

Ishikawa's Reagent – a Valuable Source for Fluoroorganic Iminium Salts

Mira Keßler,^[a] Beate Neumann,^[a] Hans-Georg Stammer,^[a] and Berthold Hoge^{*[a]}

Dedicated to Professor Thomas Klapötke on the Occasion of his 60th Birthday

Abstract. We herein report on iminium salts derived from Ishikawa's reagent $\text{Et}_2\text{N}-\text{CF}_2-\text{CHF}-\text{CF}_3$. The reaction with $\text{P}(\text{C}_2\text{F}_5)_3\text{F}_2$ afforded $[\text{Et}_2\text{N}=\text{CF}-\text{CHF}-\text{CF}_3][\text{P}(\text{C}_2\text{F}_5)_3\text{F}_3]$ as an ionic liquid. The fluorine atom in the cation in α position to the nitrogen atom is labile towards nucleophilic substitution as demonstrated by the reaction with SnCl_2 where an exchange of the fluorine by a chlorine atom took place. Upon contact with water the fluorine atom is substituted by a hydroxyl group. The reaction of Ishikawa's reagent with $\text{P}(\text{C}_2\text{F}_5)_2\text{F}$ afforded the

zwitterionic $[\text{P}(\text{C}_2\text{F}_5)_2\text{F}_3\{\text{C}(\text{NET}_2)(\text{CHF}-\text{CF}_3)\}]$. Most likely $[\text{Et}_2\text{N}=\text{CF}-\text{CHF}-\text{CF}_3][\text{P}(\text{C}_2\text{F}_5)_2\text{F}_2]$ was formed transiently. The anion is obviously sufficiently nucleophilic to attack the susceptible α -fluorine atom of the cation. During several months Ishikawa's reagent loses hydrogen fluoride, which reacts with glass producing SiF_4 which abstracts a fluoride ion from Ishikawa's reagent affording $[\text{Et}_2\text{N}=\text{CF}-\text{CHF}-\text{CF}_3][\text{SiF}_5]$.

Introduction

The application of dialkyl(fluoroalkyl)amines for preparation of fluoroacetamides through hydrolysis was first published in 1946.^[1] In the following years several dialkyl(fluoroalkyl)amines, such as 1,1,2,2-tetrafluoroethyl dimethylamine (TFEDMA),^[2,3] Yarovenko's^[2] and Ishikawa's reagent^[4,5] (Figure 1), were developed as fluorinating reagents.

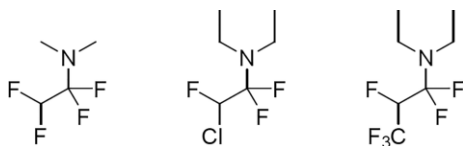
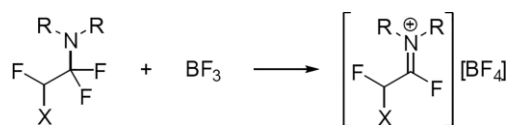


Figure 1. TFEDMA, Yarovenko's reagent, and Ishikawa's reagent from left to right.

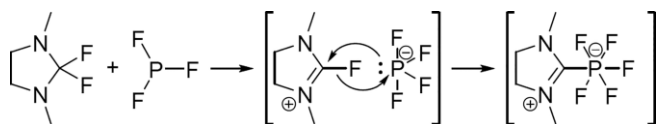
They are widely used in organic chemistry for deoxyfluorination, as illustrated by the conversion of carboxylic acids into acyl fluorides or of alcohols into alkyl or aryl fluorides.^[2,4] Their fluorinating abilities towards inorganic compounds are widely unexplored. Reactions with trifluoroborane yield iminium tetrafluoroborate salts (Scheme 1).^[6]



Scheme 1. Reaction of dialkyl(fluoroalkyl)amines with trifluoroborane (R = alkyl, X = Cl, CF_3 , F).

By treatment with a Lewis acid such as trifluoroborane an umpolung is achieved. While Ishikawa's reagent is a nucleophilic fluoride transfer reagent the corresponding iminium salts are used for an electrophilic transfer of the CHFX group, without being sufficiently characterized.^[6,7]

Moreover, similar fluorinating reagents such as cyclic and acyclic difluorobis(dialkylamino)methane served as precursors for carbene complexes of phosphorus(V) fluorides.^[8–10] The synthesis of these complexes is accomplished by the treatment of fluorophosphanes with the respective dialkylamine and involves transient phosphate(III) salts as illustrated in Scheme 2.



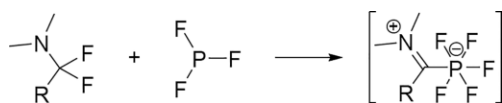
Scheme 2. Reaction of a cyclic difluorobis(dialkylamino)methane with trifluorophosphane.

Fluorinating agents of this type containing two amino groups allow a salt formation by effective delocalization of the positive charge of the cation. This results in a surprising stability of the zwitterionic phosphorus(V) compounds towards moisture and air. There are only a few examples for similar reactions of α,α -difluoroorganylamines containing only one amino group, as shown in Scheme 3.

* Prof. Dr. B. Hoge
E-Mail: b.hoge@uni-bielefeld.de

[a] Centrum für Molekulare Materialien
Fakultät für Chemie
Universität Bielefeld
Universitätsstraße 25
33615 Bielefeld, Germany

© 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.



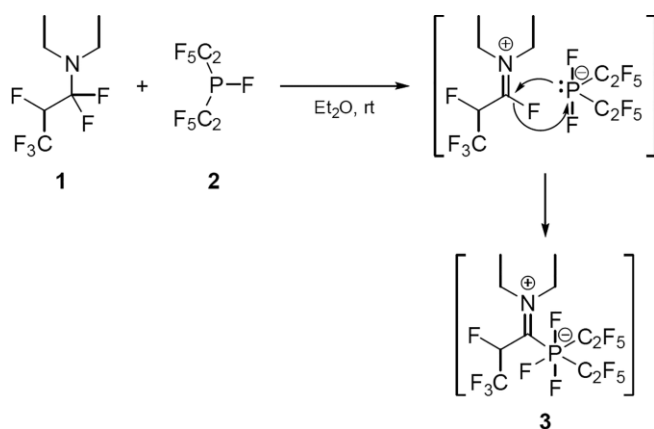
Scheme 3. Reaction of α,α -(difluoroorganyl)dimethylamines with triphosphorane (R = H, Ph, *t*Bu).^[11]

Contrary to stable bis(dialkylamino) derivatives the latter phosphorus(V) complexes decompose in solution.^[11]

The aim of this research was the isolation and characterization of iminium salts, both ionic and zwitterionic, generated from Ishikawa's reagent.

Results and Discussion

Reaction of Ishikawa's reagent (**1**) with fluorobis(pentafluoroethyl)phosphane (**2**) afforded the zwitterionic iminium phosphate **3**. Most likely, this transformation is initiated by a fluoride transfer onto the phosphorus center to give a transient iminium phosphate(III) which subsequently undergoes a formal insertion of the phosphorus atom into the C–F bond in α position to the nitrogen atom. The latter fulfills the formal requirements of an oxidative addition of the cation to the phosphate(III) ion (Scheme 4).



Scheme 4. Reaction of Ishikawa's reagent (**1**) with fluorophosphane **2** to yield iminium phosphate **3**.

Crystals of **3**, suitable for an X-ray diffraction study, were grown from dichloromethane. The compound crystallizes in the monoclinic space group $P2_1/n$. The molecular structure and selected bonding parameters are shown in Figure 2.

In accordance with structural characteristics of iminium salts the arrangement at the nitrogen atom is trigonal planar [sum of C–N–C angles: $360.0(2)^\circ$]. The bond length N1–C5 of 129.56(18) pm is in the typical range for C–N double bonds.^[12]

The observed bond length P1–C5 of 199.65(14) pm is relatively long in comparison to similar phosphorus(V) compounds (Figure 3). Compounds **C** and **D** are identical except for the substituent in *trans* position to the carbene ligand. The introduction of one pentafluoroethyl group instead of a fluorine atom, however, does not shorten the bond between the phosphorus atom and the carbene ligand significantly. The only

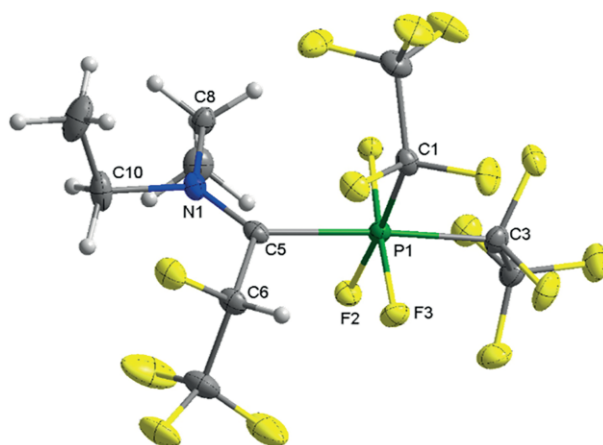


Figure 2. Molecular structure of $[P(C_2F_5)_2F_3\{C(NEt_2)(CHF-CF_3)\}]$ (**3**). Thermal ellipsoids are shown at 50% probability. Selected bond lengths /pm and angles $^\circ$: P1–F2 161.49(9), P1–F3 161.91(9), P1–C1 194.62(14), P1–C3 193.31(15), P1–C5 199.65(14), N1–C5 129.56(18), N1–C8 150.71(18), C5–C6 154.75(19), C5–N1–C8 126.14(12), C5–N1–C10 126.21(12), C8–N1–C10 107.61(11).

difference between **A** and **B** is the substituent in α position to the nitrogen atom. The P–C bond of compound **B**, featuring a bulky and electron donating *tert*-butyl group, is longer than the P–C bond of **A** featuring a hydrogen substituent. The P–C bond in **3** [199.65(14) pm] is significantly longer than in **B** [193.71(15) pm], which may indicate a weaker contact between the carbene ligand and the phosphorane fragment in **3**. It is conceivable that the electron withdrawing influence of the tetrafluoroethyl unit at C5 (Figure 2) decreases the basicity, whereas the electron donating *tert*-butyl group has the opposite effect.

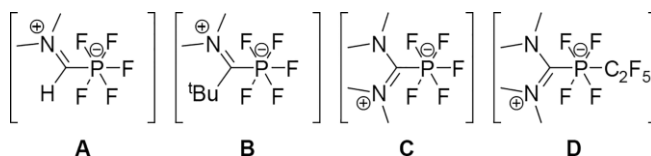
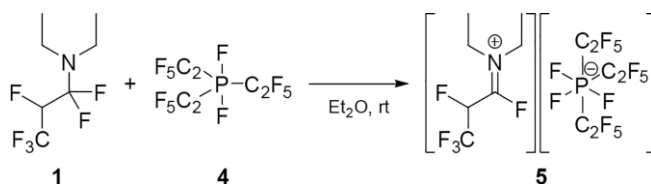


Figure 3. Zwitterionic phosphates similar to **3**. P–C bond length /pm to the formal carbene ligand: 186.27(12) (**A**),^[11] 193.71(15) (**B**),^[11] 192.49(12) (**C**),^[8] 191.6(2) (**D**).^[10] P–C bond length /pm to the pentafluoroethyl group: 191.9(2).^[10]

Upon reaction of Ishikawa's reagent with difluorotris(pentafluoroethyl)phosphane (**4**) diethyl(1,2,3,3,3-pentafluoropropyl)iminium trifluorotris(pentafluoroethyl)phosphate (**5**) was formed (Scheme 5).



Scheme 5. Reaction of Ishikawa's reagent (**1**) with phosphorane **4**.

The iminium phosphate **5** is liquid at room temperature and therefore an ionic liquid. Various trifluorotris(pentafluoroethyl)phosphate salts are already known to be ionic liquids.^[13]

An NMR spectroscopic investigation indicates that the anion was formed only in the meridional geometry. The resonances in the ^{19}F NMR spectrum are very similar to those of other trifluorotris(pentafluoroethyl)phosphate salts.^[14] The experimental and calculated resonance in the ^{31}P NMR spectrum is shown in Figure 4.

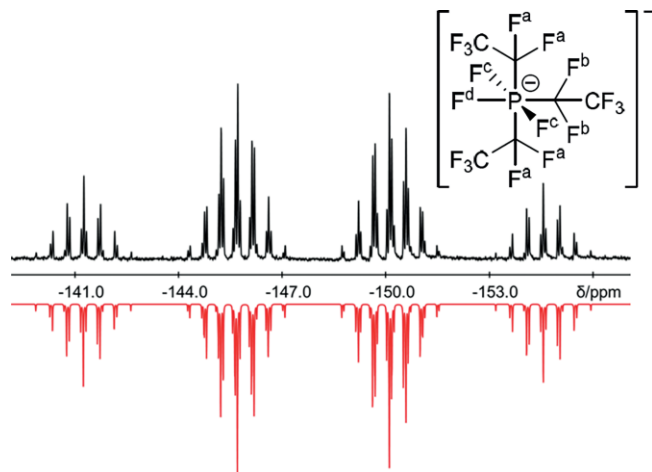
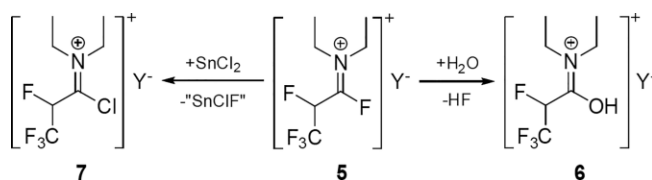


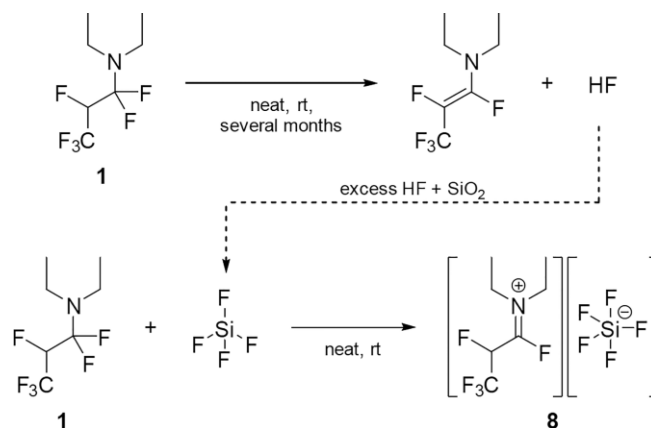
Figure 4. Section of the ^{31}P NMR spectrum of $[\text{Et}_2\text{N}=\text{CF}-\text{CHF}-\text{CF}_3][\text{P}(\text{C}_2\text{F}_5)_3\text{F}_3]$ (**5**). Experimental top, simulation^[15] bottom. $^2J(\text{F}^a, \text{P}) = 98$, $^2J(\text{F}^b, \text{P}) = 83$, $^1J(\text{F}^c, \text{P}) = 902$, $^1J(\text{F}^d, \text{P}) = 890$ Hz.

As indicated by the reaction of Ishikawa's reagent (**1**) with fluorobis(pentafluoroethyl)phosphane (**2**) the fluorine atom in α position to the nitrogen atom in the diethyl(1,2,3,3,3-pentafluoropropyl)iminium ion is prone to substitution. Thus iminium phosphate **5** readily hydrolyzes forming diethyl(2,3,3,3-tetrafluoro-1-hydroxypropyl)iminium trifluorotris(pentafluoroethyl)phosphate (**6**). Upon treatment of **5** with tin(II) chloride the α -fluorine atom is substituted by a chlorine atom yielding diethyl(1-chloro-2,3,3,3-tetrafluoropropyl)iminium trifluorotris(pentafluoroethyl)phosphate (**7**) (Scheme 6). Chloropropyliminium phosphate **7** also hydrolyzes forming **6**.



Scheme 6. Substitution of the α -fluorine atom in the diethyl(1,2,3,3,3-pentafluoropropyl)iminium ion. $\text{Y}^- = [\text{P}(\text{C}_2\text{F}_5)_3\text{F}_3]^-$.

Upon storing Ishikawa's reagent (**1**) in a glass flask for a few months a solid separated which was identified as diethyl(1,2,3,3,3-pentafluoropropyl)iminium pentafluorosilicate (**8**). This observation may be rationalized by slow elimination of hydrogen fluoride from **1**, which reacts with the glass, releasing tetrafluorosilane which finally abstracts a fluoride ion from **1** (Scheme 7). The resonances of the byproduct diethyl(1,2,3,3,3-pentafluoroprop-1-enyl)amine^[4] were observed in the ^{19}F NMR spectrum of the supernatant.



Scheme 7. Proposed formation of iminium silicate **8**.

Iminium silicate **8** sublimed at room temperature in high vacuum (10^{-3} mbar) forming colorless crystals in a receiver flask that was cooled to -196°C . It crystallizes in the monoclinic space group $P2_1/n$. The molecular structure and selected bonding parameters are shown in Figure 5.

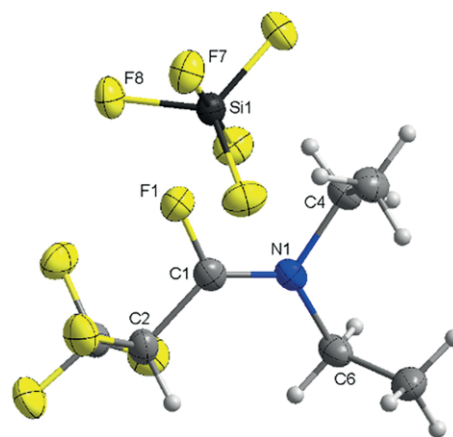


Figure 5. Molecular structure of $[\text{Et}_2\text{N}=\text{CF}-\text{CHF}-\text{CF}_3][\text{SiF}_5]$ (**8**). Thermal ellipsoids are shown at 50% probability. Selected bond lengths /pm and angles $^\circ$: Si1–F7 166.29(12), Si1–F8 160.99(12), N1–C1 127.2(3), N1–C4 150.2(2), C1–F1 130.1(2), C1–C2 151.4(3), C1–N1–C4 119.35(16), C1–N1–C6 123.30(16), C6–N1–C4 117.31(16).

The arrangement at the nitrogen atom is trigonal planar with the sum of C–N–C angles being $360.0(3)^\circ$.

Conclusions

Ishikawa's reagent (**1**) reacts with phosphanes and phosphoranes to afford iminium phosphate salts. The fluorine atom in α position to the nitrogen atom of the iminium ion $[\text{Et}_2\text{N}=\text{CF}-\text{CHF}-\text{CF}_3]^+$ is labile towards substitution. Thus the salt-like iminium phosphate(III) formed by the reaction of **1** with fluorobis(pentafluoroethyl)phosphane (**2**) undergoes a nucleophilic substitution leading to the formation of the zwitterionic iminium phosphate **3**. Diethyl(1,2,3,3,3-pentafluoropropyl)iminium trifluorotris(pentafluoroethyl)phosphate (**5**) was obtained by the treatment of difluorotris(pentafluoroethyl)phosphorane (**4**) with **1**. The iminium phosphate **5** is an

ionic liquid. Upon contact with water the α -fluorine atom is exchanged by a hydroxyl group. Treatment with tin(II) chloride led to the substitution by a chlorine atom. Upon storage at room temperature Ishikawa's reagent slowly liberates hydrogen fluoride, which attacks glass to form tetrafluorosilane, which reacts with **1** to furnish diethyl(1,2,3,3,3-pentafluoropropyl)iminium pentafluorosilicate (**8**). The solid-state structures of **3** and **8** show typical characteristics of iminium salts. The P–C bond of **3** between the phosphorus atom and the carbene ligand is relatively long which might be caused by the electron withdrawing character of the attached tetrafluoroethyl group.

Experimental Section

All chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed throughout all preparative procedures. Non-volatile compounds were handled in a dry N₂ atmosphere using Schlenk techniques. NMR spectra were recorded on a Bruker Model Avance III 500 HD (¹H 500.0 MHz; ¹³C 125.8 MHz; ¹⁹F 470.7 MHz; ³¹P 202.5 MHz). Positive shifts are downfield from the external standards Si(CH₃)₄ (¹H, ¹³C), CCl₃F (¹⁹F), H₃PO₄ (³¹P). The NMR spectra were recorded in the indicated deuterated solvent or in a non-deuterated solvent equipped with a capillary filled with acetone-D₆. ESI mass spectra were recorded using a ZQ2000 single quadrupole mass spectrometer (Waters, Manchester, UK) equipped with an ESI source (3.5 kV spray voltage). C, H, N analyses were performed with a HEKAtech Euro EA 3000 apparatus. The crystal data were collected on a Rigaku Super-

nova diffractometer using Mo-K α ($\lambda = 0.71073 \text{ \AA}$) or Cu-K α ($\lambda = 1.54184$) radiation. The crystals were kept at 100.0(1) K during data collection. Using Olex2,^[16] the structures were solved with the ShelXT^[17] structure solution program using Intrinsic Phasing and refined with the ShelXL^[18] refinement package using Least Squares minimization. Fluorobis(pentafluoroethyl)phosphane (**2**)^[19] was prepared as described in the literature. Ishikawa's reagent (**1**) was either obtained from a commercial source or prepared *in situ* after a modified literature procedure.^[4] Crystallographic data and structure refinement results for zwitterionic iminium phosphate **3** and iminium silicate **8** are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1998948 and CCDC-1998949 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthesis of Zwitterionic Iminium Phosphate 3: Diethylamine (560 mg, 6.70 mmol), hexafluoropropene (14 mmol) and ethyl ether (20 mL) were combined via condensation. Upon thawing the reaction mixture a colorless solid was initially formed which redissolved. Fluorobis(pentafluoroethyl)phosphane (1.30 g, 4.51 mmol) was added after 150 min via condensation whereby the solution turned yellow. After 90 min all volatile components were removed *in vacuo* to produce a yellow solid residue. It was dissolved in ethyl ether and an orange oil was precipitated with *n*-pentane. The supernatant was removed and the procedure was repeated three times with the residue. The solvent of the combined supernatants was evaporated. The obtained yellow solid was redissolved in ethyl ether and an orange oil was precipitated with

Table 1. Crystal data and refinement characteristics for zwitterionic iminium phosphate **3** and iminium silicate **8**.

	[P(C ₂ F ₅) ₂ F ₃ {C(NEt ₂)(CHF-CF ₃)}] (3)	[Et ₂ N=CF-CHF-CF ₃][SiF ₅] (8) ^{a)}
Empirical formula	C ₁₁ H ₁₁ F ₁₇ NP	C ₇ H ₁₁ F ₁₀ NSi
<i>M</i> /g·mol ⁻¹	511.18	327.26
<i>T</i> /K	100.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /pm	912.57(2)	651.040(10)
<i>b</i> /pm	1392.83(3)	1525.81(3)
<i>c</i> /pm	1391.03(3)	1255.71(2)
α /°	90	90
β /°	97.906(2)	100.6520(10)
γ /°	90	90
<i>V</i> /10 ⁶ ·pm ³	1751.27(7)	1225.88(4)
<i>Z</i>	4	4
ρ_{calcd} /g·cm ⁻³	1.939	1.773
μ /mm ⁻¹	0.329	2.858
<i>F</i> (000)	1008.0	656.0
Crystal size /mm ³	0.401 × 0.224 × 0.092	0.304 × 0.259 × 0.183
Radiation /Å	Mo-K α ($\lambda = 0.71073$)	Cu-K α ($\lambda = 1.54184$)
2 θ range for data collection /°	4.158 to 64.136	9.216 to 151.952
Index ranges	-13 ≤ <i>h</i> ≤ 12, -20 ≤ <i>k</i> ≤ 19, -20 ≤ <i>l</i> ≤ 20	-8 ≤ <i>h</i> ≤ 8, -18 ≤ <i>k</i> ≤ 19, -15 ≤ <i>l</i> ≤ 15
Total data collected	34053	43540
Unique data	5755 [R _{int} = 0.0407, R _{sigma} = 0.0321]	2550 [R _{int} = 0.0777, R _{sigma} = 0.0216]
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	4646	2351
Data / restraints / parameters	5755 / 0 / 315	2550 / 0 / 216
Goodness of fit on F ²	1.055	1.030
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0383 / 0.0811	0.0386 / 0.1047
<i>R</i> ₁ / <i>wR</i> ₂ [all data]	0.0530 / 0.0876	0.0411 / 0.1064
$\Delta\rho_{\text{max/min}}$ /e·Å ⁻³	0.48 / -0.36	0.63 / -0.32

a) Crystal was non-merohedrally twinned, ratio 79:21, component 2 rotated by 10.81° around [-0.01 -0.21 0.98] (reciprocal) or [0.31 -0.13 0.94] (direct). Both domains were taken into account for data reduction, only the main component for data refinement.

n-pentane. The solvent of the supernatant was evaporated and the last step was repeated once. Zwitterionic iminium phosphate **3** (1.37 g, 2.67 mmol, 59%) was obtained as a slightly yellow solid. Suitable crystals for an X-ray diffraction study were grown in dichloromethane at $-30\text{ }^{\circ}\text{C}$. Melting point: $40\text{--}48\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$ (CDCl_3 , 298 K): $\delta = 1.53$ [dd, $^3J(\text{H,H}) = ^3J(\text{H,H}) = 7\text{ Hz}$, 6 H, CH_3], 3.86 [dq, $^2J(\text{H,H}) = 13$, $^3J(\text{H,H}) = 7\text{ Hz}$, 1 H, NCH], 4.02 [dq, $^2J(\text{H,H}) = 13$, $^3J(\text{H,H}) = 7$, $^4J(\text{H,P}) = 5\text{ Hz}$, 1 H, NCH], 4.35 [ddq, $^2J(\text{H,H}) = 13$, $^3J(\text{H,H}) = 4J(\text{H,P}) = 7\text{ Hz}$, 1 H, NCH], 4.81 [ddq, $^2J(\text{H,H}) = 13$, $^3J(\text{H,H}) = 4J(\text{H,P}) = 7\text{ Hz}$, 1 H, NCH], 6.56 [d (broad), $^2J(\text{H,F}) = 47\text{ Hz}$, 1 H, CFH] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): $\delta = 14.1$ (s, 1 C, CH_3), 14.9 [d, $^4J(\text{C,P}) = 5\text{ Hz}$, 1 C, CH_3], 56.9 [d, $^3J(\text{C,P}) = 25\text{ Hz}$, 1 C, CH_2], 57.9 [dd, $^3J(\text{C,P}) = 4J(\text{C,F}) = 9\text{ Hz}$, 1 C, CH_2], 88.0 [dm, $^1J(\text{C,F}) \approx 200\text{ Hz}$, 1 C, CFH], 119.6 [m (overlap), 2 C, PCCF_3], 120.8 [qdd (overlap), $^1J(\text{C,F}) = 287$, $^2J(\text{C,F}) = 25$, $^3J(\text{C,P}) = 3\text{ Hz}$, 1 C, CHCF_3], 197.5 (m, 1 C, NCP) ppm. Note: CF_2 signal not observed. $^{19}\text{F NMR}$ (CDCl_3 , 298 K): $\delta = -190.1$ [d (broad), $^2J(\text{H,F}) = 47\text{ Hz}$, 1 F, CFH], -118.8 [dm, $^2J(\text{F,P}) = 105\text{ Hz}$, 2 F, CF_2], -111.8 / -110.6 [AB spin system, $^2J(\text{F,F}) = 315$, $^2J(\text{F,P}) = 99$ / 89 Hz , 2 F, CF_2], -82.6 (m, 3 F, CF_2CF_3), -80.1 (m, 3 F, CF_2CF_3), -75.3 [ddd (broad), $^1J(\text{F,P}) = 926$, $^2J(\text{F,F}) \approx 55$ / 55 Hz , 1 F, PF], -69.8 [ddd (broad), $^1J(\text{F,P}) = 935$, $^2J(\text{F,F}) \approx 55$ / 55 Hz , 1 F, PF], -68.3 (m, 3 F, CHCF_3), -36.5 [ddd (broad), $^1J(\text{F,P}) = 907$, $^2J(\text{F,F}) \approx 55$ / 55 Hz , 1 F, PF] ppm. $^{31}\text{P NMR}$ (CDCl_3 , 298 K): $\delta = -145.0$ (m, 1 P, P) ppm. $\text{C}_{11}\text{H}_{11}\text{F}_{17}\text{NP}$: C 26.53 (calcd. 25.85), H 2.45 (calcd. 2.17), N 2.92% (calcd. 2.74%). Note: the relatively high carbon value is reproducible upon reanalysis.

Synthesis of Diethyl(1,2,3,3,3-pentafluoropropyl)iminium trifluoro-tris(pentafluoroethyl)phosphate (5): Diethylamine (490 mg, 6.70 mmol), hexafluoropropene (10 mmol) and ethyl ether (20 mL) were combined via condensation. After thawing of the reaction mixture a colorless solid was formed which redissolved. Difluoro-tris(pentafluoroethyl)phosphorane (1.42 g, 3.34 mmol) was added after 1 h via condensation. After thawing the solution immediately turned yellow. All volatile compounds were removed under reduced pressure after 1 h and iminium phosphate **5** (2.01 g, 3.10 mmol, 93%) was obtained as a yellow liquid. $^1\text{H NMR}$ (CDCl_3 , 298 K): $\delta = 1.41$ [t, $^3J(\text{H,H}) = 7\text{ Hz}$, 3 H, CH_3], 1.43 [t, $^3J(\text{H,H}) = 7\text{ Hz}$, 3 H, CH_3], 4.01 (m, 4 H, CH_2), 6.0 [d (broad), $^2J(\text{H,F}) = 43\text{ Hz}$, 1 H, CFH] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): $\delta = 11.2$ (s, 1 C, CH_3), 11.4 (s, 1 C, CH_3), 50.9 [dd, $^3J(\text{C,F}) = 4J(\text{C,F}) = 6\text{ Hz}$, 1 C, CH_2], 51.5 [d, $^3J(\text{C,F}) = 5\text{ Hz}$, 1 C, CH_2], 82.4 [ddq, $^1J(\text{C,F}) = 210$, $^2J(\text{C,F}) = 30$ / 40 Hz , 1 C, CHF], 118.6 [qd (overlap with anion), $^1J(\text{C,F}) = 284$, $^2J(\text{C,F}) = 25\text{ Hz}$, 1 C, CHCF_3], 119.9 [m (overlap with cation), 3 C, CF_2CF_3], 163.4 [dd, $^1J(\text{C,F}) = 329$, $^2J(\text{C,F}) = 24\text{ Hz}$, 1 C, NCF] ppm. Note: CF_2 signal not observed. $^{19}\text{F NMR}$ (CDCl_3 , 298 K): $\delta = -206.2$ [ddq, $^2J(\text{H,F}) = 43$, $^3J(\text{F,F}) = 20$, $^3J(\text{F,F}) = 13\text{ Hz}$, 1 F, NCCF], -116.9 [dm, $^2J(\text{F,P}) = 98\text{ Hz}$, 4 F, PCF_2], -88.3 [dm, $^1J(\text{F,P}) = 902\text{ Hz}$, 2 F, PF], -82.6 (m, 6 F, PCCF_3), -80.9 (m, 3 F, PCCF_3), -74.9 [ddd, $^3J(\text{F,F}) = 13$, $^3J(\text{H,F}) = 6$, $^4J(\text{F,P}) = 6\text{ Hz}$, 3 F, NCCCF₃], -44.9 [dm, $^1J(\text{F,P}) = 890\text{ Hz}$, 1 F, PF], -29.8 (m, 1 F, NCF) ppm. $^{31}\text{P NMR}$ (CDCl_3 , 298 K): $\delta = -147.8$ [dtquint, $^1J(\text{F,P}) = 890$ / 902 , $^2J(\text{F,P}) = 98$ / 83 Hz , 1 P, P] ppm. $\text{C}_{13}\text{H}_{11}\text{F}_{23}\text{NP}$: C 24.54 (calcd. 24.05), H 1.94 (calcd. 1.71), N 2.52% (calcd. 2.16%). **MS** (ESI, neg) $m/z = 444.8$ ($[\text{P}(\text{C}_2\text{F}_5)_3\text{F}_3]^-$, 100%). **MS** (ESI, pos) $m/z = 202.0$ ($[\text{NEt}_2(\text{C}_3\text{H}_2\text{F}_4\text{O})]^+$, 100%), 204.1 ($[\text{NEt}_2(\text{C}_3\text{HF}_5)]^+$, <1%).

Hydrolysis of Iminium Phosphate 5 – Generation of Diethyl(2,3,3,3-tetrafluoro-1-hydroxypropyl)iminium trifluoro-tris(pentafluoroethyl)phosphate (6): An NMR tube with a solution of **5** in acetonitrile- D_3 was mixed with a drop of water and investigated by NMR spectroscopy immediately. Diethyl(2,3,3,3-tetrafluoro-1-hydroxypropyl)iminium trifluoro-tris(pentafluoroethyl)phosphate (**6**) was

formed. $^1\text{H NMR}$ (CD_3CN , 298 K): $\delta = 1.13$ [t, $^3J(\text{H,H}) = 7\text{ Hz}$, 3 H, CH_3], 1.20 [t, $^3J(\text{H,H}) = 7\text{ Hz}$, 3 H, CH_3], 3.44 (m, 4 H, CH_2), 5.82 [dq, $^2J(\text{H,F}) = 45$, $^3J(\text{H,F}) = 6\text{ Hz}$, 1 H, CFH] ppm. Note: OH signal not observed presumably due to overlap with H_2O signal. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): $\delta = 12.3$ (s, 1 C, CH_3), 13.4 (s, 1 C, CH_3), 43.5 [s (broad), 1 C, CH_2], 44.5 [s (broad), 1 C, CH_2], 83.5 [dq, $^1J(\text{C,F}) = 191$, $^2J(\text{C,F}) = 34\text{ Hz}$, 1 C, CHF], 118–124 [m (overlap of cation, anion and solvent), 4 C, CF_3], 162.4 [d, $^2J(\text{C,F}) = 23\text{ Hz}$, 1 C, NCOH] ppm. Note: CF_2 signal not observed. $^{19}\text{F NMR}$ (CD_3CN , 298 K): $\delta = -202.6$ [dq, $^2J(\text{H,F}) = 45$, $^3J(\text{F,F}) = 13\text{ Hz}$, 1 F, NCCF], -116.9 [dm, $^2J(\text{F,P}) = 98\text{ Hz}$, 4 F, PCF_2], -116.4 [dm, $^2J(\text{F,P}) = 83\text{ Hz}$, 2 F, PCF_2], -88.3 [dm, $^1J(\text{F,P}) = 902\text{ Hz}$, 2 F, PF], -82.6 (m, 6 F, PCCF_3), -80.9 (m, 3 F, PCCF_3), -76.4 [dd, $^3J(\text{F,F}) = 13$, $^3J(\text{H,F}) = 6\text{ Hz}$, 3 F, NCCCF₃], -44.9 [dm, $^1J(\text{F,P}) = 890\text{ Hz}$, 1 F, PF] ppm. $^{31}\text{P NMR}$ (CD_3CN , 298 K): $\delta = -147.9$ [dtquint, $^1J(\text{F,P}) = 890$ / 902 , $^2J(\text{F,P}) = 98$ / 83 Hz , 1 P, P] ppm. **MS** (ESI, neg) $m/z = 444.9$ ($[\text{P}(\text{C}_2\text{F}_5)_3\text{F}_3]^-$, 100%). **MS** (ESI, pos) $m/z = 202.1$ ($[\text{NEt}_2(\text{C}_3\text{H}_2\text{F}_4\text{O})]^+$, 100%).

Reaction of Iminium Phosphate 5 with Tin(II) Chloride – Generation of Diethyl(1-chloro-2,3,3,3-tetrafluoropropyl)iminium trifluoro-tris(pentafluoroethyl)phosphate (7): Iminium phosphate **5** was added to a suspension of an excess of tin(II) chloride in acetonitrile in an NMR tube. After heating to $80\text{ }^{\circ}\text{C}$ for 1 h the suspension was investigated via NMR spectroscopy. Diethyl(1-chloro-2,3,3,3-tetrafluoropropyl)iminium trifluoro-tris(pentafluoroethyl)phosphate (**7**) and hydrolysis product **6** were detected. $^1\text{H NMR}$ (CD_3CN , 298 K): $\delta = 1.48$ (m, 6 H, CH_3), 4.22 (m, 4 H, CH_2), 6.59 [dq, $^2J(\text{H,F}) = 42$, $^3J(\text{H,F}) = 5\text{ Hz}$, 1 H, CFH] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): $\delta = 11.5$ (s, 1 C, CH_3), 12.5 (s, 1 C, CH_3), 56.8 (s, 1 C, CH_2), 57.5 (s, 1 C, CH_2), 84.9 [dq, $^1J(\text{C,F}) = 204$, $^2J(\text{C,F}) = 37\text{ Hz}$, 1 C, CHF], 118–124 [m (overlap of cation, anion, solvent and **6**), 4 C, CF_3], 168.6 [m (low intensity), 1 C, NCCI] ppm. Note: CF_2 signal not observed. $^{19}\text{F NMR}$ (CD_3CN , 298 K): $\delta = -190.8$ [dq, $^2J(\text{H,F}) = 42$, $^3J(\text{F,F}) = 14\text{ Hz}$, 1 F, NCCF], -116.9 [dm, $^2J(\text{F,P}) = 98\text{ Hz}$, 4 F, PCF_2], -116.3 [dm, $^2J(\text{F,P}) = 83\text{ Hz}$, 2 F, PCF_2], -88.3 [dm, $^1J(\text{F,P}) = 902\text{ Hz}$, 2 F, PF], -82.6 (m, 6 F, PCCF_3), -80.9 (m, 3 F, PCCF_3), -74.5 [dd, $^3J(\text{F,F}) = 14$, $^3J(\text{H,F}) = 5\text{ Hz}$, 3 F, NCCCF₃], -44.8 [dm, $^1J(\text{F,P}) = 890\text{ Hz}$, 1 F, PF] ppm. $^{31}\text{P NMR}$ (CD_3CN , 298 K): $\delta = -147.9$ [dtquint, $^1J(\text{F,P}) = 890$ / 902 , $^2J(\text{F,P}) = 98$ / 83 Hz , 1 P, P] ppm. **MS** (ESI, neg) $m/z = 444.9$ ($[\text{P}(\text{C}_2\text{F}_5)_3\text{F}_3]^-$, 100%). **MS** (ESI, pos) $m/z = 202.2$ ($[\text{NEt}_2(\text{C}_3\text{H}_2\text{F}_4\text{O})]^+$, 93%), 220.1 ($[\text{NEt}_2(\text{C}_3\text{HClF}_4)]^+$, 100%).

Diethyl(1,2,3,3,3-pentafluoropropyl)iminium pentafluorosilicate (8): Ishikawa's reagent (**1**) was stored under an atmosphere of nitrogen for 10 months in a glass flask. During this time the once colorless liquid turned orange and a solid precipitated. During condensation in high vacuum (10^{-3} mbar) colorless crystals were formed in the cooled condenser ($-196\text{ }^{\circ}\text{C}$). After thawing the colorless supernatant was removed and the obtained crystals of **8** were suitable for an X-ray diffraction study. The supernatant was a mixture of diethyl(1,2,3,3,3-pentafluoroprop-1-enyl)amine and Ishikawa's reagent. Note: Because of the small amount of obtained **8** and the long reaction time no suitable NMR spectroscopic data was collected.

Acknowledgements

We thank Prof. Lothar Weber and Dr. Julia Bader for helpful discussions. Merck KGaA (Darmstadt, Germany) is gratefully acknowledged for the donation of chemicals. We acknowledge the support by the Deutsche Forschungsgemeinschaft (Core Facility GED@BI, Mi477/21–1). Open access funding enabled and organized by Projekt DEAL.

Keywords: Ishikawa's reagent; Iminium phosphate; Iminium silicate; Fluorination; Ionic liquids

References

- [1] G. W. Rigby, H. E. Schroeder, US2409315A **1946**.
- [2] N. N. Yarovenko, M. A. Raksha, *Zh. Obshch. Khim.* **1959**, *29*, 2159–2163.
- [3] V. A. Petrov, S. Swearingen, W. Hong, W. C. Petersen, *J. Fluorine Chem.* **2001**, *109*, 25–31.
- [4] A. Takaoka, H. Iwakiri, N. Ishikawa, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3377–3380.
- [5] D. C. England, L. R. Melby, M. A. Dietrich, R. V. Lindsey, *J. Am. Chem. Soc.* **1960**, *82*, 5116–5122.
- [6] C. Wakselman, M. Tordeux, *J. Chem. Soc., Chem. Commun.* **1975**, 956.
- [7] a) F. Giornal, S. Pazenok, L. Rodefeld, N. Lui, J.-P. Vors, F. R. Leroux, *J. Fluorine Chem.* **2013**, *152*, 2–11; b) F. Aribi, E. Schmitt, A. Panossian, J.-P. Vors, S. Pazenok, F. R. Leroux, *Org. Chem. Front.* **2016**, *3*, 1392–1415; c) E. Schmitt, A. Panossian, J.-P. Vors, C. Funke, N. Lui, S. Pazenok, F. R. Leroux, *Chem. Eur. J.* **2016**, *22*, 11239–11244; d) E. Schmitt, G. Landelle, J.-P. Vors, N. Lui, S. Pazenok, F. R. Leroux, *Eur. J. Org. Chem.* **2015**, 6052–6060; e) E. Schmitt, B. Rugeri, A. Panossian, J.-P. Vors, S. Pazenok, F. R. Leroux, *Org. Lett.* **2015**, *17*, 4510–4513.
- [8] T. Böttcher, O. Shyshkov, M. Bremer, B. S. Bassil, G.-V. Rösenthaller, *Organometallics* **2012**, *31*, 1278–1280.
- [9] a) R. Pajkert, T. Böttcher, M. Ponomarenko, M. Bremer, G.-V. Rösenthaller, *Tetrahedron* **2013**, *69*, 8943–8951; b) T. Böttcher, G.-V. Rösenthaller, *J. Fluorine Chem.* **2015**, *171*, 4–11.
- [10] T. Böttcher, S. Steinhauer, N. Allefeld, B. Hoge, B. Neumann, H. G. Stämmler, B. S. Bassil, M. Winter, N. W. Mitzel, G.-V. Rösenthaller, *Dalton Trans.* **2014**, *43*, 2979–2987.
- [11] T. Böttcher, B. S. Bassil, L. Zhechkov, G.-V. Rösenthaller, *Inorg. Chem.* **2013**, *52*, 5651–5653.
- [12] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, 1–19.
- [13] a) C. C. Cassol, G. Ebeling, B. Ferrera, J. Dupont, *Adv. Synth. Catal.* **2006**, *348*, 243–248; b) O. Schneider, A. Bund, A. Ispas, N. Borissenko, S. Zein El Abedin, F. Endres, *J. Phys. Chem. B* **2005**, *109*, 7159–7168; c) T. Kishi, T. Kuboki, H. Saruwatari, N. Takami, US 20060068282 **2006**.
- [14] N. Ignatyev, M. Schmidt, A. Kühner, V. Hilarius, U. Heider, A. Kucheryna, P. Sartori, H. Willner, WO2003002579A1 **2003**.
- [15] P. H. M. Budzelaar, *gNMR*, IvorySoft **2006**.
- [16] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [17] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015**, *71*, 3–8.
- [18] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.
- [19] A. V. Zakharov, Y. V. Vishnevskiy, N. Allefeld, J. Bader, B. Korscheid, S. Steinhauer, B. Hoge, B. Neumann, H.-G. Stämmler, R. J. F. Berger, N. W. Mitzel, *Eur. J. Inorg. Chem.* **2013**, 3392–3404.

Received: May 5, 2020

Published Online: July 17, 2020