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Hydridophosphates | *Very Important Paper* |

VIP

Synthesis of Stable Salts Containing the Hydridophosphate Anion $[P(C_2F_5)_3F_2H]^-$

Julia Bader,[a] Nikolai Ignat'ev,[b] and Berthold Hoge*[a]

Abstract: The reaction of the industrial product $(C_2F_5)_3PF_2$ with $LiAlH_4$ in THF solution selectively furnished the hydridophosphate anion $[P(C_2F_5)_3F_2H]^-$. The compound $[PPh_4][P(C_2F_5)_3F_2H]$ is obtained as a colorless solid on a multigram scale by salt metathesis in aqueous THF. Combining $[P(C_2F_5)_3F_2H]^-$ with various imidazolium and pyridinium cations affords ionic liquids with melting points well below room temperature. $(C_2F_5)_3PF_2$ also abstracts hydrides from amines, affording the hydridophosphate anion $[P(C_2F_5)_3F_2H]^-$ and the corresponding imminium cations which add a second amine moiety by intra- or intermolecular adduct formation.

Introduction

Weakly coordinating anions (WCAs) are of great academic as well as industrial interest. Based on the pioneering work of Strauss, Reed, and Krossing, WCAs have been established as constituents of ionic liquids, for lithium ion batteries as well as for the stabilization of reactive cations.[1] Thereby perfluorinated WCAs like $[B(C_6F_5)_4]^-$, $[Al\{OC(CF_3)_3\}_4]^-$ and $[P(C_2F_5)_3F_3]^-$ exhibit an enormous potential in synthesis and application.[2]

The familiar hexafluorophosphate anion, $[PF_6]^-$, is used as a lithium salt in lithium ion batteries[2] or in combination with organic cations like imidazolium derivatives in ionic liquids.[3–5] One disadvantage of $[PF_6]^-$, however, is the sensitivity of the PF bond towards hydrolysis.[6,7] To circumvent this obstacle, perfluoroalkyl substituents are incorporated which enhance the hydrolytic stability of the phosphate anion. Fluoroperfluoroalkylphosphate derivatives have been known for about 40 years.[8] The trifluorotris(pentafluoroethyl)phosphate ion, $[P(C_2F_5)_3F_3]^-$, which is used in commercially available ionic liquids, exhibits a significantly reduced charge density in comparison to $[PF_6]^-$. The reaction of the technical product $(C_2F_5)_3PF_2$ with an aqueous HF solution selectively affords the corresponding phosphoric acid $[H(OH_2)_n][P(C_2F_5)_3F_3]$ as a precursor of a variety of ionic liquids of surprising hydrolytic, thermal, and electrochemical stability.[9–11]

Fluorohydridophosphates are known since 1964 when Cavell and Nixon reported the formation of $[Me_2NH_2][P(CF_3)F_4H]$ by the aminolysis of CF_3PF_2 with Me_2NH.[12] $[P(CF_3)F_4H]^-$ was also synthesized selectively by the reaction of CF_3PF_2 with KHF_2 in acetonitrile.[11] KHF_2 was also used for the synthesis of $K[P(CF_3)_2F_3H]$ starting from $(CF_3)_2PF$.[13] Accordingly, treatment of PF_3 with KHF_2 resulted in the formation of $K[PF_5H]$.[14] The direct reaction of PF_3 with HF and metal fluorides afforded HPF_4, while the formation of the expected hydridophosphate $[PF_5H]^-$ could not be observed under these conditions.[15] The compound H_2PF_3 is converted into the stable hydridophosphates $M[PF_4H_2]$ (M = K, Cs) by treatment with KF and CsF.[16]

The formation of complex anions with hydrido substituents can also be achieved by the hydride abstraction from amines by strong Lewis acids. $B(C_6F_5)_3$ is able to abstract a hydride from NEt_3 to give $[B(C_6F_5)_3H]^-$,[17] but due to its high price it is not suitable for technical applications. Usually, hydrides are abstracted from amines by their reaction with carbocations like CPh_3^+.[18,19] The resulting imminium ion is a strong electrophile and reacts with excess amines under adduct formation.[20,21] With tetramethylethylenediamine (TMEDA) and 1,8-bis(dimethylamino)naphthalene (DMAN), for example, adduct formation results in a ring closing reaction to a heterocyclic cation.[17,22] Knoll and Krumm found that the imminium ion $[Me_2N{=}CH_2]^+$ forms adducts with bases with a pK_a value above 6, whereas stronger bases with a pK_a value above 10 like NEt_3 deprotonate the imminium ion.[23]

Results and Discussion

The synthesis of the difluorohydridotris(pentafluoroethyl)phosphate anion, $[P(C_2F_5)_3F_2H]^-$, from $(C_2F_5)_3PF_2$ was recently realized by a hydride transfer reaction.[24] This process strongly depends on the reaction conditions.

The reaction of neat $(C_2F_5)_3PF_2$ with $NaBH_4$ at elevated temperatures only affords $(C_2F_5)_3P$ and $(C_2F_5)_2PH$.[25] If the reduction is carried out with $LiAlH_4$ in diethyl ether, a mixture of $(C_2F_5)_3P$, $(C_2F_5)_2PH$ and $C_2F_5PH_2$ is obtained. The selective conversion of $(C_2F_5)_3PF_2$ to $Li[P(C_2F_5)_3F_2H]$ is achieved with $LiAlH_4$ in THF as a solvent (Scheme 1).

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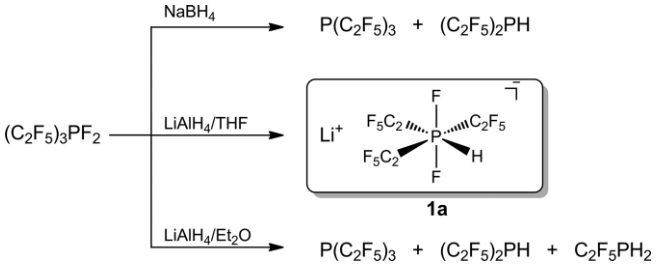
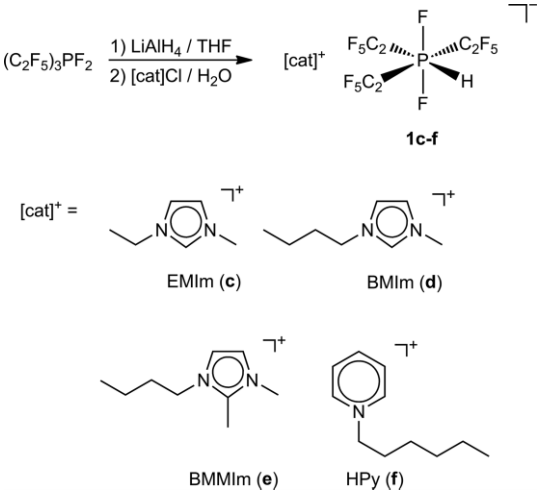


Scheme 1. Reduction products of $(C_2F_5)_3PF_2$.

$Li[P(C_2F_5)_3F_2H]$, **1a**, however, decomposed during the concentration of the reaction solution in vacuo. The preparation of a stable salt was achieved by the treatment of the dissolved $Li[P(C_2F_5)_3F_2H]$ with $[PPh_4]Cl$ in aqueous THF to give $[PPh_4][P(C_2F_5)_3F_2H]$, **1b**, as a colorless solid in an 82 % yield. The oxygen- and moisture stable salt melts at 114–116 °C. Aqueous solutions of the compound can be kept for several days at room temperature without any sign of decomposition; the pure solid can be stored under N_2 without decomposition.

The ^{19}F NMR spectrum exhibits one resonance for the fluorine atoms bound directly to the phosphorus atom at $\delta(^{19}F) = -114.7$ ppm. In addition to the $^1J(PF)$ coupling of J = 737 Hz, a $^2J(FH)$ coupling of J = 58 Hz leads to a broad doublet of doublets, as evidenced by a $^{19}F\{^1H\}$ NMR spectrum. The ^{31}P NMR spectrum (Figure 1) displays a first-order spectrum in which the coupling of the phosphorus atom to the fluorine atoms of the CF_3 units is not resolved. The signal is split into a triplets by the $^1J(PF)$ coupling to the P–F fluorine atoms F_A. A further quintet of triplets splitting results from the $^2J(PF)$ coupling to the fluorine atoms of the chemically inequivalent pentafluoroethyl groups. In addition, a doublet with a $^1J(PH)$ coupling constant of J = 678 Hz is observed. The same coupling is detected in the resonance of the hydrogen atom in the ^1H NMR spectrum which is split into a doublet of triplets of triplets at 5.6 ppm. In addition to the $^1J(PH)$ coupling, the $^2J(HF)$ coupling to the P–F fluorine atoms F_A as well as the $^3J(HF)$ coupling to the fluorine atoms of the *trans* located CF_2 unit is detected.

A cation exchange of in situ generated $Li[P(C_2F_5)_3F_2H]$, **1a**, with different imidazolium chlorides and a pyridinium salt leads to ionic liquids with melting points below room temperature (Scheme 2). These products are insoluble in water and thus can easily be separated from the aqueous reaction mixture. Their melting points are well below room temperature and range from −2.6 °C {$[BMIm][P(C_2F_5)_3F_2H]$, **1d**} over −2.4 °C {$[EMIm][P(C_2F_5)_3F_2H]$, **1c**} to +9.6 °C {$[BMMIm][P(C_2F_5)_3F_2H]$, **1e**} (see Scheme 2). For comparison, the trifluoro derivative $[BMIM][P(C_2F_5)_3F_3]$ melts at 3 °C,[26] while $[EMIm][P(C_2F_5)_3F_3]$ exhibits a melting point of −1 °C[26] (−37 °C[10]) and decomposes at 300 °C.



Scheme 2. Synthesis of ionic liquids **1c**–**f** of the $[P(C_2F_5)_3F_2H]^-$ anion.

Related hydridophosphate salts decompose at a much lower temperature {$[EMIm][P(C_2F_5)_3F_2H]$, **1c**: 176 °C; $[BMIm][P(C_2F_5)_3F_2H]$, **1d**: 177 °C; $[BMMIm][P(C_2F_5)_3F_2H]$, **1e**: 179 °C}. For the ther-

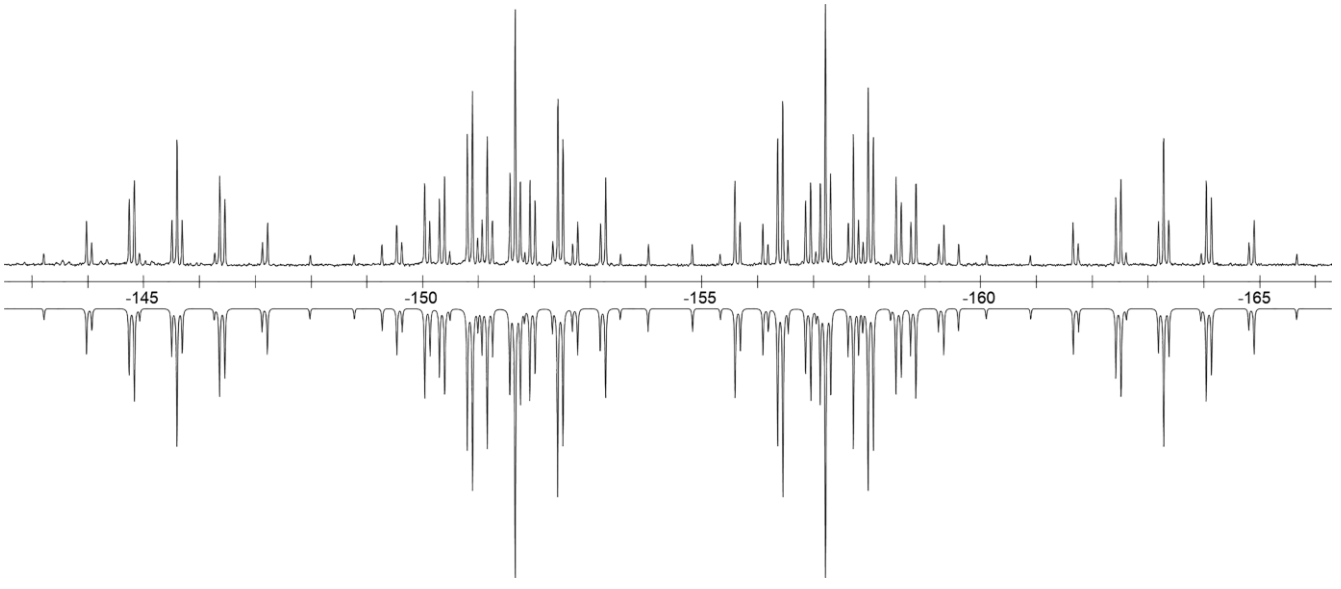


Figure 1. Experimental (top) and calculated (bottom) ^{31}P NMR spectrum of $[P(C_2F_5)_3F_2H]^-$ as $[PPh_4]^+$ salt.

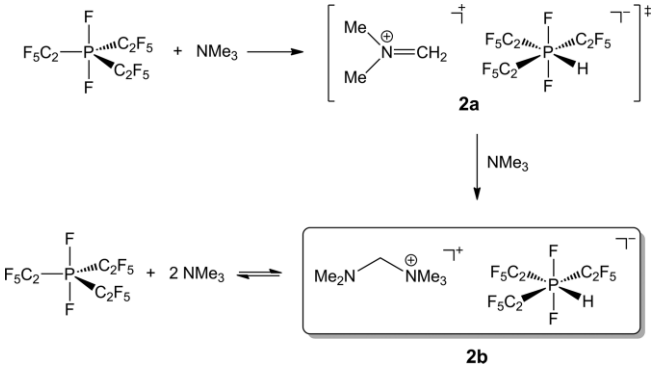
mal decomposition of the pyridinium derivative [HPy][$P(C_2F_5)_3F_2H$], **1f**, an even lower decomposition temperature of 166 °C is found.

[BMIm][$P(C_2F_5)_3F_2H$], **1d**, exhibits a density of 1.58 g/cm^3 at 20 °C (Table 1). This value is close to that of the analogous trifluoro salt [BMIm][$P(C_2F_5)_3F_3$][27] but significantly larger than that of the hexafluorophosphate salt [BMIm][PF_6].[28] The dynamic viscosity of [BMIm][$P(C_2F_5)_3F_2H$], **1d**, (96 mPa s at 20 °C) lies in the same range as [BMIm][$P(C_2F_5)_3F_3$][27] and is considerably lower than that of [BMIm][PF_6] (261 mPa s).[28]

Table 1. Density and dynamic viscosity of phosphate salts.

	ϱ /g cm^3	η /mPa s	M.p. /°C
[BMIm][$P(C_2F_5)_3F_2H$] (**1d**)	1.58	96	–2.6
[BMIm][$P(C_2F_5)_3F_3$]	1.63[27]	93[27]	+3[26]
[BMIm][PF_6]	1.36[28]	261[28]	10.4[29]

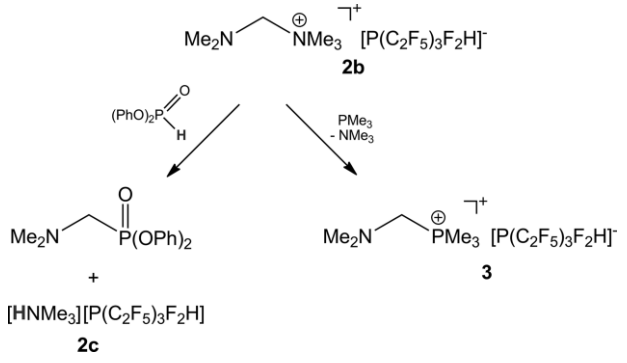
In contrast to $B(C_6F_5)_3$, which abstracts a hydride from NEt_3 to give $[B(C_6F_5)_3H]^-$,[17] PF_5 forms a colorless solid adduct with NMe_3. Substitution of three fluorine atoms of PF_5 by pentafluoroethyl groups increases the Lewis acidity of the resulting phosphorane $(C_2F_5)_3PF_2$ drastically. In keeping with this, the reaction of $(C_2F_5)_3PF_2$ with NMe_3 results in a hydride abstraction by the phosphorane with an initial formation of the imminium hydridophosphate [Me_2NCH_2][$P(C_2F_5)_3F_2H$], **2a** (Scheme 3). The Lewis acidic imminium ion adds a second equivalent of trimethylamine to form the ammonium ion $[Me_2NCH_2NMe_3]^+$.[20] The corresponding product, $[Me_2NCH_2NMe_3][P(C_2F_5)_3F_2H]$, **2b**, is isolated quantitatively as a colorless solid.



Scheme 3. Reaction of $(C_2F_5)_3PF_2$ with NMe_3.

This transformation was conducted in the absence of any solvent. Furthermore, the stoichiometry is non-relevant, as both excess $(C_2F_5)_3PF_2$ or excess NMe_3 are volatile species that can easily be removed from the solid product. Evaporating a flask with 2 g of **2b** overnight, however, results in a complete removal of the salt, which indicates that the reaction of $(C_2F_5)_3PF_2$ with NMe_3 is reversible even at room temperature.

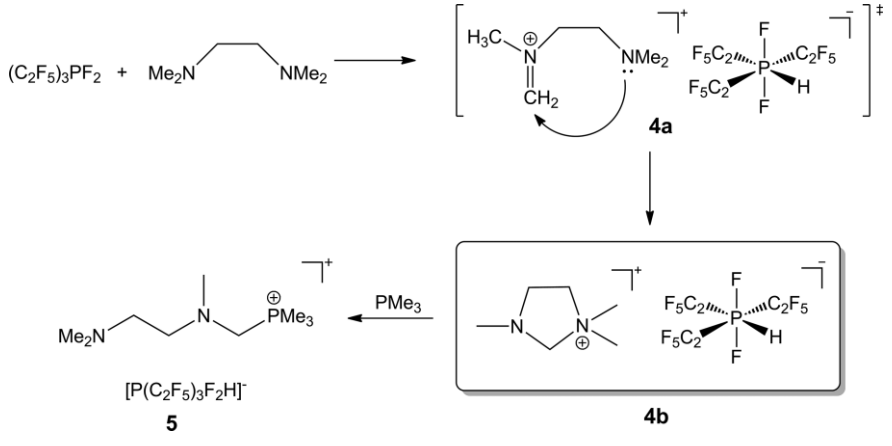
The treatment of **2b** with diphenylphosphonic ester furnishes the substituted phosphonic ester $Me_2NCH_2P(O)(OPh)_2$ and [$HNMe_3$][$P(C_2F_5)_3F_2H$], **2c** (Scheme 4). The reaction of **2b** with PMe_3 leads under liberation of NMe_3 to the phosphonium salt [$Me_2NCH_2PMe_3$][$P(C_2F_5)_3F_2H$], **3**.



Scheme 4. Reactions of the aminomethylammonium cation $[Me_2NCH_2NMe_3]^+$ with $(PhO)_2PHO$ and PMe_3.

The solvent-free reaction of $Me_2NC_2H_4NMe_2$ (tetramethylethylenediamine, TMEDA) with $(C_2F_5)_3PF_2$ was performed similarly. A hydride is transferred to the phosphorane $(C_2F_5)_3PF_2$, affording the hydridophosphate anion $[P(C_2F_5)_3F_2H]^-$. The resulting imminium cation $[H_2C(Me)NC_2H_4NMe_2]^+$ of **4a**, reacted with the second amine functionality by an intramolecular ring closing reaction[22] to afford $[C_6H_{15}N_2][P(C_2F_5)_3F_2H]$, **4b**, as a viscous hydrophobic liquid (Scheme 5). A density of 1.62 g/cm^3 and a dynamic viscosity of 298 mPa s at 20 °C were determined.

The treatment of **4b** with PMe_3 leads to the formation of the corresponding phosphonium salt **5** by ring opening (Scheme 5).



Scheme 5. Mechanism of the reaction of $(C_2F_5)_3PF_2$ with TMEDA.

Conclusions

The generation of the fluoro(perfluoroalkyl)hydridophosphate anion $[P(C_2F_5)_3F_2H]^-$ strongly depends on the reaction conditions. A selective synthesis was achieved by the reaction of $(C_2F_5)_3PF_2$ with $LiAlH_4$ in THF solution. The derivative $[PPh_4][P(C_2F_5)_3F_2H]$, **1b**, was obtained as a colorless solid by salt metathesis with $[PPh_4]Cl$. The cation exchange with differently substituted imidazolium and pyridinium salts resulted in hydrophobic room temperature ionic liquids **1c**–**f**.

Another successful generation of the $[P(C_2F_5)_3F_2H]^-$ anion makes use of the hydride abstraction from amines. The strong Lewis acid $(C_2F_5)_3PF_2$ abstracts a hydride ion from NMe_3 and TMEDA, respectively, to afford the hydridophosphate anion, $[P(C_2F_5)_3F_2H]^-$, and the corresponding imminium cations. The initially formed $[Me_2NCH_2]^+$ adds a second equivalent of NMe_3 to give the cation $[Me_2NCH_2NMe_3]^+$. The corresponding hydridophosphate salt $[Me_2NCH_2NMe_3][P(C_2F_5)_3F_2H]$, **2b**, was isolated quantitatively. The reaction between $(C_2F_5)_3PF_2$ and NMe_3 is reversible at room temperature. The imminium ion generated from TMEDA, $[H_2C(Me)NC_2H_4NMe_2]^+$, is stabilized by the second amine functionality by intramolecular cyclization. The product, $[C_6H_{15}N_2][P(C_2F_5)_3F_2H]$, **4b**, represents a hydrophobic room temperature ionic liquid. Both imminium cations display the typical behavior towards PMe_3 to furnish the corresponding phosphonium cations.

Experimental Section

$(C_2F_5)_3PF_2$ was provided by the Merck KGaA, Darmstadt, Germany. All other chemicals were obtained from commercial sources. Tetramethylethylenediamine was dried with CaH_2. All other chemicals were used without further purification. Standard high-vacuum techniques were employed throughout all preparative procedures. Nonvolatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. NMR spectra were recorded with a Bruker Avance II 300 and a Bruker Model Avance III 300 (^{1}H: 300.13 MHz; ^{13}C: 75.47 MHz; ^{19}F: 282.40 MHz; ^{31}P: 111.92 MHz) with positive shifts being downfield from the external standards [85 % orthophosphoric acid (^{31}P), CCl_3F (^{19}F) and TMS (^{1}H, ^{13}C)]. Computer simulation of the ^{31}P NMR spectrum of $[P(C_2F_5)_3F_2H]^-$ was carried out with the program gNMR.[30] C, H, and N analyses were carried out with a HEKAtech Euro EA 3000 apparatus. ESI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. The spectra were recorded with a Bruker Daltonik esquireNT 5.2 esquireControl software by the accumulation and averaging of several single spectra. Data analysis software 3.4 was used for processing the spectra. EI mass spectra were recorded with a Finnigan MAT 95 spectrometer (20 eV). Melting points were determined using a HWS Mainz 2000 apparatus. IR spectra were recorded on an Alpha FTIR spectrometer equipped with an ATR unit (Bruker) in a range of 4000 cm^{-1} to 400 cm^{-1}. The moisture content of ionic liquids was measured by a Karl-Fischer titration (831 KF-Coulometer, Metrohm) and the content of chloride and fluoride ions by ion-chromatography (830 Metrohm). Viscosity, density and thermal stability (DSC) of ionic liquids were measured using a Viscosimeter SVM 3000 (Anton Paar) and a Netzsch DSC 204 instrument.

$[PPh_4][P(C_2F_5)_3F_2H]$ (1b): $(C_2F_5)_3PF_2$ (2.38 g, 5.59 mmol) was added slowly to a $LiAlH_4$/THF solution (1 M, 5.6 mL, 5.6 mmol) at 0 °C and stirred for 20 min. The solution was hydrolyzed with formation of a colorless precipitate, before a $CHCl_3$ solution (5 mL) of $[PPh_4]Cl$ (1.89 g, 5.04 mmol) was added. The precipitate was filtered off and washed with chloroform. The aqueous phase was removed and the chloroform phase was dried in vacuo. A colorless solid remained (3.18 g, 82 %). M.p.: 114–116 °C. ^{1}H NMR ($CDCl_3$): δ = 5.6 {d, t, quin, m, ^1J(PH) = 678, ^2J(HF) = 64, $^3J(HF_{trans})$ = 13 Hz, 1 H, $[P(C_2F_5)_3F_2H]$}, 7.6–7.9 ppm {m, 20 H, $[P(C_6H_5)_4]^+$}. ^{1}H{^{19}F} NMR ($CDCl_3$): δ = 5.6 {d, ^1J(PH) = 678, ^2J(HC) = 37 Hz, 1 H, $[P(C_2F_5)_3F_2H]$}, 7.6–7.9 ppm {m, 20 H, $[P(C_6H_5)_4]^+$}. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 117.5 [d, ^1J(PC) = 90 Hz, *ipso*-C], 130.7 [d, ^2J(PC) = 13 Hz, *ortho*-C], 134.2 [d, ^3J(PC) = 13 Hz, *meta*-C], 135.7 ppm [d, ^4J(PC) = 3 Hz, *para*-C]. ^{13}C{^{19}F} NMR ($CDCl_3$): δ = 117.6 [d, ^1J(PC) = 211 Hz, *trans*-CF_2], 117.7 [d, ^1J(PC) = 102, ^2J(CH) = 37 Hz, *cis*-CF_2], 120.3 [d, ^2J(PC) = 28 Hz, *trans*-CF_3], 120.9 ppm [d, ^2J(PC) = 21 Hz, *cis*-CF_3]. ^{19}F NMR ($CDCl_3$): δ = –81.4 (m, 3 F, *trans*-CF_3), –83.1 (m, 6 F, *cis*-CF_3), –113.9 [d, d, m, ^1J(PF) = 737, ^2J(FH) = 58 Hz, 2 F, PF], –120.6 [d, m, ^2J(PF) = 104 Hz, 2 F, *trans*-CF_2], –127.3 ppm [d, m, ^2J(PF) = 93 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR ($CDCl_3$): δ = –154.9 {d, t, quin, t, ^1J(PH) = 678, ^1J(PF) = 738, $^2J(PF_{cis})$ = 93, $^2J(PF_{trans})$ = 104 Hz, $[P(C_2F_5)_3F_2H]^-$}, 23.4 ppm (m, $[PPh_4]^+$). ESI-MS (neg.): *m/z* {(%) [assignment]} = 427.2 (100) $[M]^-$, 307.2 (19) $[M - C_2F_5H]^-$. EI-MS (20 eV): *m/z* {(%) [assignment]} = 414 (13) $[\{PPh\}\{P(C_2F_5)_2F_2\}]^{\cdot+}$, 337 (53) $[PPh_4]^+$, 262 (100) $[PPh_3]^{\cdot+}$, 183 (23) $[P(C_2F_5)FH]^{\cdot+}$. IR (ATR): $\tilde{\nu}$ = 2325 (vw), 2245 (vw), 1588 (vw), 1486 (vw), 1439 (w), 1310 (w), 1271 (w), 1207 (m), 1172 (m), 1124 (m), 1108 (m), 1069 (m), 1038 (w), 997 (w), 954 (m), 768 (m), 751 (w), 737 (w), 722 (s), 688 (m), 633 (vw), 613 (w), 594 (w), 556 (m), 523 (vs), 452 (w), 440 (w), 428 (m) cm^{-1}. $C_{30}H_{21}F_{17}P_2$ (766.4): calcd. C 47.01, H 2.76; found C 47.15, H 2.87.

Synthesis of Ionic Liquids

General Procedure: $(C_2F_5)_3PF_2$ was added at 0 °C to 1.1 equiv. of a $LiAlH_4$/THF solution (1 M) and stirred for 30 min. The resulting clear solution was hydrolyzed with formation of a colorless precipitate. Thereafter, one equivalent of [cat]Cl [cat = 1-Ethyl-3-methylimidazolium (EMIm), 1-Butyl-3-methylimidazolium (BMIm), 1-Hexylpyridinium (HPy), 1-Butyl-2,3-dimethylimidazolium (BMMIm)], dissolved in 2 mL of H_2O, was added. After stirring for 20 min, the precipitate was filtered off. The filtrate consists of a two-phase system. After the removal of the aqueous phase, the ionic liquids were extracted two times with water and dried in vacuo, yielding colorless liquids (**1c**–**f**) in yields of 30–60 %.

1c: Yield 3.4 g (33 %). ^{1}H NMR ([D$_6$]acetone): δ = 1.6 [t, ^3J(HH) = 7 Hz, 3 H, CH_2CH_3], 4.0 (s, 1 H, CH_3), 4.4 [q, ^3J(HH) = 7 Hz, 2 H, CH_2], 5.7 {d, t, t, m, ^1J(PH) = 675, ^2J(FH) = 63, ^3J(FH) = 13 Hz, 1 H, $[P(C_2F_5)_3F_2H]$}, 7.7/7.8 [t, ^3J(HH) = 2, NC*H*C*H*N], 9.0 ppm (s, 1 H, NC*H*N). ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 14.5 (s, CH_2CH_3), 35.6 (s, CH_3), 44.9 (s, CH_2), 122.2 (s, EtNCHCH), 123.9 (s, MeNCHCH), 136.2 ppm (s, NCHN). ^{13}C{^{19}F} NMR ([D$_6$]acetone): δ = 119.9 (m, CF_2), 122.9 ppm (m, CF_3). ^{19}F NMR ([D$_6$]acetone): δ = –81.1 [m, d, ^4J(FH) = 1 Hz, 3 F, *trans*-CF_3], –82.3 [quin, d, ^3J(PF) = 9, ^4J(FH) = 2 Hz, 6 F, *cis*-CF_3], –114.1 [d, d, m, ^1J(PF) = 736, ^2J(FH) = 64 Hz, 2 F, PF_2], –119.7 [d, m, ^2J(PF) = 104 Hz, 2 F, *trans*-CF_2], –126.3 ppm [d, m, ^2J(PF) = 93 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR ([D$_6$]acetone): δ = –154.4 ppm {d, t, quin, t, ^1J(PH) = 678, ^1J(PF) = 735, ^2J(PF) = 93, ^2J(PF) = 104 Hz, $[P(C_2F_5)_3F_2H]^-$}.

1d: Yield 10.2 g (64 %). ^{1}H NMR ([D$_6$]acetone): δ = 0.9 [t, ^3J(HH) = 7 Hz, 3 H, CH_2CH_3], 1.4 [pseudo-sext, ^3J(HH) = 8 Hz, 2 H, CH_2CH_3], 1.9 [pseudo-quin, ^3J(HH) = 7 Hz, 2 H, $CH_2C_2H_5$], 4.0 (s, 3 H, CH_3), 4.4 [t, ^3J(HH) = 8 Hz, 2 H, $CH_2C_3H_7$], 5.7 {d, t, t, m, ^1J(PH) = 675, ^2J(FH) = 63, ^3J(FH) = 13 Hz, 1 H, $[P(C_2F_5)_3F_2H]$}, 7.7 (m, 2 H, NC*H*C*H*N), 9.1 ppm (s, 1 H, NC*H*N). ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 12.7 (s, CH_2CH_3), 19.0 (s, CH_2CH_3), 31.8 (s, $CH_2C_2H_5$), 35.7 (s, CH_3), 49.4 (s,

$CH_2C_3H_7$), 122.5 (s, MeNCHCH), 123.9 (s, BuNCHCH), 136.4 ppm (s, NCHN). $^{13}C\{^{19}F\}$ NMR ([D$_6$]acetone): δ = 118.9 (m, CF_2), 122.5 ppm (m, CF_3). ^{19}F NMR ([D$_6$]acetone): δ = –80.8 (m, 3 F, *trans*-CF_3), –81.9 (m, 6 F, *cis*-CF_3), –115.0 [d, d, m, ^1J(PF) = 724, ^2J(FH) = 65 Hz, 2 F, PF_2], –119.1 [d, m, ^2J(PF) = 107 Hz, 2 F, *trans*-CF_2], –125.7 ppm [d, m, ^2J(PF) = 92 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR ([D$_6$]acetone): δ = –154.2 ppm {d, t, quin, t, ^1J(PH) = 676, ^1J(PF) = 737, ^2J(PF) = 94, ^2J(PF) = 104 Hz, [$P(C_2F_5)_3F_2H]^-$}.

1e: Yield 9.1 g (55 %). ^1H NMR ([D$_6$]acetone): δ = 1.0 [t, ^3J(HH) = 7 Hz, 3 H, CH_2CH_3], 1.4 [pseudo-sext, ^3J(HH) = 7 Hz, 2 H, CH_2CH_3], 1.9 [pseudo-quin, ^3J(HH) = 7 Hz, 2 H, $CH_2C_2H_5$], 2.8 (s, 3 H, NCCH_3N), 3.9 (s, 1 H, CH_3), 4.3 [t, ^3J(HH) = 7 Hz, 2 H, $CH_2C_3H_7$], 5.7 {d, t, t, m, ^1J(PH) = 675, ^2J(FH) = 63, ^3J(FH) = 13 Hz, 1 H, [$P(C_2F_5)_3F_2H$]}, 7.6 ppm (m, 2 H, NCHCHN). $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 8.9 (s, NCCH$_3$N), 12.7 (s, CH_2CH_3), 19.1 (s, CH_2CH_3), 31.2 (s, $CH_2C_2H_5$), 34.6 (s, CH_3), 48.0 (s, $CH_2C_3H_7$), 120.8 (s, NCHCHN), 122.2 (s, NCHCHN), 144.4 ppm (s, NCMeN). ^{19}F NMR ([D$_6$]acetone): δ = –79.9 (m, 3 F, *trans*-CF_3), –81.1 (m, 6 F, *cis*-CF_3), –112.9 [d, d, m, ^1J(PF) = 737, ^2J(FH) = 65 Hz, 2 F, PF_2], –118.6 [d, m, ^2J(PF) = 105 Hz, 2 F, *trans*-CF_2], –125.1 ppm [d, m, ^2J(PF) = 95 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR ([D$_6$]acetone): δ = –153.7 ppm {d, t, quin, t, ^1J(PH) = 674, ^1J(PF) = 737, ^2J(PF) = 92, ^2J(PF) = 104 Hz, [$P(C_2F_5)_3F_2H]^-$}.

1f: Yield 10.0 g (59 %). ^1H NMR ([D$_6$]acetone): δ = 0.9 (m, 3 H, CH_3), 1.3–1.9 (m, 8 H, CH_2), 4.5 [t, ^3J(HH) = 7 Hz, 2 H, NCH_2], 5.6 {d, t, t, m, ^1J(PH) = 673, ^2J(FH) = 63, ^3J(FH) = 13 Hz, 1 H, [$P(C_2F_5)_3F_2H$]}, 8.0 (m, 2 H, NCHCH), 8.5 [t, ^3J(HH) = 8 Hz, 1 H, NC_2H_2CH], 8.7 ppm [d, ^3J(HH) = 6 Hz, 2 H, NCH]. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 13.1 (s, CH_3), 22.0 (s, CH_2CH_3), 25.2 (s, $CH_2C_2H_5$), 30.7 (s, $NC_2H_4CH_2$), 30.8 (s, NCH_2CH_2), 61.9 (s, NCH_2), 128.4 (s, NC_2H_2CH), 144.4 (s, NCHCH), 145.7 ppm (s, NCH). $^{13}C\{^{19}F\}$ NMR ([D$_6$]acetone): δ = 118.2 (m, CF_2), 120.9 ppm (m, CF_3). ^{19}F NMR ([D$_6$]acetone): δ = –79.9 (m, 3 F, *trans*-CF_3), –81.1 (m, 6 F, *cis*-CF_3), –112.9 [d, d, m, ^1J(PF) = 737, ^2J(FH) = 61 Hz, 2 F, PF_2], –118.6 [d, m, ^2J(PF) = 105 Hz, 2 F, *trans*-CF_2], –125.2 ppm [d, m, ^2J(PF) = 92 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR ([D$_6$]-acetone): δ = –152.7 ppm {d, t, quin, t, ^1J(PH) = 676, ^1J(PF) = 737, ^2J(PF) = 94, ^2J(PF) = 104 Hz, [$P(C_2F_5)_3F_2H]^-$} (Table 2).

[Me$_2$NCH$_2$NMe$_3$][P(C$_2$F$_5$)$_3$F$_2$H] (2b): NMe_3 (7.3 mmol) was condensed onto $(C_2F_5)_3PF_2$ (5.14 g, 12.1 mmol) and the mixture was stirred for 24 h at room temperature. Volatile compounds were removed in vacuo. A colorless solid remained (2.15 g, 100 %). ^1H NMR (CD_3CN): δ = 2.6 [s, 6 H, $(CH_3)_2N$-], 2.8 [s, 9 H, -N(CH_3)$_3$], 4.0 (s, 2 H, -NCH_2N-), 5.7 ppm {d, t, quin, ^1J(PH) = 675, ^2J(FH) = 63, ^3J(FH) = 14 Hz, 1 H, [$P(C_2F_5)_3F_2H$]}. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 45.3 [s, $(CH_3)_2N$-], 48.4 [s, -N(CH_3)$_3$], 90.5 ppm (s, -NCH_2N-). ^{19}F NMR (CD_3CN): δ = –80.6 (m, 3 F, *trans*-CF_3), –81.8 (m, 6 F, *cis*-CF_3), –113.6 [d, d, m, ^1J(PF) = 733, ^2J(FH) = 62 Hz, 2 F, PF_2], –119.1 [d, m, ^2J(PF) = 104 Hz, 2 F, *trans*-CF_2], –125.7 ppm [d, m, ^2J(PF) = 94 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR (CD_3CN): δ = –153.7 ppm {d, t, quin, t, ^1J(PH) = 674, ^1J(PF) = 733, ^2J(PF) = 94, ^2J(PF) = 104 Hz, [$P(C_2F_5)_3F_2H]^-$}.

Reaction of 2b with (PhO)$_2$PHO: Excess $(PhO)_2PHO$ was added to a solution of [$Me_2NCH_2NMe_3$][$P(C_2F_5)_3F_2H$] in CH_2Cl_2 to afford **2c** and $Me_2NCH_2P(O)(OPh)_2$. The solution was analyzed by multinuclear NMR spectroscopy. $^{13}C\{^1H\}$ NMR (CH_2Cl_2): δ = 44.7 {s, [HN(CH_3)$_3$]$^+$}, 45.1 [d, ^3J(PC) = 5 Hz, $(CH_3)_2N$], 51.4 ppm [d, ^1J(PC) = 157 Hz, Me_2NCH_2]. ^{19}F NMR (CH_2Cl_2): δ = –80.8 (m, 3 F, *trans*-CF_3), –81.9 (m, 6 F, *cis*-CF_3), –114.4 [d, d, m, ^1J(PF) = 731, ^2J(FH) = 63 Hz, 2 F, PF_2], –119.3 [d, m, ^2J(PF) = 103 Hz, 2 F, *trans*-CF_2], –125.9 ppm [d, m, ^2J(PF) = 94 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR (CH_2Cl_2): δ = 7.3 [t, ^2J(PH) = 13 Hz, $Me_2NCH_2P(O)(OPh)_2$], –153.8 ppm {d, t, quin, t, ^1J(PH) = 678, ^1J(PF) = 731, ^2J(PF) = 93, ^2J(PF) = 104 Hz, [$P(C_2F_5)_3F_2H]^-$}.

[Me$_2$NCH$_2$PMe$_3$][P(C$_2$F$_5$)$_3$F$_2$H] (3): PMe_3 (9.5 mmol) was condensed onto a solution of [$Me_2NCH_2NMe_3$][$P(C_2F_5)_3F_2H$], **2b**, (4.58 g, 8.42 mmol) in CH_2Cl_2 and the mixture was stirred for 30 min. Volatile compounds were removed in vacuo. Colorless solid **3** remained (4.72 g, 100 %). M.p.: 51.3 °C. ^1H NMR (CD_2Cl_2): δ = 1.8 {d, ^2J(PH) = 14 Hz, 9 H, [$Me_2NCH_2P(CH_3)_3$]$^+$}, 2.4 {s, 6 H, [$(CH_3)_2NCH_2PMe_3$]$^+$}, 3.3 [d, ^2J(PH) = 5 Hz, 2 H, ($Me_2NCH_2PMe_3$)$^+$], 5.7 ppm {d, t, quin, m, ^1J(PH) = 678, ^2J(FH) = 64, ^3J(FH) = 14 Hz, 1 H, [$P(C_2F_5)_3F_2H$]$^-$}. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 6.5 {d, ^1J(PC) = 54 Hz, [$Me_2NCH_2P(CH_3)_3$]$^+$}, 47.6 {d, ^3J(PC) = 7 Hz, [$(CH_3)_2NCH_2PMe_3$]$^+$}, 52.9 ppm [d, ^1J(PC) = 74 Hz, ($Me_2NCH_2PMe_3$)$^+$]. ^{19}F NMR (CD_2Cl_2): δ = –80.8 (m, 3 F, *trans*-CF_3), –82.0 (m, 6 F, *cis*-CF_3), –113.9 [d, d, m, ^1J(PF) = 730, ^2J(FH) = 63 Hz, 2 F, PF_2], –119.2 [d, m, ^2J(PF) = 105 Hz, 2 F, *trans*-CF_2], –125.7 ppm [d, m, ^2J(PF) = 93 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR (CD_2Cl_2): δ = –154.1 {d, t, quin, t, ^1J(PH) = 678, ^1J(PF) = 728, ^2J(PF) = 93, ^2J(PF) = 105 Hz, [$P(C_2F_5)_3F_2H]^-$}, 24.3 ppm [dec, t, ^2J(PH) = 13, ^2J(PH) = 4 Hz, ($Me_2NCH_2PMe_3$)$^+$]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = –154.1 {t, quin, t, ^1J(PF) = 728, ^2J(PF) = 93, ^2J(PF) = 105 Hz, [$P(C_2F_5)_3F_2H]^-$}, 24.3 ppm [s, ^1J(PC) = 74, ^1J(PC) = 54 Hz, ($Me_2NCH_2PMe_3$)$^+$]. IR (ATR): $\tilde{\nu}$ = 3375 (vw, br), 3010 (vw), 2845 (vw), 2797 (vw), 2231 (vw), 1470 (vw), 1423 (vw), 1304 (w), 1274 (w), 1203 (s), 1179 (vs), 1119 (s), 1087 (w), 1063 (m), 1041 (w), 958 (vs), 913 (vw), 880 (vw), 827 (vw), 751 (s), 691 (vw), 664 (vw), 623 (w), 614 (m), 596 (m), 557 (s), 522 (s), 428 (w) cm^{-1}.

[C$_6$H$_{15}$N$_2$][P(C$_2$F$_5$)$_3$F$_2$H] (4b): $(C_2F_5)_3PF_2$ (14.59 g, 34.25 mmol) was combined with tetramethylethylenediamine, TMEDA, (3.59 g, 30.9 mmol) and the mixture was stirred for 3 days at room temperature. Volatile compounds were removed in vacuo, whereby **4b** remained as a colorless liquid (15.89 g, 95 %). ^1H NMR (CD_3CN): δ = 2.5 [s, 3 H, -N(CH_3)], 2.8 (m, 2 H, MeNCH_2), 3.2 [s, 6 H, N(CH_3)$_2$], 3.6 (m, 2 H, Me_2NCH_2), 3.9 (s, 2 H, NCH_2N), 5.6 ppm {d, t, quin, m, ^1J(PH) = 675, ^2J(FH) = 63, ^3J(FH) = 14 Hz, 1 H, [$P(C_2F_5)_3F_2H$]$^-$}. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 37.3 [t, ^1J(C^{14}N) = 1.6 Hz, (CH_3)N], 51.8 (s, MeNCH_2), 52.8 [t, ^1J(C^{14}N) = 4.4 Hz, N(CH_3)$_2$], 64.4 [t, ^1J(C^{14}N) = 3.9 Hz, Me_2NCH_2], 86.0 ppm [t, ^1J(C^{14}N) = 3.7 Hz, NCH_2N]. ^{19}F NMR (CD_3CN): δ = –81.3 (m, 3 F, *trans*-CF_3), –82.5 (m, 6 F, *cis*-CF_3), –114.3 [d, d, m, ^1J(PF) = 734, ^2J(FH) = 63 Hz, 2 F, PF_2], –119.8 [d, m, ^2J(PF) =

Table 2. Selected analytical data for salts of the composition [cat][$P(C_2F_5)_3F_2H$], **1c**–**f**.

	1c: [EMIm][a]	**1d:** [BMIm][b]	**1e:** [BMMIm][c]	**1f:** [HPy][d]
Yield /%	33	64	55	59
Glass transition /°C	–	–86	–78	–76
Cold crystallization /°C	–	–38	–24	–
Melting point /°C	–2.4	–2.6	9.6	–
Decomposition point /°C	176	177	179	166
Content of H_2O /ppm	43.1	40.4	122.1	26.8
Content of Cl^- /ppm	< 5	< 5	5.9	142.54
Content of F^- /ppm	111.9	47.9	197.5	7175

[a] 1-Ethyl-3-methylimidazolium. [b] 1-Butyl-3-methylimidazolium. [c] 1-Butyl-2,3-dimethylimidazolium. [d] 1-Hexylpyridinium.

104 Hz, 2 F, *trans*-CF_2], –126.5 ppm [d, m, ^2J(PF) = 94 Hz, 4 F, *cis*-CF_2]. ^{31}P NMR (CD_3CN): δ = –154.4 ppm {d, t, quin, t, ^1J(PH) = 676, ^1J(PF) = 733, ^2J(PF) = 93, ^2J(PF) = 104 Hz, [$P(C_2F_5)_3F_2H]^-$}. ESI-MS (pos.): *m/z* {(%) [assignment]} = 115.0 (100) $[C_6H_{15}N_2]^+$. ESI-MS (neg.): *m/z* {(%) [assignment]} = 426.6 (46) $[P(C_2F_5)_3F_2H]^-$, 306.6 (100) $[P(C_2F_5)_2F_2]^-$, 118.8 (47) $[C_2F_5]^-$. IR (ATR): $\tilde{\nu}$ = 2986 (vw), 2865 (vw), 2823 (vw), 2795 (vw), 1472 (w), 1311 (w), 1271 (w), 1203 (s), 1175 (vs), 1122 (vs), 1070 (w), 1043 (m), 957 (s), 872 (w), 811 (w), 757 (s), 738 (m), 634 (w), 614 (m), 595 (m), 556 (s), 522 (s), 428 (m) cm^{-1}. $C_{12}H_{16}F_{17}N_2P$ (542.2): calcd. C 26.56, H 2.97, N 5.17; found C 26.71, H 2.94, N 5.23.

Reaction of 4b with PMe_3: Excess PMe_3 was added to a solution of **4b** in CH_2Cl_2. The resulting solution of **5** was analyzed by multinuclear NMR spectroscopy. ^{1}H NMR (CH_2Cl_2): δ = 1.8 [d, ^2J(PH) = 14 Hz, 9 H, $CH_2P(CH_3)_3$], 2.1 [s, 6 H, $(CH_3)_2N$], 3.1 [s, 3 H, $(CH_3)NCH_2P$], 3.4 [d, ^2J(PH) = 4 Hz, 2 H, NCH_2P], 5.6 ppm {d, t, quin, m, ^1J(PH) = 678, ^2J(FH) = 63, ^3J(FH) = 14 Hz, 1 H, $[P(C_2F_5)_3F_2H]^-$}. ^{13}C{^{1}H} NMR (CH_2Cl_2): δ = 6.6 [d, ^1J(PC) = 54 Hz, $CH_2P(CH_3)_3$], 45.0 [s, $(CH_3)_2N$], 45.4 [d, ^3J(PC) = 4 Hz, $(CH_3)NCH_2P$], 51.6 [d, ^1J(PC) = 73, NCH_2P], 56.6 [d, ^3J(PC) = 9, CH_2NCH_2P], 57.6 ppm (s, Me_2NCH_2). ^{31}P NMR (CH_2Cl_2): δ = –154.0 {d, t, quin, t, ^1J(PH) = 677, ^1J(PF) = 730, ^2J(PF) = 93, ^2J(PF) = 104 Hz, $[P(C_2F_5)_3F_2H]^-$}, 24.0 ppm {dec, t, ^2J(PH) = 14, ^2J(PH) = 4 Hz, $[Me_2NC_2H_4N(Me)CH_2PMe_3]^+$}. ^{31}P{^{1}H} NMR ($CH_2Cl_2$): δ = –154.0 {t, quin, t, ^1J(PF) = 730, ^2J(PF) = 93, ^2J(PF) = 104 Hz, $[P(C_2F_5)_3F_2H]^-$}, 24.0 {s, ^1J(PC) = 54 Hz, $[Me_2NC_2H_4N(Me)CH_2PMe_3]^+$} ppm.

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Keywords: Hydridophosphates · Anions · Hydride abstraction · Fluorine · Ionic liquids

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