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Anhydrous Phosphazenium Fluorides as Sources for Extremely Reactive Fluoride Ions in Solution

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Dedicated to Professor Albert Eschenmoser on the occasion of his 80th birthday

Abstract: Several peralkylated polyaminophosphazenium cations were evaluated for the generation of novel anhydrous F^- salts. Two of them have been characterized by X-ray analysis and are particularly soluble, even in apolar aprotic solvents like benzene or THF, one of them even at −30 °C. Such solutions probably represent the most basic metal-free and stable media known to date. Comparison of these fluorides with known F^- sources demonstrates that they are of unprecedented reactivity and selectivity in E2 elimination reactions.

Keywords: cations · elimination · fluorine · phosphazenes · phosphorus

Introduction

The F^- ion is among the most important catalysts in organic synthesis and its importance is ever growing.[1,2] A vast variety of inorganic,[2,3] organometallic,[4–7] and organic[8–28] F^- sources have been proposed, but the limited lipophilicity of resistant (metal) counterions and the instability of so far known lipophilic (organic) counterions towards the F^- ion pose severe restrictions. Metal fluorides[29] and even Me_4NF[8,9] are notoriously insoluble in aprotic (inert) solvents, whereas higher tetraalkylammonium fluorides are normally[30] notoriously unstable towards Hofmann degradation.[10,28,31]

The term "naked fluoride", first introduced by Liotta 1974 for the system KF/[18]crown-6 in MeCN,[6] has been used for F^- sources of strongly differing reactivity.[4,11–14] Truly "naked fluoride" can of course only exist in the gas phase in the absence of a counterion. All solvents and all counterions stabilize and thus deactivate to a greater or lesser extent depending on their size and their specific structure. Spectroscopic criteria for the definition of nakedness of F^- ions are not available; it has, for example, been pointed out that ^{19}F NMR data do not correlate with "nakedness".[32] Attempts have been reported to define "nakedness" by means of estimated lattice energies of the F^- salts.[33] The main problem is the reliable estimate of the lattice energy, which in the case of organic cations is certainly not solely a function of electrostatics, but also of specific short-range interactions like hydrogen bridges of F^- to α-protons in quaternary ammonium[11,34] or phosphonium ions, or partial or even full bonding with carbon in guanidinium ions[15,35] or with phosphorus in phosphonium ions, as has been often observed or calculated for tetraalkyl-,[14,16,35] tetraaryl-,[17,18] and even tetraaminophosphonium fluorides.[19,35] Preliminary ab initio calculations have recently been performed to establish a scale of "nakedness" of a limited number of organic F^- sources,[35] but no comprehensive comparison of the experimental reactivity or nucleophilicity–basicity balance of F^- sources has yet been reported.

The preceding paper deals with the unique stability of polyaminophosphazenium cations under basic conditions.[36] In this paper we detail our efforts to utilize some of these cations for the generation of stable, unsolvated, and soluble

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F$^-$ salts. Preliminary results have already been published.[37,38]

Results and Discussion

The phosphazenium fluorides presented in this paper are shown in Figure 1.

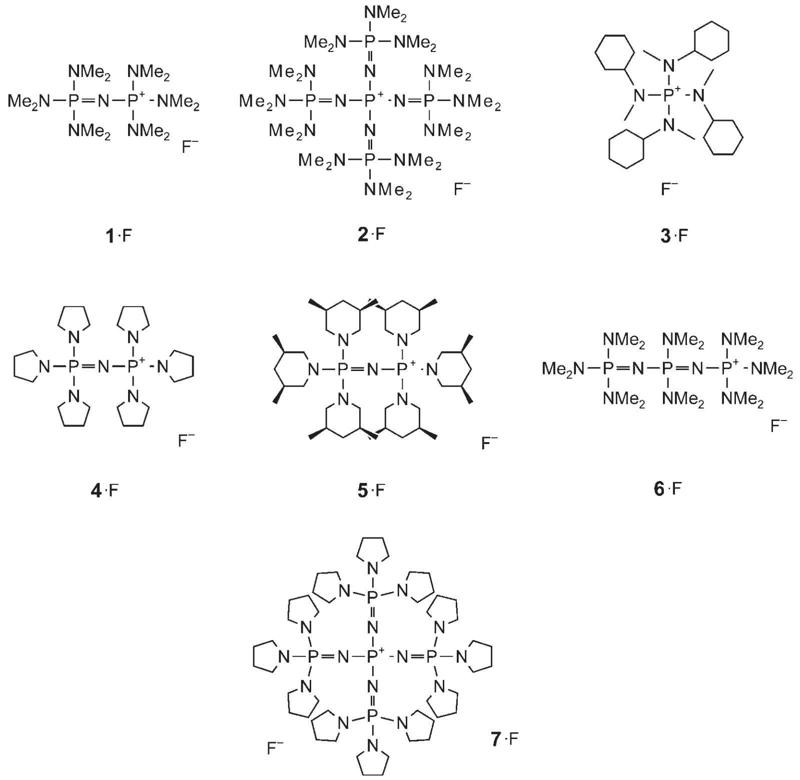


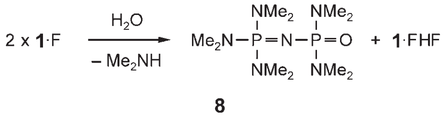
Figure 1. Phosphazenium fluorides described in this paper.

Generation of the fluoride salts: Stability of organic cations towards OH$^-$[36] and F$^-$ must not necessarily correlate closely. For example, with phosphazenium ions hydrolysis is only feasible with OH$^-$, not with anhydrous F$^-$. In tetraalkylammonium ions Hofmann degradation becomes dominant over nucleophilic dealkylation in turning from OH$^-$ to F$^-$; anhydrous tetraalkylammonium fluorides capable of Hofmann degradation are highly unstable,[28] whereas anhydrous Me$_4$NF is quite stable and well characterized.[8,9]

*Permethylated P$_2$ fluoride **1**·F*: The relative stability of Me$_4$NF prompted us to utilize the permethylated cation **1**$^+$[36] as counterion for "naked fluoride", in a first attempt. For its generation by metathesis, critical decisions had to be made concerning the choice of the F$^-$ ion source, the solvent, and the reaction conditions. We first tried to generate the F$^-$ salt by reaction of **1**·I with AgF in MeCN, analogous to a protocol described by Richman for peralkylated tetraaminophosphonium iodides.[19] The resulting dark solution deprotonated indicators with $^{DMSO}pK_a$ values of about 20. As we already knew from our work on phosphazene bases[39–41] that at such high basicity levels deprotonation of MeCN with subsequent self-condensation might be rapid, we suspected that this might be responsible for the color of the solution. Such behavior would be in accord with observations of solutions of Me$_4$NF in MeCN[8] and thus the reports by Richman must be doubted.[42]

Next we treated KF with **1**·BF$_4$ in H$_2$O. After filtration from precipitated KBF$_4$, the solution was concentrated and the residue dried in vacuo at 77–85 °C. The oily residue had the approximate theoretical weight, but ^{1}H NMR analysis revealed considerable hydrolysis of **1**$^+$ forming the diphosphazene oxide **8**[41,43] and **1**·FHF (Scheme 1). H$_2$O was thus not considered a suitable solvent.

A corresponding metathesis in MeOH (H$_2$O content less than 50 ppm) left, after filtration from precipitated KBF$_4$, a solution that was subsequently was concentrated in vacuo. Attempts to dry the residual material, directly or azeotropically, led to partial decomposition. Following the Christe procedure for anhydrous Me$_4$NF,[8,9] we then displaced MeOH by *i*PrOH before drying in high vacuum. Depending on the batch size, this improved the yield to reproducible 70–90 % after washing with THF. The crystalline material thus obtained contains 98–99 % active fluoride according to a titration with **9** (9-phenylxanthene[44] as indicator).

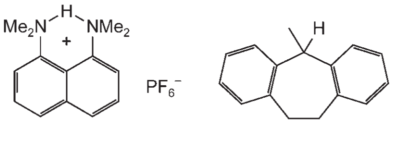


$$2 \times \mathbf{1}\cdot F \xrightarrow[-\,Me_2NH]{H_2O} Me_2N{-}P(NMe_2)_2{=}N{-}P(NMe_2)_2{=}O + \mathbf{1}\cdot FHF$$

Scheme 1. Degradation of **1**·F in presence of H$_2$O.

It can be further purified by dissolving in benzene, filtering off a small amount of insoluble material, presumably KBF$_4$, and concentrating in vacuo. Eventually it can be recrystallized from anhydrous THF, but mostly the activity of the product suffered thereby owing to contamination with traces of H$_2$O during the recrystallization process. If an excess of KF was used for the metathesis, the amount of insoluble material, probably largely a double salt **1**·F·KF, was substantial.

Salt **1**·F is extremely hygroscopic and melts at 151 °C with decomposition. A sample kept at 160 °C for 2 min was largely (ca. 70 %) decomposed. Salt **1**·F is easily soluble in benzene,[45] but surprisingly not in toluene; it is also soluble in trifluoromethylbenzene, fluorobenzene, chlorobenzene, furan, 2-methylfuran, or primary and secondary amines; however, these solvents deactivate to some extent. Salt **1**·F is sparingly soluble in ether solvents such as THF or diethyl ether. In benzene it deprotonates triphenylmethane ($^{\mathrm{DMSO}}\mathrm{p}K_a = 30.6$[46]) to a visible extent, but not **10** (Figure 2, extrapolated $^{\mathrm{DMSO}}\mathrm{p}K_a = 32.8$[47]).



9 **10**

Figure 2. Acid source **9** and indicator **10** for titration of "naked" fluorides.

The X-ray crystal structure of the benzene-soluble crystalline material revealed that it was in fact the desired "unsolvated" fluoride salt **1**·F.[37] The cubic symmetry of the lattice excludes the possibility that any solvent, ordered or disordered, might be present. The F–C distances (332 and 349 pm) are approximately 20–35 pm shorter than the sum of the van der Waal's radii of H and F plus one normal C–H bond length, indicating weak C–H···F hydrogen bridges. The linear P-N-P bridge of the cation is most probably dictated by the symmetry of the lattice and by the geometrical requirements for the maximum number of hydrogen bridges. In **1**·PF_6, in which the cation is more likely to occupy an energy-minimum conformation due to reduced interionic forces, the P-N-P bridge is bent (142°[48]).

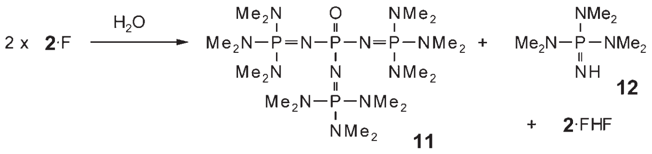
There are limitations concerning the production and application of **1**·F:

1) The batch size for the desolvation of **1**·F is limited to about 20 g.
2) Salt **1**·F is stable only up to temperatures of about 120 °C.
3) There is no non-deactivating solvent for **1**·F at temperatures below 5 °C.
4) Half molar amounts of H_2O quite rapidly destroy the activity of **1**·F irreversibly by hydrolysis of the cation.

There were good reasons to believe that larger phosphazenium cations would overcome at least part of these limitations.

*Permethylated P_5 fluoride **2**·F*: Salt **2**·F was synthesized from **2**·BF_4[36] by the protocol utilized for the synthesis of **1**·F, but in line with the expected enhanced "nakedness" taking off last traces of *i*PrOH required higher temperatures and longer reaction times. A colorless to light gray microcrystalline powder was obtained, containing at least 90 % "naked" fluoride by titration with **9** (triphenylmethane as indicator); recrystallization from 2-methyltetrahydrofuran/2,5-dimethyltetrahydrofuran enhances the titer, but proved unnecessary for most applications. Again approximately 1 % of insoluble material could be removed by filtration of the benzene (or THF) solution.

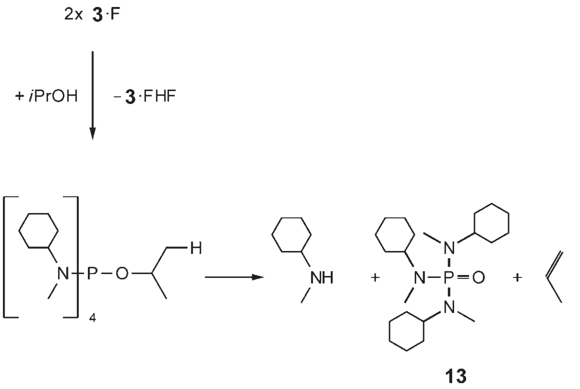
Salt **2**·F[37] melts above 260 °C. After heating to 250 °C for 30 min 90 % of the original titer of basic fluoride was retained. Again contamination with H_2O has to be excluded, dehydration at 140 °C causes partial hydrolysis, presumably (as observed by ^{1}H NMR spectroscopy) to the least basic possible primary hydrolysis products **11**[49] and **12**[36] (Scheme 2).



Scheme 2. Suspected degradation of **2**·F in presence of H_2O.

Salt **2**·F is easily soluble in benzene[45] and THF—in THF to a 0.3 M solution at room temperature and to a 0.1 M solution even at −30 °C. Like **1**·F, **2**·F is extremely hygroscopic. In THF **2**·F deprotonates **10** substantially and 4-phenyltoluene (extrapolated $^{\mathrm{DMSO}}\mathrm{p}K_a = 37.6$[50]) to a visible extent; thus its basicity exceeds even that of the strongest phosphazene bases.[41] An X-ray crystal structure reveals the "nakedness" of **2**·F.[51]

Other phosphazenium fluorides: Salt **3**·F could not be obtained by utilizing *i*PrOH as entraining agent. Before all *i*PrOH was released, a colorless distillate was formed that did not show olefinic signals in the ^{1}H NMR spectrum. Our interpretation is that *i*PrOH attacks at the phosphorus atom and releases propene by β-elimination forming the corresponding phosphoric acid triamide **13** (Scheme 3). In line with this interpretation is the fact that by exchanging *i*PrOH

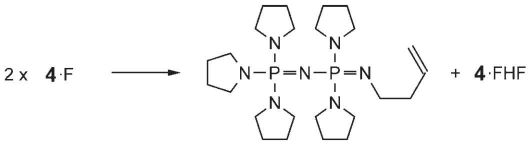


Scheme 3. Suspected degradation of **3**·F in presence of *i*PrOH.

for neopentanol, the reaction of **3**·BF$_4$[36] provided **3**·F with a content of "naked fluoride" of more than 95 %.

Fluoride salts **4**·F, **5**·F, **6**·F, and **7**·F were generated by protocols similar to those for **1**·F and **2**·F from the corresponding BF$_4$ salts.[36]

Salt **4**·F could only be obtained in a very impure form with, at most, 49 % of the "naked fluoride". Hofmann degradation leading to the formation of **14** was the dominant problem (Scheme 4); no attempts were made to obtain pure **4**·F.



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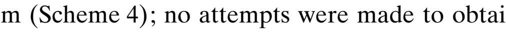
Scheme 4. Suspected thermal degradation of **4**·F.

Unlike the behavior under aqueous base phase-transfer conditions,[36] the impeded Hofmann degradation in **5**$^+$[36] made it more resistant than **4**$^+$ under anhydrous conditions; crude **5**·F had a "naked fluoride" content of about 60 %.

Surprisingly **6**$^+$ proved less resistant than **1**$^+$ under these conditions. Although the conditions were believed to be essentially anhydrous, considerable amounts of a distillate was formed, which according to ^{1}H NMR spectroscopy was most probably the triphosphazene oxide **15**[43b] (Scheme 5). According to titration the crude product contained only 38 % "naked fluoride", thus no attempts were made to obtain pure **6**·F.



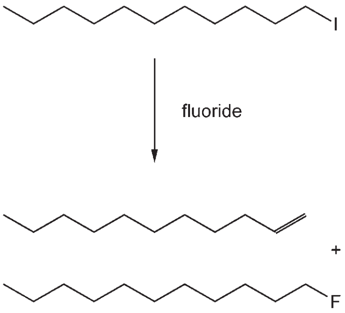
$$6\cdot F \xrightarrow[-\,Me_2NH]{H_2O} Me_2N{-}\overset{NMe_2}{\underset{NMe_2}{P}}{=}N{-}\overset{NMe_2}{\underset{NMe_2}{P}}{=}N{-}\overset{NMe_2}{\underset{NMe_2}{P}}{=}O \;+\; 6\cdot FHF$$

15

Scheme 5. Suspected degradation of **6**·F in presence of H$_2$O.

Drying of **7**·F proved even more difficult than drying of **2**·F; complete release of *i*PrOH required 48 h heating at 120 °C. The product contained 87 % "naked fluoride" according to titration.

Reactivity and selectivity of fluoride sources—"nakedness": We decided to establish a practical scale of "nakedness" based on the rate of reaction of fluoride sources with primary alkyl iodides (Scheme 6). This reaction has the advantage of telling us something not only about reactivity, but also about selectivity with respect to substitution versus elimination.



Scheme 6. Reaction of fluoride sources with 1-iodoundecane.

Table 1 includes literature values (entries 2–4) and shows that fluoride sources differ extremely in both respects. It did not make sense to derive absolute rate constants, as most of the systems are heterogeneous (the heterogenity does of course not influence the elimination/substitution balance). Nevertheless there is a fair correlation of absolute reactivity and E2 selectivity; the more reactive and thus "naked" the fluoride source, the more E2 is favored over S$_N$2.

Bu$_4$N·Ph$_3$SnF$_2$[20] (entry 1) is an excellent source of nucleophilic fluoride under somewhat enforcing conditions, more S$_N$2 selective than Bu$_4$N·FHF[21] and Bu$_4$N·Ph$_3$SiF$_2$[22] (entries 2,3). Complex [Co(Cp)$_2$]·F (entry 4) is considerably more reactive, but the claimed "nakedness"[4] is not supported by the E2 selectivity, the value being even considerably lower than for KF/[18]crown-6 (entries 5,7). Uncomplexed CsF (entry 8) is more selective than KF/[18]crown-6, indicating that the effect of the crown ether is a solubilizing one rather than an effect of cation/anion separation.[52] This is

Table 1. Conditions, half lives, and selectivities of the reaction of 1-iodoundecane with various fluoride sources.

	Fluoride source/solvent	$t_{1/2}$ [h]/T [°C] conditions	E2:S$_N$2
1	3 equiv Bu$_4$N·Ph$_3$SnF$_2$/MeCN	3.6/81	0.03:1
2	3 equiv Bu$_4$N·FHF/MeCN	4/81[a]	0.17:1
3	4 equiv Bu$_4$N·Ph$_3$SiF$_2$/MeCN	–/81[b]	0.35:1
4	[Co(Cp)$_2$]·F/THF	< 6/25[c]	0.38:1
5	3 equiv KF/0.24 equiv [18]crown-6/MeCN	41/81	0.61:1
6	2.5 equiv BnNMe$_3$F·H$_2$O/MeCN	7.2/25	0.91:1
7	3 equiv KF/3 equiv [18]crown-6/MeCN	0.9/81	0.96:1
8	3 equiv CsF/MeCN	108/81	2.1:1
9	3 equiv KF/0.24 equiv[2.2.2]-crypt/MeCN	47/81	2.2:1
10	5 equiv Me$_4$NF/THF	9/0	7.7:1
11	3 equiv KF/3 equiv[2.2.2]-crypt/MeCN	0.3/0	7.8:1
12	10 equiv Bu$_4$NF·3 H$_2$O/THF	< 0.08/0	8.5:1
13	3 equiv (Me$_2$N)$_3$S·Me$_3$SiF$_2$[23]/THF	16/0	10:1
14	10 equiv "Bu$_4$NF"[d]/THF	1.7/−40	11:1
15	2.5 equiv **1**·F + 2.75 equiv SiEt$_4$/THF	0.04/0	24:1
16	3 equiv Bu$_4$NF (**2**·F + Bu$_4$N·O$_3$SC$_4$F$_9$)/THF	6.3/−78	43:1
17	3 equiv **1**·F/THF	1/−78	90:1
18	3 equiv **2**·F/THF	0.004/−78	166:1

[a] Reaction with 1-iodooctadecane.[21] [b] Reaction with 1-iodooctane.[22] [c] Reaction with 1-iododecane.[4] [d] By drying Bu$_4$NF·3 H$_2$O in high vacuum following literature procedures.[10,24]

also indicated by the moderate effect on selectivity by increasing the amount of [18]crown-6 from catalytic to equimolar. Cryptands have a much more pronounced effect on both reactivity and selectivity; KF/[2.2.2]cryptand[7] (entries 9,11) resembles Me_4NF (entry 10) or tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF)[23] (entry 13) in reacting already at 0 °C with strong preference for the E2 reaction. It is noteworthy that $Bu_4NF{\cdot}3H_2O$ (entry 12) is comparable, even in selectivity. The product of thermal dehydration of this trihydrate reacts already at −40 °C, though surprisingly only with slightly enhanced selectivity (entry 14). From diverse titration experiments there is strong evidence that the active component (about 45 % of the material) corresponds to $Bu_4NF{\cdot}0.5H_2O$.[24] Anhydrous Bu_4NF[28] obtained in THF by metathesis of **2**·F with $Bu_4N{\cdot}O_3SC_4F_9$[53] (entry 16) has a half life of decay of only 4 h at room temperature and is considerably more reactive and selective. Thus it seems that hydration reduces selectivity, until every F^- ion can form a hydrogen bridge to a H_2O molecule and that further hydration has little influence. In line with calculations and despite the very low solubility in THF at −78 °C, **1**·F (entry 17) is clearly more reactive than tetraalkylammonium fluorides.[33,35] Salt **2**·F (entry 18) is only slightly more selective than **1**·F and in homogeneous solutions only slightly more reactive (see Table 2). However, under the conditions of limited solubility at −78 °C, salt **2**·F is about 350 times more reactive than **1**·F, thus contradicting the prognosis that enhancing the radius of the F^- counterion beyond the radius of $\mathbf{1}^+$ would have only marginal influence on reactivity.[33]

Table 2. Conditions, reaction times, and yields of the reaction of **16** with bases.

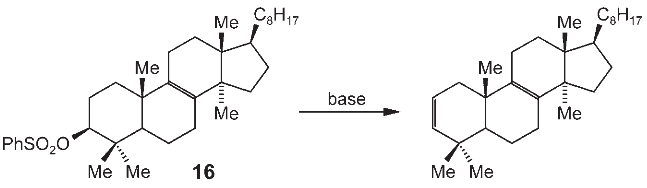
Fluoride source	Solvent	t [h]/T [°C]	Yield
KO*t*Bu	DMSO/THF 1:1	96/70	75 %[a]
Me_4NF	THF	96/65	< 5 % conversion[a]
1·F	PhH	0.08/25	99 %[b]
2·F	PhH	0.03/25	quantitative[a]
3·F	PhH	24/25	quantitative[a]
3·F	PhH/PhF 1:1	1.5/25	quantitative[a]
5·F	PhH	0.08/25	quantitative[a]
5·F	$PhCF_3$	0.11/25	quantitative[a]
5·F	THF	15/25	quantitative[a]
7·F	PhH	0.05/25	quantitative[a]
7·F	THF	0.5/25	quantitative[a]

[a] According to TLC. [b] Isolated yield.

The potential of **1**·F as F^- donor is shown by the interaction with $SiEt_4$ (entry 15), which reduces both reactivity and selectivity, presumably through the formation of $FSiEt_4^-$ in equilibrium, to date, an unknown species.[54]

For comparison of all five phosphazenium fluorides, primary alkyl iodides are not suitable substrates; due to the extreme reactivity of these fluorides half lives of the reactions can only be determined at very low temperatures at which **2**·F and particularly **1**·F are only sparingly soluble; the far lower solubility of **5**·F, **7**·F, and **3**·F would further obscure a direct comparison.

In **16** (Scheme 7) *trans*-diaxial elimination is only possible in a twisted ring A; due to this unfavorable conformational preequilibrium elimination is considerably slower than in the primary iodides, allowing estimation of reaction rates at temperatures in which solubility of the fluorides is reasonable. The crystallinity and low volatility of the product would help to follow the reaction by TLC and to determine reaction yields. The utilization of the benzene sulfonate instead of the tosylate or mesylate avoids problems with deprotonation of the acidic methyl groups in the sulfonates. Complete conversion of **16** with KO*t*Bu as base takes four days at 70 °C and leads to 75 % elimination and 25 % S−O bond scission to afford lanostenol. Me_4NF is even much less reactive. With **1**·F, **2**·F, **5**·F, and **7**·F elimination is complete within 2–30 min at room temperature without any detectable side reaction; the reaction with **3**·F is considerably slower but equally selective.



Scheme 7. Fluoride-induced elimination in **16**.

Conclusion

Due to their high solubility, their ease of synthesis, and the simplicity (transparency) of their NMR spectra,[55] **1**·F and **2**·F are the most convenient fluoride sources among the phosphazenium fluorides. Salts **1**·F and **2**·F are extremely reactive and selective elimination bases, **2**·F even at very low temperature; with this combination of properties they are certainly unprecedented. Often these fluorides provide the exclusive solution for difficult E2 elimination reactions.[56] Aliphatic epoxides are rearranged to allylic alcohols by *anti*-elimination.[57,58] Unactivated aromatic halides are converted to fluoroaromatics by means of an aryne mechanism.[58–60] “Naked hydride”[58,60] or highly reactive carbanions like naked allyl,[37,58,60] benzyl,[60] or cyclopropenyl[61] anions or ester enolates[61,62] are easily generated by anhydrous Si−(H,C,O) bond cleavage; various other applications have been reported.[63] Concerning solution chemistry, salt **2**·F is by far the best approximation to “naked fluoride” and probably the strongest stable metal-free base known to date. Salt **3**·F is considerably less reactive and might be of interest as a very easily available, somewhat less reactive fluoride source.

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, DSS = sodium 4,4-dimethyl-4-silapentanesulfonate, TSP = sodium 2,2,3,3-tetradeutero-3-trimethylsilylpropionate; in sealed NMR tubes the signals of C_6D_5H (7.15 ppm) and of [D$_7$]THF (3.70 ppm) served as references]: 90 MHz Varian CM 390, 250 MHz Bruker AC 250, and 400 MHz Bruker AM 400 spectrometers; ^{13}C NMR (internal standard TMS): 25.2 MHz Bruker WP 80 and 100.6 MHz Bruker AM 400 spectrometers; ^{31}P NMR (external standard 85 % H_3PO_4): Bruker AM 400 spectrometer; ^{19}F NMR (external standard fluorobenzene, $\delta = -116$ ppm and trifluoromethylbenzene, $\delta = -64$ ppm): 188.3 MHz Bruker AC 200, 282.0 MHz Bruker MSL 300, 470.3 MHz, Bruker AMX 500 spectrometers; analytical TLC, Merck silica gel plates with F_{254} indicator. All work with the crystalline fluoride salts was performed in a glove box under Ar (Labmaster, M. Braun GmbH). The H_2O values were below 1 ppm. Solvents were removed from the atmosphere by a special charcoal filter. Glassware was dried for at least 30 min at 100 °C and immediately transferred to the glove box via the vacuum chamber. All reactions involving anhydrous fluoride salts were performed under N_2 with rigorous exclusion of moisture.

Benzene was purchased from Fluka-Chemie AG (Switzerland), H_2O content < 0.005 %. MeOH was purchased from Fluka-Chemie AG (Switzerland) and kept over molecular sieves 3 Å, H_2O content < 0.01 %. *i*PrOH was purchased from Fluka-Chemie AG (Switzerland) and kept over molecular sieves 3 Å, H_2O content < 0.005 %.

Na_2O, $NaHCO_3$, Na_2SO_4, $MgSO_4$, BaO, $Bu_4NF{\cdot}3\,H_2O$, $Bu_4N{\cdot}Ph_3SnF_2$, EtOH, EtOAc, *i*PrOAc, Me_2CO, benzenesulfonyl chloride, 1-undecanol, [18]crown-6, [2.2.2]cryptand, $(Me_2N)_3S{\cdot}Me_3SiF_2$, and 1,8-bis(dimethylamino)naphthalene were used as purchased from Fluka-Chemie AG (Switzerland). 1-Undecene, triphenylmethane, and 4-phenyltoluene were used as purchased from Aldrich. Pentane was used as purchased from Riedel-deHaën. PhCl was distilled over P_2O_5 and stored over molecular sieves 3 Å; 1-iodoundecane was used as purchased from Lancaster. PhF was stirred with BaO, filtered, and distilled under Ar; $PhCF_3$ was distilled, a forerun amounting to half of it was discarded, the remainder was distilled and stored over molecular sieves 3 Å; THF, 2-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran, and toluene were distilled from K/Na-alloy/anthracene; neopentanol was dried by reaction with sodium metal at 60 °C, distilled, refluxed over BaO for 5 h and fractionally distilled under N_2; EtCN was stirred over $KMnO_4$ until a persistent violet color appeared, filtered, and distilled over P_2O_5; other solvents were purified by simple distillation; pyridine was distilled and stored over molecular sieves 4 Å; KF (Riedel-deHaën) was dried for 12 h in high vacuum at 240 °C. Commercial lanosterol (Sigma-Aldrich Chemical Company) was purified and hydrogenated as described in literature.[64]

General procedure for the conversion of tetrafluoroborates to fluorides: A solution of the appropriate BF_4^- salt in anhydrous MeOH (20 mL for 30 mmol if not otherwise indicated) was stirred vigorously with a solution of KF (1.05 equiv) in anhydrous MeOH (25 mL for 30 mmol) under N_2 for 10 min. After suction from precipitated KBF_4 into a 100 mL-round-bottomed flask and washing with *i*PrOH (5 mL) the solution was concentrated on a rotary evaporator in vacuo at maximum 40 °C bath temperature. The clear residue was taken up in anhydrous *i*PrOH (3 × 5 mL) and successively evaporated until the pressure in the rotary evaporator dropped to 20 mbar (the rotary evaporator was purged with Ar to keep out H_2O and CO_2). *i*PrOH (5 mL) was added before transferring the flask, equipped with a glass-covered stirring bar, to the vacuum apparatus (10 mm cross flow section, directly connected to an oil diffusion pump). The flask was then fitted to the cold trap of the vacuum apparatus. The solution was carefully concentrated in vacuo with stirring and then heated at the conditions indicated. For all operations following the first heating in vacuo rigorous exclusion of moisture (glove box) was *absolutely* essential.

1,1,1,3,3,3-Hexakis(dimethylamino)-1λ^5,3λ^5-diphosphazenium fluoride (1·F): The mixture obtained from **1**·BF_4 (12.8 g, 30 mmol) according to the general procedure was heated by raising the bath temperature to 80 °C within 1 h and the temperature was then kept at 80 °C for 1 h (during which time first crystals of solvent-free fluoride salt began to form) and at 100 °C for 1 h. The completely solidified product was scratched from the surface of the flask and dried for 1 h at 120 °C. A slurry of the product in THF (20 mL) was prepared; larger lumps were crushed with a pestle and the crystals were filtered off with a D4 glass suction filter, washed with THF (15 mL) and dried in a high vacuum, providing 9.7 g (90 %) of colorless crystals, containing 98–99 % "naked" fluoride by titration. M.p. 151 °C (partial decomp); ca. 1 % of inorganic material was removed by filtration of the benzene solution. Spectroscopic data have already been reported.[37]

Tetrakis{[tris(dimethylamino)phosphoranyliden]amino}phosphonium fluoride (2·F): The mixture obtained from **2**·BF_4[65] (10.0 g, 12.1 mmol) according to the general procedure was heated by raising the bath temperature to 80 °C over a period of 6 h. The material then contained 1 equiv of *i*PrOH; for the removal of this residual *i*PrOH the batch was divided into 5 g portions (glove box) and further dried at 100 °C and 120 °C for 4 h each, and at 130–135 °C for 6 h with efficient stirring until no *i*PrOH could be detected by ^{1}H NMR spectroscopy (D_2O; ca. 14 h). The material was recrystallized from 2-methyltetrahydrofuran/2,5-dimethyltetrahydrofuran 1:1. ^{1}H NMR (250 MHz, C_6D_6, 30 °C, TMS): $\delta = 2.52$ (d, ^3J(P,H) = 10 Hz), 18.10 ppm (t, ^1J(F,H) = 118 Hz, FHF^-); ^{19}F NMR (188.3 MHz, C_6D_6, 30 °C, 100 mg in 0.4 mL): $\delta = -72.0$ (d, ^1J(P,F) = 710 Hz, PF_6^-), −99.9 (s, F^-), −151.9 (s, BF_4^-), −155.5 ppm (d, ^1J(H,F) = 118 Hz, FHF^-); according to the integration the product contained F^- (90.3 mol %), FHF^- (8.5 mol %), BF_4^- (0.4 mol %), and PF_6^- (0.7 mol %); elemental analysis calcd (%) for $C_{24}H_{72}N_{16}FP_5$ (758.8): (for **2**·F + 1.5 H_2O; weighing of the sample was performed without exclusion of moisture): C 36.68, H 9.62, N 28.52; found: C 36.92, H 9.39, N 28.36.

Tetrakis[cyclohexyl(methyl)amino]phosphonium fluoride (3·F): The solution obtained from **3**·BF_4 (9.46 g, 16.7 mmol) in absolute MeOH (15 mL) according to the general procedure was dried until at 35 °C and 20 mbar no further solvent distilled. Then 2,2-dimethyl-1-propanol/toluene 3:1 (5 mL, instead of *i*PrOH) was added five times; after each addition the solvent was evaporated as described above. Before transferring the flask to the vacuum apparatus more of the solvent mixture (5 mL) was added. The temperature was raised to 120 °C over a period of 6 h and kept at this temperature with efficient stirring for 36 h. The resulting colorless crystalline material (7.91 g, 95 %), m.p. 248 °C, was analyzed and shown to contain 98 % "naked" fluoride, according to a titration in THF with **9** and triphenylmethane as indicator. ^{1}H NMR (250 MHz, D_2O, CD_3CN, 30 °C, TSP): $\delta = 0.90$–1.85 (m, 40 H; CH_2), 2.68 (d, ^3J(P,H) = 10 Hz, 12 H; NCH_3), 3.06 ppm (m, 4 H; NCH); ^{19}F NMR (100 MHz, C_6D_6, 30 °C): $\delta = -96.8$ (s, F^-), −154 ppm (d, J(H,F) = 125 Hz, FHF^-); ^{31}P NMR (100 MHz, $CDCl_3$, 30 °C): $\delta = 45.3$ ppm (s); elemental analysis calcd (%) for $C_{28}H_{56}N_4PF$ (498.8): (for **3**·F + 2.5 H_2O; weighing of the sample was performed without exclusion of moisture): C 61.85, H 11.30, N 10.30; found: C 61.69, H 10.88, N 10.89.

Tetrakis[(tri-1-pyrrolidinylphosphoranyliden)amino]phosphonium fluoride (7·F): The mixture obtained from **7**·BF_4 (6.55 g, 5.76 mmol) according to the general procedure was dried (attention, vigorous bumping may occur!) for 5 h at room temperature. Then the temperature was raised to 80 °C over a period of 1 h and kept at this temperature with efficient stirring until the product had completely solidified (ca. 2 h). According to ^{1}H NMR spectroscopy the material contained more than one equivalent of *i*PrOH. To guarantee a thorough mixing, the material was scratched from the wall of the flask and finely grounded under N_2 (dry box). The flask with the powdered material was then again connected to the high vacuum apparatus and heated at 80 °C for 6 h, at 100 °C for 13 h, and at 120 °C for 22 h. To avoid the formation of lumps, the bath was repeatedly replaced by an ultrasonic bath for 30 min. The resulting colorless crystalline material (5.67 g, 92 %), m.p. 235 °C (decomp), was analyzed and found to contain 87 ± 5 % "naked" fluoride, according to a titration in THF with **9** (triphenylmethane as indicator). ^{1}H NMR (250 MHz, D_2O, CD_3CN, 30 °C, TSP): $\delta = 1.75$ (m, 48 H; NCH_2CH_2), 3.18 ppm (m, 48 H; NCH_2CH_2); ^{19}F NMR (188 MHz, chlorobenzene/C_6D_6, 30 °C): $\delta = -104.8$ (s, F^-), −153.9 (s, BF_4^-), −158.8 ppm (d, J(H,F) = 113 Hz, FHF^-);

^{31}P NMR (100 MHz, chlorobenzene/C_6D_6, 30 °C): $\delta = -33.4$ (quint, ^2J(P,P) = 48.3 Hz, 1 P), −9.2 ppm (d, 4 P); elemental analysis calcd (%) for $C_{48}H_{96}N_{16}FP_5$ (1071.3): (for **2**·F + 3.5 H_2O; weighing of the sample was performed without exclusion of moisture): C 50.83, H 9.15, N 19.76; found: C 50.74, H 8.44, N 19.55.

General procedure for the reaction of 1-iodoundecane with fluoride sources: The indicated number of equivalents (amount) of the fluoride source formed a slurry or was dissolved in the corresponding solvent (4 mL mmol^{-1} of fluoride source), the appropriate number of equivalents of additives were added, and the mixture was stirred for 5 min. The mixture was brought to the indicated temperature and 1-iodoundecane (36.8 µL, 45.2 mg, 0.160 mmol) was added all at once with efficient stirring. After the indicated time at the indicated temperature, the mixture was either quenched with MeOH (250 µL) (reactions run below 0 °C) or a sample (250 µL) was taken from the reaction mixture (reactions run above 0 °C); H_2O (1 mL or the indicated amount) and pentane (1 mL or the indicated amount) were added to the reaction mixture (or the 250 µL sample), the mixture was shaken, and a sample of the pentane phase was directly subjected to GC injection. GC (analyt., Varian 3700, quartz column SE 30/25 m, integrator Varian CDS 111; column temperature 60 °C, temperature Program 10 °C min^{-1} till 150 °C, injector temperature 170 °C, detector temperature 170 °C): 8.73–9.62 min: 1-undecene; 10.43–11.21 min: 1-fluoroundecane (identified by ^{1}H NMR spectroscopy); 13.31–13.35 min: unidentified; 14.16 min: 1-undecanol; 21.34–23.88 min: 1-iodoundecane.

Lanosta-2,8-diene[66,67] from 16: A slurry of **1**·F (720 mg, 2.00 mmol) in THF (3 mL) was prepared, and a solution of **16** (378 mg, 0.660 mmol) dissolved in THF (2 mL) was added. The mixture was stirred for 30 min at room temperature. After addition of H_2O (10 mL) the mixture was extracted with Et_2O (3 × 10 mL), the combined ethereal phases were dried over Na_2SO_4, and the solvent was removed in vacuo. After filtration over a short column (silica, PE 30/50), the product was recrystallized from EtOH, affording colorless crystals (271 mg, 99 %). M.p. 86 °C (lit.[66] 83–84 °C), $R_f = 0.64$ (silica/cyclohexane); ^{1}H NMR in accord with literature values;[67] ^{13}C NMR (100.6 MHz, $CDCl_3$, 30 °C, TMS): $\delta = 138.2$ (C-2), 135.1 (C-8), 133.1 (C-9), 121.9 (C-3), 50.6 (C-17), 50.1 (C-14), 48.4 (C-5), 44.5 (C-13), 39.6 (C-24), 37.9 (C-1), 36.5 (C-20,C-22), 36.4 (C-4), 35.0 (C-10), 31.8 (C-29), 31.2 (C-12), 31.1 (C-15), 28.2 (C-16), 28.0 (C-25), 26.3 (C-7), 24.3 (C-28), 24.2 (C-23), 22.8 (C-7), 22.7 (C-26), 28.0 (C-25), 26.3 (C-7), 24.3 (C-28), 24.2 (C-23), 22.8 (C-27), 22.7 (C-26), 22.6 (C-19), 20.8 (C-11), 19.4 (C-6), 18.8 (C-21,C-30), 15.9 ppm (C-18); elemental analysis calcd (%) for $C_{30}H_{50}$ (410.7): C 87.73, H 12.27; found: C 87.65, H 12.22.

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[1] G. G. Yakobson, V. V. Bardin, *Fluoride Ions in Organic Chemistry*, Nauka, Novosibirsk, **1985**; D. J. Adams, J. H. Clark, *Chem. Soc. Rev.* **1999**, *28*, 225–231.

[2] J. H. Clark, *Chem. Rev.* **1980**, *80*, 429–452.

[3] W. T. Miller, Jr., W. Frass, P. R. Resnick, *J. Am. Chem. Soc.* **1961**, *83*, 1767–1768; L. Rand, J. V. Swisher, C. J. Cronin, *J. Org. Chem.* **1962**, *27*, 3505–3507; T. Ando, J. Yamawaki, *Chem. Lett.* **1979**, 45–46; N. Ishikawa, T. Kitazume, T. Yamazaki, Y. Mochida, T. Tatsuno, *Chem. Lett.* **1981**, 761–764; T. Ando, J. Yamawaki, T. Kawate, S. Sumi, T. Hanafusa, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2504–2507; J. H. Clark, A. J. Hyde, D. K. Smith, *J. Chem. Soc. Chem. Commun.* **1986**, 791–793; J. Ichihara, T. Matsuo, T. Hanafusa, T. Ando, *J. Chem. Soc. Chem. Commun.* **1986**, 793–794; J. Busch-Petersen, Y. Bo, E. J. Corey, *Tetrahedron Lett.* **1999**, *40*, 2065–2068.

[4] B. K. Bennett, R. G. Harrison, T. G. Richmond, *J. Am. Chem. Soc.* **1994**, *116*, 11165–11166.

[5] V. V. Grushin, *Chem. Eur. J.* **2002**, *8*, 1007–1014; M. J. Bayer, S. S. Jalisatgi, B. Smart, A. Herzog, C. B. Knobler, M. F. Hawthorne, *Angew. Chem.* **2004**, *116*, 1890–1893; *Angew. Chem. Int. Ed.* **2004**, *43*, 1854–1857.

[6] C. L. Liotta, H. P. Harris, *J. Am. Chem. Soc.* **1974**, *96*, 2250–2252.

[7] M. Gross, F. Peter, *Bull. Chim. Soc. Fr.* **1975**, 871–874.

[8] K. O. Christe, W. W. Wilson, *J. Fluorine Chem.* **1990**, *47*, 117–120.

[9] K. O. Christe, W. W. Wilson, R. D. Wilson, R. Bau, Jin-an Feng, *J. Am. Chem. Soc.* **1990**, *112*, 7619–7625.

[10] R. K. Sharma, J. L. Fry, *J. Org. Chem.* **1983**, *48*, 2112–2114.

[11] A.-R. Mahjoub, X. Zhang, K. Seppelt, *Chem. Eur. J.* **1995**, *1*, 261–265.

[12] R. Z. Gnann, R. I. Wagner, K. O. Christe, R. Bau, G. A. Olah, W. W. Wilson, *J. Am. Chem. Soc.* **1997**, *119*, 112–115; see also J. H. Clark, D. J. Nightingale, *J. Fluorine Chem.* **1996**, *78*, 91–93.

[13] R. D. Chambers, W. K. Gray, G. Sandford, J. F. S. Vaughan, *J. Fluorine Chem.* **1999**, *94*, 213–215.

[14] A. Kornath, F. Neumann, *Inorg. Chem.* **2003**, *42*, 2894–2901.

[15] A. A. Kolomeitsev, G. Bissky, J. Barten, N. Kalinovich, E. Lork, G.-V. Röschenthaler, *Inorg. Chem.* **2002**, *41*, 6118–6124.

[16] H. Schmidbaur, K.-H. Mitschke, W. Buchner, H. Stühler, J. Weidlein, *Chem. Ber.* **1973**, *106*, 1226–1237; J. Leroy, J. Bensoam, M. Humilière, C. Wakselman, F. Mathey, *Tetrahedron* **1980**, *36*, 1931–1936.

[17] S. J. Brown, J. H. Clark, *J. Chem. Soc. Chem. Commun.* **1983**, 1256–1257.

[18] S. J. Brown, J. H. Clark, D. J. Macquarrie, *J. Chem. Soc. Dalton Trans.* **1988**, 277–280.

[19] J. E. Richman, R. B. Flay, *J. Am. Chem. Soc.* **1981**, *103*, 5265–5267.

[20] M. Gingras, *Tetrahedron Lett.* **1991**, *32*, 7381–7384.

[21] P. Bosch, F. Camps, E. Chamorro, V. Gasol, A. Guerrero, *Tetrahedron Lett.* **1987**, *28*, 4733–4736.

[22] A. S. Pilcher, H. L. Ammon, P. DeShong, *J. Am. Chem. Soc.* **1995**, *117*, 5166–5167.

[23] W. J. Middleton (DuPont), US 3940402, **1976** [*Chem. Abstr.* **1976**, *85*, P 6388j]; W. B. Farnham, R. L. Harlow, *J. Am. Chem. Soc.* **1981**, *103*, 4608–4610; W. J. Middleton, *Org. Synth.* **1985**, *64*, 221–225.

[24] D. P. Cox, J. Terpinski, W. Lawrynowicz, *J. Org. Chem.* **1984**, *49*, 3216–3219; J. H. Clark, D. K. Smith, *Tetrahedron Lett.* **1985**, *26*, 2233–2236.

[25] K. M. Harmon, B. A. Southworth, K. E. Wilson, P. K. Keefer, *J. Org. Chem.* **1993**, *58*, 7294–7295.

[26] J.-ichi Hayami, N. Ono, A. Kaji, *Tetrahedron Lett.* **1968**, *9*, 1385–1386; L. N. Markovskii, V. I. Tovstenko, E. G. Martynyuk, V. E. Pashinnik, Y. G. Shermolovich, S. V. Iksanova, *Zh. Org. Khim.* **1990**, *26*, 1372–1373; *J. Org. Chem. (USSR)* **1990**, *26*, 1185–1186.

[27] J. H. Clark, *J. Chem. Soc. Chem. Commun.* **1978**, 789–791; H. Vorbrüggen, K. Krolikiewicz, *Tetrahedron Lett.* **1984**, *25*, 1259–1262; H. Vorbrüggen, *Acc. Chem. Res.* **1995**, *28*, 509–520; S. J. Brown, J. H. Clark, *J. Chem. Soc. Chem. Commun.* **1985**, 672–673; S. J. Brown, J. H. Clark, *J. Fluorine Chem.* **1985**, *30*, 251–258; R. D. Chambers, T. F. Holmes, S. R. Korn, G. Sandford, *J. Chem. Soc. Chem. Commun.* **1993**, 855–856; A. Martinsen, J. Songstad, *Acta Chem. Scand. A* **1977**, *31*, 645–650; A. A. Kolomeitsev, Y. L. Yagupol'skii, G. N. Koidan, A. P. Marchenko, A. M. Pinchuk, *Zh. Org. Khim.* **1990**, *26*, 1143–1144; *J. Org. Chem. (USSR)* **1990**, *26*, 984–985; A. A. Kolomeitsev, Y. L. Yagupol'skii, *J. Fluorine Chem.* **1991**, *54*, 319; H. Seto, Z.-hui Qian, H. Yoshioka, Y. Uchibori, M. Umeno, *Chem. Lett.* **1991**, 1185–1188; R. D. Chambers, W. K. Gray, S. R. Korn, *Tetrahedron* **1995**, *51*, 13167–13176; D. Albanese, D. Landini, M. Penso, *Tetrahedron Lett.* **1995**, *36*, 8865–8866; S. V. Pasenok, M. E. de Roos, W. K. Appel, *Tetrahedron* **1996**, *52*, 9755–9758; D. J. Adams, J. H. Clark, D. J. Nightingale, *Synth. Commun.* **1998**, *28*, 4295–4301; C. J. Handy, Y.-F. Lam, P. DeShong, *J. Org. Chem.* **2000**, *65*, 3542–3543; J. Kvíčala, P. Mysík, O. Paleta, *Synlett* **2001**, 547–549; J. Wessel, U. Behrens, E. Lork, T. Borrmann, W.-D. Stohrer, R. Mews, *Inorg. Chem.* **2002**, *41*, 4715–4721; M. Henrich, A. Marhold,

A. A. Kolomeitsev, N. Kalinovich, G.-V. Röschenthaler, *Tetrahedron Lett.* **2003**, *44*, 5795–5798.

[28] H. Sun, S. G. DiMagno, *J. Am. Chem. Soc.* **2005**, *127*, 2050–2051.

[29] M. A. Klocho, K. T. Batova, *Russ. J. Inorg. Chem.* **1960**, *5*, 1126–1127; D. A. Wynn, M. M. Roth, B. D. Pollard, *Talanta* **1984**, *31*, 1036–1040; G. Gonzalez-Trueba, C. Paradisi, G. Scorrano, *Gazz. Chim. Ital.* **1996**, *126*, 457–462.

[30] Some tetraalkylammonium fluorides incapable of Hofmann degradation have been described.[11,12,25] Anhydrous tetrabutylammonium fluoride has been recently described as an unstable crystalline material which can be stored only below −35 °C.[28]

[31] D. Landini, A. Maia, A. Rampoldi, *J. Org. Chem.* **1989**, *54*, 328–332; C. Rieux, B. Langlois, R. Gallo, *C. R. Acad. Sci. Ser. IIc* **1990**, *310*, 25–30.

[32] M. Gerken, J. A. Boatz, A. Kornath, R. Haiges, S. Schneider, T. Schroer, K. O. Christe, *J. Fluorine Chem.* **2002**, *116*, 49–58.

[33] K. O. Christe, H. D. Brooke Jenkins, *J. Am. Chem. Soc.* **2003**, *125*, 9457–9461; 14210.

[34] K. M. Harmon, I. Gennick, S. L. Madeira, *J. Phys. Chem.* **1974**, *78*, 2585–2591.

[35] T. Borrmann, E. Lorks, R. Mews, W.-D. Stohrer, *J. Fluorine Chem.* **2004**, *125*, 903–916.

[36] Preceding paper.

[37] 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.

[38] R. Link, R. Schwesinger, *Angew. Chem.* **1992**, *104*, 864; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 850.

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

[40] 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.

[41] 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.

[42] The reported yield of fluoride salt was "about 50 %".[19] This stoichiometry raises the suspicion that the salt was in fact a FHF^- salt.[8,9] Other salts of "naked fluoride" ions have been reported to be isolated from solutions in MeCN[4,13,18,26] or $CHCl_3$.[17,18] The incompatibility of "naked fluoride" with these solvents at ambient temperature has already been demonstrated.[8,9]

[43] a) M. Becke-Goehring, A. Debo, E. Fluck, W. Goetze, *Chem. Ber.* **1961**, *94*, 1383–1387; b) H. R. Allcock, N. M. Tollefson, R. A. Arcus, R. R. Whittle, *J. Am. Chem. Soc.* **1985**, *107*, 5166–5177.

[44] F. Ullmann, G. Engi, *Ber. Dtsch. Chem. Ges.* **1904**, 37, 2367–2374.

[45] **1**·F and **2**·F are both commercially available as solutions in benzene from Aldrich Chemical Company and Fluka-Chemie AG (Switzerland).

[46] W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCallum, N. R. Vanier, *J. Am. Chem. Soc.* **1975**, *97*, 7006–7014.

[47] G. Häfelinger, A. Streitwieser, Jr., *Chem. Ber.* **1968**, *101*, 657–671, 672–680.

[48] The quality of the X-ray structure was not sufficient to justify a presentation within this paper: M. Keller, University of Freiburg, unpublished results.

[49] G. N. Koidan, A. P. Marchenko, A. M. Pinchuk, *Zh. Obshch. Khim.* **1985**, *55*, 1633–1634; *J. Gen. Chem. (USSR)* **1985**, *55*, 1453.

[50] A. Streitwieser, Jr., J. R. Murdoch, G. Häfelinger, C. J. Chang, *J. Am. Chem. Soc.* **1973**, *95*, 4248–4254.

[51] H. Hillebrecht, University of Freiburg.

[52] J. M. Miller, J. H. Clark, *J. Chem. Soc. Chem. Commun.* **1982**, 1318–1319.

[53] R. M. Pomaville, C. F. Poole, *J. Chromatogr.* **1989**, *468*, 261–278.

[54] The Me_4SiF^- ion has been detected in the gas phase, but not yet in solution; according to gas-phase measurements of its free energy of formation from F^- it should be some 6 pK units more basic than $Me_3SiF_2^-$: J. W. Larson, T. B. McMahon, *J. Am. Chem. Soc.* **1985**, *107*, 766–773. This is in line with deprotonation experiments in THF involving **2**·F + Me_4Si and $(Me_2N)_3S{\cdot}Me_3SiF_2$.

[55] Fully deuterated analogues of **1**·F and **2**·F have been synthesized.[60]

[56] M. Wollenweber, R. Pinkos, J. Leonhardt, H. Prinzbach, *Angew. Chem.* **1994**, *106*, 84–87; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 117–120; V. Sharma, M. Keller, A. Weiler, D. Hunkler, H. Prinzbach, *Angew. Chem.* **1996**, *108*, 3029–3031; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2858–2861; J.-P. Melder, K. Weber, A. Weiler, E. Sackers, H. Fritz, D. Hunkler, H. Prinzbach, *Res. Chem. Intermed.* **1996**, *22*, 667–702; G. Person, M. Keller, H. Prinzbach, *Liebigs Ann.* **1996**, 507–527; T. Mathew, M. Keller, D. Hunkler, H. Prinzbach, *Tetrahedron Lett.* **1996**, *37*, 4491–4494; M. Wollenweber, M. Etzkorn, J. Reinbold, F. Wahl, T. Voss, J.-P. Melder, C. Grund, R. Pinkos, D. Hunkler, M. Keller, J. Wörth, L. Knothe, H. Prinzbach, *Eur. J. Org. Chem.* **2000**, 3855–3886; P. Landenberger, K. Scheumann, M. Keller, D. Hunkler, H. Fritz, J. Wörth, L. Knothe, H. Prinzbach, *J. Org. Chem.* **2001**, *66*, 5744–5758; J. Reinbold, E. Sackers, T. Oßwald, K. Weber, A. Weiler, T. Voss, D. Hunkler, J. Wörth, L. Knothe, F. Sommer, N. Morgner, B. von Issendorff, H. Prinzbach, *Chem. Eur. J.* **2002**, *8*, 509–524.

[57] R. Schwesinger in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), Wiley, **1995**, pp. 2657–2658.

[58] R. Link, Ph.D. Thesis, University of Freiburg (Germany), **1995**.

[59] 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].

[60] P. Wenzl, Ph.D. Thesis, University of Freiburg (Germany), **1998**.

[61] T. L. Arrowood, S. R. Kass, *J. Am. Chem. Soc.* **1999**, *121*, 7272–7273.

[62] T. Nobori, A. Shibahara, S. Kiyono, T. Hayashi, K. Funaki, I. Hara, K. Mizutani, U. Takaki (Mitsui Chemicals, Inc., Japan), EP 1044989 A1, **2000** [*Chem. Abstr.* **2000**, *133*, 310281].

[63] K. Lukin, P. E. Eaton, *J. Am. Chem. Soc.* **1995**, *117*, 7652–7656; J. Braun, R. Schwesinger, P. G. Williams, H. Morimoto, D. E. Wemmer, H.-H. Limbach, *J. Am. Chem. Soc.* **1996**, *118*, 11101–11110; M. Bertau, J. Leonhardt, A. Weiler, K. Weber, H. Prinzbach, *Chem. Eur. J.* **1996**, *2*, 570–579; M. Bertau, F. Wahl, A. Weiler, K. Scheumann, J. Wörth, M. Keller, H. Prinzbach, *Tetrahedron* **1997**, *53*, 10029–10040; R. Dorta, P. Egli, F. Zürcher, A. Togni, *J. Am. Chem. Soc.* **1997**, *119*, 10857–10858; N. Bieler, P. Egli, R. Dorta, A. Togni, M. Eyer (Lonza A. G., Switzerland), EP 909762 A2, **1999** [*Chem. Abstr.* **1999**, *130*, 305622]; M. A. Biamonte, A. Vasella, *Helv. Chim. Acta* **1998**, *81*, 695–717; R. Bischoff, J. Currie, W. Herron, R. Taylor (Dow Corning Limited, GB), EP 860461 A2, **1998** [*Chem. Abstr.* **1998**, *129*, 203429]; J. Reinbold, M. Bertau, T. Voss, D. Hunkler, L. Knothe, H. Prinzbach, D. Neschchadin, G. Gescheidt, B. Mayer, H.-D. Martin, J. Heinze, G. K. Surya Prakasch, G. A. Olah, *Helv. Chim. Acta* **2001**, *84*, 1518–1560; S. Kohlstruk, W. Poersch, M. Ewald, M. Windmueller (Degussa AG), EP 1318160 A1, **2003** [*Chem. Abstr.* **2003**, *139*, 36952].

[64] M. D. McCreary, D. W. Lewis, D. L. Wernick, G. M. Whitesides, *J. Am. Chem. Soc.* **1974**, *96*, 1038–1054.

[65] The phosphazenium salts **1**·BF_4 and **2**·Cl are commercially available from Aldrich Chemical Company or Fluka-Chemie AG (Switzerland).

[66] J. W. Huffman, *J. Org. Chem.* **1959**, *24*, 447–451; the sulfonylation was performed as described for the analogous tosylate: C. W. Shoppee, G. A. R. Johnston, *J. Chem. Soc.* **1961**, 3261–3271.

[67] G. H. Posner, G. M. Gurria, *J. Org. Chem.* **1976**, *41*, 578–580.

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