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New Lipophilic 2-Amino-*N*,*N*′-dialkyl-4,5-dimethylimidazolium Cations: Synthesis, Structure, Properties, and Outstanding Thermal Stability in Alkaline Media

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Dedicated to Professor H.-U. Reissig on the occasion of his 60th birthday

Abstract: A series of new *N*,*N*′-dialkyl-4,5-dimethylimidazolium cations possessing electron-rich 2-imidazolylidene- or phosphoranylidene-amino substituents has been efficiently synthesized from common precursors, *N*,*N*′-dialkyl-4,5-dimethylimidazol-2-ylidenes. The new lipophilic salts obtained have been found to be highly stable towards strong alkali under both biphasic and homogeneous conditions. Their exceptional aqueous base resistance, which has hitherto only been seen with peralkylated polyaminophosphazenium cations, may be attributed to three factors: aromatic stabilization, efficient resonance charge delocalization, and steric protection of the exocyclic nitrogen linkage due to bulky lipophilic *N*-alkyl substituents.

Keywords: aromatic stabilization · imidazolium cations · lipophilicity · phase-transfer catalysis · steric protection

Introduction

Phase-transfer catalysis by means of lipophilic organic cations capable of maintaining an efficient concentration of reactive anionic species in organic media has become an essential tool for both established and state-of-the-art organic synthesis.[1] Low cost, operational simplicity, and environmental benefits offered by the phase-transfer catalysis technique are attractive for industrial applications.[2] In order for the catalysis to be sustainable, the lipophilic cationic catalyst has to be compatible with the basic/nucleophilic medium under the reaction conditions. However, conventional organic cations have limited stability towards concentrated aqueous alkali hydroxides or powerful nucleophiles, especially at elevated temperatures.[3,4] For this reason, the design and synthesis of stable organic cations has become an important objective with regard to phase-transfer methodology.[4,5]

The organic phosphazenium cations developed by Schwesinger et al.[4,6] set new benchmarks in terms of thermal stability and base resistance, and hence they attracted considerable interest from industrial laboratories.[7] The commercially available tetrakis{[tris(dimethylamino)phosphoranyliden]-amino}phosphonium (P_5-phosphazenium cation) found industrial application for the production of high-quality polymeric materials.[8] However, excellent stability of the P_5-cation is attained at the expense of the high molecular weight required for the extensive resonance delocalization of the positive charge over the large dendritic network of alternating P and N atoms. Moreover, all catalysts of the PN-type exhibit potential dermal toxicity due to traces of hexaalkylphosphoramide.[5f]

It seems reasonable to assume that rational design exploiting a combination of electronic and steric effects to facilitate charge delocalization and enhance hydrolytic stability could result in the discovery of cationic structures with comparable or even greater base resistance. In a search for such structures, we turned our attention to the versatile tools and immense structural diversity offered by heterocyclic chemistry.

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Results and Discussion

In our own approach to the design of stable lipophilic cations, we assumed that accommodation of the positive charge within an aromatic system should impart additional stability and base resistance. Aromatically stabilized cationic systems appended with appropriately positioned donor substituent(s) to enable efficient delocalization of positive charge and bulky alkyl groups to provide steric protection of centres likely to be susceptible to nucleophilic cleavage were deemed likely to display the highest thermal stability. Herein, we report a new family of lipophilic cations incorporating a fully substituted[9] aromatic imidazolium core, namely 2-[1,3-dialkyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylideneamino]-1,3-dialkyl-4,5-dimethylimidazoliums $\mathbf{1}^+$ (hereinafter referred to as bis(*N*,*N*′-dialkylimidazolium)amides or BIMA), 2-[tris(dimethylamino)phosphoranylidenamino]-1,3-dialkyl-4,5-dimethylimidazoliums $\mathbf{2}^+$, and 2-[bis(dimethylamino)methyleneamino]-1,3-diisopropyl-4,5-dimethylimidazolium $\mathbf{3}^+$ (Figure 1).

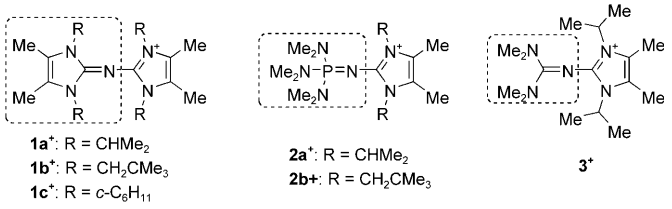
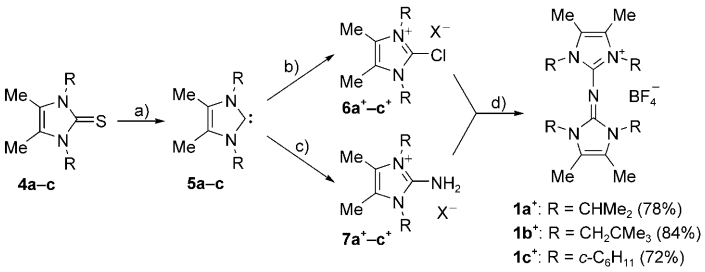


Figure 1. New lipophilic cations designed for phase-transfer applications under drastic conditions: basic/nucleophilic media at high temperature. Encircled with a dashed line are groups facilitating charge delocalization due to resonance.

Our choice of donor groups was stipulated by their ability to facilitate maximum delocalization of a positive charge, as known for Schwesinger's basicity battery cells $(R_2N)_3P{=}N$[10] or anticipated by us for the imidazol-2-ylideneamino group in BIMA $\mathbf{1}^+$. Cations $\mathbf{1}^+$ and $\mathbf{2}^+$ were found to be extremely base-resistant, with their stability towards the strong alkali base KOH being no lower than that of industrially applied $[(Me_2N)_3P{=}N]_4P^+$ (P_5-phosphazenium cation).[11]

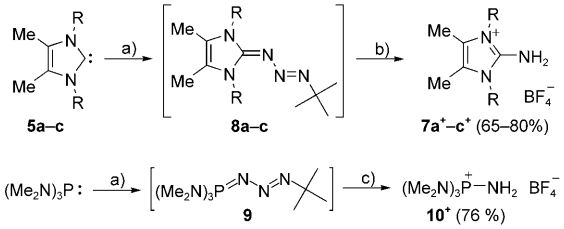
The synthesis of BIMA $\mathbf{1}^+$ was accomplished in a convergent manner starting from common precursors, stable tetraalkylimidazolin-2-ylidenes **5**[12] (Scheme 1), which were prepared on a multigram scale from 1,3-dialkyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thiones **4**[13] and stored as stock solutions in hexane at room temperature under an inert atmosphere.

The BIMA salts $\mathbf{1}{\cdot}BF_4$ were obtained by KF-mediated coupling of the intermediary salts (**6a–c**)·X with the corresponding derivatives **7**·X. We found it convenient to operate with stable, crystalline, non-hygroscopic building blocks $\mathbf{6}{\cdot}BF_4$ and $\mathbf{7}{\cdot}BF_4$. However, the viability of the protocol without isolation of the intermediates **6a**·X and **7a**·X was exemplified by the synthesis of $\mathbf{1a}{\cdot}BF_4$ from **5a** in 65% overall yield (see the Experimental Section). While chlorination of



Scheme 1. Synthesis of the BIMA salts $\mathbf{1}{\cdot}BF_4$: a) Na/K alloy, glyme, reflux; b) C_2Cl_6, THF, −40 °C; c) see **5** to $\mathbf{7}^+$ in Scheme 2; d) KF in MeCN, then aq. $NaBF_4$; yields are given for step d).

5 at C-2 to give $\mathbf{6}^+$ is documented,[14] the amination method using *tert*-butyl azide to obtain $\mathbf{7}^+$ is unprecedented in the literature.[15] We capitalized on the recently described simple, safe and efficient procedure for large-scale synthesis of *tert*-butyl azide.[16] When treated with *tert*-butyl azide, the nucleophilic carbenes **5** and tris(dimethylamino)phosphine quantitatively produce the corresponding *tert*-butyltriazenes **8** and **9** (Scheme 2).



Scheme 2. Amination with *tert*-butyl azide: a) Me_3CN_3, THF; b) NH_4BF_4, MeOH; c) CF_3CO_2H, then aqueous $NaBF_4$.

The structure of **8a** (R=$CHMe_2$) was proven by single-crystal X-ray diffraction[17] (Figure 2). Compounds **8** and **9** are relatively thermally stable intermediates. Upon mild acidic treatment, they readily release $CH_2{=}CMe_2$ and N_2, furnishing high yields of the requisite building blocks $\mathbf{7}{\cdot}BF_4$ and $\mathbf{10}{\cdot}BF_4$, respectively.

The salts $\mathbf{2}{\cdot}BF_4$ and $\mathbf{3}{\cdot}BF_4$ were obtained as shown in Scheme 3. Here again, KF-promoted coupling proved advantageous.[18]

The new imidazolium salts $(\mathbf{1–3}){\cdot}BF_4$ are stable, colourless, non-hygroscopic crystalline solids that are readily soluble in chlorinated hydrocarbons, alcohols, and polar non-protogenic organic solvents.

In a first attempt to evaluate the stability of BIMA $\mathbf{1}^+$ towards aqueous alkali, a sample of $\mathbf{1a}{\cdot}ONf$ was heated to 120 °C with an excess of 50% aqueous KOH in [D_6]DMSO. Although appreciable H/D exchange in the Me groups at the 4,5-positions occurred, the *N*-isopropyl groups remained intact, and no hydrolytic cleavage of $\mathbf{1a}^+$ was observed under these conditions. Encouraged by this result, we examined the base resistances of the cations $\mathbf{1}^+–\mathbf{3}^+$ under biphasic (PhCl/50% aqueous KOH) and homogeneous (KOH in

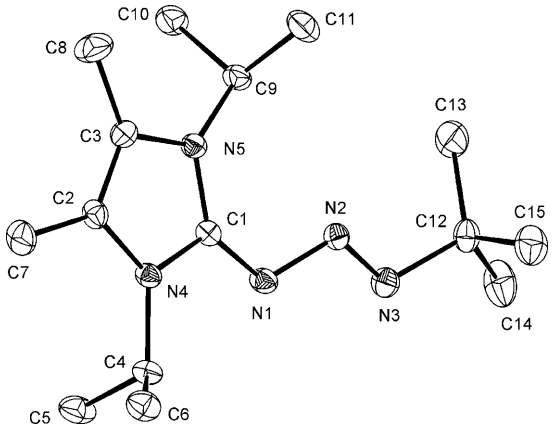
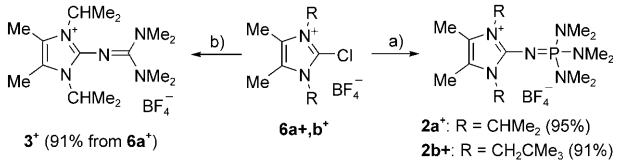


Figure 2. X-ray crystal structure of the triazene **8a**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bonds lengths and angles [Å, °]: N1–C1 1.3411(16), N4–C1 1.3638(15), N5–C1 1.3618(16), N4–C2 1.3951(16), C2–C3 1.3537(18), N5–C3 1.4115(17), N1–N2 1.3617(15), N2–N3 1.2517(16), N3–C12 1.4856(18); N5-C1-N1 134.36(11), N4-C1-N1 118.74(11), C1-N1-N2 113.83(10), N1-N2-N3 111.92(10).



Scheme 3. Synthesis of the salts **2**·BF_4 and **3**·BF_4: a) **10**·BF_4, KF in MeCN, then aq. $NaBF_4$; b) $(Me_2N)_2C{=}NH$, KF in MeCN, then aq. $NaBF_4$.

ethylene glycol) conditions, comparing them with that of commercially available tetrakis{[tris(dimethylamino)phosphoranyliden]amino}phosphonium (P_5-phosphazenium cation), the exceptional base resistance of which is commonly acknowledged. The results are summarized in Table 1.

Cation $\mathbf{3}^+$ proved to be the least stable. It was found to be slowly cleaved by 50% aqueous KOH with a loss of one Me_2N group, even at room temperature (Table 1, entry 6). Apparently, the $(Me_2N)_2C{=}N$ group in organic cations is not compatible with concentrated aqueous alkali, especially at elevated temperatures, although it was found to be advantageous in the design of cationic phase-transfer catalysts for nucleophilic fluorinations with KF (Halex process) in aprotic media.[5f]

BIMAs $\mathbf{1a}^+$,$\mathbf{c}^+$ and phosphoranylidenaminoimidazolium $\mathbf{2a}^+$ displayed much higher base resistance, their half lives ranging from 30 to 95 h in a refluxing biphasic mixture of PhCl/50% aqueous KOH at 115°C (Table 1, entries 1, 3, and 4). These stabilities are far superior to those of conventional organic cations, and comparable to those of the most stable peralkylated polyaminophosphazenium cations.[4]

The neopentyl-substituted cations $\mathbf{1b}^+$ and $\mathbf{2b}^+$ and the P_5-phosphazenium cation[4,11] proved to be the most stable of the studied series. They did not show tangible signs of decomposition in a refluxing biphasic mixture of PhCl and 50% aqueous KOH (Table 1, entries 2, 5, and 7).[19] Recognizing the temperature limitations of the above biphasic mixtures at atmospheric pressure, we turned our attention to homogeneous solutions of KOH in ethylene glycol, b.p. 197°C.

Prolonged reflux of **1b**·BF_4, **2b**·OTs, or $[(Me_2N)_3P{=}N]_4P{\cdot}BF_4$ in a 1 M solution of KOH in ethylene glycol resulted in insignificant decomposition (Table 1, entries 8–10). Based on these data, the half lives of the cations under these conditions were estimated to be well in excess of 650 h. Thus, the most stable representative of the new class of lipophilic organic cations having a tetraalkyl imidazolium core matches the permethylated P_5-cation in terms of chemical resistance towards strong alkali at high temperatures.

To gain better insight into the factors enhancing the stability of BIMA $\mathbf{1}^+$, we analyzed the alkaline hydrolysis of the cation $\mathbf{1a}^+$ (Scheme 4), and the X-ray structures of the salts **1a**·OTs (Figure 3) and **1b**·I (Figure 4).

The hydrolytic cleavage of $\mathbf{1a}^+$ proceeded cleanly, resulting in the imidazolinone derivatives **7a′**[9a] and **11**. Despite apparent favourability of the Hofmann degradation pathway for the cation possessing four *N*-isopropyl groups, no products arising from base-induced elimination of propylene could be detected.[20] Evidently, the observed hydrolysis is initiated by nucleophilic attack of OH^- at the C centre in $\mathbf{1a}^+$, as shown in Scheme 4. For this to happen, a breakdown of the 6π-aromaticity of the imidazolium ring has to occur in the rate-limiting step, hence the increase in the activation barrier resulting in enhanced base resistance.

The X-ray structure of $\mathbf{1a}^+$ in **1a**·OTs[17] (see Figure 3 and the legend) features two imidazolium rings with nearly identical structural parameters, bond lengths, and angles, and an sp^2-hybridized exocyclic N1 atom with two equal C–N bonds. It indicates an even distribution of the positive charge over both

Table 1. Half lives of the organic cations in strongly basic media. Conditions **A**: vigorously stirred biphasic mixture of PhCl/50% aqueous KOH, reflux (115°C inner temperature, 145°C oil-bath temperature). Conditions **B**: 1 M solution of KOH in ethylene glycol, reflux.

Entry	Compound	Conditions	Reaction time [h]	Conversion [%][a]	$t_{1/2}$ [h]
1	**1a**·BF_4	**A**	24	42	31
2	**1b**·BF_4	**A**	48	trace[a]	stable
3	**1c**·BF_4	**A**	21	33	36
4	**2a**·BF_4	**A**	30	20	94
5	**2b**·OTs[b]	**A**	48	trace[a]	stable
6	**3**·BF_4	**A**	16	18	58[c]
7	$[(Me_2N)_3P{=}N]_4P{\cdot}BF_4$	**A**	48	trace[a]	stable
8	**1b**·BF_4	**B**	24	<5	>650
9	**2b**·OTs[b]	**B**	24	<5	>650
10	$[(Me_2N)_3P{=}N]_4P{\cdot}BF_4$	**B**	24	<5	>650

[a] At the limit of detection by the NMR technique. [b] Obtained according to Scheme 3 followed by treatment with TsOK in 50% aqueous MeOH instead of aqueous $NaBF_4$. [c] At 25°C.

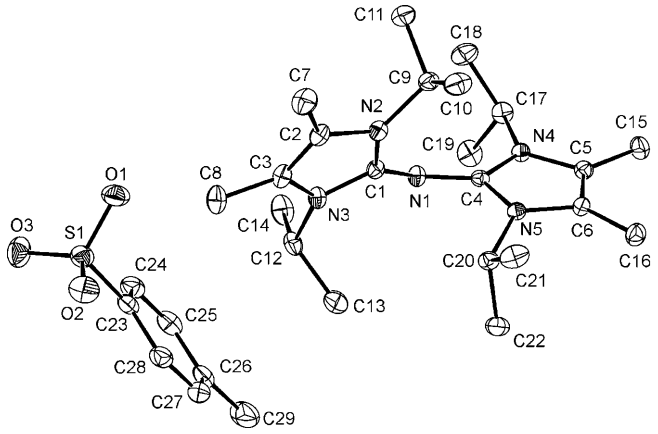


Figure 3. X-ray crystal structure of the BIMA salt **1a**·OTs. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bonds lengths and angles [Å, °]: N1–C1 1.332(2), N1–C4 1.331(2), N2–C1 1.360(2), N2–C2 1.410(3), C2–C3 1.351(3), N3–C3 1.403(2), N3–C1 1.357(2), N4–C4 1.355(2), N4–C5 1.403(2), C5–C6 1.345(3), N5–C6 1.413(2); C4-N1-C1 124.96(13). Dihedral angle between the two imidazolium rings: 73.96(11)°.

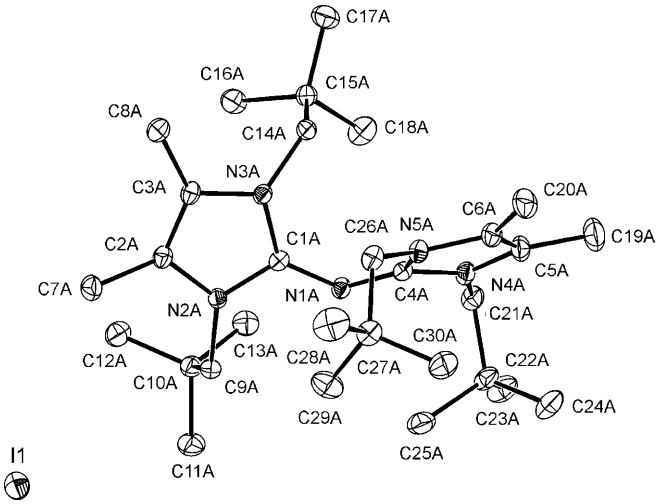


Figure 4. One of the three symmetrically independent cations observed in the X-ray crystal structure of **1b**·I. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bonds distances and angles [Å, °]: N1A–C1A 1.333(3), N1A–C4A 1.336(3), N2A–C1A 1.355(3), N2A–C2A 1.412(3), C2A–C3A 1.343(3), N3A–C3A 1.408(3), N3A–C1A 1.364(3), N4A–C4A 1.359(3), N4A–C5A 1.407(3), C5A–C6A 1.345(4), C1A-N1A-C4A 122.8(2). Dihedral angle between the two imidazolium rings: 52.9(2)°.

imidazolium rings and hence optimum electronic stabilization of the system. The spatial arrangement of the core structure displays significant deviation from planarity with a dihedral angle of 74° between the planes containing the imidazolium rings. All four $CHMe_2$ substituents are spatially arranged in such a way that they provide efficient hydrophobic protection of the C1/C4 centres from nucleophilic attack by the hydroxide anion.[21]

It is reasonable to assume that, while the electronic effects in BIMA $\mathbf{1}^+$ remain essentially the same, steric shielding by four bulky neopentyl substituents in $\mathbf{1b}^+$ appears to be the greatest (X-ray structure of **1b**·I;[17] see Figure 4 and the legend). The structural parameters of the intercyclic C1A-N1A-C4A junction in $\mathbf{1b}^+$ are almost identical to those in $\mathbf{1a}^+$, but the dihedral angle between the imidazolium rings (53°)[17,22] is smaller than that in $\mathbf{1a}^+$. Surprisingly, both CMe_3 groups of each imidazolium ring are located on the same face of the ring plane. Impending over the C1A/C4A centres, the CMe_3 groups sterically hinder the approach of OH^- from this face, whereas the opposite face of the ring plane is protected from nucleophilic attack by the neopentyl group of the neighbouring imidazolium moiety. This accounts for the highest base resistance being observed for $\mathbf{1b}^+$.

Considerable steric crowding is a likely cause of a slow dynamic process on the NMR timescale, as observed for solutions of the salt **1b**·BF_4. The process causes line-broadening and non-equivalence of CMe_3 groups and 4,5-Me groups in the ^{1}H NMR spectrum at 25 °C. In CD_3OD at −33 °C, the ^{1}H signals of two non-equivalent CH_2 groups are split into *AB* systems (Figure 5), while the ^{13}C NMR spectrum of $\mathbf{1b}^+$

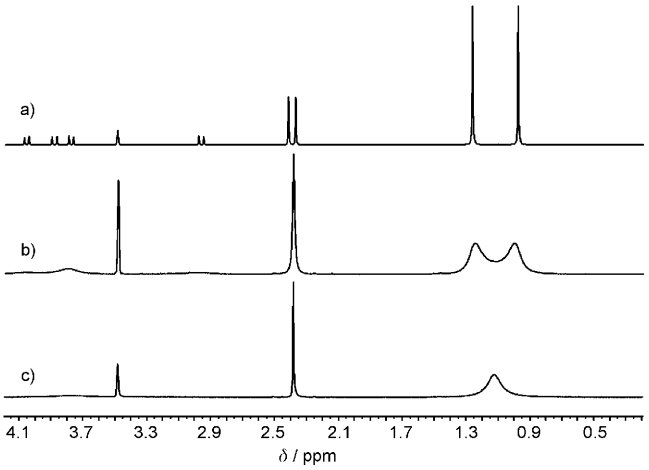
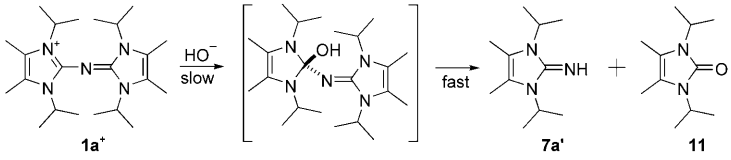


Figure 5. Temperature-dependent ^{1}H NMR spectra of the cation $\mathbf{1b}^+$ measured in CD_3OD at a) 240 K, b) 298 K, and c) 313 K.



Scheme 4. Hydrolytic cleavage of the BIMA cation.

indicates a structure with two identical imidazolium rings lacking perpendicular planes of symmetry (Figure 6). At elevated temperature (100 °C in [D_6]DMSO), the proton signals within each group become equivalent and appear as typical singlets (see the Experimental Section). In contrast, no re-

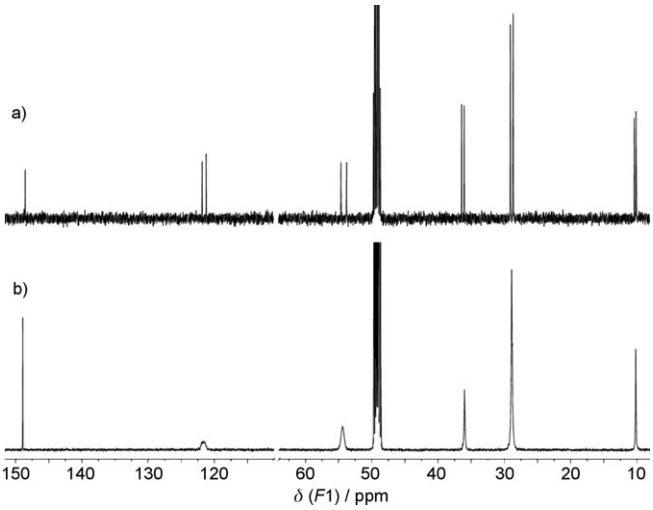
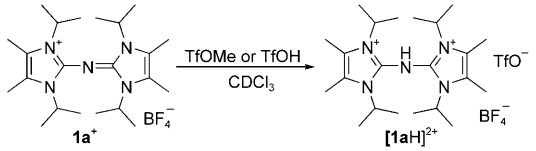


Figure 6. Temperature-dependent ^{13}C NMR spectra of the cation $\mathbf{1b}^+$ measured in CD_3OD at a) 240 K and b) 300 K.

stricted rotation was observed for the cation $\mathbf{1a}^+$, and its NMR spectra remained unchanged as a function of temperature down to −20 °C.

The observed temperature-dependent dynamics in the NMR spectra of $\mathbf{1b}^+$ could be rationalized in terms of a combination of two different processes of sterically hindered rotation with similar activation barriers (ΔG): one is due to slow rotation of the Me_3CCH_2 groups about the CH_2–N bonds causing splitting of the CH_2 signals to *AB* systems, while the other is due to slow rotation of the imidazolium rings about the exocyclic C2–N/N–C2′ bonds resulting in a loss of perpendicular planes of symmetry.

Our failure to obtain an *N*-methylated product from the reaction of $\mathbf{1a}^+$ with TfOMe points to substantial steric crowding created by the isopropyl groups around the C2-N-C2′ fragment. Instead, *N*-protonation occurred,[23] giving rise to the stable symmetrical dication $[\mathbf{1a}H]^{2+}$, the identity of which was verified independently by treatment of $\mathbf{1a}^+$ with TfOH (Scheme 5).



Scheme 5. Protonation of $\mathbf{1a}\cdot BF_4$ to give $[\mathbf{1a}H]\cdot OTf\cdot BF_4$; no methylation product was detected in the reaction with TfOMe.

Conclusions

In conclusion, we have designed and synthesized new organic cations, the alkaline base resistance of which at high temperature far exceeds that of conventional organic cations and is on a par with that of the permethylated P_5-phosphazenium cation.[4,11] The enhanced stability may be attributed to accommodation of the positive charge by an electronically stabilized aromatic imidazolium moiety, with bulky *N*-alkyl groups providing additional steric protection. Susceptibility to Hofmann degradation is strongly diminished due to the low charge density on the endocyclic nitrogen atoms or may be completely precluded, as in the case of the tetraneopentyl cation $\mathbf{1b}^+$.

The outstanding stability of the fully substituted imidazolium cations paves the way to applications for which high base resistance is a prerequisite for sustainable chemical performance, that is, phase-transfer catalysts under harsh reaction conditions, anhydrous fluoride sources, anionic reactions in aprotic media, or base-induced polymerization. Syntheses and exploratory studies of new salts based on the cations $\mathbf{1}^+$ and $\mathbf{2}^+$ combined with highly basic anions, specifically fluorides, alcoholates, and enolates, are currently underway and will be reported in due course.

Experimental Section

General: Melting points (m.p.; uncorrected): Wagner & Munz PolyTherm A apparatus; elemental analyses: PE 2400 Series II CHN analyzer. NMR spectra were measured from solutions in $CDCl_3$ on a Bruker Avance 400 spectrometer at 300 K unless stated otherwise: ^1H (400 MHz) referenced to internal standard $SiMe_4$ in $CDCl_3$ and C_6D_6 or to residual solvent peaks[24] in $[D_6]$DMSO and CD_3CN; ^{13}C (100.6 MHz) referenced to *d*-solvent signals;[24] ^{31}P (162 MHz) referenced to internal standard $(MeO)_3PO$ ($\delta = 3.0$ ppm in $CDCl_3$ or 3.5 ppm in $[D_6]$DMSO);[25] ^{19}F NMR (376.5 MHz) referenced to internal standard $PhCF_3$ ($\delta = -63.7$ ppm),[26] the signals of BF_4^- of the imidazolium salts appeared at -155 ± 0.5 ppm as two singlets due to $^{10}BF_4^-$ and $^{11}BF_4^-$ (1:4 ratio), the former 0.06 ppm downfield from the latter. Temperature-dependent NMR spectra were measured on a Bruker Avance 500 spectrometer (500 MHz for ^1H, 125.7 MHz for ^{13}C). IR spectra were recorded on a Bruker Alpha spectrometer equipped with an ATR device. ESI mass spectra were recorded using a Thermo Scientific LCQ Fleet mass spectrometer. High-resolution mass spectra (HRMS) were obtained with EI or APCI instruments.

3-Hydroxybutan-2-one, *N,N′*-diisopropylthiourea, pentan-1-ol, *tert*-butanol, MeOH, $CHCl_3$, Me_3CCN, $LiAlH_4$, cyclohexylamine, $S{=}CCl_2$, C_2Cl_6, 25% aqueous NH_3, 40% aqueous HBF_4, CF_3CO_2H, $NaBF_4$, $P(NMe_2)_3$, PhCl, ethylene glycol, TfOMe, and TfOH were used as purchased from commercial suppliers. Et_3N was dried and stored over KOH pellets. $(Me_2N)_2C{=}NH$ was freshly distilled in vacuo over BaO. NH_4BF_4 was prepared by careful neutralization of aqueous NH_3 with aqueous HBF_4 followed by removal of water under reduced pressure and drying under high vacuum.

tert-Butyl azide,[16] neopentylamine,[27] and *N,N′*-dineopentyl- and *N,N′*-dicyclohexylthioureas[28] were obtained according to the literature procedures.

All reactions were carried out in heat-gun-dried glassware equipped with magnetic stirring bars under an atmosphere of dry argon. ^1H NMR control of the reaction mixtures was routinely performed to ensure complete conversions of the starting materials. Solvents were dried by standard procedures: THF and 1,2-dimethoxyethane were distilled over Na/K alloy with added Ph_2CO; diglyme was distilled in vacuo over Na; toluene was distilled over Na; MeCN was distilled over CaH_2 and stored over 3 Å molecular sieves; hexane was distilled over P_2O_5. Commercially available "dry" KF (ca. 20 g) was placed in a mortar and maintained in an oven at 200 °C for 12 h. Then, whilst still hot, it was thoroughly ground to a fine powder using a hot pestle (thick leather gloves!). Thus, pre-dried KF was used for further activation to serve as a heterogeneous base in the synthesis of the target cations. All the products obtained were of more than 95% purity (NMR).

***N,N′*-Dialkyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thiones (4): General procedure (GP 1)** based on the method described earlier.[13] The requisite *N,N′*-dialkylthiourea (100 mmol), 3-hydroxybutanone (110 mmol), and pentan-1-ol (65 mL) were placed in a 250 mL reaction flask equipped with a magnetic stirring bar, a Dean–Stark head, and a reflux condenser. The reaction mixture was heated with an oil bath and maintained under reflux for about 48 h until no more water was produced, indicating complete conversion. We found that reflux in pentan-1-ol and the use of a Dean–Stark head provides better reaction control and affords cleaner conversions. The work-ups of the reaction mixtures and spectral data of the products were as specified below.

1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thione (4a): The heating was turned off, and the reaction mixture was allowed to slowly cool overnight with stirring while still in the oil bath, whereupon white crystals separated. The mixture was further cooled to −20 °C, and the precipitated crystals were collected by filtration, washed a few times with cold (−20 °C) methanol, and dried in high vacuum to furnish the pure product **4a** (18.05 g, 85 %) as colourless crystals. ^{1}H and ^{13}C NMR data of **4a** were in good agreement with those reported in the literature.[13]

1,3-Dineopentyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thione (4b): The reaction mixture was cooled to ambient temperature, the solvent was evaporated in vacuum, and the residual oil was distilled under high vacuum (165 °C/0.3 mbar) to give the product **4b** (21.48 g, 80 %), which slowly crystallized to a low-melting yellowish solid. ^{1}H NMR (C_6D_6): $\delta = 1.01$ (s, 18H; CMe_3), 1.60 ppm (s, 6H; Me); NCH_2 signals were not observed due to very strong broadening; ^{13}C NMR (C_6D_6): $\delta = 10.4$ (Me), 29.3 (CMe_3), 35.2 (CMe_3), 54.9 (NCH_2), 121.1 (C=C), 167.6 ppm (C=S); HRMS (EI): *m/z*: calcd for $C_{15}H_{28}N_2S$: 268.1973 [M^+]; found: 268.1965.

1,3-Dicyclohexyl-4,5-dimethyl-1*H*-imidazole-2(3*H*)-thione (4c): The reaction mixture was cooled to ambient temperature, the solvent was evaporated in vacuo, and the residual oil was dried under high vacuum (150 °C/0.05 mbar) for 2 h to give the product **4c** (28.08 g, 96 % yield) as a tawny glass. ^{1}H NMR (C_6D_6): $\delta = 0.59$–2.25 (m), 1.78 (s) (26H, all CH_2 and Me), 5.86 ppm (brs, 2H; NCH); ^{13}C NMR (C_6D_6): $\delta = 10.6$ (Me), 25.9, 26.6, 31.4 (all CH_2), 58.0 (NCH), 120.8 ppm (C=C); a C=S signal was not observed due to very low intensity; HRMS (EI): *m/z*: calcd for $C_{17}H_{28}N_2S$: 292.1973 [M^+]; found: 292.1966.

***N,N′*-Dialkyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidenes (5): General procedure (GP 2)** based on the method described earlier.[13] Na (1.61 g, 70 mmol) and K (5.47 g, 140 mmol) were sequentially added to an argon-flushed reaction flask equipped with a three-way tap. The flask was then connected to a diaphragm vacuum pump, and the Na/K eutectic was formed by cautiously melting the metals with a heat-gun under reduced pressure while gently swirling the contents of the flask. The reaction flask was then filled with argon and allowed to cool to ambient temperature. A glass-coated magnetic stirring bar was placed in the flask, and a solution of **4** (70 mmol) in 1,2-dimethoxyethane (150 mL) was cautiously added with vigorous stirring. The reaction flask was fitted with a reflux condenser, and the reaction mixture was stirred under reflux for 5 h until full conversion. It was then allowed to cool, the solvent was removed in vacuo, and the residue was diluted with dry hexane (250 mL) and stirred for 1 h. The insoluble inorganic residue was allowed to precipitate overnight. The yields and titres of the products **5** were estimated by withdrawing aliquots of clear hexane solutions, evaporating the solvent, drying under high vacuum at RT, and weighing the residues. The resulting clear homogeneous stock solutions of the products **5** (> 90 % yield in each case) could be stored for several months at ambient temperature under an inert atmosphere. Care should be taken to avoid turbidity when withdrawing aliquots from the stock solutions.

1,3-Diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene (5a): ^{1}H and ^{13}C NMR data were in good agreement with those reported in the literature.[13]

1,3-Dineopentyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene (5b): ^{1}H NMR (C_6D_6): $\delta = 1.00$ (s, 18H; CMe_3), 1.76 (s, 6H; Me), 3.69 ppm (s, 4H; NCH_2); ^{13}C NMR (C_6D_6): $\delta = 10.1$ (Me), 28.5 (CMe_3), 33.5 (CMe_3), 58.3 (NCH_2), 122.7 ppm (C=C); a C-2 signal was not observed due to very low intensity.

1,3-Dicyclohexyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene (5c): ^{1}H NMR (C_6D_6): $\delta = 1.11$–1.33 (brm, 6H), 1.44–1.61 (brm, 2H), 1.66–1.86 (brm, 10H), 1.94–2.10 (brm, 4H), 2.24–2.47 (brm, 4H) (all CH_2 and Me), 3.66 ppm (tt, $J = 11.6$ Hz, $J = 3.8$ Hz, 2H; NCH); ^{13}C NMR (C_6D_6): $\delta = 8.8$ (Me), 26.0, 26.5, 35.5 (all CH_2), 58.7 (NCH), 121.5 ppm (C=C); a C-2 signal was not observed due to very low intensity.

2-Chloro-*N,N′*-dialkyl-4,5-dimethylimidazolium tetrafluoroborates (6·BF_4): General procedure (GP 3): A stock solution of **5** (15.0 mmol) in hexane was added to a reaction flask. The hexane was removed in vacuo, THF (60 mL) was added to the solid residue, and the resulting solution was cooled to −40 °C. C_2Cl_6 (3.800 g, 16.0 mmol) was added in one portion under vigorous stirring, and the reaction mixture was allowed to gradually warm to ambient temperature and stirred for 24 h. It was then poured into a separating funnel containing a two-phase mixture of $CHCl_3$ (100 mL)/10 % aqueous $NaBF_4$ (100 mL), which was vigorously shaken. The organic phase was separated, and the aqueous phase was extracted once with $CHCl_3$ (20 mL). The combined organic phases were washed with 10 % aqueous $NaBF_4$ solution (100 mL), dried ($MgSO_4$), and filtered. The volatiles were removed in vacuo, and the solid residue was dried under high vacuum at 50 °C overnight to remove residual traces of C_2Cl_6, yielding pure product **6** as a yellowish crystalline solid.

2-Chloro-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate (6a·BF_4): 69 % yield, m.p. 156–158 °C (from AcOEt/MeOH, 20:1); ^{1}H NMR: $\delta = 1.64$ (d, $^3J = 7.0$ Hz, 12H; $CHMe_2$), 2.35 (s, 6H; Me), 4.85 ppm (sept, $^3J = 7.0$ Hz, 2H; NCH); ^{13}C NMR: $\delta = 9.9$ (Me), 20.4 ($CHMe_2$), 52.8 (NCH), 126.4 (C-Cl), 128.2 ppm (C=C); these NMR data are in good agreement with those described earlier for the tetrachloroaluminate salt;[14] IR: $\tilde{\nu} = 899$, 1032, 1044, 1093, 1377, 1454, 1506 cm^{-1}; HRMS (ESI$^+$): *m/z*: calcd for $C_{11}H_{20}{}^{35}ClN_2{}^+$: 215.1310 [$M^+$]; found: 215.1311; elemental analysis calcd (%) for $C_{11}H_{20}BClF_4N_2$: C 43.67, H 6.66, N 9.26; found: C 43.77, H 6.69, N 9.12.

2-Chloro-1,3-dineopentyl-4,5-dimethylimidazolium tetrafluoroborate (6b·BF_4): 95 % yield, m.p. 130–132 °C (from AcOEt); ^{1}H NMR (CD_3CN): $\delta = 1.04$ (s, 18H; CMe_3), 2.30 (s, 6H; Me), 4.00 ppm (s, 4H; NCH_2); ^{13}C NMR (CD_3CN): $\delta = 10.8$ (Me), 28.1 (CMe_3), 35.5 (CMe_3), 57.6 (CH_2), 130.3 (C=C), 131.6 ppm (C-Cl); IR: $\tilde{\nu} = 1034$, 1048, 1101, 1484, 1506 cm^{-1}; HRMS (ESI$^+$): *m/z*: calcd for $C_{15}H_{28}{}^{35}ClN_2{}^+$: 271.1936 [$M^+$]; found: 271.1935; elemental analysis calcd (%) for $C_{15}H_{28}BClF_4N_2$: C 50.23, H 7.87, N 7.81; found: C 50.50, H 7.95, N 7.67.

2-Chloro-1,3-dicyclohexyl-4,5-dimethylimidazolium tetrafluoroborate (6c·BF_4): 65 % yield, m.p. 102–104 °C (from AcOEt); ^{1}H NMR: $\delta = 1.14$–1.33 (m, 2H), 1.35–1.54 (m, 4H), 1.69–1.82 (m, 2H), 1.86–2.16 (m, 12H) (all CH_2), 2.36 (s, 6H; Me), 4.25–4.46 ppm (m, 2H; NCH); ^{13}C NMR: $\delta =$ 10.3 (Me), 24.8, 25.8, 30.2 (all CH_2), 61.0 (NCH), 126.6 (C-Cl), 128.4 ppm (C=C); IR ($CDCl_3$): $\tilde{\nu} = 1026$, 1070, 1443, 1496 cm^{-1}; HRMS (ESI$^+$): *m/z*: calcd for $C_{17}H_{28}{}^{35}ClN_2{}^+$: 295.1936 [$M^+$]; found: 295.1936; elemental analysis calcd (%) for $C_{17}H_{28}BClF_4N_2$: C 53.36, H 7.38, N 7.32; found: C 53.49, H 7.39, N 7.20.

2-Amino-*N,N′*-dialkyl-4,5-dimethylimidazolium tetrafluoroborates (7): General procedure (GP 4): A stock solution of **5** (15.0 mmol) in hexane was added to a reaction flask. The hexane was removed in vacuo, and the solid residue was redissolved in THF (15 mL). A solution of *tert*-butyl azide (1.640 g, 16.5 mmol) in toluene (16.5 mL) was then slowly added under vigorous stirring. After 5 min, the reaction mixture was heated to 60 °C and stirred for 30 min yielding the triazene **8** (NMR control). The volatiles were removed in vacuo, and the residue was redissolved in MeOH (15 mL). Solid NH_4BF_4 (2.360 g, 22.5 mmol) was then slowly added (Caution: Effervescence due to evolution of N_2 and isobutylene!) and the reaction mixture was stirred for 15 min. After aqueous work-up as described in GP 3, the pure product **7** was isolated as a colourless crystalline solid.

2-Amino-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate (7a·BF_4): 80 % yield, m.p. 119–122 °C (from Et_2O/AcOEt 1:1); ^{1}H NMR: $\delta = 1.52$ (d, $^3J = 7.0$ Hz, 12H; $CHMe_2$), 2.18 (s, 6H; Me), 4.52 (sept, $^3J =$ 7.0 Hz, 2H; NCH), 5.82 ppm (s, 2H; NH_2); ^{13}C NMR: $\delta = 9.7$ (Me), 20.6 ($CHMe_2$), 48.5 (NCH), 119.9 (C=C), 143.3 ppm (C-NH_2); IR: $\tilde{\nu} = 1020$, 1514, 1647, 2941, 2987, 3364, 3445 cm^{-1}. Treatment of the sample of **7a** with MeONa in MeOH gave a quantitative yield of the conjugated base,

1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-imine (**7a′**), the NMR data of which matched those reported in the literature.[9a] HRMS (ESI$^+$): *m*/*z*: calcd for $C_{11}H_{22}N_3^+$: 196.1808 [M^+]; found: 196.1807; elemental analysis calcd (%) for $C_{11}H_{22}BF_4N_3$: C 46.67, H 7.83, N 14.84; found: C 46.81, H 7.88, N 14.69.

2-Amino-1,3-dineopentyl-4,5-dimethylimidazolium tetrafluoroborate (7b·BF$_4$): 80% yield, m.p. 198–200°C (from AcOEt/MeOH, 50:1); ^{1}H NMR: $\delta = 1.03$ (s, 18H; CMe_3), 2.11 (s, 6H; Me), 3.70 (s, 4H; NCH_2), 6.09 ppm (s, 2H; NH_2); ^{13}C NMR: $\delta = 9.7$ (Me), 28.1 (C*Me*$_3$), 34.9 (*C*Me$_3$), 53.6 (CH_2), 120.3 (C=C), 147.1 ppm (C-NH_2); IR: $\tilde{\nu} = 1017$, 1036, 1531, 1656, 2959, 3361, 3424 cm^{-1}; HRMS (ESI$^+$): *m*/*z*: calcd for $C_{15}H_{30}N_3^+$: 252.2434 [M^+]; found: 252.2435; elemental analysis calcd (%) for $C_{15}H_{30}BF_4N_3$: C 53.11, H 8.91, N 12.39; found: C 53.25, H 8.97, N 12.27.

2-Amino-1,3-dicyclohexyl-4,5-dimethylimidazolium tetrafluoroborate (7c·BF$_4$): 65% yield, m.p. 178–180°C (from AcOEt); ^{1}H NMR: $\delta = 1.14$–1.36 (m, 2H), 1.41–1.64 (m, 4H), 1.65–1.79 (m, 2H), 1.79–2.11 (m, 12H) (all CH_2), 2.20 (s, 6H; Me), 3.94–4.12 (m, 2H; NCH), 5.89 ppm (s, 2H; NH_2); ^{13}C NMR: $\delta = 10.1$ (Me), 24.8, 25.6, 30.6 (all CH_2), 56.8 (NCH), 119.9 (C=C), 143.5 ppm (C-NH_2); IR: $\tilde{\nu} = 1018$, 1515, 1656, 2862, 2936, 3352, 3414 cm^{-1}; HRMS (ESI$^+$): *m*/*z*: calcd for $C_{17}H_{30}N_3^+$: 276.2434 [M^+]; found: 276.2435; elemental analysis calcd (%) for $C_{17}H_{30}BF_4N_3$: C 56.21, H 8.32, N 11.57; found: C 56.18, H 8.41, N 11.33.

(*E*)-2-(*tert*-Butyltriaz-2-enylidene)-1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazole (8a): A sample of intermediate **8a** was obtained from **5a** and *tert*-butyl azide as described in GP 4; >99% yield, beige crystalline solid that gradually turned dark on exposure to air. ^{1}H NMR (C_6D_6): $\delta = 1.21$ (br d, $^3J = 7.2$ Hz, 12H; CH*Me*$_2$), 1.49 (s, 9H; CMe_3), 1.63 (s, 6H; Me), 5.13 ppm (br, 2H; NCH); ^{13}C NMR: $\delta = 10.1$ (Me), 21.4 (CH*Me*$_2$), 29.4 (C*Me*$_3$), 47.9 (NCH), 60.0 (*C*Me$_3$), 117.8 (C=C), 153.2 ppm (C=N).

Tris(dimethylamino)(amino)phosphonium tetrafluoroborate (10·BF$_4$): P-$(NMe_2)_3$ (7.670 g, 47.0 mmol) was carefully added dropwise to a solution of *tert*-butyl azide (5.520 g, 55.7 mmol) in toluene (5 mL) at −20°C under vigorous stirring. The reaction mixture was gradually allowed to warm to ambient temperature overnight, yielding the triazene **9**.[29] The mixture was then cooled to −20°C, whereupon CF_3CO_2H (8.04 g, 70.5 mmol) was added dropwise over a period of 10 min. The cooling bath was then removed, and the reaction mixture was stirred for an additional 15 min. After aqueous work-up as described in GP 3, the pure product **10** was isolated as a colourless crystalline solid (11.4 g, 91%). The spectral data of **10** were in good agreement with those reported in the literature.[10]

Bis(*N*,*N*′-dialkyl-4,5-dimethylimidazolium-2-yl)amide tetrafluoroborates (1) and 2-[tris(dimethylamino)phosphoranylidenamino]-1,3-dialkyl-4,5-dimethylimidazolium tetrafluoroborates (2): General procedure (GP 5): Pre-dried KF (1.400 g, 24.0 mmol) was placed in a reaction flask and strongly heated with a heat-gun under high vacuum for a few minutes to remove all traces of moisture. It was then cooled under argon, and the flask was equipped with a magnetic stirring bar. The requisite salt **6** (3.00 mmol), **7** (3.00 mmol), or **10** (0.800 g, 3.00 mmol) was added, followed by MeCN (6 mL), and the reaction mixture was stirred for 48 h at ambient temperature (synthesis of **1a**,**c** and **2a**) or at 60°C (synthesis of **1b** and **2b**). ^{1}H NMR spectra of the reaction mixtures indicated full conversion of the starting materials. Each mixture was then poured into a separating funnel containing a two-phase mixture of $CHCl_3$ (50 mL)/12% aqueous $NaBF_4$ (110 mL), which was vigorously shaken. The organic phase was separated, and the aqueous phase was extracted once with $CHCl_3$ (20 mL). The combined organic phases were washed with 12% aqueous $NaBF_4$ solution (50 mL), dried ($MgSO_4$), and filtered. The volatiles were removed in vacuo, and the solid residue was dried under high vacuum to afford the pure product **1** or **2** as a beige crystalline solid.

Bis(1,3-diisopropyl-4,5-dimethylimidazolium-2-yl)amide tetrafluoroborate (1a·BF$_4$): 1.080 g, 78% yield, m.p. 151–153°C (from hexane/AcOEt 1:6); ^{1}H NMR: $\delta = 1.44$ (d, $^3J = 7.0$ Hz, 24H; CH*Me*$_2$), 2.19 (s, 12H; Me), 4.21 ppm (sept, $^3J = 7.0$ Hz, 4H; NCH); ^{13}C NMR: $\delta = 10.2$ (Me), 21.2 (CH*Me*$_2$), 48.0 (NCH), 119.5 (C=C), 144.5 ppm (CNC); IR: $\tilde{\nu} = 1051$, 1096, 1367, 1425, 1573 cm^{-1}; HRMS (ESI$^+$): *m*/*z*: calcd for $C_{22}H_{40}N_5^+$: 374.3278 [M^+]; found: 374.3279; elemental analysis calcd (%) for $C_{22}H_{40}BF_4N_5$: C 57.27, H 8.74, N 15.18; found: C 57.06, H 8.56, N 14.78.

Bis(1,3-dineopentyl-4,5-dimethylimidazolium-2-yl)amide tetrafluoroborate (1b·BF$_4$): 1.667 g, 84% yield; recrystallization from hexane/AcOEt (1:1) gave the inclusion compound **1b**·AcOEt, m.p. 145–148°C; after further crystallization, the m.p. was increased to 202–204°C; ^{1}H NMR (CD_3OD, 499.84 MHz, 313 K): $\delta = 0.95$ (br s, 36H; CMe_3), 2.21 (s, 12H; Me), 3.59 ppm (br s, 8H; NCH_2); ^{13}C NMR (CD_3OD, 125.7 MHz): $\delta =$ 10.0 (br, Me), 28.7 (br, C*Me*$_3$), 35.9 (br, *C*Me$_3$), 54.3 (br, NCH_2), 121.4 (br, C=C), 148.8 ppm (CNC); ^{1}H NMR ([D$_6$]DMSO, 499.84 MHz, 373 K): $\delta = 0.92$ (s, 36H; CMe_3), 2.18 (s, 12H; Me), 2.89 ppm (br s, 8H, NCH_2); ^{1}H NMR (CD_3OD, 499.84 MHz, 240 K): $\delta = 0.80$ (s, 18H), 1.09 (s, 18H) (both CMe_3), 2.20 (s, 6H), 2.24 (s, 6H) (both Me), 2.79 (d, $^2J = 15.3$ Hz, 2H; NCH_2), 3.60 (d, $^2J = 14.1$ Hz, 2H; NCH_2), 3.71 (d, $^2J = 15.3$ Hz, 2H; NCH_2), 3.88 ppm (d, $^2J = 14.1$ Hz, 2H; NCH_2); ^{13}C NMR (CD_3OD, 125.7 MHz, 240 K): $\delta = 9.9$ and 10.2 (Me), 28.4 and 28.9 (C*Me*$_3$), 35.8 and 36.2 (*C*Me$_3$), 53.6 and 54.4 (NCH_2), 121.0 and 121.6 (C=C), 148.3 ppm (CNC); IR (for **1b**·BF$_4$): $\tilde{\nu} = 1030$, 1048, 1397, 1475, 1580 cm^{-1}; HRMS (ESI$^+$): *m*/*z*: calcd for $C_{30}H_{56}N_5^+$: 486.4530 [M^+]; found: 486.4527; elemental analysis calcd (%) for $C_{30}H_{56}BF_4N_5$: C 62.82, H 9.84, N 12.21; found: C 62.56, H 9.79, N 12.18.

Bis(1,3-dicyclohexyl-4,5-dimethylimidazolium-2-yl)amide tetrafluoroborate (1c·BF$_4$): 1.622 g, 87% yield, m.p. 76–78°C; ^{1}H NMR: $\delta = 1.05$–1.30 (br m) and 1.61–2.12 (br m) (40H, all CH_2), 2.21 (s, 12H; Me), 3.68 ppm (br t, 4H; NCH); ^{13}C NMR: $\delta = 10.5$ (Me), 25.0, 26.2, 31.1 (all CH_2), 57.0 (NCH), 119.4 (C=C), 144.6 ppm (CNC); IR: $\tilde{\nu} = 1048$, 1378, 1413, 1585 cm^{-1}; HRMS (ESI$^+$): *m*/*z*: calcd for $C_{34}H_{56}N_5^+$: 534.4530 [M^+]; found: 534.4529; elemental analysis calcd (%) for $C_{34}H_{56}BF_4N_5$: C 65.69, H 9.08, N 11.27; found: C 65.39, H 8.97, N 10.99.

2-[Tris(dimethylamino)phosphoranylidenamino]-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate (2a·BF$_4$): 1.266 g, 95% yield, m.p. 99–101°C (from hexane/AcOEt 1:5); ^{1}H NMR: $\delta = 1.47$ (d, $^3J = 7.1$ Hz, 12H; CH*Me*$_2$), 2.21 (s, 6H; CMe), 2.72 (d, ^3J(H,P) = 10.0 Hz, 18H; NMe_2), 4.68 ppm (sept, $^3J = 7.1$ Hz, 2H; NCH); ^{13}C NMR: $\delta = 10.1$ (Me), 21.3 (CH*Me*$_2$), 37.1 (d, ^2J(C,P) = 4.2 Hz; NMe_2), 47.5 (NCH), 119.2 (C=C), 142.3 ppm (d, ^2J(C,P) = 14.8 Hz; CNP); ^{31}P NMR: $\delta = 17.88$ ppm; IR: $\tilde{\nu} = 737$, 756, 974, 1035, 1048, 1408, 1568 cm^{-1}; HRMS (ESI$^+$): *m*/*z*: calcd for $C_{17}H_{38}N_6P^+$: 357.2890 [M^+]; found: 357.2889; elemental analysis calcd (%) for $C_{17}H_{38}BF_4N_6P$: C 45.96, H 8.62, N 18.92; found: C 45.80, H 8.43, N 18.90.

2-[Tris(dimethylamino)phosphoranylidenamino]-1,3-dineopentyl-4,5-dimethylimidazolium tetrafluoroborate (2b·BF$_4$): 1.366 g, 91% yield. According to the procedure given for **1a**·OTs (see below), a sample **2b**·BF_4 was converted into **2b**·OTs. ^{1}H NMR: $\delta = 0.98$ (s, 18H; CMe_3), 2.17 (d, ^6J(H,P) = 0.6 Hz, 6H; CMe), 2.30 (s, 3H; Me, OTs), 2.65 (d, $^3J = 9.9$ Hz, 18H; NMe_2), NCH_2 peaks not observed due to strong broadening, 7.08 (d, $^3J = 8$ Hz, 2H; CH_m, OTs), 7.84 ppm (d, $^3J = 8$ Hz, 2H; CH_o, OTs); ^{13}C NMR: $\delta = 10.4$ (Me), 21.3 (Me, OTs), 28.3 (C*Me*$_3$), 34.8 (*C*Me$_3$), 37.2 (d, ^2J(C,P) = 3.9 Hz; NMe_2), 52.8 (NCH_2), 120.2 (C=C), 126.3 and 128.2 (both CH, OTs), 138.1 (*C*Me, OTs), 145.0 (C-S, OTs), 148.2 ppm (d, ^2J(C,P) = 10.15 Hz; CNP); ^{31}P NMR: $\delta = 22.73$ ppm; IR: $\tilde{\nu} = 561$, 680, 744, 977, 1182, 1549 cm^{-1}; HRMS (ESI$^+$): *m*/*z*: calcd for $C_{21}H_{46}N_6P^+$: 413.3516 [M^+]; found: 413.3510; elemental analysis calcd (%) for $C_{28}H_{53}N_6O_3PS$: C 57.51, H 9.13, N 14.37; found: C 57.36, H 9.00, N 14.11.

Bis(1,3-diisopropyl-4,5-dimethylimidazolium-2-yl)amide tetrafluoroborate (1a·BF$_4$) from 1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-2(3*H*)-ylidene (5a): One-pot procedure: A stock solution of **5a** in hexane was added to a reaction flask. The hexane was removed in vacuo, and the resulting crystalline residue (1.140 g, 6.32 mmol) was redissolved in diglyme (6.3 mL). A solution of *tert*-butyl azide (0.323 g, 3.16 mmol) in toluene (3.16 mL) was slowly added under vigorous stirring. After 5 min, the reaction mixture was heated to 60°C and stirred for 30 min, then cooled to −40°C, whereupon C_2Cl_6 (0.748 g, 3.16 mmol) was added in one portion. The resulting mixture was gradually allowed to warm to ambient temperature and stirred for 24 h. It was then cooled to −20°C, TfOH (0.280 mL, 3.16 mmol) was carefully added, and the resulting mixture was stirred for 15 min before being allowed to gradually warm to ambient temperature. The volatiles were removed under high vacuum (0.05 mbar), and the residual mixture of **6a**·X and **7a**·X was diluted with dry MeCN (6.3 mL) and combined with KF (1.540 g, 26.0 mmol), activated as described in

GP 5. The resulting mixture was stirred for 48 h at ambient temperature. Aqueous work-up as described in GP 5 followed by recrystallization of the solid residue from AcOEt/hexane (6:1) gave the pure product **1a**·BF_4 (770 mg, 65%) as yellowish crystals.

2-[Bis(dimethylamino)methyleneamino]-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate (3·BF_4): Pre-dried KF (0.232 g, 4.00 mmol) was placed in a reaction flask and strongly heated with a heat-gun under high vacuum for a few minutes to remove all traces of moisture. It was then cooled under argon, and the flask was equipped with a magnetic stirring bar. MeCN (2 mL), $(Me_2N)_2C{=}NH$ (0.126 mL, 1.00 mmol), and the salt **6a**·BF_4 (0.303 g, 1.00 mmol) were successively added. The reaction mixture was stirred for 24 h at ambient temperature. Aqueous work-up as described in GP 5 furnished the pure product **3**·BF_4 (0.347 g, 91%) as a yellowish crystalline solid. M.p. 169–171 °C; ^{1}H NMR: $\delta = 1.46$ (d, $^3J = 7.1$ Hz, 12H; CHMe_2), 2.24 (s, 6H; Me), 2.88 (s, 12H; NMe_2), 4.28 ppm (sept, $^3J = 7.1$ Hz, 2H; NCH); ^{13}C NMR: $\delta = 10.1$ (Me), 21.0 (CHMe_2), 39.7 (NMe_2), 48.5 (NCH), 120.6 (C=C), 145.7 (C_{im}N), 161.4 ppm (N=*C*(NMe_2)$_2$); IR: $\tilde{\nu} = 1034$, 1045, 1399, 1430, 1533 cm^{-1}; HRMS (ESI$^+$): *m*/*z*: calcd for $C_{16}H_{32}N_5^+$: 294.2652 [M^+]; found: 294.2653; elemental analysis calcd (%) for $C_{16}H_{32}BF_4N_5$: C 50.40, H 8.46, N 18.37; found: C 50.15, H 8.43, N 18.08.

Reactions of the salt 1a·BF_4 with TfOMe or TfOH: Bis(1,3-diisopropyl-4,5-dimethylimidazolium-2-yl)amine tetrafluoroborate triflate, [1aH]·OTf·BF_4: A sample of **1a**·BF_4 (0.046 g, 0.10 mmol) in $CDCl_3$ was treated with TfOMe (0.018 g, 0.11 mmol). No reaction occurred after 24 h at ambient temperature. Heating of the sample for a week at 80 °C resulted in disappearance of the signal of TfOMe and the formation of **1a**·HOTf, the authenticity of which was verified by matching the NMR data with those of a reference sample obtained by protonation of **1a**·BF_4 (0.046 g, 0.10 mmol) with an equimolar amount of TfOH in $CHCl_3$ (ca. −80 °C to RT, then high vacuum) to give a quantitative yield of [**1a**H]·OTf·BF_4 as a yellow oil. ^{1}H NMR (CD_3CN): $\delta = 1.49$ (d, $^3J = 7.0$ Hz, 24H; CHMe_2), 2.35 (s, 12H; Me), 4.50 (sept, $^3J = 7.0$ Hz, 4H; NCH), 8.69 ppm (brs; NH, integral intensity reduced due to H/D exchange); ^{13}C NMR (CD_3CN): $\delta = 10.7$ (Me), 21.1 (CHMe_2), 52.2 (NCH), 121.8 (q, ^1J(C,F) = 320 Hz; CF_3SO_3), 127.1 (C=C), 134.8 ppm (CNC).

Stability tests of cations 1^+–3^+ and P_5^+ under phase-transfer conditions: Method A: A 50% aqueous KOH solution (1.5 mL) was added to a Schlenk tube containing a solution of the corresponding tetrafluoroborate salt (0.50 mmol) in chlorobenzene (1.5 mL). As a quantitative NMR standard, dibenzo-[18]crown-6 or [18]crown-6 was chosen, in order to avoid overlaps of the NMR signals with those of the cations to be tested. The resulting two-phase mixture was kept under the conditions specified in Table 1. The progress of the alkaline cleavage was monitored by ^{1}H and ^{31}P NMR (if applicable) of aliquots taken from the chlorobenzene phase and diluted with [D_6]DMSO. The authenticities of compounds **7a′** and **11** resulting from the cleavage of $\mathbf{1a}^+$ (see Scheme 4) were proven by matching the NMR data with those of a reference sample (see the synthesis of **7a**·BF_4 above) and HRMS, respectively; **11**, HRMS (EI): *m*/*z*: calcd for $C_{11}H_{20}N_2O$: 196.1576 [M^+]; found: 196.1572.

Stability tests of cations $\mathbf{1b}^+$, $\mathbf{2b}^+$, and P_5^+ under homogeneous conditions: Method B: The salt **1b** (0.115 g, 0.20 mmol) and $[(Me_2N)_3P{=}N]_4P{\cdot}BF_4$ were added to a solution of KOH (1 mmol) in ethylene glycol (1 mL). After 24 h of reflux (see Table 1), a few small side signals in the characteristic areas of both the ^{1}H and ^{31}P (for $\mathbf{P_5}^+$) NMR spectra appeared, although no appreciable change in relative ratio of the characteristic ^{1}H signals of the starting cations **1b** and $\mathbf{P_5}^+$ was observed. Subjecting the salt **2b** (0.100 g, 0.20 mmol) to the same conditions led to a similar degree of decomposition.

Anion exchange in the products 1a·BF_4 and 1b·BF_4 to obtain salts 1a·OTs and 1b·I for X-ray analysis: A solution of the tetrafluoroborate salt **1** (1.00 mmol) in MeOH (10 mL) was treated with an at least tenfold excess of TsOK (concentrated solution in 50% aqueous MeOH) or a saturated KI solution in MeOH and the mixtures were stirred for 1 h at RT and then set aside for 24 h at 4 °C (refrigerator). Thereafter, the volatiles were removed in vacuo, and the residue obtained was dried under high vacuum and then treated with $CHCl_3$ (10 mL). The resulting suspension was vigorously stirred for 15 min at ambient temperature and then filtered through a 0.2 μm syringe filter. The clear filtrate was concentrated in vacuo to afford yellowish crystals of **1a**·OTs or **1b**·I free from tetrafluoroborate (^{19}F NMR control).

X-ray structures of the salts 1a·OTs and 1b·I and of the triazene 8a:[17] Slow cooling of a saturated solution of **1a**·OTs in AcOEt or of **1b**·I in AcOEt/hexane (1:1) afforded crystals suitable for X-ray analysis. Suitable crystals of **8a** were obtained by crystallization from Et_3N. Crystal data for **1a**·OTs: $C_{22}H_{40}N_5{\cdot}C_7H_7O_3S$, $M_r = 545.78$, *orthorhombic*, space group $Pna2_1$; $a = 21.7539(4)$, $b = 8.77290(10)$, $c = 15.6722(3)$ Å; $V = 2990.96(9)$ Å^3; $Z = 4$; dimensions of colourless crystal $0.5 \times 0.4 \times 0.1$ mm; 150(2) K; $\mu(Mo_{K\alpha}) = 0.15$ mm^{-1}; $R[F^2 > 2\sigma(F^2)] = 0.036$, $wR2$ (all data) = 0.091, $S = 1.04$, reflections/parameters 5606/356; max/min residual electron density 0.12/−0.28 e Å^{-3}. The hydrogen atoms in all structures were recalculated in idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2$–$1.5\ U_{eq}$ (pivot atom); **1b**·I: $3(C_{30}H_{56}N_5){\cdot}C_4H_8O_2{\cdot}3(I)$, $M_r = 1929.20$, *triclinic*, space group $P\bar{1}$ (No. 2); $a = 10.76990(10)$, $b = 16.8764(2)$, $c = 30.3494(4)$ Å, $\alpha = 74.8719(7)$, $\beta = 89.6370(9)$, $\gamma = 83.1406(7)°$; $V = 5285.16(11)$ Å^3; $Z = 2$; colourless crystal $0.3 \times 0.2 \times 0.1$ mm; 150(2) K; $\mu(Mo_{K\alpha}) = 0.94$ mm^{-1}; $R[F^2 > 2\sigma(F^2)] = 0.035$, $wR2$ (all data) = 0.079, $S = 0.89$, reflections/parameters 20711/1021; max/min residual electron density 0.74/−0.76 e Å^{-3}. **8a**: $C_{15}H_{29}N_5$, $M_r = 279.43$, *orthorhombic*, space group $Pna2_1$, $a = 12.6964(2)$, $b = 14.7323(3)$, $c = 9.1166(2)$ Å; $V = 1705.23(6)$ Å^3; $Z = 4$; colourless crystal $0.4 \times 0.4 \times 0.3$ mm; 150(2) K; $\mu(Mo_{K\alpha}) = 0.07$ mm^{-1}; $R[F^2 > 2\sigma(F^2)] = 0.036$, $wR2$ (all data) = 0.097, $S = 1.05$, reflections/parameters 3753/190; max/min residual electron density 0.19/−0.15 e Å^{-3}.

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[1] E. V. Dehmlow, S. S. Dehmlow, *Phase Transfer Catalysis*, 3rd ed., VCH, Weinheim, **1993**.

[2] a) B. Langlois, L. Gilbert, G. Forat, in *Industrial Chemistry Library, Vol. 8* (Eds.: J.-R. Desmurs, S. Ratton), Elsevier, Amsterdam, **1996**, pp. 244–292; b) M. E. Halpern, in *Process Chemistry in the Pharmaceutical Industry* (Ed.: K. G. Gadamasetti), Marcel Dekker, New York, **1999**, pp. 283–298; c) M. Makosza, M. Fedorynski, in *Interfacial Catalysis* (Ed.: A. G. Volkov), Marcel Dekker, New York, **2003**, pp. 159–201; d) D. Albanese, in *Interfacial Catalysis* (Ed.: A. G. Volkov), Marcel Dekker, New York, **2003**, pp. 203–226.

[3] a) E. V. Dehmlow, V. Knufinke, *J. Chem. Res. Synop.* **1989**, 224–225; b) J. G. Dawber, J. C. Tebby, A. A. C. Waite, *J. Chem. Soc. Perkin Trans. 2* **1983**, 1923–1925.

[4] R. Schwesinger, R. Link, P. Wenzl, S. Kossek, M. Keller, *Chem. Eur. J.* **2006**, *12*, 429–437, and references therein.

[5] a) D. J. Brunelle, D. A. Singleton, *Tetrahedron Lett.* **1984**, *25*, 3383–3386; b) D. Albanese, D. Landini, A. Maia, M. Penso, *J. Mol. Catal. A* **1999**, *150*, 113–131; c) D. Albanese, D. Landini, A. Maia, M. Penso, *Ind. Eng. Chem. Res.* **2001**, *40*, 2396–2401; d) M. Makosza, R. Bujok, *Tetrahedron Lett.* **2002**, *43*, 2761–2763; e) M. Henrich, A. Marhold, A. A. Kolomeitsev, N. Kalinovich, G.-V. Roeschenthaler, *Tetrahedron Lett.* **2003**, *44*, 5795–5798; f) A. Pleschke, A. Marhold, M. Schneider, A. Kolomeitsev, G.-V. Roeschenthaler, *J. Fluorine Chem.* **2004**, *125*, 1031–1038.

[6] a) R. Schwesinger, R. Link, G. Thiele, H. Rotter, D. Honert, H.-H. Limbach, F. Maennle, *Angew. Chem.* **1991**, *103*, 1376–1378; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1372–1375; b) R. Link, R. Schwesinger, *Angew. Chem.* **1992**, *104*, 864; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 850; c) R. Schwesinger, R. Link, P. Wenzl, S. Kossek, *Chem. Eur. J.* **2006**, *12*, 438–445.

[7] a) M. Fischer (BASF AG, Germany), EP 0691334A1, **1996**; [*Chem. Abstr.* **1996**, *124*, 264009]; b) P. Hupfield, A. Surgenor, R. Taylor

(Dow Corning, USA), EP 1008610A2, **2000**; [*Chem. Abstr.* **2000**, *133*, 31350]; c) G. Moloney, P. Hupfield, A. Surgenor, R. Taylor (Dow Corning, USA), EP 1008612A2, **2000**; [*Chem. Abstr.* **2000**, *133*, 31352]; d) T. Nobori, S. Fujiyoshi, I. Hara, T. Hayashi, A. Shibahara, K. Funaki, K. Mizutani, S. Kiyono (Mitsui Chemicals Inc., Japan), US 6469224 B1, **2002**; [*Chem. Abstr.* **2001**, *135*, 344378]; N. Yoshimura, S. Kiyono, K. Mizutani, I. Hara, T. Hayashi, T. Nobori, Y. Yamamoto, M. Konno, Y. Inoue, A. Matsuura, T. Ohkubo (Mitsui Chemicals Polyurethanes, Japan), EP 1775301A1, **2007**; [*Chem. Abstr.* **2006**, *144*, 129398].

[8] a) T. Nobori, T. Suzuki, S. Kiyono, M. Kouno, K. Mizutani, Y. Sonobe, U. Takaki (Mitsui Toatsu Chemicals, Japan), EP 0791600A1, **1997**; [*Chem. Abstr.* **1997**, *127*, 234743]; b) T. Nobori, T. Hayashi, S. Kiyono, U. Takaki (Mitsui Chemicals Inc., Japan), EP 0879838A2, **1998**; [*Chem. Abstr.* **1999**, *130*, 38836]; c) T. Nobori, T. Hayashi, T. Urakami, S. Yamasaki, *Catalysis* **2001**, *43*, 532–537; [*Chem. Abstr.* **2001**, *135*, 372004]; d) T. Nobori, T. Hayashi, S. Fujiyoshi, *Petrotech* **2002**, *25*, 516–520; [*Chem. Abstr.* **2002**, *137*, 358613]; e) T. Nobori, T. Hayashi, A. Shibahara, S. Fujiyoshi, *Chem. Eng.* **2002**, *47*, 365–370; [*Chem. Abstr.* **2002**, *137*, 329748].

[9] The Me groups at the 4- and 5-positions are believed to be essential to protect the structures from possible side reactions: a) M. Tamm, D. Petrovic, S. Randoll, S. Beer, T. Bannenberg, P. G. Jones, J. Grunenberg, *Org. Biomol. Chem.* **2007**, *5*, 523–530; b) I. Tommasi, F. Sorrentino, *Tetrahedron Lett.* **2006**, *47*, 6453–6456.

[10] 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.

[11] The chloride salt is commercially available from Fluka-Chemie AG (Switzerland).

[12] The steadily developing chemistry of these compounds has been summarized in recent review articles: a) N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev.* **2005**, *249*, 829–857, and references therein; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.

[13] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561–562. For the synthesis of **5** from **4**, we found it advantageous to use Na/K alloy in refluxing glyme instead of K in THF as it provides higher conversions in shorter reaction times.

[14] a) N. Kuhn, J. Fahl, R. Fawzi, C. Maichle-Moessmer, M. Steimann, *Z. Naturforsch. B* **1998**, *53*, 720–726; b) N. Kuhn, A. Abu-Rayyan, M. Göhner, M. Steimann, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1721–1723.

[15] The chemistry and coordinating properties of the conjugated bases, 2-iminoimidazolines, have been reviewed: a) N. Kuhn, M. Göhner, M. Grathwohl, J. Wiethoff, G. Frenking, Y. Chen, *Z. Anorg. Allg. Chem.* **2003**, *629*, 793–802. For original experimental results indicating high basicity and nucleophilicity of the exocyclic N atom, see: b) N. Kuhn, R. Fawzi, M. Steimann, J. Wiethoff, D. Bläser, R. Boese, *Z. Naturforsch. B* **1995**, *50*, 1779–1784; c) N. Kuhn, R. Fawzi, M. Steimann, J. Wiethoff, *Chem. Ber.* **1996**, *129*, 479–482; d) N. Kuhn, R. Fawzi, M. Steimann, J. Wiethoff, *Z. Anorg. Allg. Chem.* **1997**, *623*, 554–560; e) N. Kuhn, R. Fawzi, M. Steimann, J. Wiethoff, *Z. Anorg. Allg. Chem.* **1997**, *623*, 769–774; f) N. Kuhn, R. Fawzi, M. Steimann, J. Wiethoff, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1577–1582; g) N. Kuhn, R. Fawzi, M. Grathwohl, H. Kotowski, M. Steimann, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1937–1939; h) N. Kuhn, H. Kotowski, J. Wiethoff, *Phosphorus Sulfur Silicon Relat. Elem.* **1998**, *133*, 237–244; ref.[9a].

[16] J. C. Bottaro, P. E. Penwell, R. J. Schmitt, *Synth. Commun.* **1997**, *27*, 1465–1467.

[17] CCDC 729001 (**8a**), 729002 (**1a**·OTs), and 729003 (**1b**·**I**) 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

[18] It induces the synthesis of **2a**,**b** from **6a**,**b** and $(Me_2N)_3P{=}NTMS$ equally well.

[19] The half-life of $[(Me_2N)_3P{=}N]_4P{\cdot}Cl$ in 50% NaOH/PhCl at 110°C has been reported to be 33 h.[4]

[20] The insignificance of Hofmann degradation in alkaline cleavage of cations with extended resonance conjugation was noted earlier by Schwesinger et al.[4]

[21] Steric repulsion between 4,5-Me and $CHMe_2$ groups seems to contribute to this arrangement. The distances between all but one CH_3 carbons of the isopropyl groups and each C1/C4 centre are relatively short and fall in a narrow range from 3.1 to 4.1 Å.

[22] The dihedral angle ranges from 52.9(2)° to 58.3(2)° for three symmetrically independent cations observed in the crystal structure of **1b**·I.

[23] Similar outcomes resulting in protonation rather than methylation have been observed in reactions of sterically hindered 2,6-di-*tert*-butylpyridine derivatives with $MeOSO_2F$ under atmospheric pressure: a) H. Weber, J. Pant, M. Liedigk, H. Wunderlich, *Chem. Ber.* **1981**, *114*, 1455–1463; b) C. J. Hou, Y. Okamato, *J. Org. Chem.* **1982**, *47*, 1977–1979. It was conjectured that the protonation occurs due to α-elimination from the methylating agent or hydrolysis by traces of stray moisture.

[24] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.

[25] R. Streck, A. J. Barnes, *Spectrochim. Acta Part A* **1999**, *55*, 1049–1058.

[26] D. Naumann, B. Wilkes, J. Kischkewitz, *J. Fluorine Chem.* **1985**, *30*, 73–87.

[27] W. Meister, R. D. Guthrie, J. L. Maxwell, D. A. Jaeger, D. J. Cram, *J. Am. Chem. Soc.* **1969**, *91*, 4452–4458.

[28] M. Hernández-Rodríguez, E. Juaristi, *Tetrahedron* **2007**, *63*, 7673–7678.

[29] Spectral data of the intermediate **9** are in good agreement with those reported in the literature: J. R. Goerlich, M. Farkens, A. Fischer, P. G. Jones, R. Schmutzler, *Z. Anorg. Allg. Chem.* **1994**, *620*, 707–715.

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