Table 2.

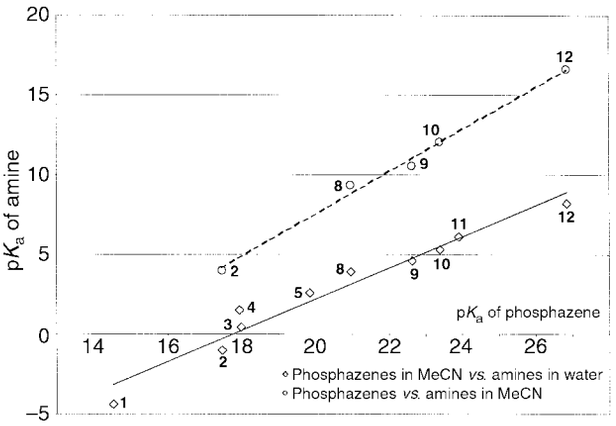

Fig. 1 The dependence between pK_as of phosphazenes and corresponding amines (RNH_2).[11] The numbering of points corresponds to Table 2.

Comparison of pK_a-values

It is seen from Table 2 that the obtained pK_a-values for the phosphazenes obtained using different indicators differ somewhat from each other. Those differences were usually not larger than was the precision of the ΔpK_a determinations, which by repeated measurements was better than ±0.2 pK_a units. However, there were some noticeable deviations from the overall picture. The obscure region was the range from 19 to 22 pK_a units, which includes the phosphazenes **4**–**6** and **8**. The pK_a-values for **5** obtained using MMS, pyrrolidine and TMG differed considerably. If we used for MMS the literature[12] pK_a-value, 21.6, and for pyrrolidine the corresponding value, 19.58, then the calculated pK_a-values for **5** are correspondingly 21.3 and 19.8, *i.e.*, the difference is 1.5 pK_a units. This is a much larger difference than could be introduced only by experimental error. To solve this inconsistency we compared the basicities of MMS and pyrrolidine with each other in their mixture and found that their apparent ΔpK_a is ≈0.7–0.8 pK_a units. Compared with their ΔpK_a-value obtained using the literature pK_a-values our ΔpK_a-value is significantly lower and incomparable with it within experimental error. We feel that the literature pK_a of pyrrolidine seems to be closer to its actual value than does the corresponding value for MMS. This opinion is based on a comparison of the obtained pK_a-values for the phosphazenes (**3**–**5** and **16**) using different indicators (EA, TEA, pyrrolidine, PhTMG and MMS). The usage for MMS of the pK_a-value 20.3 instead of 21.6 reduces the scatter of pK_a-values for **5** and **16** obtained using different indicators. Therefore, we assume that the conjugate anion of MMS is actually not as strong a base, *i.e.* its apparent pK_a is lower than its literature pK_a-value.[12] In Table 2 are shown pK_a-values for **5**, **6** and **16** calculated on the basis of the both MMS pK_a-values (21.6 and 20.3). The average phosphazene pK_a-values for them in Table 2 and the corresponding values in Fig. 1 are calculated without the ΔpK_a data obtained using MMS and $C_6H_5CO_2H$ as indicators.

It is necessary to keep in mind that, in principle, the obtained ΔpK_a-values are rather quantities for the equilibrium where, besides ions, the solution contains some ion-pairs, and, correspondingly, can contain some contribution from specific solvation effects.[13] In particular this can be the situation in the case of carboxylic acids used as indicators. Therefore the obtained ΔpK_a-values should be considered as apparent values for the phosphazenes. However, the calculated pK_a-values are not only of qualitative importance reflecting whether the indicator used or the phosphazene measured was a stronger base. Their quantitative value is observable by plotting them *versus* basicities of amines in water (Fig. 1). The correlation of pK_a-values of phosphazenes in acetonitrile with the corresponding values of anilines (amines) in water[10] is rather good and has a slope which is close to unity [$pK_a(RN{=}PPyrr_3) = 0.97 \cdot pK_a(RNH_2) + 17.90$]. This value of the slope confirms that solvent-specific interactions have no large effect on the measured pK_a-values of the phosphazenes or that these effects are cancelled out.[14] A satisfactory correlation coefficient ($R^2 = 0.96$) of this correlation with pK_a-values in polar solvents where the ion pairing is much less probable than in the case of acetonitrile in the present study supports the quite small significance of solvent-specific effects.

There are only a few literature pK_a-values for anilines in acetonitrile available.[10] However, a similar correlation between pK_a-values of these compounds exists and is observable in Fig. 1. An analogous correlation is found between pK_a-values of *s*-$C_6H_5N{=}P(CH_2CH_3)_2C_6H_5$ phosphazenes and the corresponding anilines in nitromethane.[15]

The analysis of the pK_a-values of anilines in water and in acetonitrile and of those for phosphazenes in acetonitrile reveals that the transfer of anilines from water to acetonitrile increases their basicity by approximately 5 pK_a units and that substitution of the hydrogens of the aniline (amine) amino group by the $=P(Pyrr)_3$ group increases the basicity approximately by 10–12 pK_a units.

Experimental

General procedures

The standard 1D ^1H and proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AC-200 NMR spectrometer at 200 MHz and 50 MHz, correspondingly. Solutions were prepared and sealed off in 5 mm NMR tubes. The concentration of measured solutions was 0.11–0.12 M. Chemical shifts were determined relative to TMS as internal standard. Nondeuterated acetonitrile was used as solvent and the preparations were performed under dry nitrogen. *J*-Values are in Hz. C, H, N elemental analysis was done on a Perkin-Elmer Analyzer 2400 ser. II, or a Perkin-Elmer Elemental Analyzer 240. Mps (uncorrected) were determined on a Gallenkamp mp apparatus with a digital thermometer (SG 95/09/223). Ion exchangers used were APA-8π (Reachim) or Dowex Monosphere 550 A, the strongly basic anion-exchange resins (Cl^- form). The exchange of anions for Cl^- was performed by means of a column with MeOH as solvent.

Materials

$NaBF_4$, $NaBPh_4$ (Fluka), KOMe (Merck), DAB (Ferak Berlin), 2,5-dichloroaniline, 70% aq. $EtNH_2$ and 60% aq. HPF_6 (Aldrich) were commercial products and were used without additional purification. CH_2Cl_2 (Merck), CCl_4 (Reakhim) were distilled from P_2O_5 and stored on NaOH. Pyrrolidine (Merck) was distilled and stored on molecular sieves 4 Å. Et_3N (Reakhim) was distilled and stored on NaOH. THF and benzene were distilled from $LiAlH_4$. Aniline and 4-(dimethylamino)aniline were distilled from Zn powder, α-naphthylamine, *p*-anisidine (all Reakhim), and 4-bromoaniline (Fluka) were recrystallized from an ethanol–water mixture. 2,6-Dichloroaniline, 4-chloro-2-nitroaniline and MMS were synthesized by standard procedures. PhTMG[3d] and $C_6H_5N{=}P(NMe_2)_3$ **16**[2d] were prepared as described in the literature. Anhydrous hydrazine was prepared from hydrazine hydrate (Reakhim). Romil Super Purity MeCN was used for spectral measurements. The reaction conditions (and therefore the isolated yields) for all synthesized phosphazene compounds were not optimized.

(2,4-Dinitrophenylimino)tripyrrolidinophosphorane 1 (Scheme 1). To a solution of 10 mmol of (2,4-dinitrophenylimino)phosphorus(v) trichloride[6] [**7**, R = 2,4-$(NO_2)_2C_6H_3$] in 15 ml of THF at −50 °C was added 60 mmol of pyrrolidine in 5 ml of THF under N_2. The mixture was stirred and the temperature was allowed to warm to ambient, and the mixture was left

overnight. Settled pyrrolidine·HCl salt was filtered off and the solvent removed at reduced pressure. To the residue, 3.5 g of a brown viscous mass, was added 20 ml of 70% aq. $EtNH_2$. Light yellow crystals were precipitated, and were recrystallized from 70% aq. $EtNH_2$.[1] Product **1** was dried under high vacuum to give **1** (2.7 g, 63%), mp 97.1–97.4 °C; δ_H 1.83 (12H, m, $NCH_2C\mathit{H}_2$), 3.16 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.8, $NC\mathit{H}_2CH_2$), 6.87 (1H, d, $^3J_{H\text{-}H}$ 9.4, Ar 6-H), 7.96 (1H, dd, $^3J_{H\text{-}H}$ 9.4, $^4J_{H\text{-}H}$ 2.9, Ar 5-H), 8.36 (1H, t, $^4J_{H\text{-}H} = {}^5J_{P\text{-}H} = 2.9$, Ar 3-H); δ_C 27.0 ($^3J_{P\text{-}C}$ 8.0, $NCH_2\mathit{C}H_2$), 47.6 ($^2J_{P\text{-}C}$ 4.2, $N\mathit{C}H_2CH_2$), 121.9 ($^4J_{P\text{-}C}$ 2.1, Ar C-3), 123.8 ($^3J_{P\text{-}C}$ 10.1, Ar C-6), 127.7 (Ar C-5), 134.8 (Ar C-4), 143.4 ($^3J_{P\text{-}C}$ 28.0, Ar C-2), 153.7 ($^2J_{P\text{-}C}$ 6.8, Ar C-1) [Calc. for $C_{18}H_{27}N_6O_4P$ (M: 422.40): C, 51.18; H, 6.44; N, 19.89. Found: C, 51.25; H, 6.65; N, 19.33%].

1·HPF$_6$. To 1.28 mmol of **1** in 5 ml of MeOH was added 10 ml of 0.6 M HCl (6 mmol, excess). The solution was filtered and a calculated amount of 30% HPF_6 was added. The pale crystals were collected by suction filter, washed successively with water and cold MeOH and dried *in vacuo*: mp 199–205 °C; δ_H 1.9 (12H, overlapped by the solvent, $NCH_2C\mathit{H}_2$), 3.34 (12H, dt, $^3J_{H\text{-}H}$ 6.8, $^3J_{P\text{-}H}$ 3.7, $NC\mathit{H}_2CH_2$), 7.47 (1H, dd, $^3J_{H\text{-}H}$ 9.3, Ar 6-H), 8.46 (1H, dd, $^3J_{H\text{-}H}$ 9.3, $^4J_{H\text{-}H}$ 2.7, Ar 5-H), 9.03 (1H, dd, $^4J_{H\text{-}H}$ 2.7, $^5J_{P\text{-}H}$ 1.5, Ar 3-H), 9.1 (1H, br d, $^2J_{P\text{-}H}$ 9.8, NH); δ_C 26.9 ($^3J_{P\text{-}C}$ 8.7, $NCH_2\mathit{C}H_2$), 48.8 ($^2J_{P\text{-}C}$ 5.1, $N\mathit{C}H_2CH_2$), 121.4 ($^3J_{P\text{-}C}$ 3.1, Ar C-6), 123.9 (Ar C-3), 131.7 (Ar C-5), 137.1 ($^3J_{P\text{-}C}$ 9.3, Ar C-2), 141.6 ($^2J_{P\text{-}C}$ 3.1, Ar C-1), 143.0 (Ar C-4) [Calc. for $C_{18}H_{28}F_6N_6O_4P_2$ (M: 568.39): C, 38.04; H, 4.97; N, 14.79. Found: C, 38.18; H, 4.86; N, 14.39%].

(4-Chloro-2-nitrophenylimino)tripyrrolidinophosphorane 2 (Scheme 1). To 13.1 mmol (2.26 g) of 4-chloro-2-nitroaniline solution in 10 ml of CCl_4 was added 13.1 mmol (2.7 g) of PCl_5 at room temperature. The mixture was heated and refluxed until the HCl evolution ceased. The solvent was removed. The residue, raw (4-chloro-2-nitrophenylimino)phosphorus(v) trichloride (**7**, R = 4-Cl-2-$NO_2C_6H_3$), in the form of a pale yellow solid (2.9 g, 9 mmol), mp 91–93 °C was dissolved in 40 ml of dried benzene and a solution of 4.8 g of pyrrolidine in 10 ml of benzene was added at room temperature by means of a dropping funnel. The mixture was heated to 50 °C and stirred for *ca.* 1 h. The mixture was cooled to 5 °C, pyrrolidine·HCl salt was filtered off and the solvent removed at reduced pressure (60 °C/5 mmHg). From the dark brown residue the product **2** was precipitated by addition of 70% aq. $EtNH_2$. Product **2** was recrystallized from 70% aq. $EtNH_2$[1] and dried under high vacuum to give yellow crystals (1.7 g, 33%); mp 87.6–87.9 °C; δ_H 1.80 (12H, m, $NCH_2C\mathit{H}_2$), 3.14 (12H, dt, $^3J_{H\text{-}H}$ 6.7, $^3J_{P\text{-}H}$ 4.0, $NC\mathit{H}_2CH_2$), 6.85 (1H, br d, $^3J_{H\text{-}H}$ 9.0, Ar 6-H), 7.11 (1H, dd, $^3J_{H\text{-}H}$ 9.0, $^4J_{H\text{-}H}$ 2.8, Ar 5-H), 7.46 (1H, br t, $^4J_{H\text{-}H}$ 2.8, $^5J_{H\text{-}P}$ 2.5, Ar 3-H); δ_C 27.0 ($^3J_{P\text{-}C}$ 7.8, $NCH_2\mathit{C}H_2$), 47.6 ($^2J_{P\text{-}C}$ 4.0, $N\mathit{C}H_2CH_2$), 117.6 ($^5J_{P\text{-}C}$ 4.2, Ar C-4), 124.3 ($^4J_{P\text{-}C}$ 1.9, Ar C-3), 126.5 ($^3J_{P\text{-}C}$ 9.1, Ar C-6), 132.5 (Ar C-5), 145.1 ($^3J_{P\text{-}C}$ 26, Ar C-2), 146.2 ($^2J_{P\text{-}C}$ 7.4, Ar C-1) [Calc. for $C_{18}H_{27}ClN_5O_2P$ (M: 411.86): C, 52.49; H, 6.61; N, 17.00. Found: C, 52.34; H, 6.57; N, 16.76%].

2·HPF$_6$. To a methanolic solution of 0.72 g of **2** at −50 °C was added a calculated amount of 60% HPF_6. The yellowish precipitated salt was filtered off and washed with MeOH. The salt was dissolved in $CHCl_3$ and reprecipitated by adding MeOH until turbidity persisted ($CHCl_3$–MeOH ≈1:2). The mixture was warmed to lose the turbidity and left for crystallization. The pale crystals (0.26 g) were collected by suction, washed with MeOH and dried *in vacuo*: mp 214.0–214.4 °C; δ_H 1.9 (12H, overlapped by solvent, $NCH_2C\mathit{H}_2$), 3.30 (12H, dt, $^3J_{H\text{-}H}$ 6.7, $^3J_{P\text{-}H}$ 3.7, $NC\mathit{H}_2CH_2$), 7.31 (1H, d, $^3J_{H\text{-}H}$ 9.0, Ar 6-H), 7.71 (1H, dd, $^3J_{H\text{-}H}$ 9.0, $^4J_{H\text{-}H}$ 2.6, Ar 5-H), 8.28 (1H, dd, $^4J_{H\text{-}H}$ 2.6, $^5J_{H\text{-}P}$ 1.5, Ar 3-H), 8.6 (1H, br, NH); δ_C 26.9 ($^3J_{P\text{-}C}$ 8.6, $NCH_2\mathit{C}H_2$), 48.7 ($^2J_{P\text{-}C}$ 5.0, $N\mathit{C}H_2CH_2$), 122.9 ($^3J_{P\text{-}C}$ 2.9, Ar C-6), 127.3 (Ar C-3), 128.9 (Ar C-4), 134.9 ($^2J_{P\text{-}C}$ 2.4, Ar C-1), 137.3 (Ar C-5), 138.9 ($^3J_{P\text{-}C}$ 8.8, Ar C-2) [Calc. for $C_{18}H_{28}F_6ClN_5O_2P_2$ (M: 557.82): C, 38.76; H, 5.06; N, 12.55. Found: C, 38.44; H, 4.95; N, 12.04%].

(2,6-Dichlorophenylimino)tripyrrolidinophosphorane 3 (Scheme 1). To 15.6 mmol of 2,6-dichloroaniline solution in 17 ml of CCl_4 was added 15.6 mmol of PCl_5. HCl was evolved and the corresponding salt of 2,6-dichloroaniline settled out. The mixture was stirred, heated and refluxed until the HCl evolution ceased. The cooled solution was filtered and solvent was removed *in vacuo* (eventually 80 °C/3 mmHg). The light yellow oil (3 g, 10 mmol), raw (2,6-dichlorophenylimino)-phosphorus(v) trichloride (**7**, R = 2,6-$Cl_2C_6H_3$), was dissolved in 40 ml of dry benzene. A solution of 5.2 g of pyrrolidine in 10 ml of benzene was added. The mixture was stirred and refluxed for 1 h, stored at 5 °C for 36 h, after which the settled pyrrolidine·HCl salt was filtered off. The solvent was removed at reduced pressure. The thick residue was treated with 70% aq. $EtNH_2$ (≈10 ml) and the precipitate was separated by suction. For recrystallization it was dissolved in warm 70% aq. $EtNH_2$ (≈120 ml) and the warm solution was filtered. Precipitated crystals were collected by suction, washed with dil. aq. $EtNH_2$ and dried under high vacuum to give white crystals (2.2 g, 35%); mp 79.8–81.0 °C; δ_H 1.75 (12H, m, $NCH_2C\mathit{H}_2$), 3.18 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.4, $NC\mathit{H}_2CH_2$), 6.50 (1H, ddd, $^3J_{H\text{-}H}$ 7.6, $^3J_{H\text{-}H}$ 8.1, $^6J_{P\text{-}H}$ 1.9, Ar 4-H), 7.15 [2H, dd, $^3J_{H\text{-}H}$ 7.9, $^5J_{P\text{-}H}$ 1.4, Ar 3(5)-H]; δ_C 27.1 ($^3J_{P\text{-}C}$ 8.2, $NCH_2\mathit{C}H_2$), 47.6 ($^2J_{P\text{-}C}$ 4.5, $N\mathit{C}H_2CH_2$), 117.8 ($^5J_{P\text{-}C}$ 2.4, Ar C-4), 128.7 [Ar C-3(5)], 130.3 [$^3J_{P\text{-}C}$ 8.9, Ar C-2(6)], 146.3 ($^2J_{P\text{-}C}$ 9.7, Ar C-1) [Calc. for $C_{18}H_{27}Cl_2N_4P$ (M: 401.32): C, 53.87; H, 6.78; N, 13.96. Found: C, 53.79; H, 6.77; N, 13.84%].

3·HPF$_6$. To a cold methanolic solution of free base **3** the calculated amount of 60% HPF_6 solution was added. The white precipitate was separated by suction and washed with cold MeOH. Recrystallization from methanolic solution gave 0.45 g of nearly colorless crystals; mp 240–244 °C; δ_H 1.83 (12H, m, $NCH_2C\mathit{H}_2$), 3.23 (12H, dt, $^3J_{H\text{-}H}$ 6.7, $^3J_{P\text{-}H}$ 2.7, $NC\mathit{H}_2CH_2$), 6.2 (1H, s, NH), 7.32 (1H, ddd, $^3J_{H\text{-}H}$ 7.1, $^3J_{H\text{-}H}$ 9.0, $^6J_{P\text{-}H}$ 1.5, Ar 4-H), 7.50 [2H, dt, $^3J_{H\text{-}H}$ 7.9, Ar3(5)-H]; δ_C 26.8 ($^3J_{P\text{-}C}$ 9.0, $NCH_2\mathit{C}H_2$), 48.3 ($^2J_{P\text{-}C}$ 5.1, $N\mathit{C}H_2CH_2$), 130.5 [$^4J_{P\text{-}C}$ 1.5, Ar C-3(5)], 130.8 ($^5J_{P\text{-}C}$ 2.1, Ar C-4), 132.6 (Ar C-1), 136.6 [$^3J_{P\text{-}C}$ 3.8, ArC-2(6)] [Calc. for $C_{18}H_{28}Cl_3F_6N_4O_2P_2$ (M: 547.29): C, 39.50; H, 5.16; N, 10.24. Found: C, 39.60; H, 5.06; N, 10.08%].

(2,5-Dichlorophenylimino)tripyrrolidinophosphorane 4 (Scheme 1). This compound was prepared analogously to the synthesis of **3**. 4.1 g of (2,5-dichlorophenylimino)-phosphorus(v) trichloride (**7**, R = 2,5-Cl_2-C_6H_3; mp 120.1–120.4 °C) were used for the synthesis. Finally, after purification, 1.6 g of **4** in the form of white crystals were obtained (yield 30.8%); mp 82.7–83.4 °C; δ_H 1.80 (12H, m, $NCH_2C\mathit{H}_2$), 3.16 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.9, $NC\mathit{H}_2CH_2$), 6.45 (1H, ddd, $^3J_{H\text{-}H}$ 8.4, $^4J_{H\text{-}H}$ 2.5, $^6J_{P\text{-}H}$ 0.4, Ar 4-H), 6.72 (1H, dd, $^4J_{H\text{-}H}$ 2.5, $^4J_{P\text{-}H}$ 1.2, Ar 6-H), 7.12 (1H, dd, $^3J_{H\text{-}H}$ 8.4, $^5J_{P\text{-}H}$ 2.5, Ar 3-H); δ_C 27.0 ($^3J_{P\text{-}C}$ 7.7, $NCH_2\mathit{C}H_2$), 47.6 ($^2J_{P\text{-}C}$ 3.9, $N\mathit{C}H_2CH_2$), 116.2 (Ar C-4), 122.4 ($^3J_{P\text{-}C}$ 8.8, Ar C-6), 126.7 ($^3J_{P\text{-}C}$ 26.9, Ar C-2), 130.6 (Ar C-3), 132.6 (Ar C-5), 151.0 ($^2J_{P\text{-}C}$ 7.0, Ar C-1) [Calc. for $C_{18}H_{27}Cl_2N_4P$ (M: 401.32): C, 53.87; H, 6.78; N, 13.96. Found: C, 53.93; H, 6.83; N, 13.86%].

4·HPF$_6$. This compound was prepared as described for **3**·HPF_6 with the following parameters: yield 61%; mp 202.5–203 °C; δ_H 1.88 (12H, m, $NCH_2C\mathit{H}_2$), 3.27 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.6, $NC\mathit{H}_2CH_2$), 6.2 (1H, br s, NH) 7.18 (1H, m, Ar 4-H), 7.23 (1H, d, $^4J_{P\text{-}H}$ 2.3, Ar 6-H), 7.50 (1H, dd, $^3J_{H\text{-}H}$ 8.5, $^5J_{P\text{-}H}$ 1.3, Ar 3-H); δ_C 26.8 ($^3J_{P\text{-}C}$ 8.6, $NCH_2\mathit{C}H_2$), 48.6 ($^2J_{P\text{-}C}$ 5.0, $N\mathit{C}H_2CH_2$), 124.1 ($^3J_{P\text{-}C}$ 2.4, Ar C-6), 127.18 ($^3J_{P\text{-}C}$ 8.5, Ar C-2),

127.21 (Ar C-4), 132.4 (Ar C-3), 134.2 (Ar C-5), 136.4 ($^2J_{P\text{-}C}$ 1.9, Ar C-1).

(2-Chlorophenylimino)tripyrrolidinophosphorane 5 (Scheme 1). 11.3 mmol of (2-chlorophenylimino)phosphorus(v) trichloride[6] were slurried in 50 ml of dry benzene, and 71 mmol of pyrrolidine was added at room temperature by means of a dropping funnel. The mixture was stirred and warmed to 50 °C and then left to cool. The precipitate of pyrrolidine·HCl salt was filtered off, and the solvent was removed. The residue, a dark viscous oil, was treated with a 25-fold quantity of 70% aq. $EtNH_2$ and stored at −15 °C for a week. Crystals of **5** were collected and recrystallized from abundant 70% aq. $EtNH_2$[1] as white crystals (1.5 g, 36%), mp 49.3–50.6 °C; δ_H 1.78 (12H, m, NCH_2CH_2), 3.16 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 4.0, NCH_2CH_2), 6.45 (1H, dddd, $^3J_{H\text{-}H}$ 7.1, $^3J_{H\text{-}H}$ 7.8, $^4J_{H\text{-}H}$ 1.7, $^6J_{P\text{-}H}$ 0.7, Ar 4-H), 6.77 (1H, ddd, $^3J_{H\text{-}H}$ 8.1, $^4J_{H\text{-}H}$ 1.7, $^4J_{P\text{-}H}$ 1.1, Ar 6-H), 6.91 (1H, ddd, $^3J_{H\text{-}H}$ 7.1, $^3J_{H\text{-}H}$ 8.1, $^4J_{H\text{-}H}$ 1.7, Ar 5-H), 7.15 (1H, ddd, $^3J_{H\text{-}H}$ 7.8, $^4J_{H\text{-}H}$ 1.7, $^5J_{P\text{-}H}$ 2.6, Ar 3-H); δ_C 27.0 ($^3J_{P\text{-}C}$ 7.6, NCH_2CH_2), 47.6 ($^2J_{P\text{-}C}$ 3.8, NCH_2CH_2), 116.9 (Ar C-4), 123.7 ($^3J_{P\text{-}C}$ 8.0, Ar C-6), 127.8 (Ar C-5), 128.1 ($^3J_{P\text{-}C}$ 22, Ar C-2), 130.0 ($^4J_{P\text{-}C}$ 1.9, Ar C-3), 149.7 ($^2J_{P\text{-}C}$ 7.8, Ar C-1) [Calc. for $C_{18}H_{28}ClN_4P$ (M: 366.83): C, 58.93; H, 7.69; N, 15.27. Found: C, 58.97; H, 7.78; N, 15.21%].

5·HPF$_6$. To a methanolic solution (7.5 ml) of **5** (1.5 g) was added the calculated amount of 60% HPF_6 at −40 °C. The mixture was allowed to warm to ambient temperature, and crystals of **5**·HPF_6 were collected by suction and recrystallized from a 2:3 mixture of $CHCl_3$ and MeOH (eventually at −15 °C). White crystals (0.75 g) were collected; mp 173.7–175.6 °C; δ_H 1.87 (12H, m, NCH_2CH_2), 3.26 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.7, NCH_2CH_2), 6.1 (1H, br d, $^2J_{P\text{-}H}$ 11, NH), 7.2–7.3 (3H, br m, Ar 4-, 5- and 6-H), 7.5 (1H, br d, $^3J_{H\text{-}H}$ 8, Ar 3-H); δ_C 26.8 ($^3J_{P\text{-}C}$ 8.5, NCH_2CH_2), 48.4 ($^2J_{P\text{-}C}$ 4.8, NCH_2CH_2), 124.9 (Ar C-6), 127.6 (Ar C-4), 128.8 ($^3J_{P\text{-}C}$ 9, Ar C-2), 129.3 (Ar C-5), 131.2 (Ar C-3), 135.0 ($^2J_{P\text{-}C}$ 1.6, Ar C-1) [Calc. for $C_{18}H_{29}ClF_6N_4P_2$ (M: 512.79): C, 42.16; H, 5.70; N, 10.93. Found: C, 42.65; H, 5.64; N, 10.73%].

(α-Naphthylimino)tripyrrolidinophosphorane 6 (Scheme 1). 25 mmol (3.5 g) of α-naphthylamine were dissolved in 20 ml of CCl_4 and 25 mmol (5.2 g) of PCl_5 were added. The mixture was heated at 70 °C for *ca.* 4 h up to the end of evolution of HCl. The precipitate was filtered off and washed successively with CCl_4, benzene, and diethyl ether. The bluish crystals of (α-naphthylamino)phosphorus(v) trichloride (**7**, R = α-naphthyl) were dried *in vacuo* (mp 150–152 °C) and 6 mmol of this was slurried in 60 ml of benzene. The mixture was heated to 80 °C and 40 mmol of pyrrolidine was added by means of a dropping funnel. The mixture was stirred and kept at 80 °C for 4 h and then cooled. 1,1,2-Trichloroethylene was added and the HCl salt of pyrrolidine was filtered off. Solvent was removed and to the dark viscous residue was added 30 ml of 70% aq. $EtNH_2$. The mixture was left for two days after which the formed crystals were filtered off, then recrystallized from 40-fold excess of 70% aq. $EtNH_2$ (eventually at −15 °C) and light beige crystals of **6** were collected (1 g, 44%), mp 81.0–82.5 °C; δ_H 1.78 (12H, m, NCH_2CH_2), 3.21 (12H, dt, $^3J_{H\text{-}H}$ 6.5, $^3J_{P\text{-}H}$ 3.8, NCH_2CH_2), 6.67 (1H, dt, $^3J_{H\text{-}H}$ 7.4, ArH), 7.00 (1H, d, $^3J_{H\text{-}H}$ 8.0, ArH), 7.14 (1H, dt, $^3J_{H\text{-}H}$ 7.5, $^3J_{H\text{-}H}$ 8.0, ArH), 7.28 (2H, m, ArH), 7.62 (1H, m, ArH), 8.53 (1H, m, ArH); δ_C 27.1 ($^3J_{P\text{-}C}$ 7.6, NCH_2CH_2), 47.7 ($^2J_{P\text{-}C}$ 3.8, NCH_2CH_2), 114.8 ($^3J_{P\text{-}C}$ 8.3, Ar C-2), 115.5 (Ar C-4), 123.7 (Ar C), 126.0 (Ar C), 126.6 (Ar C), 127.8 (Ar C), 127.9 ($J_{P\text{-}C}$ 1.4, Ar C-3), 132.2 ($^3J_{P\text{-}C}$ 24.1, Ar C-9), 136.2 ($^4J_{P\text{-}C}$ 2.7, Ar C-10), 150.0 ($^2J_{P\text{-}C}$ 4.9, Ar C-1) [Calc. for $C_{22}H_{31}N_4P$ (M: 382.49): C, 69.08; H, 8.17; N, 14.65. Found: C, 69.12; H, 8.51; N, 14.40%].

6·HPF$_6$. 140 mg of **6** were dissolved in diethyl ether and **6**·HCl was precipitated by adding an ethereal solution of HCl. The precipitate was dissolved in MeOH and a calculated amount of 60% HPF_6 solution was added. The solution (Et_2O and most from MeOH) was drawn up and cooled. The crystals were filtered off, washed with cold MeOH and dried *in vacuo*. 80 mg of white crystals of **6**·HPF_6 were obtained, mp 198–202 °C; δ_H 1.81 (12H, m, NCH_2CH_2), 3.27 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.6, NCH_2CH_2), 6.5 (1H, d, $^2J_{P\text{-}H}$ 11.2, NH), 7.34 (1H, br d, $^3J_{H\text{-}H}$ 7.3, ArH), 7.48 (1H, dd, $^3J_{H\text{-}H}$ 8.3, $^3J_{H\text{-}H}$ 7.3, ArH), 7.63 (2H, m, ArH), 7.84 (1H, br d, $^3J_{H\text{-}H}$ 8.3, ArH), 7.96 (1H, m, ArH), 8.16 (1H, m, ArH); δ_C 26.8 ($^3J_{P\text{-}C}$ 8.5, NCH_2CH_2), 48.5 ($^2J_{P\text{-}C}$ 4.8, NCH_2CH_2), 122.6 ($^3J_{P\text{-}C}$ 3.1, Ar C-2), 123.1 (Ar C), 126.7 ($J_{P\text{-}C}$ 1.6, Ar C-4), 127.6 ($J_{P\text{-}C}$ 1.2, Ar C), 127.8 (Ar C), 127.9 (Ar C), 129.5 (Ar C), 130.6 ($^3J_{P\text{-}C}$ 6.9, Ar C-9), 133.3 (Ar C-10), 135.6 (Ar C-1) [Calc. for $C_{22}H_{32}F_6N_4P_2$ (M: 528.45): C, 49.62; H, 6.10; N, 10.60. Found: C, 49.96; H, 5.92; N, 10.24%].

(4-Bromoanilino)tripyrrolidinophosphonium tetraphenylborate 8·HBPh$_4$ (Scheme 2). The chlorophosphonium salt **13** was synthesized from 12.5 mmol of PCl_5 and 37.4 mmol of pyrrolidine in CH_2Cl_2.[1] Et_3N was used to eliminate the evolving HCl. The precipitate of Et_3N·HCl was filtered off and CH_2Cl_2 replaced with 30 ml of THF. 12.5 mmol of 4-bromoaniline and then 12.5 mmol of Et_3N were added at −20 °C to the solution after which it was stirred and the temperature was allowed to rise to ambient. Then the solution was warmed to 50 °C and kept for 30 min at this temperature. Formed Et_3N·HCl was filtered off and solvent was removed *in vacuo*. The obtained dark brown viscous residue was dissolved in MeOH and an equimolar amount of $NaBPh_4$ as a solution in MeOH was added. The precipitated **8**·$HBPh_4$ was filtered off and recrystallized from MeOH–$CHCl_3$ (2:1) to give yellowish crystals (3.1 g, 34%), mp 184.6–186.5 °C; δ_H 1.85 (12H, m, NCH_2CH_2), 3.20 (12H, dt, $^3J_{H\text{-}H}$ 6.7, $^3J_{P\text{-}H}$ 3.4, NCH_2CH_2), 6.83 (4H, t, $^3J_{H\text{-}H}$ 7.1, $\overset{+}{B}Ph_4$ 4-H), 6.94 [2H, d, $^3J_{H\text{-}H}$ 8.9, Ar 2(6)-H], 6.99 [8H, t, $^3J_{H\text{-}H}$ 7.1, $\overset{+}{B}Ph_4$ 3(5)-H], 7.27 [8H, m, $\overset{+}{B}Ph_4$ 2(6)-H], 7.46 [2H, d, $^3J_{H\text{-}H}$ 8.9, Ar 3(5)-H]; δ_C 26.9 ($^3J_{P\text{-}C}$ 8.7, NCH_2CH_2), 48.4 ($^2J_{P\text{-}C}$ 5.2, NCH_2CH_2), 117.0 (Ar C-4), 122.7 ($\overset{+}{B}Ph_4$ C-4), 122.8 [$^3J_{P\text{-}C}$ 7.0, Ar C-2(6)], 126.5 [$^2J_{B\text{-}C}$ 2.8, $\overset{+}{B}Ph_4$ C-2(6)], 133.6 [Ar C-3(5)], 136.8 [$\overset{+}{B}Ph_4$ C-3(5)], 138.4 (Ar C-1), 164.9 ($^1J_{P\text{-}C}$ 49.4, $\overset{+}{B}Ph_4$ C-1).

(4-Bromophenylimino)tripyrrolidinophosphorane 8. To a solution of **8**·$HBPh_4$ in 10 ml of acetonitrile was added the calculated amount of 25% methanolic KOMe. The precipitated $KBPh_4$ was filtered off, methanol was removed, and the obtained residue was extracted with *n*-hexane. After evaporation of hexane, white crystals of **8** were obtained, mp 98.8–99.6 °C; δ_H 1.78 (12H, m, NCH_2CH_2), 3.13 (12H, dt, $^3J_{H\text{-}H}$ 6.5, $^3J_{P\text{-}H}$ 3.6, NCH_2CH_2), 6.55 [2H, d, $^3J_{H\text{-}H}$ 8.7, Ar 2(6)-H], 7.05 [2H, d, $^3J_{H\text{-}H}$ 8.7, Ar 3(5)-H]; δ_C 27.0 ($^3J_{P\text{-}C}$ 7.9, NCH_2CH_2), 47.6 ($^2J_{P\text{-}C}$ 3.8, NCH_2CH_2), 107.2 (Ar C-4), 125.2 [$^3J_{P\text{-}C}$ 18.1, Ar C-2(6)], 132.0 [$^4J_{P\text{-}C}$ 1.0, Ar C-3(5)], 153.1 ($^2J_{P\text{-}C}$ 2.9, Ar C-1).

8·HPF$_6$ was prepared as described above for **5**·HPF_6: mp 191.5–192.6 °C; δ_H 1.89 (12H, m, NCH_2CH_2), 3.24 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.3, NCH_2CH_2), 6.5 (1H, br d, $^2J_{P\text{-}H}$ 9.5, NH), 6.97 [2H, d, $^3J_{H\text{-}H}$ 8.8, Ar 2(6)-H], 7.48 [2H, d, $^3J_{H\text{-}H}$ 8.8, Ar 3(5)-H]; δ_C 26.9 ($^3J_{P\text{-}C}$ 8.8, NCH_2CH_2), 48.4 ($^2J_{P\text{-}C}$ 5.1, NCH_2CH_2), 117.0 (Ar C-4), 122.8 [$^3J_{P\text{-}C}$ 6.7, Ar C-2(6)], 133.5 [Ar C-3(5)], 138.5 (Ar C-1).

(Phenylimino)tripyrrolidinophosphorane 9 (Scheme 2). Chlorophosphonium salt **13** was synthesized from 50 mmol of PCl_5 and 150 mmol of pyrrolidine in CH_2Cl_2.[1] Et_3N was used to eliminate the evolving HCl. The precipitate of Et_3N·HCl was filtered off and CH_2Cl_2 was replaced with 50 ml of dry THF. 55 mmol of aniline and 55 mmol of Et_3N were added subsequently to the solution at −10 °C. The mixture was stirred and its temperature was allowed to rise to ambient after which it was heated for a short time to 60 °C. The mixture was left for

two days and the formed $Et_3N{\cdot}HCl$ was filtered off. Solvent was removed *in vacuo* and the residue was recrystallized twice from aq. $EtNH_2$.[1] Compound **9** was obtained (12 g, 72%), mp 50.8–51.8 °C; δ_H 1.78 (12H, m, NCH_2CH_2), 3.14 (12H, dt, $^3J_{H\text{-}H}$ 6.5, $^3J_{P\text{-}H}$ 3.6, NCH_2CH_2), 6.48 (1H, t, $^3J_{H\text{-}H}$ 7.2, Ar 4-H), 6.63 [2H, d, $^3J_{H\text{-}H}$ 7.9, Ar 2(6)-H], 6.96 [2H, t, $^3J_{H\text{-}H}$ 7.6, Ar 3(5)-H]; δ_C 25.4 ($^3J_{P\text{-}C}$ 7.6, NCH_2CH_2), 45.9 ($^2J_{P\text{-}C}$ 3.6, NCH_2CH_2), 116.4 (Ar C-4), 123.5 [$^3J_{P\text{-}C}$ 17.5, Ar C-2(6)], 129.4 [Ar C-3(5], 153.4 ($^2J_{P\text{-}C}$ 2.9, Ar C-1) [Calc. for $C_{19}H_{29}N_4P$ (M: 332.38): C, 65.04; H, 8.79; N, 16.85. Found: C, 64.83; H, 9.20; N, 16.47%].

9·HPF$_6$. 1.5 g of free base **9** were dissolved in 15 ml of 70% aq. $EtNH_2$ and a calculated amount of 30% HPF_6 was added (pH > 7). The mixture was warmed to 40 °C and approximately 2 ml of water were added, the precipitate (≈2.2 g) was collected by suction, dissolved in 9 ml of MeOH, and the solution was filtered. To the slightly warmed filtrate were added 5 ml of water and the solution was left overnight. The formed crystals were filtered off, washed with dil. MeOH, and dried *in vacuo*. 1.6 g of **9**·HPF_6 were obtained, mp 154.0–154.9 °C; δ_H 1.88 (12H, m, NCH_2CH_2), 3.23 (12H, dt, $^3J_{H\text{-}H}$ 6.7, $^3J_{P\text{-}H}$ 3.4, NCH_2CH_2), 6.4 (1H, s, NH), 7.1 [3H, m, Ar 2(6)-H and 4-H], 7.4 [2H, t, Ar 3(5)-H]; δ_C 26.8 ($^3J_{P\text{-}C}$ 8.5, NCH_2CH_2), 48.4 ($^2J_{P\text{-}C}$ 5.1, NCH_2CH_2), 121.3 [$^3J_{P\text{-}C}$ 6.4, Ar C-2(6)], 125.0 (Ar C-4), 130.7 [Ar C-3(5)], 138.9 (Ar C-1) [Calc. for $C_{18}H_{30}F_6N_4P_2$ (M: 478.34): C, 45.20; H, 6.32; N, 11.71. Found: C, 45.39; H, 6.28; N, 11.66%].

(4-Methoxyanilino)tripyrrolidinophosphonium tetrafluoroborate 10·HBF$_4$ (Scheme 2). Chlorophosphonium salt **13** was synthesized from 25 mmol of PCl_5 and 75 mmol of pyrrolidine in CH_2Cl_2.[1] Et_3N was used to eliminate the evolving HCl. The precipitate of $Et_3N{\cdot}HCl$ was filtered off and solvent CH_2Cl_2 was replaced with 50 ml of THF. 25 mmol of *p*-anisidine in 10 ml of THF and 25 mmol of triethylamine were added subsequently at −20 °C. The temperature of the mixture was allowed to rise to ambient, after which it was warmed to 65 °C for 4 h, then left overnight. The formed $Et_3N{\cdot}HCl$ was filtered off and solvent was removed *in vacuo*. The residue, **10**·HCl, was dissolved in 70% aq. $EtNH_2$, a calculated amount of aq. $NaBF_4$ (as concentrated as possible) was added, and the precipitate of formed **10**·HBF_4 was filtered off. The following recrystallization from aq. $EtNH_2$ yielded 2.1 g (25%) of beige crystals of **10**·HBF_4, mp 164.5–165.7 °C; δ_H 1.86 (12H, m, NCH_2CH_2), 3.22 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.5, NCH_2CH_2), 3.76 (3H, s, OCH_3), 6.9 [2H, d, $^3J_{H\text{-}H}$ 9.0, Ar 3(5)-H], 7.0 [2H, d, $^3J_{H\text{-}H}$ 9.0, Ar 2(6)-H]; δ_C 26.8 ($^3J_{P\text{-}C}$ 8.6, NCH_2CH_2), 48.3 ($^2J_{P\text{-}C}$ 4.9, NCH_2CH_2), 56.3 (OCH_3); 115.9 [Ar C-3(5)], 125.0 [$^3J_{P\text{-}C}$ 5.5, Ar C-2(6)], 130.9 (Ar C-1), 158.2 (Ar C-4) [Calc. for $C_{19}H_{32}BF_4N_4OP$ (M: 450.20): C, 50.68; H, 7.16; N, 12.40. Found: C, 50.58; H, 7.51; N, 12.12%].

10·HPF$_6$. **10**·HBF_4 was dissolved in a small amount of MeOH and the BF_4^- anion was exchanged for Cl^- by means of a column of strongly basic anion-exchange resin APA–8π using MeOH as eluent. The solvent was removed and the residue, **10**·HCl, was dissolved in water. A calculated amount of 15% HPF_6 was added to the aqueous solution, and the precipitated white crystals of **10**·HPF_6 were recrystallized from aq. MeOH, mp 135.8–136.1 °C; δ_H 1.86 (12H, m, NCH_2CH_2), 3.2 (12H, br dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.4, NCH_2CH_2), 3.8 (3H, br s, OCH_3), 6.1 (1H, br d,$^2J_{P\text{-}H}$ 11.4, NH), 6.9 [2H, br d, $^3J_{H\text{-}H}$ 9, Ar 3(5)-H], 7.0 [2H, br d, $^3J_{H\text{-}H}$ 9, Ar 2(6)-H]; δ_C 26.8 ($^3J_{P\text{-}C}$ 8.5, NCH_2CH_2), 48.3 ($^2J_{P\text{-}C}$ 4.8, NCH_2CH_2), 56.3 (OCH_3), 115.9 [Ar C-3(5)], 125.2 [$^3J_{P\text{-}C}$ 5.5, Ar C-2(6)], 130.8 (Ar C-1), 158.3 (Ar C-4) [Calc. for $C_{19}H_{32}F_6N_4OP_2$ (M: 508.43): C, 44.89; H, 6.34; N, 11.02. Found: C, 45.03; H, 6.35; N, 10.85%].

(4-Methoxyphenylimino)tripyrrolidinophosphorane 10. To a methanolic solution of **10**·HBF_4 was added the calculated amount of KOMe solution in MeOH. The precipitated KBF_4 was filtered off, solvent was removed, and the residue was extracted with *n*-hexane. The solvent was removed *in vacuo* and **10** in form of a yellowish oil, was obtained: δ_H 1.77 (12H, m, NCH_2CH_2), 3.13 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.8, NCH_2CH_2), 3.64 (3H, s, OCH_3), 6.6 [4H, br s, Ar 2(6)-H and Ar 3(5)-H]; δ_C 27.0 ($^3J_{P\text{-}C}$ 7.7, NCH_2CH_2), 47.6 ($^2J_{P\text{-}C}$ 4.9, NCH_2CH_2), 56.2 (OCH_3), 115.1 [Ar C-3(5)], 123.9 [$^3J_{P\text{-}C}$ 16.9, Ar C-2(6)], 147.0 ($^2J_{P\text{-}C}$ 2.8, Ar C-1), 151.8 (Ar C-4).

[4-(Dimethylamino)anilinotripyrrolidinophosphonium] perchlorate 11·HClO$_4$ (Scheme 2). The chlorophosphonium salt **13** was prepared from 25 mmol of PCl_5 and 75 mmol of pyrrolidine in CH_2Cl_2.[1] Et_3N was used to eliminate the evolving HCl. The precipitated $Et_3N{\cdot}HCl$ was filtered off, and CH_2Cl_2 removed *in vacuo* and replaced with 20 ml of THF. 25 mmol of 4-(dimethylamino)aniline in 10 ml of THF and 25.5 mmol of Et_3N were added subsequently at −10 °C. The mixture was refluxed for 3 h and left overnight. The formed $Et_3N{\cdot}HCl$ was filtered off and solvent was removed *in vacuo* to give a dark-brown viscous residue. The obtained product was dissolved in 80 ml of 70% aq. $EtNH_2$ and 25 mmol of $NaClO_4{\cdot}H_2O$ in 50 ml of water was added to precipitate **11**·$HClO_4$. After recrystallization from aq. $EtNH_2$, light pink crystals of **11**·$HClO_4$ were obtained (4 g, 34%), mp 117.9–118.6 °C; δ_H 1.85 (12H, m, NCH_2CH_2), 2.89 (6H, s, NCH_3), 3.22 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.5, NCH_2CH_2), 6.1 (1H, br d, $^2J_{P\text{-}H}$ 12.2, NH), 6.7 [2H, br d, $^3J_{H\text{-}H}$ 9, Ar 3(5)-H], 7.0 [2H, br d, $^3J_{H\text{-}H}$ 9, Ar 2(6)-H]; δ_C 26.8 ($^3J_{P\text{-}C}$ 8.5, NCH_2CH_2), 41.1 (NCH_3), 48.3 ($^2J_{P\text{-}C}$ 4.7, NCH_2CH_2), 114.6 [Ar C-3(5)], 125.7 [$^3J_{P\text{-}C}$ 5.1, Ar C-2(6)], 127.0 (Ar C-1), 149.6 (Ar C-4) [Calc. for $C_{20}H_{35}ClN_5O_4P$ (M: 475.93): C, 50.47; H, 8.09; N, 14.71. Found: C, 50.57; H, 7.83; N, 14.52%].

[4-(Dimethylamino)phenylimino]tripyrrolidinophosphorane 11. A sample of **11** was liberated from intermediate **11**·HBF_4 by means of KOMe as described earlier in the case of base **10**, to give pink viscous oily phosphazene **11**. After storage in a refrigerator at 5 °C the phosphazene **11** afforded yellowish crystals; δ_H 1.77 (12H, m, NCH_2CH_2), 2.71 (6H, s, NCH_3), 3.13 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.8, NCH_2CH_2), 6.55 [4H, s, Ar 3(5)-H and Ar 2(6)-H]; δ_C 27.0 ($^3J_{P\text{-}C}$ 7.7, NCH_2CH_2), 42.7 (NCH_3), 47.6 ($^2J_{P\text{-}C}$ 3.5, NCH_2CH_2), 116.5 [Ar C-3(5)], 123.9 [$^3J_{P\text{-}C}$ 16.8, Ar C-2(6)], 143.8 (Ar C-4), 145.0 ($^2J_{P\text{-}C}$ 2.8, Ar C-1).

Hydrazinotripyrrolidinophosphonium hexafluorophosphate 12·HPF$_6$ (Scheme 2). Chlorophosphonium salt **13** was prepared from 25 mmol of PCl_5 and 75 mmol of pyrrolidine in 35 ml of CH_2Cl_2.[1] Et_3N was used to eliminate the evolving HCl. The precipitated $Et_3N{\cdot}HCl$ was filtered off and 100 mmol of hydrazine was added at −15 °C. The mixture was left to warm to room temperature. Approximately 20 ml of the solvent were removed by evaporation and the residue was stored at −15 °C for 24 h. The precipitate of $H_2NNH_2{\cdot}HCl$ containing some $Et_3N{\cdot}HCl$ was filtered off and solvent was removed *in vacuo* to give 7 g of a brown viscous residue. This product was dissolved in 40 ml of 40% aq. $EtNH_2$ and the calculated amount (with regard to the phosphazene base **12**) of 30% HPF_6 solution was added to settle the brownish oil. The aqueous layer was decanted and the remaining oil was stirred with glass stick several times with portions of fresh water to give 4.6 g of yellowish crystals of **12**·HPF_6. Recrystallization of the product was performed from aq. $EtNH_2$, mp 108.0–109.3 °C; δ_H 1.88 (12H, m, NCH_2CH_2), 3.21 (12H, dt, $^3J_{H\text{-}H}$ 6.6, $^3J_{P\text{-}H}$ 3.9, NCH_2CH_2) 3.6 (2H, d, $^3J_{P\text{-}H}$ 10.1, $NHNH_2$), 5.4 (1H, d, $^2J_{P\text{-}H}$ 33.6, $NHNH_2$); δ_C 26.9 ($^3J_{P\text{-}C}$ 8.1, NCH_2CH_2), 48.0 ($^2J_{P\text{-}C}$ 4.2, NCH_2CH_2) [Calc. for $C_{12}H_{27}F_6N_5P_2$ (M: 417.32): C, 34.54; H, 6.52; N, 16.78. Found: C, 34.49; H, 6.50; N, 16.74%].

(Anilino)tris(dimethylamino)phosphonium hexafluorophosphate 16·HPF$_6$. 0.3 g of $C_6H_5N{=}P(NMe_2)_3$ **16** were dissolved in

1.5 ml of 70% aq. $EtNH_2$ and 1.4 ml of 30% HPF_6 solution were added with caution. From the obtained slightly alkaline solution the formed white precipitate was filtered off, washed with water, and then dissolved in methanol to give a slightly turbid solution of **16**·HPF_6. The solution was filtered and methanol removed to give 0.35 g of product in the form of white crystals which had no sharp mp (melted between 92 and 106 °C): δ_H 2.72 (18H, d, $^3J_{P\text{-}H}$ 10.1, NCH_3), 7.06 [2H, d, $^3J_{H\text{-}H}$ 8.2, Ar 2(6)-H], 7.16 (1H, t, $^3J_{H\text{-}H}$ 7.6, Ar 4-H), 7.37 [2H, t, $^3J_{H\text{-}H(av)}$ 7.9, Ar 3(5)-H]; δ_C 37.6 ($^2J_{P\text{-}C}$ 4.9, NCH_3), 122.3 [$^3J_{P\text{-}C}$ 6.0, Ar C-2(6)], 125.5 (Ar C-4), 130.8 [Ar C-3(5)], 138.8 (Ar C-1) [Calc. for $C_{12}H_{24}F_6N_4P_2$ (M: 400.28): C, 36.01; H, 6.04; N, 13.99. Found: C, 36.10; H, 6.06; N, 13.60%].

Acknowledgements

This work was supported by grants 3366, 3370, 1867, 3992 from the Estonian Science Foundation and from the German Government (BMFT X-112.4). We extend our gratitude to Professor Dr R. Schwesinger for valuable advice and suggestions regarding the manuscript.

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