Acid−Base Equilibria in Nonpolar Media. 2.[1] Self-Consistent Basicity Scale in THF Solution Ranging from 2-Methoxypyridine to EtP_1(pyrr) Phosphazene

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Relative ion-pair basicities ΔpK_{ip} of 25 substituted aryl and alkyl iminophosphoranes (phosphazenes) and 20 other N-bases (various pyridines, amines, amidines) have been measured in THF medium using the UV−Vis and/or ^{13}C NMR methods. The ΔpK_{ip} values were corrected for ion pairing using the Fuoss equation to obtain relative ionic basicities ΔpK_{α}. Based on the measurements, a basicity scale ranging from 2-methoxypyridine to EtP_1(pyrr) and having a total span over 18 pK units has been created. The scale has been anchored to the pK_{α} value of triethylamine (pK_{α} = 12.5). The results are compared to pK_a values in various other solvents and in the gas phase. The pK_{α} values give better correlations than the pK_{ip} values, thus indirectly validating the procedure of correction for ion pairing. The predictability of the basicity together with suitable spectral properties in the UV range make the phenylphosphazenes convenient neutral indicators in the high basicity range where the choice of neutral indicators is very limited.

Introduction

Numerous acidity studies, mostly focused on CH-acids, have been carried out in THF.[2,3,4] Alkali metal amides or carbanions with alkali metal counterions have mostly been used as deprotonating agents. On the basis of these measurements, ion-pair acidity scales have been developed relative to 9-phenylfluorene or fluorene.[2,3,4] Those scales have been anchored to the pK_a values of these reference compounds in aqueous sulfolane and DMSO, respectively. This approach has also been used in constructing acidity scales in various other nonpolar media—cyclohexylamine,[5] benzene,[6,7] dimethoxyethane,[8] diethyl ether,[9] etc.

Contrary to acidity measurements, studies on basicity in THF are scarce. Recently, the Morris group compiled an acidity scale in THF based on NMR measurements including numerous metal hydrides, phosphines, etc.[10] The observed pK_{ip} values were corrected for ion-pairing using the Fuoss equation.[11] Besides the phosphines the pK_{ip} values for a number of other organic compounds were established and the pK_{α} (here and henceforth the term "pK_a of the base" is understood as the acidity of conjugate acid of the base, and its definition is given in eq 1) value 12.5 of triethylamine was suggested as the secondary standard for anchoring acidity and basicity scales in THF.[10]

In nonpolar media the measured equilibrium constants do not generally reflect the free ion acidity but rather refer to ion pairs. An attempt to suppress the interactions between cations and anions of the CH-acids in nonpolar media was made by the Konovalov group.[12,2] They have used lithium [2.1.1]cryptate as the counterion for the anions of CH-acids. In this cryptate the [2.1.1]cryptand acts as a layer of solvent molecules separating the ions and so eliminating the specific interactions. In a previous work by some of us phosphazene *t*-BuP_4(dma) (here and henceforth "dma" denotes dimethylamino ($N(CH_3)_2$) and "pyrr" denotes 1-pyrrolidinyl ($N(CH_2\,CH_2)_2$) radical) was used as the deprotonating agent to create an acidity scale in *n*-heptane.[1] Protonated *t*-BuP_4(dma) is a large cation with a delocalized charge and has very weak interaction with anions.

We have found earlier that aryl-substituted P_1 phosphazenes $ArN{=}P(R)_3$, where R = dma or pyrr, are suitable indicators together with amines to compile a basicity scale in acetonitrile (AN).[13,14]

In this paper we report a basicity scale in THF medium that incorporates aryl and alkyl P_1 phosphazenes

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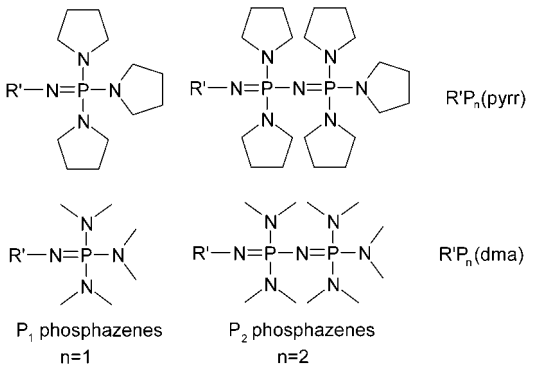
Scheme 1



R′N═P(R)$_3$ (see Scheme 1), some aryl P$_2$ phosphazenes R′N═P(R)$_2$N═P(R)$_3$, various substituted pyridines, and several other bases.

For a better comparison with the THF data and as a further extension of the earlier established basicity scale in AN, some additional pK_a values for several bases were also measured in the latter solvent.

In a polar solvent S (water, AN, etc.) at low or moderate concentrations the basicity of base B is defined using eq 1 and is expressed as dissociation constant K_a (eq 2) of the respective conjugate acid HB^+ of the base B or, more commonly, its negative logarithm pK_a

$$HB^+ + S \overset{K_a}{\rightleftharpoons} B + HS^+ \quad (1)$$

$$K_a = \frac{a(B)a(HS^+)}{a(HB^+)} \quad (2)$$

In media of low polarity ($D \leq 15-20$)[15] there is an extensive ion-pairing and formation of aggregates between ions and neutral molecules (homo- and heteroconjugation) that has to be considered. The extent of ion-pairing depends on the solvent, the size of the ions, and the charge distribution in ions. The general trend is that small ions tend to form solvent-separated ion-pairs (SSIP) (eq 3) while large ions with delocalized charge tend to form contact ion-pairs (CIP) (eq 4).

$$HB^+ + A^- \rightleftarrows HB^+_s \cdot A^-_s \quad (3)$$

$$HB^+ + A^- \rightleftarrows [HBA]_s \quad (4)$$

In media of low polarity the homo- and heteroconjugation processes (eqs 5 and 6, respectively) occur to a much lower extent as compared to ion-pairing. At a low concentration these conjugation processes between ions and neutrals can be neglected because most of the ions present in the solution are ion-paired.

$$HB^+ + B \rightleftarrows BHB^+ \quad (5)$$

$$HB^+ + B_1 \rightleftarrows BHB_1^+ \quad (6)$$

To exclude the necessity for measuring the hydrogen ion activity (see eq 2), the equilibrium between two (ion-paired) bases B_1 and B_2 was studied:

$$B_2 + HB_1^+A^- \overset{K_d^{HB_1^+A^-}}{\rightleftharpoons} B_2 + HB_1^+ + A^- \overset{K}{\rightleftharpoons} HB_2^+ + B_1 + A^- \overset{1/K_d^{HB_2^+A^-}}{\rightleftharpoons} HB_2^+A^- + B_1 \quad (7)$$

The K_d are the dissociation constants of the respective ion pairs. The directly measured quantity is the relative ion-pair basicity, ΔpK_{ip}, of bases B_1 and B_2. It is expressed as follows:

$$\Delta pK_{ip} = pK_{ip}(HB_2^+A^-) - pK_{ip}(HB_1^+A^-) = \log \frac{KK_d^{HB_1^+A^-}}{K_d^{HB_2^+A^-}} = \log \frac{a(HB_2^+A^-)a(B_1)}{a(HB_1^+A^-)a(B_2)} \quad (8)$$

If the K_d values can be measured or estimated then the pK_α (an estimate of the pK_a) can be found as follows:

$$\Delta pK_\alpha = pK_\alpha(HB_2^+) - pK_\alpha(HB_1^+) = \Delta pK_{ip} - \log \frac{K_d^{HB_1^+A^-}}{K_d^{HB_2^+A^-}} \quad (9)$$

Experimental Section

Chemicals. Most of the compounds were the same as used earlier.[13,14] The following compounds were of commercial origin and were used without further purification: TMG (Aldrich, 99%), 1,8-bisdimethylaminonaphthalene (DMAN) (Aldrich, >99%), *tert*-butylimino-tris(dimethylamino)phosphorane (*t*-BuP_1(dma)) base (Fluka, >98%), *tert*-butylimino-tris(pyrrolidino)phosphorane (*t*-BuP_1(pyrr)) base (Fluka, ≥98%), and all substituted anilines (Aldrich) used for synthesis of new phosphazenes. Aniline (Reakhim) was purified by refluxing with acetone and following recrystallization of HCl salt.[16] *N*,*N*-Dimethylaniline (Reakhim) was purified by refluxing with acetic anhydride and following recrystallization of HCl salt.[16] *o*-Toluidine (Reakhim) was distilled twice, the second time from CaH_2. Pyrrolidine (Merck or Fluka, >98%) was distilled from NaOH and was kept over NaOH. 2-Methoxypyridine (Aldrich, 98%) was distilled fractionally from $MgSO_4$ under reduced pressure.

Solutions of trifluoromethanesulfonic acid (TfOH) (Aldrich, 99+%) or methanesulfonic acid ($MeSO_3H$) (Fluka, >99%) were used as acidic titrants. Phosphazene bases EtP_1(pyrr)[17] or EtP_2-(dma) (Fluka, >98%) were used as basic titrants.

Solvents. THF was used as purchased (Romil, >99.9%, Super Purity Solvent, water content <0.005%) or purified (REAKHIM, pure) as follows:[16] THF was kept on KOH pellets and then boiled 2−2.5 h on CaH_2 in the flow of dried Ar. After that, THF was distilled through the 60 cm long column filled with steel rings, and the fraction with bp 66.2−66.5 °C was collected. To this distillate was added $LiAlH_4$, and then it was boiled with same column for 1 h under Ar and then distilled fractionally, fraction with bp 66.2−66.3 °C was collected. For syntheses was used THF stored over KOH and distilled from $LiAlH_4$. CCl_4 was distilled from P_2O_5, benzene from $LiAlH_4$ (all Reakhim).

We observed that ~0.2 M TfOH polymerizes THF within a few hours, and in dilute solutions the active concentration of this acid was lower than analytical concentration. Also we observed that with some batches of THF the absorbance below 280 nm decreased upon addition of TfOH.

AN (Romil, >99.9%, Super Purity Solvent (far UV), water content <0.005%) was the same used in previous work[14] and was used without further purification.

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General Method for the Synthesis of the P_1 Phosphazenes. New phenyl-substituted P_1 phosphazenes (s-PhP$_1$(pyrr)) were synthesized by the Kirsanov reaction[18] according to the scheme:

$$\text{s-PhNH}_2 + \text{PCl}_5 \xrightarrow[\text{CCl}_4]{} \text{s-PhN=PCl}_3 \xrightarrow[\text{Bz or THF}]{\text{PyrrH}} \text{s-PhP}_1\text{(pyrr)} \quad (10)$$

An amount of 20 mmol of the corresponding aniline was dissolved in 20 mL of CCl_4, and 20 mmol of PCl_5 was added (in some cases it was necessary to cool the mixture in the beginning of the reaction). The mixture was warmed and refluxed until the evolution of HCl finished. Insoluble in CCl_4, trichlorophosphazenes were filtered off and washed successively with CCl_4, benzene, and diethyl ether. When the trichlorophosphazene was soluble in CCl_4, the solvent was removed on a rotavapor, and the residue was dried in vacuo.

An amount of 15 mmol of obtained phenylimino trichlorophosphazene was dissolved in 40 mL of dried THF (in the case of 2-NO_2-4-CF_3 and 5-Cl-2-NO_2 substituents, 50 mL of dry benzene was used instead), and 90 mmol of pyrrolidine (solution in 15 mL of THF) was added by means of a dropping funnel. The mixture was heated to 50 °C and stirred ca. 1 h. Then the mixture was cooled to +5 °C, the HCl salt of pyrrolidine was filtered off, and the solvent was removed at reduced pressure (60 °C/5 Torr). The brown residue was washed with 70% aqueous solution of $EtNH_2$. The crystals of the product were collected, washed with 40% aqueous $EtNH_2$ solution, dried in vacuo, and recrystallized (2-NO_2-4-CF_3-$C_6H_3P_1$(pyrr) was isolated as HBF_4 salt).

4-CF_3-$C_6H_4P_1$(pyrr). According to the general method, after recrystallization from 70% $EtNH_2$ aq soln, 1.9 g of colorless crystals was obtained, yield 32%, mp 102.4−103.3 °C. Anal. Calcd for $C_{19}H_{28}F_3N_4P$: C, 56.99%; H, 7.07%; N 13.99%. Found: C, 57.18%; H, 7.12%; N, 14.01%. ^{1}H NMR (200 MHz, CD_3Cl) δ 1.83 (m, 12H), 3.19 (dt, 12H, $J_{H-H} = 6.6$, $J_{P-H} = 3.4$), 6.78 (d, 2H, $J_{H-H} = 8.5$), 7.27 (d, 2H, $J_{H-H} = 8.5$). ^{13}C NMR (50 MHz, CD_3Cl) δ 26.4 (d, $J_{C-P} = 8.0$), 46.9 (d, $J_{C-P} = 4.0$), 117.3 (q, $J_{C-F} = 32.3$), 122.2 (d, $J_{C-P} = 18.2$), 125.72 (d, $J_{C-P} = 2.7$), 125.74 (q, $J_{C-F} = 270.3$), 155.7.

5-Cl-2-NO_2-$C_6H_3P_1$(pyrr). According to the general method, after recrystallization from 70% $EtNH_2$ aq soln, 4.5 g of yellowish crystals was obtained, yield 73%, mp 82.7−83.2 °C. Anal. Calcd for $C_{18}H_{27}ClN_5O_2P$: C, 52.49%; H, 6.61%; N, 17.0%. Found: C, 52.47%; H, 6.59%; N, 16.80%. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 12H), 3.19 (dt, 12H, $J_{H-H} = 6.7$, $J_{P-H} = 4.2$), 6.42 (dd, 1H, $J_{H-H} = 8.6$, 2.2), 6.77 (dd, 1H, $J_{H-H} = 2.2$, $J_{P-H} = 1.0$), 7.42 (dd, 1H, $J_{H-H} = 8.6$, $J_{P-H} = 2.4$). ^{13}C NMR (50 MHz, THF) δ 27.0 (d, $J_{C-P} = 7.7$), 47.6 (d, $J_{C-P} = 3.7$), 114.34, 124.2 (d, $J_{C-P} = 9.4$), 126.0, 137.4, 144.2 (d, $J_{C-P} = 24.3$), 147.9 (d, $J_{C-P} = 7.4$).

2-NO_2-4-CF_3-$C_6H_3P_1$(pyrr). The raw product (4.9 g) synthesized according to the general method was dissolved in 40 mL of 5% aq HCl, and the solution of 1.3 g of $NaBF_4$ in water was added. The precipitate was filtered, dried, and recrystallized from ethyl acetate. A 3.3 g (6.2 mmol) amount of light yellow crystals of the HBF_4 salt of the phosphazene (mp 186−187 °C) was dissolved in the mixture of 8 mL MeOH and 12 mL AN. A 6.2 mmol amount of MeOK as 25% solution in MeOH was added. The solvent was removed, and the residue was refluxed with hexane for 0.5 h. The mixture was filtered, and the hexane was removed under the reduced pressure. The brownish solid residue was recrystallized from 70% $EtNH_2$ aq soln to give 2.0 g (yield 72.5%, mp 70.5−71.2 °C) of light yellow crystals of the product. Anal. Calcd for $C_{19}H_{21}F_3N_5O_2P$: C, 51.23%; H, 6.11%; N, 15.72%. Found: C, 51.42%; H, 6.12%; N, 15.66%. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 12H), 3.20 (dt, 12H, $J_{H-H} = 6.7$, $J_{P-H} = 4.2$), 6.90 (d, 1H, $J_{H-H} = 8.8$), 7.29 (dd, 1H, $J_{H-H} = 8.8$, 2.5, $J_{P-H} = 0.6$), 7.72 (br m, 1H, $J_{H-H} = 2.5$). ^{13}C NMR (50 MHz, THF) δ 27.1 (d, $J_{C-P} = 7.7$), 47.6 (d, $J_{C-P} = 4.0$), 115.5 (q, $J_{C-F} = 33.8$), 122.4 (br m), 125.0 (d, $J_{C-P} = 9.2$), 125.7 (q, $J_{C-F} = 270.2$), 128.2 (m), 144.9 (d, $J_{C-P} = 26.3$), 150.0 (d, $J_{C-P} = 7.8$).

2,6-Cl_2-4-NO_2-$C_6H_2P_1$(pyrr). According to the general method, 4.2 g (yield 63,2%, mp 95.3−96.9 °C, recrystallized from 70% $EtNH_2$ aqueous solution or from hexane) of yellow crystals was obtained. Anal. Calcd for $C_{18}H_{26}Cl_2N_5O_2P$: C, 48.77%; H, 5.91%; N, 15.8%. Found: C, 48.37%; H, 5.87%; N, 15.80%. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.82 (m, 12H), 3.21 (dt, 12H, $J_{H-H} = 6.6$, $J_{P-H} = 3.4$), 8.13 (d, $J_{P-H} = 1.2$). ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.4 (d, $J_{C-P} = 8.6$), 47.0 (d, $J_{C-P} = 5.0$), 124.0, 128.2 (d, $J_{C-P} = 9.0$), 136.1, 151.4 (d, $J_{C-P} = 11.7$).

2,6-(NO_2)$_2$-$C_6H_3P_1$(pyrr). According to the general method, 3.6 g (yield 57%, mp 132.5−132.8 °C, recrystallized from 3:1 mixture MeOH−$CHCl_3$) of orange crystals was obtained. Anal. Calcd for $C_{18}H_{27}N_6O_4P$: C, 51.17%; H, 6.44%; N, 19.89%. Found: C, 50.77%; H, 6.36%; N, 19.89%. ^{1}H NMR (200 MHz, CD_3Cl) δ 1.81 (m, 12H), 3.09 (dt, 12H, $J_{H-H} = 6.6$, $J_{P-H} = 3.0$), 6.59 (dt, 1H, $J_{H-H} = 8.0$, $J_{P-H} = 1.3$), 7.56 (dd, 2H, $J_{H-H} = 8.0$, $J_{P-H} = 1.2$). ^{13}C NMR (50 MHz, CD_3Cl) δ 26.4 (d, $J_{C-P} = 8.7$), 46.6 (d, $J_{C-P} = 5.1$), 113.4, 126.6, 137.6 (d, $J_{C-P} = 12.8$), 148.1 (d, $J_{C-P} = 7.7$).

2,5-Cl_2-$C_6H_3P_1$(pyrr).[13] ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 12H), 3.05 (dt, 12H, $J_{H-H} = 6.7$, $J_{P-H} = 4.3$), 6.37 (ddd, 1H, $J_{H-H} = 8.4$, 2.5, $J_{P-H} = 0.5$), 6.68 (dd, 1H, $J_{H-H} = 2.5$, $J_{P-H} = 1.2$), 7.05 (dd, 1H, $J_{H-H} = 8.4$, $J_{P-H} = 2.5$). ^{13}C NMR (50 MHz, THF) δ 27.0 (d, $J_{C-P} = 7.5$), 47.6 (d, $J_{C-P} = 3.7$), 115.9, 122.3 (d, $J_{C-P} = 8.3$), 127.3 (d, $J_{C-P} = 26.4$), 130.1 (d, $J_{C-P} = 1.5$), 132.2, 150.5 (d, $J_{C-P} = 5.8$).

Synthesis of $HBPh_4$ Salts of the P_2 Phosphazenes. 2-Cl-$C_6H_4P_2$(pyrr)·$HBPh_4$. In three-necked flask, equipped with magnetic stirrer, powder adding system, and rubber gas balloon with Ar, of 15 mL (140 mmol) of 2-chloroaniline was added 0.28 g (12 mmol) of NaH. The mixture was heated slowly to 60 °C. After the evolution of H_2 was ceased, the mixture was stirred and cooled to room temperature, and 2.6 g (4.7 mmol) Cl-P(pyrr)$_2$=N-P$^+$(pyrr)$_3$·BF_4^- was added gradually by means of powder adding system.[19] The mixture was heated again to 60 °C, held at that for 6 h, and then left for 2 days. The excess of chloroaniline was removed under reduced pressure (110 °C/6 mmHg). To the residue dissolved in CH_2Cl_2 was added some water, and the CH_2Cl_2 extract of product HBF_4 salt was washed with acidified water to remove the rest of chloroaniline. The CH_2Cl_2 was removed in vacuo, the residue, 0.8 g of dark oil, was dissolved in 10 mL MeOH, treated with charcoal, and product was precipitated as $HBPh_4$ salt by adding 0.43 g of $NaBPh_4$ solution in 1.5 mL of MeOH. It was filtered and recrystallized from a 1:1 mixture of EtOH and AN. Yield 0.2 g (18%, mp 155.0−156.1 °C) of nearly colorless crystals. Anal. Calcd for $C_{50}H_{65}BClN_7P_2$: C, 68.84%; H, 7.51%; N, 11.24%. Found: C, 68.82%; H, 7.71%; N, 11.20%. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 20H), 2.95 (dt, 12H, $J_{H-H} = 6.6$, $J_{P-H} = 3.6$), 3.22 (m, 8H), 6.34 (br d, 1H, $J_{P-H} = 11.4$), 6.69 (t, 4H, $J_{H-H} = 7.2$), 6.84 (t, 8H, $J_{H-H(av)} = 7.4$), 7.0 (m, 2H), 7.19 (d, 1H, $J_{H-H} = 4.5$), 7.26 (m, 8H), 7.39 (d, 1H, $J_{H-H} = 4.5$). ^{13}C NMR (50 MHz, THF) δ 26.9 (d, $J_{C-P} = 9.0$), 27.1 (d, $J_{C-P} = 9.4$), 47.5 (d, $J_{C-P} = 5.2$), 47.9 (d, $J_{C-P} = 5.7$), 121.7, 121.8 (d, $J_{C-P} = 2.9$), 124.8, 125.6 (m, $J_{C-B} = 2.9$), 128.5, 130.5, 130.6 (d, $J_{C-P} = 5.0$) 137.2 (m, $J_{C-B} = 1.5$), 137.5 (d, $J_{C-P} = 2.7$), 165.3 (m, $J_{C-B} = 49.9$).

PhP_2(dma)·$HBPh_4$. The same procedure was used as for 2-Cl−$C_6H_4P_2$(pyrr)·$HBPh_4$. To 15 mL of aniline (distilled from Zn-dust) was added 15.2 mmol of NaH, and the mixture was heated for a short time. At room temperature 7.6 mmol (5.2 g) of ClP(dma)$_2$=N−P$^+$(dma)$_3$·BPh_4^- (made from BF_4^- salt[19]) was added. The excess of aniline was washed out with acidified water and the residue extracted with warm 70% $EtNH_2$ aq soln. By diluting this extract with water, a brownish precipitate of desired (raw) product as a $HBPh_4$ salt was collected. The recrystallization from 70% $EtNH_2$ aq soln and finally from

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ethyl acetate gave 1.0 g of crystals with gentle violet tint (yield 18.8%, mp 135.2−136.3 °C). Anal. Calcd for $C_{40}H_{56}BN_7P_2$: C, 67.89%; H, 7.99%; N, 13.85%. Found: C, 67.30%; H, 8.07%; N, 13.87%. ^{1}H NMR (200 MHz, THF) δ 2.41 (d, 18H, J_{P-H} = 10.2), 2.63 (d, 12H, J_{P-H} = 10.8), 6.70 (t, 4H, J_{H-H} = 7.2), 6.85 (t, 8H, $J_{H-H(av)}$ = 7.4), 6.9−7.0 (m, 3H), 7.2 (m, 2H), 7.28 (m, 8H). ^{13}C NMR (50 MHz, THF) δ 36.9 (d, J_{C-P} = 5.2), 119.9 (d, J_{C-P} = 7.1), 121.7, 123.2, 125.6 (m, J_{C-B} = 2.8), 130.0, 137.2, 140.8, 165.2 (m, J_{C-B} = 49.5).

$PhP_2(pyrr)\cdot HBPh_4$. The same procedure was used as for 2-Cl−$C_6H_4P_2$(pyrr)·$HBPh_4$, except that NaH was not used. To 5 mL of aniline 5 mmol (2.4 g) of $ClP(pyrr)_2{=}N{-}P^+(pyrr)_3\cdot BF_4^-$ was added,[19] and the mixture was stirred and heated at 150 °C for 20 h. Then aniline was removed under the reduced pressure. The residue was extracted with 10 mL of CH_2Cl_2, and the extract was washed twice with water and acidified water, respectively. The extract was concentrated, and a dark sticky residue (1.9 g) was dissolved in 8 mL of MeOH. The solution was filtered, and a solution of 1.22 g (3.5 mmol) of $NaBPh_4$ in 3.5 mL MeOH was added. Collected violet crystals of product were recrystallized from 70% $EtNH_2$ aq soln as described in ref 19 or from 4:1 mixture of MeOH/$CHCl_3$. A 1.8 g (yield 44%, mp 179.2−180.2 °C) amount of crystals with beige tint was obtained. Anal. Calcd for $C_{50}H_{66}BN_7P_2$: C, 71.67%; H, 7.94%; N, 11.70%. Found: C, 71.64%; H, 7.90%; N, 11.64%. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 20H), 2.99 (dt, 12H, J_{H-H} = 6.6, J_{P-H} = 3.6), 6.68 (t, 4H, J_{H-H} = 7.2), 6.83 (t, 8H, $J_{H-H(av)}$ = 7.5), 6.9−7.0 (m, 3H), 7.19 (d, 2H, J_{H-H} = 7.6), 7.25 (m, 8H). ^{13}C NMR (50 MHz, THF) δ 27.0 (d, J_{C-P} = 8.6), 27.1 (d, J_{C-P} = 9.2), 47.5 (d, J_{C-P} = 5.2), 47.7 (d, J_{C-P} = 5.8) 119.8 (d, J_{C-P} = 7.2), 121.6, 123.0, 125.6 (m, J_{C-B} = 2.8), 129.9, 137.2 (br m), 141.2, 165.3 (m, J_{C-B} = 49.5).

4-MeO-$C_6H_4P_2$(pyrr)·$HBPh_4$. 5 mmol (0.61 g) of anisidine, 5 mmol (2.75 g) of $Cl{-}P(pyrr)_2{=}N{-}P^+(pyrr)_3\cdot BF_4^-$ and 5 mmol (0.5 g) of Et_3N were mixed in a 20 mL solution of THF/AN (1:2) at room temperature. The mixture was refluxed for 20 h. The solvent was removed under reduced pressure, and the residue, 2.2 g of viscous oil, was dissolved in 10 mL of AN. A 1.7 g amount of $NaBPh_4$ in 5 mL of MeOH was added. An oily substance separated. The solution was decanted from the oily substance, and the substance was twice extracted with 40 mL of hot MeOH. The crystals collected from the methanolic solutions were recrystallized from 1:4:9 mixture of water−AN−MeOH. Yield 0.7 g (16%, mp 165.0−166.4 °C) of colorless crystals. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 20H), 2.98 (dt, 12H, J_{H-H} = 6.5, J_{P-H} = 3.6), 3.7 (overlapped by solvent, 3H), 6.54 (d, 4H, J_{H-H} = 12.0), 6.68 (t, 4H, J_{H-H} = 7.2), 6.8 (br m, 12H,), 7.25 (m, 8H). ^{13}C NMR (50 MHz, THF) δ 27.0 (d, J_{C-P} = 8.6), 27.1 (d, J_{C-P} = 9.2), 47.5 (d, J_{C-P} = 5.0), 47.7 (d, J_{C-P} = 5.7), 55.7, 115.2, 121.7, 122.0 (d, J_{C-P} = 6.7), 125.6 (m, J_{C-B} = 2.8), 133.6, 137.2, 156.8, 165.3 (m, J_{C-B} = 49.5).

Liberation of P_2 Phosphazene Bases from Their HBPh_4 Salts with KOMe. The corresponding $HBPh_4$ salt was dissolved in a possibly small amount of dried MeOH, and a calculated (with light excess) amount of 25% KOMe solution in MeOH was added. The precipitated $KBPh_4$ was filtered off in a glovebox, and MeOH was removed under reduced pressure. The residue was extracted with hexane, the extract was filtered, and hexane was removed in vacuo. The free bases were used for spectrometric measurements.

2-Cl-$C_6H_4P_2$(pyrr): colorless crystals. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 20H), 3.12 (dt, 12H, J_{H-H} = 6.6, J_{P-H} = 4.2), 3.23 (m, 8H), 6.17 (ddd, 1H, J_{H-H} = 7.7, 6.8, 1.9), 6.71 (ddd, 1H, J_{H-H} = 8.1, 6.8, 1.7), 6.79 (ddd, 1H, J_{H-H} = 8.1, 1.9, J_{P-H} = 1.2), 7.01 (ddd, 1H, J_{H-H} = 7.7, 1.7, J_{P-H} = 2.6). ^{13}C NMR (50 MHz, THF) δ 27.1 (d, J_{C-P} = 8.2), 27.4 (d, J_{C-P} = 8.4), 47.4 (d, J_{C-P} = 4.6), 47.9 (d, J_{C-P} = 4.0), 113.8, 122.1 (d, J_{C-P} = 11.9), 126.5, 127.9 (d, J_{C-P} = 30.7), 129.4 (d, J_{C-P} = 2.7), 151.3 (d, J_{C-P} = 5.1).

PhP_2(dma): colorless crystals. ^{1}H NMR (200 MHz, THF) δ 2.55 (d, 18H, J_{P-H} = 10.1), 2.65 (d, 12H, J_{P-H} = 10.0), 6.27 (ddt, 1H, J_{H-H} = 7.1, 1.5, J_{P-H} = 1.2), 6.60 (br d, 2H,, J_{H-H} = 7.9), 6.82 (br t, 2H,, $J_{H-H(av)}$ = 7.5). ^{13}C NMR (50 MHz, THF) δ 37.3 (d, J_{C-P} = 4.4), 38.1 (d, J_{C-P} = 2.6), 114.3, 123.2 (d, J_{C-P} = 20.1), 128.4 (d, J_{C-P} = 1.7), 154.9.

PhP_2(pyrr): colorless needles. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 20H), 3.12 (dt, 20H, J_{H-H} = 6.7, J_{P-H} = 4.3), 6.58 (m, 2H, J_{H-H} = 8.3), 6.78 (m, 2H). ^{13}C NMR (50 MHz, THF) δ 27.1 (d, J_{C-P} = 8.1), 27.3 (d, J_{C-P} = 8.4), 47.4 (d, J_{C-P} = 4.7), 47.9 (d, J_{C-P} = 3.8), 113.9, 122.9 (d, J_{C-P} = 20.8), 128.3 (d, J_{C-P} = 1.9), 155.3.

Synthesis of $HBPh_4$ Salts of P_1 Phosphazenes and Amines. A methanolic solution of bases (10 mmol in 10 mL MeOH) was acidified with 15% HCl aq soln, and a slight excess of $NaBPh_4$ solution in small quantity of MeOH was added. Precipitate of the salt was filtered, washed several times with MeOH, recrystallized (except TBD) from a 4:1 mixture of MeOH and $CHCl_3$, and dried in vacuo.

$Et_3N\cdot HBPh_4$: mp 184−187 °C (dec); ^{1}H NMR (200 MHz, THF) δ 0.88 (t, 3H, J_{H-H} = 7.4) 2.53 (q, 2H, J_{H-H} = 7.4), 6.75 (t, 4H, J_{H-H} = 7.2), 6.89 (t, 8H, $J_{H-H(av)}$ = 7.4), 7.31 (m, 8H). ^{13}C NMR (50 MHz, THF) δ 9.3, 47.8, 122.0, 125.9 (m, J_{C-P} = 2.7), 137.1, 165.1 (m, J_{C-P} = 49.5).

2-Cl-$C_6H_4P_1$(dma)·$HBPh_4$: mp 162.0−163.3 °C. ^{1}H NMR (200 MHz, THF) δ 2.47 (d, 18H, J_{P-H} = 10.2), 6.72 (t, 4H, J_{H-H} = 7.2), 6.86 (t, 8H, $J_{H-H(av)}$ = 7.6), 7.10 (m, 1H), 7.2 (m, 2H) 7.28 (m, 8H), 7.47 (m, 1H). ^{13}C NMR (50 MHz, THF) δ 37.3 (d, J_{C-P} = 4.4), 121.9, 125.7 (m, J_{C-B} = 2.8), 128.7 (d, J_{C-P} = 2.0), 129.2 (d, J_{C-P} = 5.7), 131.3, 132.1 (d, J_{C-P} = 6.6), 134.3, 137.2, 165.1 (m, J_{C-B} = 49.5).

2,5-Cl_2-$C_6H_3P_1$(pyrr)·$HBPh_4$: mp 153.4−153.6 °C. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 12H), 3.06 (dt, 12H, J_{H-H} = 6.7, J_{P-H} = 3.7), 6.71 (t, 4H, J_{H-H} = 7.2), 6.86 (t, 8H, $J_{H-H(av)}$ = 7.4), 7.13 (dd, 1H, J_{H-H} = 2.4, J_{P-H} = 1.1), 7.22 (ddd, 1H, J_{H-H} = 8.6, 2.4, J_{P-H} = 0.9), 7.26 (m, 8H), 7.44 (dd, 1H, J_{H-H} = 8.6, J_{P-H} = 1.2). ^{13}C NMR (50 MHz, THF) δ 26.8 (d, J_{C-P} = 8.5), 48.4 (d, J_{C-P} = 4.7), 121.8, 125.6 (m, J_{C-B} = 2.9), 125.7 (overlapped by anions peak), 128.0, 128.7 (d, J_{C-P} = 8.0), 132.4, 134.1 (d, J_{C-P} = 1.7), 136.2, 137.1 (m, J_{C-B} = 1.4), 165.2 (m, J_{C-B} = 49.5).

***t*-BuP_1(dma)·$HBPh_4$**: mp 266−267 °C (dec). ^{1}H NMR (200 MHz, THF) δ 1.22 (d, 9H, J_{P-H} = 1.0), 2.50 (d, 18H, J_{P-H} = 10.0), 4.5 (br d, 1H, J_{P-H} = 9.7), 6.71 (t, 4H, J_{H-H} = 7.2), 6.86 (t, 8H, $J_{H-H(av)}$ = 7.4), 7.28 (m, 8H). ^{13}C NMR (50 MHz, THF) δ 31.5 (d, J_{C-P} = 4.6), 37.8 (d, J_{C-P} = 4.7), 53.2, 121.8, 125.7 (m, J_{C-B} = 2.8), 137.2, 165.2 (m, J_{C-B} = 49.5).

TBD·$HBPh_4$ (1,5,7-triazabicyclo[4.4.0]dec-5-enyltetraphenylborate): mp 240−241 °C (dec); ^{1}H NMR (200 MHz, DMSO-d_6) δ 1.81 (q, 4H, $J_{H-H(av)}$ = 5.9), 3.13 (t, 4H, J_{H-H} = 5.8), 3.18 (t, 4H, J_{H-H} = 6.0). ^{13}C NMR (50 MHz, DMSO-d_6) δ 20.2, 37.5, 46.2, 121.5, 125.3 (m, J_{C-B} = 2.7), 135.5 (m, J_{C-B} = 1.2), 150.6, 163.3 (m, J_{C-B} = 49.5).

***t*-BuP_1(pyrr)·$HBPh_4$**: mp 233−235 °C. ^{1}H NMR (200 MHz, THF) δ 1.24 (d, 9H, J_{P-H} = 0.8), δ 1.8 (overlapped by solvent, 12H), 3.05 (dt, 12H, J_{H-H} = 6.7, J_{P-H} = 3.7), 6.71 (t, 4H, J_{H-H} = 7.2), 6.85 (t, 8H, $J_{H-H(av)}$ = 7.4), 7.26 (m, 8H).^{13}C NMR (50 MHz, THF) δ 26.8 (d, J_{C-P} = 8.2), 31.7 (d, J_{C-P} = 4.5), 48.4 (d, J_{C-P} = 4.7), 53.2 (d, J_{C-P} = 0.8) 121.8, 125.7 (m, J_{C-B} = 2.8), 137.2, 165.2 (m, J_{C-B} = 49.5).

H_2NP_1(pyrr)·$HBPh_4$: mp 183.0−184.3 °C. ^{1}H NMR (200 MHz, THF) δ 1.8 (overlapped by solvent, 12H), 3.05 (dt, 12H, J_{H-H} = 6.6, J_{P-H} = 3.8), 3.35 (d, 2H, J_{P-H} = 10.4), 5.50 (d, 1H, J_{P-H} = 35.6), 6.73 (t, 4H, J_{H-H} = 7.2), 6.87 (t, 8H, J_{H-H} = 7.2), 7.28 (m, 8H). ^{13}C NMR (50 MHz, THF) δ 26.9 (d, J_{C-P} = 8.1), 47.9 (d, J_{C-P} = 4.0), 121.9, 125.8 (m, J_{C-B} = 2.8), 137.1, 165.2 (m, J_{C-B} = 49.7).

EtP_1(pyrr)·$HBPh_4$: ^{1}H NMR (200 MHz, THF) δ 1.08 (dt, 3H, J_{H-H} = 7.4, J_{P-H} = 1.2), δ 1.8 (overlapped by solvent, 12H), 2.82 (dq, 2H, J_{H-H} = 7.4, J_{P-H} = 9.0), 3.03 (dt, 12H, J_{H-H} = 6.7, J_{P-H} = 3.8), 6.71 (t, 4H, J_{H-H} = 7.2), 6.86 (t, 8H, $J_{H-H(av)}$ = 7.4), 7.26 (m, 8H). ^{13}C NMR (50 MHz, THF) δ 17.3 (d, J_{C-P} = 7.1), 26.9 (d, J_{C-P} = 8.0), 36.8, 48.0 (d, J_{C-P} = 4.6), 121.8, 125.7 (m, J_{C-B} = 2.8), 137.2, 165.2 (m, J_{C-B} = 49.5).

UV−Vis Spectrophotometric Determination of pK_a in AN and pK_{ip} in THF. The spectrophotometric titration method in THF and in AN media in the glovebox was similar to that used in the previous work.[14] Perkin-Elmer Lambda 2S or Lambda 40 spectrophotometer equipped with quartz fiber

Table 1. Ionic Radii Used for Correction for Ion Pairing

ion	ion-pair radius, Å[a]	ion	ion-pair radius, Å[a]
$RNH^+{=}PR'_3$; $RNH^+{=}PR''_3$	4	pyrrolidineH^+	2
$RNH^+{=}PR'_2N{=}PR'_3$	4.8	$DMANH^+$	3.2
$RNH^+{=}PR''_2N{=}PR''_3$	5.4	X-anilineH^+; X-pyridineH^+	2
$TBDH^+$	3	N,N-Me_2-anilineH^+	2.2
$DBUH^+$; $DABH^+$[b]	2.5	2,6-X_2-pyridineH^+	2.2
$TMGH^+$; $TEAH^+$	2.2	$CF_3SO_3^-$; $CH_3SO_3^-$	2.5
$PhTMGH^+$	2.7	BPh_4^-	4.4

[a] Ionic radii from literature (ref 10) were used when available. In cases when no literature data were available, the radii were estimated by PM3 calculations; R = alkyl or aryl; R′ = dma; R″ = pyrr; X = H or substituent. [b] DAB = 1,4-diaminobutane.

optic system, and an external sample compartment positioned into the glovebox was used. Two different gloveboxes were used. Earlier measurements were carried out in a Mecaplex glovebox in the atmosphere of nitrogen, continuously purified from water vapor, volatile acidic and basic impurities with molecular sieves, powdered P_2O_5, and KOH pellets. Later measurements were carried out in MBraun glovebox in the atmosphere of argon that was constantly circulated through a purification system containing molecular sieves and activated copper for removal of water vapor and oxygen, respectively. The residual concentrations of water and oxygen in the atmosphere of the glovebox during the measurements were constantly monitored and were generally below 1 ppm.

All solutions were prepared in glovebox and were made fresh daily. The concentrations of acidic titrants were from 1 to 3 mM, and basic titrants were from 0.5 to 5.5 mM. Higher concentrations (up to 0.36 and 0.025 M for methanesulfonic acid and EtP_1(pyrr), respectively) were made for studying relative ion-pair basicity dependence from concentrations in THF. The concentrations of studied bases were generally in mM range; higher concentrations (up to 0.23 M) were used for studying relative ion-pair basicity dependence from concentrations.

The phosphazene bases are more stable and convenient to handle if they are used as salts. Several counterions (BPh_4^-, PF_6^-, ClO_4^-) were used in the salts. From these, only salts with tetraphenylborate anion were soluble enough in THF.

Various disturbances were frequently observed with the tetraphenylborate anion both in UV−Vis (strange behavior of the spectra upon titration and the nonreversibility of the spectra upon back-titration, change of spectrum in time) and NMR measurements (change of spectrum in time, appearance of alien peaks). This could be due to the somewhat unstable nature of this anion. Therefore, we avoided this anion as counterion in UV−Vis spectrophotometric measurements and used free bases instead.

Calculation Methods for UV−Vis Spectrophotometric Measurements. The ΔpK_a calculation methods in AN are similar to those of the previous works.[1,20] The essence of the general calculation method is the following. When two partially protonated bases B_1 and B_2 are in the same solution, then the following equation holds for absorbance A at wavelength λ (1 cm path length):

$$A^\lambda = [HB_1^+]\epsilon^\lambda_{HB_1^+} + [B_1]\epsilon^\lambda_{B_1} + [HB_2^+]\epsilon^\lambda_{HB_2^+} + [B_2]\epsilon^\lambda_{B_2} \quad (11)$$

The molar absorptivities ϵ can be found separately from the spectra of the free bases and fully protonated bases. If we use concentrations, that are normalized to 1 then we may write: $[HB_1^+] = 1 - [B_1]$ and $[HB_2^+] = 1 - [B_2]$. After a mathematical transformation of eq 11 we get

$$\frac{A^\lambda - \epsilon^\lambda_{HB_1^+} - \epsilon^\lambda_{HB_2^+}}{(\epsilon^\lambda_{B_2} - \epsilon^\lambda_{HB_2^+})} = [B_1]\cdot\frac{(\epsilon^\lambda_{B_1} - \epsilon^\lambda_{HB_1^+})}{(\epsilon^\lambda_{B_2} - \epsilon^\lambda_{HB_2^+})} + [B_2] \quad (12)$$

If the spectra are recorded over a range of wavelengths then $[B_1]$ and $[B_2]$ can be found from eq 12 as the slope and intercept of a regression line. From the values of $[B_1]$ and $[B_2]$, the calculation of ΔpK_a of the bases is straightforward. In many cases (for example, when the bases have absorption maxima in different wavelength ranges) it was possible to use various simpler calculation procedures (see refs 1 and 20). The mixture of bases as well as both bases separately was titrated with an optically transparent acid and/or base, and the data for ΔpK_a calculations was obtained from UV−Vis spectra. From each titration experiment, the ΔpK_a was determined as the mean of 5−20 values.

In THF the general principle of the ΔpK calculations is the same. As UV−Vis spectrophotometry does not make any difference between free ions, solvent separated ion-pairs, and loosely bonded contact ion-pairs (these last two are the main forms of monocharged ions at concentration below 0.01 M in THF),[10] we get ΔpK_{ip}s instead of ΔpK_as. The ΔpK_{ip} values given in Table 2 are a mean of 5−23 measurements. The correction for ion pairing was calculated using the Fuoss equation as described in ref 10, and a ΔpK_α is then obtained. The ionic radii that were used are given in Table 1.

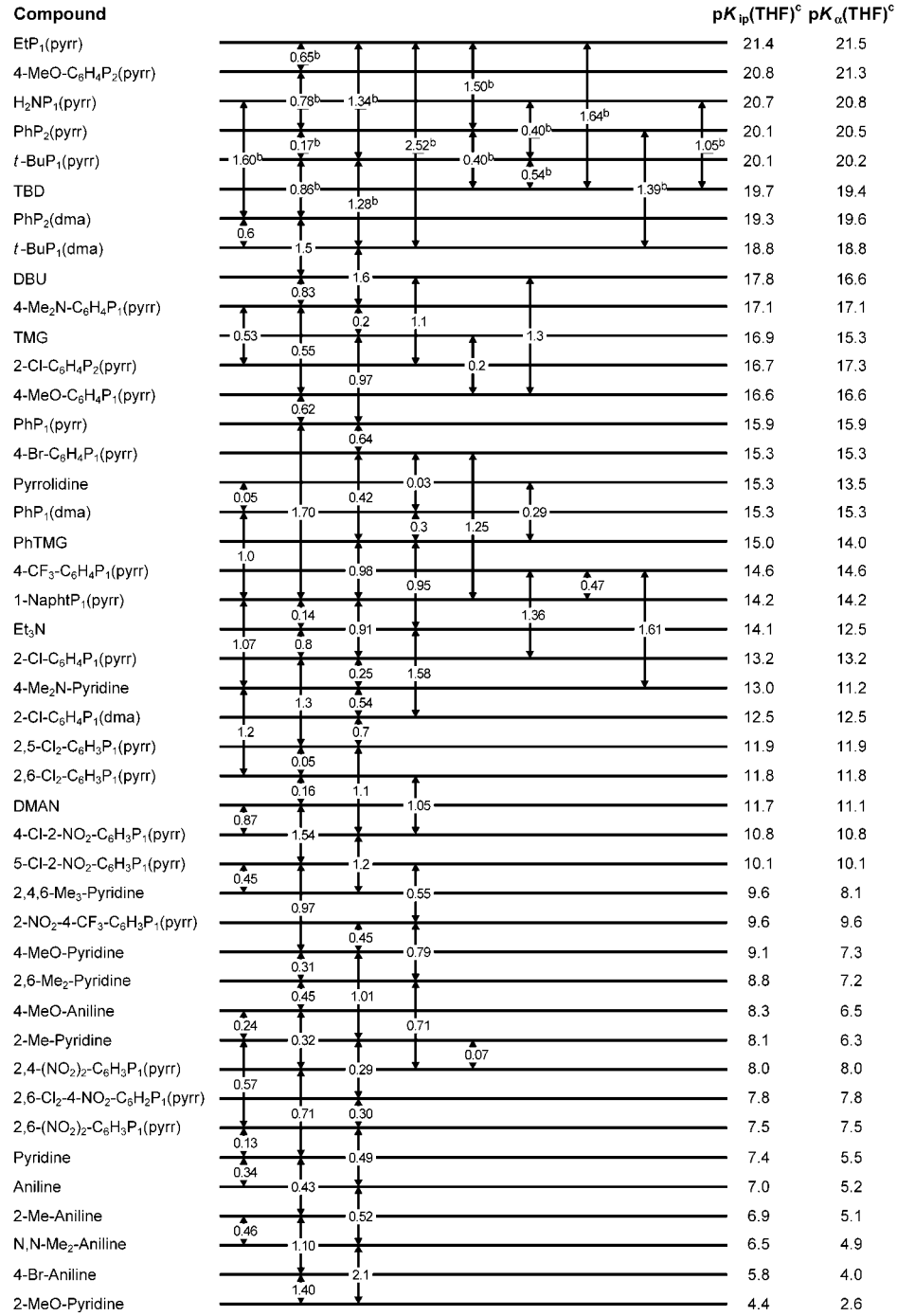
In some cases ("invisible bases", e.g., aliphatic amines (pyrrolidine and triethylamine) and t-BuP_1(dma), also DBU and TMG versus "visible" aromatic bases) the calculations have been carried out on a molar basis. The solution containing a mixture of known amounts (in moles) of "invisible" and visible base was titrated with titrant of known concentration. From the added titrant mass and its concentration, the amount (in moles) of titrant in the cell was found. Combining the spectra of solutions containing both bases fully deprotonated, fully protonated, and the mixture of protonated and deprotonated forms, we calculated the indicator ratio of the visible base, and knowing the amounts of the visible base and titrant added, we calculated the indicator ratio for "invisible" base. The ΔpK_{ip} calculation is then straightforward. The agreement between relative ion-pair basicities obtained with different calculation methods was satisfactory.

NMR pK_{ip} Determination. The standard 1D ^1H and proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AC-200 NMR spectrometer at 200 and 50 MHz, correspondingly. Solutions (∼ 0.1 M) were prepared and sealed off in 5 mm NMR tubes. Chemical shifts were determined relative to TMS as an internal standard.

The NMR spectra of phosphazenes and the method used for determination of their ΔpK_{ip} in THF were analogous to the corresponding NMR spectra and ΔpK_a calculations applied for phosphazenes in the AN.[13] There is no large difference of the ^{13}C and ^1H chemical shifts for phosphazenes in THF as compared to the corresponding shifts in AN. Usually, the differences were below 1 ppm for ^{13}C and 0.1 ppm for ^1H. The ΔpK_{ip}s of phosphazenes were determined using approximately equimolar mixture of phosphazene and indicator in THF. As it was in the case of AN solutions, there is the fast (in NMR time scale) exchange between phosphazene and indicator base and acid forms leading to the coalescence of NMR lines in the ^{13}C and ^1H spectra. Correspondingly, the chemical shifts of these forms were determined separately from the single component THF solutions of these species. The ΔpK_{ip} values were calculated as it was done previously with ΔpK_a values.[13] The indicator ratios for eq 8 were calculated (eqs 13 and 14) from chemical shifts of the individual species (both neutral and protonated forms of the bases) and their averaged values in the mixtures containing both forms.

(20) Leito, I.; Kaljurand, I.; Koppel, I. A.; Yagupolskii, L. M.; Vlasov, V. M. *J. Org. Chem.* **1998**, *63*, 7868−7874.

Table 2. Continuous Self-consistent Basicity Scale of Neutral Bases in THF Solution[a]



[a] The numbers on the arrows are the direct experimental ΔpK_{ip} values (uncorrected for ion pairing) obtained from UV−Vis spectrophotometric measurements if not indicated otherwise. [b] NMR measurements. [c] Absolute pK_{ip}(THF) and pK_{α}(THF) estimated values for conjugate acids of the respective bases.

$$\frac{a(HB_2^+A^-)}{a(B_2)} = \frac{\delta_{B_2} - \delta}{\delta - \delta_{HB_2^+A^-}} \qquad (13)$$

$$\frac{a(B_1)}{a(HB_1^+A^-)} = \frac{\delta - \delta_{B_1}}{\delta_{HB_1^+A^-} - \delta} \qquad (14)$$

In the case of alkylphosphazenes, the differences of the ^{13}C chemical shifts for alkyl substituent between phosphazene base and acid forms are markedly lower as compared to the corresponding differences of the arylic carbons of arylphosphazenes[13] and were in the range of 3−6 ppm for the ones measured.

Results

Altogether 96 individual acid−base equilibrium measurements in THF involving 45 bases were carried out using the UV−Vis spectrophotometric or ^{13}C NMR method. These measurements give a continuous basicity scale in THF as presented in Table 2, and some ^{13}C NMR results are given in Table 3.

Multiple overlapping measurements make the results more reliable and help to estimate their self-consistency. The entire basicity range covered involves at least two independent pathways of measurements and the relative basicity of any two bases can be obtained by combining

Table 3. ^{13}C NMR ΔpK_{ip}[a] Results Not Included in Table 2

base	reference base	ΔpK_{ip}
t-BuP$_1$(dma)	PhP$_2$(dma)	0.39
DBU	*t*-BuP$_1$(dma)	0.77
	2-Cl−C$_6$H$_4$P$_2$(pyrr)	0.00
	4-Me$_2$N-C$_6$H$_4$P$_1$(pyrr)	0.48
TMG	PhP$_1$(pyrr)	−1.11
DAB	2-Cl-C$_6$H$_4$P$_1$(pyrr)	−0.53
DMAP	2-Cl-C$_6$H$_4$P$_1$(dma)	0.38
	2,5-Cl$_2$-C$_6$H$_3$P$_1$(pyrr)	−0.45
Et$_3$N	2-Cl-C$_6$H$_4$P$_1$(dma)	0.87
	2,5-Cl$_2$-C$_6$H$_3$P$_1$(pyrr)	0.08
	4-Cl-2-NO$_2$-C$_6$H$_3$P$_1$(pyrr)	−0.94
DMAN	2,5-Cl$_2$-C$_6$H$_3$P$_1$(pyrr)	0.31
	Et$_3$N	0.25

[a] $\Delta pK_{ip} = pK_{ip(\text{conjugate acid of the reference base})} - pK_{ip(\text{conjugate acid of the base})}$.

at least two independent sets of measurements. Reversibility of protonation/deprotonation process of all bases was checked. All equilibria presented in Table 2 were reached in minutes and were stable. Both ion-pair (pK_{ip}) values and values corrected for ion pairing (pK_α) are given in Table 2. Although somewhat arbitrary, the correction for ion-pairing is useful because it makes our data comparable to the data by the Morris group.[10]

The absolute pK_α values have been obtained by anchoring the scale to the pK_α value of triethylamine in THF ($pK_\alpha = 12.5$),[10] a secondary standard proposed by the Morris' group. This is not a perfect choice, but is the most suitable anchoring point available for our data. See Discussion for additional comments.

It is not easy to find a suitable anchoring point for the ion-pair pK_{ip} values. The amount of available absolute pK_{ip} values of bases in THF is scarce. The data on acids is abundant but not directly comparable to pK_{ip} data of bases (see ref 21 for further discussion). Therefore the pK_{ip} values have been anchored to the pK_α value of PhP$_1$-(pyrr). This anchorage is arbitrary, but this way the core of the scale—the P$_1$ phosphazenes—have all practically the same values in both scales, which facilitates the discussion.

The absolute pK_α values were calculated as in the previous papers[14,20] by minimizing the sum of squares u of differences between directly measured ΔpK_α^i values and the assigned pK_α values while keeping the pK_α value of triethylamine constant and equal to 12.5.

$$u = \sum_{i=1}^{n_m} (\Delta pK_\alpha^i - (pK_\alpha(HB_2^+A^-) - pK_\alpha(HB_1^+A^-))) \quad (15)$$

It should be stressed that the absolute pK_α values of bases given in Table 2 are not as accurate as the relative pK_αs. One could anchor the scale to any other absolute pK_α value, and the relative basicities will remain the same. Precision s of the measurements was calculated as in the previous papers:[14,20]

$$s = \sqrt{\frac{u}{n_m - n_c}} \quad (16)$$

The number of measurements is $n_m = 83$; the number of pK_αs determined $n_c = 43$. For our results, $s = 0.10$ (for pK_{ip}, $s = 0.09$). Some previously published pK_a values in AN[14] (Table 4) have minor corrections (up to 0.03 pK_a units) due to the new measurements.

Table 4. Basicity Data of the Bases in AN, H$_2$O, and the Gas Phase

base	pK_a values in AN[a]	GB (kcal/mol)[b]	pK_a values in H$_2$O[c]
EtP$_1$(pyrr)	28.89[d]		
t-BuP$_1$(pyrr)	28.35[d]		
PhP$_2$(dma)	26.28		
TBD	25.96[e]	244.3	
t-BuP$_1$(dma)	26.88[d]		
2-Cl-C$_6$H$_4$P$_2$(pyrr)	25.24		
4-Me$_2$N-C$_6$H$_4$P$_1$(pyrr)	23.71		
DBU	24.16	239.6	
4-MeO-C$_6$H$_4$P$_1$(pyrr)	22.95		
PhP$_1$(pyrr)	22.17		
4-Br-C$_6$H$_4$P$_1$(pyrr)	21.05		
TMG	23.3[f]	238.4	13.6
PhP$_1$(dma)	21.07		
4-CF$_3$-C$_6$H$_4$P$_1$(pyrr)	19.93		
1-NaphtP$_1$(pyrr)	20.42		
PhTMG	20.63	236.9	12.18[g]
pyrrolidine	19.34	218.8	11.1
2-Cl-C$_6$H$_4$P$_1$(pyrr)	19.97		
2-Cl-C$_6$H$_4$P$_1$(dma)	18.87		
Et$_3$N	18.63	227	10.7
2,5-Cl$_2$-C$_6$H$_3$P$_1$(pyrr)	18.32		
2,6-Cl$_2$-C$_6$H$_3$P$_1$(pyrr)	18.36		
DMAP	17.75	232.1	9.53
DMAN	18.42	238.0	12.1[h]
4-Cl-2-NO$_2$-C$_6$H$_3$P$_1$(pyrr)	17.48		
5-Cl-2-NO$_2$-C$_6$H$_3$P$_1$(pyrr)	17.07		
2-NO$_2$-4-CF$_3$-C$_6$H$_3$P$_1$(pyrr)	16.33		
2,4,6-Me$_3$-pyridine	14.78		
2,4-(NO$_2$)$_2$-C$_6$H$_3$P$_1$(pyrr)	14.68		
2,6-Cl$_2$-4-NO$_2$-C$_6$H$_2$P$_1$(pyrr)	14.25		
2,6-(NO$_2$)$_2$-C$_6$H$_3$P$_1$(pyrr)	13.91		
4-MeO-pyridine	14.04	222.2	6.5
2,6-Me$_2$-pyridine	13.92	222.5	6.70
4-MeO-aniline	11.66	207.6	5.3
2-Me-pyridine	13.11	219.2	5.94
pyridine	12.33[i]	214.7	5.25
aniline	10.42	203.3	4.6
2-Me-aniline			4.4
N,*N*-Me$_2$-aniline	11.23	217.3	5.1
4-Br-aniline	9.25		3.9
2-MeO-pyridine			3.1

[a] Slightly revised pK_a values of conjugate acids of corresponding bases obtained in previous work (ref 14) or in this work if not noted otherwise. [b] Gas-phase basicities from ref 25. [c] pK_a values of conjugate acids of corresponding bases from refs 24 or 23 if not noted otherwise. [d] Reference 17. [e] Reference 26. [f] Reference 27. [g] Reference 28. [h] Reference 29. [i] Anchor of AN scale; value taken from ref 22.

Discussion

pK_α Values of Iminophosphoranes. Unsubstituted PhP$_1$(pyrr) is a strong base with basicity ($pK_\alpha = 15.9$) between those of TMG and DBU. By substitution of the phenyl ring, the basicity can be varied over a wide pK_α range. In this work the pK_α values of substituted PhP$_1$-(pyrr) range from 7.5 (2,6-dinitro-) to 17.1 (4-(dimethylamino)-), that is − by almost 10 orders of magnitude. The influence of substituents in the phenyl ring on the basicity of the phosphorane is easily predictable giving the possibility to conveniently "tune" the basicity of the phosphorane.

Alkyliminophosphoranes are significantly stronger bases than aryliminophosphoranes. Thus, EtP$_1$(pyrr) is by ca. 5.5 and *t*-BuP$_1$(pyrr) by ca. 4 orders of magnitude stronger than PhP$_1$(pyrr). The inductive effect and some delocalization of the lone electron pair of the imino

(21) Streitwieser, A.; Kim, Y.-J. *J. Am. Chem. Soc.* **2000**, *122*, 11783−11786.

nitrogen into the aromatic ring (see ref 14 for discussion on this topic) are most probably the reasons.

As can be expected, the P_2 phenyliminophosphoranes are stronger bases than the corresponding P_1 phenyliminophosphoranes. The difference is ca. 4−5 pK units. For alkyliminophosphoranes the same difference is ca. 6 pK units in acetonitrile.[19] We do not have data on P_2 alkyliminophosphoranes in THF, so direct comparison is not possible.

The relatively good predictability of the basicity together with suitable spectral properties in the UV range make the phenyliminophosphoranes convenient neutral indicators in the medium to high basicity range. The choice of neutral indicators in the high basicity range is currently very limited.

Comparison of Basicities in THF with Those in Other Media. Correlation of pK_{ip} and pK_α values in THF with pK_a values in acetonitrile yields the following equations: pK_{ip}(THF) = (−2.68 ± 0.55) + (0.83 ± 0.03)·pK_a(AN); n = 39; r^2 = 0.959; s = 0.89. pK_α(THF) = (−5.08 ± 0.39) + (0.92 ± 0.02)·pK_a(AN); n = 39; r^2 = 0.983; s = 0.63. Correlation of pK_{ip} and pK_α values in THF with pK_a values in water yields the following equations: pK_{ip}(THF) = (1.78 ± 0.64) + (1.08 ± 0.08)·pK_a(H_2O); n = 17; r^2 = 0.926; s = 1.05. pK_α(THF) = (−0.31 ± 0.49) + (1.14 ± 0.06)·pK_a(H_2O); n = 17; r^2 = 0.960; s = 0.80. Correlation of pK_{ip} and pK_α values in THF with gas-phase basicity pK_a values (pK_a(GB) = GB (kcal·mol^{-1})/1.364 (kcal·mol^{-1})) is poor and yields the following equations: pK_{ip}(THF) = (−53.29 ± 12.52) + (0.39 ± 0.08)·pK_a(GB); n = 15; r^2 = 0.676; s = 2.57. pK_α(THF) = (−61.34 ± 12.48) + (0.43 ± 0.08)·pK_a(GB); n = 15; r^2 = 0.718; s = 2.56.

From these correlations it appears that the differentiating ability of THF for basicities is between water and AN. One can see that the transfer of this reaction series from THF to AN increases slightly its sensitivity toward substituent effects both in case of pK_{ip} and pK_α whereas the transfer from THF into water leads to the opposite result.

It is interesting to note that in all cases the correlation is better with the pK_α than with the pK_{ip} values. This result indirectly validates the method of correction for ion-pairing.

Concentration Dependence of pK_{ip} Values. If we assume that no larger associates than 1:1 ion pairs exist in the solution then the pK_{ip} values should not show any concentration dependence. The concentrations in the NMR measurements are intrinsically higher than in UV−Vis measurements, and the agreement between these two methods serves as a good indicator. According to the data in Tables 2 and 3, the results of the two methods agree well for the ΔpK_{ip} values of arylphosphazenes. With bases of smaller size, however, disagreements are observed. When comparing the results of the measurement of the same equilibrium carried out by different methods, the following is observed: the ΔpK_{ip} between DBU and 4-Me_2N−$C_6H_4P_1$(pyrr) according to the UV−Vis measurements is 0.83, according to NMR it is 0.48; according to the UV−Vis measurements DMAP is by 0.54 pK_{ip} units stronger base than 2-Cl−$C_6H_4P_1$(dma), whereas according to the NMR measurements DMAP is by 0.38 units weaker. The situation is even more serious with triethylamine: according to the UV−Vis measurements it is by 1.58 pK_{ip} units stronger base than 2-Cl−$C_6H_4P_1$(dma), according to the NMR it is by 0.87 pK_{ip} units weaker. These discrepancies are larger than the possible uncertainties of these measurements. On the UV−Vis measurements we did not observe noticeable ΔpK_{ip} dependence (see Table S1 in Supporting Information) on concentrations while changing the concentration of Et_3N over the wide range (from 4.5 × 10^{-5} M to 2.3 × 10^{-2} M) and keeping the 2-Cl−$C_6H_4P_1$(pyrr) concentration 10^{-4} to 10^{-5} M.

The disagreements can be due to the formation of aggregates of 1:1 ion pairs at higher concentrations, especially at those used in the NMR method. Due to this concentration dependence, the NMR measurements involving bases of small size were not included in the scale (Table 2).

We used the Streitwieser method[30] to estimate the mean aggregation numbers of the ion pairs. For the UV−Vis data these were around 1, indicating that no significant aggregation of the ion pairs was taking place during the measurements. In principle the method also permits to find the mean aggregation constants; however, due to the very low extent of aggregation we could not get reliable estimates for the aggregation constants. Also, it was not possible to apply that method to the NMR data, because it is necessary that one of the protonated bases would be in the solution only in the form of a monomeric ion pair. This condition is not met at the concentrations used for the NMR measurements.

Anchoring of the Scale. These disagreements cast some doubt on the suitability of triethylamine as anchoring point for our data: the pK_α value of triethylamine was determined by the Morris group using NMR measurements (concentrations were in the range of 0.02−0.07 M).[10] The other two compounds common in this work and ref 10, *N*,*N*-dimethylaniline (pK_α = 6.0)[10] and TMG (estimated pK_α = 15),[10] are not as suitable because they are, respectively, either at the very bottom of the scale or have a pK_α value that has only been estimated, not measured. They are of similar size to triethylamine, so that similar concentration dependence problems can be anticipated. The pK_α values of *N*,*N*-dimethylaniline and TMG from this work are 4.9 and 15.3, respectively. Thus, in the case of *N*,*N*-dimethylaniline there is a disagreement, but the general picture would remain the same if one of these two compounds would be used as the anchoring point. To the best of our knowledge, besides the work of the Morris group,[10] there is no other absolute basicity data in THF available in the literature that could be used to anchor our scale.

Conclusions

Relative ion-pair basicities ΔpK_{ip} of 25 substituted aryl and alkyl iminophosphoranes and 20 other N-bases

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(various pyridines, amines, amidines) have been measured in THF medium using the UV−Vis and/or ^{13}C NMR methods. The ΔpK_{ip} values were corrected for ion pairing using the Fuoss equation to obtain relative ionic basicities ΔpK_{α}. Based on these measurements, a basicity scale ranging from 2-methoxypyridine to EtP_1(pyrr) and having a total span over 18 pK units has been created. The scale has been anchored to the pK_{α} value of triethylamine ($pK_{\alpha} = 12.5$). It is practically impossible to give any truly absolute pK_{ip} values at this time, because absolute pK_{ip} data of neutral bases in THF is almost nonexistent in the literature.

The results are compared to pK_a values in various other solvents and in the gas phase. The pK_{α} values give better correlations than the pK_{ip} values, thus indirectly validating the procedure of correction for ion pairing.

The predictability of the basicity together with suitable spectral properties in the UV range make the phenyliminophosphoranes convenient neutral indicators in the high basicity range where the choice of neutral indicators is very limited.

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Supporting Information Available: Table (Table S1) of detailed experimental data (includes data for all the UV−vis equilibrium measurements: concentrations, acid used, calculation method) and ^{13}C NMR spectra of selected compounds (Figures S2). This information is available free of charge via the Internet at http://pubs.acs.org.

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