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Hexaalkylguanidinium and 2-(Dialkylamino)-1,3-dimethylimidazolinium Trimethyldifluorosiliconates and Perfluoroalkoxides. Accidental Isolation and Molecular Structure of $[C(NMe_2)_3]^+F^-\cdot 6CH_2Cl_2$[§]

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Hexaalkylguanidinium and 2-(dialkylamino)-1,3-dimethylimidazolinium trimethyldifluorosiliconates, precursors for two stable hexaalkylguanidinium perfluoroalkoxides, were synthesized by treating commercially available bis(dialkylamino)-difluoromethane derivatives with (dialkylamino)trimethylsilanes in aprotic media. With hexamethylguanidinium pentafluoroethoxide the introduction of the lipophilic and electronegative C_2F_5O group was straightforwardly achieved in the case of primary and secondary alkyl triflates to furnish the respective fluorinated ethers. The molecular structures of $[(CH_2NMe)_2C(NEt_2)]^+[Me_3SiF_2]^-$ and $[C(NMe_2)_3]^+F^-\cdot 6CH_2Cl_2$ were determined, showing in the latter case a fluoride anion octahedrally coordinated by six methylene chloride molecules via hydrogen bridges with a F···H distance of 205 pm (C···F distance 270.0(3) pm).

Introduction

Among the most commonly used methods of introducing fluorine and fluorinated moieties into organic and inorganic molecules are nucleophilic displacement reactions requiring a respective reagent of reasonable high solubility in aprotic organic solvents, e.g. fluorides with lipophilic counterions $Q^+ = Alk_4N^+$, $\{[(Me_2N)_3P]_2N\}^+$, $[S(NMe_2)_3]^+$ (TAS^+), $[C(NMe_2)_3]^+$ (HMG^+), $TDAE^{2+}$ (TDAE = tetrakis(dimethylamino)ethylene), $[P(NAlk_2)_4]^+$, and Bu_4P^+.[1−8] The onium fluorides with the best solubility in THF or monoglyme contain at least one phosphorus atom: $\{[(Me_2N)_3P]_2N\}^+F^-$;[6] $[P(NAlk_2)_4]^+F^-$;[7] $Bu_4P^+F^-$.[8] An increasing countercation size also decreases the Q^+F^- lattice energy, favorable for the nucleophilic fluorination and perfluoroalkoxylation, too.[2,3] The advantages of $Me_4N^+F^-$ (TMAF) are the high thermal and chemical stability of the Me_4N^+ cation and the high nucleophilicity of the very weak solvated fluoride ion.[1−4] A drawback of this salt is its low solubility in etheral solvents. It was also mentioned that the high symmetry of Me_4N^+ often leads to disordered crystal structures.[9] Another approach to fluoride-ion sources includes the use of hypervalent fluorosilicon, e.g. $TAS^+[Me_3SiF_2]^-$, or fluorotin onium derivatives showing excellent fluorinating power and being useful sources of highly nucleophilic fluoride, as well.[10−18] There

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is a need in new effective and selective reagents for the introduction of lipophilic CF_3O or C_2F_5O moieties into organic molecules, which could then be more able to traverse the lipid cell membranes than their nonfluorinated counterparts. Recently Blazejewski et al. have proposed 2-(trifluoromethoxy)ethyl triflate as a synthon, however, limited to trifluoromethoxy derivatives only.[19] The salts $TAS^+CF_3O^-$ and $TAS^+C_2F_5O^-$ were used to substitute bromine or triflate in alkyl bromides or triflates.[18,20,21] Because of the low yields of alkyl trifluoromethyl ethers in the reactions with the most synthetically useful functionalized secondary triflates, the low selectivity (20−75% content of alkyl fluoride byproducts), the high cost of TASF, and the toxicity of one of its precursor, SF_4, these compounds have not found broad application as anionic perfluoroalkoxylating reagents.

The perfluorinated carbanionic species $HMG^+[C(CF_3)_3]^-$, prepared from $HMG^+HF_2^-$ or HMG^+F^- and perfluoroisobutene, was found to be a stable solid.[22,23] The lipophilic and robust HMG^+ could be the cation of choice to get stable HMG^+ perfluoroalkoxides since the positive charge is distributed over three nitrogen atoms. Searching for a general route to pure hexaalkylguanidinium fluorides containing no HF_2^- as precursors for hexaalkylguanidinium perfluoroalkoxides avoiding SF_4 and its derivatives, we decided to study the reactions of bis(dialkylamino)methane derivatives with (dialkylamino)trimethylsilanes.[24]

Experimental Section

Materials and Apparatus. Chemicals were obtained from commercial sources and used without further purification. 2-Chloro-1,3-dimethylimidazolidinium chloride and tetramethylchloroformamidinium chloride were prepared according to published methods.[25] Bis(dimethylamino)difluoromethane and 2,2-difluoro-1,3-dimethylimidazoline (DFI) were synthesized by the method disclosed in a Mitsui patent.[26] Bis(dimethylamino)difluoromethane and 2,2-difluoro-1,3-dimethylimidazoline (DFI) solutions in CH_3CN and 1,3-dimethylimidazolidinone (DMI) were also prepared by modification of the patent procedure: after fluorination of 2-chloro-1,3-dimethylimidazolinium chloride and tetramethyl-chloroformamidinium chloride with KF in CH_3CN or DMI and separation of inorganic salts, the resulting mixtures were distilled in vacuo to give colorless solution of DFI and bis(dimethylamino)difluoromethane in CH_3CN or DMI, respectively. The synthesis of hexaalkylguanidinium trimethyldifluorosilicates were performed either with these solutions or with CH_3CN or DMI solutions of pure DFI and bis(dimethylamino)difluoromethane obtained after fractionation in vacuo. CH_3CN was distilled from phosphorus pentoxide and then stored over calcium hydride. DMI was distilled in vacuo and stored over (4 Å) molecular sieves. All reactions and manipulations were conducted under an atmosphere of dry nitrogen. The NMR spectra were recorded on a Bruker DPX-200 NMR instrument (^{13}C, 50.32 MHz; ^{19}F, 188.31 MHz; ^{1}H, 200.13 MHz), with positive shifts being downfield from the external standards CCl_3F (^{19}F) and TMS (^{13}C and ^{1}H).

General Method for the Preparation of Hexaalkylguanidinium Trimethyldifluorosiliconates. To a solution of (0.28 mol) bis(dialkylamino)difluoromethane in 300 mL of acetonitrile cooled to −30 °C was added dropwise (0.41 mol) (trimethylsilyl)-dimethylamine. The reaction mixture was stirred at −30 °C for 4 h. During a period of 4 h, the reaction temperature was raised from −30 °C to room temperature and the mixture was stirred additionaly for 1 h at room temperature. After cooling of the resulting solution to 0 °C, half of the solvent, 150 mL, was pumped off in vacuo and 250 mL of Et_2O was added. The precipitated colorless solid was filtered off under nitrogen, washed with 100 mL of Et_2O, and finally dried in vacuo at room temperature for 0.5 h to yield pure products in the yields noted.

Hexamethylguanidinium difluorotrimethylsiliconate ($[(Me_2N)_3C]^+[Me_3SiF_2]^-$; 96%) (1): colorless powder with mp 166−167 °C (from CH_2Cl_2). NMR data (acetonitrile-d_3, 233 K): $C(NMe_2)_3^+$ ion, $\delta(^{1}H)$ 2.8 ppm (s, 18H); $Me_3SiF_2^-$ ion, $\delta(^{1}H)$ −0.2 ppm (s, CH_3, 9H); $\delta(^{13}C)$ 6.3 ppm (s, CH_3 of the $Me_3SiF_2^-$ ion); $\delta(^{13}C)$ 39.7 ppm (s, $(CH_3)_2N$); $\delta(^{13}C)$ 163.3 ppm (s, C^+); $\delta(^{19}F)$ −59.3 ppm (s, 2F, $Me_3SiF_2^-$). Anal. Calcd for $C_{10}H_{27}F_2N_3Si$: C, 47.02; H, 10.65. Found: C, 46.86; H, 10.80.

N,N,N′,N′-Tetramethyl-N″,N″-diethylguanidinium trimethyldifluorsiliconate ($[(NMe_2)_2CNEt_2]^+[Me_3SiF_2]^-$; 95%) (2): colorless powder with mp 87−89 °C. NMR data (acetonitrile-d_3, 233 K): $C(NEt_2)(NMe_2)_2^+$ ion, $\delta(^{1}H)$ 1.2 ppm (t, CH_3, 6H); $\delta(^{1}H)$ 3.1 ppm (s, 12H); $\delta(^{1}H)$ 3.4 ppm (q, $^3J_{HH} = 4.4$ Hz, CH_2, 4H); $Me_3SiF_2^-$ ion, $\delta(^{1}H)$ −0.2 ppm (s, CH_3, 9H); $\delta(^{13}C)$ 5.2 ppm (s, CH_3 of the $Me_3SiF_2^-$ ion); $\delta(^{13}C)$ 13.1 ppm (s, CH_3); $\delta(^{13}C)$ 36.0 ppm (s, $(CH_3)_2N$); $\delta(^{13}C)$ 45.7 ppm (s, CH_2); $\delta(^{13}C)$ 163.9 ppm (s, C^+); $\delta(^{19}F)$ −60.0 ppm (s, 2F, $Me_3SiF_2^-$). Anal. Calcd for $C_{12}H_{31}F_2N_3Si$: C, 50.84; H, 11.02. Found: C, 50.45; H, 11.25.

2-(Dimethylamino)-1,3-dimethylimidazolinium trimethyldifluorsiliconate ($[(CH_2NMe)_2CNMe_2]^+[Me_3SiF_2]^-$; 95% in CH_3CN, 70% in DMI) (3): colorless powder with mp 79−82 °C. NMR data (acetonitrile-d_3, 233 K): $[CH_2N(Me)]_2C(NMe_2)^+$ ion, $\delta(^{1}H)$ 2.9 ppm (s, CH_3, 6H); $\delta(^{1}H)$ 3.0 ppm (s, CH_3, 6H); $\delta(^{1}H)$ 3.6 ppm (s, CH_2, 4H); $Me_3SiF_2^-$ ion, $\delta(^{1}H)$ −0.3 ppm (s, CH_3, 9H); $\delta(^{13}C)$ 6.0 ppm (s, CH_3 of the $Me_3SiF_2^-$ ion); $\delta(^{13}C)$ 36.5 ppm (s, CH_3, $(CH_3)_2N$); $\delta(^{13}C)$ 40.3 ppm (s, CH_3); $\delta(^{13}C)$ 50.1 ppm (s, CH_2); $\delta(^{13}C)$ 164.2 ppm (s, C^+); $\delta(^{19}F)$ −61.6 ppm (s, 2F, $Me_3SiF_2^-$). Anal. Calcd for $C_{10}H_{25}F_2N_3Si$: C, 47.40; H, 9.94. Found: C, 47.26; H, 9.88.

2-(Diethylamino)-1,3-dimethylimidazolinium trimethyldifluorosiliconate ($[(CH_2NMe)_2CNEt_2]^+[Me_3SiF_2]^-$; 95%) (4): colorless powder with mp 67−73 °C. NMR data (acetonitrile-d_3, 233 K): $[CH_2N(Me)]_2C(NMe_2)^+$ ion, $\delta(^{1}H)$ 1.1 ppm (t, CH_3, 6H); $\delta(^{1}H)$ 2.8 ppm (s, CH_2, 4H); $\delta(^{1}H)$ 3.0 ppm (s, CH_3, 6H); $\delta(^{1}H)$ 3.3 ppm (q, $^3J_{HH} = 4.5$ Hz, CH_2, 4H); $Me_3SiF_2^-$ ion, $\delta(^{1}H)$ −0.2 ppm (s, CH_3, 9H); $\delta(^{13}C)$ 4.5 ppm (s, CH_3 of the $Me_3SiF_2^-$ ion); $\delta(^{13}C)$

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13.1 ppm (s, CH_3); $\delta(^{13}C)$ 36.0 ppm (s, CH_3,); $\delta(^{13}C)$ 44.0 ppm (s, CH_2); $\delta(^{13}C)$ 49.4 ppm (s, CH_2); $\delta(^{13}C)$ 164.5 ppm (s, C^+); $\delta(^{19}F)$ −59.3 ppm (s, 2F, $Me_3SiF_2^-$). Anal. Calcd for $C_{12}H_{29}F_2N_3Si$: C, 51.21; H, 10.39. Found: C, 50.78; H, 10.19.

Hexamethylguanidinium Heptafluoroisopropanolate ($[Me_2N]_3C^+[(CF_3)_2CFO]^-$, 95%) (6). This salt was prepared by adding $(CF_3)_2C{=}O$ to $(Me_2N)_3C^+$ $Me_3SiF_2^-$ following the procedure to synthesize $(Me_2N)_3C^+C_2F_5O^-$: colorless powder with mp 86−90 °C. NMR data (methylene chloride-d_2, 200 K): $C(NMe_2)_3^+$ ion, $\delta(^1H)$ 2.9 ppm (s, 18H); $\delta(^{19}F)$ −68.7 ppm (s, CF, 1F); $\delta(^{19}F)$ −81.4 ppm (s, CF_3, 3F). Anal. Calcd for $C_{10}H_{18}F_7N_3O$: C, 36.48; H, 5.51. Found: C, 36.38; H, 5.61.

Hexamethylguanidinium Pentafluoroethanolate ($(Me_2N)_3C^+C_2F_5O^-$) (7). Into a well-stirred suspension of 3.3 g (12.9 mmol) of $(Me_2N)_3C^+Me_3SiF_2^-$ in 20 mL of monoglyme cooled to −50 °C was condensed 1.8 g (15.5 mmol) of trifluoracetyl fluoride. During a period of 1 h, the reaction temperature was raised from −50 °C to ambient temperature. All volatile products were pumped off in vacuo to leave a colorless solid, which was washed two times with Et_2O (2 × 5 mL) and dried in vacuo. $(Me_2N)_3C^+C_2F_5O^-$ (3.4 g, 12.19 mmol, 95%) was obtained as a white powder with mp 167−170 °C. NMR data (methylene chloride-d_2, 200 K): $C(NMe_2)_3^+$ ion, $\delta(^1H)$ 2.9 ppm (s, 18H); $\delta(^{13}C)$ 39.7 ppm (s, $(CH_3)_2N$); $\delta(^{13}C)$ 163.3 ppm (s, C^+); $\delta(^{19}F)$ −35.2 ppm (s, CF_2, 2F); $\delta(^{19}F)$ −85.7 ppm (s, CF_3, 3F). Anal. Calcd for $C_9H_{18}F_5N_3O$: C, 38.71; H, 6.50. Found: C, 38.61; H, 6.85.

Ethyl 2-(Pentafluoroethoxy)propionate ($MeCH(OC_2F_5)COOEt$, 87.4%) (8). To a well-stirred solution of 4.9 g (17.6 mmol) of hexamethylguanidinium pentafluoroethanolate in 30 mL of CH_3CN cooled with ice was added dropwise 4.0 g (16.0 mmol) of ethyl 2-(trifluoromethylsulfonyloxy)propionate dissolved in 4 mL of CH_3CN during a period of 1 h. The temperature was raised to ambient temperature and the mixture stirred for 1 h. The mixture was poured in sodium hydrocarbonate solution (3%, 50 mL) and extracted with pentane (3 × 50 mL). The combined organic extracts were washed with water and dried over $MgSO_4$. The final purification by distillation under reduced pressure gave pure ethyl 2-(pentafluoroethoxy)propionate. $CH_3C(H)(OC_2F_5)(COOC_2H_5)$ (3.3 g, 13.98 mmol, 87.4%) is a colorless liquid with bp 61−62 °C/55 Torr. NMR data (chloroform-d_3): $\delta(^1H)$ 1.3 ppm (t, $^3J(HH) = 7.3$ Hz, CH_3); $\delta(^1H)$ 1.5 ppm (d, $^3J(HH) = 7.2$ Hz, CH_3); $\delta(^1H)$ 4.2 ppm (q, CH_2), $\delta(^1H)$ 4.8 ppm (q, CH); $\delta(^{19}F)$ −87.7 (s, CF_3) ppm, $\delta_A(^{19}F)$ −90.3, $\delta_B(^{19}F)$ −91.5 (AB system, $J_{AB} = 146.8$ Hz, CF_2); $\delta(^{13}C)$ 14.0 ppm (s, CH_3), $\delta(^{13}C)$ 18.5 ppm (s, CH_3); $\delta(^{13}C)$ 60.1 ppm (s, CH_2); $\delta(^{13}C)$ 70.7 ppm (t, $^4J(CF) = 4.5$ Hz, CH); $\delta(^{13}C)$ 115.3 ppm (tq, $^1J(CF) = 271.9$ Hz, $^2J(CF) = 42.0$ Hz, CF_2)); $\delta(^{13}C)$ 116.9 ppm (qt, $^1J(CF) = 281.1$ Hz, $^2J(CF) = 44.8$ Hz, CF_3); $\delta(^{13}C)$ 169.7 ppm (s, CH). Anal. Calcd for $C_7H_9F_5O_3$: C, 35.60; H, 3.84. Found: C, 35.28; H, 3.99.

1,1,1,2,2-Pentafluoro-2-(2,2,2-trifluoroethoxy)ethane ($CF_3CF_2OCH_2CF_3$, 71.6%) (9). To a vessel with a Teflon stopcock containing a magnetically stirred mixture of 1.2 g (5 mmol) of hexamethylguanidinium pentafluoroethanolate and 5 mL of diglyme was added in one portion 1.15 g (5 mmol) of (2,2,2-trifluoroethyl)trifluoromethanesulfonate. The vessel was closed and the mixture stirred at 55 °C for 3.5 h. After being cooled to 20 °C, the product was pumped off in vacuo using a water aspirator pump into a trap cooled with liquid nitrogen. The final trap-to-trap vacuum distillation gave 0.78 g of 1,1,1,2,2-pentafluoro-2-(2,2,2-trifluoroethoxy)ethane. NMR data (chloroform-d_3): $\delta(^1H)$ 4.3 ppm (q, 2H, $^3J(HF) = 7.5$ Hz, CH_2O); $\delta(^{19}F)$ −76.3 ppm (t, 3F, $^3J(HF) = 7.5$ Hz, CF_3); $\delta(^{19}F)$ −87.6 (s, 3F, CF_3); −92.8 ppm (s, 2F, OCF_2).[27,28]

1,1,1,2,2-Pentafluoro-2-methoxyethane ($CF_3CF_2OCH_3$, 95%) (10).[27−29] This compound was synthesized by adding methyl trifluoromethanesulfonate to $(Me_2N)_3C^+C_2F_5O^-$ at 0 °C followed by stirring for 3 h at 20 °C in a glass vessel with a Teflon stopcock. The workup is as for $CF_3CF_2OCH_2CF_3$. NMR data (chloroform-d_3): $\delta(^1H)$ 2.0 ppm (s 3H, CH_3O); $\delta(^{19}F)$ −87.2 ppm (s, 3F, CF_3); −87.6 ppm (s, 2F, OCF_2); $\delta(^1H)$ 4.3 ppm (q, 2H, $^3J(HF) = 7.5$ Hz, CH_2O); $\delta(^{19}F)$ −76.3 ppm (t, 3F, $^3J(HF) = 7.5$ Hz, CF_3); $\delta(^{19}F)$ −87.6 (s, 3F, CF_3); −92.8 ppm (s, 2F, OCF_2). MS (CI/NH_3; *m/z*): 150 (M^-, 7); 169 (M^+F^-, 67); 135 ($M - CH_3^-$, 100). MS (EI; *m/z*): 131 (M − F, 29); 119 ($M - OCH_3$, 57); 81 ($M - CF_3$, 100); 69 (CF_3, 73).

Crystal Structure Determination. Crystals of $[(CH_2NMe)_2CNEt_2]^+[Me_3SiF_2]^-$, **4**, were grown from a concentrated solution in acetonitrile (1 g in 4 mL), which was cooled with liquid nitrogen, and diethyl ether (4 mL) was condensed into the solid. The flask was placed into a cryostate at −30 °C and allowed to stand for 7 d at this temperature. The crystals of $[C(NMe_2)_3]^+Me_3SiF_2^-$, **1**,[30] were obtained in a similar way from methylene chloride/ether at −30 °C. Along with the crystals of **1** some crystals of $[C(NMe_2)_3]^+F^-$ were also found and subjected to crystal structure analysis. The single-crystal X-ray data of the compounds were collected at 173(2) K using graphite-monochromatized Mo Kα radiation ($\lambda = 71.073$ pm) on Siemens P4 (**4**) and STOE IPDS (**5**) diffractometers. The structures were solved by direct methods and anisotropically refined based on F^2 using the SHELX-97 program package.[31] The hydrogen atoms were placed in calculated positions, assigned common isotropic thermal parameters, and allowed to ride on their parent atoms. For the HMG^+ cation two sets of N positions were found, related to a 60° rotation with a 1:1 occupancy ratio. The carbon atoms were not effected by this disorder. Further details are given in Table 1. Complete structural data are found in the Supporting Information.

Results and Discussion

Bis(dialkylamino)difluoromethane derivatives, $(R_2N)_2CF_2$, as precursors for fluorinated hexaalkylguanidinium salts have been chosen for the following reasons: (1) They are easily available[25,26] via chlorination of tetraalkylurea derivatives with oxalyl chloride followed by fluorination of $(Alk_2N)_2CCl^+Cl^-$ with KF in CH_3CN or DMI. (2) Their solutions in aprotic solvents are stable in glass vessels, and as a result of the elongated C−F bonds due to two α-dialkylamino groups, the compounds are very useful fluorinating agents, especially for the fluorination of alcohols.[26] (3) The use of hexaalkylguanidinium fluorides is a useful alternative to TASF, excluding the necessity to operate with highly toxic sulfur tetrafluoride. (4) It was possible to study the stabilizing influence of the hexaalkylguanidinium (HAG) cation on different anionic species to develop, on the basis of hexaalkylguanidinium fluorides, new anionic perfluoroalkoxy reagents for introducing the lipophilic and electrononegative R_FO^- groups into organic molecules.

Synthesis of Hexaalkylguanidinium Trimethyldifluorosiliconates. The reactions of bis(dialkylamino)difluor-

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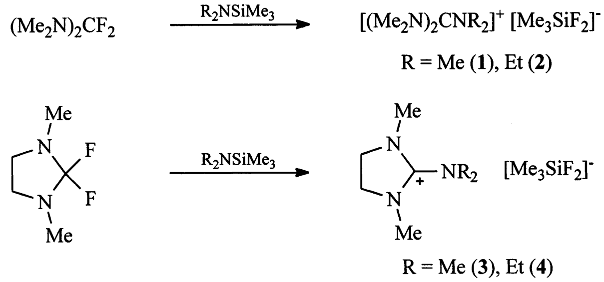
Table 1. Crystal Data and Details of Data Collection and Structure Refinement for Compounds **4** and **5**$\cdot 6CH_2Cl_2$

param	$C_{12}H_{29}F_2N_3Si$	$C_7H_{18}N_3F\cdot 6CH_2Cl_2$
fw	281.47	672.80
cryst system	monoclinic	rhombohedral
space group	$P2/n$	$R\bar{3}$
lattice params	$a = 913.5(2)$ pm, $\alpha = 90°$ $b = 860.0(2)$ pm, $\beta = 96.99(3)°$ $c = 1058.0(2)$ pm, $\gamma = 90°$	$a = 1425.85(8)$ pm, $\alpha = 90°$ $b = 1425.85(8)$ pm, $\beta = 90°$ $c = 1301.66(8)$ pm, $\gamma = 120°$
cell vol, nm^3	0.8250(3)	2.2918(2)
formula units/unit cell	2	3
D_{calcd}, Mg/m^3	1.133	1.462
μ_{calcd}(Mo Kα), mm^{-1}	0.152	1.101
$F(000)$	308	1026
cryst size, mm^3	$0.50 \times 0.40 \times 0.20$	$0.50 \times 0.50 \times 0.40$
2θ range, deg	2.78−26.04	2.86−27.50
obsd reflcns	11 447	1537
indpdt reflcns	1621 ($R_{int} = 0.0829$)	1140 ($R_{int} = 0.0282$)
goodness of fit	1.070	1.055
R1; wR2 [$I > 2\sigma(I)$]	0.0496; 0.1377	0.0411; 0.0954
R1, wR2 (all data)	0.0657, 0.1456	0.0562; 0.1035
$\Delta\rho_{min/max}$, pm^{-3}	$(-0.196/0.216) \times 10^{-6}$	$(-0.321/0.437) \times 10^{-6}$

Scheme 1



methane derivatives with silylated secondary amines have not been studied so far. Because of the lack of the full analytical data in our brief communication, we have not exactly assigned the structure of the reaction product to $(Me_2N)_3C^+F^-$.[24] Its full characterization has shown that it is not hexamethylguanidinium fluoride but $(Me_2N)_3C^+Me_3SiF_2^-$.[32] Here we describe the preparation of the structurally diverse hexaalkylguanidinium and 2-(dialkylamino)-1,3-dimethylimidazolinium trimethyldifluorosiliconates. The rate of the reaction of bis(dimethylamino)difluoromethane with (dimethylamino)trimethylsilane depends strongly on the solvent used. In pentane or diethyl ether no reaction was observed in a period of 24 h at 20 °C. An addition of catalytic amounts of CH_3CN, CH_2Cl_2, NMP, or 1,3-dimethylimidazolidinone (DMI) accelerated the reaction. It is most convenient to operate with CH_3CN or DMI solutions of bis(dialkylamino)-difluoromethane derivatives prepared according to a Mitsui patent:[26] after fluorination of $(Alk_2N)_2CCl^+Cl^-$ with KF followed by filtration from inorganic salts, $(Alk_2N)_2CF_2$ reagents along with a solvent were distilled to give ca. 13% weight solution of $(Alk_2N)_2CF_2$ in CH_3CN or DMI. Stirring of bis(dialkylamino)difluoromethanes with (dimethylamino)trimethylsilanes in CH_3CN during 4 h at −30 °C followed by warming up to ambient temperature and stirring for 1 h leads to nearly quantitative formation of e.g. $(Alk_2N)_3C^+Me_3SiF_2^-$ salts as colorless powders (Scheme 1).

The chemistry of the previously synthesized hexamethylguanidinium fluoride (HMGF) has not been developed, apparently because of its difficult access from HMG^+ pivaloate and Et_2NSF_3 and the extreme basicity of HMGF.[23] In contrast to $(Me_2N)_3C^+F^-$, which shows a 50% HF_2^- impurity even in DMF solution,[23] due to F^- complexation with Me_3SiF, the basicity of $(Me_2N)_3C^+Me_3SiF_2^-$ is reduced compared with HMGF. In our case no significant HF_2^- concentration in $(Me_2N)_3C^+Me_3SiF_2^-$ solutions was detected; e.g. a saturated solution of $(Me_2N)_3C^+Me_3SiF_2^-$ in CH_3CN formed only 5.5% of HF_2^- within 24 h at 20 °C. In $HMG^+Me_3SiF_2^-$ solutions in DMF at 20 °C only 0.2−0.5% HF_2^- was observed; no HF_2^- was detected in monoglyme solution at 20 °C. CH_3CN and DMF solutions of this salt obtained at −30 °C show no hydrogen difluoride content. Until now there was no evidence for $(Me_2N)_3S^+F^-$ existing in substance or in solution, e.g. TASF, $(Me_2N)_3S^+Me_3SiF_2^-$, decomposed in a vacuum or after being dissolved in CH_3CN at the ambient temperature losing immediately Me_3SiF to give no $(Me_2N)_3S^+F^-$ but $TAS^+HF_2^-$ along with sulfur-containing unidentified products of TAS^+ decomposition.[10] A similar decomposition in CH_3CN at 20 °C was reported also for $(Me_2N)_3S(O)^+Me_3SiF_2$.[33] Christe et al. tried to synthesize hexamethylguanidinium fluoride, $(Me_2N)_3C^+F^-$, similar to the synthesis of anhydrous $Me_4N^+F^-$,[1] reacting $(Me_2N)_3C^+OH^-$ in water with HF and removing water in vacuo. But their attempts failed, and instead of $(Me_2N)_3C^+F^-$ the hexafluorosilicate $[(Me_2N)_3C^+]_2SiF_6^{2-}$ was isolated and characterized by X-ray diffraction.[9] $(Me_2N)_3C^+Me_3SiF_2^-$ can be easily recrystallized from CH_3CN/ether or methylene chloride/ether solutions prepared at −30 to −40 °C. Presumably due to the dynamic equilibria between $(Me_2N)_3C^+Me_3SiF_2^-$ and $Me_3SiF/(Me_2N)_3C^+F^-$ (Scheme 2), from the methylene chloride/ether solution of $(Me_2N)_3C^+Me_3SiF_2^-$ obtained at −30 °C were isolated and characterized by solid-state X-ray diffraction both salts, $(Me_2N)_3C^+Me_3SiF_2^-$ and hexamethylguanidinium fluoride, $(Me_2N)_3C^+F^-$, as a solvate with six methylene chloride molecules.

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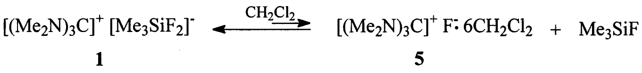
(32) Kolomeitsev, A. A.; Bissky, G.; Röschenthaler, G.-V. *16th International Symposium on Fluorine Chemistry*; Royal Society of Chemistry: Durham, U.K., 2000; Abstract 1P-107.

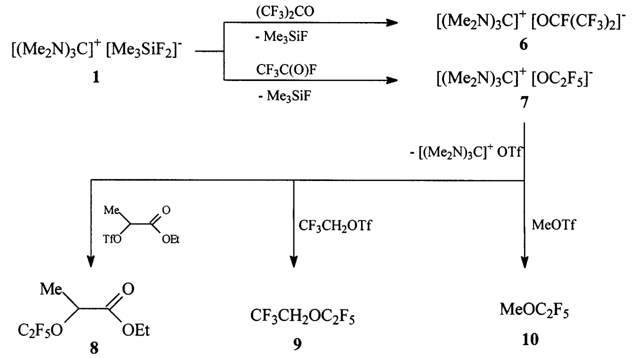
(33) Wessel, J.; Behrens, U.; Lork, E.; Borrman, T.; Stohrer, W.-D.; Mews, R. *Inorg. Chem.* **2002**, *41*, 4715−4721.

Scheme 2



$$[(Me_2N)_3C]^+[Me_3SiF_2]^- \underset{\mathbf{1}}{} \xrightleftharpoons{CH_2Cl_2} [(Me_2N)_3C]^+F^- \cdot 6CH_2Cl_2 \underset{\mathbf{5}}{} + Me_3SiF$$

Scheme 3



It was quite surprising that $(Me_2N)_3C^+F^-$ does not fluorinate methylene chloride at −30 °C. In this case HMGF is similar to Me_4NF which fluorinates CH_2Cl_2 at ambient temperature,[34] but its methylene chloride solution obtained at −30 °C is stable at this temperature for many hours. In this case both, fluorination and deprotonation of the solvent do not occur. [2,35]

We have also tried to prepare $(Me_2N)_3C^+F^-$ in accordance with our procedure to synthesize anhydrous (TMA)F.[4] The methathesis of $[C(NMe_2)_3]^+BF_4^-$ salt with a solution of oven-dried KF in anhydrous methanol (in 2-propanol KF is sparingly soluble) proceeds quantitatively to afford $[C(NMe_2)_3]^+F^-$ in CH_3OH solution [$\delta(^{19}F)$ $CH_3OH = -147.9$ ppm (s), $\delta(^{19}F)$ $H_2O = -119.0$ ppm (s)]. But after removal of methanol (20−130 °C, 0.01 mbar) $[C(NMe_2)_3]^+HF_2^-$ was obtained [$\delta(^1H)$ (acetonitrile-d_3) = 2.83 ppm (s); ($\delta^{19}F$) = −147.7 ppm (d), $J(HF) = 120.7$ Hz].

Synthesis of $(Me_2N)_3C^+C_2F_5O^-$ and $(Me_2N)_3C^+(CF_3)_2CFO^-$. Hexamethylguanidinium difluorotrimethylsiliconate is easy to handle under nitrogen and a very reactive source of highly nucleophilic fluoride. $(Me_2N)_3C^+Me_3SiF_2^-$ reacts with trifluoroacetyl fluoride and hexafluoroacetone in CH_3CN, THF, or monoglyme to give the colorless salts $(Me_2N)_3C^+C_2F_5O^-$ and $(Me_2N)_3C^+(CF_3)_2CFO^-$, respectively, stable until their melting points (Scheme 3). Thus, because of easy availability and high activity of hexamethylguanidinium difluorotrimethylsiliconate and relative salts **2**−**4**, there is no need to operate with hexamethylguanidinium fluoride, difficult to prepare and to handle.

Trainor[21] studied $TAS^+CF_3O^-$ in the reactions with carbohydrate triflate esters. The trifluoromethoxide anion replaced the primary triflate group under generally mild reaction conditions, but a significant alkyl fluoride impurity was detected. The more sterically hindered secondary carbohydrate triflates require harsher reaction conditions, and the alkyl fluoride formation increased, becoming in some cases the main reaction product.

Table 2. Comparison of the Reactions of $HMG^+OC_2F_5^-$ and $TAS^+OC_2F_5^-$ with $TfOCH(Me)CO_2Et$ (0.2 mmol)

	yield, %[b]	
	$C_2F_5OC(Me)CO_2Et$	$FCH(Me)CO_2Et$
$TAS^+OC_2F_5^-$ [a]	43	16
$HMG^+OC_2F_5^-$ [a]	74	3

[a] 0.2 mmol, 0.5 mL of CH_3CN, 1 h, 20 °C. [b] Yield from ^{19}F NMR, reference $PhCF_3$.

The properties of $(Me_2N)_3C^+C_2F_5O^-$ (**7**) as a $C_2F_5O^-$ transfer reagent were compared with those of $(Me_2N)_3S^+$-$C_2F_5O^-$.[20] The ^{19}F NMR study of a 1 mol L^{-1} solution of $HMG^+OC_2F_5^-$ in CH_3CN at 20 °C revealed a 5.8% mol of $CF_3C(O)F$. The signal of the $-OCF_2-$ group was observed as a broad singulet ($\Delta_{1/2} = 1074$ Hz). In the case of $TAS^{+-}OC_2F_5^-$ (1 mol L^{-1}, 20 °C) a higher $CF_3C(O)F$ content (16.4%) was observed ($\Delta_{1/2} = 1800$ Hz). The 0.4 mol L^{-1} solutions of both salts in CH_3CN (see Table 2) were tested in 1:1 ratio reactions with ethyl 2-(trifluoromethylsulfonyloxy)propionate. The ^{19}F NMR analysis of the reaction mixtures in 1 h has shown that $(Me_2N)_3C^+C_2F_5O^-$ gave 2-(pentafluoroethoxy)propionic acid ethyl ester (**8**) in 74% yield along with 3% 2-(fluoroethyl)propionic acid ethyl ester[36] and that $TAS^+OC_2F_5^-$ in 1 h gave 43% 2-(pentafluoroethoxy)propionic acid ethyl ester and 15.9% 2-(fluoroethyl)propionic acid ethyl ester as a byproduct.

The optimization of the conditions (see Experimental Section) for $(Me_2N)_3C^+C_2F_5O^-$ (**7**) reacting with ethyl 2-(trifluoromethylsulfonyloxy)propionate 2-(pentafluoroethoxy)propionic acid ethyl ester (**8**) gave 2-(pentafluoroethoxy)propionic acid ethyl ester in 87% isolated yield. Moreover, only 0.4 mol % of 2-(fluoroethyl)propionic acid ethyl ester was detected in the reaction mixture. The less electrophilic 2,2,2-trifluorethyl-trifluormethansulfonate required more severe conditions. Treatment of the alkoxide (**7**) with it at 55 °C for 3.5 h afforded 1,1,1,2,2-pentafluoro-2-(2,2,2-trifluoroethoxy)ethane (**9**)[28] in 71% isolated yield. $(Me_2N)_3C^+C_2F_5O^-$ easily reacts at 20 °C also with methyl triflate to form 1,1,1,2,2-pentafluoro-2-methoxyethane (**10**) (95%).[29] In both cases no alkyl fluoride byproduct was observed. These ethers, $CF_3CF_2OCH_3$ and $CF_3CF_2OCH_2CF_3$, were recently found to be the most promising hydrofluorocarbons (HFCs) to substitute the chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Alternative methods to prepare these alkyl perfluoroalkyl ethers include high-temperature fluorination of methyl and trifluoroethyl trifluorovinyl ethers with high valence metal fluorides such as cobalt trifluoride or manganese trifluoride.[27,28] $CF_3CF_2OCH_3$ and $CF_3CF_2OC_2H_5$ can be prepared also from a $CF_3C(O)F$/KF(CsF) mixture and dialkyl sulfates at elevated temperatures. In this case the formation of MeF or EtF byproducts is not dramatic as far as both alkyl fluorides could be easily separated from alkyl perfluoroalkyl ethers.[29] When this paper had been accepted for publication, a similar protocol describing oxalyl fluoride/KF(CsF) reactions with CH_3CH_2OTf and

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(34) Christe, K. O.; Wilson, W. W. *J. Fluorine Chem.* **1990**, *47*, 117−120.
(35) Frohn, H.-J. Private communication.
(36) Thenappan, A.; Burton, D. J. *J. Org. Chem.* **1990**, *55*, 2311−2317.

CF_3CH_2OTf was published.[37] It was mentioned that especially for CF_3CH_2OTf the competing fluorination reaction caused serious separation problems. $HMG^+OC_2F_5^-$ is superior to the $TAS^+CF_3O^-$, $TAS^+OC_2F_5^-$, and $CF_3C(O)F/KF$-(CsF) systems because of better product yields, reaction selectivity, and product isolation. Compound **7** forms practically pure alkyl pentafluoroethyl ethers, in contrary to $TAS^+R_FO^-$ reactions with alkyl triflates where up to 75% of AlkF byproducts were formed. The increased reactivity of $HMG^+OC_2F_5^-$ can be explained by the higher chemical stability of the carbocation $(Me_2N)_3C^+$ over $(Me_2N)_3S^+$. Moreover, $(Me_2N)_3C^+$, as we demonstrated above, is a better stabilizer for perfluoroalkoxy anions in solution than $(Me_2N)_3S^+$. The stabilizing effect of the counterion on R_FO^- anions depends not only on its large size but also on the degree of charge delocalization. There is no doubt that HMG^+, where the positive charge is distributed over the three nitrogen atoms, acts as a better nonpolarizing stabilizer for perfluoroalkoxide species than TAS^+, since for $S(NH_2)_3^+$ the main part of the Mulliken positive charge (+0.92e) is located on the sulfur atom,[17] whereas HMG^+ should be regarded as an imminium cation rather than a carbenium ion.[9]

In conclusion, the methodology reported herein is expected to be quite general for selective pentafluoroalkoxylation of primary and secondary carbon atoms of alkyl triflates. The ready availability of hexaalkylguanidinium trimethyldifluorosiliconates, variety of perfluorocarboxyl fluorides and of triflate esters, mild reaction conditions, and selectivity for pentafluoroalkoxylation reaction suggest that this metodology should be quite versatile to be applied for complex systems. Further study will be focused on straightforward synthesis of hexaalkylguanidinium fluorides based on DFI type reagents and their comparison with HAG^+ trimethyldifluorosiliconates in "Halex" reactions. The progress in this field will be reported in due course.

Crystal Structure of $[(CH_2NMe)_2CNEt_2]^+Me_3SiF_2^-$. The compound is ionic, with discrete $[(CH_2NMe)_2CNEt_2]^+$ cations structurally analyzed by X-ray diffraction the first time and $Me_3SiF_2^-$ anions (Figure 1). The CN_3 framework is planar, the sum of the angles being almost 360° [111.2(3)° for N(1)#2−C(3)−N(1) (endocyclic) and 248.76(13)° (exocyclic) for N(1)−C(3)−N(2) and N(1)#2−C(3)−N(2)]. The endocyclic C(3)−N(1) [133.9(2) pm] and exocyclic C(3)−N(2) [134.9(4) pm] bond distances differing by 1.0 pm only are somewhat longer than an average C=N double bond (130 pm) indicating that the cation can be considered an iminium species.[9,38] Similar bond lengths were found in the hexamethylguanidinium salts[30] $[(Me_2N)_3C]^+[Me_3SiF_2]^-$. The geometry at the nitrogen atoms N(1) and N(2) is essentially planar. The five-membered ring is twisted on C(5)−C(5)#2 [C(4)−N(1)−C(3)−N(1)#2 = −158.3(2)°, C(4)−N(1)−C(5)−C(5)#2 = −146.7(2)°] with −9.0(2) pm deviation at N(1), 0.00(18) pm at C(3), +9.0(2) pm at N(1)#2, −14.6(3) pm at C(5)#2, and +14.6(3) pm at C(5). The trigonal-bipyramidal $Me_3SiF_2^-$ anion shows structural parameters similar to those of refs 30 and39 with the bond lengths Si(1)−F(1) = 177.25(15) pm, Si(1)−C(2) = 187.8(4) pm, and Si(1)−C(1) = 189.0(3) pm and angles F(1)−Si(1)−F(1)#1 = 179.62(13)°, F(1)−Si(1)−C(2) = 89.81(6)°, F(1)−Si(1)−C(1) = 90.47(10)°, and C(1)−Si(1)−C(2) = 119.83(10)°.[30,39] Both fluorine atoms are bridging to the *N*-methyl groups of two neighboring cations by $H_2C(4)-$*H*···*F*−Si contacts (241.6 pm) slightly less than the sum of the van der Waals radii of 255 pm. There are also C(1)−*H*···*F*−Si contacts of 245.6 and 247.7 pm in the $Me_3SiF_2^-$ anion.

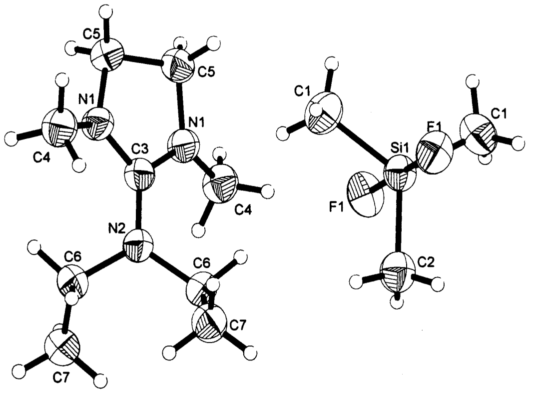

Figure 1. X-ray crystal structure representation of $[(CH_2NMe)_2CNEt_2]^+Me_3SiF_2^-$ with 50% thermal ellipsoids. Selected bond lengths (pm) and angles (deg) for the cation: C(3)−N(1) 133.9(2), C(3)−N(2) 134.9(4), N(1)−C(4) 145.6(3), N(1)−C(5) 147.1(3), N(2)−C(6) 147.6(3); N(1)#2−C(3)−N(1) 111.2(3), (13) N(1)−C(3)−N(2) 124.38, C(3)−N(1)−C(4) 127.1(2), C(3)−N(1)−C(5) 109.33(18), C(4)−N(1)−C(5) 122.27(19), C(3)−N(2)−C(6) 120.87(13), C(6)−N(2)−C(6)#2 120.87(13), N(1)−C(5)−C(5)#2 101.87(12); C(4)−N(1)−C(3)−N(1)#2 −158.3(2), C(4)−N(1)−C(5)−C(5)#2 −146.7(2)°.

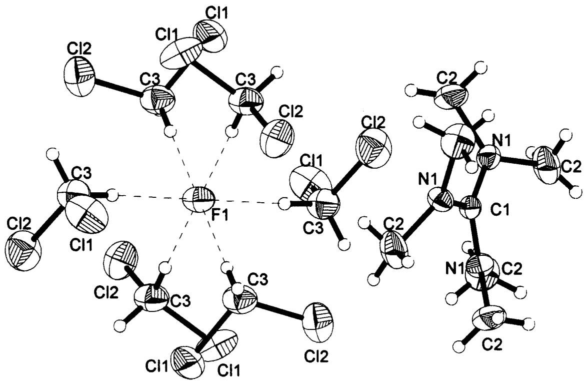

Figure 2. X-ray crystal structure representation of $[C(NMe_2)_3]^+F^-{\bullet}6CH_2Cl_2$ with 50% thermal ellipsoids

Crystal Structure of $[C(NMe_2)_3]^+F^-{\cdot}6CH_2Cl_2$. The structure shows discrete HMG^+ cations and F^- anions, octahedrally coordinated by six methylene chloride molecules (Figure 2). The structural parameters of the HMG^+ cation are in accord with already published data.[9] The CN_3 unit is planar, with N(1)−C(1)−N(1)#2 = 119.992(6)°. The C(1)−N(1) bond distance was found to be 133.9 pm, proving the iminium cation character (see above and refs 7 and 27); the

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(38) Wilson, A. J. C. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C, p 697.

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N(1)−C(2) distance is 152.1(4) pm. The geometry around the nitrogen atoms is planar with the sum of the angles [C(1)−N(1)−C(2) = 117.5(3)°, C(1)−N(1)−C(2)#5 = 117.5(3)°, C(2)−N(1)−C(2)#5 = 125.3(3)°] being 360.3°. The structure of the methylene chloride with C(3)−Cl(1) [176.4(3) pm], C(3)−Cl(2) [177.2(3)], and Cl(1)−C(3)−Cl(2) [110.36(15)°] is similar to what is found for the pure compound (C−Cl = 176.8 pm, Cl−C−Cl = 112.01°).[40] One hydrogen of each CH_2Cl_2 molecule forms a hydrogen bridge to the fluoride anion [H···F = 205(3) pm, C−H···F = 178(2)°]. In the case of 1,1,3,3,5,5-hexamethylpiperidinium fluoride, an adduct with four CH_2F_2 molecules was found with H···F contacts less than 220 pm.[2]

Acknowledgment. A.A.K. is grateful to the Deutsche Forschungsgemeinschaft (Grant 436 UKR 113/36/0) for financial support.

Supporting Information Available: Crystallographic data for $[(CH_2NMe)_2CNEt_2]^+Me_3SiF_2^-$ and $[C(NMe_2)_3]^+F^-\cdot 6CH_2Cl_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Kawaguchi, T.; Tanaka, K.; Takeuchi, T.; Watanabe, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 62.