DOI: 10.1002/chem.200500837

Extremely Base-Resistant Organic Phosphazenium Cations

Reinhard Schwesinger,*[a] Reinhard Link,[b] Peter Wenzl,[c] Sebastian Kossek,[d] and Manfred Keller[a]

Abstract: A series of peralkylated polyaminophosphazenium cations exhibiting extraordinary base resistance under phase-transfer conditions were efficiently synthesized from readily available starting materials. Their half lives under these conditions exceed those of the most stable conventional organic cations by factors of up to 3000.

Keywords: cations · phase-transfer catalysis · phosphazenes · phosphorus

Introduction

Lipophilic organic cations in molar or catalytic amounts are indispensable auxiliaries for solubilization of anionic reagents in organic media. The catalytic application, phase-transfer catalysis, has become an essential methodology particularly for industrial processes.[1] Among these the most important processes are base catalyzed and often utilize aqueous alkali hydroxides as second phase. A vast variety of organic cations has been used as catalysts for such reactions, but conventional organic cations have limited base resistance. This instability can be due to Hofmann degradation,[2–4] nucleophilic dealkylation,[4,5] Sommelet–Hauser rearrangement, or benzylic deprotonation with subsequent Stevens rearrangement in the case of quaternary ammonium ions[6] or by hydrolysis in the case of bis(triphenylphosphane)iminium ion,[4] tetraphenylarsonium[4] and -phosphonium ions[7] (Table 1), tetraalkylphosphonium,[3,7,8] and *N*-alkyl-4-dialkylaminopyridinium ions.[4]

In context with our work on extremely strong uncharged bases we[9–11] and others[4,12–15] learnt about the unique stability of polyaminophosphazenium cations under basic conditions. In this paper we detail our longstanding efforts to identify or develop phosphazenium cations with maximum base resistance.

Results and Discussion

A survey of phosphazenium ions to be discussed in this paper is given in Figure 1. The parameters considered were the size of the conjugated system and the nature of the alkyl substituents on nitrogen atoms.

Table 1. Half lives of phase transfer catalysts in 50% NaOH/chlorobenzene at 100°C.

Entry	Compound	$t_{1/2}$ [h]
1	$Bu_4P^+Cl^-$	0.08/20°C[4]
2	$Ph_4As^+Cl^-$	2/20°C[a]
3	$Ph_3PNPPh_3^+Cl^-$	1.1/20°C[a]
4	$Bu_4N^+Cl^-$	0.33
5	**1a**·Cl	0.33
6	**1b**·Cl	0.9
7	**1e**·Cl	67
8	**1f**·Cl	6
9	**2a**·Cl	8 (9[4])
10	**2b**·Cl	21
11	**2c**·Cl	7
12	**2d**·Cl	8
13	**3**·Cl	3.7
14	**4a**·Cl	33/110°C
15	**4b**·Cl	477/110°C

[a] CH_2Cl_2 as solvent.[4]

[a] Prof. Dr. R. Schwesinger, Dr. M. Keller
Chemisches Laboratorium
Institut für Organische Chemie und Biochemie
der Universität Freiburg
Albertstrasse 21, 79104 Freiburg (Germany)
Fax: (+49) 761-203-8712
E-mail: rschwesi@chemie.uni-freiburg.de

[b] Dr. R. Link
Current address: CU-Chemie Uetikon GmbH
Raiffeisenstrasse 4, 77933 Lahr (Germany)

[c] Dr. P. Wenzl
Current address: Fluka-Chemie AG, Industrie-Strasse 25
9471 Buchs, SG (Switzerland)

[d] Dr. S. Kossek
Current address: Protiveris
9700 Great Seneca Hwy, Rockville, MD 20850 (USA)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

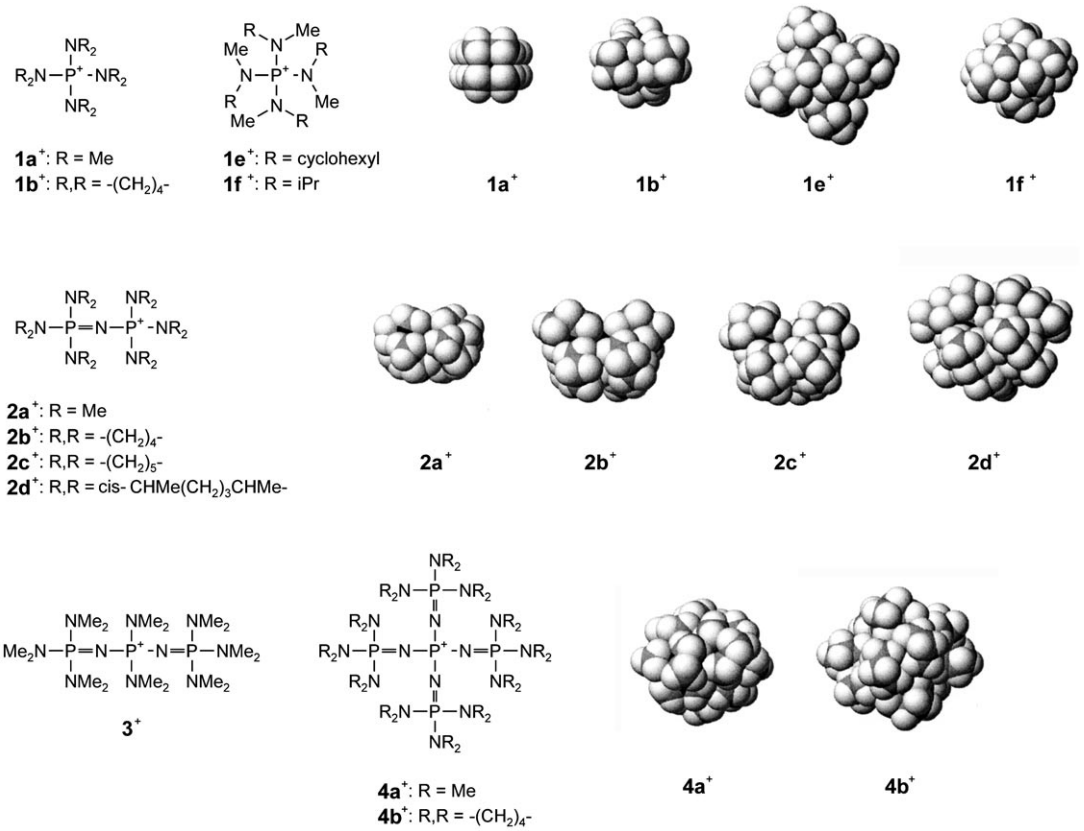
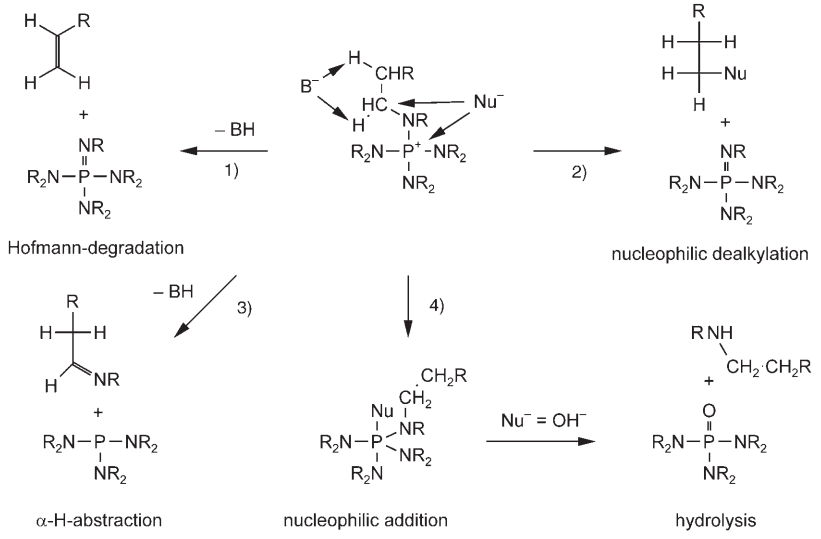


Figure 1. Phosphazenium ions and their structures described in this paper derived from molecular modeling studies.

For the conception of phosphazenium ions of maximum base resistance it is essential to know their potential paths of decay. For tetrakis(dialkylamino)phosphonium ions $\mathbf{1}^+$ four such paths have been observed (Scheme 1):[16]

1) Hofmann degradation.
2) Nucleophilic substitution on (alkyl-)carbon.
3) β-Elimination with formation of an imine and a phosphorous acid amide.
4) Hydrolysis by attack of hydroxide at the phosphorus atom.



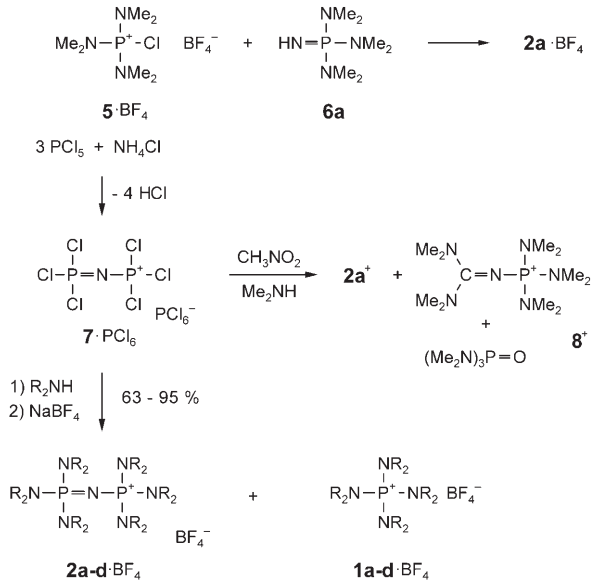
Scheme 1. Modes of decay of peralkylated tetraaminophosphonium cations (paths 1–4).

It was reasonable to assume that the ease of decay of peralkylated polyaminophosphazenium ions like $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{3}^+$, and $\mathbf{4}^+$ correlates with the degree of charge delocalization (hence with the base strength of the product of dealkylation by means of path 1 or 2), as in all four modes of decay merely complete loss of the cationic resonance in the rate-limiting step is involved. The rate of decay in path 4 also depends on steric shielding at the phosphorus nuclei. The relative importance of the two factors was, a priori, not evident.

To evaluate the influence of the size of the conjugated system we first investigated the stabilities within the series of permethylated cations $\mathbf{1a}^+$, $\mathbf{2a}^+$, $\mathbf{3}^+$, and $\mathbf{4a}^+$.

Permethylated systems: The P_1 cation $\mathbf{1a}^+$[17,18] has long been known, yet prepared rather inefficiently. An improved synthesis from our lab has been reported.[19]

For $\mathbf{2a}^+$[20] we envisioned an improvement of our original route (Scheme 2)[9] through the coupling of $\mathbf{5}\cdot BF_4$[21] and **6a**,[11,18,22,23] now starting with the readily available perchlorodiphosphazenium salt $\mathbf{7}\cdot PCl_6$.[24,26,27]

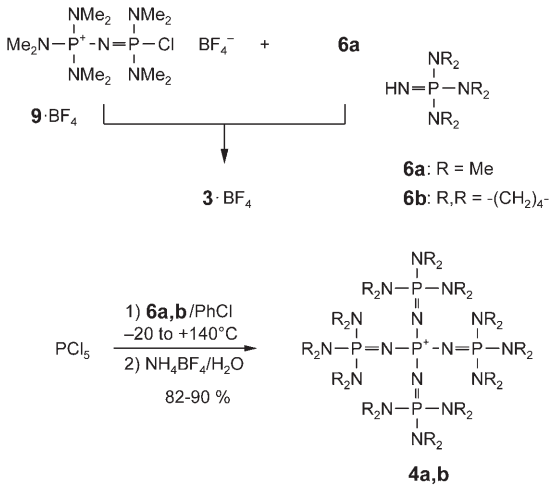


Scheme 2. Syntheses of $\mathbf{2}\cdot BF_4$.

For the exchange of the PCl_6^- ion in $\mathbf{7}\cdot PCl_6$ there is no straight forward protocol.[28] We thus had to settle with the fact that aminolysis also produced equimolar amounts of the corresponding P_1 cations $\mathbf{1}^+$. For a one-pot conversion a solvent was needed that is stable to PCl_5 as well as secondary amines. Reaction of PCl_5 with NH_4Cl in a 3:1 molar ratio in $MeNO_2$ furnished $\mathbf{7}\cdot PCl_6$, which on reaction with dimethylamine provided $\mathbf{2a}^+$ as the BF_4^- salt in good yield together with two unexpected products, HMPA and $\mathbf{8}\cdot BF_4$.[25] When PCl_5 was used instead of $\mathbf{7}\cdot PCl_6$ the $\mathbf{8}^+$ ion was also formed and presumably arises from a cascade reaction of $MeNO_2$ with $\mathbf{5}^+$ involving a fulminate→cyanate rearrangement,[29] possibly via a tris(dimethylamino)isocyanatophosphonium ion as intermediate.[20]

Because of literature reports on the potentially explosive nature of $MeNO_2$ in presence of strong Lewis acids, the explosive nature of fulminates, and the environmental concerns about HMPA as a molar byproduct, this one-pot protocol was rejected in favor of a two-step alternative with $POCl_3$ as solvent for the first step.[24,27] Taking off the solvent in vacuo, aminolysis of $\mathbf{7}\cdot PCl_6$ in chlorobenzene and treatment with NH_4BF_4 afforded $\mathbf{2a}\cdot BF_4$ together with $\mathbf{1a}\cdot BF_4$, from which $\mathbf{2a}\cdot BF_4$ can be separated readily by crystallization.

The P_3 and P_5 systems $\mathbf{3}\cdot BF_4$ and $\mathbf{4a}\cdot BF_4$, respectively, could be obtained through the coupling of **6a** and $\mathbf{9}\cdot BF_4$[11] and through the reaction of **6a** with PCl_5 in chlorobenzene followed by anion exchange with NH_4BF_4, respectively (Scheme 3).



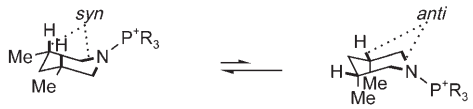
Scheme 3. Syntheses of $\mathbf{3}\cdot BF_4$ and $\mathbf{4}\cdot BF_4$.

The stability of the phosphazenium cations $\mathbf{1a}^+$, $\mathbf{2a}^+$, $\mathbf{3}^+$, and $\mathbf{4a}^+$ was evaluated by determining their half lives as chlorides in the system 50% NaOH/chlorobenzene at 100°C (Table 1). The order of increasing stability is $P_1{}^+ < P_3{}^+ < P_2{}^+ < P_5{}^+$ (entries 5, 9, 13, 14), with $\mathbf{1a}^+$ already being as stable as Bu_4N^+. Except for $P_3{}^+ < P_2{}^+$, this is the order of increasing resonance.

Pyrollidinyl-substituted systems: Substitution of the dimethylamino groups for 1-pyrrolidinyl groups enhances the basicity of phosphazene bases by some 1.5 p*K* units[10,11] and should, therefore, improve the stability of cations by enhancing resonance. On the other hand, this substitution allows for the competition by Hofmann degradation and, due to reduction of the C-N-C angle, possibly reduces steric shielding of the phosphorus nuclei against attack by hydroxide (path 4). Due to the relatively low stability of $\mathbf{3}^+$, only the $\mathbf{1a}^+$, $\mathbf{2a}^+$, and $\mathbf{4a}^+$ ions were modified. The ions $\mathbf{1b}^+$[30] and $\mathbf{2b}^+$ were synthesized in excellent yields in analogy to the permethylated systems. Ion $\mathbf{4b}^+$ was synthesized from **6b**.[11] It turned out, that $\mathbf{1b}^+$, $\mathbf{2b}^+$, and $\mathbf{4b}^+$ are more stable than the appropriate methylated system by factors of 2.7 to 15 (Table 1).

Piperidinyl-substituted systems: Substitution of dimethylamino groups by 1-piperidinyl groups in the P_2 system ($\mathbf{2c}^+$), unexpectedly, did not enhance stability.

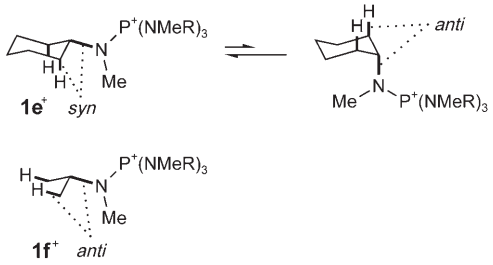
To impede Hofmann degradation in $\mathbf{2c}^+$, methyl groups were introduced by reaction of $\mathbf{7}\cdot PCl_6$ with *cis*-3,5-dimethylpiperidine. These methyl groups in $\mathbf{2d}^+$ enforce either *syn*-elimination or *anti*-elimination from a ring-inverted conformer with two axial methyl groups (Scheme 4). The latter path would cost some 6 kcal mol^{-1} of conformational energy according to force-field modeling studies.



Scheme 4. Conformational preequilibrium for the Hofmann elimination in *cis*-3,5-dimethylpiperidinyl-substituted phosphazenium cations.

Experimentally the methyl groups had no significant influence on the stability towards aqueous NaOH (Table 1), indicating that in phosphazenium ions with two or more phosphorus atoms the Hofmann degradation (path 1) is not dominant in the destruction of the cations by hydroxide. In fact, according to modeling studies (Figure 1) the additional methyl groups in $\mathbf{2d}^+$ do not significantly enhance steric shielding at phosphorus atom relative to $\mathbf{2c}^+$.

***sec*-Alkyl-substituted systems**: If in fact path 4 governs the decay, *sec*-alkyl groups provide better steric protection from degradation. Cyclohexyl-substituted phosphazenium cations again would have to either undergo *syn*-elimination or switch to *anti*-elimination from an energetically disfavored ring-inverted conformer with axial leaving group (Scheme 5).

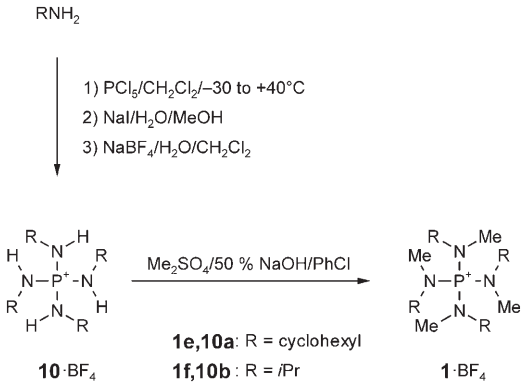


Scheme 5. Conformational prerequisites for the Hofmann elimination in *sec*-alkyl(methyl)aminophosphonium cations $\mathbf{1e}$,$\mathbf{f}^+$.

In the series of quaternary ammonium ions this concept has so far not been rewarding; the extremely crowded tricyclohexylmethylammonium ion is less stable towards bases than a tetra-*N*-alkylammonium ion.[4] The much higher release of steric energy in the transition state of the Hofmann degradation of the former presumably outbalances conformational effects.

As the Hofmann degradation is not dominant under phase-transfer conditions in systems with two (or more) phosphorus atoms, we envisioned being able to apply this concept to the more readily available P_1 systems. As a P_1 cation with four dicyclohexylamino substituents seemed inaccessible for steric reasons, $\mathbf{1e}^+$ with four cyclohexyl(methyl)amino substituents was the next target.

The synthesis of $\mathbf{10a}$·I has already been reported.[31a] We utilized a modified protocol with improved yield. Ion $\mathbf{1e}^+$ proved to be very easily obtainable by means of phase-transfer methylation of $\mathbf{10a}$·BF_4 (Scheme 6).



Scheme 6. Synthesis of $\mathbf{1e}$,$\mathbf{f}$·BF_4.

According to modeling studies, the ion $\mathbf{1e}^+$ can occur in three nearly isoenergetic symmetrical conformations (within 1.8 kcal mol^{-1}; Figure 2).

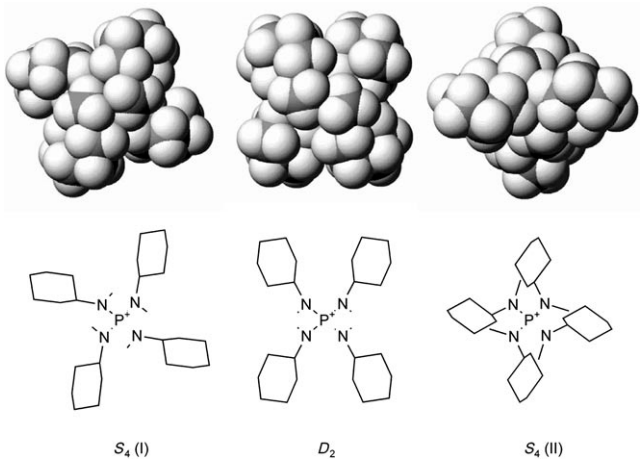


Figure 2. Low-energy conformations derived from molecular modeling studies of $\mathbf{1e}^+$ in the order of increasing energy.

In all the conformers the nitrogen atoms are in equatorial positions. One nitrogen atom in an axial position should raise the energy by some 5 kcal mol^{-1}. The total release of strain on Hofmann degradation of conformer S_4(I) was predicted to be only approximately 8–9 kcal mol^{-1}, so that the much lower release of steric strain in the transition state should probably not outbalance the unfortunate conformational prerequisites.

X-ray analyses of $\mathbf{1e}$·BF_4 (Figure 3), $\mathbf{1e}$·PF_6, and $\mathbf{1e}$·$O_3SC_4F_9$[32] provided further insight into the conformational situation. In all three salts the same low-energy S_4(I) conformation depicted in Figure 2 is met. In contrast to the structure derived from molecular modeling studies, the tetrahedral geometry around the phosphorus atom is slightly distorted with two N-P-N angles at 110.8–112.1° and two at 104.3–105.4°.

In fact, although only a P_1 system, $\mathbf{1e}^+$ turned out to be extremely stable under phase-transfer conditions; it is comparable to the P_5 system $\mathbf{4a}^+$ and is only beaten by $\mathbf{4b}^+$.

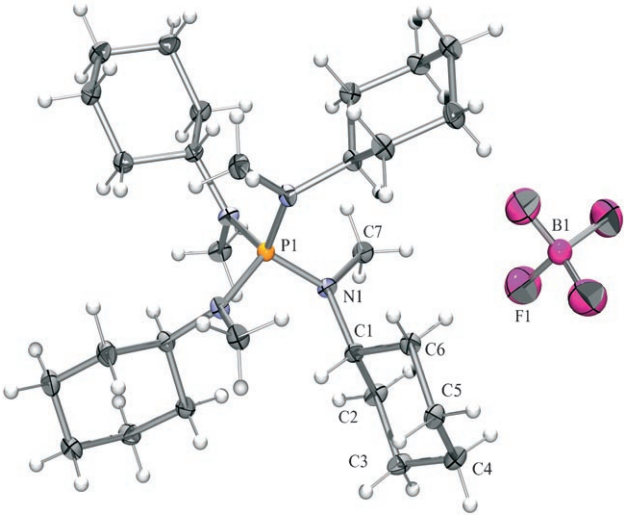


Figure 3. X-ray crystal structure of $\mathbf{1e}\cdot BF_4$.

In the isopropyl-substituted ion $\mathbf{1f}^+$, synthesized analogously from $\mathbf{10b}\cdot I$,[31] *anti*-periplanar N-C-C-H alignments are present in all conformers (Scheme 5). In $\mathbf{1f}^+$, the calculated energy window of the three conformers is only 1.3 kcal mol^{-1} with the same sequence as in $\mathbf{1e}^+$. X-ray analysis of $\mathbf{1f}\cdot BF_4$ confirms the preference of $\mathbf{1f}^+$ for the S_4(I)-conformation (Figure 4).

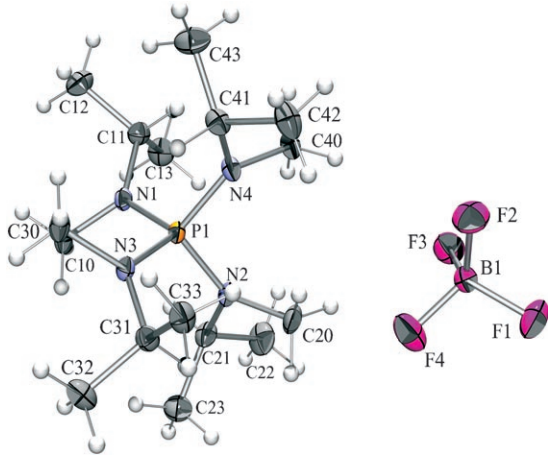


Figure 4. X-ray crystal structure of $\mathbf{1f}\cdot BF_4$.

Indeed, $\mathbf{1f}^+$ (Table 1) turned out clearly less stable than $\mathbf{1e}^+$.

Conclusion

The novel phosphazenium ions offer several advantages as counterions particularly in reactions with strongly basic and/or strongly nucleophilic anions. These advantages include:

1) Greatly enhanced stability towards aqueous base.
2) High anionic reactivity due to comparatively weak short-range cation–anion interactions (e.g. like hydrogen bridges in Bu_4N^+[33])
3) With respect to a given molecular weight the comparatively spherical shape of the novel cations (e.g. versus Bu_4N^+, see Figure 1) leads to a maximized cation–anion separation in the ion pairs and thus improves anion reactivities for electrostatic reasons.

In particular, ball-shaped $\mathbf{4a}^+$ has already found broad application.[13–15,34] A number of the described cations have been evaluated as counterions for the generation of anhydrous fluoride salts.[35]

Experimental Section

General: Melting points (m.p.; uncorrected): Apparatus Dr. Tottoli and Bock Monoscop M; IR: Perkin–Elmer 457 and Philips PU 9706 spectrometers; elemental analyses: Perkin–Elmer Elemental Analyzer 240; ^{1}H NMR (internal standards TMS = tetramethylsilane): 90 MHz Varian CM 390, 250 MHz Bruker AC 250, and 400 MHz Bruker AM 400 spectrometer; ^{13}C NMR (internal standard TMS): 25.2 MHz Bruker WP 80 and 100.6 MHz Bruker AM 400 spectrometer; ^{31}P NMR (external standard): Bruker AM 400 spectrometer. MM2-based modeling studies were performed with PCModel 8.5 with additional parameters gained by fitting to X-ray structures.

MeCN was purchased from Fluka Chemie AG (Switzerland) and stored over molecular sieves 3 Å, H_2O content $< 0.001\,\%$.

Aqueous NH_3, powdered charcoal, Na_2O, NaOH, NaCl, Na_2SO_4, $NaBPh_4$, $NaBF_4$, NH_4BF_4, KI, $MgSO_4$, BaO, H_3PO_4, EtOH, EtOAc, MeOAc, *i*PrOAc, and Me_2CO were used as purchased from Fluka Chemie AG (Switzerland). KCl and PCl_5 were used as purchased from Riedel-deHaën. 70 % aqueous $EtNH_2$ was used as purchased from Merck/Darmstadt. $POCl_3$ was distilled under N_2; $MeNO_2$ was distilled from $CaCl_2$ and stored over molecular sieves 3 Å; CH_2Cl_2 and PhCl, specified as "absolute" were distilled over P_2O_5 and stored over molecular sieves 3 Å; EtCN was stirred over $KMnO_4$ until the violet color persisted, filtered and distilled over P_2O_5; other solvents were purified by simple distillation; NEt_3 was first distilled from *p*-toluenesulfonyl chloride (ca. 2 mol-%), then over Na_2O or BaO; pyrrolidine, piperidine, gaseous amines, and NH_3 were distilled or passed over Na_2O or BaO; MeI was distilled and stored over 4 Å molecular sieves. NH_4Cl was dried in high vacuum for 1 h at 50 °C.

Tetrakis(cyclohexylamino)phosphonium iodide ($\mathbf{10a}\cdot I$)[31a] and tetrakis(cyclohexylamino)phosphonium tetrafluoroborate ($\mathbf{10a}\cdot BF_4$): Cyclohexylamine (54.56 g, 550 mmol) was dissolved in absolute CH_2Cl_2 (125 mL) and cooled to −40 °C. With cooling in a dry-ice bath, PCl_5 (11.45 g, 55 mmol) was added at such a rate that the temperature did not exceed −30 °C. The mixture was then allowed to warm to room temperature until all PCl_5 had dissolved. It was then gradually heated to reflux, held at reflux for 4 h, and cooled to room temperature. The solvent was removed, the residue was dissolved in H_2O/MeOH 2:1 (ca. 750 mL), KI (10.0 g, 60 mmol) in H_2O (20 mL) was added, and the was mixture kept at 4 °C for 20 h. The precipitate was isolated by suction, washed with a small amount of H_2O/MeOH 2:1 at −4 °C, and dried in high vacuum, affording colorless crystals (27.5 g, 90 %). M.p. 256 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 30 °C, TMS): $\delta = 1.02$–2.11 (m, 40H; CH_2), 3.04 (m, 4H; CH), 4.18 ppm (m, 4H; NH).

$\mathbf{10a}\cdot BF_4$: $\mathbf{10a}\cdot I$ was dissolved in CH_2Cl_2 and shaken three times with a twofold excess of saturated aqueous $NaBF_4$. The organic layer was dried with $MgSO_4$ and the solvent was removed in vacuo, affording a crystal-

line residue (m.p. 222 °C). The ^{1}H NMR spectrum corresponded to that of **10a**·I.

Tetrakis[cyclohexyl(methyl)amino]phosphonium tetrafluoroborate (1e·BF$_4$): In a two-necked 500 mL flask with dropping funnel and reflux condenser chlorobenzene (100 mL) and 50 % aqueous NaOH (100 mL) were added to **10a**·BF$_4$ (15.0 g, 29.0 mmol). Dimethyl sulfate (18.53 g, 147 mmol) was added with vigorous stirring, whereby the mixture warmed up to boiling temperature and **10a**·BF$_4$ dissolved completely. After 12 h of stirring, the mixture was quenched with H_2O (200 mL), the organic phase was diluted with CH_2Cl_2 (100 mL) and separated, and the aqueous phase was extracted once with CH_2Cl_2 (100 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo. Recrystallization from *i*PrOH afforded colorless crystals (14.65 g, 88 %). M.p. 315 °C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$, 30 °C, TMS): $\delta = 1.00$–2.00 (m, 40H; CH_2), 2.68 (d, $^3J(P,H) = 10$ Hz, 12H; CH_3), 3.01 ppm (m, 4H; CH); ^{31}P NMR (202 MHz, $CDCl_3$, 30 °C, 85 % H_3PO_4): $\delta = 45.9$ ppm (s); IR (KBr): $\tilde{\nu} = 2934$ (s), 2861 (s), 1475 (s), 1454 (m), 1386 (w), 1276 (m), 1223 (m), 1171 (m), 1150 (m), 1087 (vs), 1050 (vs), 1008 (vs), 977 (vs), 898 (w), 856 (w), 819 (w), 609 cm^{-1} (w); elemental analysis calcd (%) for $C_{28}H_{56}N_4BF_4P$ (566.6): C 59.36, H 9.96, N 9.89; found: C 59.16, H 9.84, N 9.87.

X-ray structures of 1e·BF$_4$, 1e·PF$_6$, and 1f·BF$_4$: Suitable crystals of **1e**·BF$_4$ were obtained by slowly cooling a hot saturated solution of the salt in *i*PrOH. Suitable crystals of **1e**·PF$_6$ were obtained by slow evaporation of a saturated solution of the salt in Me_2CO. Suitable crystals of **1f**·BF$_4$ were obtained by slowly cooling a hot saturated solution of the salt in *i*PrOH/H_2O. Radiation: $Mo_{K\alpha}$ wavelength 0.71073 Å; absorption correction: semiempirical from equivalents. The structures were solved with SIR97[36] and refined with full-matrix least-squares methods on F^2 with SHELXL-97.[37] Details of the data collection and refinement are given in Table 2. The coordinates of the H atoms were calculated in idealized positions and refined in a riding model. CCDC-270539 (**1f**·BF$_4$), CCDC-270540 (**1e**·PF$_6$), and CCDC-270541 (**1e**·BF$_4$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1,1,1,3,3,3-Hexakis(dimethylamino)-1λ^5,3λ^5-diphosphazenium tetrafluoroborate (2a·BF$_4$) and tetrakis(dimethylamino)phosphonium tetrafluoroborate (1a·BF$_4$)

Method 1: see reference [24]: Yield 103–127 g, 72–89 %; IR (KBr): $\tilde{\nu} =$ 3056, 2900, 2854, 2808, 2350, 2036, 1814, 1756, 1663, 1638, 1617, 1559, 1491, 1466, 1417, 1395, 1297, 1179, 1095, 1067, 1053, 981, 741, 631 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{36}N_7BF_4P_2$ (427.2): C 33.74, H 8.49, N 22.55; found: C 33.85, H 8.50, N 22.78.

For the isolation of **1a**·BF$_4$, a solution of $NaBF_4$ (66 g, 0.60 mol) in H_2O (300 mL) was added with vigorous stirring to the combined aqueous phases from which the salts of **2a**$^+$ were extracted. The solvent was evaporated to dryness, and the residue was extracted with CH_2Cl_2 and filtered from inorganic salts. The solvent was again evaporated to dryness and the crude product was recrystallized from EtOH, yielding colorless crystals (58 g, 60 %); m.p. >260 °C.

Methods 2 and 3: see the Supporting Information.

[Bis(dimethylamino)methyleneimino]tris(dimethylamino)phosphonium tetrafluoroborate (8·BF$_4$) (*potentially hazardous*): A slurry of PCl_5 (20.8 g, 0.100 mol) in $MeNO_2$ (50 mL) was prepared. Under N_2 and cooling with an ice bath, Me_2NH (45 g, 1.00 mol) was passed into the solution at such a rate that the temperature did not exceed 10 °C. The mixture was then stirred for 2 h at room temperature and set aside for 7 d. Excess Me_2NH and $MeNO_2$ were removed in vacuo at 30 °C bath temperature and the residue was dried in high vacuum. The residue was dissolved in ice/H_2O (50 mL), and $NaBF_4$ (20.0 g, 0.18 mol) dissolved in H_2O (50 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic phases were concentrated in vacuo, dried in high vacuum, digested several times with *i*PrOAc, and once more dried in high vacuum, affording colorless needles (12.1 g, 33 %). M.p. 91 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 30 °C, TMS): $\delta =$ 2.73 (d, $^3J(P,H) = 10.5$ Hz, 18H; $PN(CH_3)_3$), 2.99 ppm (d, $^5J(P,H) = 0.5$ Hz, 12H; $CN(CH_3)_2$); IR (KBr): $\tilde{\nu} = 3450$, 2928, 1656, 1546, 1478, 1422, 1406, 1389, 1295, 1181, 1084, 988, 934, 761, 687 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{30}N_6BF_4P$ (364.2): C 36.28, H 8.30, N 23.07; found: C 35.53, H 8.13, N 22.34. As the purification of **8**·BF$_4$ proved troublesome (no suitable solvent for recrystallization was found) the corresponding PF_6^- and BPh_4^- salts (see the Supporting Information) were prepared.

1,1,1,3,3,3-Hexa-1-pyrrolidinyl-1λ^5,3λ^5-diphosphazenium tetrafluoroborate (2b·BF$_4$) and tetra-1-pyrrolidinylphosphonium tetrafluoroborate (1b·BF$_4$): A slurry of **7**·PCl_6 (from 0.333 mol of NH_4Cl[24]) in absolute chlorobenzene (300 mL) was prepared. At −20 °C (dry-ice bath) pyrrolidine (570 g, 8.00 mol) was added with vigorous mechanical stirring. The mixture was then allowed to warm to room temperature, and was stirred for 1 h at room temperature and then for 1 h at 60 °C. $NaBF_4$ (36.7 g, 0.334 mol) in H_2O (500 mL) was added with vigorous stirring. The organic phase was separated and the aqueous phase (kept for isolation of **1b**·BF$_4$) was extracted once with chlorobenzene (100 mL). The

Table 2. Experimental details and results of the X-ray diffraction analyses of the compounds **1e**·BF$_4$, **1e**·PF$_6$, and **1e**·BF$_4$.

	1e·BF$_4$	**1e**·PF$_6$	**1f**·BF$_4$
formula	$C_{28}H_{56}N_4BF_4P$	$C_{28}H_{56}N_4F_6P_2$	$C_{16}H_{40}N_4BF_4P$
M_r	566.55	624.71	406.30
T [K]	100 (2)	100 (2)	100 (2) K
crystal system	tetragonal	tetragonal	orthorhombic
space group	$I\bar{4}$	$I\bar{4}$	$Pna2_1$
a [Å]	11.4833 (2)	11.6343 (2)	19.0700 (3)
b [Å]	11.4833 (2)	11.6343 (2)	8.6740 (3)
c [Å]	12.0802 (3)	12.0541 (2)	13.5409 (3)
V [Å^3]	1592.97 (6)	1631.61(7)	2239.84 (10)
Z/ρ_{calcd} [g cm^{-3}]	2/1.181	2/1.272	4, 1.205
μ [mm^{-1}]	0.133	0.192	0.163
$F(000)$	616	672	880
crystal size [mm]	0.35 × 0.3 × 0.22	0.4 × 0.4 × 0.2	0.50 × 0.40 × 0.10
θ range [°]	2.45–27.47	2.43–27.44	2.14–27.48
index range	$-14 \le h \le 14$	$-15 \le h \le 15$	$-24 \le h \le 24$
	$-14 \le k \le 14$	$-15 \le k \le 15$	$-11 \le k \le 11$
	$-14 \le l \le 15$	$-15 \le l \le 15$	$-17 \le l \le 17$
reflections collected	7887/1830	7958/1858	19116/4379
	[R(int) = 0.0266]	[R(int) = 0.0239]	[R(int) = 0.0371]
completeness	100 % (θ = 25.00°)	99.9 % (θ = 27.44°)	99.9 %
max/min transmission	0.968/0.927	0.967/0.880	0.979/0.859
data/restraints/parameters	1830/0/142	1858/0/147	4379/1/247
goodness of fit on F^2	1.079	1.088	1.044
final R indices [$I > 2\sigma$]	$R1 = 0.0258$	$R1 = 0.0242$	$R1 = 0.0284$
	$wR2 = 0.0662$	$wR2 = 0.0628$	$wR2 = 0.0779$
R indices all data	$R1 = 0.0289$	$R1 = 0.0247$	$R1 = 0.0351$
	$wR2 = 0.0674$	$wR2 = 0.0632$	$wR2 = 0.0812$
absolute structure parameter	−0.09 (8)	0.01 (7)	−0.03 (7)
largest difference peak/hole [e Å^{-3}]	0.228/−0.320	0.163/−0.348	0.379/−0.540

combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was recrystallized once from MeOH/H_2O 1:2 (750 mL, mother liquor kept for isolation of **1b**·BF_4) and twice from EtOAc (450 mL), to afford 148 g (84%) of colorless crystals. M.p. 153°C; ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): $\delta = 1.85$–1.93 (m, 24H; NCH_2CH_2), 3.06–3.17 ppm (m, 24H; NCH_2CH_2); IR (KBr): $\tilde{\nu} = 2954$ (CH), 2870, 1640, 1512, 1490 (*N*-CH_3), 1457, 1362, 1342, 1293 (BF), 1278, 1238, 1202, 1120, 1081, 1048, 1014 (NC), 911, 868, 761 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{48}N_7BF_4P_2$ (583.5): C 49.41, H 8.29, N 16.80; found: C 49.41, H 8.24, N 16.68.

Salt 1b·BF_4: The two aqueous phases were combined, and $NaBF_4$ (36.7 g, 0.334 mmol) dissolved in H_2O (100 mL) was added; the mixture was extracted twice with CH_2Cl_2 (2×200 mL). The solvent was removed in vacuo and the residue was dried in high vacuum. Recrystallization from EtOAc afforded colorless crystals (118 g, 90%). M.p. 158°C; ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): $\delta = 1.98$ (m, 16H; NCH_2CH_2), 3.25 ppm (m, 16H; NCH_2CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$, 30°C, TMS): $\delta =$ 26.2 (NCH_2CH_2), 47.2 ppm (NCH_2CH_2); IR (KBr): $\tilde{\nu} = 2950$, 2858, 1478, 1457, 1338, 1292, 1248, 1204, 1114, 1047, 907, 869, 763 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{32}N_4BF_4P$ (398.2): C 48.26, H 8.10, N 14.07; found: C 48.13, H 8.01, N 13.95.

1,1,1,3,3,3-Hexa-1-piperidinyl-1λ^5,3λ^5-diphosphazenium tetrafluoroborate (2c·BF_4): A slurry of **7**·PCl_6 (from 0.167 mol of NH_4Cl[24]) in absolute chlorobenzene (400 mL) was prepared. Piperidine (340 g, 4.00 mol) was added with vigorous mechanical stirring at such a rate that the temperature did not exceed 0°C (dry-ice bath). Then the mixture was allowed to warm to room temperature and kept for 5 d. The solvent was evaporated in vacuo and traces of chlorobenzene and excess piperidine were removed azeotropically with a small amount of H_2O. The product was dissolved in MeOH (500 mL), and cleared with powdered charcoal. $NaBF_4$ (36.7 g, 0.334 mol) in H_2O (500 mL) was then added with vigorous stirring, and MeOH was removed in vacuo until crystallization occurred. The crystals were collected by suction, and the crude product was recrystallized once from Me_2CO/EtOAc 3:1, to afford colorless crystals (96 g, 87%). M.p. 225°C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): $\delta = 1.56$ (m, 24H; NCH_2CH_2), 1.64 (m, 12H; $NCH_2CH_2CH_2$), 3.04 ppm (m, 24H; NCH_2CH_2); IR (KBr): $\tilde{\nu} = 2916$, 2836, 1446, 1393, 1351, 1275, 1203, 1157, 1109, 1068, 1021, 952, 852, 718, 658 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{48}N_7BF_4P_2$ (667.6): C 53.97, H 9.06, N 14.63; found: C 53.96, H 9.03, N 14.58.

***cis*-3,5-Dimethylpiperidine**: see the Supporting Information.

1,1,1,3,3,3-Hexakis[1-(*cis*-3,5-dimethylpiperidinyl)]-1λ^5,3λ^5-diphosphazenium tetrafluoroborate (2d·BF_4): A slurry of **7**·PCl_6 (21.76 mmol of crude product[24]) in absolute chlorobenzene (20 mL) was prepared. At −40°C, *cis*-3,5-dimethylpiperidine (26.56 g, 0.237 mol) and NEt_3 (22.01 g, 0.217 mol) were then successively added at such a rate that the temperature did not exceed −20°C. The mixture was then slowly warmed to reflux. After refluxing for 12 h the mixture was cooled to room temperature, and the solvent was removed in vacuo. A solution of $NaBF_4$ (4.0 g, 36 mmol) in H_2O (150 mL) was added, and the mixture was extracted with CH_2Cl_2 (3×100 mL). The combined organic phases were concentrated in vacuo, and the residue was dried in high vacuum and recrystallized from aqueous $EtNH_2$ (ca. 0.5 L, 70%) to give colorless crystals (4.0 g, 33%). M.p. 215°C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): $\delta = 0.75$ (dt, $^2J(4,4) = 13.1$ Hz, $^3J(4,3/5) = 11.8$ Hz, 6H; 4-H), 0.90 (d, $^3J(3/5,CH_3) = 6.4$ Hz, 36H; CH_3), 1.52 (m, 12H; 3-,5-H), 1.88 (dt, 6H; 4-H), 2.15 (dd, $^2J(2/6,2/6) = 11.3$ Hz, $^3J(2/6,3/5) = 12.2$ Hz, 12H; 2-,6-H), 3.27 ppm (dd, $^3J(2/6,3/5) = 4.9$ Hz, 12H; 2-,6-H); ^{13}C NMR (100 MHz, $CDCl_3$, 30°C, TMS): $\delta = 19.1$ (CH_3), 32.0 (d, $^3J(2/6,3/5) = 4.9$ Hz, CH), 32.1 (CH), 41.9 (γ-CH_2), 52.5 ppm (α-CH_2); ^{31}P NMR (202 MHz, $CDCl_3$, 30°C, 85% H_3PO_4): $\delta = 7.7$ ppm (s); IR (KBr): $\tilde{\nu} = 2948$ (s, br), 2868 (s, br), 1461 (m), 1390 (m, br) 1352 (s), 1290 (w), 1190 (s), 1164 (m), 1128 (s, br), 1088 (m), 1051 (vs), 1037 (s, br), 952 (m), 929 (m), 851 (m), 800 (m), 747 cm^{-1} (w); elemental analysis calcd (%) for $C_{42}H_{84}N_7BF_4P_2$ (835.9): C 60.35, H 10.13, N 11.73; found: C 60.39, H 9.98, N 11.73.

1,1,1,3,3,5,5,5-Octakis(dimethylamino)-1λ^5,3λ^5,5λ^5-triphosphazadienium tetraphenylborate (3·BPh_4): Salt **9**·BF_4[11] (9.7 g, 23.0 mmol) dissolved in absolute chlorobenzene (10 mL) was added to a solution of **6a** (10.2 g, 57.3 mmol) in absolute chlorobenzene (10 mL) at such a rate that the temperature did not exceed 0°C (ice/NaCl bath). Then the mixture was allowed to warm to room temperature, was stirred for 1 h at this temperature and then was heated to 110°C. After 3 h the mixture was cooled, the solvent was removed in vacuo, and the residue was dried in high vacuum. The resulting oil was dissolved in MeOH (100 mL) and a solution of $NaBPh_4$ (10 g) in MeOH (100 mL) was added. Brownish crystals were collected by suction and recrystallized three times from MeOH, to afford colorless crystals (9.6 g, 56%). M.p. 120°C; ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): $\delta = 2.55$ (d, $^3J(P,H) = 10.5$ Hz, 12H; 3-CH_3), 2.59 (d, $^3J(P,H) = 10.5$ Hz, 36H; 1, 5-CH_3), 6.90 (t, ^3J(p-H,m-H) = 7 Hz, 1H; Ar-p-H), 7.06 (t, ^3J(o-H,m-H) = 7 Hz, 1H; Ar-o-H), 7.44 ppm (br m, 2H; Ar-m-H); IR (KBr): $\tilde{\nu} = 3044$, 2992, 2924, 2800, 1932, 1803, 1753, 1574, 1475, 1448, 1353, 1318, 1287, 1185, 1061, 1028, 982, 839, 796, 736, 727, 702, 650 cm^{-1}; elemental analysis calcd (%) for $C_{40}H_{68}N_{10}BP_3$ (792.8): C 60.60, H 8.65, N 17.67; found: C 60.62, H 8.58, N 17.56.

1,1,1,3,3,5,5,5-Octakis(dimethylamino)-1λ^5,3λ^5,5λ^5-triphosphazadienium tetrafluoroborate (3·BF_4): A slurry of **3**·BPh_4 (9.00 g, 11.3 mmol) in MeOH (100 mL) was prepared, and Lewatit M500 (50 g, strongly basic anion exchange resin, Cl^- form) was added. The mixture was stirred by rotating the flask on a rotary evaporator (without vacuum) until the salt had dissolved (ca. 12 h). The resin was filtered off and washed with MeOH, and the filtrate was concentrated in vacuo. After dissolving in H_2O (100 mL) and clearing with powdered charcoal, a solution of $NaBF_4$ (2.0 g, 18 mmol) in H_2O (50 mL) was added. Precipitated **3**·BF_4 was isolated by suction, dried in high vacuum, and recrystallized from ethyl pivalate (crystallized at −100°C), to afford colorless crystals (3.9 g, 62%). M.p. 205°C; ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): $\delta = 2.59$ (d, $^3J(P,H) = 11$ Hz, 12H; 3-CH_3), 2.66 ppm (d, $^3J(P,H) = 10$ Hz, 36H; 1, 5-CH_3); IR (KBr): $\tilde{\nu} = 3500$, 2992 (CH), 2916, 2802, 1804, 1725, 1541, 1481 (*N*-CH_3), 1355, 1316 (BF), 1185, 1087, 1047, 981 (NC), 844, 791, 740, 647 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{48}N_{10}BF_4P_3$ (560.4): C 34.30, H 8.63, N 25.00; found: C 34.06, H 8.51, N 24.49.

Tetrakis{[tris(dimethylamino)phosphoranyliden]amino}phosphonium tetrafluoroborate (4a·BF_4): Compound **6a**[11,22,23] (330 g, 1.85 mol) was dissolved in absolute chlorobenzene (280 mL) and cooled to −20°C under N_2. With cooling in a dry-ice bath, PCl_5 (42.4 g, 0.20 mol) was added at such a rate that the temperature did not exceed −10°C. Then the mixture was gradually heated to reflux, was held at reflux for 6 h, and was cooled to room temperature. A solution of NH_4BF_4 (130 g, 1.24 mol) in H_2O (700 mL) was added, the mixture was carefully shaken in a separating funnel, and the organic phase (lower layer) was separated. The aqueous phase was extracted once with chlorobenzene (100 mL), and the combined organic phases were washed once with H_2O (100 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The residue was dried in high vacuum, was recrystallized from MeOH/H_2O 2:1 (600 mL) and again was dried in high vacuum. Recrystallization from THF (600 mL, cooling to −20°C) yielded colorless crystals (149 g, 90%). M.p. >270°C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): $\delta =$ 2.62 ppm (d, $^3J(P,H) = 10$ Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$, 30°C, TMS): $\delta = 37.1$ ppm (d, $^2J(P,C) = 4.7$ Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$, 30°C): $\delta = -34.8$ (quint, $^2J(P,P) = 54,3$ Hz, 1P), 6.3 ppm (d, 4P); IR (KBr): $\tilde{\nu} = 3086$, 2992, 2882, 2798, 1482, 1457, 1394, 1288, 1190, 1090, 1066, 1051, 996, 814, 734 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{72}N_{16}BF_4P_5$ (826.5): C 34.87, H 8.78, N 27.11; found: C 35.00, H 8.76, N 27.01.

Tetrakis[(tri-1-pyrrolidinylphosphoranyliden)amino]phosphonium tetrafluoroborate (4b·BF_4): Compound **6b**[11] (46.4 g, 182 mmol) was dissolved in absolute chlorobenzene (40 mL) and cooled to −30°C under N_2. With cooling in a dry-ice bath, PCl_5 (4.24 g, 20 mmol) was added at such a rate that the temperature did not exceed −10°C. Then the mixture was allowed to warm to room temperature until all PCl_5 had dissolved. It was then gradually heated to reflux, was held at reflux for 10.5 h, and was cooled to room temperature. A solution of NH_4BF_4 (12.8 g, 122 mmol) in H_2O (100 mL) was added, the mixture was carefully shaken in a separating funnel, and the organic (lower) phase was separated. The aqueous phase was extracted once with chlorobenzene (100 mL) and the combined organic phases were washed once with H_2O (100 mL), dried over

$MgSO_4$, and concentrated in vacuo. The tan residue was dried in high vacuum, was recrystallized from MeOH/H_2O 7:1 (300 mL), and again was dried in high vacuum to afford colorless crystals (18.6 g, 82%). M.p. >210°C (decomp); **6b**·HBF_4 could be recovered almost quantitatively from the mother liquor; ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): δ = 1.75 (m, 48H; NCH_2CH_2), 3.14 ppm (m, 48H; NCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 30°C, TMS): δ = 26.4 (d, ^3J(P,C) = 9 Hz, NCH_2CH_2), 46.4 ppm (d, ^2J(P,C) = 6 Hz, NCH_2CH_2); ^{31}P NMR (202 MHz, $CDCl_3$, 30°C, 85% H_3PO_4): δ = −33.8 (quint, ^2J(P,P) = 51 Hz, 1P), 6.25 ppm (d, 4P); IR (KBr): $\tilde{\nu}$ = 2956 (vs), 2860 (vs), 2660 (w), 2080 (w), 1480 (w), 1453 (m), 1355 (s), 1263 (vs, br), 1196 (s), 1124 (s), 1082 (vs), 1047 (vs), 1008 (vs), 909 (w), 867 (w), 803 (m), 760 (w), 721 cm^{-1} (w); elemental analysis calcd (%) for $C_{48}H_{96}N_{16}BF_4P_5$ (1139.1): C 50.62, H 8.50, N 19.67; found: C 50.46, H 8.53, N 19.56.

Stability test of phosphonium- and phosphazenium cations under phase-transfer conditions: The corresponding tetrafluoroborate salt (0.500 mmol) was dissolved in a minimum amount of MeOH, a solution of KCl (45 mg, 0.600 mmol) in H_2O (150 μL) was added with stirring, the precipitate was filtered off, and the solution concentrated in vacuo, yielding the crude chloride. Chlorobenzene (7 mL), H_2O (3.5 mL), and NaOH (3.5 g) were added and the mixture was heated to 100°C (if not otherwise indicated) in a Teflon flask with stirring. Then both phases were diluted by addition of chlorobenzene (20 mL) as well as H_2O (20 mL) and separated; the aqueous phase was extracted with chlorobenzene (2×30 mL) and the combined organic phases were washed with brine (20 mL). The combined organic phases were concentrated in vacuo, the residue was dissolved in MeOH (25 mL), and $NaBPh_4$ or $NaBF_4$ (200 mg) in MeOH (5 mL) was added. The colorless precipitates were filtered off, washed with a small amount of MeOH, and dried in vacuo to afford the corresponding salts. From the yield (assuming first-order kinetics with respect to the cation) the half lives of the cations were calculated. In case of **4a**$^+$ the precipitate contained cation salts derived from decomposition products;[35] a ^{1}H NMR analysis was performed to evaluate the amount of undecomposed **4a**$^+$.

Salt 1a·BF_4: 26 mg, 88 μmol, 18% after 75 min; $t_{1/2}$ = 20 min.

Salt 1b·BPh_4: 243 mg, 387 μmol, 77% after 20 min; $t_{1/2}$ = 54 min; m.p. 213°C; ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): δ = 1.88 (m, 16H; NCH_2CH_2), 3.13 (m, 16H; NCH_2CH_2), 6.88 (m, 4H; p-H_{arom}), 7.22 (m, 8H; o-H_{arom}), 7.45 ppm (m, 8H; m-H_{arom}).

Salt 1e·BPh_4: 561 mg, 603 μmol, 65% after 42.5 h; $t_{1/2}$ = 67 h, m.p. 230°C; ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): δ = 1.00–1.95 (m, 40H; CH_2), 2.50 (d, ^3J(P,H) = 10 Hz, 12H; CH_3), 2.92 (m, 4H; CH), 6.80–7.08 (m, 12H; H_{arom}), 7.25–7.42 ppm (m, 8H; H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$, 30°C, TMS): δ = 25.1 (s, CH_2), 26.1 (s, CH_2), 29.9 (d, ^2J(P,C) = 3.2 Hz, CH), 30.5 (s, CH_2), 55.8 (d, ^2J(P,C) = 4.7 Hz, CH_3), 116.8, 121.8, 125.6 (^2J(B,C) = 2.6 Hz), 136.2 ppm; elemental analysis calcd (%) for $C_{52}H_{76}N_4BP$ (799.0): C 78.17, H 9.59, N 7.01; found: C 78.15, H 9.61, N 7.07.

Salt 1f·BPh_4: 539 mg, 1327 μmol, 85% after 1.5 h; $t_{1/2}$ = 6 h; m.p. 234°C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): δ = 1.10 (d, ^3J = 8 Hz, 24H; CCH_3), 2.35 (d, ^3J(P,H) = 10 Hz, 12H; NCH_3), 3.30 (sept, 4H; CH), 6.90 (m, 4H; H_{arom}), 7.05 (m, 8H; H_{arom}), 7.42 ppm (m, 8H; H_{arom}); elemental analysis calcd (%) for $C_{40}H_{60}N_4BP$ (638.7): C 75.22, H 9.47, N 8.77; found: C 75.28, H 9.49, N 8.85.

Salt 2a·BF_4: 130 mg, 304 μmol, 61% after 6 h; $t_{1/2}$ = 8 h.

Salt 2b·BF_4: 239 mg, 410 μmol, 82% after 6 h; $t_{1/2}$ = 21 h.

Salt 2c·BF_4: 265 mg, 265 μmol, 53% after 6 h; $t_{1/2}$ = 7 h.

Salt 2d·BF_4: 253 mg, 301 μmol, 60% after 6 h; $t_{1/2}$ = 8 h.

Salt 4a·BPh_4: 29.2 mg, 28.9 μmol, 2.2% after 184 h at 110°C; $t_{1/2}$ = 33 h.

Salt 4b·BPh_4: 524 mg, 460 μmol, 91% after 65 h at 110°C, $t_{1/2}$ = 477 h; m.p. 248°C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): δ = 1.74 (m, 48H; NCH_2CH_2), 3.13 (m, 48H; NCH_2CH_2), 6.90 (m, 4H; *p*-H_{arom}), 7.07 (m, 8H; *m*-H_{arom}), 7.44 ppm (m, 8H; *o*-H_{arom}); for the analysis of the decomposition products, the mother liquor was concentrated in vacuo and the residue checked by NMR spectroscopy: ^{1}H NMR (250 MHz, $CDCl_3$, 30°C, TMS): δ = 1.75 (m, integr. 70 mm), 3.03 (m, 22 mm), 3.15 (m, 34 mm) 6.78–7.02 (m, 10.5 mm), 7.08 (m, 15 mm), 7.30–7.50 (m, 19 mm), 7.62 ppm (m, 2 mm).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft.

[1] M. E. Halpern, *Process Chemistry in the Pharmaceutical Industry* **1999**, pp. 283–298; M. Makosza, M. Fedorynski in *Interfacial Catalysis* (Ed.: A. G. Volkov), Dekker, New York, Basel, **2003**, pp. 159–201; D. Albanese in *Interfacial Catalysis* (Ed.: A. G. Volkov), Dekker, New York, Basel, **2003**, pp. 203–226.

[2] D. Landini, A. Maia, *J. Chem. Soc. Chem. Commun.* **1984**, 1041–1042; D. Landini, A. Maia, A. Rampoldi, *J. Org. Chem.* **1986**, *51*, 5475–5476.

[3] D. Landini, A. Maia, A. Rampoldi, *J. Org. Chem.* **1986**, *51*, 3187–3191.

[4] E. V. Dehmlow, V. Knufinke, *J. Chem. Res. Synop.* **1989**, 224–225.

[5] H. J.-M. Dou, R. Gallo, P. Hassanaly, J. Metzger, *J. Org. Chem.* **1977**, *42*, 4275–4276.

[6] I. E. Markó in *Comprehensive Organic Synthesis, Vol. 3* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 913–974; E. M. Arnett, P. C. Wernett, *J. Org. Chem.* **1993**, *58*, 301–303; X.-M. Zhang, F. G. Bordwell, M. Van Der Puy, H. E. Fried, *J. Org. Chem.* **1993**, *58*, 3060–3066; L. Vial, M.-H. Gonçalves, P.-Y. Morgantini, J. Weber, G. Bernardinelli, J. Lacour, *Synlett* **2004**, 1565–1568.

[7] J. G. Dawber, J. C. Tebby, A. A. C. Waite, *J. Chem. Soc. Perkin Trans. 2* **1983**, 1923–1925.

[8] G. W. Fenton, C. K. Ingold, *J. Chem. Soc.* **1929**, 2342–2357.

[9] R. Schwesinger, H. Schlemper, *Angew. Chem.* **1987**, *99*, 1212–1214; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1167–1169.

[10] R. Schwesinger, C. Hasenfratz, H. Schlemper, L. Walz, E.-M. Peters, K. Peters and H. G. von Schnering, *Angew. Chem.* **1993**, *105*, 1420–1422; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1361–1363.

[11] R. Schwesinger, H. Schlemper, C. Hasenfratz, J. Willaredt, T. Dambacher, T. Breuer, C. Ottaway, M. Fletschinger, J. Boele, H. Fritz, D. Putzas, H. W. Rotter, F. G. Bordwell, A. V. Satish, G.-Z. Ji, E.-M. Peters, K. Peters, H. G. von Schnering, L. Walz, *Liebigs Ann.* **1996**, 1055–1081.

[12] A. P. Marchenko, G. N. Koidan, A. M. Pinchuk, *Zh. Obshch. Khim.* **1983**, *53*, 670–677; *J. Gen. Chem.* **1983**, *53*, 583–589.

[13] E. V. Dehmlow, U. Fastabend, *Gazz. Chim. Ital.* **1996**, *126*, 53–55; T. Nobori, T. Suzuki, S. Kiyono, M. Kouno, K. Mizutani, Y. Sonobe, U. Takaki (Mitsui Toatsu Chemicals, Inc., Japan), EP 791600 A1, **1997** [*Chem. Abstr.* **1997**, *127*, 234743]; T. Nobori, T. Hayashi, S. Kiyono, U. Takaki (Mitsui Chemicals, Inc., Japan), EP 879838 A2, **1998** [*Chem. Abstr.* **1999**, *130*, 38836]; M. Isobe, K. Ohkubo, S. Sakai, U. Takaki, T. Nobori, T. Izukawa, S. Yamasaki (Mitsui Toatsu Chemicals, Inc., Japan), EP 897940 A2, **1999** [*Chem. Abstr.* **1999**, *130*, 197636]; S. Yamasaki, I. Hara, S. Tamura, F. Yamazaki, H. Watanabe, M. Matsufuji, S. Matsumoto, A. Nishikawa, T. Izukawa, M. Aoki, T. Nobori, U. Takaki (Mitsui Chemicals, Inc., Japan), EP 916686 A1, **1999** [*Chem. Abstr.* **1999**, *130*, 52838]; P. C. Hupfield, R. G. Taylor, *J. Inorg. Organomet. Polym.* **1999**, *9*, 17–34; P. Hupfield, A. Surgenor, R. Taylor (Dow Corning Corporation, USA), EP 1008610 A2, **2000** [*Chem. Abstr.* **2000**, *133*, 31350]; G. Moloney, P. Hupfield, A. Surgenor, R. Taylor (Dow Corning Corporation, USA), EP 1008612 A2, **1999** [*Chem. Abstr.* **2000**, *133*, 31352]; M. Isobe, K. Ohkubo, S. Sakai (Mitsui Toatsu Chemicals, Inc., Japan), EP 1028133 A1, **2000** [*Chem. Abstr.* **2000**, *133*, 164974]; D. Baskaran, A. H. E. Müller, *Macromol. Rapid Commun.* **2000**, *21*, 390–395; S. Yamasaki, Y. Hara, T. Kunihiro, F. Yamazaki, M. Matsufuji, A. Nishikawa, S. Matsumoto, T. Izukawa, M. Isobe, K. Ohkubo, K. Ueno (Mitsui Toatsu Chemicals, Inc., Japan), EP 104100 A1, **2000** [*Chem. Abstr.* **2000**, *132*, 308867]; S. Ota, S. Moriya, R. Mori, T. Koda, J. Tan, S. Kojoh, H. Kaneko, S. Hama, T. Nobori, T. Matsugi, N. Kashiwa (Mitsui Chemicals, Inc., Japan), EP 1275670 A1, **2001** [*Chem. Abstr.* **2001**, *135*, 137856]; A. Grzelka, J. Chojnowski, M. Cypryk, W. Fortuniak, P. C. Hupfield, R. G. Taylor, *J. Organomet. Chem.* **2002**, *660*, 14–26; A. Grzelka, J. Chojnowski, W. Fortuniak,

R. G. Taylor, P. C. Hupfield, *J. Inorg. Organomet. Polym.* **2004**, *14*, 85–99.
[14] T. Nobori, S. Fujiyoshi, I. Hara, T. Hayashi, A. Shibahara, K. Funaki, K. Mizutani, S. Kiyono (Mitsui Chemicals, Inc., Japan), EP 1275630 A1, **2001** [*Chem. Abstr.* **2001**, *135*, 344378].
[15] The phosphazenium salts **2a**·BF_4 and **4a**·Cl are commercially available.[22,23]
[16] A. P. Marchenko, G. N. Koidan, A. M. Pinchuk, *Zh. Obshch. Khim.* **1984**, *54*, 2691–2696; *J. Gen. Chem.* **1984**, *54*, 2405–2409.
[17] H. G. Ang, G. Manoussakis, Y. O. El Nigumi, *J. Inorg. Nucl. Chem.* **1968**, *30*, 1715–1717; Y. O. El Nigumi, H. J. Emeléus, *J. Inorg. Nucl. Chem.* **1970**, *32*, 3211–3212; K. Issleib, M. Lischewski, *Synth. React. Inorg. Met.-Org. Chem.* **1973**, *3*, 255–266.
[18] G. N. Koidan, A. P. Marchenko, A. A. Kudryavtsev, A. M. Pinchuk, *Zh. Obshch. Khim.* **1982**, *52*, 2001–2011; *J. Gen. Chem.* **1982**, *52*, 1779–1787.
[19] R. Schwesinger, J. Willaredt, H. Schlemper, M. Keller, D. Schmitt, H. Fritz, *Chem. Ber.* **1994**, *127*, 2435–2454.
[20] A. P. Marchenko, S. I. Shaposhnikov, G. N. Koidan, A. V. Kharchenko, A. M. Pinchuk, *Zh. Obshch. Khim.* **1988**, *58*, 2230–2237; *J. Gen. Chem.* **1988**, *58*, 1985–1992.
[21] H. Nöth, H. J. Vetter, *Chem. Ber.* **1965**, *98*, 1981–1987; B. Castro, J.-R. Dormoy, B. Dourtoglou, G. Evin, C. Selve, J.-C. Ziegler, *Synthesis* **1976**, 751–752; J.-R. Dormoy, B. Castro, *Tetrahedron Lett.* **1979**, *20*, 3321–3322.
[22] Commercially available from Aldrich Chemical Company.
[23] Commercially available from Fluka Chemie AG (Switzerland).
[24] R. Link, R. Schwesinger, *Angew. Chem.* **1992**, *104*, 864; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 850.
[25] R. Schwesinger, R. Link. G. Thiele, H. Rotter, D. Honert, H.-H. Limbach, F. Männle, *Angew. Chem.* **1991**, *103*, 1376–1378; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1372–1375.
[26] M. Becke-Goehring, W. Lehr, *Chem. Ber.* **1961**, *94*, 1591–1594.
[27] L. Seglin, M. R. Lutz, H. Stange (FMC Corporation, US), US 3231327, **1966** [*Chem. Abstr.* **1966**, *64*, 58007]; D. Bougeard, C. Brémard, R. de Jaeger, Y. Lemmouchi, *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *79*, 147–159.
[28] E. Fluck, E. Schmid, W. Haubold, *Z. Anorg. Allg. Chem.* **1977**, *433*, 229–236.
[29] H. Wieland, A. Höchtlein, *Justus Liebigs Ann. Chem.* **1933**, *505*, 237–247.
[30] The chloride salt **1b**·Cl has already been described: B. Schiemenz, T. Wessel, R. Pfirmann, A. Beck, W. Hahn, (Clariant GmbH, Germany), EP 11070724, **2001** [*Chem. Abstr.* **2001**, *134*, 101014].
[31] a) No spectroscopic data have been reported for the compound: T. B. Cameron, H. N. Hanson, G. F. de la Fuente, J. E. Huheey, *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *78*, 37–46; b) V. G. Kostina, E. K. Rutkovskii, N. G. Feshchenko, *Zh. Obshch. Khim.* **1987**, *57*, 1072–1077; *J. Gen. Chem.* **1987**, *57*, 955–960.
[32] The quality of the X-ray structure of **1e**·$O_3SC_4F_9$ was not sufficient to justify a presentation within this paper: M. Keller, University of Freiburg, unpublished results.
[33] K. M. Harmon, I. Gennick, S. L. Madeira, *J. Phys. Chem.* **1974**, *78*, 2585–2591; A.-R. Mahjoub, X. Zhang, K. Seppelt, *Chem. Eur. J.* **1995**, *1*, 261–265; R. Goddard, H. M. Herzog, M. T. Reetz, *Tetrahedron* **2002**, *58*, 7847–7850, and references therein.
[34] E. V. Dehmlow, S. Schrader, *Z. Naturforsch. B* **1990**, *45*, 409–412; E. V. Dehmlow, G. O. Torossian, *Z. Naturforsch. B* **1990**, *45*, 1091–1092; E. V. Dehmlow, J. Wilkenloh, *Liebigs Ann. Chem.* **1990**, 125–128; E. V. Dehmlow, R. Richter, *Chem. Ber.* **1993**, *126*, 2765–2766; E. V. Dehmlow, U. Fastabend, *J. Chem. Soc. Chem. Commun.* **1993**, 1241–1242; E. V. Dehmlow, R. Richter, A. B. Zhivich, *J. Chem. Res. Synop.* **1993**, 504–505; E. V. Dehmlow, R. Klauck, *J. Chem. Res. Synop.* **1994**, 448–449; E. V. Dehmlow, J. Kinnius, *J. Prakt. Chem.* **1995**, *337*, 153–155; S. Schrader, E. V. Dehmlow, *Org. Prep. Proced. Int.* **1996**, *28*, 634–637; M. Fischer (BASF Aktiengesellschaft, Ludwigshafen), EP 0691334 A1, **1996** [*Chem. Abstr.* **1996**, *124*, 264009]; M. Missfeldt, J. Willsau, R. Büscher, P. Bell, H.-U. Borst (Agfa-Gevaert AG, Germany), EP 0762202 A1, **1997** [*Chem. Abstr.* **1997**, *126*, 257014]; H. Jin Lee, U. Sun Kong, D. Kwon Lee, J. Ho Shin, H. Nam, G. Sig Cha, *Anal. Chem.* **1998**, *70*, 3377–3383; M. Hwan Kim, K. Moon Lee, H. Joon Oh, H. Choll Cho, D. Hoe Cho, H. Nam, G. Sig Cha, K.-J. Paeng, *Anal. Sci.* **2001**, *17*, 995–997; E. V. Dehmlow, M. Kaiser, J. Bollhöfer, *New J. Chem.* **2001**, *25*, 588–590; W. Klein, M. Jansen, *Z. Naturforsch. B* **2001**, *56*, 287–292; N. Okawa (Dow Corning Toray Silicone Co. Ltd., Japan), JP 2003073476 A2, **2003** [*Chem. Abstr.* **2003**, *138*, 222300]; T. Okawa (Dow Corning Toray Silicone Co. Ltd., Japan), JP 2003252996 A2, **2003** [*Chem. Abstr.* **2003**, *139*, 231135]; S. Funaki, Y. Taniguchi, T. Nobori, Y. Yamamoto, I. Hara, T. Hayashi, K. Mizutani, S. Kiyono, EP 1486479 A1, **2004** [*Chem. Abstr.* **2004**, *142*, 55652].
[35] Succeeding paper.
[36] A. Altonare, M. C. Burla, M. Carnalli, G. Gascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagan, *J. Appl. Crystallogr.* **1999**, *32*, 115–122.
[37] G. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen (Germany).

Received: May 2, 2005
Revised: July 18, 2005
Published online: September 28, 2005

