Novel, Very Strong, Uncharged Auxiliary Bases; Design and Synthesis of Monomeric and Polymer-Bound Triaminoiminophosphorane Bases of Broadly Varied Steric Demand☆

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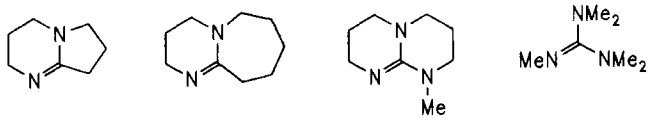
The synthesis and properties of a number of very strong iminophosphorane bases up to an extremely high level of steric hindrance are described. They cover a range of ca. 4 p*K* units in basicity and a range of more than 11 orders of magnitude in their rates of methylation with methyl iodide. Most of the systems are readily prepared in up to molar quantities, conveniently recovered from their salts and are of high chemical and thermal stability. Crystal structures were determined in order to parametrize a force field, which is utilized in molecular modeling studies offering a rationalization of the observed differences in steric hindrance and basicity. Depending on the degree of steric protection of the basic center, these novel bases are proposed as unprecedented, versatile auxiliary bases in E2 eliminations and in reactions involving deprotonation in the presence of more or less strong electrophiles.

A number of uncharged nitrogen bases are well established standard reagents in organic synthesis; in many applications replacement by ionic bases would prove highly disadvantageous. Nevertheless, concerning the strongest of the until recently commercially available bases, tetramethylguanidine[1], DBN, and DBU[2], little efforts have been undertaken to vary their structure[3] in order to generate a palette of bases, each of them optimized with respect to its availability and to a given application. Successful efforts to construct bases stronger than DBU had been limited to some guanidine derivatives[4] and to kinetically extremely sluggish proton-chelating tertiary amine derivatives[8].

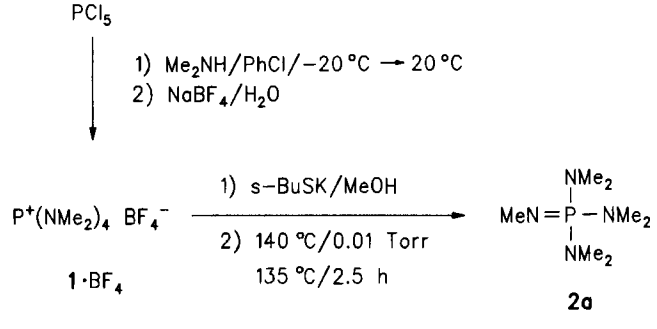
In the course of our studies[9,10] aimed at the design and synthesis of new base systems, our attention was drawn to the hardly explored structural type of peralkylated triaminoiminophosphoranes[5]; the "archetype" of these systems **2a**[11,12] has been known for two decades, but no data concerning its basicity, no optimized synthetic procedure, and no application as auxiliary base have been reported. We found that **2a** has distinct advantages over amidine- and guanidine-type bases in being considerably more basic and extremely stable towards basic hydrolysis.

Design and Synthesis of Sterically Unhindered Systems

The range of applications of sterically unhindered bases is restricted mainly to reactions of substrates of limited electrophilicity, where proton abstraction is involved in the rate determining step, e.g. E2 elimination of hydrogen halide from secondary halides. Between DBU and KO*t*Bu, two of the standard bases used for such conversions, there is a large gap concerning both basicity and reactivity, so it was felt that bases of intermediate basicity would be of considerable interest. As the dehydrohalogenation of secondary halides is an important application of sterically unhindered to moderately sterically hindered bases, the proportion of base alkylation to elimination in the reaction with isopropyl bromide was chosen as a practical measure of the steric demand of known and new uncharged bases.



DBN DBU MTBD PMG



2a

With respect to this criterion, DBU and MTBD (other than DBN or PMG) are nearly optimal compromises concerning the degree of steric hindrance (see Table 1); they allow quite rapid eliminations with a generally tolerable amount of base alkylation. Compound **2a** features a similarly favorable range of steric demand, making it a promising candidate for a new type of more reactive dehydrohalogenating reagents.

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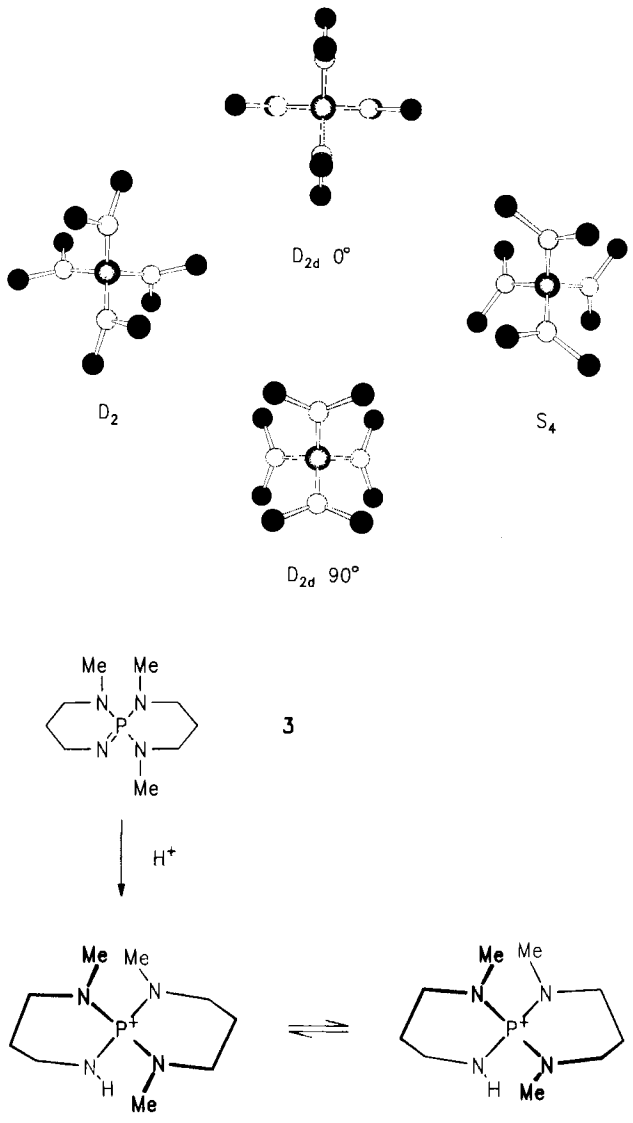
As the reported multistep procedures are not suitable for a large-scale preparation of **2a**, a novel high-yield two-step protocol was developed. Reaction of phoshorus pentachloride with dimethylamine affords the peralkylated cation $\mathbf{1}^{+}$[13] as tetrafluoroborate, which is then demethylated with thiolate. The high basicity of triaminoiminophosphoranes necessitates drastic reaction conditions, the required reaction temperature being more than 80°C higher than for quaternary ammonium salts.

Incorporation of amino groups into rings has been demonstrated to enhance the basicity of guanidine bases by curtailing conformational diversity to those conformers, which are favorable for delocalization of charge in the conjugate cation as in (essentially planar) MTBD[5] versus nonplanar PMG (see Table 1). A similarly advantageous effect was also suspected for previously unknown peralkylated mono-, bi-, or tricyclic triaminoiminophosphoranes.

Compared to guanidine bases, the optimum spatial arrangement of ligands in triaminoiminophosphorane bases for high basicity is much more difficult to evaluate due to considerable conformational diversity. But it seemed a reasonable assumption that, disregarding the detailed nature of the PN bond[15], in (local) minimum-energy conformations of symmetrically substituted (or conformationally unrestricted) tetraaminophosphonium ions all amino groups have spatial arrangements related (or approximately related) by symmetry; due to reduced symmetry, the free bases should have less conformational restrictions. Thus, substitution patterns favoring such symmetrical arrangements in the cation by steric effects were suspected to more or less reduce their acidity. From a critical consideration of possible conformations of these cations (shown with trigonal-planar amino groups) two principal symmetrical conformations emerged, D_2 and S_4. Symmetry is retained if the torsional angles R–N–P–N and the pyramidalization of nitrogen are simultaneously adjusted for all amino groups. The D_2 and S_4 symmetrical conformers are interconvertible via two arrangements with D_{2d} symmetry, special cases of the former with the torsional angle R–N–P–N being either 0° with trigonal-planar nitrogen atoms (D_{2d} 0°), or 90° where pyramidalization of nitrogen is again a free parameter and all alkyl groups are in positions equivalent by symmetry (D_{2d} 90°). Molecular modeling studies revealed, that in acyclic systems representatives of one or the other of these arrangements are sterically favorable, the most favorable conformation depending on the bulkiness of the nitrogen substituents and the assumed equilibrium N–P–N angles. But generally, as in the permethylated cation $\mathbf{1}^{+}$, only unrealistic values of more than 140° for one pair of N–P–N angles can reduce the two quasi-*peri* interactions of alkyl groups to the extent that a D_{2d} 0° conformer becomes feasible. A compound **3** with an enforced (approximate) D_{2d} 0° conformation in the cation was thus felt to fill a gap in the conformational hyperplane and to be helpful in defining the upper limit of basicity of triaminoiminophosphorane systems.

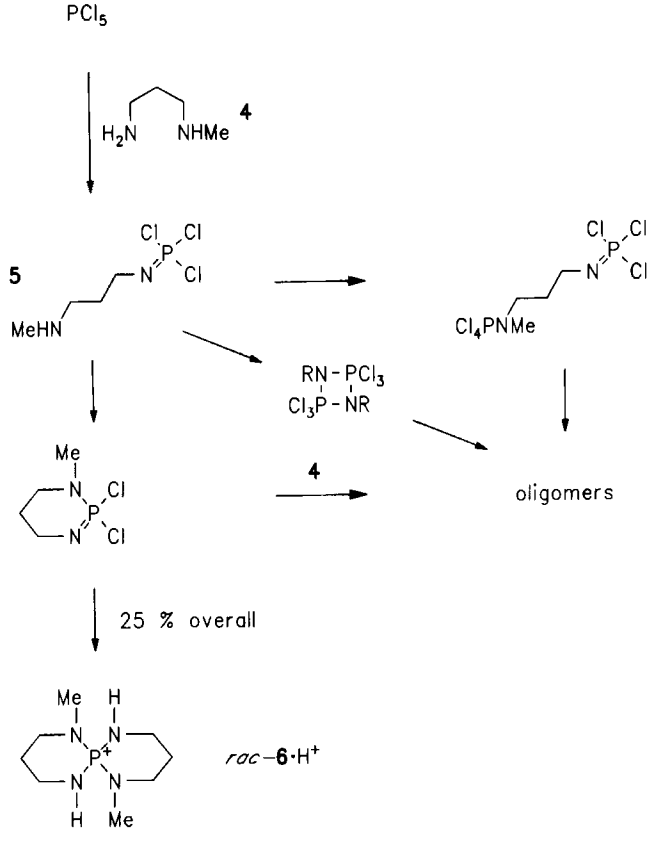
First attempts to synthesize the spiro derivative *rac*-**6** · H^{+} by reaction of phosphorus pentachloride with the diamine



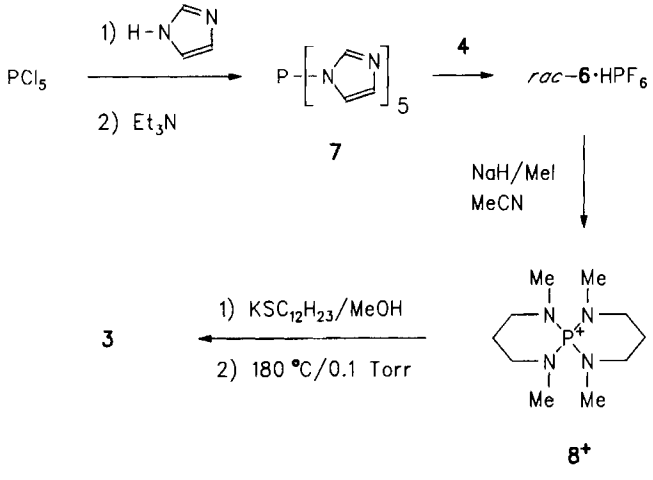
4 ended up with disappointingly low yields, even when dilution techniques were applied. Thus, at least for the generation of compounds with sterically less favorable ring systems than in *rac*-**6**, alternative synthetic routes had to be worked out[5].

The reason for the difficulties encountered with direct substitution of chlorine in phosphorus pentachloride is most probably the high tendency of intermediates to enter into competing intermolecular reaction channels. Due to a strong decrease in reactivity of intermediates on subsequent replacement of chlorine by amino functions, intermediates like **5** are supposed to react faster with more electrophilic phosphorus pentachloride than to undergo intramolecular attack at the iminophosphorus trichloride functionality. Dimerization of **5** or other intermediates possibly accounts for further decrease in yield[16,17].

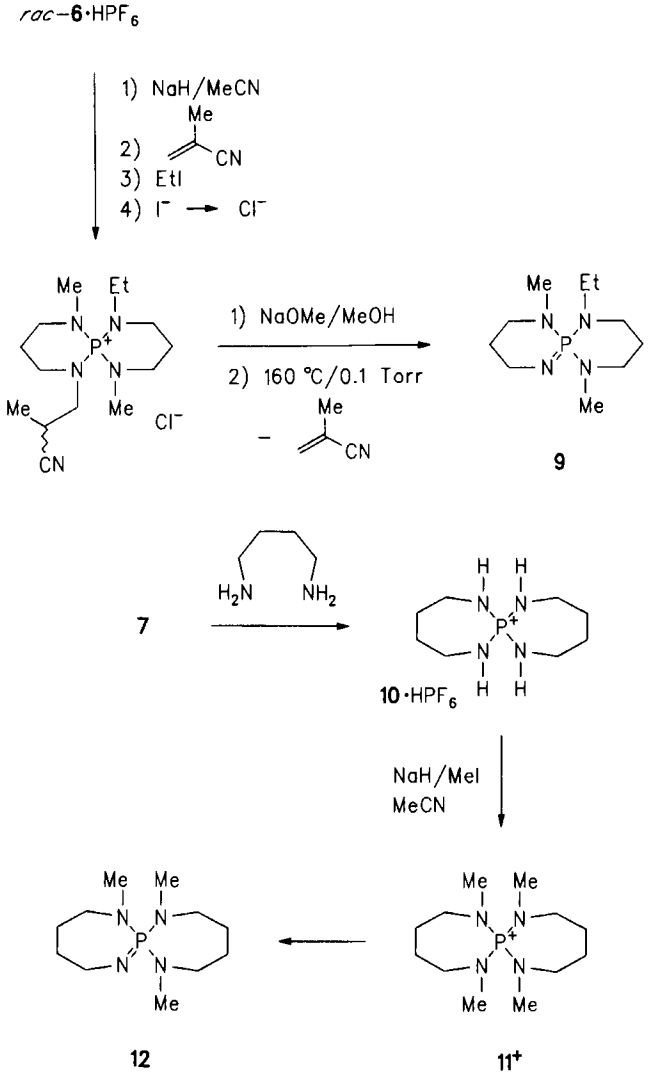
For such reasons a less reactive P^{5+} synthon, more sterically hindered at phosphorus, was given better chances. In fact, reaction of diamine **4** with a species produced from phosphorus pentachloride and imidazole provided 70% of the desired spiro bicyclic *rac*-**6** as hexafluorophosphate salt.



The detailed nature of this P^{5+} synthon remains to be clarified; the stoichiometry of the reaction concerning precipitated triethylammonium chloride indicates the neutral phosphorane **7**. The conversion of the peralkylated cation $\mathbf{8}^+$, obtained by base-promoted twofold methylation of *rac*-**6**, into the peralkylated base **3** was again accomplished by thiolate-induced demethylation.



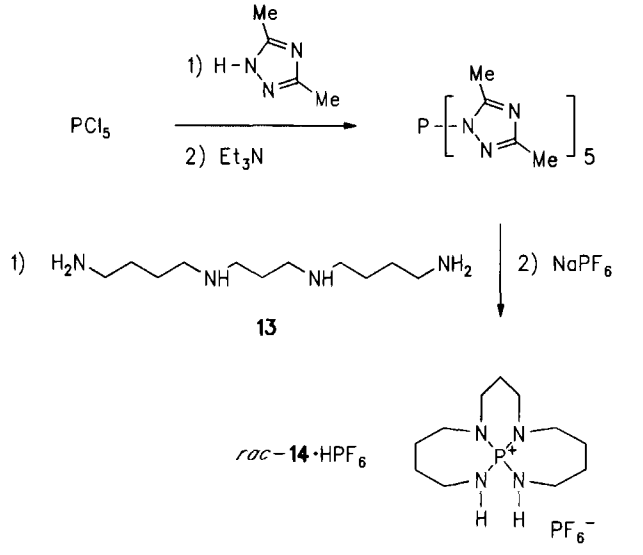
The free base **3**, the least sterically hindered unstrained triaminoiminophosphorane base available, turned out to be a solid; this fact complicates its purification by distillation and its dosage by means of a syringe. Aiming at a liquid derivative, we elaborated a synthetic strategy for selective monoalkylation with higher alkyl halides, consisting of selective protection of the NH function in the free base *rac*-**6** by treatment with a Michael acceptor, monoalkylation of this protected derivative, and basic deprotection by a retro Michael reaction. Acrylonitrile turned out too reactive, inducing extensive polymerization, but methacrylonitrile was found to be well suited. Monoethylation of the Michael adduct provided the liquid, distillable base *rac*-**9**. Utilizing the phosphorus imidazolide synthon **7** and the dealkylation concept also allows the synthesis of a [6,6]spiro compound **10** starting from tetramethylenediamine, but yield diminished to 30%. Permethylation of **10** to the cation $\mathbf{11}^+$ and demethylation as described for $\mathbf{8}^+$ affords the liquid base **12**.

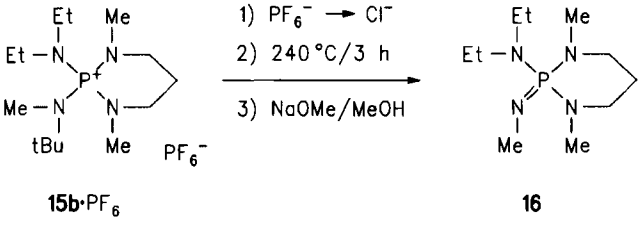


Yields of tricyclic tetraaminophosphonium salts like salts of *rac*-**14** via linear tetramines like **13** were even inferior; replacement of imidazole by the more nucleofugic and more sterically hindered 3,5-dimethyl-1,2,4-triazole enhanced yields only slightly; thus, for practical reasons, no attempts were made to convert these systems to peralkylated bases.

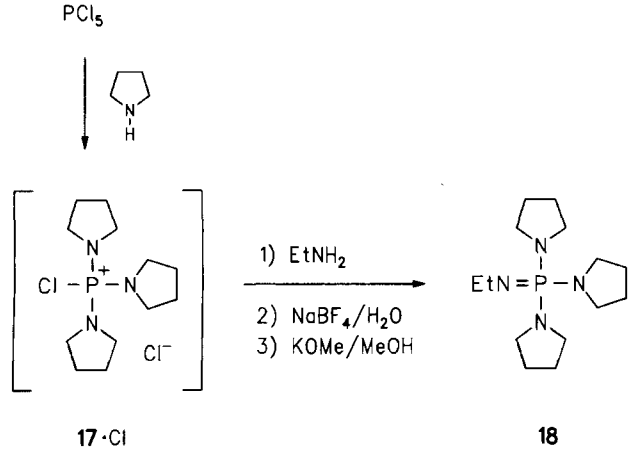
Thermal elimination of isobutene from the peralkylated cation salt **15b** · Cl, a side product of the synthesis of the sterically hindered base **23b** (see below), provided the hydrochloride of the monocyclic base **16**.

The reported principal strategy for the synthesis of the archetype base **2a** via the chlorotris(dimethylamino)phosphonium salt **19**[11b], produced by chlorine addition to hexamethylphosphorous triamide[11b,18] or by chlorination of HMPA with phosgene[19], phosphorus oxychloride[20], or thionyl chloride[21], was adopted for the synthesis of the new liquid base **18**. A more convenient direct synthesis of chlorophosphonium salts by selective threefold substitution of phosphorus pentachloride proved feasible, as long as the threefold substitution reaction was carefully controlled, allowing a one-pot synthesis of **18** via **17**.





15b·PF$_6$ **16**

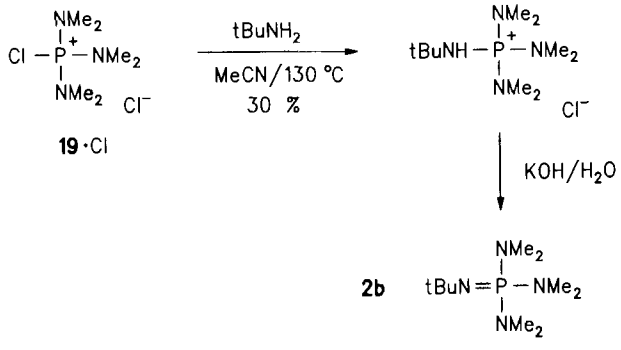


17·Cl **18**

Design and Synthesis of Sterically Hindered Systems

Only sterically rather uncongested and hence rather nucleophilic, throughout *n*-alkylated triaminoiminophosphorane systems[11,12,22] like **2a** had been fully described[23], so it was felt that the generation of non-nucleophilic bases would fill a gap.

Extensive molecular modeling studies revealed that generally for a certain level of steric hindrance the most economic acyclic structures (concerning molecular mass) are those, where bulkiness of the alkyl groups is localized on the imine substituent. Furthermore, they uncovered that within the series of isomeric alkyl groups those built from *tert*-butyl and methyl groups throughout are most effective in any position. The synthetic efforts were therefore first aimed at the minimal structure **2b**.



Application of the reported strategy for the synthesis of **2a** by means of chlorophosphonium salt **19** did not allow the introduction of strongly sterically hindered primary amine components in satisfactory yields. For example, in the reaction with *tert*-butylamine at 130°C in a sealed tube partial decomposition of **19**[17] led to an intractable mixture of partially demethylated products and ca. 30% of **2b**[5].

The Staudinger reaction had occasionally been utilized for the synthesis of sterically unhindered iminophosphorane bases[12], but suitable azides for sterically hindered bases are not readily available and should furthermore be too hazardous to be used as a large-scale starting material. The rational design of bases of broadly varied steric hindrance therefore asked for a systematic investigation of novel synthetic routes.

Depending on the degree of steric bulk of the proper base system, a number of conceptionally different strategies were envisioned and realized. These all have in common that they ultimately start from phosphorus pentachloride and a *tert*-alkyl-substituted primary amine via intermediate (alkylimino)phosphorus trichlorides:

i) Persubstitution of (alkylimino)phosphorus trichlorides with a secondary amine component.

ii) Monosubstitution of (alkylimino)phoshorus trichlorides with a secondary amine component, cyclization with a 1,3-diamine component and alkylation of eventually remaining NH groups.

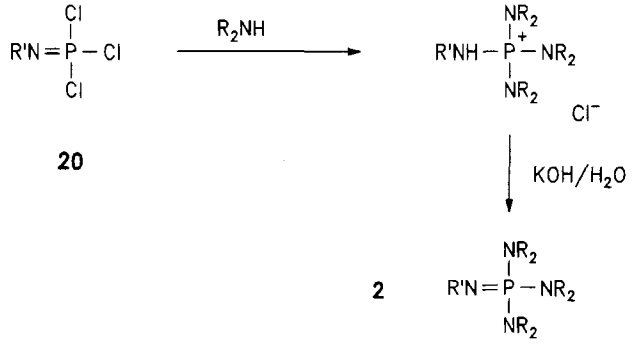
iii) Persubstitution of (alkylimino)phosphorus trichlorides with another sterically less congested primary amine component, followed by selective threefold alkylation (presumably methylation) of the three less sterically hindered amino functionalities.

iv) Direct persubstitution of phosphorus pentachloride with a primary amine component followed by selective threefold methylation.

Strategy i: Compound **2b** was in fact easily available by starting with **20a**[24]. This route and the reported strategy[11] for the synthesis of **2a** are complementary, as (alkylimino)phosphorus trichlorides are only stable towards dimerization, when the bulkiness of the alkyl group on nitrogen exceeds that of isopropyl[16].

Compound **2b**[5] is a relatively volatile, mobile liquid, insensitive to oxygen and easily recoverable from its salts by treatment with alkali metal hydroxides without any detectable hydrolysis. According to strategy i, but employing commercially available *tert*-octylamine instead of *tert*-butylamine, we secured the more sterically hindered base **2c** (*t*Oct-P_1) via **20b**.

No primary amine was commercially available that would induce even stronger steric hindrance. Structure **2d** with the 1,1,2,2-tetramethylpropyl (*tert*-heptyl) substituent was then envisaged, as the reported synthesis of *tert*-heptylamine is straightforward[25]. The reaction sequence worked out for **2b** and **2c** provided the highly sterically hindered base **2d** via **20c** in high yield without the necessity of applying rigorous reaction conditions.



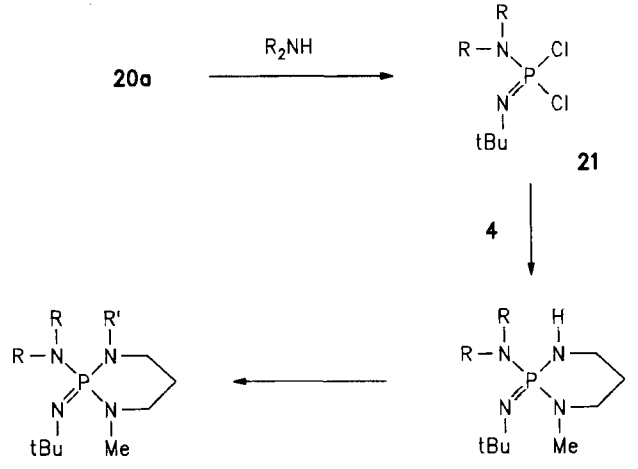
20 **2**

R′ = *t*Bu	R′ = CMe_2CH_2tBu	R′ = CMe_2tBu
20a	**20b**	**20c**
2b: R = Me	**2c**: R = Me	**2d**: R = Me
2e: R_2 = $-[CH_2]_4-$		**2f**: R_2 = $-[CH_2]_4-$

In order to obtain bases with enhanced basicity, pyrrolidine instead of dimethylamine was employed as secondary amine component yielding the bases **2e** and **2f**.

Strategy ii: Ring closure was suspected to enhance basicity, as discussed for the sterically unhindered bases. Furthermore, according to molecular modeling studies, incorporation of two amino groups into a six-membered ring induces a conformation, where one of the alkyl groups of the singular dialkylamino group would be in a quasi *peri* position with respect to the lone pair on the imino nitrogen (or NH bond in the cation). This offers the opportunity of economically controlling steric hindrance of the system by proper choice of the single (monofunctional) secondary amine component.

The respective minimal structure **23a** was principally available from inexpensive commercial compounds via the demethylated compound *rac*-**22a**, but the yield was only moderate due to limited selectivity for monosubstitution in the reaction of **20a** with dimethylamine leading to the intermediate **21a**. Good selectivity was obtained with diethylamine providing **21b**, **23b** having the additional advantage of being more sterically hindered and slightly more basic than **23a**. The monodealkylated intermediate *rac*-**22b** offers the opportunity of attachment to a Merrifield polymer, thus providing a sterically hindered, immobilized base **23d** of comparable strength. These two bases are commercially available and are on the way to being established as special reagents for critical reactions in a basicity range exceeding that of DBU by more than 3 p*K* units[10,26].



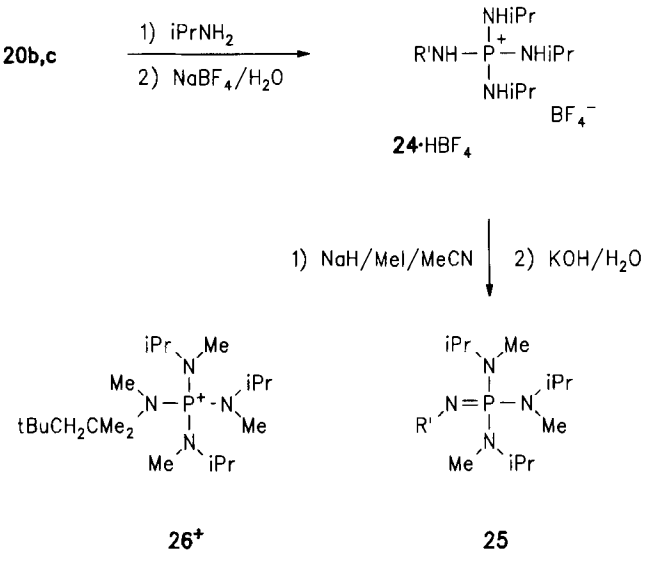
23a–c: R′ = Me
23d: R′ = CH_2Po; R = Et
Po = Polymer

21, **22**, **23a**: R = Me
b: R = Et
c: R = *i*Pr

Reaction of diisopropylamine with **20a** requires reflux conditions and produces **21c** in only moderate yield, as E2 elimination of isobutene competes with substitution. Attempted catalysis of the substitution reaction with *N*-methylimidazole or *p*-(dimethylamino)pyridine speeds up the conversion of **20a** drastically, presumably proceeding via polyonio compounds[27], but E2 elimination becomes the only detectable reaction. Further substitution and cyclization of **21c** with diamine **4** again afforded only moderate yields under varied conditions, but the final methylation proceeded almost quantitatively.

Strategy iii: The low yield of **23c** stimulated the search for other backbones suitable for extremely sterically hindered bases. Strategy iii affords a sufficient kinetic differentiation between the two principal sites of methylation, the primary amine generating the basic center had to be considerably more bulky than those providing the alkyl(methyl)amino groups. Isopropylamine was selected for the threefold substitution of an iminophosphorus trichloride, because for this strategy (see also strategy iv) this amine was suspected to induce high steric demand in the respective iminophosphorane base and yet to retain the possibility of high kinetic differentiation between the principal sites of

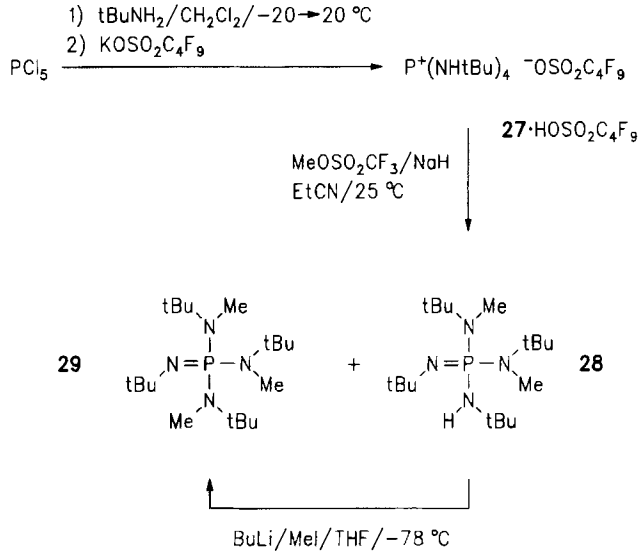
subsequent methylation. The reaction of isopropylamine with **20b** afforded salts of **24a**; but methylation led to only fair yields of **25a** along with some quarternized salt of $\mathbf{26}^+$ and some presumably dimethylated material which was removed by reaction with pivaloyl chloride. Obviously, methylation had not occurred with the desired selectivity.



24a, **25a**: R′ = CMe_2CH_2tBu
24b, **25b**: R′ = CMe_2tBu

To better define the influence of the R′ group upon the nucleophilicity of bases of type **25** and to cope with the problem of selective methylation, the *tert*-heptyl base **25b** was prepared analogously from **20c**. In fact, **24b** underwent threefold methylation with high selectivity.

Strategy iv: According to molecular modeling studies, a base with four isopropyl groups would exhibit steric hindrance at a rather moderate level, less than the more readily available **2b**. For **29**, a base with four *tert*-butyl groups instead, the predicted level of steric hindrance is so high, that the permethylation was expected to be the critical step of the synthesis. In fact, the symmetrical cation $\mathbf{27} \cdot H^+$ is very easily available as chloride salt[28], but attempts to perform three- or fourfold methylation of a number of different, rather sparingly soluble salts with standard methylating agents (methyl iodide, methyl tosylate) failed; only incomplete monomethylation could be achieved in benzonitrile under rigorous conditions, leading to partial decomposition. Molecular modeling studies of the cations revealed, that the increment of steric strain imposed on the substitution of a methyl group for a NH proton increases considerably with the degree of methylation with a particularly large increment for the third methylation step. It was therefore felt that standard methylating agents would not be sufficiently reactive. Utilization of methyl triflate as methylating agent and NaH in propionitrile provided a good yield of twofold **28** ($\cdot H^+$) along with some minor amounts of threefold alkylation product **29** ($\cdot H^+$) at room temperature. Already in the twofold alkylation product **28** the steric hindrance is sufficient to slow down the intra- or intermolecular proton transfer of the NH proton to the imino nitrogen below the level of the NMR time scale. The corresponding (sharp) signals for the N*t*Bu and the NH*t*Bu group are separated by 25 Hz in unpurified [D_6]benzene at room temperature.



Liberation of the mixture of bases from the tetrafluoroborates with KOH and treatment of this mixture with butyllithium and subsequently with methyl iodide yielded the free base **29** in good yield.

Discussion

The basicity of novel and known imine bases was determined by titration in acetonitrile[29] (see Table 1).

Table 1. $^{MeCN}pK_{BH^+}$ values[29,30] and proportion of alkylation in the reaction of some commercially available bases and of sterically unhindered triaminoiminophosphoranes with isopropyl bromide

Compound	$^{MeCN}pK_{BH^+}$ value	% Alkylation with iPrBr
DBN	23.79	91
DBU	24.33	21
PMG	25.00	66
MTBD	25.44	8
23b	27.63	0
30	32.72	5
2a	27.55	13
16	27.99	22
***rac*-9**	28.31	49
12	28.38	10
18	28.89	2

Surprisingly, replacement of the dimethylamino groups in **2a** by pyrrolidine rings (**18**) enhances basicity even more than bridging of different dimethylamino groups, as in *rac*-

9, **12**, and **16**. Compound **18** is the most basic iminophosphorane known.

The ratio of rates of alkylation to elimination in the reaction with isopropyl bromide have been determined in order to define the intrinsic relative nucleophilicity of the sterically unhindered bases (see Table 1). Except for *rac*-**9** and **16** all iminophosphorane bases are less prone to alkylation than DBU.

In Figure 1 the rates of base-induced dehydrohalogenation of 2-phenylethyl chloride with different bases in acetonitrile are plotted versus the $^{MeCN}pK_{BH^+}$ values of the bases. A straight line defining equal relative nucleophilicity is fitted to the points for **2a**, **18**, and **30** and corresponds to a linear correlation of log *k* with the $^{MeCN}pK_{BH^+}$ value with a Brönstedt coefficient of 0.46, a value lying in the expected range[31]. The most reactive iminophosphorane base is *rac*-**9**, but according to its low steric demand it is relatively nucleophilic. The least reactive base employed is **23b**, 2–3 orders of magnitude less reactive than *rac*-**9** due to considerable steric hindrance. The well balanced steric hindrance in **18** suppresses alkylation with secondary alkyl halides effectively and makes **18** a particularly interesting dehydrohalogenation reagent which is about 2 orders of magnitude more reactive than DBU.

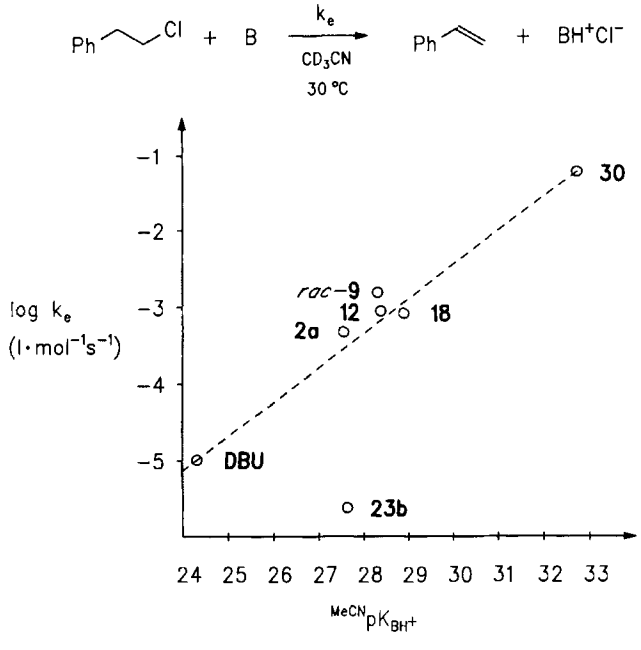
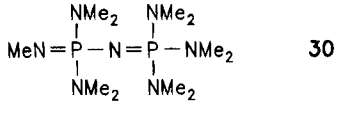


Figure 1. Correlation of the rate constant of E2 elimination of 2-phenylethyl chloride with the $^{MeCN}pK_{BH^+}$ value of the employed base



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The plot does not reveal structural effects of the bases other than their intrinsic steric hindrance, which is directly related to the deviation of their points from the correlation line; bases above the correlation line are more, bases below this line are less prone to alkylation than the reference bases. This does not generally rule out large entropic effects, but it rules out that they differ substantially in the two types of reactions, base alkylation and E2 elimination. It thus seems that from a practical point of view, concerning nucleophilic side reactions of the bases, the two parameters base strength and a practically defined steric hindrance are sufficient for the evaluation of an imine as auxiliary base.

The $^{MeCN}pK_{BH^+}$ values and the relative rates of methylation of sterically hindered triaminoiminophosphorane bases are listed in Table 2 in the order of decreasing methylation rate, i.e. increasing steric hindrance. Hygroscopicity decreases drastically down the row; while **3** is very hygroscopic, **29** gives correct analytical data even after handling in air.

Table 2. $^{MeCN}pK_{BH^+}$ values[29,30] and relative rates of methylation of triaminoiminophosphorane bases

Compound	$^{MeCN}pK_{BH^\oplus}$ value	k_{MeI}(rel.)
3		1
2a	27.55	0.17
18	28.89	0.17
2e	28.35	$1.4 \cdot 10^{-4}$
23a	27.57	$5.6 \cdot 10^{-5}$
2b	26.88	$2.6 \cdot 10^{-5}$
23b	27.63	$9.7 \cdot 10^{-6}$
2c	26.49	$9.1 \cdot 10^{-7}$
25a	26.68	$3.8 \cdot 10^{-7}$
2f	27.28	$1.3 \cdot 10^{-7}$
23c	26.77	$2.4 \cdot 10^{-8}$
2d	25.96	$2.2 \cdot 10^{-8}$
25b	25.38	$4.9 \cdot 10^{-10}$
29	24.71	$> 3 \cdot 10^{-11}$

As with the sterically unhindered systems, the presence of pyrrolidinyl groups instead of dimethylamino groups, as in **2e** vs. **2b** and in **2f** vs. **2d**, enhances the basicity by ca. 1.3 p*K* units.

All sterically hindered bases down to **25a** are liquids; the most sterically hindered bases below **25a** are solids, certainly due to some restrictions in conformational mobility. But even these bases and their conjugate cations show only averaged signals for magnetically equivalent atoms in the ^1H-, ^{13}C-, and ^{15}N-NMR spectra.

Crystal structure analyses were performed in order to shed some light on their conformational preferences. The structures of both **2f**[34] and **2f** · HBF_4[34] are complicated by molecular disorder caused by inversions of the pyrrolidine rings. In the free base, two almost identical conformers exist in the unit cell, only one is shown in Figure 2. The P1–N1 (P2–N5) double bond in **2f** is 14.3 pm (average) shorter than the other P–N bonds. In **2f** · HBF_4 (Figure 3) all P–N bonds are roughly equalized. The mean values for all four P–N bonds (and thus the sum of the P–N bond

orders) in **2f** and **2f** · HBF_4 are almost identical. Apart from this structural difference, the conformation of the free base and the cation are in fact rather similar (approximately mirror images); the conformations correspond approximately to S_4 with two sets of torsional angles C–N–P–N of ca. 169 ± 4 and 33 ± 19° for **2f** and of ca. 160 ± 8 and 36 ± 4° for **2f** · HBF_4. They differ by the torsional angle C–C–N–P of the *tert*-heptyl group and by the degree of pyramidalization on nitrogen; due to reduced participation of the nitrogen lone pairs in bonding, this is as expected somewhat stronger for the amino groups in the free base **2f**. If the MM2 force field[35] is adjusted to reproduce the conformations of the free base and of the cation[36], respectively, the parameters tell that in both cases the PN_4 tetrahedrons are considerably stretched along the axis defining the approximate S_4 symmetry; the structure of **2f** is only reproduced correctly, if all but one pair of equilibrium N–P–N angles are made strongly unequal, uncovering considerable stereoelectronic effects. The conformational change on protonation of **2f**, as observed in the crystal structures, does not offer an obvious explanation for its low basicity compared to **18**; according to MM2 both sets of principal conformations (related either to the structure of **2f** or of **2f** · HPF_6 by generating all invertomers of the pyrrolidine ring) should be very similar in steric energy for both, **2f** and **2f** · H^+.

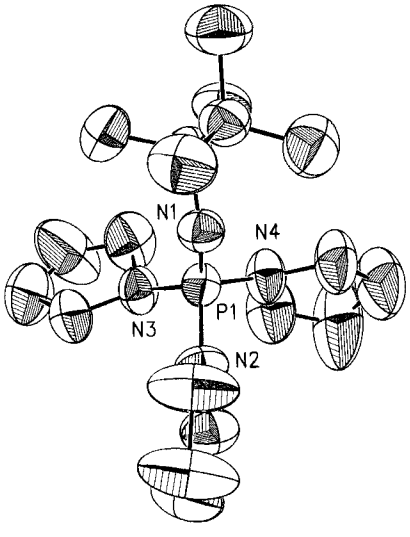


Figure 2. ORTEP drawing[39] of the structure of **2f**. Characteristic bond lengths [pm] and angles [°]: P1–N1 151.1, P1–N2 164.4, P1–N3 167.3, P1–N4 165.6; N1–P1–N2 105.0, N1–P1–N3 123.9, N1–P1–N4 115.3, N2–P1–N3 102.4, N2–P1–N4 109.8, N3–P1–N4 99.4

The less constrained cation **31** · H^+ in the hexafluorophosphate[38] and the unsubstituted tetraaminophosphonium ion in the iodide[40] have a D_{2d} 90° like conformation in the crystal, suggesting that the S_4 conformation, which is sterically enforced (but almost ideally realized) for **2f** and **2f** · H^+, is less favorable for some stereoelectronic reasons.

Defining steric hindrance as the amount of additional MM2 energy caused by replacement of the NH proton in the conjugate cation of a base by a methyl group, summarized over all conformers found within a 3-kcal/mol window with a simple force field (based on the crystal structures), allows us to define a linear Brönstedt-like correlation of this difference in steric energy with the pK values of the bases with a slope of 0.19 (r = 0.954, Figure 4), indicating that the decrease of basicity with increasing bulkiness of the substituents is mainly a sterical phenomenon. Such a trend is also often met with tertiary amines[2b,32] or fully alkylated guanidines[2b], but not with the related phosphazene systems[33]. As with guanidines (see PMG vs. MTBD, Table 1), cyclic structures are particularly strong bases, **12** and **23a**, **b** lying above the averaged correlation line. *rac*-**9** with a D_{2d} 0°-like conformation and **12** with a D_{2d} 90° (or perhaps a S_4)-like conformation in the cation are almost equally basic. It thus seems that concerning basicity there are no pronounced inherent conformational effects, as long as symmetric arrangements of amino groups around phosphorus are realized. The basicity of **16** is intermediate between that of the acyclic base **2a** and that of the spirobicyclic bases *rac*-**9** and **12**. The lower basicity of acyclic structures is most probably an effect of a more negative protonation entropy, a function of a particularly high conformational mobility of the free bases compared to the cations, caused by the lower P–N (or C–N) bond order. In line with this rationalization, this effect is not observed with the extremely sterically hindered acyclic bases, **23c** and **25a** e.g. being almost equally basic. The correlation between steric hindrance and basicity is thus improved along the series of the structurally related systems **2a**–**2b**–**2c**–**2d**, **18**–**2e**–**2f**, **16**–**23b**, **25a**–**25b**, **2a**–**29**, **2b**–**29**, and **23a**–**23c**; **23a**–**23b** and **2c**–**25a** are the only exceptions. The molecular modeling studies reveal that for the cations of the noncyclic bases **2b** and **2c** and to some extent also for **2a**, **2d**, and **29** it is more difficult than for the other systems discussed to adopt symmetrical arrangements of ligands around phosphorus. In fact, **2b**, **2c**, and also **29** fall deepest, **2d** to some extent below the correlation line; **2a** also falls considerably below

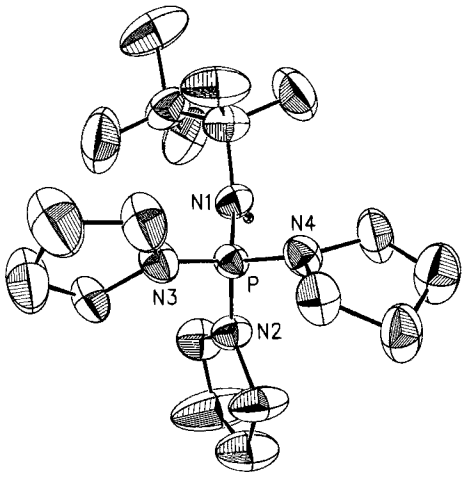
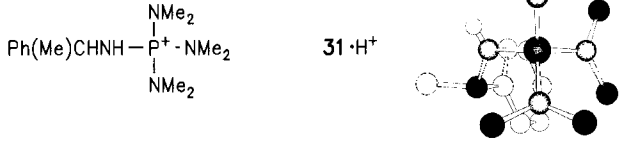


Figure 3. ORTEP drawing of the structure of the cation in **2f** · HBF_4. Characteristic bond lengths [pm] and angles [°]: P–N1 162.8, P–N2 162.2, P–N3 161.5, P–N4 162.5; N1–P–N2 101.5, N1–P–N3 116.8, N1–P–N4 111.3, N2–P–N3 109.4, N2–P–N4 112.6, N3–P–N4 105.4

Table 3. Experimental details and results of the X-ray diffraction analyses of the compounds **2f**, **2f** · HBF_4, and **25b**[41]

Cpd.	**25b**	**2f**	**2f**·HBF_4
Molecular formula	$C_{19}H_{45}N_4P$	$C_{19}H_{39}N_4P$	$C_{19}H_{40}BF_4N_4P$
Molecular mass	360.57	354.52	442.34
Crystal system	triclinic	monoclinic	orthorhombic
Space group	P1	P21/c	$P2_12_12_1$
a [pm]	10.153(2)	11.3495(1)	8.1245(3)
b [pm]	10.394(3)	21.1034(8)	15.9168(8)
c [pm]	11.251(3)	18.817(1)	18.308(1)
α	85.86(2)		
ß	86.68(2)	106.256(3)	
γ	78.28(2)		
V [pm^3]·10^{-6}	1158.3(6)	4326.6(2)	2367.5(2)
Z	2	8	4
d(calcd) [$g \cdot cm^{-3}$]	1.034	1.088	1.241
Size of the crystal [mm]	0.5x0.4x0.28	0.6x0.5x0.35	0.6x0.45x0.25
No. of measured reflections	4704	13175	5163
Symmetry-independent reflections	4467	6590	2582
Observed reflections $I>2\sigma(I)$	4187	4676	2279 [$I>3\sigma(I)$]
Linear absorpt. coeff. [mm^{-1}]	1.082	1.158	1.405
Absorption correction	-	Ψ-Scan	Ψ-Scan
Ratio $F_{obs.}$/parameters	10.52	10.77	8.63
R	0.043	0.054	0.069
R_W	0.051	0.064	0.071
Diff.Four. ρ_{max}[$eÅ^{-3}$]	0.264	0.247	0.397



the correlation line, but here the steric effect is certainly superposed by a missing inductive stabilization of the cation by β-alkyl groups on the basic center; the difference in basicity between the *N*-methyl bases **2a** and **16** is less than between the corresponding *N*-*tert*-butyl bases **2b** and **23b**. As **25a** has a very favorable conformation concerning the symmetry of the arrangement of amino groups, an enhancement in basicity is observed in going from **2c** to the more sterically hindered **25a**, which is not observed with **2d/25b** and thus is not simply explained by an inductive effect of the additional β-alkyl groups in **25a/25b**. Thus, there seems to be some evidence for a relationship between the degree of symmetry of the arrangement of amino groups in the cation and the basicity of the free base, but with 0.3–0.6 p*K* units the effect is not large enough do be separated unambiguously from the other effects discussed here.

The relative rates of methylation of the bases were determined by concurrent reaction of a complete series of suitable pairs of free bases with methyl iodide (Figure 5). The order of increasing steric effects of the substituents is as expected Me < Et < *i*Pr < *t*Bu < *t*Oct < *t*Hept. A linear Brönstedt-like correlation between the MM2 energies of protonated and methylated base and log*k* exists ($r = 0.984$) with a slope of 0.62, a value lying in the expected range.

Such Brönstedt-like correlations would certainly allow us to predict the basicities and the relative rates of methylation of many other free bases correctly and thus allow us to classify them concerning their inherent steric shielding of the basic center. But overgrowing conformational complexity, as observed with the pyrrolidine-substituted bases **2e** and **2f**, can become a limiting factor; in a qualitative sense, back tying of the α-carbons of the dialkylamino groups by the incorporation into pyrrolidine rings as in **2e** and **2f** causes a slight decrease in steric shielding compared to the compounds **2b** and **2d** bearing dimethylamino groups (see Table 2).

Compound **25a** was found to be only moderately more sterically hindered than **2c**, somewhat less than estimated by the MM2 analysis (perhaps incomplete, 119 conformers of **25a** · H^+ were found).

The shielding effect of three isopropyl groups was considerably stronger in the *tert*-heptyl compound. A crystal structure analysis of the free base **25b**[34] was expected to reveal clear-cut information, due to unambiguous conformational identity. The crystal structure (Figure 6) is excellently reproduced by the force field developed from the structure of **2f** and corresponds to the second best conformation, being only 0.35 kcal/mol above the global minimum in MM2 steric energy; thus, stereoelectronic factors beyond those responsible for the deformations of the

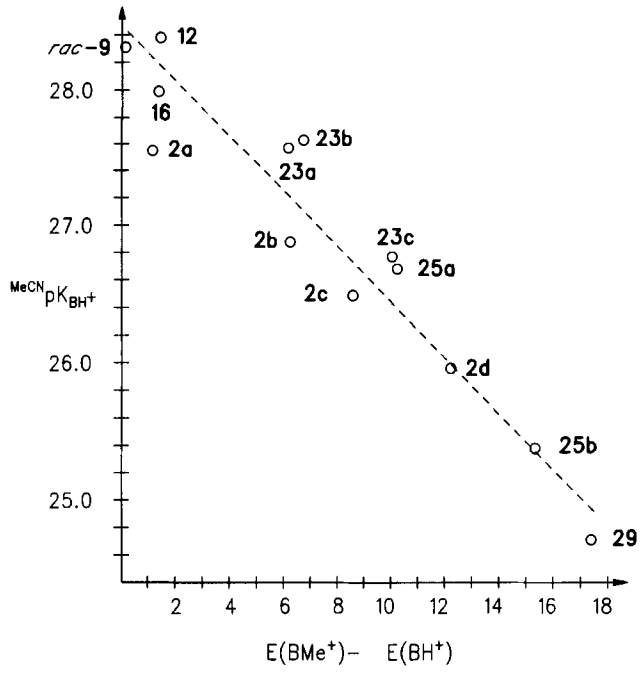


Figure 4. Correlation between the $^{MeCN}pK_{BH^+}$ value of different bases B and the calculated differences in steric energy of B · H^+ and B · Me^+ (see text)

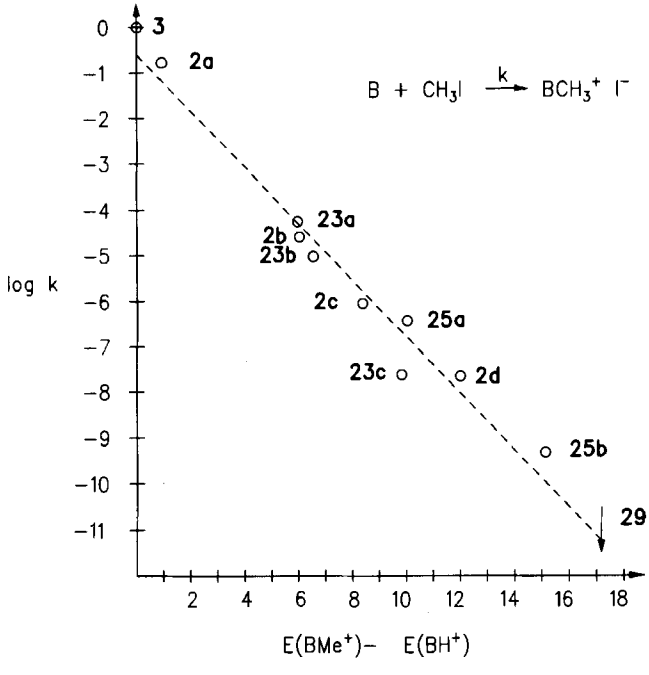


Figure 5. Correlation between the relative methylation rates of different bases B and the calculated differences in steric energy of B · H^+ and B · Me^+ (see text) using **3** as reference

N–P–N and N–P=N angles are probably not important in the free bases; again the conformation of the free base was predicted to be also favorable for the cation, so that no new explanation for the observed low basicity appeared.

The steric effect of the *tert*-heptyl substituent versus *tert*-butyl in the relative rate of methylation of **2b** vs. **2d** and **2e** vs. **2f** is very similar to that observed with the corresponding P_4 bases[33]. The strong effect is induced by the backbone of the bases, placing the *tert*-butyl subunit of *tert*-heptyl above the lone pair of the imine nitrogen (or the NH proton), as shown in the crystal structures of **2f**, **2f** · H^+ and **25b**.

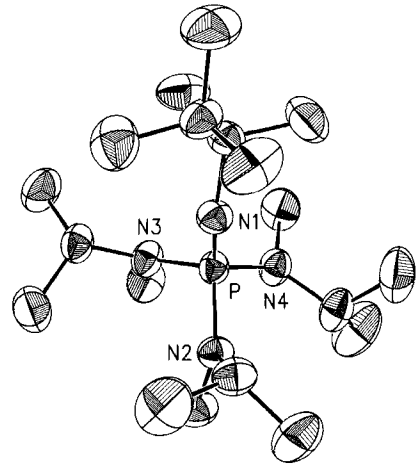


Figure 6. ORTEP drawing of the structure of **25b**. Characteristic bond lengths [pm] and angles [°]: P–N1 152.6, P–N2 166.5, P–N3 167.2, P–N4 167.8; N1–P–N2 106.52, N1–P–N3 114.69, N1–P–N4 122.67, N2–P–N3 108.71, N2–P–N4 103.25, N3–P–N4 99.97

Among the *tert*-butylimino compounds a particularly large shielding effect of the dialkylamino group was expected in **23c** and **29**. In the most stable, symmetrical conformation of **23c** two methyl groups shield the basic nitrogen like an umbrella, attack of electrophiles except protons causing a rotation of the diisopropylamino group by almost 90°. This rotation is expected to reduce orbital overlap considerably (more than in **15b**$^+$ or **15a**$^+$) and thus to cause an unfavorable enthalpy contribution, which is not covered by the force field. For **23c** the observed rate of methylation is in fact lower than expected from the molecular modeling studies. The related cation **15a**$^+$ adopts a conformation in the crystal lattice of the hexafluorophosphate salt which resembles the predicted minimum energy conformation of **15c**$^+$, the *tert*-butyl(methyl)amino group being twisted by 90°C out of the plane defined by a D_{2d} 0°-like conformation[42]. But contrasting the situation with **15c**$^+$, the force field evaluates this X-ray conformation of **15a**$^+$ to be some 2 kcal/mol higher in energy than a more D_{2d} 0°-like conformation. Additionally, as with **15c**$^+$, it is considered quite unfavorable concerning "conjugation". Thus the driving force for this unexpected conformational behavior of **15a**$^+$ has to be identified before a reliable rationalization of the unexpected low methylation rate of **23c** can be given. Once more (see discussion of the basicity of the other systems) it seems, that stereoelectronic influences on basicity or nucleophilicity of iminophosphoranes might in the end prove quite difficult to be evaluated. MO calculations might help to shed some light on such stereoelectronic presuppositions[15].

For the permethylated cation **32**$^+$ molecular modeling studies confirm the expected conformation with an ideal S_4 symmetry and for the free base **29** the conformation shown

in Figure 8. Due to extreme steric crowding in **29**, the principal arrangement of two of the three strongly shielding *tert*-butyl groups around the basic center (see Figure 7) should be preserved on methylation of the imino nitrogen. Compound **29** is therefore even more sterically hindered than **23c** and surprisingly, at a first glance, also more than **25b**. In fact, no methylation of **29** could be induced so far; reaction with methyl triflate in dichloromethane at room temperature led to almost complete decomposition, no novel cationic compound could be detected; with methyl iodide in propionitrile/chlorobenzene in a sealed tube no reaction occurred within four days at 100°C.

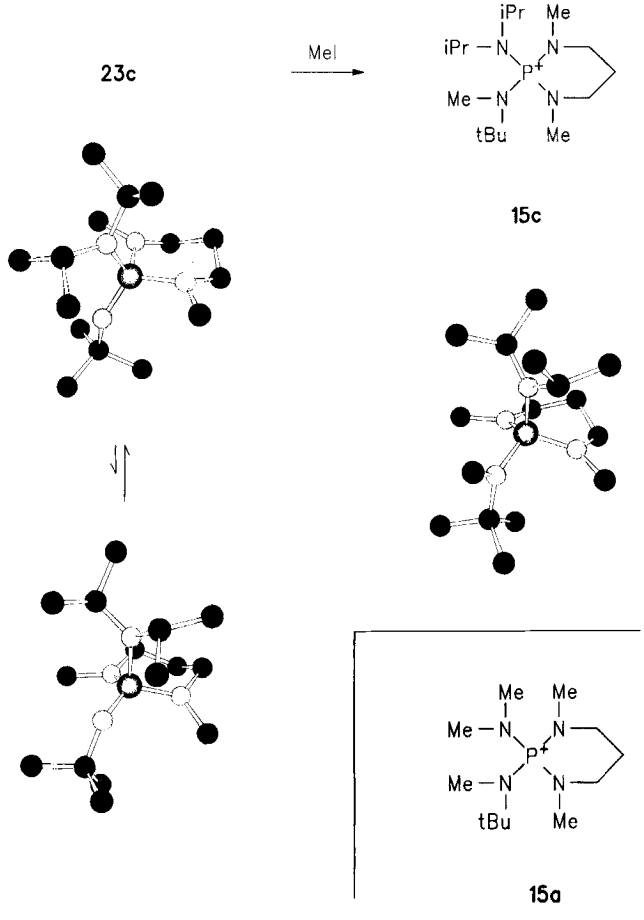


Figure 7. Schakal plots of the most stable conformers of **23c** and **15c** according to molecular modeling, without hydrogen atoms

Critical evaluation of all relevant properties of the different iminophosphorane bases like availability, boiling point (molecular mass), melting point, solubility, basicity, stability towards oxidation (on long-time storage, somewhat depending on the number of secondary alkyl groups), and steric hindrance nourishes the expectation, that among the sterically unhindered bases **2a** and **18** are most suitable as auxiliary bases, especially for E2 eliminations. Among the sterically hindered systems, **2e** and the polymer base **23d**[5,26l] are probably the most promising standard bases, e.g. for alkylation reactions. Compound **29** is one of the least nucleophilic non-chelating bases known. According to molecular modeling studies, among the commercially available bases only with 2,6-di-*tert*-butylpyridine[43] methylation is even slower. But **29** is about 12 pK units more basic and thus within its basicity range unique. It is more readily available than the other extremely sterically hindered systems described here and will certainly prove to be an exceptionally useful, essentially non-nucleophilic strong base for many reactions involving even small aggressive electrophiles like methylating agents, iodine and organic or inorganic acyl chlorides.

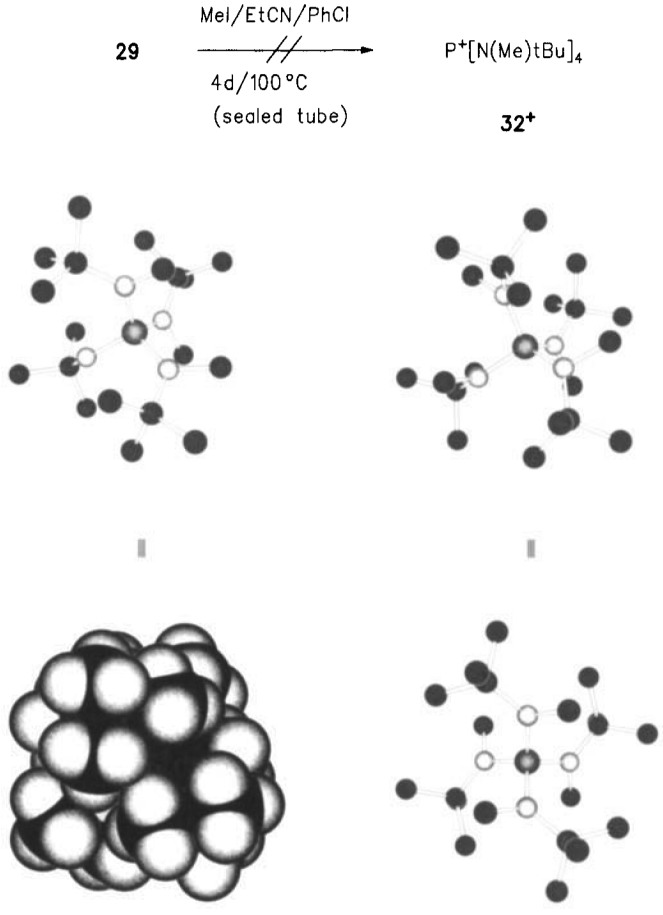


Figure 8. Schakal plots of the most stable conformers of **29** and $\mathbf{32}^+$ according to molecular modeling, ball-stick models without hydrogen atoms. The basic nitrogen in the space filling model of **29** is drawn white

Experimental

^{1}H NMR [internal standard TMS, in D_2O: sodium 4,4-dimethyl-4-silapentanesulfonate (DSS, δ = 0.00)]: Varian EM 390, Bruker AC 250, and Bruker AM 400 (30°C). – ^{13}C NMR (internal standard TMS): Bruker WP 80 and Bruker AM 400 (30°C). – ^{15}N and ^{31}P NMR (external standard [^{15}N]nitromethane δ = 380.2 and H_3PO_4, resp.): Bruker AM 400 (30°C). – IR: Perkin-Elmer 457 and Philips PU 9706. – Elemental analyses: Perkin-Elmer Elemental Analyzer 240; in the case of hygroscopicity of a compound (most of the free bases) CHN analyses were renounced. – GC: Varian Model 3700. – Melting points (uncorrected): Apparatus Dr. Tottoli and Reichert Kofler bench. – Ion Exchange: Amberlite IRA-400 and Lewatit M 500, strongly basic anion exchange resins (Cl^- form); exchange of anions for Cl^- was performed by means of a column with MeOH as solvent.

Acetonitrile (MeCN) and propionitrile (EtCN) were used in an essencially anhydrous quality, which dissolves $KMnO_4$ without decomposition; THF and cyclohexane were distilled over K/Na/anthracene; hexane was distilled over K/Na alloy; CH_2Cl_2 and chlorobenzene specified as "absolute" were distilled over P_2O_5; other solvents were purified by simple distillation; NEt_3

was first distilled over *p*-toluenesulfonyl chloride (ca. 2 mol-%), then over Na_2O (or BaO); other, also gaseous, amines and pyridine were distilled or passed over Na_2O (or BaO); NaOMe in MeOH specified as "anhydrous" was prepared from anhydrous MeOH and sodium metal; dry *i*PrOH, PCl_5, and KOMe were used as purchased by Fluka/Switzerland.

Tetrakis(dimethylamino)phosphonium Tetrafluoroborate (**1** · BF_4): In a 1.5-l four-necked flask, equipped with a mechanical stirrer, two gas inlets with bubble counters (for N_2 and amines), a gas outlet with bubble counter, and thermometer, 208 g (1.00 mol) of PCl_5 was slurried in 400 ml of absolute chlorobenzene. Under N_2 400 g (8.80 mol) of Me_2NH was passed into the mixture with vigorous stirring (gas inlet above surface of the solution) at a rate that kept the temp. of the solution at −20°C (dry ice bath). The solution was then held at this temp. for 4 h, allowed to warm to 20°C within 5 h and set aside for 36 h. The solvent was removed at reduced pressure and the residue dried in high vacuo. The product was dissolved in 1 l of water, traces of chlorobenzene were removed azeotropically, and a solution of 110 g (1.00 mol) of $NaBF_4$ and 160 g (4.00 mol) of NaOH in 500 ml of water was added, dimethylamine was removed in vacuo, and the product extracted twice with 300 ml of CH_2Cl_2. The solvent was removed in vacuo and the residue recrystallized from EtOH, furnishing 285 g (97%) of colorless crystals, m.p. >260°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.77 (d, $^3J_{P,H}$ = 10 Hz). – IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2950, 2862, 2824, 1807, 1755, 1644, 1596, 1548, 1490, 1467, 1416, 1367, 1304, 1246, 1191, 1171, 1094, 1050, 994, 865, 835, 768, 753. – $C_8H_{24}BF_4N_4P$ (294.1): calcd. C 32.67, H 8.23, N 19.05; found C 32.59, H 8.18, N 18.93.

Tris(dimethylamino)(methylimino)phosphorane (**2a**) *and Tris(dimethylamino)(methylamino)phosphonium Hexafluorophosphate* (**2a** · HPF_6): 58.8 g (200 mmol) of **1** · BF_4 was slurried in 50 ml of MeOH, and 220 mmol of anhydrous KOMe was added all at once under N_2. The mixture was stirred for 10 min after which time exactly 19.84 g (210 mmol) of (disulfide-free) 2-butanethiol was added under N_2. The mixture was concentrated in vacuo (after precipitated KBF_4 had eventually been filtered off under N_2, especially for runs on a scale larger than described here), and the residue was heated in a bath at 140°C for 30 min in high vacuo. The solid amorph residue was liquidified by heating at 160°C for 2.5 h under N_2, whereby some residual MeOH and part of the formed methylated thiol (b.p. 112°C/740 Torr) was slowly distilled off under N_2. After cooling the methylated thiol was distilled off in reduced vacuo (100°C bath temp./100 Torr), then the product was slowly distilled rising the bath temp. from 90 to 180°C, until the distillation from the solid redidue of KBF_4 ceased. Depending on the quality of the thiol the distillate contained some traces of sulfur compounds (e.g. disulfide); after dilution with 3 volumes of distilled water these impurities could be removed by distilling off the water azeotropically in vacuo; the residue was heated in high vacuo until it began to boil. Na_2O (or BaO) was added, and the product was distilled yielding 34.5 g (90%) of a colorless liquid, b.p. 42°C/0.4 Torr (ref.[11b] 55°C/0.3 Torr). – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 2.47 [d, $^3J_{P,H}$ = 9.2 Hz, 18H, $(CH_3)_2N$], 3.29 (d, $^3J_{P,H}$ = 23.2 Hz, 3H, CH_3N). – ^{15}N NMR (40 MHz, [D$_6$]benzene): δ = 23.17 (d, $^1J_{P,N}$ = −18.0 Hz, NMe_2), 24.45 (d, $^1J_{P,N}$ = 18.4 Hz, NMe). – For characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous $EtNH_2$ and recrystallized from water, m.p. >310°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.70 (dd, $^3J_{H,H}$ = 6.3, $^3J_{P,H}$ = 13.3 Hz, 3H, CH_3NH), 2.78 [d, $^3J_{P,H}$ = 9 Hz, 18H, $(CH_3)_2N$], 4.50 (br., 1H, NH). – ^{15}N NMR (40 MHz, [D$_6$]DMSO): δ = 21.68 (d, $^1J_{P,N}$ = −32.8 Hz, NMe_2), 24.02 (d, $^1J_{P,N}$ = −32.2 Hz, NMe). – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (NH), 3002, 2950, 2920, 2868, 2832, 1650, 1590, 1515, 1397, 1310, 1185, 1170, 1108, 1070, 998, 835, 761, 751, 557. – $C_7H_{22}F_6N_4P_2$ (338.2): calcd. C 24.86, H 6.56, N 16.57; found C 24.76, H 6.82, N 16.36.

(±)-1,7-Dimethyl-1,5,7,11-tetraaza-6-phosphoniaspiro[5.5]undecane Hexafluorophosphate (*rac*-**6** · HPF_6): In a 4-l three-necked flask, equipped with a mechanical stirrer, gas inlet, dropping funnel with gas outlet, and thermometer, a solution of 340 g (5.00 mol) of imidazole (dried in high vacuo at 50°C) in 600 ml of pyridine and then 700 ml (508 g, 5.02 mol) of Et_3N were added dropwise with stirring to a slurry of 208 g (1.00 mol) of PCl_5 in 1 l of absolute CH_2Cl_2 under N_2 at below 10°C (the addition of the first mol of total base being strongly exothermic). After stirring for further 30 min, the precipitated Et_3N · HCl was filtered off under N_2, washed with a small amount of absolute CH_2Cl_2, and the isolated Et_3N · HCl dried in vacuo and weighed. The filtrate was concentrated in vacuo until CH_2Cl_2 could no longer be detected (^{1}H NMR). The total volume was brought to 1 l by the addition of pyridine. Compound **4** [(4.8−1/2 · isolated Et_3N · HCl, see above) mol] was added quickly with stirring and cooling to room temp. The mixture was refluxed for 1 h and the solvent distilled off under normal pressure, the temp. of the residue rising to 240°C. The residue was cooled to ca. 100°C and then 1 l of cold water added all at once. The solution was cooled to below 10°C and 105 ml (1.0 mol) of 75% HPF_6 added with cooling in an ice bath. The precipitate was collected by suction and washed with icecold/water. The mother liquor was once extracted with CH_2Cl_2, the (ice-cold) organic phase washed with a small amount of icecold dil. H_2SO_4, then concentrated by rotary evaporation. The residue and the dried crystals were recrystallized from water affording 243 g (70%) of colorless crystals, m.p. 102−103°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97 (m_c, 4H, 3,9-H), 2.75 (d, $^3J_{P,H}$ = 10.5 Hz, 6H, CH_3), 3.18−3.53 (m_c, 8H, 2,4,8,10-H), 3.78 (br. m, 2H, HN). – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (NH), 2975, 2945, 1490, 1448, 1420, 1392, 1356, 1341, 1280, 1200, 1144, 1110, 1065, 1000, 955, 840, 736, 625, 560, 455, 420. – $C_8H_{20}F_6N_4P_2$ (348.2): calcd. C 27.60, H 5.79, N 16.09; found C 27.86, H 5.85, N 16.21.

1,5,7,11-Tetramethyl-1,5,7,11-tetraaza-6-phosphoniaspiro[5.5]undecane Hexafluorophosphate (**8** · PF_6): In a 250-ml two-necked flask, equipped with a magnetic stirrer, gas inlet, and powder addition funnel with gas outlet, 13.23 g (38.0 mmol) of *rac*-**6** · HPF_6 was dissolved in 50 ml of MeCN and 2.52 g (105 mmol) of hexane-washed NaH gradually added under N_2 at 0°C. After cooling to −20°C, 5.93 ml (13.5 g, 95 mmol) of MeI was added gradually and the mixture stirred at room temp. until the gas evolution ceased (ca. 2 h). Excess NaH was cautiously destroyed with MeOH and the solvent evaporated in vacuo. From the residue MeCN was removed azeotropically with 100 ml of water at reduced pressure. The crude PF_6 salt was collected by suction and recrystallized from MeOH. Yield 13.2 g (92%) of colorless crystals, m.p. >300°C (dec.). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.02 (m_c, 4H, 3,9-H), 2.67 (d, $^3J_{P,H}$ = 10.7 Hz, 12H, CH_3), 3.35 (m_c, 8H, 2,4,8,10-H). – ^{13}C NMR (20 MHz, $CDCl_3$): δ = 24.9 (d, $^3J_{P,C}$ = 4.1 Hz, C-3,9), 34.2 (d, $^2J_{P,C}$ = 4.0 Hz, CH_3), 51.4 (d, $^2J_{P,C}$ = 1.7 Hz, C-2,4,8,10). – ^{15}N NMR (40 MHz, $CDCl_3$): δ = 28.0 (d, $^1J_{P,N}$ = 29.6 Hz). – ^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.7. – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 1465, 1436, 1370, 1350, 1338, 1255, 1202, 1172, 1108, 1040, 1004, 957, 875, 853, 835, 730, 725, 488. – $C_{10}H_{24}F_6N_4P_2$ (376.3): calcd. C 31.92, H 6.43, N 14.89; found C 31.95, H 6.58, N 14.79.

5,7,11-Trimethyl-1,5,7,11-tetraaza-6λ^5-phosphaspiro[5.5]undec-1(6)-ene (**3**) *and 1,5,7-Trimethyl-1,5,7,11-tetraaza-6-phosphoniaspiro[5.5]undecane Hexafluorophosphate* (**3** · HPF_6): In 3.24 g (8.6 mmol) of **8** · PF_6 the anion was exchanged for Cl^- and, after clearing with charcoal and removal of the solvent at reduced pressure, the product was dried in high vacuo at 120°C. It was subsequently dissolved in 5 ml of MeOH, and exactly 1.74 g (8.6 mmol) of (disulfide-free) 1-dodecanethiol and 8.7 mmol of anhydrous NaOMe in MeOH were added under N_2. Precipitated NaCl was filtered off, the filtrate concentrated in vacuo, and the residue distilled in high vacuo at 180−190°C bath temp. The distillate was diluted with 3 volumes of diethyl ether, extracted three times with equal volumes of distilled water, the combined aqueous phases were concentrated in vacuo, and the residue was heated in high vacuo until it began to boil. Na_2O (or BaO) was added and the product distilled. Yield up to 1.51 g (81%) of a colorless solid, depending on the accuracy of the added amount of 1-dodecanethiol, b.p. 72°C/0.03 Torr, m.p. 68−71°C. – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.34 (m, 1H, 9-H), 1.62 (m, 1H, 9-H), 1.77 (m_c, 2H, 3-H), 2.29 (d, $^3J_{P,H}$ = 8 Hz, 3H, 5-CH_3), 2.42 (d, $^3J_{P,H}$ = 12 Hz, 6H, 7,11-CH_3), 2.57 (m, 2H, 4-H), 2.96 (m, 4H, 8,10-H), 3.75 (dt, $^3J_{P,H}$ = 20, $^3J_{H,H}$ = 5.6 Hz, 2H, 2-H). – ^{15}N NMR (40 MHz, [D$_6$]benzene): δ = 28.0 (d, $^1J_{P,N}$ = 7.2 Hz), 36.9 (d, $^1J_{P,N}$ = 16.8 Hz), 45.0 (d, $^1J_{P,N}$ = 25.8 Hz, N-7,11). – For characterization, a sample was precipitated as **3** · HPF_6 with 75% HPF_6 from dil. aqueous NH_3 and recrystallized from water, m.p. >230°C (dec.). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95 (m_c, 4H, 3,9-H), 2.63 (d, $^3J_{P,H}$ = 10 Hz, 3H, 7-CH_3), 2.67 (d, $^3J_{P,H}$ = 11 Hz, 6H, 1,5-CH_3), 3.13 (m_c, 2H, CH_2N), 3.29−3.45 (m, 6H, CH_2N), 4.03 (br. s, 1H, HN). – ^{15}N NMR (40 MHz, $CDCl_3$, $HOSO_2CF_3$ salt): δ = 26.2 (d, $^1J_{P,N}$ = 34.1 Hz), 30.9 (d, $^1J_{P,N}$ = 28.0 Hz), 34.8 (d, $^1J_{P,N}$ = 25.1 Hz). – IR (KBr): $\tilde{\nu}$ = 3380 cm^{-1} (NH), 2950, 2880, 2765, 1485, 1468, 1448, 1433, 1424, 1412, 1388, 1360, 1338, 1282, 1258, 1152, 1115 (s), 1055, 1000, 982, 950, 929, 908, 888, 838 (s), 740, 560 (s). – $C_9H_{22}F_6N_4P_2$ (362.2): calcd. C 29.84, H 6.12, N 15.47; found C 29.72, H 6.29, N 15.46.

(±)-7-Ethyl-5,11-dimethyl-1,5,7,11-tetraaza-6λ^5-phosphaspiro[5.5]undec-1(6)-ene (*rac*-**9**) *and (±)-1-Ethyl-5,11-dimethyl-1,5,7,11-tetraaza-6-phosphoniaspiro[5.5]undecane Hexafluorophosphate* (*rac*-**9** · HPF_6): In a 1-l three-necked flask, equipped with a magnetic stirrer, gas inlet, powder addition funnel with gas outlet, and thermometer, 244 g (0.70 mol) of pure *rac*-**6** · HPF_6 was dissolved in 200 ml of MeCN. Then 19.2 g (0.80 mol) of hexane-washed NaH was gradually added to the resulting solution, excess NaH being filtered off under N_2 immediately after gas evolution had ceased. 64 ml (51.7 g, 0.77 mol) of methacrylonitrile was added to the filtrate with stirring under N_2 and the mixture kept at 20°C for 24 h; 57 ml (84 g, 0.77 mol) of EtBr was added with cooling to room temp. and the mixture again kept at room temp. for 24 h under N_2. The precipitated NaBr was filtered off, the solvent removed at reduced pressure, the residue dissolved in MeOH, the anion exchanged for Cl^-, the solvent removed at reduced pressure, and the residue dried in high vacuo at 100°C. 0.70 mol of NaOMe in MeOH was added, NaCl filtered off under N_2, the filtrate concentrated in vacuo, and the residue distilled in high vacuo at a bath temp. of 160°C. The crude base was dissolved in 1.5 l of water, the aqueous solution extracted three times

with diethyl ether (the extracts were discarded), the aqueous solution freed from ether at reduced pressure, and cleared with charcoal. Water was distilled off in high vacuo until the base began to boil. A small amount of potassium metal was added and the product distilled in high vacuo furnishing 150 g (93%) of a colorless oil, b.p. 83°C/0.03 Torr. – ^{1}H NMR (250 MHz, CD_3CN): δ = 1.05 (t, $^3J_{H,H}$ = 7 Hz, 3H, CH_3CH_2), 1.64–1.85 (m, 4H, 3,9-H), 2.45 (d, $^3J_{P,H}$ = 11 Hz, 3H, CH_3N), 2.45 (d, $^3J_{P,H}$ = 10 Hz, 3H, CH_3N), 2.73 (m_c, 2H, CH_2Me), 2.96–3.22 (m, 6H, 4,8,10-H), 3.27 (m_c, 1H, 2-H), 3.35 (m_c, 1H, 2-H). – ^{15}N NMR (40 MHz, [D$_6$]benzene): δ = 30.8 (d, $^1J_{P,N}$ = −4.0 Hz, N-5), 36.6 (d, $^1J_{P,N}$ = −18.3 Hz, N-11), 47.7 (d, $^1J_{P,N}$ = 25.3 Hz, N-1), 49.1 (d, $^1J_{P,N}$ = −22.0 Hz, N-7). – For characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous NH_3, m.p. ca. 270°C (dec.). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{H,H}$ = 7 Hz, 3H, CH_3CH_2), 1.87–2.02 (m, 4H, 3,9-H), 2.62 (d, $^3J_{P,H}$ = 10.5 Hz, 3H, CH_3N), 2.66 (d, $^3J_{P,H}$ = 10.5 Hz, 3H, CH_3N), 2.88–3.45 (m, 10H, 2,4,8,10-H and CH_2Me), 3.79 (br. m, 1H, HN). – ^{15}N NMR (40 MHz, [D$_6$]DMSO): δ = 27.8 (d, $^1J_{P,N}$ = −30.6 Hz, N-5), 31.9 (d, $^1J_{P,N}$ = −27.5 Hz, N-11), 36.9 (d, $^1J_{P,N}$ = 26.6 Hz, N-7), 45.1 (d, $^1J_{P,N}$ = −28.8 Hz, N-1). – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (NH), 2975, 2940, 1630, 1490, 1387, 1357, 1342, 1329, 1280, 1235, 1120, 1058, 995, 953, 840, 725, 560. – $C_{10}H_{24}F_6N_4P_2$ (376.3): calcd. C 31.92, H 6.43, N 14.89; found C 31.84, H 6.80, N 14.74.

1,6,8,13-Tetraaza-7-phosphoniaspiro[6.6]tridecane Hexafluorophosphate (**10** · HPF_6): By analogy with the procedure used for the preparation of *rac*-**6** · HPF_6, **4** was exchanged for tetramethylenediamine. The reduced lipophilicity of **10** · HPF_6 compared to *rac*-**6** · HPF_6 affords numerous extractions from aqueous solution. Yield 105 g (30%) of colorless crystals, m.p. 228–230°C. – ^{1}H NMR (250 MHz, CD_3OD): δ = 1.62 (m_c, 8H, 3,4,10,11-H), 3.02 (m_c, $^3J_{P,H}$ = 19.5 Hz, 8H, 2,5,9,12-H). – IR (KBr): $\tilde{\nu}$ = 3410 cm^{-1}, 3195 (NH), 2955, 2867, 1630, 1453, 1415, 1363, 1285, 1275, 1220, 1180, 1120, 1103, 1053, 1008, 980, 959, 830, 560, 520, 435. – $C_8H_{20}F_6N_4P_2$ (348.2): calcd. C 27.60, H 5.79, N 16.09; found C 27.66, H 6.16, N 16.29.

1,6,8,13-Tetramethyl-1,6,8,13-tetraaza-7-phosphoniaspiro[6.6]tridecane Hexafluorophosphate (**11** · PF_6): In a 250-ml two-necked flask, equipped as described above, 8.7 g (25 mmol) of **10** · HPF_6 was dissolved in 125 ml of MeCN and 3.36 g (140 mmol) of hexane-washed NaH gradually added under N_2. After cooling to −20°C, 8.80 ml (20.0 g, 140 mmol) of MeI was slowly added and the mixture stirred at room temp., until the gas evolution ceased (ca. 2 h). Excess NaH was cautiously destroyed with *t*BuOH and the solvent removed in high vacuo. From the residue MeCN was removed azeotropically with 100 ml of water at reduced pressure. The crude PF_6 salt was collected by suction and recrystallized from MeOH/water, affording 9.8 g (97%) of colorless crystals, m.p. >300°C (dec.). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.70 (m_c, 8H, 3,4,10,11-H), 2.75 (d, $^3J_{P,H}$ = 10.5 Hz, 12H, CH_3), 3.21 (m_c, $^3J_{P,H}$ = 13.5 Hz, 8H, 2,5,9,12-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3 (d, $^2J_{P,C}$ = 5.1 Hz, C-2,5,9,12), 34.2 (d, $^2J_{P,C}$ = 6.1 Hz, CH_3), 51.2 (s, C-3,4,10,11). – ^{15}N NMR (40 MHz, $CDCl_3$): δ = 32.0 (d, $^1J_{P,N}$ = 33.6 Hz). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 1465, 1436, 1370, 1350, 1338, 1255, 1202, 1172, 1108, 1040, 1004, 957, 875, 853, 835, 730, 725, 488. – $C_{12}H_{28}F_6N_4P_2$ (404.3): calcd. C 35.65, H 6.98, N 13.86; found C 35.66, H 6.98, N 13.80.

6,8,13-Trimethyl-1,6,8,13-tetraaza-7λ^5-phosphaspiro[6.6]tridec-1(7)-ene (**12**) *and 1,6,8-Trimethyl-1,6,8,13-tetraaza-7-phosphoniaspiro[6.6]tridecane Hexafluorophosphate* (**12** · HPF_6): According to the procedure used for the preparation of **3**, 10 g (25 mmol) of **11** · PF_6 gave up to 5.6 g (92%) of a colorless liquid, b.p. 85°C/0.1 Torr. – ^{1}H NMR (250 MHz, CD_3CN): δ = 1.42–1.70 (m, 8H, 3,4,10,11-H), 2.66 (d, $^3J_{P,H}$ = 8.5 Hz, 9H, CH_3), 2.91 (m, 6H, 5,9,12-H), 3.15 (m_c, 2H, 2-H). – ^{15}N NMR (40 MHz, [D$_6$]benzene): δ = 33.9 (d, $^1J_{P,N}$ = −24.5 Hz, N-8,13), 40.5 (d, $^1J_{P,N}$ = −3.0 Hz, N-6), 49.3 (d, $^1J_{P,N}$ = 20.1 Hz, N-1). – For characterization, a sample was precipitated as **12** · HPF_6 with 75% HPF_6 from dil. aqueous NH_3 and recrystallized from water, m.p. 225–228°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.60–1.78 (m, 8H, 3,4,10,11-H), 2.76 (d, $^3J_{P,H}$ = 9.5 Hz, 6H, 1,6-CH_3), 2.77 (d, $^3J_{P,H}$ = 9.5 Hz, 3H, 8-CH_3), 3.10–3.30 (m_c, 8H, 2,5,9,12-H), 4.21 (m_c, 1H, HN). – IR (KBr): $\tilde{\nu}$ = 3390 cm^{-1} (NH), 2932, 1455, 1433, 1405, 1380, 1347, 1334, 1252, 1208, 1191, 1140, 1106, 1084, 1056, 1020, 1005, 965, 954, 834, 727, 555, 513. – $C_{11}H_{26}F_6N_4P_2$ (390.3): calcd. C 33.85, H 6.71, N 14.36; found C 33.24, H 6.65, N 14.20.

5,9-Diaza-1,13-tridecanediamine[44] (**13**): At 30°C 15.7 g (0.100 mol) of 1-bromo-3-chloropropane was added to 176 g (2.00 mol) of tetramethylenediamine over a 30-min period with stirring, whereby the temp. rose to ca. 60°C. Stirring was continued for 3 h at room temp., the unconsumed tetramethylenediamine then distilled off in high vacuo. 13.5 g (0.241 mol) of finely powdered KOH was added and the mixture distilled in high vacuo affording 15.7 g (72.6%) of a viscous oil, b.p. 135–140°C/0.01 torr. – ^{1}H NMR (250 MHz, D_2O): δ = 1.46 (m, 8H, 2,3,11,12-H), 1.63 (m, 2H, 7-H), 2.56 (m, 12H, 1,4,6,8,10,13-H). – The further characterization was performed as **13** · 4 HCl. – ^{1}H NMR (250 MHz, D_2O): δ = 1.77 (m_c, 8H, 2,3,11,12-H), 2.14 (m_c, 2H, 7-H), 3.00–3.22 (m, 12H, 1,4,6,8,10,13-H). – IR (KBr): $\tilde{\nu}$ = 3424 cm^{-1} (NH), 2946, 2800, 2512, 2018, 1595, 1510, 1450, 1404, 1351, 1253, 1103, 1028, 873, 836. – $C_{11}H_{32}Cl_4N_4$ (362.2): calcd. C 36.48, H 8.91, N 15.47; found C 36.31, H 8.84, N 15.30.

(±)-2,7,11,16-Tetraaza-1-phosphoniatricyclo[9.5.0.0^{1,7}]hexadecane Hexafluorophosphate (*rac*-**14** · HPF_6): In a 250-ml two-necked flask, equipped with a mechanical stirrer, gas inlet, dropping funnel with gas outlet, and thermometer, 5.2 g (25 mmol) of PCl_5 was suspended in 50 ml of absolute CH_2Cl_2 and a solution of 12.5 g (125 mmol) of 3,5-dimethyl-1,2,4-triazole[45] (dried in vacuo at 60°C) in 45 ml of pyridine added dropwise to the suspension at 5–10°C under N_2 over a 45-min period. Then 17.4 ml (12.6 g, 125 mmol) of Et_3N was added at 5–10°C and the mixture stirred for an additional 1.5 h, during which time the formerly flesh-colored solution turned red-brown. The mixture was filtered under N_2 and the precipitate washed with 20 ml of absolute CH_2Cl_2. 5.45 g (25 mmol) of **13** was added to the filtrate and CH_2Cl_2 carefully removed at reduced pressure. From the residual solution first Et_3N (ca. 1 h), then pyridine (ca. 2 h) were slowly distilled off, until the temp. of the residue rose to 260°C. After cooling to ca. 100°C, 125 ml of water was added, and the solution was cooled to ca. 10°C. 33 ml (31 mmol) of 75% HPF_6 was added with cooling, the mixture extracted 5 times with 50-ml portions of CH_2Cl_2, the combined organic phases were thoroughly washed with 50 ml of ice-cold 38% H_2SO_4 and then with a $NaHCO_3$ solution; subsequently CH_2Cl_2 was removed in vacuo. Yield 2.69 g (29%) of crude product. An analytical sample as colorless crystals was obtained by recrystallization from water with charcoal, m.p. 153–155°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60–1.75 (m, 8H, 4,5,13,14-H), 2.03 (m_c, 2H, 9-H), 2.85–2.97 (m, 4H), 3.07–3.22 (m, 2H), 3.24–3.32 (m, 2H), 3.32–3.43 (m, 2H), 3.55 (m_c, 2H), 4.15 (m_c, 2H, HN). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2 (C-5,13), 26.4 (d, $^2J_{P,C}$ = 5.5 Hz, C-9), 30.0 (C-4,14), 40.8 (d, $^2J_{P,C}$ = 1.1 Hz, C-3,15), 48.3 (d, $^2J_{P,C}$ = 3.4 Hz, C-8,10), 48.7 (d, $^2J_{P,C}$ = 5.4 Hz, C-6,12). – IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1} (NH), 2930, 1455, 1435, 1405, 1360, 1320, 1260, 1245, 1215, 1195, 1150, 1115, 1100, 1075, 1060, 975, 950, 840, 775, 740, 715, 560, 520, 433. – $C_{11}H_{24}F_6N_4P_2$ (388.3): calcd. C 34.03, H 6.23, N 14.43; found C 34.25, H 6.58, N 14.27.

(Ethylimino)tris(1-pyrrolidinyl)phosphorane (**18**) *and (Ethylamino)tris(1-pyrrolidinyl)phosphonium Hexafluorophosphate* (**18** · HPF_6): In a 3-l four-necked flask, equipped with a mechanical stirrer, dropping funnel, two gas inlets with bubble counters (for N_2 and $EtNH_2$), a gas outlet, and thermometer, 208 g (1.00 mol) of PCl_5 was slurried in 1500 ml of CH_2Cl_2 under N_2, and 248 ml (213 g, 3.00 mol) of pyrrolidine and then 557 ml (405 g, 4.00 mol) of Et_3N were slowly added with stirring to the cooled mixture (dry ice bath) at such a rate that the temp. of the solution was kept below −30°C. The mixture was then allowed to warm to room temp., stirred for 2 h, and recooled to 0°C. 62.3 ml (49.6 g, 1.10 mol) of $EtNH_2$ was passed into the mixture which was again allowed to warm to room temp., the precipitated Et_3N · HCl was filtered off, the filtrate concentrated to ca. 400 ml and shaken with a solution of 132 g (1.20 mol) of $NaBF_4$ in 250 ml of water. The organic phase was separated and the aqueous phase extracted with 50 ml of CH_2Cl_2. The combined organic phases were concentrated by rotary evaporation, the residue was dissolved in 250 ml of MeOH and the solution again concentrated by rotary evaporation in order to remove last traces of CH_2Cl_2 (control by ^{1}H NMR!). The residue was dissolved in 350 ml of MeOH and a solution of 70 g (1.00 mol) of KOMe in 400 ml of MeOH added. After the precipitated KBF_4 had settled it was filtered off under N_2, the solvent was removed at reduced pressure and the residue heated in high vacuo until it began to boil. After addition of 0.5 g of Na_2O (or BaO) the product was fractionated in vacuo, the first fraction (8 ml) being discarded. Yield 236 g (83%) of a colorless oil, b.p. 95°C/5 · 10^{-2} Torr. – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.53 (m, 15H, CH_2CH_3 and CH_2CH_2N), 3.12 (m, 12H, CH_2CH_2N), 3.54 (dq, $^3J_{P,H}$ = 17.3 Hz, 2H, CH_2Me). – For further characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous $EtNH_2$ and recrystallized from MeOH/water, m.p. 221°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (dt, $^3J_{H,H}$ = 7, $^4J_{P,H}$ = 1.2 Hz, 3H, CH_3CH_2), 1.94 (m, 12H, CH_2CH_2N), 2.99 (ddq, $^3J_{H,H}$ = 7, $^3J_{H,HN}$ = 7, $^3J_{P,H}$ = 9 Hz, CH_2Me), 3.23 (m, 12H, CH_2CH_2N), 3.78 (br. m, 1H, HN). – IR (KBr): $\tilde{\nu}$ = 3378 cm^{-1} (NH), 3052, 2974, 2876, 1458, 1416, 1215, 1087, 837. – $C_{14}H_{30}F_6N_4P_2$ (430.4): calcd. C 39.07, H 7.03, N 13.02; found C 39.39, H 7.04, N 12.85.

General Procedure for the Precipitation or Recrystallization of Tetrafluoroborate, Perchlorate, Iodide, and Hexafluorophosphate Salts from Aqueous Ethylamine: The crude product was dissolved in ca. 10 parts (or the indicated amount) of 70% aqueous $EtNH_2$ and the solution eventually cleared with charcoal. A 20% excess (based on a 100% yield of the desired salt) or the indicated amount of NaI, $NaBF_4$, or $NaClO_4$ (dissolved in a minimum amount of water) or 75% HPF_6 and/or (for precipitation/recrystallization) water was added to the hand-warm solution until turbidity persisted. After clearing of the solution by addition of a minimum amount of 70% aqueous $EtNH_2$, it was allowed to cool to room temp. or to the temp. indicated and, if necessary, stirred with a glass-covered stirring bar to favor crystallization.

After several days the crystals were collected by suction, washed with aqueous $EtNH_2$ of the same concentration as the mother liquor, and dried in high vacuo at 60°C.

General Procedure for the Liberation of Triaminophosphorane Bases from their Salts with 50% aqueous KOH Solution: The crude salt was dried in high vacuo. At least 3 equivalents of a 50% aqueous KOH solution was added with stirring, and eventually so much water was added that the two phases could be separated (precipitated KCl favors formation of emulsions). For the control of complete separation of the base, the aqueous phase was extracted with diethyl ether. The organic phases were combined, the solvent was removed in vacuo, and the residue heated in high vacuo until it began to boil. After addition of ca. 0.5 g of Na_2O (or BaO), the crude product was fractionated in vacuo.

tert-Butylammonium Chloride: 527 ml (366 g, 5.00 mol) of *tert*-butylamine was added to a solution of 524 ml (839 g, 5.00 mol) of 1,1,2,2-tetrachloroethane in 750 ml of trichloroethylene at such a rate that the reaction remained under control (reaction temp. 25°C or higher). After the mixture had been kept at 50°C for 2 h the precipitate was collected by suction, washed with trichloroethylene, and dried in high vacuo at ca. 40–50°C providing 520 g (95%) of colorless leaves. The mother liquor could serve as solvent for the next batch.

(tert-Butylimino)phosphorus Trichloride[24] (**20a**): A 4-l one-necked flask was charged with 822 g (7.50 mol) of *tert*-butylammonium chloride, 1562 g (7.50 mol) of PCl_5, and 2.0 l of PCl_3, and the slurry was refluxed for 5–6 d (jacketed coil condenser, b.p. of PCl_3 is only 75°C, and 22.5 mol of HCl gas are evolved!). PCl_3 was then distilled off under normal pressure, until the temp. had reached 105–110°C (caution, **20a** is thermally unstable). After cooling to 20°C, the solution was saturated with SO_2 (destruction of excess PCl_5). $SOCl_2$, PCl_3, and $POCl_3$ were distilled off at 75 Torr (cooling agent at −20°C), then an intermediate fraction up to ca. 78°C, finally 1120 ml (1380 g, 88.3%) of the desired product as a colorless liquid at 61°C/22 Torr.

(tert-Butylimino)tris(dimethylamino)phosphorane (**2b**) *and (tert-Butylamino)tris(dimethylamino)phosphonium Hexafluorophosphate* (**2b** · HPF_6): A 500-ml three-necked flask, equipped with a mechanical stirrer, two gas inlets with bubble counters (for N_2 and amine), a dry ice condenser with gas outlet and bubble counter, and thermometer, was charged with 34.2 ml (41.7 g, 0.200 mol) of **20a**. At −15 to −20°C (just above the freezing point of **20a**) 144 g (3.20 mol) of Me_2NH was added by condensation. After 2 h the solution was allowed to warm to room temp. and refluxed for 1 h; excess Me_2NH was distilled off and the base liberated with a 50% KOH solution according to the general procedure affording 31 g (80%) of a colorless liquid, b.p. 32°C/0.02 Torr. – ^1H NMR (90 MHz, CD_3CN): δ = 1.10 [d, $^4J_{P,H}$ = 1 Hz, 9H, $(CH_3)_3C$], 2.50 [d, $^3J_{P,H}$ = 9 Hz, 18H, $(CH_3)_2N$]. – ^{15}N NMR (40 MHz, [D$_6$]benzene): δ = 23.9 (d, $^1J_{P,N}$ = −21.9 Hz, NMe_2), 67.1 (d, $^1J_{P,N}$ = −12.2 Hz, N*t*Bu). – For characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous $EtNH_2$ and recrystallized from MeOH/water, m.p. >310°C (dec.). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.32 [d, $^4J_{P,H}$ > 1 Hz, 9H, $(CH_3)_3C$], 2.77 (d, $^3J_{P,H}$ = 10 Hz, 18H, CH_3N), 3.57 (br. d, $^2J_{P,H}$ = 10 Hz, 1H, HN). – ^{15}N NMR (40 MHz, $CDCl_3$, **2b** · $HOSO_2C_4F_9$): δ = 22.8 (d, $^1J_{P,N}$ = −33.5 Hz, NMe_2), 63.3 (d, $^1J_{P,N}$ = −30.5 Hz, N*t*Bu). – IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1}, 3360 (NH), 2950, 1630, 1470, 1420, 1394, 1371, 1307, 1230, 1185, 1063, 992, 837, 768, 753, 560. – $C_{10}H_{28}F_6N_4P_2$ (380.3): calcd. C 31.58, H 7.42, N 14.73; found C 31.63, H 7.51, N 14.70.

(tert-Butylimino)tris(1-pyrrolidinyl)phosphorane (**2e**) *and (tert-Butylamino)tris(1-pyrrolidinyl)phosphonium Tetrafluoroborate* (**2e** · HBF_4): A 250-ml three-necked flask, equipped with a mechanical stirrer, dropping funnel, gas inlet, reflux condenser with gas outlet, and thermometer, was charged with 116.0 ml (99.6 g, 1.400 mol) of pyrrolidine under N_2. Cooling in a MeOH/dry ice bath, 34.2 ml (41.7 g, 0.200 mol) of **20a** was slowly added at such a rate that the temp. of the solution was kept below −40°C. The mixture was allowed to warm to 80°C and then refluxed for 2 h. After cooling, 300 ml of a 50% KOH solution was added with stirring, the organic phase separated, and the aqueous phase extracted with 50 ml of pyrrolidine. From the combined organic phases pyrrolidine was distilled off at atmospheric pressure, the residue heated in high vacuo until it began to boil, then 0.5 g of Na_2O (or BaO) was added and the base fractionated in high vacuo to afford 59.9 g (96.0%) of a slightly yellowish liquid, b.p. 108°C/5 · 10^{-2} Torr, m.p. −24°C. – ^1H NMR (250 MHz, [D$_6$]benzene): δ = 1.55 (m, 12H, CH_2CH_2N), 1.57 [s, 9H, $(CH_3)_3C$], 3.11 (m, 12H, CH_2CH_2N). – For further characterization a sample was converted to the HBF_4 salt according to the general procedure, m.p. 95–97°C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 [s, 9H, $(CH_3)_3C$], 1.94 (m, 12H, CH_2CH_2N), 3.25 (m, 12H, CH_2CH_2N), 4.25 (br. d, $^2J_{P,H}$ = 10 Hz, 1H, HN). – IR (KBr): $\tilde{\nu}$ = 3293 cm^{-1} (NH), 3056, 2962, 2866, 1465, 1432, 1390, 1364, 1226, 1205, 1083, 1029. – $C_{16}H_{34}BF_4N_4P$ (400.3): calcd. C 48.02, H 8.56, N 14.00; found C 48.38, H 8.58, N 13.77.

(1,1,3,3-Tetramethylbutylimino)phosphorus Trichloride (**20b**): In a 500-ml one-necked flask, 56.3 g (0.340 mol) of pure (1,1,3,3-tetramethylbutyl)ammonium chloride (from crude "*tert*-octylamine" and HCl gas in EtOH, suction, and drying in high vacuo) and 70.8 g (0.340 mol) of PCl_5 were slurried in 200 ml of PCl_3, and the mixture was heated under reflux for 48 h (jacketed coil condenser, b.p. of PCl_3 is only 75°C, and 1.02 mol of HCl gas are evolved!). After 24 h it became homogeneous, and the HCl evolution was strongly reduced. The solvent was distilled off at normal pressure, and after cooling to 20°C, the residue was saturated with SO_2 (destruction of excess PCl_5) and the product fractionated in vacuo. After cooling the product was purged with N_2. Yield 75.4 ml (85.1 g, 95%) of a colorless liquid, b.p. 73°C/2 Torr (48°C/0.5 Torr). d_4^{20} = 1.13. – Because of extensive sensitivity of the material towards hydrolysis, a CHN analysis was renounced. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.02 [s, 9H, $(CH_3)_3C$], 1.38 [s, 6H, $(CH_3)_2C$], 1.49 (d, $^4J_{P,H}$ = 7.7 Hz, 2H, CH_2). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.51 [s, $(CH_3)_3C$], 33.46 [d, $^3J_{P,C}$ = 11 Hz, $(CH_3)_2C$], 56.72 (CH_2), 56.93 (CMe_3); CMe_2 signal hidden by noise.

Tris(dimethylamino)(1,1,3,3-tetramethylbutylimino)phosphorane (**2c**) *and Tris(dimethylamino)(1,1,3,3-tetramethylbutylamino)phosphonium Hexafluorophosphate* (**2c** · HPF_6): In a 1-l four-necked flask, equipped with a mechanical stirrer, two gas inlets (for N_2 and amine), a dropping funnel, dry ice condenser with gas outlet and bubble counter, and thermometer, 118.0 ml (90.0 g, 2.00 mol) of Me_2NH were condensed under N_2 by external cooling in a MeOH/dry ice bath. Then a solution of 58.5 ml (66.0 g, 0.250 mol) of **20b** in 200 ml of THF was gradually added within 2 h at −70°C. After stirring for 1 h, the mixture was allowed to warm to room temp. slowly and set aside for 12 h. Precipitated Me_2NH · HCl was filtered off and the residue washed with two 30-ml portions of warm THF. The filtrate was concentrated by rotary evaporation and the product dried in high vacuo. Yield 80.1 g (98%) of a tan solid. The base was liberated with a 50% KOH solution according to the general procedure affording 68.9 g (97%) of a colorless liquid, b.p. 81°C/0.1 Torr, m.p. −28°C. – ^1H NMR (250 MHz, [D$_6$]benzene): δ = 1.32 [s, 9H, $(CH_3)_3C$], 1.46 [s, 6H, $(CH_3)_2C$], 1.72 (d, $^4J_{P,H}$ = 3 Hz, 2H, CH_2), 2.48 [d, $^3J_{P,H}$ = 9.5 Hz, 18H, $(CH_3)_2N$]. – For further characterization, a sample was precipitated as HPF_6 salt according to the general procedure, m.p. 96°C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.04 [s, 9H, $(CH_3)_3C$], 1.39 [s, 6H, $(CH_3)_2C$], 1.63 (s, 2H, CH_2), 2.76 [d, $^3J_{P,H}$ = 9.8 Hz, 18H, $(CH_3)_2N$], 3.58 (br. d, $^2J_{P,H}$ = 8.6 Hz, 1H, HN). – IR (KBr): $\tilde{\nu}$ = 3336 cm^{-1} (NH), 2948, 1478, 1381, 1366, 1301, 1184, 1066, 1044, 995, 851. – $C_{14}H_{36}F_6N_4P_2$ (436.4): calcd. C 38.53, H 8.32, N 12.84; found C 39.23, H 8.27, N 12.96.

2,3,3-Trimethyl-1-butene: 10 ml of concd. H_3PO_4 was added to crude (ether-containing) 2,3,3-trimethyl-1-butanol (prepared from 0.66 mol of pinacolon according to ref.[25]) and the mixture refluxed for 3 h. The resulting solution was fractionated (effective column with sufficient refluxing) affording a forerun of diethyl ether and a fraction containing the product as olefin/water azeotrope (b.p. 67°C). After phase separation, some sodium metal was added and the product once more distilled over a 20-cm Vigreux column affording 52.9 g (82%, ref.[25] 82%) of a colorless liquid, b.p. 76–77°C (ref.[25] 76–79°C). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.06 [s, 9H, $(CH_3)_3C$], 1.74 (dd, $^4J_{H,H}$ = 1.5, $^4J_{H,H}$ = 0.75 Hz, 3H, CH_3CtBu), 4.64–4.73 (m, 2H, CH_2).

N-(1,1,2,2-Tetramethylpropyl)formamide: The procedure described in ref.[25] was applied, but starting from 2,3,3-trimethyl-1-butene rather than from 2,3,3-trimethyl-1-butanol; the workup was also slightly altered: The reaction mixture was poured on 1 kg of ice and brought to pH 7–8 with a 50% NaOH solution with external cooling with an ice/NaCl bath. The mixture was extracted with three 300-ml portions of diethyl ether, and the combined ethereal phases were dried with Na_2SO_4. After removal of the solvent in vacuo, the residue was recrystallized from a small amount of hexane affording 59.5 g (78%, ref.[25] 85%) of colorless crystals, m.p. 139°C (ref.[25] 138–139°C). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.96 [s, 9H, $(CH_3)_3C$], 1.30 [s, 6H, $(CH_3)_2CtBu$], 6.27 (br., 1H, HN), 8.22 (d, $^3J_{H,H}$ = 12 Hz, 1H, CHO).

(1,1,2,2-Tetramethylpropyl)ammonium Chloride[25]: Preparation according to a literature procedure, yield 57 g (90%, ref.[25] 93%) as colorless crystals, m.p. >164°C (subl.) (ref.[25] 305–306°C). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.08 [s, 9H, $(CH_3)_3C$], 1.42 [s, 6H, $(CH_3)_2CtBu$], 8.28 (br. s, 3H, H_3N^+).

(1,1,2,2-Tetramethylpropylimino)phosphorus Trichloride (**20c**): According to the procedure used for the synthesis of **20b**, but refluxing of the mixture was prolonged to 72 h. The reaction of 31.8 g (0.210 mol) of (1,1,2,2-tetramethylpropyl)ammonium chloride afforded 37.6 ml (46.5 g, 89%) of a colorless liquid, b.p. 46°C/1.2 Torr. d_4^{20} = 1.24. – Because of extensive sensitivity of **20c** towards hydrolysis a CHN analysis was renounced. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.91 [s, 9H, $(CH_3)_3C$], 1.28 [s, 6H, $(CH_3)_2CtBu$].

Tris(dimethylamino)(1,1,2,2-tetramethylpropylimino)phosphorane (**2d**) *and Tris(dimethylamino)(1,1,2,2-tetramethylpropylamino)phosphonium Hexafluorophosphate* (**2d** · HPF_6): In a 250-ml three-necked flask, equipped with a mechanical stirrer, two gas inlets (for N_2 and amine), a dropping funnel, and dry ice condenser with gas outlet and bubble counter, 50.0 ml (38.0 g, 844

mmol) of Me_2NH were condensed under N_2 with external cooling in a dry ice bath. Then 10.1 ml (12.5 g, 50.0 mmol) of **20c** was slowly added neat within 2 h to the gently refluxing mixture (ice bath, b.p. Me_2NH: 7°C). The mixture was refluxed for an additional 3 h, after which time excess Me_2NH was distilled off. The base was liberated with a 50% KOH solution according to the general procedure. Drying of the free base in high vacuo afforded 12.8 g (93%) of a colorless solid, which could be purified by distillation or sublimation (10^{-3} Torr), b.p. 81°C/5 · 10^{-2} Torr, m.p. 56°C. – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.30 [s, 9H, $(CH_3)_3C$], 1.33 [s, 6H, $(CH_3)_2CtBu$], 2.48 [d, $^3J_{P,H}$ = 9.5 Hz, 18H, $(CH_3)_2N$]. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 1455, 1316, 1189, 1156, 1060, 962, 778, 719, 702. – $C_{13}H_{33}N_4P$ (276.4): calcd. C 56.49, H 12.03, N 20.27; found C 56.30, H 11.74, N 20.24. – For further characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous $EtNH_2$ and recrystallized from MeOH/water, m.p. 218–219°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 [s, 9H, $(CH_3)_3C$], 1.26 [s, 6H, $(CH_3)_2CtBu$], 2.78 [d, $^3J_{P,H}$ = 10.1 Hz, 18H, $(CH_3)_2N$], 3.22 (br. d, $^2J_{P,H}$ = 7.3 Hz, 1H, HN). – IR (KBr): $\tilde{\nu}$ = 3374 cm^{-1} (NH), 2954, 1475, 1386, 1302, 1188, 1168, 1142, 1062, 1043, 995, 841. – $C_{13}H_{34}F_6N_4P_2$ (422.4): calcd. C 36.97, H 8.11, N 13.26; found C 37.26, H 8.15, N 13.13.

Tris(1-pyrrolidinyl)(1,1,2,2-tetramethylpropylimino)phosphorane (**2f**) *and Tris(1-pyrrolidinyl)(1,1,2,2-tetramethylpropylamino)phosphonium Tetrafluoroborate* (**2f** · HBF_4): According to the procedure used for the preparation of **2d**, 20.2 ml (25.0 g, 100 mmol) of **20c** gave 31.9 g (90%) of a colorless solid, m.p. 61°C, b.p. 133°C/10^{-2} Torr. – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.35 [s, 9H, $(CH_3)_3C$], 1.44 [s, 6H, $(CH_3)_2CtBu$], 1.55 (m, 12H, CH_2CH_2N), 3.10 (m, 12H, CH_2CH_2N). – IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1}, 2858, 1465, 1351, 1330, 1315, 1148, 1080, 998. – $C_{19}H_{39}N_4P$ (354.5): calcd. C 64.37, H 11.09, N 15.80; found C 64.65, H 11.26, N 15.51. – For further characterization a sample was precipitated as **2f** · HBF_4 from aqueous $EtNH_2$ according to the general procedure, m.p. 193°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00 [s, 9H, $(CH_3)_3C$], 1.29 [s, 6H, $(CH_3)_2CtBu$], 1.96 (m, 12H, CH_2CH_2N), 3.26 (m, 12H, CH_2CH_2N), 3.65 (br. d, $^2J_{P,H}$ = 8.2 Hz, 1H, HN). – IR (KBr): $\tilde{\nu}$ = 3298 cm^{-1} (NH), 2964, 2876, 1458, 1394, 1378, 1368, 1296, 1234, 1108. – $C_{19}H_{40}BF_4N_4P$ (442.3): calcd. C 51.59, H 9.12, N 12.67; found C 51.52, H 9.22, N 12.57.

(tert-Butylimino)(diethylamino)phosphorus Dichloride[46] (**21b**): In a three-necked flask, equipped with a mechanical stirrer, gas inlet, dropping funnel with gas outlet, and thermometer, 17.1 ml (20.9 g, 100 mmol) of **20a** was dissolved in 100 ml of cyclohexane under N_2. 15.6 ml (11.0 g, 150 mmol) of Et_2NH and 20.9 ml (15.2 g, 150 mmol) of Et_3N were successively added at such a rate that the reaction remained under control (eventually cooling). After 12 h at room temp., the mixture was heated to 50°C for 6 h. After cooling the precipitated Et_3N · HCl was filtered off under N_2, the solvent removed at reduced pressure, and the product distilled in vacuo, affording 21.8 g (89%) of a colorless liquid, b.p. 72°C/2.5 Torr. – Due to sensitivity of the material to hydrolysis a CHN analysis was renounced. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.16 (t, $^3J_{H,H}$ = 7 Hz, 6H, CH_3CH_2), 1.32 [d, $^4J_{P,H}$ = 1 Hz, 9H, $(CH_3)_3C$], 3.28 (dq, $^3J_{P,H}$ = 17.5 Hz, 4H, CH_2Me).

(±)-2-(tert-Butylimino)-2-(diethylamino)-1-methyl-1,3,2λ^5-diazaphosphinane (*rac*-**22b**) *and (±)-2-(tert-Butylamino)-2-(diethylamino)-1-methyl-1,3,2-diazaphosphinanium Hexafluorophosphate* (*rac*-**22b** · HPF_6) *from* **21b**: In a 500-ml four-necked flask, equipped with a mechanical stirrer, gas inlet, two dropping funnels, a reflux condenser with gas outlet, and thermometer, 349 ml (367.7 g, 1.50 mol) of **21b** and a solution of 233 ml (198 g, 2.25 mol) of **4** in 117 ml of MeCN were synchronously added dropwise within 24 h to 900 ml of MeCN, while the mixture was kept at ca. 50°C. After cooling, precipitated **4** · 2 HCl was filtered off and the solvent removed in vacuo. The base was liberated from the residue by the addition of a 50% KOH solution according to the general procedure and rapidly distilled in high vacuo (<0.05 Torr), until the temp. of the distillation residue had reached 170°C or until formation of non-condensing components (cloud tracks) was observed. The crude product was fractionated; an occasionally occurring yellowish forerun could be decolorized by treatment with sodium metal at 100°C; it could be avoided, if the dehydrated crude product was treated with sodium metal; but the base slowly reacted with sodium with the formation of a salt and therefore an amount of base equivalent to the added sodium remained in the distillation residue. Yield 271 g (69%) of a colorless oil. From intermediate fractions and residues the base was precipitated with $NaBF_4$ from aqueous solution and liberated from the latter with excess KOH in MeOH. After filtration of KBF_4 and concentration of the filtrate at reduced pressure, further product was obtained and purified by distillation, b.p. 72°C/5 · 10^{-3} Torr. – ^{1}H NMR (250 MHz, CD_3CN): δ = 1.00 (t, $^3J_{H,H}$ = 7 Hz, 6H, CH_3CH_2), 1.14 [d, $^4J_{P,H}$ = 1.4 Hz, 9H, $(CH_3)_3C$], 1.79 (m_c, 2H, 5-H), 2.41 (d, $^3J_{P,H}$ = 10 Hz, 3H, CH_3N), 3.00 (m, 8H, 4,6-H, and CH_2Me); HN proton exchanged with CD_3CN. – For characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous NH_3, m.p. 172–174°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15 (t, $^3J_{H,H}$ = 7.5 Hz, 6H, CH_3CH_2), 1.34 [s, 9H, $(CH_3)_3C$], 1.67 (br. s, 1H, HN*t*Bu), 1.92 (m_c, 2H, 5-H), 2.72 (d, $^3J_{P,H}$ = 10 Hz, 3H, CH_3N), 3.0–3.4 (m, 8H, 4,6-H and CH_2Me), 3.69 (m_c, 1H, 3-H). – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (NH), 2980, 1625, 1475, 1416, 1395, 1385, 1372, 1330, 1287, 1230, 1205, 1168, 1114, 1100, 1070, 1028, 990, 955, 840, 748, 703, 560. – $C_{12}H_{30}F_6N_4P_2$ (406.3): calcd. C 35.47, H 7.44, N 13.79; found C 35.54, H 7.71, N 13.56.

rac-**22b** *from* **20a**: A 10-l three-necked flask, equipped with a mechanical stirrer, gas inlet, dropping funnel with gas outlet, and thermometer, was charged with 513 ml (626 g, 3.00 mol) of **20a**, 2.5 l of absolute CH_2Cl_2. At 5°C, 343 ml (241 g, 3.30 mol) of Et_2NH and 460 ml (334 g, 3.30 mol) of Et_3N were added successively under N_2, both over a 1-h period. After 48 h, 5.4 l of absolute CH_2Cl_2 and, with cooling to 5°C, 714 ml (608 g, 6.90 mol) of **4** were added within 1 h. After 4 d at room temp., precipitated **4** · 2 HCl was filtered off and the solvent removed in vacuo. From the residue CH_2Cl_2 was completely removed (^{1}H-NMR control!) azeotropically with water at reduced pressure. Workup as described above afforded 554–562 g (71–72%) of a colorless oil.

2-(tert-Butylimino)-2-(diethylamino)-1,3-dimethyl-1,3,2λ^5-diazaphosphinane (BEMP, **23b**), *2-(tert-Butylamino)-2-(diethylamino)-1,3-dimethyl-1,3,2-diazaphosphinanium Hexafluorophosphate* (**23b** · HPF_6), *and 2-(tert-Butylmethylamino)-2-(diethylamino)-1,3-dimethyl-1,3,2-diazaphosphinanium Hexafluorophosphate* (**15b** · PF_6): In a 1-l three-necked flask, equipped with a mechanical stirrer, dropping funnel with gas outlet, and thermometer, 231 ml (280 g, 2.00 mol) of trimethyl phosphate was rapidly added with stirring under N_2 to a mixture of 137 g (0.50 mol) of **23b** and 390 g (1.50 mol) of *rac*-**22b** at such a rate that the temp. of the solution was kept below 100°C. The mixture was then heated for 7 h at 100°C and cooled to room temp. Then 9.6 g (80 mmol) of *t*BuCOCl and 6 mol of a 50% KOH solution were successively added with stirring, stirring being continued for 3 h. The organic phase was separated and the aqueous phase extracted with diethyl ether. The combined organic phases were concentrated at reduced pressure and the product heated in high vacuo until it began to boil. After cooling to room temp., 9.6 g (80 mmol) of *t*BuCOCl was added and the product distilled. After taking off a forerun (excess *t*BuCOCl), the product was fractionated affording 493 g (87%, based on *rac*-**22b**) of a colorless oil, b.p. 70°C/0.03 Torr. – ^{1}H NMR (250 MHz, CD_3CN): δ = 1.00 (t, $^3J_{H,H}$ = 7 Hz, 6H, CH_3CH_2), 1.14 [d, $^4J_{P,H}$ = 1.4 Hz, 9H, $(CH_3)_3C$], 1.81 (m_c, 2H, 5-H), 2.42 (d, $^3J_{P,H}$ = 10 Hz, 6H, CH_3N), 2.93–3.15 (m, 8H, 4,6-H, and CH_2Me). – ^{15}N NMR (40 MHz, [D$_6$]benzene): δ = 34.6 (d, $^1J_{P,N}$ = 4.5 Hz, N-1,3), 47.5 (d, $^1J_{P,N}$ = 46.3 Hz, NEt_2), 68.3 (s, N*t*Bu). – For characterization, a sample was precipitated as HPF_6 salt from dil. aqueous NH_3 with 75% HPF_6, m.p. ca. 300°C (dec.). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H,H}$ = 7 Hz, 6H, CH_3CH_2), 1.35 [s, 9H, $(CH_3)_3C$], 1.68 (d, $^2J_{P,H}$ = 2 Hz, 1H, HN), 2.02 (m_c, 2H, 5-H), 2.68 (d, $^3J_{P,H}$ = 10 Hz, 6H, CH_3N), 3.11 (m_c, 4H, CH_2Me), 3.28 (m_c, 4H, 4,6-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 (d, $^3J_{P,C}$ = 1.9 Hz, CH_3CH_2), 24.1 (d, $^3J_{P,C}$ = 4.8 Hz, C-5), 30.6 [d, $^3J_{P,C}$ = 4.6 Hz, $(CH_3)_3C$], 35.1 (d, $^2J_{P,C}$ = 4.6 Hz, CH_3N), 39.3 (d, $^2J_{P,C}$ = 4.1 Hz, CH_2Me), 50.1 (d, $^2J_{P,C}$ = 1.7 Hz, C-4,6), 53.3 (d, $^2J_{P,C}$ = 1.7 Hz, CMe_3). – ^{15}N NMR (40 MHz, $CDCl_3$, **23b** · $HOSO_2C_4F_9$): δ = 27.9 (d, $^1J_{P,N}$ = −28.4 Hz, N-1,3), 51.0 (d, $^1J_{P,N}$ = −27.1 Hz, NEt_2), 59.4 (d, $^1J_{P,N}$ = −30.5 Hz, NH*t*Bu). – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (NH), 2976, 2940, 1630, 1475, 1390, 1371, 1293, 1268, 1226, 1198, 1163, 1130, 1055, 1018, 990, 955, 838, 757, 739, 695, 560. – $C_{13}H_{32}F_6N_4P_2$ (420.4): calcd. C 37.15, H 7.67, N 13.33; found C 37.11, H 8.01, N 13.29.

From the separated aqueous phase (concd. KOH) **15b** · PF_6 was precipitated by addition of 75% HPF_6, m.p. >250°C (dec.). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, $^3J_{H,H}$ = 7 Hz, 6H, CH_3CH_2), 1.37 [s, 9H, $(CH_3)_3C$], 2.07 (m_c, 2H, 5-H), 2.70 [d, $^3J_{P,H}$ = 11 Hz, 3H, CH_3NtBu], 2.73 (d, $^3J_{P,H}$ = 10 Hz, 6H, CH_3NCH_2), 3.07 (m_c, 4H, CH_2Me), 3.22 (m_c, 4H, 4,6-H). – ^{13}C NMR (100 MHz, $CDCl_3$, 233 K): δ = 14.0 (d, $^3J_{P,C}$ = 0.9 Hz, CH_3CH_2), 22.9 (d, $^3J_{P,C}$ = 8.4 Hz, C-5), 28.0 [d, $^3J_{P,C}$ = 2.8 Hz, $(CH_3)_3C$], 31.8 (d, $^2J_{P,C}$ = 7.3 Hz, CH_3NtBu), 37.5 (d, $^2J_{P,C}$ = 4.7 Hz, 1,3-CH_3), 40.7 (d, $^2J_{P,C}$ = 4.6 Hz, CH_2Me), 49.8 (d, $^2J_{P,C}$ = 3.4 Hz, C-4,6), 58.2 (d, $^2J_{P,C}$ = 2.1 Hz, CMe_3). – ^{15}N NMR (40 MHz, $CDCl_3$, **15b** · $OSO_2C_4F_9$): δ = 31.4 (d, $^1J_{P,N}$ = −34.0 Hz, N-1,3), 48.2 (d, $^1J_{P,N}$ = −28.1 Hz, NEt_2), 58.4 (d, $^1J_{P,N}$ = −26.7 Hz, NMe*t*Bu). – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2940, 2895, 1630, 1475, 1384, 1373, 1290, 1275, 1264, 1206, 1168, 1091, 1063, 1052, 1023, 960, 925, 877, 837, 739, 720, 670, 560. – $C_{14}H_{34}F_6N_4P_2$ (434.4): calcd. C 38.71, H 7.89, N 12.90; found C 38.76, H 8.09, N 12.82.

Polymer-BEMP **23d**: In a 1-l four-necked flask, equipped with a mechanical stirrer, dropping funnel, gas inlet, and reflux condenser with gas outlet, 100 g of Merrifield polymer (5 mmol Cl/g resin = 500 mmol) was slurried in 240 ml of THF/MeCN (1:1) under N_2 and 161 ml (154 g, 0.59 mol) of *rac*-**22b** added in one batch; after the exothermic reaction had ceased, the mixture was heated for 7 h in an oil bath kept at 70°C (caution, vigorously bumping occurred on heating above the boiling point). The reaction mixture was poured on a column with a sintered-glass plate and the polymer first rinsed with 92–117 g of *rac*-**22b** in 400 ml of THF/MeCN (1:1), until the

last eluted base fraction was free from Cl^- ($AgNO_3$/dil. HNO_3); then the polymer was rinsed with THF/MeCN, until all soluble base had been extracted. The polymer was dried in high vacuo at 100−150°C (the hose coupling must contain a sintered glass plate!). After removal of the solvent, excess *rac*-**22b** could be recovered from the mother liquor as described above. − Elemental analysis: C 68.87 H 9.84 Cl 1.48 N 12.04. − The remaining chlorine in the polymer could not be replaced by nucleophiles like thiolate, indicating that it was not bound ionically and not in a reactive benzylic position.

2-(Diethylamino)-1,3-dimethyl-2-(methylimino)-1,3,2λ⁵-diazaphosphinane (**16**) *and 2-(Diethylamino)-1,3-dimethyl-2-(methylamino)-1,3,2-diazaphosphinanium Hexafluorophosphate* (**16** · HPF_6): In 43.4 g (100 mmol) of **15b** · PF_6 the anion was exchanged for Cl^-. After removal of the solvent at reduced pressure, the residue was heated for 3 h to 240°C in high vacuo. Then 100 mmol of NaOMe in MeOH was added to the residue, precipitated NaCl filtered off, the solvent removed at reduced pressure, and the residue subjected to fractional distillation in high vacuo, affording 16.0 g (70%) of a colorless oil, b.p. 70°C/0.01 Torr. − ^1H NMR (250 MHz, CD_3CN): δ = 1.03 (t, $^3J_{H,H}$ = 7 Hz, 6H, CH_3CH_2), 1.79 (m_c, 2H, 5-H), 2.49 (d, $^3J_{P,H}$ = 10 Hz, 6H, 1,3-CH_3), 2.61 (d, $^3J_{P,H}$ = 23 Hz, 3H, CH_3N), 2.97−3.13 (m, 8H, 4,6-H, and CH_2Me). − ^{15}N NMR (40 MHz, [D_6]benzene): δ = 24.5 (d, $^1J_{P,N}$ = 26.2 Hz, P=NMe), 33.6 (d, $^1J_{P,N}$ = −6.2 Hz, N-1,3), 49.5 (d, $^1J_{P,N}$ = −28.3 Hz, NEt_2). − For further characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous NH_3. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H,H}$ = 7 Hz, 6H, CH_3CH_2), 2.00 (m_c, 2H, 5-H), 2.61 (dd, $^3J_{H,H}$ = 5.5, $^3J_{P,H}$ = 13 Hz, 3H, CH_3NH), 2.68 (d, $^3J_{P,H}$ = 10 Hz, 6H, 1,3-CH_3), 3.13 (m_c, 4H, CH_2Me), 3.28 (m_c, 4H, 4,6-H), 3.66 (m_c, 1H, HN). − ^{15}N NMR (40 MHz, [D_6]DMSO): δ = 22.1 (d, $^1J_{P,N}$ = 29.7 Hz, NHMe), 26.6 (d, $^1J_{P,N}$ = 27.2 Hz, N-1,3), 50.3 (d, $^1J_{P,N}$ = 29.2 Hz, NEt_2). − IR (KBr): $\tilde{\nu}$ = 3405 cm^{-1} (NH), 2975, 2940, 2910, 1630, 1470, 1384, 1293, 1266, 1212, 1168, 1131, 1095, 1056, 1029, 989, 961, 932, 835, 795, 741, 718, 560, 518, 487. − $C_{10}H_{26}F_6N_4P_2$ (378.3): calcd. C 31.75, H 6.93, N 14.81; found C 31.67, H 7.30, N 14.76.

(±)-2-(tert-Butylimino)-2-(dimethylamino)-1-methyl-1,3,2λ⁵-diazaphosphinane (*rac*-**22a**) *and (±)-2-(tert-Butylamino)-2-(dimethylamino)-1-methyl-1,3,2-diazaphosphinanium Hexafluorophosphate* (*rac*-**22a** · HPF_6): In a 1-l four-necked flask, equipped with a mechanical stirrer, two gas inlets (for N_2 and amine), a dropping funnel with gas outlet and bubble counter, and thermometer, 34.2 ml (41.7 g, 0.200 mol) of **20a** was dissolved in 100 ml of absolute CH_2Cl_2 under N_2 and 9.0 g (0.200 mol) of Me_2NH passed into the solution over a 1-h period at −50°C. At the same temp. 30.7 ml (22.2 g, 0.220 mol) of Et_3N was then added dropwise within 1 h. After 48 h at room temp., 300 ml of absolute CH_2Cl_2 was added within 1 h at 5°C, followed by 47.6 ml (40.5 g, 0.460 mol) of **4**. After 2 d at room temp., precipitated **4** · 2 HCl was filtered off and the solvent removed in vacuo. From the residue CH_2Cl_2 was *completely* removed (^1H NMR control!) azeotropically with water at reduced pressure. Workup, as described for *rac*-**22b**, yielded 36.2 g (52%) of a colorless oil, b.p. 92°C/0.01 Torr, which crystallized after some time, m.p. 47−48°C. − For characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous NH_3 and recrystallized from water, m.p. 208−209°C. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 [s, 9H, $(CH_3)_3C$], 2.09 (m_c, 3H, 5-H and HN), 2.72 [d, $^3J_{P,H}$ = 10 Hz, 6H, $(CH_3)_2N$], 2.73 (d, $^3J_{P,H}$ = 10 Hz, 3H, 1-CH_3), 3.16−3.4 (m, 4H, 4,6-H), 3.45 (m_c, 1H, HN). − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (NH), 2970, 1625, 1478, 1416, 1395, 1372, 1335, 1293, 1230, 1198, 1178, 1150, 1118, 1065, 988, 940, 840 (s), 752, 738, 716, 558 (s). − $C_{10}H_{26}F_6N_4P_2$ (378.3): calcd. C 31.75, H 6.93, N 14.81; found C 31.68, H 7.15, N 14.43.

2-(tert-Butylimino)-2-(dimethylamino)-1,3-dimethyl-1,3,2λ⁵-diazaphosphinane (**23a**) *and 2-(tert-Butylamino)-2-(dimethylamino)-1,3-dimethyl-1,3,2-diazaphosphinanium Hexafluorophosphate* (**23a** · HPF_6): *rac*-**22a** was methylated as described under **23b**, yield 78% (based on *rac*-**22a**), b.p. 58°C/0.04 Torr. − ^1H NMR (250 MHz, CD_3CN): δ = 1.15 [s, 9H, $(CH_3)_3C$], 1.63−1.92 (m, 2H, 5-H), 2.48 (d, $^3J_{P,H}$ = 9 Hz, 6H, CH_3N), 2.58 (d, $^3J_{P,H}$ = 9 Hz, 6H, CH_3N), 3.05 (m_c, 4H, 4,6-H). − For characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous NH_3 and recrystallized from water/MeOH, m.p. >310°C (dec.). − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 [s, 9H, $(CH_3)_3C$], 2.01 (m_c, 2H, 5-H), 2.70 (d, $^3J_{P,H}$ = 10 Hz, 6H, 1,3-CH_3), 2.74 [d, $^3J_{P,H}$ = 10 Hz, 6H, $(CH_3)_2N$], 3.26 (m_c, 4H, 4,6-H), 3.44 (d, $^2J_{P,H}$ = 10 Hz, 1H, HN). − ^{13}C NMR (100 MHz, $CDCl_3$, 240 K): δ = 24.4 (d, $^3J_{P,C}$ = 5.2 Hz, C-5), 30.8 [d, $^3J_{P,C}$ = 4.6 Hz, $(CH_3)_3C$], 35.1 (d, $^2J_{P,C}$ = 4.2 Hz, 1,3-CH_3), 37.2 [d, $^2J_{P,C}$ = 4.0 Hz, $(CH_3)_2N$], 50.4 (d, $^2J_{P,C}$ = 1.8 Hz, C-4,6), 53.3 (d, $^2J_{P,C}$ = 1.6 Hz, CMe_3). − ^{15}N NMR (40 MHz, $CDCl_3$, **23a** · $HOSO_2C_4F_9$): δ = 27.9 (d, $^1J_{P,N}$ = −27.2 Hz, N-1,3), 25.1 (d, $^1J_{P,N}$ = −28.5 Hz, NMe_2), 60.0 (d, $^1J_{P,N}$ = −30.2 Hz, NH*t*Bu). − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (NH), 2976, 2940, 1630, 1475, 1390, 1371, 1293, 1268, 1226, 1198, 1163, 1130, 1055, 1018, 990, 955, 838, 757, 739, 695, 560. − $C_{11}H_{28}F_6N_4P_2$ (392.3): calcd. C 33.68, H 7.19, N 14.28; found C 33.70, H 7.69, N 14.21.

(tert-Butylimino)(diisopropylamino)phosphorus Dichloride (**21c**): 34.2 ml (41.7 g, 200 mmol) of **20a** and a solution of 57.0 ml (40.5 g, 400 mmol) of iPr_2NH in 100 ml of MeCN were heated under reflux for 5 d under N_2. After cooling, iPr_2NH · HCl was filtered off under N_2, the filtrate concentrated by rotary evaporation and filtered again. First the parent compound was distilled at 70°C/22 Torr (2.3 g, 5%), then the desired product in high vacuo. Yield 28.9 g (53%, not optimized) of a colorless liquid, b.p. 65°C/0.1 Torr. About 6.3 g (20%) of oligophosphazenes remained in the distillation residue. − Because of extensive sensitivity to hydrolysis a CHN analysis was renounced. − ^1H NMR (250 MHz, CD_3CN): δ = 1.33 [d, $^3J_{H,H}$ = 6.3 Hz, 12H, $(CH_3)_2CH$], 1.37 [d, $^4J_{P,H}$ = 1.8 Hz, 9H, $(CH_3)_3C$], 3.81 [dsept, $^3J_{P,H}$ = 29.3 Hz, 2H, $(CHMe_2)_2N$]. − ^{15}N NMR (40 MHz, $CDCl_3$): δ = 88.0 ($^1J_{P,N}$ = −43.5 Hz, N*i*Pr_2), 128.1 ($^1J_{P,N}$ = −15.5 Hz, N*t*Bu).

(±)-2-(tert-Butylamino)-2-(diisopropylamino)-1-methyl-1,3,2-diazaphosphinanium Hexafluorophosphate (*rac*-**22c** · HPF_6): In a 500-ml four-necked flask, equipped with a mechanical stirrer, gas inlet, two dropping funnels, a reflux condenser with gas outlet, and thermometer, 13.7 g (50.0 mmol) of **21c** was dissolved in 50 ml of EtCN and the resulting solution then heated to reflux. 7.8 ml (6.6 g, 75 mmol) of **4** was added dropwise within 6 h, the mixture being refluxed for additional 36 h. After cooling and filtration from **4** · 2 HCl EtCN was removed in vacuo. After the residue had been dissolved in 80 ml of 70% aqueous $EtNH_2$, the HPF_6 salt was precipitated according to the general procedure and recrystallized from MeOH/water. Drying in high vacuo provided 10.5 g (48%, not optimized) of colorless crystals; for characterization a sample of *rac*-**22c** · $HClO_4$ was prepared by precipitation with $NaClO_4$ according to the general procedure, m.p. 234−235°C (dec.). − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, $^3J_{H,H}$ = 7 Hz, 6H, MeCHCH_3), 1.14 (d, $^3J_{H,H}$ = 7 Hz, 6H, CH_3CHMe), 1.21 [d, $^4J_{P,H}$ ≈ 0.8 Hz, 9H, $(CH_3)_3C$], 1.76 (m_c, 2H, 5-H), 2.55 (d, $^3J_{P,H}$ = 10 Hz, 3H, CH_3N), 2.92 (br. d, $^2J_{P,H}$ ≈ 10 Hz, 1H, HN*t*Bu), 3.0−3.4 (m, 4H, 4,6-H), 3.33 (dsept, $^3J_{P,H}$ = 18.8 Hz, 2H, $CHMe_2$), 4.18 (br. dt, $^2J_{P,H}$ = 10.5, $^3J_{H,H}$ = 3.5 Hz, 1H, 3-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8 (d, $^3J_{P,C}$ = 2.0 Hz, MeCHCH_3), 22.7 (d, $^3J_{P,C}$ = 2.5 Hz, CH_3CHMe), 24.2 (d, $^2J_{P,C}$ = 7.0 Hz, C-5), 30.7 [d, $^3J_{P,C}$ = 4.5 Hz, $(CH_3)_3C$], 35.2 (d, $^2J_{P,C}$ = 4.5 Hz, CH_3N), 40.8 (d, $^2J_{P,C}$ = 2.5 Hz, C-4), 46.5 (d, $^2J_{P,C}$ = 5.5 Hz, $CHMe_2$), 50.1 (d, $^2J_{P,C}$ = 1.8 Hz, C-6), 53.2 (d, $^2J_{P,C}$ = 2.5 Hz, CMe_3). − ^{15}N NMR (40 MHz, $CDCl_3$): δ = 30.3 ($^1J_{P,N}$ = 30.8 Hz, N-1), 40.2 ($^1J_{P,N}$ = 25.9 Hz, N-3), 70.9 ($^1J_{P,N}$ = 27.3 Hz, NH*t*Bu), 75.5 ($^1J_{P,N}$ = 23.4 Hz, N*i*Pr_2). − ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.96. − IR (KBr): $\tilde{\nu}$ = 3512 cm^{-1}, 3420 (NH), 2974, 1482, 1413, 1387, 1369, 1291, 1262, 1224. − $C_{14}H_{34}ClN_4O_4P$ (388.9): calcd. C 43.24, H 8.81, N 14.41; found C 42.97, H 8.65, N 14.29.

2-(tert-Butylamino)-2-(diisopropylamino)-1,3-dimethyl-1,3,2-diazaphosphinanium Hexafluorophosphate (**23c** · HPF_6): In a 100-ml three-necked flask, equipped with a magnetic stirrer, gas inlet, powder addition funnel with gas outlet, and thermometer, to a solution of 3.80 g (8.70 mmol) of *rac*-**22c** · HPF_6 in 50 ml of MeCN were added several portions of a total of 3.00 g (125 mmol) of hexane-washed NaH under N_2 at room temp. After complete addition, the mixture was sonificated for 30 min at ambient temp., followed by addition of 0.57 ml (1.30 g, 9.2 mmol) of MeI within 15 min. The slurry was allowed to warm to 42°C and further stirred for 12 h. Excess NaH was filtered off under N_2, to the filtrate cautiously added ca. 1 ml of MeOH, and the solvent removed at reduced pressure. The residue was partitioned between 50 ml of CH_2Cl_2 and 50 ml of water, the organic phase concentrated by rotary evaporation, and the residue crystallized from ca. 10 ml of EtOAc at 0°C. Drying in high vacuo furnished 3.52 g (90%) of colorless crystals. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.31 [d, $^3J_{H,H}$ = 7 Hz, 12H, $(CH_3)_2CH$], 1.38 [d, $^4J_{P,H}$ ≈ 0.8 Hz, 9H, $(CH_3)_3C$], 2.06 (m_c, 2H, 5-H), 2.69 (d, $^3J_{P,H}$ = 10 Hz, 6H, CH_3N), 3.36 (m, 4H, 4,6-H), 3.62 (dsept, $^3J_{P,H}$ = 20 Hz, 2H, $CHMe_2$); HN signal not identified. − For IR spectra and CHN analysis a sample was precipitated as $HClO_4$ salt with $NaClO_4$ from an aqueous solution, m.p. 277°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3578 cm^{-1}, 3508, 3412 (NH), 2970, 2934, 2870, 1468, 1414, 1386, 1285, 1261, 1225, 1196, 1171, 1132, 1089 (s), 1053 (s), 996, 981, 729. − $C_{15}H_{36}ClN_4O_4P$ (402.9): calcd. C 44.72, H 9.01, N 13.91; found C 45.00, H 8.81, N 13.83.

2-(tert-Butylimino)-2-(diisopropylamino)-1,3-dimethyl-1,3,2λ⁵-diazaphosphinane (**23c**): 3.14 g (7.00 mmol) of **23c** · HPF_6 was dissolved in 50 ml of MeOH and the anion exchanged for Cl^-. After clearing with charcoal, the solvent was removed in vacuo and the residue partitioned between 5 ml of a 50% KOH solution and ca. 80 ml of diethyl ether. The ether was removed at reduced pressure, the residue dried in high vacuo and sublimed at 80°C/5 · 10^{-3} Torr, affording 1.93 g (91%) of colorless crystals, m.p. 120−122°C. − ^1H NMR (250 MHz, [D_6]benzene): δ = 1.32 [d, $^3J_{H,H}$ = 6.5 Hz, 12H, $(CH_3)_2CH$], 1.47 [d, $^3J_{P,H}$ = 1 Hz, 9H, $(CH_3)_3C$], 1.42−1.51 (m, 2H, 5-H), 2.47 (d, $^3J_{P,H}$ = 9.8 Hz, 6H, CH_3N), 2.51−2.91 (m, 4H, 4,6-H), 3.28 (dsept, $^3J_{P,H}$ = 19.5 Hz, 2H, $CHMe_2$). − ^1H NMR (250 MHz, CCl_4): δ = 1.13 [s, 9H, $(CH_3)_3C$], 1.20 [d, $^3J_{H,H}$ = 7 Hz, 12H, $(CH_3)_2CH$], 1.73−1.98 (m, 2H, 5-H), 2.51 (d, $^3J_{P,H}$ = 9.8 Hz, 6H, CH_3N), 2.89−3.18 (m, 4H, 4,6-H), 3.29 (dsept, $^3J_{P,H}$ = 21 Hz, 2H, $CHMe_2$).

Tris(isopropylamino)(1,1,3,3-tetramethylbutylamino)phosphonium Iodide (**24a** · HI): In a 500-ml two-necked flask, equipped with a mechanical stirrer, gas inlet, dropping funnel with gas outlet, and thermometer, 47.3 ml (32.5 g, 550 mmol) of *i*PrNH$_2$ was dissolved in 200 ml of absolute CH_2Cl_2 at −30°C and a solution of 23.4 ml (26.5 g, 100 mmol) of **20b** in 40 ml of absolute CH_2Cl_2 gradually added under N_2. After removal of the cooling bath, stirring was continued for 12 h at room temp. The precipitated *i*PrNH$_2$ · HCl was filtered off, the crude product dissolved in 70 ml of 70% aqueous EtNH$_2$ and converted to the HI salt according to the general procedure affording 44.2 g (96%) of colorless needles. For further characterization a sample was precipitated as HBF_4 salt from aqueous EtNH$_2$ according to the general procedure, m.p. 102−103°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 [s, 9H, $(CH_3)_3C$], 1.27 [d, $^3J_{H,H}$ = 5 Hz, 18H, $(CH_3)_2CH$], 1.45 [s, 6H, $(CH_3)_2CCH_2$], 1.65 (s, 2H, CH_2), 3.34−3.62 (m, 7H, HN and C*H*Me$_2$). − IR (KBr): ṽ = 3350 cm^{-1}, 3204 (NH), 2976, 1477, 1462, 1423, 1384, 1364, 1348, 1320, 1229, 1161, 1123, 1036, 947, 919, 849, 664. − $C_{17}H_{42}BF_4N_4P$ (420.3): calcd. C 48.58, H 10.07, N 13.33; found C 48.55, H 9.93, N 12.93.

Tris(isopropylmethylamino)(1,1,3,3-tetramethylbutylimino)phosphorane (**25a**) *and Tris(isopropylmethylamino)(1,1,3,3-tetramethylbutylamino)phosphonium Hexafluorophosphate* (**25a** · HPF_6): In a 100-ml three-necked flask, equipped with a magnetic stirrer, gas inlet, powder addition funnel with gas outlet, and thermometer, 6.90 g (15.0 mmol) of **24a** · HI was dissolved in 40 ml of EtCN under N_2. Then 1.8 g (75.0 mmol) of hexane-washed NaH was slowly added with stirring at room temp. After the strong H_2 evolution had ceased, the mixture was cooled to −40°C, 3.0 ml (6.8 g, 48 mmol) of MeI gradually added, and then the mixture allowed to warm to −20°C. The reaction was maintained at this temp., until the H_2 evolution had ceased. Then the mixture was allowed to warm to 0°C. Excess of NaH and MeI were destroyed by cautious addition of 30 ml of MeOH, the mixture was neutralized with dil. HCl, the solvent removed at reduced pressure, and the residue partitioned between 250 ml of water and 50 ml of CH_2Cl_2. The organic phase was separated, the solvent distilled off at reduced pressure, and the remaining yellowish oil dried in high vacuo. The base was liberated by addition of a 50% KOH solution according to the general procedure. The crude product was contaminated by small amounts of (isopropylamino)bis-(isopropylmethylamino)(1,1,3,3-tetramethylbutylimino)phosphorane, which was acylated by addition of 36 µl (0.30 mmol) of *t*BuCOCl and heating to 80°C for 30 min. The base was again liberated according to the general procedure affording 3.68 g (65.0%) of a colorless oil, b.p. 100°C/1 Torr. − ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.04 [d, $^3J_{H,H}$ = 6.7 Hz, 18H, $(CH_3)_2CH$], 1.27 [s, 9H, $(CH_3)_3C$], 1.50 [s, 6H, $(CH_3)_2CCH_2$], 1.76 (d, $^4J_{P,H}$ = 2.5 Hz, 2H, CH_2), 2.27 (d, $^3J_{P,H}$ = 9.8 Hz, 9H, CH_3N), 4.25 (dsept, $^3J_{P,H}$ = 9.5 Hz, 3H, C*H*Me$_2$). − For further characterization, a sample was precipitated as HPF_6 salt from aqueous EtNH$_2$ according to the general procedure, m.p. 113°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.03 [s, 9H, $(CH_3)_3C$], 1.23 [d, $^3J_{H,H}$ = 6.7 Hz, 18H, $(CH_3)_2CH$], 1.45 [d, $^4J_{P,H}$ = 0.9 Hz, 6H, $(CH_3)_2CCH_2$], 1.72 (s, 2H, CH_2), 2.62 (d, $^3J_{P,H}$ = 10.1 Hz, 9H, CH_3N), 3.25 (br. d, $^2J_{P,H}$ = 7.3 Hz, 1H, HN), 3.70 (dsept, $^3J_{P,H}$ = 10.1 Hz, 3H, C*H*Me$_2$). − IR (KBr): ṽ = 3318 cm^{-1} (NH), 2968, 1478, 1385, 1365, 1249, 1181, 1053, 972, 873, 838. − $C_{20}H_{48}F_6N_4P_2$ (520.6): calcd. C 46.15, H 9.29, N 10.76; found C 46.53, H 9.47, N 10.90.

Tris(isopropylamino)(1,1,2,2-tetramethylpropylamino)phosphonium Iodide (**24b** · HI): In a 500-ml two-necked flask, equipped as described for the preparation of **24a** · HI, 47.3 ml (32.5 g, 550 mmol) of *i*PrNH$_2$ was dissolved in 200 ml of absolute CH_2Cl_2 at −30°C, and to the resulting solution a solution of 20.2 ml (25.0 g, 100 mmol) of **20c** in 40 ml of absolute CH_2Cl_2 was gradually added under N_2. After removal of the cooling bath, the temperature of the solution rose to ca. 40°C. Stirring was continued for 20 h at room temp. After cooling to 0°C, the precipitated *i*PrNH$_2$ · HCl was filtered off and the crude product converted to the HI salt according to the general procedure, affording 41.8 g (94%) of colorless needles. For further characterization a sample was converted to the HBF_4 salt according to the general procedure, m.p. 147°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.98 [s, 9H, $(CH_3)_3C$], 1.28 [d, $^3J_{H,H}$ = 6.1 Hz, 18H, $(CH_3)_2CH$], 1.34 [s, 6H, $(CH_3)_2CtBu$], 3.15 (br. d, $^2J_{P,H}$ = 7.6 Hz, HN*t*Hept), 3.42 (m, 6H, $CHMe_2$ and HN*i*Pr). − IR (KBr): ṽ = 3326 cm^{-1} (NH), 2970, 1463, 1425, 1385, 1369, 1134, 1052, 903. − $C_{16}H_{40}BF_4N_4P$ (406.3): calcd. C 47.30, H 9.92, N 13.79; found C 46.84, H 10.05, N 13.62.

Tris(isopropylmethylamino)(1,1,2,2-tetramethylpropylimino)phosphorane (**25b**) *and Tris(isopropylmethylamino)(1,1,2,2-tetramethylpropylamino)phosphonium Tetrafluoroborate* (**25b** · HBF_4): In a 250-ml three-necked flask, equipped as described for the preparation of **25a** · HPF_6, 8.93 g (20.0 mmol) of **24b** · HI was dissolved in 50 ml of EtCN under N_2 and the resulting solution cooled to −15°C. Then 2.88 g (120 mmol) of NaH and 5.0 ml (11.0 g, 80 mmol) of MeI were added alternately with stirring in ten portions, new portions of NaH being added only after H_2 evolution had ceased. After addition of all reagents, the mixture was sonificated for 2 h at ambient temp. Excess NaH and MeI were destroyed by cautious addition of 20 ml of MeOH, the mixture was subsequently carefully neutralized with dil. HCl and the solvent removed in vacuo. The residue was partitioned between 250 ml of water and 100 ml of CH_2Cl_2. Then CH_2Cl_2 was removed in vacuo to constant weight and the residual oil converted to the HBF_4 salt according to the general procedure furnishing 7.27 g (81%) of colorless needles, m.p. 225°C. In a two-necked flask, equipped with a magnetic stirrer, gas inlet, and dropping funnel with gas outlet, 5.55 g (12.4 mmol) of **25b** · HBF_4 was dissolved in 20 ml of MeOH and a solution of 0.87 g (12.4 mmol) of KOMe in 3.5 ml of MeOH added under N_2. After settling of precipitated KBF_4 for 1 h, the supernatant liquor was filtered and the precipitate washed with THF. The combined filtrates were concentrated by rotary evaporation, the residue was dissolved in THF and filtered once more. The solvent was then removed from the filtrate at reduced pressure and the solid base dried in high vacuo. Recrystallization from EtCN afforded colorless leaves, yield 2.41 g (54%, not optimized), m.p. 58°C. − ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.04 [d, $^3J_{H,H}$ = 6.7 Hz, 18H, $(CH_3)_2CH$], 1.27 [s, 9H, $(CH_3)_3C$], 1.36 [s, 6H, $(CH_3)_2CtBu$], 2.25 (d, $^3J_{P,H}$ = 9.8 Hz, 9H, CH_3N), 4.27 (br. dsept, $^3J_{P,H}$ = 8.9 Hz, 3H, $CHMe_2$). − IR (KBr): ṽ = 2966 cm^{-1}, 1467, 1328, 1195, 1041, 963, 844. − $C_{19}H_{45}N_4P$ (360.6): calcd. C 63.29, H 12.58, N 15.54; found C 63.38, H 12.57, N 15.22. − For further characterization, a sample was precipitated as HPF_6 salt with 75% HPF_6 from dil. aqueous EtNH$_2$ and recrystallized from MeOH/water, m.p. 296°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.04 [s, 9H, $(CH_3)_3C$], 1.24 [d, $^3J_{H,H}$ = 6.7 Hz, 18H, $(CH_3)_2CH$], 1.30 [s, 6H, $(CH_3)_2CtBu$], 2.64 (d, $^3J_{P,H}$ = 10.4 Hz, 9H, CH_3N), 2.80 (br. d, $^2J_{P,H}$ = 6.4 Hz, 1H, HN), 3.73 (dsept, $^3J_{P,H}$ = 9.5 Hz, 3H, C*H*Me$_2$). − IR (KBr): ṽ = 3316 cm^{-1} (NH), 2966, 1477, 1384, 1365, 1248, 1164, 1052, 1038, 833. − $C_{19}H_{46}F_6N_4P_2$ (506.5): calcd. C 45.05, H 9.15, N 11.06; found C 45.34, H 9.28, N 11.10.

Tetrakis(tert-butylamino)phosphonium Nonafluorobutanesulfonate (**27** · $HOSO_2C_4F_9$): 7.10 g (20.0 mmol) of **27** · HCl[28] was dissolved in 20 ml of warm water and a solution of 7.44 g (22.0 mmol) of potassium nonafluorobutanesulfonate in 20 ml of water added all at once. The precipitate was filtered off, dried in vacuo, and recrystallized from ethyl acetate yielding 11.9 g (96%) of colorless crystals, m.p. 213°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 [d, $^4J_{P,H}$ = 0.6 Hz, 36H, $(CH_3)_3C$], 3.07 (d, $^2J_{P,H}$ = 9.8 Hz, 4H, NH). − IR (KBr): ṽ = 3340 cm^{-1} (NH), 2976, 1475, 1413, 1390, 1368, 1290, 1239, 1195, 1132, 1109, 1054, 1036, 1016, 923, 843, 800, 733, 679, 652, 634, 613. − $C_{20}H_{40}F_9N_4O_3PS$ (618.6): calcd. C 38.84, H 6.52, N 9.06; found C 39.04, H 6.49, N 9.08.

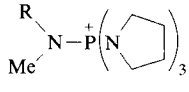
Bis(tert-butylamino)bis(tert-butylmethylamino)phosphonium Tetrafluoroborate (**28** · HBF_4): In a 100-ml two-necked flask, equipped with a magnetic stirrer, gas inlet, and powder addition funnel with gas outlet, 1.48 g (2.39 mmol) of **27** · $HOSO_2C_4F_9$ was dissolved in 30 ml of EtCN under N_2 at room temp. Then 0.315 g (95%, 12.5 mmol) of NaH and 1.64 ml (2.46 g, 15.0 mmol) of methyl triflate were added alternately with stirring in three portions, new portions of NaH being added only after H_2 evolution had ceased. After stirring for 72 h at ambient temp., excess NaH and methyl triflate were destroyed by cautious addition of 10 ml of MeOH, and the solvent was removed in vacuo. The residue was triturated three times with 10 ml of diethyl ether, the ethereal solutions were discharged. The residue was recrystallized from aqueous EtNH$_2$ according to the general procedure providing 1.35 g of a 6:1 mixture of **28** · $HOSO_2C_4F_9$ and **29** · $HOSO_2C_4F_9$. The mixture was dissolved in 10 ml of MeOH, and 155 mg (2.20 mmol) of KOMe in 3 ml of MeOH was added to the resulting solution. Precipitated $KOSO_2C_4F_9$ was filtered off under N_2, and the solvent was removed in vacuo. The residue was dried in high vacuo, then dissolved in 10 ml of *n*-hexane, insoluble material being filtered off from the solution. The solvent was removed from the filtrate in vacuo, and the residue was directly methylated as described below. For the separation of **28** and **29**, the residue was dissolved in 10 ml of CH_2Cl_2 and partitioned with a solution of 330 mg (3.00 mmol) of $NaBF_4$ and 500 mg (12.5 mmol) of NaOH in 10 ml of water. The organic phase was separated and concentrated in vacuo yielding a mixture of **28** · HBF_4 and **29**, from which **28** · HBF_4 was extracted with 10 ml of conc. aqueous EtNH$_2$. Dilution with water according to the general procedure afforded 750 mg (72%) of **28** · HBF_4, m.p. 129°C, and 95 mg (11%) of **29** (see below). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.47 [d, $^4J_{P,H}$ = 0.6 Hz, 18H, $(CH_3)_3CNMe$], 1.49 [s, 18H, $(CH_3)_3CNH$], 2.78 (d, $^3J_{P,H}$ = 11 Hz, 6H, CH_3NtBu), 2.96 (br. d, $^2J_{P,H}$ = 11 Hz, 2H, NH). − IR (KBr): ṽ = 3366 cm^{-1} (NH), 2976, 1474, 1391, 1271, 1255, 1227, 1208, 1186, 1134, 1097, 1053, 1015, 948, 914, 798, 731, 650. − $C_{18}H_{44}BF_4N_4P$ (434.4): calcd. C 49.78, H 10.21, N 12.90; found C 49.51, H 9.99, N 12.77.

(tert-Butylamino)(tert-butylimino)bis(tert-butylmethylamino)phosphorane (**28**): 750 mg (1.73 mmol) of **28** · HBF_4 was dissolved in 5 ml of MeOH and a solution of 0.125 g (1.78 mmol) of KOMe in 2 ml of MeOH added to the resulting solution under N_2. After settling of precipitated KBF_4 for 1 h, the supernatant liquor was filtered under N_2 and the precipitate washed with THF. The combined filtrate and washing was concentrated by rotary evaporation, the residue was dissolved in 10 ml of dry *n*-hexane, and the solution

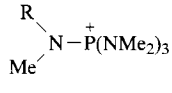
filtered once more. The solvent was then removed from the filtrate at reduced pressure and the solid base dried in high vacuo yielding 550 mg (92%) of a colorless solid, m.p. 87°C. – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.30 [s, 18H, $(CH_3)_3CNMe$], 1.42 [d, $^4J_{P,H}$ = 0.6 Hz, 9H, $(CH_3)_3CNH$], 1.54 [d, $^4J_{P,H}$ = 1.2 Hz, 9H, $(CH_3)_3CN{=}P$], 2.57 (d, $^3J_{P,H}$ = 10.7 Hz, 6H, CH_3NtBu).

(tert-Butylimino)tris(tert-butylmethylamino)phosphorane (**29**): 520 mg (1.50 mmol) of **28** was dissolved in 5 ml of THF and 21 µl (15 mg) of iPr_2NH added under N_2 to the obtained solution. After cooling to −20°C, 112 µl (255 mg) of MeI and 850 µl (1.81 mmol) of a 2.13 M solution of *n*-butyllithium in *n*-hexane were slowly added. After stirring for 3 h at −20°C, the solution was allowed to warm to room temp. Then 5 ml of MeOH was added, the solvent removed in vacuo, and the residue dried in high vacuo. The bases were liberated with 20 ml of a 50% KOH and extracted twice with 10 ml of diethyl ether. Unreacted **28** was separated as described above providing (not optimized) 420 mg (78%) of **29**, m.p. 139°C. – ^{1}H NMR (250 MHz, [D$_6$]benzene): δ = 1.41 [s, 27H, $(CH_3)_3CNMe$], 1.57 [d, $^4J_{P,H}$ = 1.2 Hz, 9H, $(CH_3)_3CN{=}P$], 2.42 (d, $^3J_{P,H}$ = 10.4 Hz, 9H, CH_3NtBu). – IR (KBr): ṽ = 2968 cm^{-1}, 1480, 1384, 1355, 1259, 1205, 1104, 1016, 928, 896, 785, 694, 626. – $C_{19}H_{45}N_4P$ (360.6): calcd. C 63.29, H 12.58, N 15.54; found C 63.64, H 12.56, N 15.36. – For further characterization, a sample was dissolved in CH_2Cl_2 and partitioned with a solution of HPF_6 in an excess of aqueous ammonia. The organic phase was concentrated in vacuo and the residue recrystallized from aqueous $EtNH_2$ according to the general procedure yielding colorless crystals, m.p. >300°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.48 [s, 27H, $(CH_3)_3CNMe$], 1.51 [d, $^4J_{P,H}$ = 1.5 Hz, 9H, $(CH_3)_3CNH$], 2.56 (br. d, $^3J_{P,H}$ = 5.8 Hz, 1H, NH), 2.73 (d, $^3J_{P,H}$ = 10.7 Hz, 9H, CH_3NtBu). – IR (KBr): ṽ = 3392 cm^{-1} (NH), 2984, 1467, 1396, 1366, 1266, 1214, 1194, 1176, 1083, 1038, 1015, 959, 937, 911, 837. – $C_{19}H_{46}F_6N_4P_2$ (448.4): calcd. C 45.05, H 9.15, N 11.06; found C 44.95, H 9.19, N 10.99.

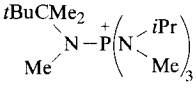
(Ethylmethylamino)tris(1-pyrrolidinyl)phosphonium Hexafluorophosphate (**33** · PF_6): 312 µl (710 mg, 5.00 mmol) of MeI was added to a solution of 284 mg (1.00 mmol) of **18** in 1 ml of chlorobenzene/EtCN (1:1) and the mixture stirred under N_2 for 12 h. Then MeOH was added and the solvent distilled off in vacuo. The residue was dissolved in dil. aqueous $EtNH_2$, the methylated base precipitated as HPF_6 salt by addition of 75% HPF_6 and recrystallized from aqueous MeOH according to the general procedure. Yield 410 mg (93%) of colorless crystals, m.p. 266°C (dec.). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, $^3J_{H,H}$ = 7.3 Hz, 3H, CH_3CH_2N), 1.97 (m, 12H, CH_2CH_2N), 2.73 (d, $^3J_{P,H}$ = 10.1 Hz, 3H, CH_3NEt), 3.04 (dq, $^3J_{P,H}$ = 10.1 Hz, 2H, CH_2Me), 3.22 (m, 12H, CH_2CH_2N). – IR (KBr): ṽ = 2966, 2886, 1481, 1457, 1380, 1345, 1240, 1204, 1174, 1130, 1094, 930, 844, 696 cm^{-1}. – $C_{15}H_{32}F_6N_4P_2$ (444.4): calcd. C 40.54, H 7.26, N 12.61; found C 40.36, H 7.21, N 12.61.



33: R = Et
35: R = *t*Bu
38: R = *t*BuMe$_2$C



34: R = *t*Bu
36: R = *t*BuCH$_2$Me$_2$C
37: R = *t*BuMe$_2$C



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(tert-Butylmethylamino)tris(dimethylamino)phosphonium Hexafluorophosphate (**34** · PF_6): 0.62 ml (1.42 g, 10.0 mmol) of MeI was added to 234 mg (1.00 mmol) of **2b** and the mixture stirred under N_2 for 36 h. MeOH was added and the solvent distilled off in vacuo. The residue was dissolved in dil. aqueous $EtNH_2$, the methylated base precipitated as HPF_6 salt by addition of 75% HPF_6 and recrystallized from aqueous $EtNH_2$ according to the general procedure or from MeOH/water. Yield 340 mg (86%) of colorless crystals, m.p. >310°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.36 [s, 9H, $(CH_3)_3C$], 2.74 (d, $^3J_{P,H}$ = 9.8 Hz, 3H, CH_3NtBu), 2.75 [d, $^3J_{P,H}$ = 9.8 Hz, 18H, $(CH_3)_2N$]. – IR (KBr): ṽ = 2918 cm^{-1}, 1470, 1299, 1181, 1066, 989, 834, 750. – $C_{11}H_{30}F_6N_4P_2$ (394.3): calcd. C 33.51, H 7.67, N 14.21; found C 33.64, H 7.65, N 13.95.

(tert-Butylmethylamino)tris(1-pyrrolidinyl)phosphonium Hexafluorophosphate (**35** · PF_6): According to the procedure used for the preparation of **34** · PF_6, treatment of 312 mg (1.00 mmol) of **2e** with 0.62 ml (1.42 g, 10.0 mmol) of MeI, heated at 50°C for 48 h, gave 400 mg (85%) of colorless crystals, m.p. >310°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37 [s, 9H, $(CH_3)_3C$], 1.97 (m, 12H, CH_2CH_2N), 2.75 (d, $^3J_{P,H}$ = 10.1 Hz, 3H, CH_3NtBu), 3.23 (m, 12H, CH_2CH_2N). – IR (KBr): ṽ = 2968 cm^{-1}, 2878, 1468, 1368, 1268, 1206, 1127, 1086, 1019, 835. – $C_{17}H_{36}F_6N_4P_2$ (472.5): calcd. C 43.22, H 7.68, N 11.86; found C 43.29, H 7.67, N 11.79.

Tris(dimethylamino)[methyl(1,1,3,3-tetramethylbutyl)amino]phosphonium Hexafluorophosphate (**36** · PF_6): According to the procedure used for the preparation of **34** · PF_6, treatment of 290 mg (1.00 mmol) of **2c** with 0.64 ml (1.42 g, 10.0 mmol) of MeI, stirred at room temp. for 72 h, gave 420 mg (93%) of colorless crystals, m.p. 160°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.03 [s, 9H, $(CH_3)_3C$], 1.44 [s, 6H, $(CH_3)_2C$], 1.66 (s, 2H, CH_2), 2.74 (d, $^3J_{P,H}$ = 9.8 Hz, 3H, CH_3NtOct), 2.75 [d, $^3J_{P,H}$ = 9.8 Hz, 18H, $(CH_3)_2N$]. – IR (KBr): ṽ = 2956 cm^{-1}, 1467, 1389, 1371, 1303, 1257, 1215, 1186, 1139, 1062, 1029, 996, 951, 936, 868, 842, 750. – $C_{15}H_{38}F_6N_4P_2$ (450.4): calcd. C 40.00, H 8.50, N 12.44; found C 40.13, H 8.37, N 12.40.

Tris(dimethylamino)[methyl(1,1,2,2-tetramethylpropyl)amino]phosphonium Hexafluorophosphate (**37** · PF_6): 276 mg (1.00 mmol) of **2d** was dissolved in 0.5 ml of chlorobenzene/EtCN (1:1) and allowed to react with 1.25 ml (2.84 g, 20.0 mmol) of MeI at 50°C for 120 h. After completion of the reaction, excess MeI was destroyed by cautious addition of MeOH and the solvent distilled off in vacuo. The residue was dissolved in dil. aqueous $EtNH_2$, **37** precipitated from the solution as PF_6 salt by addition of 75% HPF_6 and recrystallized from aqueous $EtNH_2$ according to the general procedure affording 390 mg (89%) of colorless crystals, m.p. >310°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.04 [s, 9H, $(CH_3)_3C$], 1.38 [s, 6H, $(CH_3)_2CtBu$], 2.76 [d, $^3J_{P,H}$ = 9.5 Hz, 18H, $(CH_3)_2N$], 2.87 (d, $^3J_{P,H}$ = 10.1 Hz, 3H, $CH_3NtHept$). – IR (KBr): ṽ = 2990 cm^{-1}, 1465, 1382, 1297, 1186, 1166, 1062, 990, 948, 837, 751. – $C_{14}H_{36}F_6N_4P_2$ (436.4): calcd. C 38.53, H 8.32, N 12.84; found C 38.45, H 8.39, N 12.50.

[Methyl(1,1,2,2-tetramethylpropyl)amino]tris(1-pyrrolidinyl)phosphonium Hexafluorophosphate (**38** · PF_6): According to the procedure used for the preparation of **37** · PF_6, treatment of 355 mg (1.00 mmol) of **2f** with 1.25 ml (2.84 g, 20.0 mmol) of MeI in 1 ml of chlorobenzene/EtCN (1:1), heated at 50°C for 120 h, gave 468 mg (91%) of colorless crystals, m.p. >310°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 [s, 9H, $(CH_3)_3C$], 1.39 [s, 6H, $(CH_3)_2CtBu$], 1.96 (m, 12H, CH_2CH_2N), 2.88 (d, $^3J_{P,H}$ = 10.4 Hz, 3H, $CH_3NtHept$), 3.21 (m, 12H, CH_2CH_2N). – IR (KBr): ṽ = 2976 cm^{-1}, 1459, 1381, 1255, 1213, 1083, 1019, 949, 835. – $C_{20}H_{42}F_6N_4P_2$ (514.5): calcd. C 46.69, H 8.23, N 10.89; found C 46.76, H 8.19, N 10.85.

2-(tert-Butylmethylamino)-2-(dimethylamino)-1,3-dimethyl-1,3,2-diazaphosphinanium Hexafluorophosphate (**15a** · PF_6): According to the procedure used for the preparation of **37** · PF_6, treatment of 123 mg (0.500 mmol) of **23a** with 156 µl (355 mg, 2.50 mmol) of MeI, stirred for 48 h at room temp., gave 191 mg (94%) of colorless crystals, m.p. >310°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37 [s, 9H, $(CH_3)_3C$], 2.02 (m, 2H, 5-H), 2.74 (d, $^3J_{P,H}$ = 10.7 Hz, 3H, CH_3NtBu), 2.75 (d, $^3J_{P,H}$ = 10.4 Hz, 6H, CH_3N), 2.77 [d, $^3J_{H,H}$ = 10 Hz, 6H, $(CH_3)_2N$], 3.23 (m_c, 4H, 4,6-H). – IR (KBr): ṽ = 2983 cm^{-1}, 2832, 1505, 1474, 1302, 1266, 1178, 1005, 833, 744, 687, 559, 492. – $C_{12}H_{30}F_6N_4P_2$ (406.3): calcd. C 35.47, H 7.44, N 13.79; found C 35.57, H 7.37, N 13.89.

2-(tert-Butylmethylamino)-2-(diisopropylamino)-1,3-dimethyl-1,3,2-diazaphosphinanium Hexafluorophosphate (**15c** · PF_6): According to the procedure used for the preparation of **37** · PF_6, treatment of 151 mg (0.500 mmol) of **23c** with 0.62 ml (1.42 g, 10.0 mmol) of MeI in 1 ml of chlorobenzene/EtCN (1:1), heated at 50°C for 48 h, gave 200 mg (86%) of colorless crystals, m.p. >300°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 [s, 9H, $(CH_3)_3C$], 1.39 [d, $^3J_{H,H}$ = 7 Hz, 12H, $(CH_3)_2CH$], 1.99–2.23 (m, 2H, 5-H), 2.79 (d, $^3J_{P,H}$ = 10.1 Hz, 6H, CH_3N), 2.88 (d, $^3J_{P,H}$ = 11.3 Hz, 3H, CH_3NtBu), 3.19 (dd, $^3J_{P,H}$ = 8.2, $^3J_{H,H}$ = 4.3 Hz, 2H, 4,6-H), 3.23 (ddd, $^3J_{P,H}$ = 8.6, $^3J_{H,H}$ = 4.6, $^3J_{H,H}$ = 2.4 Hz, 2H, 4,6-H), 3.55 [dsept, $^3J_{P,H}$ = 14 Hz, 2H, $CHMe_2$]. – IR (KBr): ṽ = 2970 cm^{-1}, 2924, 1488, 1409, 1369, 1261, 1171, 1069, 1052, 837. – $C_{16}H_{38}F_6N_4P_2$ (462.5): calcd. C 41.56, H 8.28, N 12.12; found C 41.61, H 8.25, N 12.10.

Tris(isopropylmethylamino)[methyl(1,1,3,3-tetramethylbutyl)amino]phosphonium Hexafluorophosphate (**26** · PF_6): In a 100-ml three-necked flask, equipped with a magnetic stirrer, gas inlet, and powder addition funnel with gas outlet, 6.35 g (13.8 mmol) of **24a** · HI was dissolved in 35 ml of EtCN under N_2. Then 1.60 g (69.0 mmol) of hexane-washed NaH was slowly added with stirring at room temp. to the obtained solution. After the strong H_2 evolution had ceased, 5.18 ml (11.80 g, 82.8 mmol) of MeI was gradually added by a syringe, the mixture allowed to warm to room temp., and excess NaH and MeI were destroyed by cautious addition of 20 ml of MeOH. The solvent was removed at reduced pressure and the residue converted to the PF_6 salt according to the general procedure. Yield 5.36 g (73%) of colorless needles, m.p. 188°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.03 [s, 9H, $(CH_3)_3C$], 1.25 [d, $^3J_{H,H}$ = 6.7 Hz, 18H, $(CH_3)_2CH$], 1.49 [s, 6H, $(CH_3)_2CCH_2$], 1.73 (s, 2H, CH_2), 2.61 (d, $^3J_{P,H}$ = 10.5 Hz, 9H, CH_3NiPr), 2.71 (d, $^3J_{P,H}$ = 10.5 Hz, 3H, CH_3NtOct), 3.63 (dsept, $^3J_{P,H}$ = 8.2 Hz, 3H, $CHMe_2$). – IR (KBr): ṽ = 2972 cm^{-1}, 1470, 1386, 1369, 1242, 1180, 1162, 1035, 968, 923, 873, 836. – $C_{21}H_{50}F_6N_4P_2$ (534.6): calcd. C 47.18, H 9.43, N 10.48; found C 46.97, H 9.60, N 10.46.

Table 4. Concurrent methylations of two bases with methyl iodide

Base pair A/B	Conditions	Analyzed products (molar ratios) analyzed signals A·H⊕	A·Me⊕	B·H⊕	B·Me⊕
3/2a	5°C/12 h	**3**·H⊕ (29) CH_3N	**8**⊕ (71) CH_3N	**2a**·H⊕ (71) $(CH_3)_2N$; CH_3NH	**1**⊕ (29) $(CH_3)_2N$
2a/18	25°C/12 h	**2a**·H⊕ (50) $(CH_3)_2N$; CH_3NH	**1**⊕ (50) $(CH_3)_2N$	**18**·H⊕ (50) CH_3CH_2N	**33**⊕ (50) CH_3CH_2N
2a/2e	25°C/12 h	**2a**·H⊕ (2) $(CH_3)_2N$[b]	**1**⊕ (98) $(CH_3)_2N$[b]	**2e**·H⊕ (96) $(CH_3)_3C$	**35**⊕ (4) $(CH_3)_3C$
2e/23b	25°C/16 h and 50°C/6 h[a]	**2e**·H⊕ (25) $(CH_3)_3C$	**35**⊕ (75) $(CH_3)_3C$	**23b**·H⊕ (83) CH_3CH_2N	**15b**⊕ (17) CH_3CH_2N
23a/2b	25°C/12 h	**23a**·H⊕ (47) $(CH_3)_3C$	**15a**⊕ (53) $(CH_3)_3C$	**2b**·H⊕ (66) $(CH_3)_3C$	**34**⊕ (34) $(CH_3)_3C$
2b/23b	25°C/16 h and 50°C/6 h[a]	**2b**·H⊕ (38) $(CH_3)_3C$	**34**⊕ (62) $(CH_3)_3C$	**23b**·H⊕ (62) CH_3CH_2N	**15b**⊕ (38) CH_3CH_2N
23b/2c	25°C/36 h[a]	**23b**·H⊕ (23) CH_3CH_2N	**15b**⊕ (77) CH_3CH_2N	**2c**·H⊕ (76) $(CH_3)_3C$	**36**⊕ (24) $(CH_3)_3C$
2c/25a	50°C/48 h[a]	**2c**·H⊕ (61) $(CH_3)_2N$[c]	**36**⊕ (39) $(CH_3)_2N$[c]; CH_3NtOct	**25a**·H⊕ (79) CH_3NiPr[c]	**26**⊕ (21) CH_3NiPr[c]; CH_3NtOct
25a/23c	50°C/48 h[a]	**25a**·H⊕ (52) $(CH_3)_2C$[c]	**26**⊕ (48) $(CH_3)_2C$[c]	**23c**·H⊕ (94) CH_3NCH_2[c]	**15c**⊕ (5.5) CH_3NCH_2[c]; CH_3NtBu
2f/23c	50°C/140 h	**2f**·H⊕ (36) $(CH_3)_3C$	**38**⊕ (64) $(CH_3)_3C$	**23c**·H⊕ (76) CH_3NCH_2	**15c**⊕ (24) CH_3NCH_2; CH_3NtBu
23c/2d	50°C/120 h	**23c**·H⊕ (63) CH_3NCH_2	**15c**⊕ (37) CH_3NCH_2; CH_3NtBu	**2d**·H⊕ (65) $(CH_3)_2N$	**37**⊕ (35) $(CH_3)_2N$; $CH_3NtHept$
2d/25b	80°C/72 h[d]	**2d**·H⊕ (52) $(CH_3)_2N$	**37**⊕ (48) $(CH_3)_2N$; $CH_3NtHept$	**25b**·H⊕ (98) CH_3NiPr; $(CH_3)_3C$	**39**⊕ (2) CH_3NiPr; $(CH_3)_3C$; $CH_3NtHept$

[a] Without solvent. – [b] The signals of **2a** · H^+ and $\mathbf{1}^+$ were not clearly separated; the mixture was thus converted to the Cl^- salts by anion exchange, dried in high vacuo and treated with an excess of 50% KOH. The free bases **2a** and **2e** were extracted with diethyl ether, the solvent was removed from the extract in vacuo and the residue converted to the HPF_6 salts with KPF_6 in water, which were then extracted with CH_2Cl_2. The ^{1}H-NMR analysis of the mixture indicated the given amount of **2a** · H^+. – [c] 250 MHz ^{1}H-NMR. – [d] Excess MeI in a sealed tube.

Tris(isopropylmethylamino)[methyl(1,1,2,2-tetramethylpropyl)amino]phosphonium Hexafluorophosphate (**39** · PF_6): According to the procedure used for the preparation of **37** · PF_6, treatment of 180 mg (0.500 mmol) of **25b** in 0.5 ml of chlorobenzene/EtCN (1:1) with 0.62 ml (1.42 g, 10.0 mmol) of MeI, heated at 50°C for 120 h, gave 240 mg (92%) of colorless crystals, m.p. >300°C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06 [s, 9H, $(CH_3)_3C$], 1.26 [d, $^3J_{H,H}$ = 6.4 Hz, 18H, $(CH_3)_2CH$], 1.40 [s, 6H, $(CH_3)_2CtBu$], 2.62 (d, $^3J_{P,H}$ = 10.1 Hz, 9H, CH_3NiPr), 2.78 (d, $^3J_{P,H}$ = 11.3 Hz, 3H, $CH_3NtHept$), 3.65 (dsept, $^3J_{P,H}$ = 8.9 Hz, 3H, $CHMe_2$). – IR (KBr): $\tilde{\nu}$ = 2982 cm^{-1}, 1468, 1385, 1368, 1240, 1162, 1034, 960, 836. – $C_{20}H_{48}F_6N_4P_2$ (520.6): calcd. C 46.15, H 9.29, N 10.76; found C 45.90, H 9.13, N 10.60.

Concurrent Methylation of Two Bases, General Procedure: 1.00 mmol of MeI was added to a mixture of 1.00 mmol of each base in 1 ml of chlorobenzene/EtCN (1:1) and the mixture stirred under the conditions indicated. Then MeOH was added and the solvent distilled off in vacuo. The residue was dissolved in dil. aqueous NH_3, subsequently 1 ml of 75% HPF_6 was added to the obtained solution, and the precipitated PF_6 salts were extracted twice with an equal volume of CH_2Cl_2. The combined organic phases were concentrated in vacuo and the residue dried in high vacuo. By ^{1}H-NMR analysis (400 MHz, $CDCl_3$) the methylated compounds as well as the protonated bases could all be identified and quantified separately by means of the signals indicated.

Determination of Rates of HCl Elimination from 2-Phenylethyl Chloride with Different Bases: In a NMR tube 12 mg (85 μmol) of 2-phenylethyl chloride and 85 μmol of the corresponding base were dissolved in 0.5 ml of dry CD_3CN. The mixture was kept at 30°C for a time close to the half-life, and the second order rate constants were calculated from the integrations of signals of 2-phenylethyl chloride (α and/or β protons), styrene (olefinic protons), and of the corresponding base. The estimated standard deviation of log*k* was ± 0.05.

X-Ray Diffraction Analyses were performed from colorless transparent crystals. The cell parameters were determined on the basis of 25 reflections. The numbers of reflections reported in Table 3 were obtained with Cu-K_α radiation and $2\Theta_{max} = 140°$ (graphite monochromator). Measurements were carried out with the system Enraf-Nonius CAD4. For computations the program MolEN[34] was employed. The structures were solved by direct methods and refined anisotropically by the last-squares method. The weighting scheme for R_w was $1/\sigma^2$. The positions of hydrogen atoms were calculated and included in the refinement with isotropic description.

☆ Dedicated to Professor *Christoph Rüchardt* on the occasion of his 65th birthday.

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