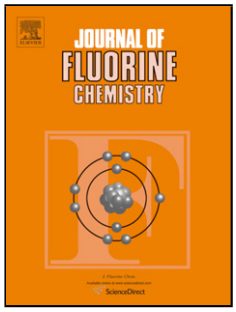

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Reaction of N-heterocyclic carbene (NHC) with different HF sources and ratios – a free fluoride reagent based on imidazolium fluoride

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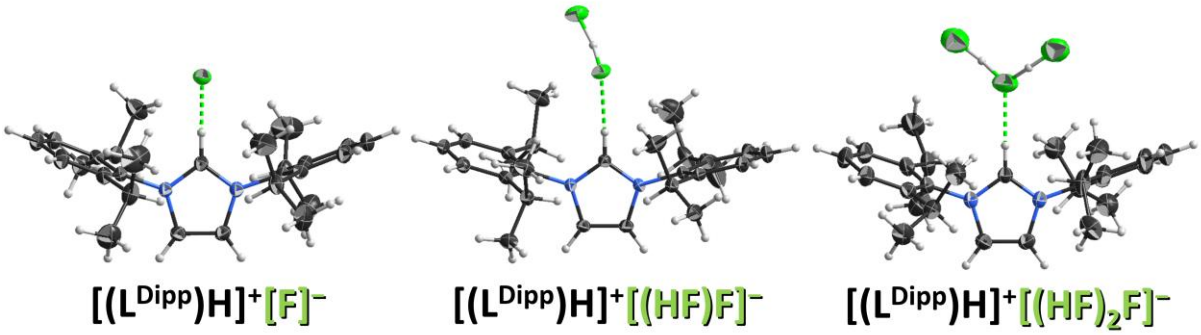
Graphical abstract



Highlights

- water-free synthesis of imidazolium fluoride $[(L^{Dipp})H]^+[F]^-$ (1) which shows characteristics of free fluoride reagent
- synthesis of imidazolium poly(hydrogen fluoride) salts $[(L^{Dipp})H]^+[F(HF)]^-$ (2) and $[(L^{Dipp})H]^+[F(HF)_2]^-$ (3)
- different synthetic approaches for preparation of (1) (2) and (3)
- X-ray analysis, NMR and Raman spectroscopic analysis and chemical determination of free fluoride of all products (1)-(3)

Abstract

Treatment of N-heterocyclic carbene (1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene; (L^{Dipp})) with different sources of hydrofluoric acid ($Et_3N{\cdot}3HF$, anhydrous hydrofluoric acid and KHF_2) in 1:1, 1:2, 1:3 ratios affords $[(L^{Dipp})H]^+[F]^-$ (**1**), $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**) and $[(L^{Dipp})H]^+[(HF)_2F]^-$ (**3**) salts respectively. Different fluoride sources all yield the same products, but ease of manipulation and isolation can influence the choice in the future use.

Compound (**1**), which shows characteristics of a free fluoride reagent, can be obtained with good yield and without the contaminants usually present in such compounds. All products were characterized by X-Ray crystallography, NMR spectroscopy and elemental analysis.

Keywords: N-heterocyclic carbene, HF, imidazolium salts, crystal structure, fluoride

1. Introduction

Imidazolium salts represent a large family of ionic compounds with a discrete cation and anion pair and high tuning abilities. Different substituents on both nitrogen atoms, ranging from symmetric to asymmetric and from aromatic to aliphatic, can be incorporated in order to tune their properties according to the need. Additionally, substituents on C2, C4 and C5 positions of imidazole ring, together with anion type, can also be manipulated with different synthetic approaches [1-3]. Because of these properties their use expands over many fields of chemistry. Most notably, imidazolium salts are applied in the field of ionic liquids (ILs) as potential replacement for volatile organic solvents [4, 5] and as precursors for N-heterocyclic carbene ligands (NHCs) which are increasingly substituting bulky phosphine ligands across

organic chemistry [6]. In biological systems, these compounds exhibits anti-tumour and anti-bacterial properties, that are also being studied in detail [7].

Most of the work on imidazolium fluorides was implemented in the area of ILs. The first ILs with fluoride ions were imidazolium tetrafluoridoborate [8] and hexafluoridophosphate [9] which showed stability towards oxygen and moisture. However, as found later [10], during the synthesis of imidazolium hexafluoridophosphate, imidazolium fluoride is formed to some extent as a side product. Further, ionic liquid of [bmim][F] synthesised in 2014 shows extremely good results for nucleophilic substitution of different leaving groups with various substrates [11].

Methods for the incorporation of F^- to imidazolium salts differ from other halides. While synthesis of imidazolium halides can be performed with quarterisation of imidazole nitrogen atoms, the same methods cannot be applied with F^- because of the strength of C−F bonds [12]. As reported so far, the imidazolium fluorides can be obtained:

a) during synthesis of imidazolium hexafluoridophosphate, as a side product [10].

b) from imidazolium halide (halide = Cl, Br, I) and subsequent anion exchange with HF or MF salts [11-13]

c) with Anion Exchange Resins (AER method) [14, 15]

Herein we report new imidazolium fluoride $[(L^{Dipp})H]^+[F]^-$ (**1**) and two imidazolium poly(hydrogen fluorides) $[(L^{Dipp})H]^+[(HF)_nF]^-$ (n = 1, 2) derived from persistent N-heterocyclic carbene with introduction of HF in stoichiometric 1:1, 1:2 and 1:3 ratios respectively.

2. Results and Discussion

When 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (L^{Dipp}) is treated with stoichiometric quantities of HF source, in the form of $Et_3N{\cdot}3HF$, in ratios (L^{Dipp}:HF) 1:1, 1:2 and 1:3, it affords $[(L^{Dipp})H]^+[F]^-$ (**1**), $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**) and $[(L^{Dipp})H]^+[(HF)_2F]^-$ (**3**) respectively. Reaction in excess of HF source afforded only crystals of $[(L^{Dipp})H]^+[(HF)_2F]^-$ (**3**) and no higher poly(hydrogen fluoride) anion was observed, even when anhydrous HF (aHF) was used as a reagent and solvent, at room temperature (Scheme 1).

In order to ease the synthetic procedure, we have searched for an alternative reagent to aHF and the choice fell onto triethylamine trihydrofluoride ($Et_3N{\cdot}3HF$), which allowed us to perform the reactions with ease, in laboratory glassware, without any signs of glass etching by the reagent. Moreover, addition of equimolar quantities of HF with $Et_3N{\cdot}3HF$ is far simpler than use of anhydrous HF. Purification and isolation of the products is effortless since remaining Et_3N has a substantial vapour pressure at room temperature and can be removed under reduced pressure.

When reacting one equivalent of HF with (L^{Dipp}) at room temperature, kinetically favoured $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**) can be isolated first. Prolonged reaction at room temperature in CH_3CN leads to formation of $[(L^{Dipp})H]^+[F]^-$ (**1**) in quantitative yields. Additionally, reaction of $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**) or KHF_2 with equivalent of (L^{Dipp}) in acetonitrile also affords $[(L^{Dipp})H]^+[F]^-$ (**1**).

2.1 Crystal structure determination of $[(L^{Dipp})H]^+[F]^-$ (1), $[(L^{Dipp})H]^+[(HF)F]^-$ (2) and $[(L^{Dipp})H]^+[(HF)_2F]^-$ (3)

A series of structures with dialkyl imidazolium poly(hydrogen fluoride) were published by Hagiwara *et al.* [13, 16-20], but our goal was obtaining similar product with sterically hindered and widely used (L^{Dipp}), which forms diaryl N-substituted imidazolium fluoride and

poly(hydrogen fluoride) salts. Crystal data for $[(L^{Dipp})H]^+[F]^-$ (**1**), $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**) and $[(L^{Dipp})H]^+[(HF)_2F]^-$ (**3**) are listed in Table 1.

All three products crystalize in monoclinic lattice; (**1**) in *P2₁/c*, (**2**) in *P2₁/n* and (**3**) in *C2/c* space group. N−C−N angle of imidazolium ring is increasing with higher poly(hydrogen fluoride) anions from 106.9° in (**1**) to 108.2°in (**3**) which is expected in terms of the electronegativity of F^- anion, pulling on the C(2)−H(2) proton. Same trend is observed in imidazolium poly(hydrogen fluoride) structures published by Hagiwara *et al*., although we have to note that in the highest poly(hydrogen fluoride) anion, $[(FH)_3F]^-$, published in that research, the angle decreases from 109.6(3)° in $DMIm(FH)_2F$ to 108.7° in $DMIm(FH)_3F$ [16].

F^- anion in compound (**1**) is stabilized by four hydrogen bonds in the crystal structure. The strongest arises from C(2)−H(2)···F(1) being 1.72 Å. Second hydrogen bond is formed with C(5)−H(5)···F(1) proton from imidazolium backbone of symmetrically generated unit with 1.97 Å, third from acetonitrile methyl proton C(30)−H(30B)···F(1) with 2.07 Å and the weakest from para proton on diisopropybenzene "wingtip" C(21)−H(21)···F(1) with 2.23 Å, from another symmetrically generated (L^{Dipp}) (Figure 1).

When crystallization of (**1**) was attempted from chloroform, an ion exchange was observed and single crystals of $[(L^{Dipp})H]^+[Cl]^-$ were isolated. Such reactivity is consistent with reactivity of a free fluoride reagent, as observed for different free fluoride reagents in the literature [21-23].

$[(HF)F]^-$ anion of compound (**2**) is stabilized by four hydrogen bonds. Three come from chloroform molecules and one from protonated imidazolium ring C(2)−H(2)···F(1), which has the strongest interaction with the distance of 1.99 Å. From three chloroform molecules, one is directed towards proton in $[(HF)F]^-$ anion. Observed electron density peak that could be

assigned to hydrogen atom in F(1)−H(1)−F(2) anion showed a slightly bent structure of anion with 164° angle (Figure 2, Table 2). The C(31)−H(31) proton from the chloroform molecule forms bifurcated, three-centred interaction with F(1) and F(2) atoms and has geometry consistent for other reported bifurcated bonds [24]. Result of such interaction is a short H(1)···H(31) nonbonded contact interaction of 2.07 Å (Figure 2). Although this H···H nonbonded distance is at the beginning of distribution curve of reported H···H nonbonded contact interactions [25], it is still far from the shortest reported in the literature [26, 27].

Structure (**3**) is the most symmetrical of the three, with asymmetric unit containing only half of imidazolium cation and anion. $[(HF)_2F]^-$ anion of product (**3**) is packed between four imidazolium cations. Terminal F(2) and symmetrically generated F(2)' atoms are each stabilized by C(4)−H(4)···F(2) hydrogen bond and with hydrogen bond arising from meta proton on diisopropybenzene "wingtip" of imidazolium cation C(7)−H(7)···F(2) (Figure 3). We would like to stress that these two interactions should be viewed with some scepticism as they are on the upper limit, as far as angles and distances are concerned, for such interaction and can be probably attributed to packing in crystal structure (Table 2). The disordered central F^-, that was modelled in three positions with approximately 1/3 occupancy each, is loosely stabilized by C(2)−H(2)···F(1) hydrogen bond. The $[(HF)_2F]^-$ anion should be completely planar but due to the disorder of central F^- in the crystal structure it is impossible to describe such shape in product (**3**) (Figure 3).

2.2 NMR analysis

NMR analysis was performed at room temperature for all three products and is in agreement with their X-ray crystal structures. We weren't able to observe separate peak for C(2)−H(2) proton in ^{1}H NMR of $[(L^{Dipp})H]^+[F]^-$ (**1**). When we dissolved monocrystals of (**1**) in

deuterated acetonitrile, ^{19}F NMR analysis showed a characteristic doublet peak for $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**) at −147.15 and −147.59 ppm ($^1J_{HF}$ = 124.03 Hz) respectively. After 24h at room temperature the doublet disappeared and a singlet for $[(L^{Dipp})H]^+[F]^-$ (**1**) at −147.94 ppm could be observed. This indicates that with introduction of acetonitrile to the crystals of (**1**), the two imidazolium fluorides form $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**) and a free carbene moiety as kinetically controlled products, and with time, thermodynamically more stable product, $[(L^{Dipp})H]^+[F]^-$ (**1**), can be quantitatively isolated and crystalized from solution (Scheme 2).

^{1}H NMR of (**2**) shows C(2)−H(2) proton peak at 10.01 ppm. The proton-fluoride coupling for $[(HF)F]^-$, with characteristic triplet at 16.06 ppm in ^{1}H NMR, and doublet at −147.50 ppm in ^{19}F NMR spectra, can also be seen. The coupling constant, $^1J_{HF}$, for such system should be around 121−125 Hz according to the literature [28, 29] and when (**2**) is formed in reaction mixture from (**1**) upon addition of acetonitrile. However, we have observed slightly lower coupling constant value, $^1J_{HF}$ = 115.14 Hz, for the pure isolated $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**) in ^{1}H NMR spectra. This can be attributed to broadened signals of $[(HF)F]^-$ in ^{1}H and ^{19}F spectra, where the exact point of peak can be somewhat arbitrarily chosen to the extent of ± 0.02 ppm. The heteronuclear coupling constant, $^1J_{HF}$, in ^{1}H NMR of $[(HF)F]^-$ is in agreement with ^{19}F NMR coupling constant where its value is $^1J_{HF}$ = 114.24 Hz. Again, discrepancies of $\Delta^1J_{HF} \approx 1$Hz between ^{1}H and ^{19}F spectra can arise due to broadened peaks. Repeated synthesis of (**2**) and NMR analysis gave the same results.

NMR analysis of (**3**) agrees with crystal structure obtained on single crystals. C(2)−H(2) proton shows a signal at 9.10 ppm, characteristic for imidazolium salts. It is even split in to a triplet with a small coupling constant of 1.5 Hz with C(4)−H(4) and C(4')−H(4)

protons. Further downfield at 13.36 ppm in ^{1}H NMR spectra is a broad peak that integrates for two and is characteristic for $[(HF)_2F]^-$ anion [28]. Proton-fluoride heterocoupling can't be observed at room temperature. The same is true for ^{19}F spectra of $[(HF)_2F]^-$ anion, where only a singlet peak at −167.28 ppm can be observed at room temperature and no proton-fluoride heterocoupling or fluoride-fluoride coupling can be seen.

3. Conclusions

Reactions of N-heterocyclic carbene with $Et_3N{\cdot}3HF$ reagent readily affords $[(L^{Dipp})H]^+[(HF)_nF]^-$ (n = 0−2) salts with 1:1, 1:2, 1:3 ratios of HF. Product (**1**) shows a free fluoride reagent characteristics and can be selectively synthesised from reactions of (L^{Dipp}) with stoichiometric quantities of $Et_3N{\cdot}3HF$ or KHF_2 without any halide or water impurities on a gram scale. All products were characterized with NMR, X-Ray, Raman and free fluoride (F_f^-) chemical analysis. Reactions of $Et_3N{\cdot}3HF$ or KHF_2 with (L^{Dipp}) were performed in glassware with no sign of glass etching by the reagents.

4. Experimental

4.1. General Experimental Procedure and Reagents

All experiments and manipulations were carried out under an inert atmosphere of dried argon, either in glovebox (M. Braun) or using standard Schlenk techniques. THF was dried in a mixture of sodium and benzophenone for at least two days, distilled under argon atmosphere and stored over 3 Å molecular sieves. Acetonitrile was stored over 3 Å molecular sieves and left for at least 48h prior to use. Deuterated solvents were dried over 3 Å molecular sieves (at least 20% w/w). Glassware was oven-dried overnight at 150 °C.

Anhydrous HF was handled in an all PTFE (polytetrafluoroethylene) vacuum line equipped with PTFE valves. The reaction was carried out in FEP (tetrafluoroethylene-

hexafluoropropylene; Polytetra GmbH, Germany) reaction vessels (height 250−300 mm with inner diameter 15.5 mm and outer diameter 18.75 mm) equipped with PTFE valves and PTFE coated stirring bars. T-shaped reaction vessels from PTFE were used for the crystallization process. Caution: aHF must be handled in a well-ventilated fume hood, and protective clothing must be worn at all times.

4.1.1 Manipulation and preparation of starting materials

$Et_3N{\cdot}3HF$ 98% (Sigma-Aldrich) was used without further treatment.

$KHF_2 \geq 99.0\%$ (Sigma-Aldrich) was used without further treatment

(L^{Dipp}) was synthesised after standard literature procedures [30].

Anhydrous HF (Linde, 99.995 %) was treated with K_2NiF_6 (Advance Research Chemicals, Inc.) for several hours prior to use.

4.1.2 NMR spectroscopy

NMR spectra (^1H and ^{19}F) were recorded on Agilent Technologies Unity Inova 300 MHz; (^1H at 303 MHz and ^{19}F at 285.1 MHz). The chemical shifts are referenced: ^1H to residual signals of deuterated solvent peaks and ^{19}F to $CFCl_3$ as an external standard.

4.1.3 Raman spectroscopy

Raman spectra were recorded at room temperature on a Horiba Jobin Yvon Labram-HR spectrometer coupled with an Olympus BXFM-ILHS microscope. Samples were excited by the 633-nm emission line of a 24.3-mW He-Ne laser with a power output of 14 mW on the sample. The samples were loaded into vacuum dried 0.5-mm quartz capillaries inside the glove box. The spectra obtained from the powdered samples corresponded completely with the spectra

taken from several, randomly oriented, single crystals, of which the identity was additionally confirmed by the unit-cell measurement on the diffractometer.

4.1.4 Free fluoride analysis

All reagents were of analytical grade and all solutions were prepared using deionized and additionally double-distilled water. The amount of free fluoride (F_f^-) was determined in aqueous solution of the sample using fluoride ion selective electrode [31].

4.1.5 Crystal structure determination

Single-crystal data for all compounds were collected on a Gemini A diffractometer equipped with an Atlas CCD detector, using graphite monochromated Cu Kα radiation. The data were treated using the CrysAlisPro software suite program package [32]. Analytical absorption correction has been applied to all data sets [33]. Structures were solved with direct methods using the ShelXT program [34]. Structure refinement has been performed with the ShelXL-2015 software [35] implemented in the program package Olex2 [36]. Figures were prepared using Diamond 4.0 software [37].

4.2. Synthesis of products

4.2.1 Synthesis of $[(L^{Dipp})H]^+[F]^-$ (1)

(L^{Dipp}) (n = 1.03 mmol; m = 400 mg) was weighed into 100 mL Schlenk flask and dissolved in 40 mL of THF or 20 ml MeCN. Solution was then cooled to 193 K, to which $Et_3N{\cdot}3HF$ (n = 0.34 mmol (1 eq. of HF); m = 55.31 mg; ρ = 0.989 mg μL^{-1}; V = 55.9 µL) was added dropwise via syringe and left to warm up to R.T. and stirred for 16 hours. Solvent was then slowly removed under vacuum. Solid residue was washed with toluene to afford single crystals of $[(L^{Dipp})H]^+[F]^-$ (**1**) in quantitative yields.

Yield 370 mg (88%).

Melting point [°C] = 130 (decomposition)

^{1}H NMR (303 MHz, CD_3CN, 25°C): δ 7.53 − 7.37 (m, 7H, ArH), 2.59 (singlet (broad), 4H, CH), 1.22 (d, *J* = 6.8 Hz, 12H, $(CH_3)_2$), 1.16 (d, *J* = 6.9 Hz, 12H, $(CH_3)_2$) ppm.

^{19}F NMR (285.05 MHz, CD_3CN, 25°C): δ −147.94 (s, 1F, F^-) ppm.

Free fluoride determination: 4.4% (experimental), 4.6% (theoretical)

Alternative synthesis of (**1**):

(L^{Dipp}) (n = 2.57 mmol; m = 1000 mg) was weighed into 100 mL Schlenk flask and dissolved in 35 mL of MeCN. KHF_2 (n = 2.56 mmol; m = 200 mg) was added and stirred for 16 hours. Reaction mixture was then filtered through 0.45μm syringe PTFE fliter, and the filtrate was left to slowly evaporate at room temperature, to afford single crystals of $[(L^{Dipp})H]^+[F]^-$ (**1**).

4.2.2 Synthesis of $[(L^{Dipp})H]^+[(HF)F]^-$ (2)

(L^{Dipp}) (n = 0.51 mmol; m = 200 mg) was weighed into 100 mL Schlenk flask and dissolved in 20 mL of THF. Solution was then cooled to 193 K, to which a THF solution of $Et_3N{\cdot}3HF$ (n = 0.34 mmol (2 eq. of HF); m = 55.31 mg; ρ = 0.989 mg μL^{-1}; V = 55.9 μL) was added dropwise via syringe and left to warm up to room temperature and stirred for an additional hour. Solvent was then removed under vacuum. Compound (**2**) was then crystalized with slow evaporation of chloroform.

Yield 201 mg (91%)

Melting point [°C] = 223.4 − 227.1 (decomposition)

^{1}H NMR (303 MHz, CD_3CN, 25°C): δ 16.44 − 15.68 (t, 1H, $^{1}J_{HF}$ = 115 Hz, $[(HF)F]^-$), 10.01 (s, 1H, C(2)H), 7.83 (s, 2H, CH=CH), 7.66 − 7.60 (m, 2H, ArH), 7.47 − 7.44 (m, 4H, ArH), 2.43 (hept, *J* = 6.5 Hz, 4H, CH), 1.26 (d, *J* = 6.9 Hz, 12H, $(CH_3)_2$), 1.19 (d, *J* = 6.9 Hz, 12H, $(CH_3)_2$) ppm.

^{19}F NMR (285.05 MHz, CD_3CN, 25°C): δ −147.50 (d, 2F, $^{1}J_{HF}$ = 114 Hz, $[(HF)F]^-$) ppm.

Free fluoride determination: 8.6% (experimental), 8.8% (theoretical)

4.2.3 Synthesis of $[(L^{Dipp})H]^+[(HF)_2F]^-$ (3)

(L^{Dipp}) (n= 6.43 mmol; m = 2500 mg) was weighed to FEP vessel and frozen in liquid nitrogen. Approximately 10 ml of aHF was condensed over the frozen (L^{Dipp}) and left to warm to room temperature. Clear red-brown solution was evaporated on the vacuum line after 30 minutes. Single crystals of (**3**) were obtained from crystallization in FEP crystallization vessel where a small temperature gradient (10 K) was used for evaporation of aHF from the crystallization part.

Yield 2300 mg (80%)

Melting point [°C] = 232.1 − 235.1 (decomposition)

^{1}H NMR (303 MHz, CD_3CN, 25°C): δ 13.36 (s (broad), 2H, $[(HF)_2F]^-$), 9.10 (t, *J* = 1.5 Hz, 1H, C(2)H), 7.90 (d, *J* = 1.5 Hz, 2H, CH=CH), 7.69 − 7.64 (m, 2H, ArH), 7.50 − 7.47 (m, 4H, ArH), 2.43 (hept, *J* = 6.7 Hz, 4H, CH), 1.28 (d, *J* = 6.7 Hz, 12H, $(CH_3)_2$), 1.20 (d, *J* = 6.9 Hz, 12H, $(CH_3)_2$) ppm.

^{19}F NMR (285.05 MHz, CD_3CN, 25°C): δ −167.28 (s, 2F, $[(HF)_2F]^-$) ppm.

Free fluoride determination: 13.3% (experimental), 12.7% (theoretical)

Alternative synthesis of (**3**):

(L^{Dipp}) (n = 0.51 mmol; m = 200 mg) was weighed into 100 mL Schlenk flask and dissolved in 20 mL of THF. Solution was then cooled to 193 K, to which a THF solution of $Et_3N{\cdot}3HF$ (n = 1.02 mmol (6 eq. of HF); m = 164.4 mg; ρ = 0.989 mg μL^{-1}; V = 167 µL) was added dropwise via syringe and left to warm to room temperature and stirred for an additional hour. Solvent and excess reagent was then removed under vacuum which afforded spectroscopically pure product (**3**).

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7. References

[1] A. Kruger, L.J.L. Haller, H. Muller-Bunz, O. Serada, A. Neels, S.A. Macgregor, M. Albrecht, Smooth C(alkyl)-H bond activation in rhodium complexes comprising abnormal carbene ligands, Dalton Trans. 40(38) (2011) 9911–9920.
[2] K. Hirano, S. Urban, C. Wang, F. Glorius, A Modular Synthesis of Highly Substituted Imidazolium Salts, Org. Lett. 11(4) (2009) 1019–1022.
[3] C. Kison, T. Opatz, Synthesis of Highly Substituted Unsymmetrical 1,2-Diamines, 1,2-Diimines, Imidazolium Salts and Imidazolylidenes by Aldimine Cross-Coupling, Synthesis 2006(21) (2006) 3727-3738.
[4] J.P. Hallett, T. Welton, Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2, Chem. Rev. 111(5) (2011) 3508-3576.
[5] T. Welton, Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis, Chem. Rev. 99(8) (1999) 2071-2084.
[6] M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, An overview of N-heterocyclic carbenes, Nature 510(7506) (2014) 485–496.
[7] S.N. Riduan, Y. Zhang, Imidazolium salts and their polymeric materials for biological applications, Chem. Soc. Rev. 42(23) (2013) 9055–9070.
[8] J.S. Wilkes, M.J. Zaworotko, Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, J. Chem. Soc., Chem. Commun. (13) (1992) 965–967.
[9] J. Fuller, R.T. Carlin, H.C. De Long, D. Haworth, Structure of 1-ethyl-3-methylimidazolium hexafluorophosphate: model for room temperature molten salts, J. Chem. Soc., Chem. Commun. (3) (1994) 299–300.
[10] R.P. Swatloski, J.D. Holbrey, R.D. Rogers, Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate, Green Chem. 5(4) (2003) 361-363.
[11] S. Bouvet, B. Pégot, J. Marrot, E. Magnier, Solvent free nucleophilic introduction of fluorine with [bmim][F], Tetrahedron Lett. 55(4) (2014) 826-829.
[12] Z.-Q. Zhu, M.-Y. Jiang, C.-G. Zheng, J.-C. Xiao, Efficient synthesis of 1-alkyl-3-methylimidazolium fluorides and possibility of the existence of hydrogen bonding between fluoride anion and C(sp3)–H, J. Fluorine Chem. 133 (2012) 160-162.
[13] R. Hagiwara, Y. Ito, Room temperature ionic liquids of alkylimidazolium cations and fluoroanions, J. Fluorine Chem. 105(2) (2000) 221–227.
[14] E. Alcalde, I. Dinarès, A. Ibáñez, N. Mesquida, A Simple Halide-to-Anion Exchange Method for Heteroaromatic Salts and Ionic Liquids, Molecules 17(4) (2012) 4007.
[15] I. Dinares, C. Garcia de Miguel, A. Ibanez, N. Mesquida, E. Alcalde, Imidazolium ionic liquids: A simple anion exchange protocol, Green Chem. 11(10) (2009) 1507–1510.
[16] T. Enomoto, Y. Nakamori, K. Matsumoto, R. Hagiwara, Ion−Ion Interactions and Conduction Mechanism of Highly Conductive Fluorohydrogenate Ionic Liquids, J. Phys. Chem. C 115(10) (2011) 4324-4332.
[17] K. Matsumoto, R. Hagiwara, R. Yoshida, Y. Ito, Z. Mazej, P. Benkic, B. Zemva, O. Tamada, H. Yoshino, S. Matsubara, Syntheses, structures and properties of 1-ethyl-3-methylimidazolium salts of fluorocomplex anions, Dalton Trans. (1) (2004) 144-149.
[18] K. Matsumoto, T. Tsuda, R. Hagiwara, Y. Ito, O. Tamada, Structural characteristics of 1-ethyl-3-methylimidazolium bifluoride: HF-deficient form of a highly conductive room temperature molten salt, Solid State Sci. 4(1) (2002) 23-26.
[19] R. Hagiwara, T. Hirashige, T. Tsuda, Y. Ito, A Highly Conductive Room Temperature Molten Fluoride: EMIF · 2.3 HF J. Electrochem. Soc. 149(1) (2002) D1-D6.
[20] R. Hagiwara, T. Hirashige, T. Tsuda, Y. Ito, Acidic 1-ethyl-3-methylimidazolium fluoride: a new room temperature ionic liquid, J. Fluorine Chem. 99(1) (1999) 1–3.
[21] V.V. Grushin, Generation of "Naked" Fluoride Ions in Unprecedentedly High Concentrations from a Fluoropalladium Complex, Angew. Chem. Int. Ed. 37(7) (1998) 994-996.

[22] A.R. Mahjoub, X. Zhang, K. Seppelt, Reactions of the "Naked" Fluoride Ion: Syntheses and Structures of SeF 62− and BrF 6−, Chem. Eur. J. 1(4) (1995) 261-265.
[23] K.O. Christe, W.W. Wilson, Reaction of the fluoride anion with acetonitrile. Chloroform and methylene chloride, J. Fluorine Chem. 47(1) (1990) 117-120.
[24] I. Rozas, I. Alkorta, J. Elguero, Bifurcated Hydrogen Bonds: Three-Centered Interactions, J. Phys. Chem. A 102(48) (1998) 9925-9932.
[25] R.S. Rowland, R. Taylor, Intermolecular Nonbonded Contact Distances in Organic Crystal Structures: Comparison with Distances Expected from van der Waals Radii, J. Phys. Chem. 100(18) (1996) 7384-7391.
[26] O. Ermer, S.A. Mason, F.A.L. Anet, S.S. Miura, Ultrashort nonbonded hydrogen...hydrogen distance in a half-cage pentacyclododecane, J. Am. Chem. Soc. 107(8) (1985) 2330-2334.
[27] J. Zong, J.T. Mague, R.A. Pascal, Exceptional Steric Congestion in an in,in-Bis(hydrosilane), J. Am. Chem. Soc. 135(36) (2013) 13235-13237.
[28] I.G. Shenderovich, S.N. Smirnov, G.S. Denisov, V.A. Gindin, N.S. Golubev, A. Dunger, R. Reibke, S. Kirpekar, O.L. Malkina, H.-H. Limbach, Nuclear magnetic resonance of hydrogen bonded clusters between F− and (HF)n: Experiment and theory, Ber. Bunsenge. Phys. Chem. 102(3) (1998) 422-428.
[29] K.O. Christe, W.W. Wilson, Nuclear magnetic resonance spectrum of the fluoride anion, J. Fluorine Chem. 46(2) (1990) 339-342.
[30] L. Hintermann, Expedient syntheses of the N-heterocyclic carbene precursor imidazolium salts IPr·HCl, IMes·HCl and IXy·HCl, Beilstein J. Org. Chem. 3 (2007) 22.
[31] M. Ponikvar, B. Sedej, B. Pihlar, B. Žemva, Determination of fluoride in M(SbF6)x compounds, Anal. Chim. Acta 418(1) (2000) 113-118.
[32] CrysAlisPro, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET) (compiled Mar 27 2014,17:12:48)
[33] R. C. Clark, J. S. Reid, The Analytical Calculation of Abosorbtion in Multifaceted Crystals, Acta Cryst. A51 (1995) 887-897
[34] G. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, Acta Crystallogr. A 71(1) (2015) 3-8.
[35] G. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallogr. C 71(1) (2015) 3-8.
[36] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, J. Appl. Crystallogr. 42(2) (2009) 339-341.
[37] Diamond - Crystal and Molecular Structure Visualization Crystal Impact - Dr. H. Putz & Dr. K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany

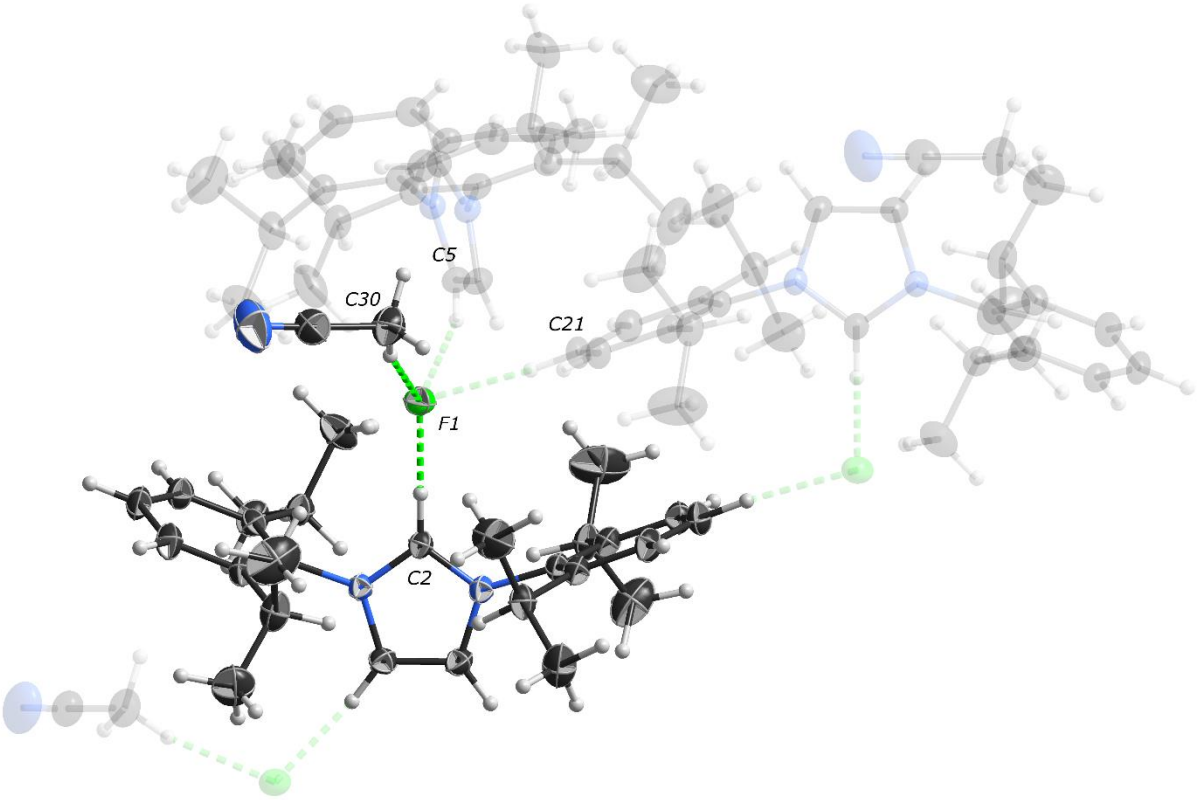


*Figure 1: Asymmetric unit (bold) and packing (blurred) of structure $[(L^{Dipp})H]^+[F]^-$ (**1**). Ellipsoids are drawn with 50% probability.*

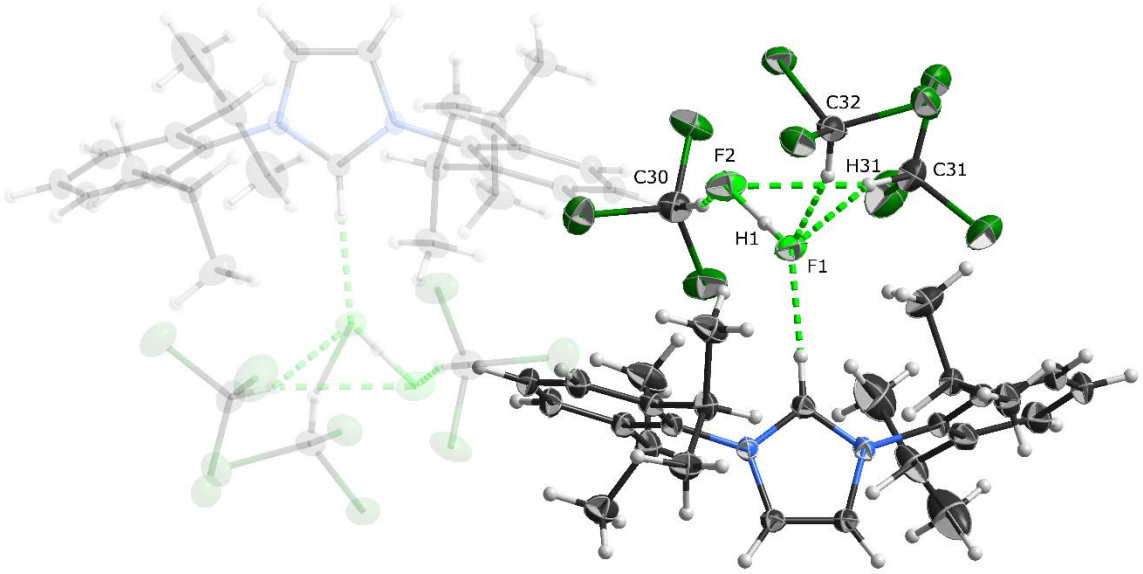


*Figure 2: Asymmetric unit (bold) and packing (blurred) of structure $[(L^{Dipp})H]^+[(HF)F]^-$ (**2**). Ellipsoids are drawn with 50% probability.*

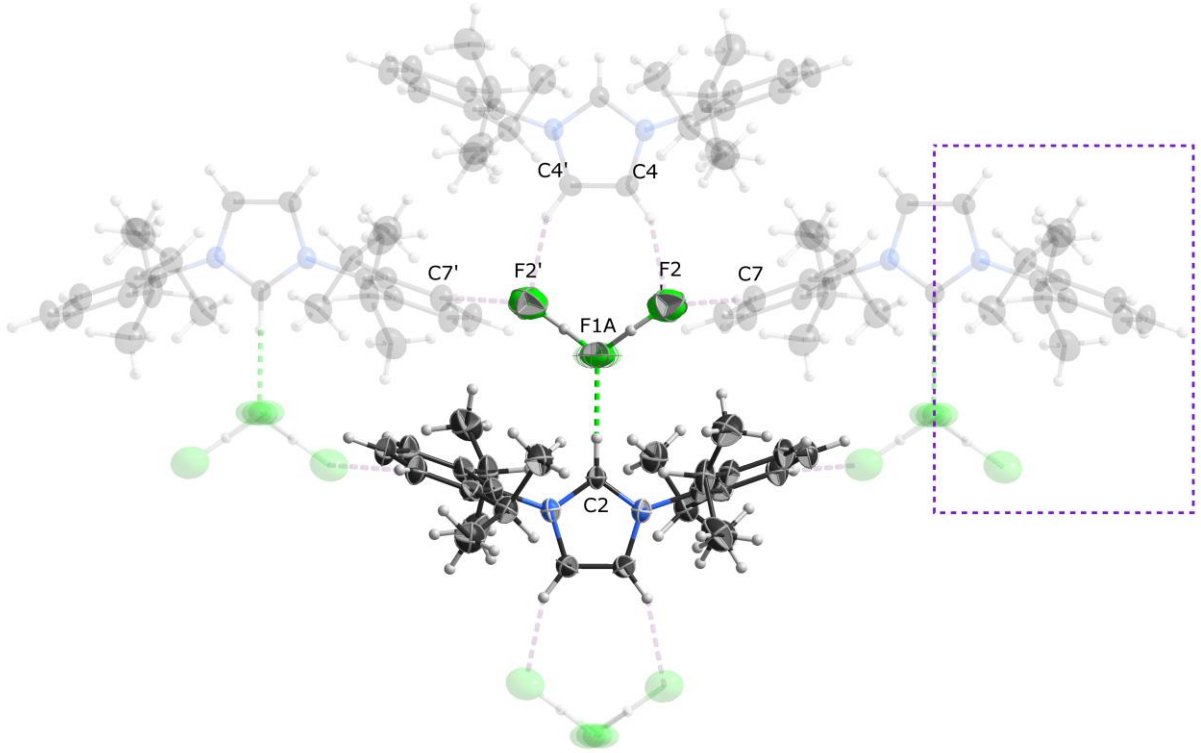
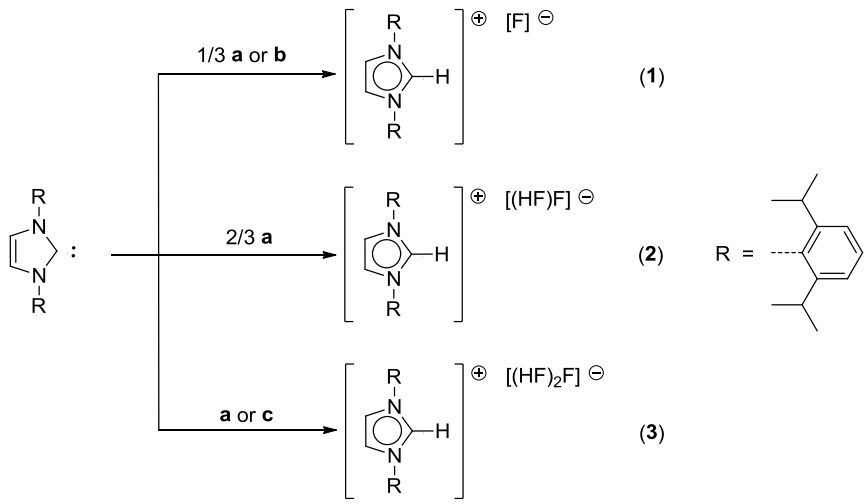
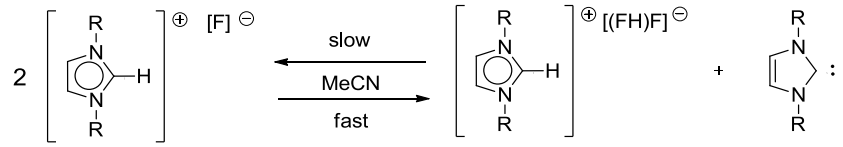


*Figure 3: Asymmetric unit (squared) and packing of structure $[(L^{Dipp})H]^+[(HF)_2F]^-$ (**3**). Ellipsoids are drawn with 50% probability.*



*Scheme 1: Synthesis of $[L(^{Dipp})H]^+[(HF)_nF]^-$ (n = 0−2) (**1**−**3** salts);*

***a**: $Et_3N{\cdot}3HF$ in MeCN or THF; **b**: KHF_2 in MeCN, **c**: aHF(reagent and solvent)*



*Scheme 2: Equilibrium in the acetonitrile solution of $[(L^{Dipp})H]^+[F]^-$ (**1**).*

*Table 1: X-ray data for compounds (**1**), (**2**) and (**3**)*

	(**1**)	(**2**)	(**3**)
CCDC ref. code	1488081	1488080	1488079
Formula	$C_{27}H_{37}N_2F{\cdot}C_2H_3N$	$C_{27}H_{37}N_2\ F_2H$ $\cdot 3(CHCl_3)$	$C_{27}H_{37}N_2{\cdot}F_3H_2$
FW [g/mol]	449.64	786.70	448.60
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/n$	$C2/c$
a [Å]	13.2812 (1)	9.6958 (2)	16.6130(2)
b [Å]	16.2775 (1)	36.5259(8)	9.0171(1)
c [Å]	13.6886 (1)	11.1478(3)	17.2328(2)
α [°]	90	90	90
β [°]	114.174 (1)	104.114(2)	90.866(1)
γ [°]	90	90	90
V [$Å^3$]	2699.76 (4)	3828.8(2)	2581.20(5)
Z	4	4	4
Crystal size [mm^3]	0.43 × 0.31 × 0.24	0.64 × 0.11 × 0.10	0.50 × 0.39 × 0.12
Temperature[K]	150	100	150
Θ range [°]	67.1−3.7	73.0−4.3	67.1−5.1
Reflections collected	24568	25470	13440
Independ. Reflect., R(int)	4821, 0.018	7495, 0.037	2308, 0.018
Completeness	1.000	0.996	0.999
Data/restraints/parameters	4821, 0, 307	7495, 0, 400	2308, 0, 158
Goodness-of-fit on F^2	1.03	1.02	1.06
Final R indices [I>2σ(I)]	R = 0.043	R =0.050	R = 0.043
	wR = 0.113	wR = 0.136	wR = 0.112
R indices (all data)	R = 0.045	R = 0.064	R = 0.044

*Table 2: Specified hydrogen bonds for (**1**), (**2**) and (**3**)*

	D–H	*H···A*	*D···A*	*<(DHA)*
			$[(L^{Dipp})H]^+[F]^-$ (**1**)	
C2–H2···F1	0.93	1.72	2.644(1)	176.9
C5–H5···F1_$1	0.93	1.97	2.867(1)	160.5
C21–H21···F1_$2	0.93	2.22	3.147(1)	170.9
C30–H30B···F1_$3	0.96	2.07	3.002(2)	164.4
			$[(L^{Dipp})H]^+[(HF)F]^-$ (**2**)	
C2–H2···F1	0.93	1.99	2.920(3)	176.0
C31–H31···F1	0.98	2.30	3.234(4)	159.0
C31–H31···F2	0.98	2.58	3.377(3)	138.9
C32–H32···F1	0.98	2.08	3.011(3)	157.2
C30–H30···F2	0.98	2.06	3.004(3)	160.8
F1–H1–F2	1.08	1.22	2.277(2)	164
			$[(L^{Dipp})H]^+[(HF)_2F]^-$ (**3**)	
C2–H2···F1A	0.93	1.98	2.91(2)	180.0
C2–H2···F1B	0.93	2.00	2.92(1)	168.0
C4–H4···F2	0.93	2.45	3.213(2)	138.9
C7–H7···F2	0.93	2.52	3.421(2)	162.9
F2–H1A···F1A	1.08	1.31	2.334(9)	154.5