Journal of Fluorine Chemistry 130 (2009) 1183–1191

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Electrochemical fluorination (Simons process) – A powerful tool for the preparation of new conducting salts, ionic liquids and strong Brønsted acids

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ARTICLE INFO

Article history:
Received 29 June 2009
Received in revised form 19 September 2009
Accepted 24 September 2009
Available online 30 September 2009

Keywords:
Electrochemical fluorination
Perfluoroalkyl-fluorophosphate
Ionic liquids
Conducting salts
Brønsted acids

ABSTRACT

Electrochemical fluorination (Simons process) provides a cheap commercial access to a series of tris(perfluoroalkyl)diflurophosphoranes. These substances are convenient starting material for the preparation of various fluoro-chemicals. The synthesis of new conducting salts and ionic liquids with perfluoroalkyl-fluorophosphate (FAP) and perfluoroalkyl-phosphinate anions is described. FAP ionic liquids exhibit excellent hydrolytic stability, low viscosity and high electrochemical and thermal stability. Organic and inorganic salts with FAP anions possess high electrochemical stability and conductivity that makes them attractive for application in several electrochemical devices (Li-ion batteries, super-capacitors, etc.). The possible application of $H[(R_F)_3PF_3]$ (HFAP), $(R_F)_2P(O)(OH)$ and $(R_F)P(O)(OH)_2$ as components of proton-conducting membranes is discussed.

1. Results and discussion

Electrochemical fluorination (ECF, Simons process) in anhydrous HF (aHF) was developed in the late 1930s at the Pensylvania State University by the American scientist Joseph Simons [1]. The fluorination of organic materials dissolved in aHF proceeds via a NiF_2/NiF_3 mediated mechanism which was proposed and proved recently [2,3]. Since its invention the Simons process is one of the favoured processes in the production of highly fluorinated materials [4]. For example, ECF of CH_3SO_2Cl is the key step in the production of triflic acid, CF_3SO_2OH [5]. Triflic acid is widely used as catalyst and starting material for the production of triflates, for instance alkyl triflates, CF_3SO_2OR. Methyl and ethyl triflate provide convenient access to ionic liquids (ILs) with triflate anion via direct alkylation of amines, phosphines or heterocyclic compounds. These very strong alkylating reagents can be easily prepared via new methods recently developed by Merck KGaA [6,7] (Scheme 1 and 2).

Method (**A**) (see Scheme 1) [6] provides a very convenient access to methyl triflate, which is produced in a very good yield with CO_2 as the only side product. The disadvantage in this method is the use of relatively expensive starting material: triflic acid anhydride. The production costs can be substantially reduced if triflic acid is used in combination with acyl or aryl chlorides, for instance with cheap benzoyl chloride, in this process (method **B**) [7] (Scheme 2).

Ethyl triflate can be easily separated from the reaction mixture via distillation, and the remaining ethyl benzoate is also a valuable product.

Alkyl triflates can also be used in solvent free metathesis reactions to eliminate chloride or bromide and synthesize highly unsymmetrical triflates ionic liquids with low halide content [8,9]. Scheme 3 presents an example:

Alkyl bis(perfluoroalkyl)phosphinates are slightly less reactive than alkyl triflates in this reaction (Scheme 4) [9,10].

Alkyl and aryl sulfonates, alkyl sulfates and alkyl phosphates can react with organic halides in the same way (Scheme 5) resulting in the formation of corresponding ionic liquids in quantitative or near to quantitative yield [8–11].

Anhydrides or silyl esters of triflic acid and trifluoroacetic acid or silyl ester of bis(perfluoroalkyl)phosphinic acid can be used in this type of reactions instead of alkyl triflates, alkylphosphinates or alkyl trifluoroacetates (Scheme 6) [8–10]. The products (ILs) are formed in quantitative or near to quantitative yield.

Oxonium and sulfonium salts are also active in such metathesis reactions (Scheme 7) forming the products in quantitative yield [12,13]:

The above described methodology offers the possibility to synthesize highly unsymmetrical ionic liquids with low content of halide. According to these methods the structures of cation and anion in ionic liquid can be built up independently.

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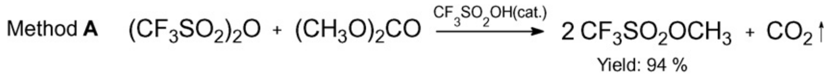
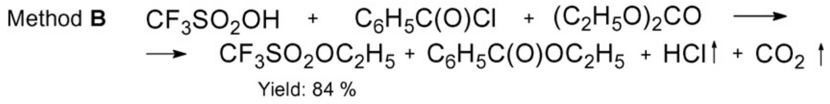
doi:10.1016/j.jfluchem.2009.09.016



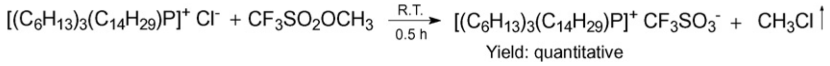
$$\text{Method A}\quad (CF_3SO_2)_2O + (CH_3O)_2CO \xrightarrow{CF_3SO_2OH(cat.)} 2\,CF_3SO_2OCH_3 + CO_2\uparrow$$

Scheme 1.



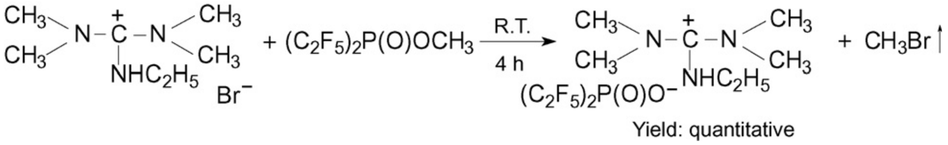
$$\text{Method B}\quad CF_3SO_2OH + C_6H_5C(O)Cl + (C_2H_5O)_2CO \longrightarrow CF_3SO_2OC_2H_5 + C_6H_5C(O)OC_2H_5 + HCl\uparrow + CO_2\uparrow$$

Scheme 2.



$$[(C_6H_{13})_3(C_{14}H_{29})P]^+\,Cl^- + CF_3SO_2OCH_3 \xrightarrow[0.5\,h]{R.T.} [(C_6H_{13})_3(C_{14}H_{29})P]^+\,CF_3SO_3^- + CH_3Cl\uparrow$$

Scheme 3.



Scheme 4.

Ionic liquids (ILs) possess very interesting properties that makes these new materials very attractive for practical applications. ILs based upon chloride or bromide anions are very viscous liquids or even solid material at room temperature. Ionic liquids based upon tetrafluoroborate BF_4^- and hexafluorophosphate PF_6^- anions are less viscous, but they are not very hydrolytically stable [14]. In particular, hexafluorophosphates are water sensitive. Trying both to decrease the viscosity and increase the hydrolytic stability, we have developed new ILs with tris(perfluoroalkyl)trifluorophosphate $[(R_F)_3PF_3]^-$ (FAP) anion.

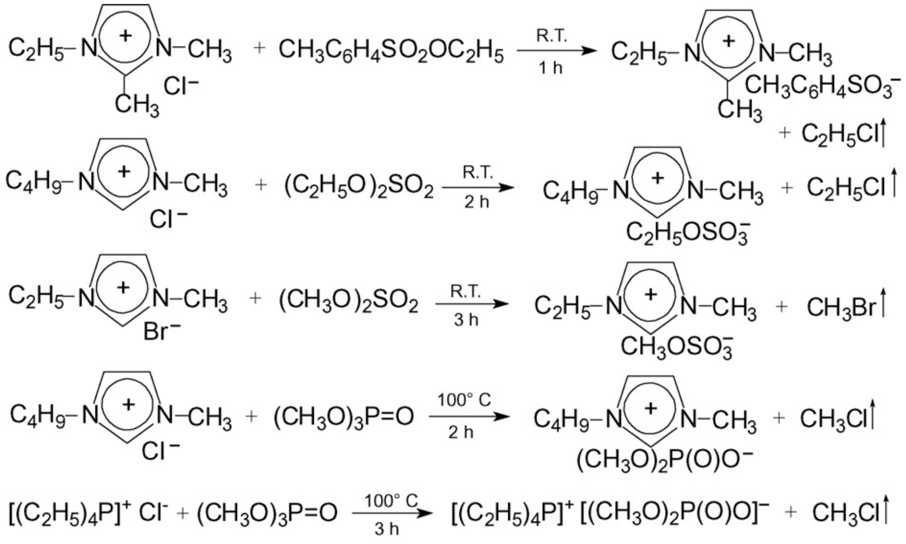
The key for these ILs is the electrochemical fluorination of trialkylphosphines, R_3P, that results in the formation of tris(perfluoroalkyl)difluorophosphoranes, $(R_F)_3PF_2$ [15,16] in a good yield. Tris(perfluoroalkyl)difluorophosphoranes are very reactive compounds and can be easily converted into several derivatives which are attractive for practical applications (Scheme 8).

Tris(perfluoroalkyl)difluorophosphoranes are strong Lewis acids which are able to abstract fluoride anion from BF_4^- or PF_6^- anions, for example (see Scheme 9) [13]:

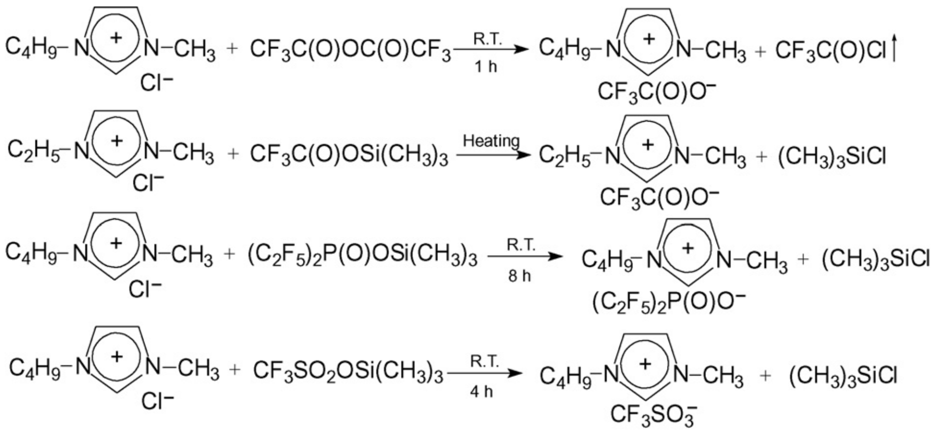
The high fluoride affinity of fluoroalkyl-fluorophosphoranes is known from the literature [17]. For, example, mono- and tris(perfluoroalkyl)difluorophosphoranes are readily react with NaF, KF or CsF [17,18]. We have used this reaction also to prepare lithium tris(pentafluoroethyl)trifluorophosphate, $Li[(C_2F_5)_3PF_3]$ (LiFAP) [19,20], that can be easily obtained via interaction of tris(pentafluoroethyl)difluorophosphorane with LiF in polar organic solvents or organic solvent mixtures (Scheme 10).

LiFAP is of interest for application in Li-ion batteries as new conducting salt to replace the hydrolytically unstable $LiPF_6$ [20].

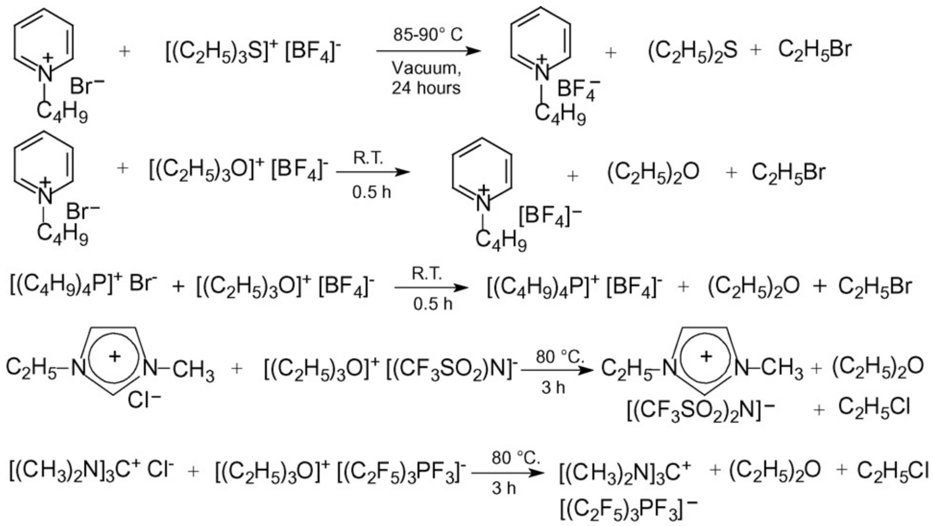
Tris(perfluoroalkyl)difluorophosphoranes are moisture sensitive compounds, but the fluoride affinity of these substances is so high that in contact with aqueous HF the hydrolysis is negligible;



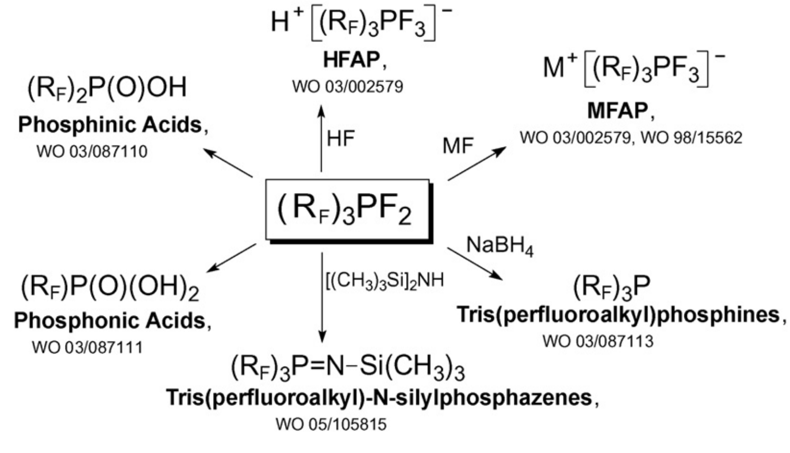
Scheme 5.



Scheme 6.



Scheme 7.

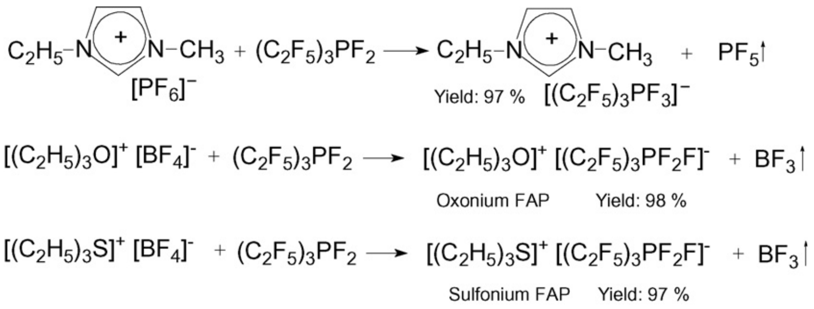


Scheme 8.

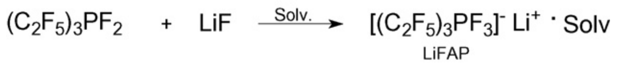
this interaction results in the addition of fluoride to phosphorus and formation, for example, of tris(pentafluoroethyl)trifluorophosphoric acid, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (HFAP) (Scheme 11) [21].

HFAP is formed as a mixture of two possible isomers: meridional (C_s symmetry) and facial (C_{3v} symmetry). ^{19}F NMR spectra show that the HFAP with meridional structure is preferably generated in this reaction. HFAP or alkali metal salts of this acid are convenient starting material for the synthesis of ILs with FAP anion (Scheme 12) [21,22].

FAP-based ILs possess high hydrolytic, thermal and electrochemical stability [22]. $(R_F)_3PF_2$ can be converted into tris(perfluoroalkyl)phosphine oxides, $(R_F)_3P{=}O$ [23] or hydrolyzed into

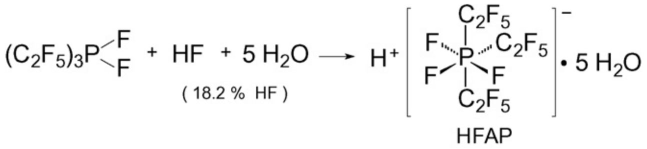


Scheme 9.



$$(C_2F_5)_3PF_2 + LiF \xrightarrow{Solv.} [(C_2F_5)_3PF_3]^- Li^+ \cdot Solv$$

Scheme 10.



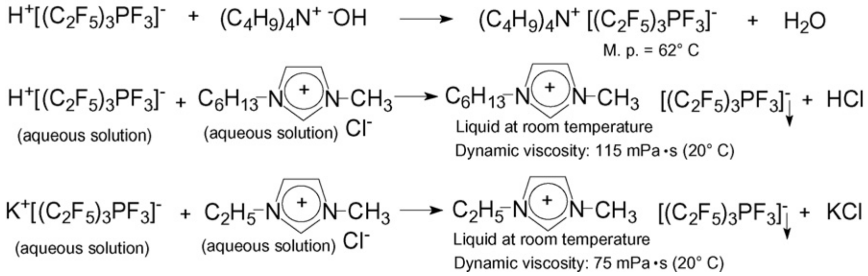
Scheme 11.

bis(perfluoroalkyl)phosphinic, $(R_F)_2P(O)OH$ and perfluoroalkylphosphonic acids, $R_FP(O)(OH)_2$ [24,25], or reduced to tris(perfluoroalkyl)phosphines, $(R_F)_3P$ [26]. $H[(R_F)_3PF_3]$, $(R_F)_2P(O)OH$ and $(R_F)P(O)(OH)_2$ are new strong Brønsted acids, which are of interest as components of proton-conducting membranes for fuel cells application [27,28].

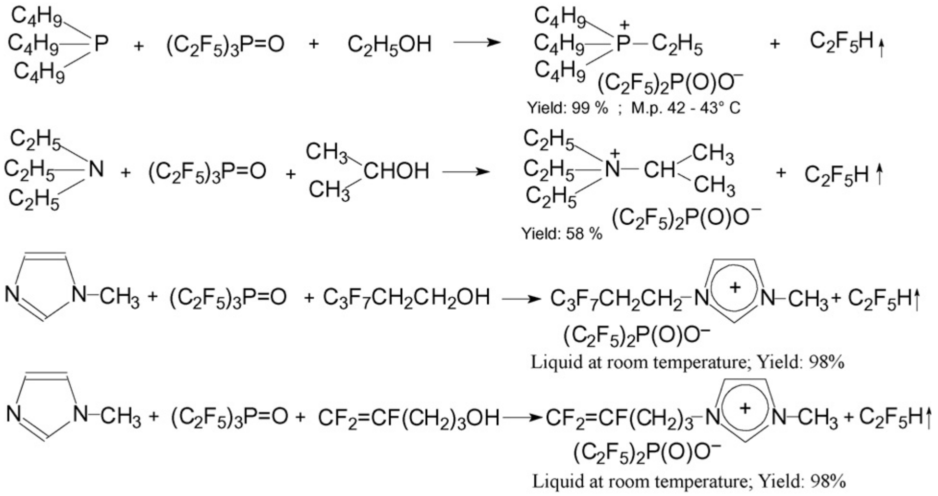
$(R_F)_3P{=}O$ give access to a new method for the alkylation of organic bases with alcohols resulting in quaternary salts with the bis(perfluoroalkyl)phosphinate anion (Scheme 14) [29]. This new reaction class results in the formation of hydrophilic (water soluble) ILs in good yield and the only side product in this process is C_2F_5H (F 125) which can be utilised for practical use. This process opens the door to the alkylation of organic compounds with alcohols – cheap and in many cases non-toxic source of alkyl groups (Scheme 13).

ILs based upon the bis(pentafluoroethyl)phosphinate anion can be easily converted into ILs with another anions, for example: $[(C_2F_5)_3PF_3]^-$, $[(CF_3SO_2)_2N]^-$, $[B(CN)_4]^-$ (Scheme 14) [29].

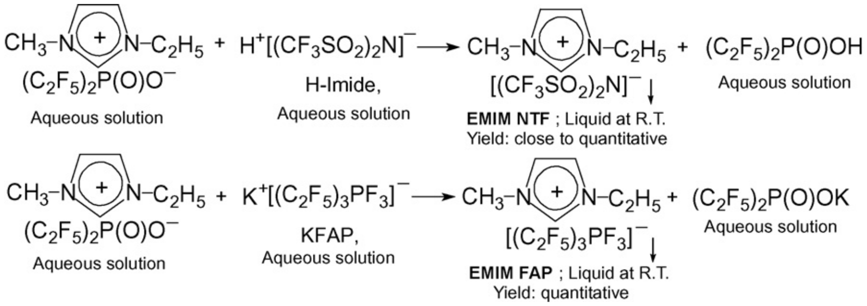
Treatment of bis(perfluoroalkyl)phosphinates or perfluoroalkylphosphonates with aHF leads to the formation of the corresponding bis(perfluoroalkyl)-tetrafluorophosphates or perfluoroalkyl-pentafluorophosphates (Scheme 15) [21].



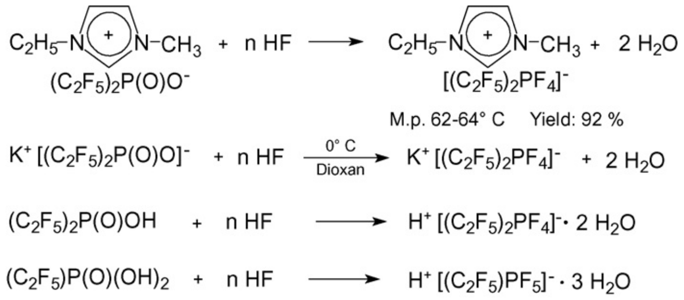
Scheme 12.



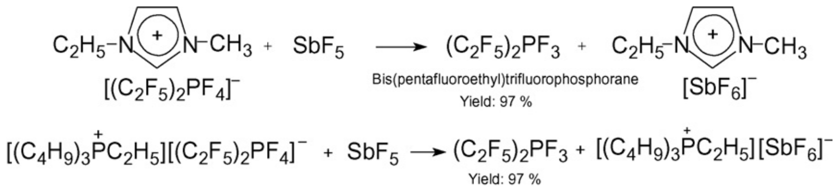
Scheme 13.



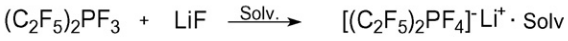
Scheme 14.



Scheme 15.



Scheme 16.



Scheme 17.

By abstraction of fluoride using SbF_5 or another strong Lewis acids, volatile bis(perfluoroalkyl)trifluorophosphoranes or perfluoroalkyltetrafluorophosphoranes and salts (ILs) with the SbF_6 anion are formed (Scheme 16) [30].

Bis(perfluoroalkyl)trifluorophosphoranes and perfluoroalkyltetrafluorophosphoranes are very reactive compounds and can be used in the same manner like tris(perfluoroalkyl)-difluorophosphoranes (see above), for instance in the synthesis of $Li[(C_2F_5)_2PF_4]$ (Scheme 17) [19].

This salt, dissolved in an organic solvent mixture of EC:DMC (1:1 w/w), shows very similar conductivity in comparison to the bench mark ($LiPF_6$ in the same solvents mixture), but has much better hydrolytic stability than $LiPF_6$. The hydrolysis rate is of about 1% (^{31}P NMR measurements) at room temperature within 48 h after addition 20% of water to the electrolyte shown below.

Electrolyte: 1 mol/l in EC:DMC (1:1, w/w)								
Temperature, °C:	−40	−20	−10	0	20	40	60	80
Conductivity, mS/cm								
Li[(C2F5)2PF4]	0.15	2.7	4.1	5.6	9.4	13.7	18.5	23.5
LiPF6		3.2	4.7	6.4	10.5	15.2	19.8	

It means, that two pentafluoroethyl-groups are enough to keep high hydrolytic stability and to enhance the conductivity in comparison to $Li[(C_2F_5)_3PF_3]$ (LiFAP) salt [20]. In contrast to LiFAP, $Li[(C_2F_5)_2PF_4]$ forms only one isomer, which nearly D_{4h} symmetry as confirmed by ^{31}P NMR and ^{19}F NMR measurements (see Fig. 1).

The symmetry of FAP-type anions has a strong influence on the melting point of the salts with these anions. For instance, 1-ethyl-3-methylimidazolium $[(C_2F_5)_3PF_3]$ (EMIM FAP) is a liquid at room temperature, but 1-ethyl-3-methylimidazolium $[(C_2F_5)_2PF_4]$ is a solid material at room temperature (m.p. = 62–64 °C), in spite of its reduced molecular weight. If we lower the symmetry of the $[(C_2F_5)_2PF_4]$ anion by removing one C_2F_5-group more to obtain C_{4v} symmetry, we yield a liquid at room temperature 1-ethyl-3-methylimidazolium $[(C_2F_5)_1PF_5]$ of low viscosity (see Fig. 2).

Recently we have described the influence of the coordination between the anion and cation on the viscosity of ILs [31]. The viscosity decreases dramatically if the IL consists of weekly coordinating anions, for instance FAP, and weekly coordinating cations, for example imidazolium cation [22]. The results above demonstrate not only the influence on the viscosity and melting point effected by the coordinating strength of the anion (all FAP-type anions are weekly coordinating anions), but also the influence of the bulkiness and symmetry of the anion.

ILs with FAP anions possess high electrochemical stability and good conductivity (see Fig. 3) that makes these new salts attractive for application in super-capacitors.

Tris(perfluoroalkyl)difluorophosphoranes are not only of interest as precursors for stable weekly coordination anions, but also to

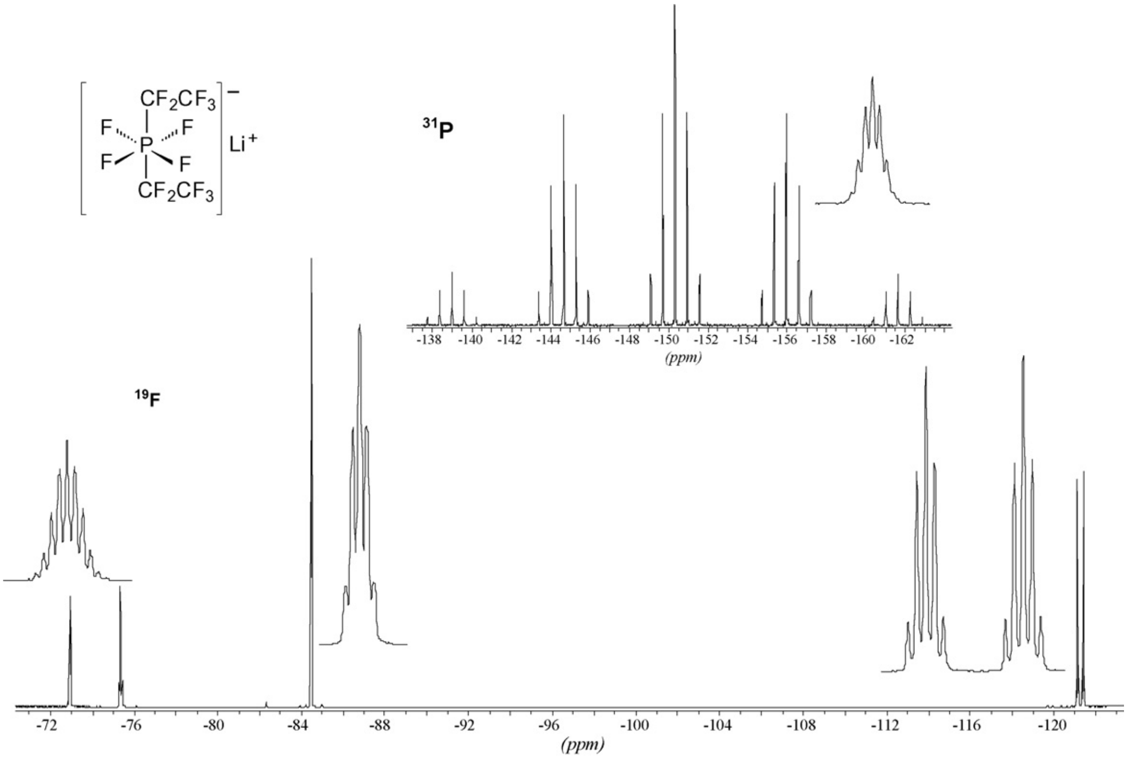
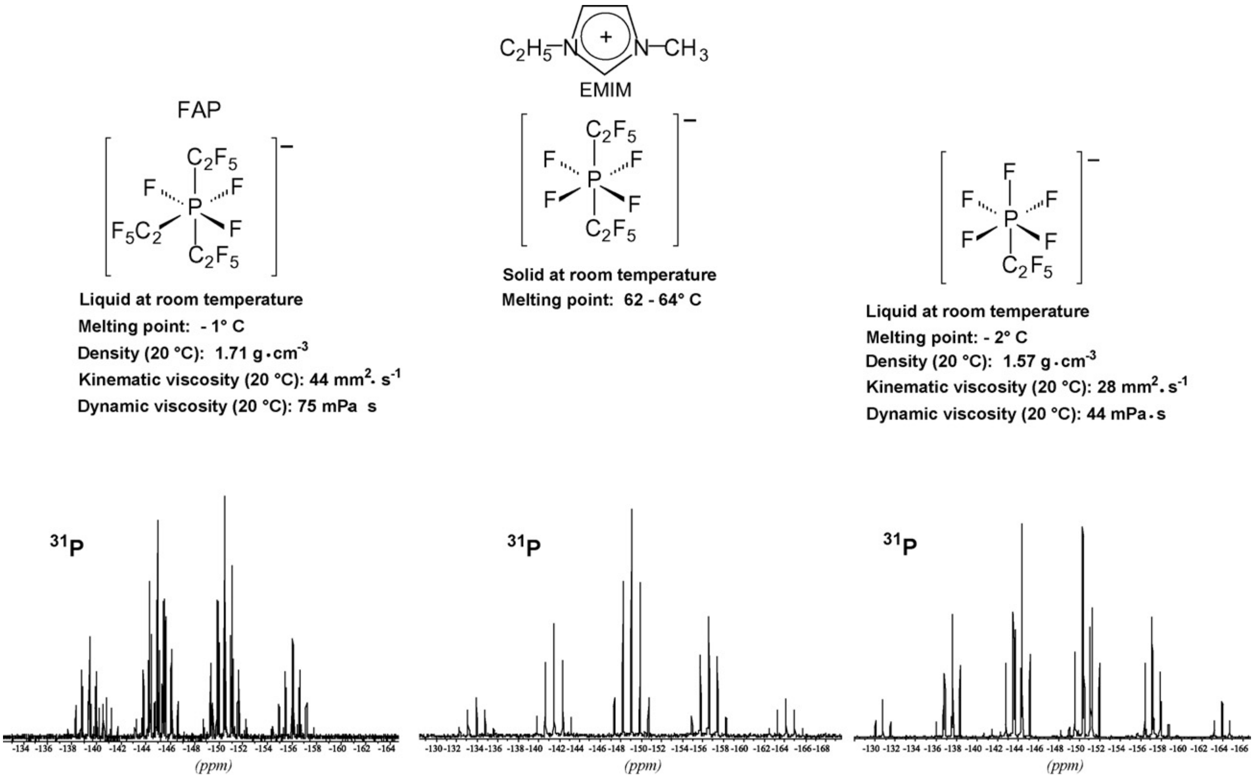


Fig. 1. Structure and 31P NMR spectra of Li[$(C_2F_5)_2PF_4$] in the mixture of the organic solvents EC:DMC.



Liquid at room temperature
Melting point: - 1° C
Density (20 °C): 1.71 g·cm^{-3}
Kinematic viscosity (20 °C): 44 mm^2· s^{-1}
Dynamic viscosity (20 °C): 75 mPa s

Solid at room temperature
Melting point: 62 - 64° C

Liquid at room temperature
Melting point: - 2° C
Density (20 °C): 1.57 g·cm^{-3}
Kinematic viscosity (20 °C): 28 mm^2· s^{-1}
Dynamic viscosity (20 °C): 44 mPa·s

Fig. 2. Structure, melting point, viscosity and ^{31}P NMR spectra of 1-ethyl-3-methylimidazolium ionic liquids with [$(C_2F_5)_3PF_3$], [$(C_2F_5)_2PF_4$] and [$(C_2F_5)_1PF_5$] anions.

produce fine fluoro-chemicals, for instance tris(perfluoroalkyl)-N-trimethylsilylphosphazenes $(R_F)_3P{=}N{-}Si(CH_3)_3$ (Scheme 18) [32].

$(R_F)_3P{=}N{-}Si(CH_3)_3$ can serve as transfer reagent for the perfluoroalkyl-group [32], similar to well known trimethyl(trifluoromethyl)silane, $(CH_3)_3SiCF_3$ (Scheme 19).

The mechanism of this new reaction is not studied yet. We suppose that fluoride anion can attack phosphorus (reversibly) or silicon (irreversibly) resulting in the formation of the reactive intermediate – tris(perfluoroalkyl)phosphanitrile-anion, $[(C_2F_5)_3P(N]^-$.

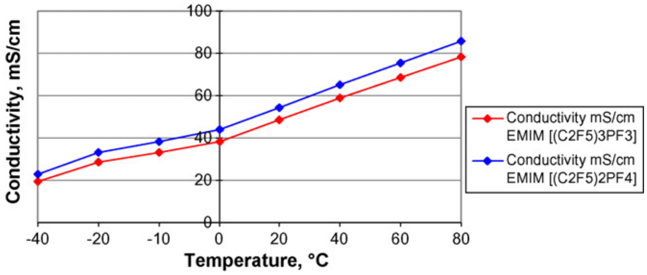
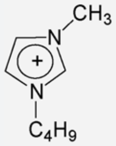


Fig. 3. Conductivity of EMIM $[(C_2F_5)_3PF_3]$ and EMIM $[(C_2F_5)_2PF_4]$ (1 M solution in CH_3CN).

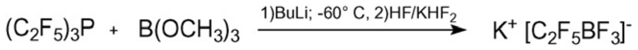
Table 1
Comparison of the thermal stability of 1-butyl-3-methyl imidazolium ionic liquids with $[(C_2F_5)BF_3]^-$ and $[(CF_3)BF_3]^-$ anions.

Ionic liquid		Conversion into $[BF_4]^-$, mol%	
Cation	Anion	150 °C, 1 h	150 °C, 5 h
	$[(CF_3)BF_3]^-$	1	60
	$[(C_2F_5)BF_3]^-$	0	0

Tris(perfluoroalkyl)phosphine oxides, $(R_F)_3P{=}O$, and tris(perfluoroalkyl)phosphines, $(R_F)_3P$ were also applied as alkylating reagents in the synthesis of perfluoroalkyl alcohols, for example $C_6H_5CH(OH)C_2F_5$, and perfluoroalkylborates (Scheme 20) [23,26].

$K[(C_2F_5)BF_3]$ is a convenient reagent in the synthesis of various salts (hydrophobic ILs) containing the $[(C_2F_5)BF_3]^-$ anion (Scheme 21) [32].

ILs with the $[(C_2F_5)BF_3]^-$ anion are much less viscous then ILs with $[BF_4]^-$ anion. Again, the low coordination ability of this anion plays an important role in reducing the viscosity of ionic liquids. ILs containing the $[(C_2F_5)BF_3]^-$ anion possess not only low viscosity but also high thermal stability, which is much better than that of ionic liquids with $[(CF_3)BF_3]^-$ anion (see Table 1).



Scheme 20.

The thermal instability of $[(CF_3)BF_3]^-$ anion is probably due to the ability to loose difluorocarbon CF_2 and to form the thermodynamically favoured $[BF_4]^-$ anion.

2. Experimental part

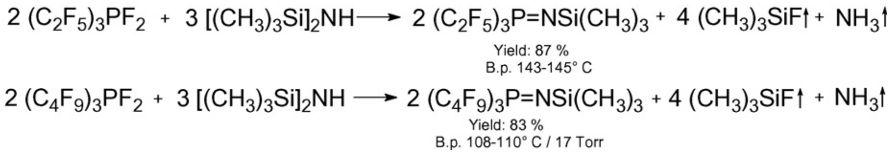
2.1. Chemicals

Tris(perfluoroalkyl)difluorophosphoranes were synthesized via electrochemical fluorination of trialkylphosphines in anhydrous HF (Simons process) as described in [15,16]. All other fluorochemicals (except fluorinated alcohols, HF, LiF, SbF_5, $[BF_4]$- and $[PF_6]$-salts, triflic acid and triflic acid anhydride) were prepared as described in the citations related to patents or patents applications referred below, owned by Merck KGaA.

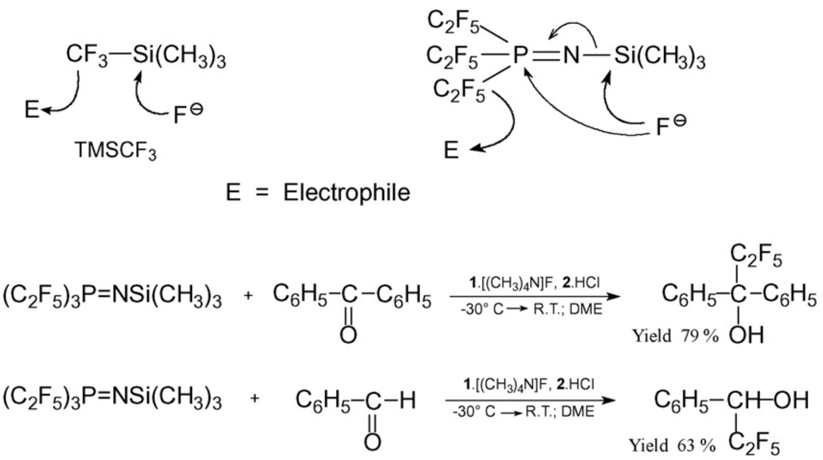
2.2. Analytical procedures

^1H, ^{19}F and ^{31}P NMR spectra were measured on a Brucker Avance III – 400 (400.17 MHz for ^1H, 376.536 MHz for ^{19}F and 161.992 MHz for ^{31}P). CCl_3F and TMS were used as references for ^{19}F NMR and the proton spectra correspondingly. For ^{31}P NMR spectra the external reference, 85% H_3PO_4 in D_2O, was used.

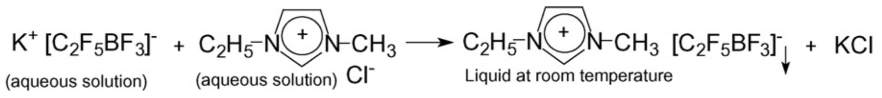
The purity (quality) of FAPs ionic liquids was controlled by measuring the residual water (Karl–Fischer titration; 831 KF-Coulometr, Metrohm) and halides (ion-chromatography, Metrohm Advanced IC System; stationary phase: Metrosep A



Scheme 18.



Scheme 19.



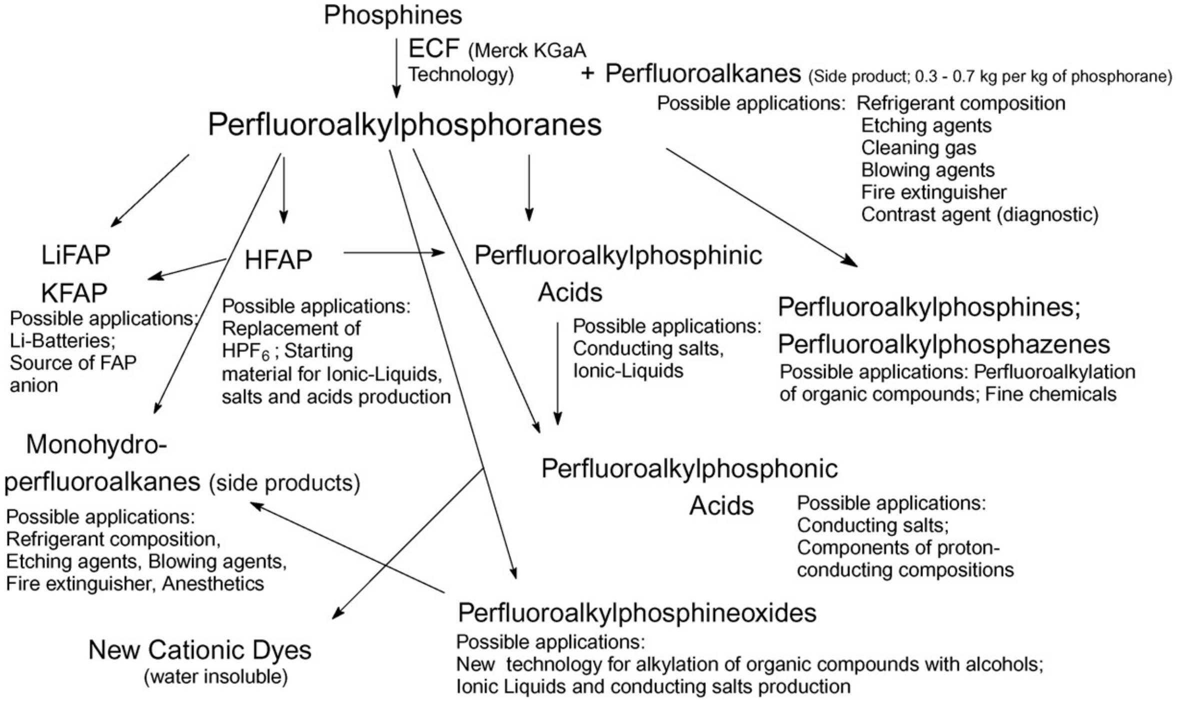
Scheme 21.

SUPP4 – 150). Contents of residual water and halides were below 50 ppm.

Viscosity and density of ionic liquids were measured on Viscosimeter SVM 3000 (Anton Paar). Conductivity was measured on Conductometer 703 (Knick); cyclic voltammograms were recorded for 0.5 M solutions in CH_3CN at glassy carbon (gc) working electrode using an Autolab PGSTAT 30 (Eco Chemie), a Pt auxiliary electrode and a Ag/$AgNO_3$ (CH_3CN) reference electrode.

3. Conclusion

FAP Chemistry – broad applications:



Acknowledgements

Authors thank Dr. P. Barthen (Heinrich-Heine University of Düsseldorf) and Dipl.-Chem. A. Wenda (Bergische University of Wuppertal) for the synthesis of the salts with $[(C_2F_5)_2PF_4]$ and $[(C_2F_5)PF_5]$ anions. Mrs. A. Amann (Merck KGaA) and Dr. Ja. Huebner (Bergische University of Wuppertal) for the analytic and measurements of viscosity and conductivity of ionic liquids and Li-salts.

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