

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



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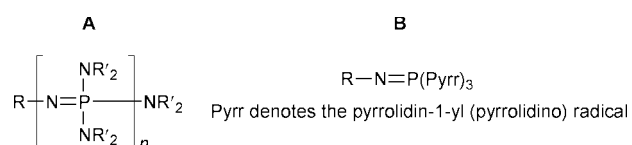
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A series of RN=P(Pyrr)₃ iminophosphoranes (P₁ phosphazenes), where R is amino-, *α*-naphthyl- or substituted phenyl group, is prepared by the Kirsanov reaction and characterized by FT NMR and other properties. The Δp*K*_a-values of the 12 different synthesized phosphazenes and C₆H₅N=P(NMe₂)₃ are determined in acetonitrile relative to the reference bases using ¹³C NMR spectroscopy. The obtained p*K*_a-values are compared with the corresponding values of RNH₂ amines. The p*K*_a-values of the synthesized phosphazenes in acetonitrile range from 14.6 to 26.8 p*K*_a units.

Introduction

The alkylphosphazenes (A) and some other classes of novel

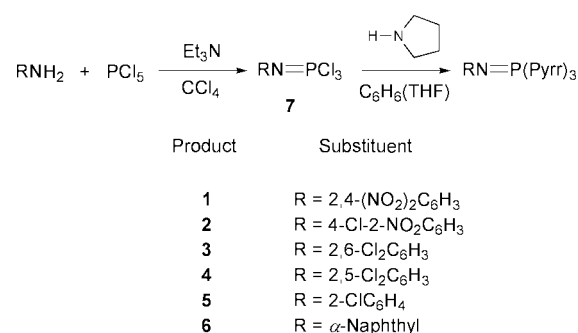


non-ionic bases are known to be very strong uncharged bases.^{1,2} The basicity of MeN=P(NMe₂)₃, which is a rather weak base, is comparable with or even higher than the basicity of cyclic or acyclic alkylated amidine and guanidine bases like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (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 p*K*_a is within the range 26–47 p*K*_a-units.^{1,2a} At the same time, in acetonitrile the basicity range from 18 to 26 p*K*_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.*^{3a} which partially cover that region). The analogous problem exists in the case of DMSO solutions where the corresponding basicity interval between aliphatic amines (p*K*_a < 11) and phosphazenes (p*K*_a > 15) is not tightly covered.⁴ To extend the basicity scale of phosphazenes in acetonitrile towards the lower p*K*_a-values in the present work we synthesized *α*-naphthyl- and a series of substituted [2,4-(NO₂)₂-, 4-Cl-2-NO₂-, 2,6-Cl₂-, 2,5-Cl₂-, 2-Cl-, 4-Br-, H-, 4-MeO- and 4-Me₂N-substituted phenyl]tripyrrolidinophosphazenes (B) and determined their Δp*K*_a-values in acetonitrile by ¹³C NMR spectroscopic methods using reference compounds with suitable p*K*_a-values. Also, C₆H₅N=P(NMe₂)₃ and H₂NN=P(Pyrr)₃ were synthesized and their p*K*_a-values were determined.

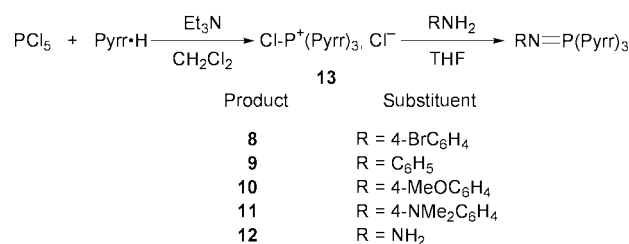
Results and discussion

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 (P₁) by the Kirsanov reaction according to Schemes 1 and 2.



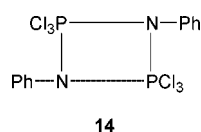
Scheme 1



Scheme 2

The Cl atoms in intermediate 7 are reactive and can be readily replaced by such nucleophiles as C₆H₅MgBr, H₂O, C₆H₅ONa, amines, *etc.* Usually the aryl-substituted compounds 7 are crystalline dimeric compounds such as the diazadiphos-

phetidines **14**. According to Zhmurova and Kirsanov⁶ 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



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 group¹ then dimethylamine, isopropylamine and pyrrolidine are capable of replacing all three chlorine atoms in **7**. In the case of C₆H₅SO₂ as the R-group, Me₂NH permits complete substitution (the mono- and di-substituted products were not formed), Et₂NH replaces only two chlorine atoms and Me₂NCH₂NMe₂ **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 PCl₃ group with -NMe₂. 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 C₆H₅-, 4-MeO-C₆H₄- and 4-Me₂NC₆H₄ 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 CH₂Cl₂ to THF.

For the pK_a measurements of the phosphazenes in acetonitrile the HPF₆ (or HClO₄) salts of compounds **1–6**, **8–12** and C₆H₅N=P(NMe₂)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 ¹³C 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 C¹ carbon of phosphazene and its HPF₆ or HClO₄ salt ranges from 11 to 18 ppm and for the C⁴ 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 HPF₆ or HClO₄ salt causes a decrease of the C¹ chemical shift and an increase of the C⁴ chemical shift for the aromatic ring. This phenomenon is

Table 1 The δ_C-values of the C¹ (δ_{C1}) and C⁴ (δ_{C4}) carbons of the phosphazene phenyl substituent and their differences [δ_{C(b)} - δ_{C(s)}] for the free phosphazene bases and their HPF₆ or HClO₄ salts in acetonitrile

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

analogous to that for the anilines where the transformation of aniline to its salt causes similar effects for the aniline C¹ and C⁴ 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 HPF₆ or HClO₄ 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-CH₂-CH₂- an increase, for >N-CH₂-CH₂- a decrease) accompanied the transformation from neutral phosphazene to the phosphazene HPF₆ or HClO₄ salt.

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}

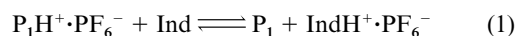
However, there are very few data available for *N*-phenyl-substituted iminophosphoranes. Yurchenko has measured by potentiometric titration the pK_a of **16** and some other analogous imino(amino)phosphazenes in nitromethane.¹¹ Using the indicator bases with known pK_a-values as reference compounds the ΔpK_a-values of phosphazenes were calculated from ¹³C (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

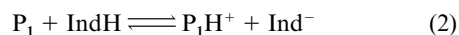
Phosphazene (R substituent)	Indicator	pK_a of indicator ¹¹	ΔpK_a of phosphazene	pK_a of phosphazene	Average pK_a of phosphazene
1 [2,4(NO ₂) ₂ C ₆ H ₃]	Lutidine	13.99	0.67	14.7	14.5
	Collidine	14.38	0.05	14.4	
2 (4-Cl-2-NO ₂ C ₆ H ₃)	EA	17.53	-0.06	17.5	17.5
	3 (2,6-Cl ₂ C ₆ H ₃)	TEA	18.45	-0.32	
4 (2,5-Cl ₂ C ₆ H ₃)	EA	17.53	0.29	17.8	17.9
	TEA	18.45	-0.58	17.9	
5 (2-ClC ₆ H ₄)	EA	17.53	0.45	18.0	19.8
	Pyrrolidine	19.58	0.18	19.8	
	MMS ^a	21.6; 20.3 ^b	-0.33	21.3; 20.0 ^b	
6 (<i>a</i> -Naphthyl)	DAB	20.12	-0.22	19.9	20.7 ^b
	MMS ^a	21.6; 20.3 ^b	0.37	22.0; 20.7 ^b	
8 (4-BrC ₆ H ₄)	PhTMG	20.6	0.35	21.0	21.0
	C ₆ H ₅ CO ₂ H ^a	20.7	0.68	21.4	
9 (C ₆ H ₅)	TMG	23.3	-0.68	22.6	22.6
	10 (4-MeOC ₆ H ₄)	TMG	23.3	0.01	
11 (4-Me ₂ NC ₆ H ₄)	DBU	24.3	-0.87	23.5	23.9
	TMG	23.3	0.64	23.9	
12 (H ₂ N)	DBU	24.3	-0.44	23.9	26.8
	TBD	25.97	0.86	26.8	
16 C ₆ H ₅ N=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 ₆ H ₅ CO ₂ H ^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 HPF₆ salt solution to give the equilibrium (1).



Monomethyl succinate (methyl hydrogen succinate) (MMS) and benzoic acid (C₆H₅CO₂H) as neutral weak protonic acids were added to the phosphazene solution to give the equilibrium (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 HPF₆ salts (P₁·HPF₆) and TBD, DBU, DAB, TMG, PhTMG, TEA, lutidine, pyrrolidine, collidine or EA (Ind), equation (3) holds.

$$\Delta pK_a = \lg([P_1 \cdot \text{HPF}_6][\text{Ind}]/[\text{Ind} \cdot \text{HPF}_6][P_1]) \quad (3)$$

In the case of a neutral phosphazene and MMS or C₆H₅CO₂H (IndH), then equation (4) applies.

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

In these equations, P₁ 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 P₁, 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 (HPF₆ or HClO₄ salts), and indicators and their protonated or deprotonated forms, in acetonitrile were prepared and the corresponding ¹H and ¹³C 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 [P₁·HPF₆]/[P₁] and [Ind]/[Ind·HPF₆], *etc.*, quotients. The investigated phosphazenes were mainly phenyl-substituted ones where the δ_C - as well as the δ_H -values of the phenylic substituent atoms in the base and salt forms are significantly different. The chemical shifts of C¹ and C⁴ 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

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

phosphazene salt form and [P₁] + [P_{1s}] is equal to the total amount of the phosphazene in solution. For the indicator the calculation was performed according to equation (6).

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

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

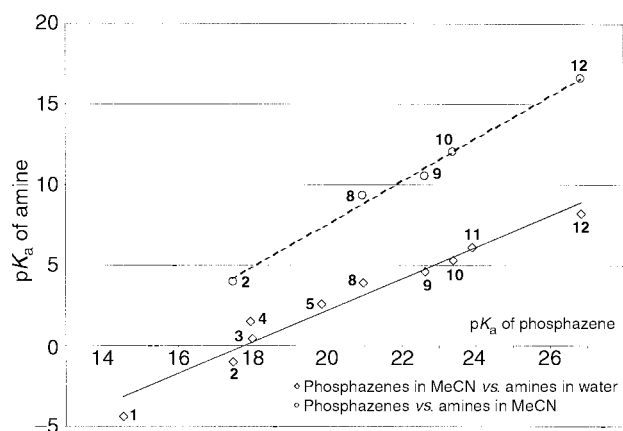


Fig. 1 The dependence between pK_a s of phosphazenes and corresponding amines (RNH_2).¹¹ The numbering of points corresponds to Table 2.

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 literature¹² 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 water¹⁰ 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 $s\text{-}C_6H_5N=P(CH_2CH_3)_2C_6H_5$ 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-8 π (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. HPF₆ (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, *a*-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) trichloride⁶ [$R = 2,4-(NO_2)_2C_6H_3$] in 15 ml of THF at $-50^\circ C$ 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. EtNH₂. Light yellow crystals were precipitated, and were recrystallized from 70% aq. EtNH₂.¹ 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, NCH₂CH₂), 3.16 (12H, dt, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.8, NCH₂CH₂), 6.87 (1H, d, $^3J_{\text{H-H}}$ 9.4, Ar 6-H), 7.96 (1H, dd, $^3J_{\text{H-H}}$ 9.4, $^4J_{\text{H-H}}$ 2.9, Ar 5-H), 8.36 (1H, t, $^4J_{\text{H-H}} = ^5J_{\text{P-H}} = 2.9$, Ar 3-H); δ_{C} 27.0 ($^3J_{\text{P-C}}$ 8.0, NCH₂CH₂), 47.6 ($^2J_{\text{P-C}}$ 4.2, NCH₂CH₂), 121.9 ($^4J_{\text{P-C}}$ 2.1, Ar C-3), 123.8 ($^3J_{\text{P-C}}$ 10.1, Ar C-6), 127.7 (Ar C-5), 134.8 (Ar C-4), 143.4 ($^3J_{\text{P-C}}$ 28.0, Ar C-2), 153.7 ($^2J_{\text{P-C}}$ 6.8, Ar C-1) [Calc. for C₁₈H₂₇N₆O₄P (M: 422.40): C, 51.18; H, 6.44; N, 19.89. Found: C, 51.25; H, 6.65; N, 19.33%].

1·HPF₆. 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% HPF₆ 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, NCH₂CH₂), 3.34 (12H, dt, $^3J_{\text{H-H}}$ 6.8, $^3J_{\text{P-H}}$ 3.7, NCH₂CH₂), 7.47 (1H, dd, $^3J_{\text{H-H}}$ 9.3, Ar 6-H), 8.46 (1H, dd, $^3J_{\text{H-H}}$ 9.3, $^4J_{\text{H-H}}$ 2.7, Ar 5-H), 9.03 (1H, dd, $^4J_{\text{H-H}}$ 2.7, $^5J_{\text{P-H}}$ 1.5, Ar 3-H), 9.1 (1H, br d, $^2J_{\text{P-H}}$ 9.8, NH); δ_{C} 26.9 ($^3J_{\text{P-C}}$ 8.7, NCH₂CH₂), 48.8 ($^2J_{\text{P-C}}$ 5.1, NCH₂CH₂), 121.4 ($^3J_{\text{P-C}}$ 3.1, Ar C-6), 123.9 (Ar C-3), 131.7 (Ar C-5), 137.1 ($^3J_{\text{P-C}}$ 9.3, Ar C-2), 141.6 ($^2J_{\text{P-C}}$ 3.1, Ar C-1), 143.0 (Ar C-4) [Calc. for C₁₈H₂₈F₆N₆O₄P₂ (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 CCl₄ was added 13.1 mmol (2.7 g) of PCl₅ 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-NO₂C₆H₃), 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. EtNH₂. Product **2** was recrystallized from 70% aq. EtNH₂¹ 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, NCH₂CH₂), 3.14 (12H, dt, $^3J_{\text{H-H}}$ 6.7, $^3J_{\text{P-H}}$ 4.0, NCH₂CH₂), 6.85 (1H, br d, $^3J_{\text{H-H}}$ 9.0, Ar 6-H), 7.11 (1H, dd, $^3J_{\text{H-H}}$ 9.0, $^4J_{\text{H-H}}$ 2.8, Ar 5-H), 7.46 (1H, br t, $^4J_{\text{H-H}}$ 2.8, $^5J_{\text{H-P}}$ 2.5, Ar 3-H); δ_{C} 27.0 ($^3J_{\text{P-C}}$ 7.8, NCH₂CH₂), 47.6 ($^2J_{\text{P-C}}$ 4.0, NCH₂CH₂), 117.6 ($^5J_{\text{P-C}}$ 4.2, Ar C-4), 124.3 ($^4J_{\text{P-C}}$ 1.9, Ar C-3), 126.5 ($^3J_{\text{P-C}}$ 9.1, Ar C-6), 132.5 (Ar C-5), 145.1 ($^3J_{\text{P-C}}$ 26, Ar C-2), 146.2 ($^2J_{\text{P-C}}$ 7.4, Ar C-1) [Calc. for C₁₈H₂₇ClN₅O₂P (M: 411.86): C, 52.49; H, 6.61; N, 17.00. Found: C, 52.34; H, 6.57; N, 16.76%].

2·HPF₆. To a methanolic solution of 0.72 g of **2** at –50 °C was added a calculated amount of 60% HPF₆. The yellowish precipitated salt was filtered off and washed with MeOH. The salt was dissolved in CHCl₃ and reprecipitated by adding MeOH until turbidity persisted (CHCl₃–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, NCH₂CH₂), 3.30 (12H, dt, $^3J_{\text{H-H}}$ 6.7, $^3J_{\text{P-H}}$ 3.7, NCH₂CH₂), 7.31 (1H, d, $^3J_{\text{H-H}}$ 9.0, Ar 6-H), 7.71 (1H, dd, $^3J_{\text{H-H}}$ 9.0, $^4J_{\text{H-H}}$ 2.6, Ar 5-H), 8.28 (1H, dd, $^4J_{\text{H-H}}$ 2.6, $^5J_{\text{H-P}}$ 1.5, Ar 3-H), 8.6 (1H, br, NH); δ_{C} 26.9 ($^3J_{\text{P-C}}$ 8.6, NCH₂CH₂), 48.7 ($^2J_{\text{P-C}}$ 5.0, NCH₂CH₂), 122.9 ($^3J_{\text{P-C}}$ 2.9, Ar

C-6), 127.3 (Ar C-3), 128.9 (Ar C-4), 134.9 ($^2J_{\text{P-C}}$ 2.4, Ar C-1), 137.3 (Ar C-5), 138.9 ($^3J_{\text{P-C}}$ 8.8, Ar C-2) [Calc. for C₁₈H₂₈F₆ClN₅O₂P₂ (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 CCl₄ was added 15.6 mmol of PCl₅, 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-Cl₂C₆H₃), 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. EtNH₂ (≈ 10 ml) and the precipitate was separated by suction. For recrystallization it was dissolved in warm 70% aq. EtNH₂ (≈ 120 ml) and the warm solution was filtered. Precipitated crystals were collected by suction, washed with dil. aq. EtNH₂ 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, NCH₂CH₂), 3.18 (12H, dt, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.4, NCH₂CH₂), 6.50 (1H, ddd, $^3J_{\text{H-H}}$ 7.6, $^3J_{\text{H-H}}$ 8.1, $^6J_{\text{P-H}}$ 1.9, Ar 4-H), 7.15 [2H, dd, $^3J_{\text{H-H}}$ 7.9, $^5J_{\text{P-H}}$ 1.4, Ar 3(5)-H]; δ_{C} 27.1 ($^3J_{\text{P-C}}$ 8.2, NCH₂CH₂), 47.6 ($^2J_{\text{P-C}}$ 4.5, NCH₂CH₂), 117.8 ($^3J_{\text{P-C}}$ 2.4, Ar C-4), 128.7 [Ar C-3(5)], 130.3 [$^3J_{\text{P-C}}$ 8.9, Ar C-2(6)], 146.3 ($^2J_{\text{P-C}}$ 9.7, Ar C-1) [Calc. for C₁₈H₂₇Cl₂N₄P (M: 401.32): C, 53.87; H, 6.78; N, 13.96. Found: C, 53.79; H, 6.77; N, 13.84%].

3·HPF₆. To a cold methanolic solution of free base **3** the calculated amount of 60% HPF₆ 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, NCH₂CH₂), 3.23 (12H, dt, $^3J_{\text{H-H}}$ 6.7, $^3J_{\text{P-H}}$ 2.7, NCH₂CH₂), 6.2 (1H, s, NH), 7.32 (1H, ddd, $^3J_{\text{H-H}}$ 7.1, $^3J_{\text{H-H}}$ 9.0, $^6J_{\text{P-H}}$ 1.5, Ar 4-H), 7.50 [2H, dt, $^3J_{\text{H-H}}$ 7.9, Ar 3(5)-H]; δ_{C} 26.8 ($^3J_{\text{P-C}}$ 9.0, NCH₂CH₂), 48.3 ($^2J_{\text{P-C}}$ 5.1, NCH₂CH₂), 130.5 [$^4J_{\text{P-C}}$ 1.5, Ar C-3(5)], 130.8 ($^5J_{\text{P-C}}$ 2.1, Ar C-4), 132.6 (Ar C-1), 136.6 [$^3J_{\text{P-C}}$ 3.8, Ar C-2(6)] [Calc. for C₁₈H₂₈Cl₃F₆N₄O₂P₂ (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-Cl₂-C₆H₃; 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, NCH₂CH₂), 3.16 (12H, dt, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.9, NCH₂CH₂), 6.45 (1H, ddd, $^3J_{\text{H-H}}$ 8.4, $^4J_{\text{H-H}}$ 2.5, $^6J_{\text{P-H}}$ 0.4, Ar 4-H), 6.72 (1H, dd, $^4J_{\text{H-H}}$ 2.5, $^4J_{\text{P-H}}$ 1.2, Ar 6-H), 7.12 (1H, dd, $^3J_{\text{H-H}}$ 8.4, $^5J_{\text{P-H}}$ 2.5, Ar 3-H); δ_{C} 27.0 ($^3J_{\text{P-C}}$ 7.7, NCH₂CH₂), 47.6 ($^2J_{\text{P-C}}$ 3.9, NCH₂CH₂), 116.2 (Ar C-4), 122.4 ($^3J_{\text{P-C}}$ 8.8, Ar C-6), 126.7 ($^3J_{\text{P-C}}$ 26.9, Ar C-2), 130.6 (Ar C-3), 132.6 (Ar C-5), 151.0 ($^2J_{\text{P-C}}$ 7.0, Ar C-1) [Calc. for C₁₈H₂₇Cl₂N₄P (M: 401.32): C, 53.87; H, 6.78; N, 13.96. Found: C, 53.93; H, 6.83; N, 13.86%].

4·HPF₆. This compound was prepared as described for **3·HPF₆** with the following parameters: yield 61%; mp 202.5–203 °C; δ_{H} 1.88 (12H, m, NCH₂CH₂), 3.27 (12H, dt, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.6, NCH₂CH₂), 6.2 (1H, br s, NH) 7.18 (1H, m, Ar 4-H), 7.23 (1H, d, $^4J_{\text{P-H}}$ 2.3, Ar 6-H), 7.50 (1H, dd, $^3J_{\text{H-H}}$ 8.5, $^5J_{\text{P-H}}$ 1.3, Ar 3-H); δ_{C} 26.8 ($^3J_{\text{P-C}}$ 8.6, NCH₂CH₂), 48.6 ($^2J_{\text{P-C}}$ 5.0, NCH₂CH₂), 124.1 ($^3J_{\text{P-C}}$ 2.4, Ar C-6), 127.18 ($^3J_{\text{P-C}}$ 8.5, Ar C-2),

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

(2-Chlorophenylimino)tripyrrolidinophosphorane 5 (Scheme 1). 11.3 mmol of (2-chlorophenylimino)phosphorus(v) trichloride⁶ 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. EtNH₂ and stored at -15 °C for a week. Crystals of **5** were collected and recrystallized from abundant 70% aq. EtNH₂¹ as white crystals (1.5 g, 36%), mp 49.3–50.6 °C; δ_H 1.78 (12H, m, NCH₂CH₂), 3.16 (12H, dt, $^3J_{H-H}$ 6.6, $^3J_{P-H}$ 4.0, NCH₂CH₂), 6.45 (1H, dddd, $^3J_{H-H}$ 7.1, $^3J_{H-H}$ 7.8, $^4J_{H-H}$ 1.7, $^6J_{P-H}$ 0.7, Ar 4-H), 6.77 (1H, ddd, $^3J_{H-H}$ 8.1, $^4J_{H-H}$ 1.7, $^4J_{P-H}$ 1.1, Ar 6-H), 6.91 (1H, ddd, $^3J_{H-H}$ 7.1, $^3J_{H-H}$ 8.1, $^4J_{H-H}$ 1.7, Ar 5-H), 7.15 (1H, ddd, $^3J_{H-H}$ 7.8, $^4J_{H-H}$ 1.7, $^5J_{P-H}$ 2.6, Ar 3-H); δ_C 27.0 ($^3J_{P-C}$ 7.6, NCH₂CH₂), 47.6 ($^2J_{P-C}$ 3.8, NCH₂CH₂), 116.9 (Ar C-4), 123.7 ($^3J_{P-C}$ 8.0, Ar C-6), 127.8 (Ar C-5), 128.1 ($^2J_{P-C}$ 22, Ar C-2), 130.0 ($^4J_{P-C}$ 1.9, Ar C-3), 149.7 ($^2J_{P-C}$ 7.8, Ar C-1) [Calc. for C₁₈H₂₈ClN₄P (M: 366.83): C, 58.93; H, 7.69; N, 15.27. Found: C, 58.97; H, 7.78; N, 15.21%].

5·HPF₆. To a methanolic solution (7.5 ml) of **5** (1.5 g) was added the calculated amount of 60% HPF₆ at -40 °C. The mixture was allowed to warm to ambient temperature, and crystals of **5·HPF₆** were collected by suction and recrystallized from a 2:3 mixture of CHCl₃ 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, NCH₂CH₂), 3.26 (12H, dt, $^3J_{H-H}$ 6.6, $^3J_{P-H}$ 3.7, NCH₂CH₂), 6.1 (1H, br d, $^2J_{P-H}$ 11, NH), 7.2–7.3 (3H, br m, Ar 4-, 5- and 6-H), 7.5 (1H, br d, $^3J_{H-H}$ 8, Ar 3-H); δ_C 26.8 ($^3J_{P-C}$ 8.5, NCH₂CH₂), 48.4 ($^2J_{P-C}$ 4.8, NCH₂CH₂), 124.9 (Ar C-6), 127.6 (Ar C-4), 128.8 ($^3J_{P-C}$ 9, Ar C-2), 129.3 (Ar C-5), 131.2 (Ar C-3), 135.0 ($^2J_{P-C}$ 1.6, Ar C-1) [Calc. for C₁₈H₂₉ClF₆N₄P₂ (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 CCl₄ and 25 mmol (5.2 g) of PCl₅ 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 CCl₄, 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. EtNH₂. The mixture was left for two days after which the formed crystals were filtered off, then recrystallized from 40-fold excess of 70% aq. EtNH₂ (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, NCH₂CH₂), 3.21 (12H, dt, $^3J_{H-H}$ 6.5, $^3J_{P-H}$ 3.8, NCH₂CH₂), 6.67 (1H, dt, $^3J_{H-H}$ 7.4, ArH), 7.00 (1H, d, $^3J_{H-H}$ 8.0, ArH), 7.14 (1H, dt, $^3J_{H-H}$ 7.5, $^3J_{H-H}$ 8.0, ArH), 7.28 (2H, m, ArH), 7.62 (1H, m, ArH), 8.53 (1H, m, ArH); δ_C 27.1 ($^3J_{P-C}$ 7.6, NCH₂CH₂), 47.7 ($^2J_{P-C}$ 3.8, NCH₂CH₂), 114.8 ($^3J_{P-C}$ 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-C} 1.4, Ar C-3), 132.2 ($^3J_{P-C}$ 24.1, Ar C-9), 136.2 ($^4J_{P-C}$ 2.7, Ar C-10), 150.0 ($^2J_{P-C}$ 4.9, Ar C-1) [Calc. for C₂₂H₃₁N₄P (M: 382.49): C, 69.08; H, 8.17; N, 14.65. Found: C, 69.12; H, 8.51; N, 14.40%].

6·HPF₆. 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% HPF₆ solution was added. The solution (Et₂O 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·HPF₆** were obtained, mp 198–202 °C; δ_H 1.81 (12H, m, NCH₂CH₂), 3.27 (12H, dt, $^3J_{H-H}$ 6.6, $^3J_{P-H}$ 3.6, NCH₂CH₂), 6.5 (1H, d, $^2J_{P-H}$ 11.2, NH), 7.34 (1H, br d, $^3J_{H-H}$ 7.3, ArH), 7.48 (1H, dd, $^3J_{H-H}$ 8.3, $^3J_{H-H}$ 7.3, ArH), 7.63 (2H, m, ArH), 7.84 (1H, br d, $^3J_{H-H}$ 8.3, ArH), 7.96 (1H, m, ArH), 8.16 (1H, m, ArH); δ_C 26.8 ($^3J_{P-C}$ 8.5, NCH₂CH₂), 48.5 ($^2J_{P-C}$ 4.8, NCH₂CH₂), 122.6 ($^3J_{P-C}$ 3.1, Ar C-2), 123.1 (Ar C), 126.7 (J_{P-C} 1.6, Ar C-4), 127.6 (J_{P-C} 1.2, Ar C), 127.8 (Ar C), 127.9 (Ar C), 129.5 (Ar C), 130.6 ($^3J_{P-C}$ 6.9, Ar C-9), 133.3 (Ar C-10), 135.6 (Ar C-1) [Calc. for C₂₂H₃₂F₆N₄P₂ (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·HBPh₄ (Scheme 2). The chlorophosphonium salt **13** was synthesized from 12.5 mmol of PCl₅ and 37.4 mmol of pyrrolidine in CH₂Cl₂.¹ Et₃N was used to eliminate the evolving HCl. The precipitate of Et₃N·HCl was filtered off and CH₂Cl₂ replaced with 30 ml of THF. 12.5 mmol of 4-bromoaniline and then 12.5 mmol of Et₃N 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 Et₃N·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 NaBPh₄ as a solution in MeOH was added. The precipitated **8·HBPh₄** was filtered off and recrystallized from MeOH–CHCl₃ (2:1) to give yellowish crystals (3.1 g, 34%), mp 184.6–186.5 °C; δ_H 1.85 (12H, m, NCH₂CH₂), 3.20 (12H, dt, $^3J_{H-H}$ 6.7, $^3J_{P-H}$ 3.4, NCH₂CH₂), 6.83 (4H, t, $^3J_{H-H}$ 7.1, BPh₄ 4-H), 6.94 [2H, d, $^3J_{H-H}$ 8.9, Ar 2(6)-H], 6.99 [8H, t, $^3J_{H-H}$ 7.1, BPh₄ 3(5)-H], 7.27 [8H, m, BPh₄ 2(6)-H], 7.46 [2H, d, $^3J_{H-H}$ 8.9, Ar 3(5)-H]; δ_C 26.9 ($^3J_{P-C}$ 8.7, NCH₂CH₂), 48.4 ($^2J_{P-C}$ 5.2, NCH₂CH₂), 117.0 (Ar C-4), 122.7 (BPh₄ C-4), 122.8 ($^3J_{P-C}$ 7.0, Ar C-2(6)), 126.5 [$^2J_{B-C}$ 2.8, BPh₄ C-2(6)], 133.6 [Ar C-3(5)], 136.8 [BPh₄ C-3(5)], 138.4 (Ar C-1), 164.9 ($^1J_{P-C}$ 49.4, BPh₄ C-1).

(4-Bromophenylimino)tripyrrolidinophosphorane 8. To a solution of **8·HBPh₄** in 10 ml of acetonitrile was added the calculated amount of 25% methanolic KOMe. The precipitated KBPh₄ 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, NCH₂CH₂), 3.13 (12H, dt, $^3J_{H-H}$ 6.5, $^3J_{P-H}$ 3.6, NCH₂CH₂), 6.55 [2H, d, $^3J_{H-H}$ 8.7, Ar 2(6)-H], 7.05 [2H, d, $^3J_{H-H}$ 8.7, Ar 3(5)-H]; δ_C 27.0 ($^3J_{P-C}$ 7.9, NCH₂CH₂), 47.6 ($^2J_{P-C}$ 3.8, NCH₂CH₂), 107.2 (Ar C-4), 125.2 [$^3J_{P-C}$ 18.1, Ar C-2(6)], 132.0 [$^4J_{P-C}$ 1.0, Ar C-3(5)], 153.1 ($^2J_{P-C}$ 2.9, Ar C-1).

8·HPF₆ was prepared as described above for **5·HPF₆**; mp 191.5–192.6 °C; δ_H 1.89 (12H, m, NCH₂CH₂), 3.24 (12H, dt, $^3J_{H-H}$ 6.6, $^3J_{P-H}$ 3.3, NCH₂CH₂), 6.5 (1H, br d, $^2J_{P-H}$ 9.5, NH), 6.97 [2H, d, $^3J_{H-H}$ 8.8, Ar 2(6)-H], 7.48 [2H, d, $^3J_{H-H}$ 8.8, Ar 3(5)-H]; δ_C 26.9 ($^3J_{P-C}$ 8.8, NCH₂CH₂), 48.4 ($^2J_{P-C}$ 5.1, NCH₂CH₂), 117.0 (Ar C-4), 122.8 [$^3J_{P-C}$ 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 PCl₅ and 150 mmol of pyrrolidine in CH₂Cl₂.¹ Et₃N was used to eliminate the evolving HCl. The precipitate of Et₃N·HCl was filtered off and CH₂Cl₂ was replaced with 50 ml of dry THF. 55 mmol of aniline and 55 mmol of Et₃N 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 $\text{Et}_3\text{N}\cdot\text{HCl}$ 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, $^3J_{\text{H-H}}$ 6.5, $^3J_{\text{P-H}}$ 3.6, NCH_2CH_2), 6.48 (1H, t, $^3J_{\text{H-H}}$ 7.2, Ar 4-H), 6.63 [2H, d, $^3J_{\text{H-H}}$ 7.9, Ar 2(6)-H], 6.96 [2H, t, $^3J_{\text{H-H}}$ 7.6, Ar 3(5)-H]; δ_{C} 25.4 ($^3J_{\text{P-C}}$ 7.6, NCH_2CH_2), 45.9 ($^2J_{\text{P-C}}$ 3.6, NCH_2CH_2), 116.4 (Ar C-4), 123.5 [$^3J_{\text{P-C}}$ 17.5, Ar C-2(6)], 129.4 [Ar C-3(5)], 153.4 ($^2J_{\text{P-C}}$ 2.9, Ar C-1) [Calc. for $\text{C}_{19}\text{H}_{29}\text{N}_4\text{P}$ (M: 332.38): C, 65.04; H, 8.79; N, 16.85. Found: C, 64.83; H, 9.20; N, 16.47%].

9-HPF₆. 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-HPF₆** were obtained, mp 154.0–154.9 °C; δ_{H} 1.88 (12H, m, NCH_2CH_2), 3.23 (12H, dt, $^3J_{\text{H-H}}$ 6.7, $^3J_{\text{P-H}}$ 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 ($^3J_{\text{P-C}}$ 8.5, NCH_2CH_2), 48.4 ($^2J_{\text{P-C}}$ 5.1, NCH_2CH_2), 121.3 [$^3J_{\text{P-C}}$ 6.4, Ar C-2(6)], 125.0 (Ar C-4), 130.7 [Ar C-3(5)], 138.9 (Ar C-1) [Calc. for $\text{C}_{18}\text{H}_{30}\text{F}_6\text{N}_4\text{P}_2$ (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-HBF₄ (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 $\text{Et}_3\text{N}\cdot\text{HCl}$ 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 $\text{Et}_3\text{N}\cdot\text{HCl}$ 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-HBF₄** was filtered off. The following recrystallization from aq. EtNH_2 yielded 2.1 g (25%) of beige crystals of **10-HBF₄**, mp 164.5–165.7 °C; δ_{H} 1.86 (12H, m, NCH_2CH_2), 3.22 (12H, dt, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.5, NCH_2CH_2), 3.76 (3H, s, OCH_3), 6.9 [2H, d, $^3J_{\text{H-H}}$ 9.0, Ar 3(5)-H], 7.0 [2H, d, $^3J_{\text{H-H}}$ 9.0, Ar 2(6)-H]; δ_{C} 26.8 ($^3J_{\text{P-C}}$ 8.6, NCH_2CH_2), 48.3 ($^2J_{\text{P-C}}$ 4.9, NCH_2CH_2), 56.3 (OCH_3), 115.9 [Ar C-3(5)], 125.0 [$^3J_{\text{P-C}}$ 5.5, Ar C-2(6)], 130.9 (Ar C-1), 158.2 (Ar C-4) [Calc. for $\text{C}_{19}\text{H}_{32}\text{BF}_4\text{N}_4\text{OP}$ (M: 450.20): C, 50.68; H, 7.16; N, 12.40. Found: C, 50.58; H, 7.51; N, 12.12%].

10-HPF₆. **10-HBF₄** 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-8 μ 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-HPF₆** 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, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.4, NCH_2CH_2), 3.8 (3H, br s, OCH_3), 6.1 (1H, br d, $^2J_{\text{P-H}}$ 11.4, NH), 6.9 [2H, br d, $^3J_{\text{H-H}}$ 9, Ar 3(5)-H], 7.0 [2H, br d, $^3J_{\text{H-H}}$ 9, Ar 2(6)-H]; δ_{C} 26.8 ($^3J_{\text{P-C}}$ 8.5, NCH_2CH_2), 48.3 ($^2J_{\text{P-C}}$ 4.8, NCH_2CH_2), 56.3 (OCH_3), 115.9 [Ar C-3(5)], 125.2 [$^3J_{\text{P-C}}$ 5.5, Ar C-2(6)], 130.8 (Ar C-1), 158.3 (Ar C-4) [Calc. for $\text{C}_{19}\text{H}_{32}\text{F}_6\text{N}_4\text{OP}_2$ (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-HBF₄** 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, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 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 ($^3J_{\text{P-C}}$ 7.7, NCH_2CH_2), 47.6 ($^2J_{\text{P-C}}$ 4.9, NCH_2CH_2), 56.2 (OCH_3), 115.1 [Ar C-3(5)], 123.9 [$^3J_{\text{P-C}}$ 16.9, Ar C-2(6)], 147.0 ($^2J_{\text{P-C}}$ 2.8, Ar C-1), 151.8 (Ar C-4).

[4-(Dimethylamino)anilino]tripyrrolidinophosphonium perchlorate 11-HClO₄ (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 $\text{Et}_3\text{N}\cdot\text{HCl}$ 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 $\text{Et}_3\text{N}\cdot\text{HCl}$ 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 $\text{NaClO}_4\cdot\text{H}_2\text{O}$ in 50 ml of water was added to precipitate **11-HClO₄**. After recrystallization from aq. EtNH_2 , light pink crystals of **11-HClO₄** 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, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.5, NCH_2CH_2), 6.1 (1H, br d, $^2J_{\text{P-H}}$ 12.2, NH), 6.7 [2H, br d, $^3J_{\text{H-H}}$ 9, Ar 3(5)-H], 7.0 [2H, br d, $^3J_{\text{H-H}}$ 9, Ar 2(6)-H]; δ_{C} 26.8 ($^3J_{\text{P-C}}$ 8.5, NCH_2CH_2), 41.1 (NCH_3), 48.3 ($^2J_{\text{P-C}}$ 4.7, NCH_2CH_2), 114.6 [Ar C-3(5)], 125.7 [$^3J_{\text{P-C}}$ 5.1, Ar C-2(6)], 127.0 (Ar C-1), 149.6 (Ar C-4) [Calc. for $\text{C}_{20}\text{H}_{35}\text{ClN}_5\text{O}_4\text{P}$ (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-HBF₄** 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, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.8, NCH_2CH_2), 6.55 [4H, s, Ar 3(5)-H and Ar 2(6)-H]; δ_{C} 27.0 ($^3J_{\text{P-C}}$ 7.7, NCH_2CH_2), 42.7 (NCH_3), 47.6 ($^2J_{\text{P-C}}$ 3.5, NCH_2CH_2), 116.5 [Ar C-3(5)], 123.9 [$^3J_{\text{P-C}}$ 16.8, Ar C-2(6)], 143.8 (Ar C-4), 145.0 ($^2J_{\text{P-C}}$ 2.8, Ar C-1).

Hydrazinotripyrrolidinophosphonium hexafluorophosphate 12-HPF₆ (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 $\text{Et}_3\text{N}\cdot\text{HCl}$ 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 $\text{H}_2\text{NNH}_2\cdot\text{HCl}$ containing some $\text{Et}_3\text{N}\cdot\text{HCl}$ 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-HPF₆**. 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, $^3J_{\text{H-H}}$ 6.6, $^3J_{\text{P-H}}$ 3.9, NCH_2CH_2), 3.6 (2H, d, $^3J_{\text{P-H}}$ 10.1, NHNH_2), 5.4 (1H, d, $^2J_{\text{P-H}}$ 33.6, NHNH_2); δ_{C} 26.9 ($^3J_{\text{P-C}}$ 8.1, NCH_2CH_2), 48.0 ($^2J_{\text{P-C}}$ 4.2, NCH_2CH_2) [Calc. for $\text{C}_{12}\text{H}_{27}\text{F}_6\text{N}_5\text{P}_2$ (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-HPF₆. 0.3 g of $\text{C}_6\text{H}_5\text{N}=\text{P}(\text{NMe}_2)_3$ **16** were dissolved in

1.5 ml of 70% aq. EtNH₂ and 1.4 ml of 30% HPF₆ 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**·HPF₆. 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-H} 10.1, NCH₃), 7.06 [2H, d, ³J_{H-H} 8.2, Ar 2(6)-H], 7.16 (1H, t, ³J_{H-H} 7.6, Ar 4-H), 7.37 [2H, t, ³J_{H-H(av)} 7.9, Ar 3(5)-H]; δ_C 37.6 (²J_{P-C} 4.9, NCH₃), 122.3 [³J_{P-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 C₁₂H₂₄F₆N₄P₂ (M: 400.28): C, 36.01; H, 6.04; N, 13.99. Found: C, 36.10; H, 6.06; N, 13.60%].

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