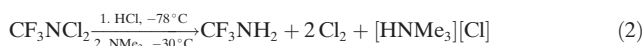**Fluoroalkyl Ammonium Salts**

Convenient Access to α-Fluorinated Alkylammonium Salts

Amanda F. Baxter, Karl O. Christe, and Ralf Haiges*

Dedicated to Prof. Dr. Manfred Schneider on the occasion of his 75th birthday

Abstract: A series of novel α-fluoroalkyl ammonium salts was obtained from the corresponding cyano compounds or nitriles by reaction with anhydrous HF. Room-temperature stable trifluoromethyl ammonium salts were obtained in quantitative yield in a one-step reaction at ambient temperature from the commercially available starting materials BrCN or ClCN. The novel cations $[CF_3CF_2NH_3]^+$, $[HCF_2CF_2NH_3]^+$, and $[(NH_3CF_2)_2]^{2+}$ were obtained from CF_3CN, HCF_2CN, and $(CN)_2$, respectively, and anhydrous HF. The aforementioned fluorinated ammonium cations were isolated as room temperature stable $[AsF_6]^-$ and/or $[SbF_6]^-$ salts, and characterized by multi-nuclear NMR and vibrational spectroscopy. The salts $[HCF_2NH_3][AsF_6]$ and $[CF_3NH_3][Sb_2F_{11}]$ were characterized by their X-ray crystal structure.

$\mathbf{S}$imilar to α-fluoroalcohols, α-fluoroalkylamines are unstable at room temperature and undergo facile HF elimination. Both, the most simple perfluorinated alcohol and amine, namely, trifluoromethanol and trifluoromethylamine, were first prepared by Seppelt et al. in 1977 from the corresponding chloro derivatives, CF_3OCl and CF_3NCl_2, with HCl at low temperature [Eqs. (1) and (2)].[1]

$$CF_3OCl + HCl \xrightarrow{-120\,°C} CF_3OH + Cl_2 \qquad (1)$$

$$CF_3NCl_2 \xrightarrow[2.\ NMe_3,\ -30\,°C]{1.\ HCl,\ -78\,°C} CF_3NH_2 + 2\,Cl_2 + [HNMe_3][Cl] \qquad (2)$$

The thermally unstably compounds CF_3OCl and CF_3NCl_2 are not readily available and were prepared according to relatively cumbersome procedures starting from COF_2 and ClF or BrCN and SF_4.[1b,2] Small amounts of CF_3NH_2 and $C_2F_2NH_2$ have also been obtained from the corresponding N-chloro compounds and Me_3SiH[3] or the corresponding perfluoroalkylsulfinylamines, R_fNSO (R_f = perfluorated alkyl group) and HCl.[4] Since the initial syntheses of CF_3OH and CF_3NH_2, a wealth of computational work has been published relating to α-fluoroalkyl alcohols and amines[5] demonstrating the relevance of these compounds to the scientific community. By comparison, however, there has been a lack of reports relating to the bulk syntheses of these or higher primary, perfluorinated analogues,[3,4,6] which

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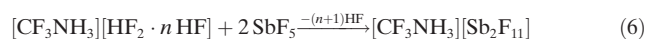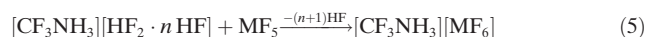Los Angeles, CA 90089-1661 (USA)
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is likely due to the cumbersome preparation of the precursor compounds.

Recently, we found that HF adds across the C=O double bond of carbonyl fluoride, establishing an equilibrium of CF_3OH with COF_2 and HF.[7] Herein we extend the concept of HF addition across C=O double bonds to HF additions across C≡N triple bonds. Only a few examples of HF additions to cyano compounds or nitriles have been reported to date.[8] Solutions of HCN in anhydrous HF were reported as unstable at 20°C and to form the $[HCF_2NH_3]^+$ cation, which was isolated as the $[AsF_6]^-$ salt and characterized by NMR and vibrational spectroscopy.[8a,9] While small amounts of CF_3NH_2 were identified by IR spectroscopy in the reaction products when FCN was added to anhydrous HF at −78°C,[8b] it was found that HF catalyzes the explosive polymerization of FCN.[1d]

Whereas the reaction of HCN with HF in the presence of an Lewis acid, such as AsF_5, results in protonation and formation of the $[HCNH]^+$ cation,[10] we have prepared $[HCF_2NH_3]^+$ by dissolving HCN in a large excess of anhydrous HF and stirring the resulting solution at ambient temperature for three days. While the resulting polybifluoride salt $[HCF_2NH_3][HF_2 \cdot nHF]$, is only stable in HF solution and decomposed upon removal of the solvent, room-temperature stable $[MF_6]^-$ (M = As, Sb) salts are obtained after the addition of stoichiometric amounts of MF_5 [Eq. (3)].

$$HCN + (n+4)\,HF \xrightarrow{72\,h} [HCF_2NH_3][HF_2 \cdot n\,HF] \xrightarrow[-(n+1)HF]{+MF_5} [HCF_2NH_3][MF_6] \qquad (3)$$
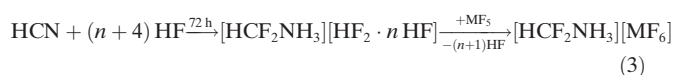
Removal of the volatile compounds in vacuo resulted in colorless, crystalline solids that were identified as $[HCF_2NH_3][MF_6]$ by their multi-nuclear NMR and vibrational spectra which were in good agreement with the ones previously reported.[8a,9] In addition, $[HCF_2NH_3][AsF_6]$ was characterized by its X-ray single-crystal structure.

In analogy to the synthesis of $[HCF_2NH_3]^+$, the simplest perfluoroalkyl ammonium cation, $[CF_3NH_3]^+$ should be accessible by treating FCN with HF. Cyanogen fluoride, however, is not readily available and must be prepared by the thermolysis of cyanuric fluoride.[11] Furthermore, it is unstable at ambient temperature and tends to polymerize explosively. We therefore explored the possibility of synthesizing $[CF_3NH_3]^+$ through an in situ generation of FCN through fluorination of HCN. However, when a freshly prepared solution of HCN in HF was exposed to an excess of 100% fluorine at room temperature, only the $[HCF_2NH_3]^+$ cation was obtained and no evidence for the formation of $[CF_3NH_3]^+$ could be found. Therefore, it must be concluded that the HF

addition to HCN proceeds faster than its fluorination to FCN, and that $[HCF_2NH_3]^+$ does not react with F_2 at ambient temperature and pressure.

Ultimately we were able to find a practical method for the preparation of the $[CF_3NH_3]^+$ cation employing the commercially available starting materials XCN (X = Br, Cl). The reaction of cyanogen bromide or cyanogen chloride with an excess of anhydrous HF results in the release of HX and a HF solution of the polybifluoride salt, $[CF_3NH_3][HF_2 \cdot n\,HF]$, is obtained [Eq. (4)].

$$XCN + (n+5)HF \xrightarrow{\geq 6\,h} [CF_3NH_3][HF_2 \cdot n\,HF] + HX \qquad (4)$$

This reaction proceeds fastest with ClCN, requiring about six hours reaction time, while four days are required in the case of BrCN as starting material. After the addition of stoichiometric amounts of MF_5 (M = As, Sb) and the removal of the HF solvent in vacuo, the resulting salts $[CF_3NH_3][MF_6]$ or $[CF_3NH_3][Sb_2F_{11}]$ were obtained in quantitative yields [Eqs. (5) and (6)].

$$[CF_3NH_3][HF_2 \cdot n\,HF] + MF_5 \xrightarrow{-(n+1)HF} [CF_3NH_3][MF_6] \qquad (5)$$

$$[CF_3NH_3][HF_2 \cdot n\,HF] + 2\,SbF_5 \xrightarrow{-(n+1)HF} [CF_3NH_3][Sb_2F_{11}] \qquad (6)$$

These novel $[CF_3NH_3]^+$ salts were identified and characterized by multinuclear NMR and vibrational spectroscopy. Additionally, $[CF_3NH_3][Sb_2F_{11}]$ was structurally characterized by single-crystal X-ray diffraction.

To probe the generality of our method of adding HF across C≡N triple bonds, we attempted HF addition reactions with a variety of other fluorinated and non-fluorinated nitriles. The reactions of CF_3CN and HCF_2CN with HF afforded the expected, novel fluorinated higher ammonium cations $[CF_3CF_2NH_3]^+$ and $[HCF_2CF_2NH_3]^+$ which, after addition of AsF_5, were isolated in over 90% yield as the corresponding $[AsF_6]^-$ salts [Eqs. (7) and (8)].

$$CF_3CN \xrightarrow[\text{2. +AsF}_5]{\text{1. xs HF, 48 h}} [CF_3CF_2NH_3][AsF_6] \qquad (7)$$

$$HCF_2CN \xrightarrow[\text{2. +AsF}_5]{\text{1. xs HF, 48 h}} [HCF_2CF_2NH_3][AsF_6] \qquad (8)$$

The first α-fluorinated diammonium salt $[NH_3CF_2CF_2NH_3][AsF_6]_2$ was obtained as an off-white solid in near quantitative yield from cyanogen $(CN)_2$ and anhydrous HF, followed by the addition of AsF_5 [Eq. (9)]. The aforementioned α-fluoroalkylammonium salts $[HCF_2NH_3][MF_6]$, $[CF_3NH_3][MF_6]$, $[CF_3NH_3][Sb_2F_{11}]$, $[CF_3CF_2NH_3][MF_6]$, $[HCF_2CF_2NH_3][MF_6]$, and $[H_3NCF_2CF_2NH_3][MF_6]$ are moisture sensitive but room-temperature stable solids that can be stored in the dry nitrogen atmosphere of a glove box for at least several months.

$$(CN)_2 \xrightarrow[\text{2. +AsF}_5]{\text{1. xs HF, 48 h}} [H_3NCF_2CF_2NH_3][AsF_6]_2 \qquad (9)$$

When the non-fluorinated nitriles CH_3CN and C_2H_5CN and the partially fluorinated compound CF_3CH_2CN were dissolved in anhydrous HF and the reaction monitored by multinuclear NMR spectroscopy, the corresponding ammonium cations $[RF_2C-NH_3]^+$ where not the exclusive reaction products. Even after reaction times of several days at ambient temperature, mixtures of the corresponding nitrilium cations $[RC≡NH]^+$, iminium cations $[RFC=NH_2]^+$ and ammonium cations were obtained (Figure 1), indicating the presence of the equilibria shown in Scheme 1.

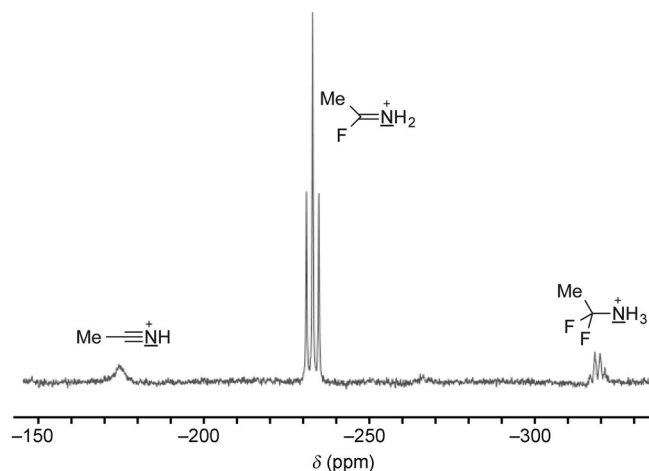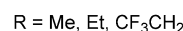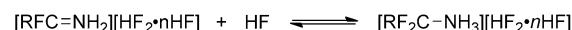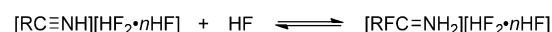*Figure 1.* The ^{14}N NMR spectrum of a 0.2 mol% CH_3CN solution in HF after 7 days at ambient temperature.

Scheme 1. Stepwise HF addition across C≡N triple bonds of nitriles.

The nitriles are immediately protonated in anhydrous HF solution and form the corresponding nitrilium cations. Even at temperatures as low as −70°C it was not possible to detect any unprotonated nitrile in HF solution. The following stepwise HF addition proceeded slower and resulted in the formation of equilibria between the corresponding nitrilium, iminium, and ammonium cations, which took about seven days to establish. While the final equilibrium concentrations were influenced by the nature of the nitrile (Table 1), the α-difluoroammonium species were formed in only 12–33% yield in the cases of acetonitrile and propionitrile. The major species in the equilibria were the α-fluoroiminium ions and in the case of CF_3CH_2CN the nitrilium cation. This is in stark contrast to the reactions of HCN, BrCN, ClCN, CF_3CN, HCF_2CN, or $(CN)_2$ in anhydrous HF for which the corresponding α-fluoroammonium species were the sole reaction products.

Details of the crystallographic data collection and refinement parameters for the structurally characterized compounds $[HCF_2NH_3][AsF_6]$ and $[CF_3NH_3][Sb_2F_{11}]$ are given in the Supporting Information.

$[HCF_2NH_3][AsF_6]$ crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the asymmetric unit ($Z = 4$, $Z' =$

Table 1: Final product ratio for the reaction of nitriles with anhydrous HF.[a]

R	[RCNH]$^+$	[RCFNH$_2$]$^+$	[RCF$_2$NH$_3$]$^+$
CH$_3$	13%	75%	12%
C$_2$H$_5$	n.o.	85%	15%
CF$_3$CH$_2$	60%	7%	33%
CF$_3$	n.o.	n.o.	100%
HCF$_2$	n.o.	n.o.	100%
H	n.o.	n.o.	100%

[a] Determined by NMR spectroscopy from a solution of 5% RCN in HF after 7 days at ambient temperature; n.o.: not observed.
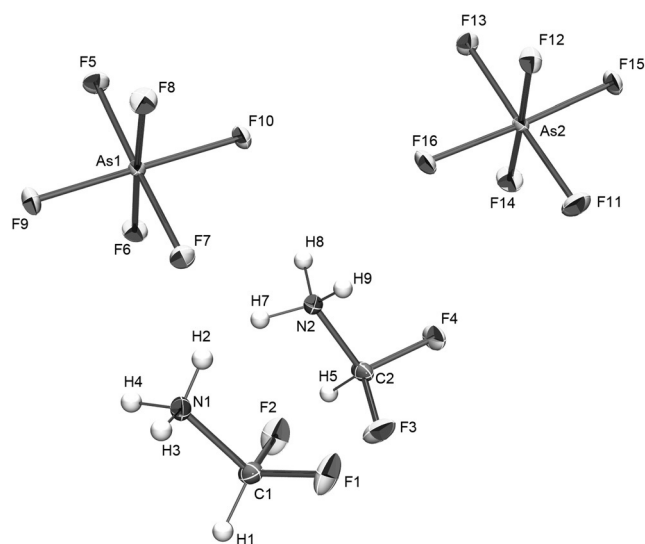

Figure 2. The asymmetric unit in the crystal structure of [HCF$_2$NH$_3$]-[AsF$_6$]. Thermal ellipsoids are set at 50% probability. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Selected bond lengths [Å] and angles [°]: C1–F2 1.326(3), C1–F1 1.338(3), C1–N1 1.470(3), C2–F3 1.325(3), C2–F4 1.342(3), C2–N2 1.475(3); F2-C1-F1 108.4(2), F2-C1-N1 107.5(2), F1-C1-N1 106.9(2), F3-C2-F4 108.7(2), F3-C2-N2 107.7(2), F4-C2-N2 106.8(2).

2). The crystal structure contains [HCF$_2$NH$_3$]$^+$ cations and [AsF$_6$]$^-$ anions (Figure 2) that are associated through hydrogen bonding between the NH$_3$ groups of the cations and the F atoms of anions. The shortest N-H···F distances are found at 2.787(2) Å. The [HCF$_2$NH$_3$]$^+$ cation exhibits a staggered conformation, with a pseudo-tetrahedral substituent arrangement around the carbon and nitrogen atoms.

[CF$_3$NH$_3$][Sb$_2$F$_{11}$] crystallizes in the monoclinic space group $P2_1/m$ with two symmetry-related formula units per unit cell. The solid-state structure contains isolated [CF$_3$NH$_3$]$^+$ cations and [Sb$_2$F$_{11}$]$^-$ anions (Figure 3) that are associated through hydrogen bonding between the H atoms of the cations and the F atoms of anions. The shortest N−H···F distances are found at 2.754(5) Å. As expected and similar to the [HCF$_2$NH$_3$]$^+$ cation, the [CF$_3$NH$_3$]$^+$ cation exhibits a staggered conformation. While the average C–F distance of the [CF$_3$NH$_3$]$^+$ cation is significantly shorter (by 0.023 Å) than in the [HCF$_2$NH$_3$]$^+$ cation, the C−N bond lengths remain constant within one standard deviation.
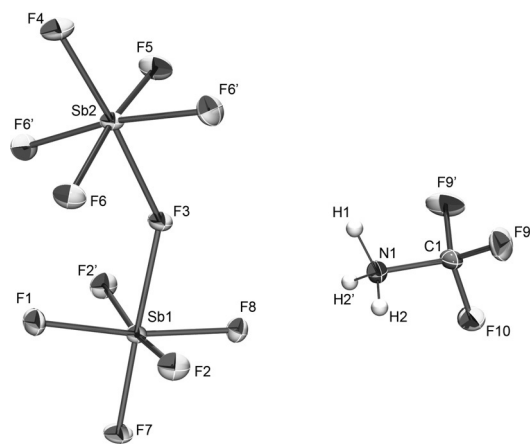

Figure 3. The asymmetric unit in the crystal structure of [CF$_3$NH$_3$]-[Sb$_2$F$_{11}$]. Hydrogen atom positions were determined from the electron density map and are depicted as spheres of arbitrary radius. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: F9–C1 1.307(3), F10–C1 1.312(5), N1–C1 1.469(6); F9-C1-F9 110.7(4), F9-C1-F10 110.1(3), F9-C1-N1 108.3(3), F10-C1-N1 109.5(4).

In summary, the HF addition across C≡N triple bonds of nitriles is a versatile and convenient method for the preparation of α-fluoroalkylammonium salts. In anhydrous HF, the cyano compounds are immediately protonated under formation of nitrilium ions. The successive stepwise HF addition across the C≡N triple bond results in the formation of fluoroiminium and, ultimately, α-fluoroalkylammonium ions. The reactions of HCN, CF$_3$CN, HCF$_2$CN, and (CN)$_2$ with anhydrous HF resulted in the formation of the corresponding α-fluoroalkylammonium ions [HCF$_2$NH$_3$]$^+$, [CF$_3$CF$_2$H$_3$]$^+$, [HCF$_2$CF$_2$NH$_3$]$^+$, and [H$_3$NCF$_2$CF$_2$NH$_3$]$^{2+}$, respectively, cyanogen bromide and cyanogen chloride, XCN (X = Br, Cl) reacted under HX evolution and formation of [CF$_3$NH$_3$]$^+$, whereas the nitriles CH$_3$CN, CH$_3$CH$_2$CN, and CF$_3$CH$_2$CN, formed mixtures of the corresponding nitrilium, iminium, and ammonium ions in anhydrous HF. Room-temperature stable but moisture sensitive α-fluoroalkylammonium salts were obtained and isolated after the addition of the Lewis acids AsF$_5$ or SbF$_5$. All species were fully characterized by multinuclear NMR and, in most cases, vibrational spectroscopy. In addition, the crystal structures of [HCF$_2$NH$_3$][AsF$_6$] and [CF$_3$NH$_3$][Sb$_2$F$_{11}$] were obtained. The conversion of the α-fluoroalkylammonium ions into the corresponding free amines, and their reaction chemistry are the subjects of ongoing studies and will be discussed in subsequent papers.

Experimental Section

Caution! Anhydrous HF can cause severe burns and contact with the skin must be avoided. HCN, BrCN, ClCN, (CN)$_2$, and AsF$_5$ are volatile and highly poisonous and should only be handled in a well ventilated fume hood. Appropriate safety precautions should be taken when working with these materials.

Materials and apparatus: All reactions were carried out in either Teflon–FEP ampules or NMR tubes that were closed by stainless steel valves. Volatile materials were handled in a stainless steel/Teflon–FEP vacuum line.[12] Reaction vessels and the vacuum line were passivated with ClF$_3$ prior to use.

Crystal-structure determinations: The single-crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO diffractometer using Mo Kα radiation. The structures were solved by the direct method and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.[13] ORTEP drawings were prepared using the ORTEP-3 for Windows V2.02 program.[14] CCDC 1413581 ($[CF_3NH_3][Sb_2F_{11}]$) und 1413581 ($[HCF_2NH_3][AsF_6]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

For further experimental details please see the Supporting Information.

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