Journal of Fluorine Chemistry 207 (2018) 12–17

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Metal-free dehydrogenation of tri- and diethylamine with $(C_2F_5)_3PF_2$

Julia Bader[a], Beate Neumann[a], Hans-Georg Stammler[a], Nikolai Ignat'ev[b], Berthold Hoge[a,*]

[a] *Centrum für Molekulare Materialien, Fakultät für Chemie, Anorganische Chemie, Universität Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany*[1]
[b] *Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany, Germany*

ARTICLE INFO

In memoriam Professor George A. Olah.

Keywords:
Hydride abstraction
Phosphate
Pentafluoroethyl
Fluorine
Amines

ABSTRACT

The reaction of the strong Lewis acid $(C_2F_5)_3PF_2$ with triethylamine leads to an initial hydride abstraction, resulting in the formation of the hydridophosphate anion $[P(C_2F_5)_3F_2H]^-$ and the iminium ion $[CH_3CH = NEt_2]^+$. The latter is deprotonated by a second molecule NEt_3 which corresponds to a formal hydrogen abstraction from the amine. The resulting nucleophilic enamine is trapped by a second equivalent of $(C_2F_5)_3PF_2$, ultimately yielding the β-aminovinylphosphorane derivative $(C_2F_5)_2PF_2C_2H_2NEt_2$. The β-aminovinylphosphorane reacts with CsF to the corresponding trifluorophosphate derivative, $[P(C_2F_5)_2F_3C_2H_2NEt_2]^-$, which hydrolyzes to the aldehyde $[P(C_2F_5)_2F_3CH_2CHO]^-$, while the reaction with anhydrous HF yields the zwitterionic species $[P(C_2F_5)_2F_3C_2H_3NEt_2]$.

1. Introduction

Transition-metal complexes play an important role in the dehydrogenation of amines. Secondary amines can be converted into imines via a ruthenium-catalyzed hydrogen transfer under reflux conditions [1]. Tertiary amines undergo an iridium-catalyzed dehydrogenation to form enamines, however, this reaction requires a catalyst load of 10 mol-% and heating for several hours [2]. In contrast, tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, allows a metal-free dehydrogenation of secondary and tertiary amines [3–6], yielding in a stoichiometric amount the ammonium hydridoborate $[HNEt_3][B(C_6F_5)_3H]$ and the iminium borate $[(C_6F_5)_3BCH_2CH = NEt_2]$. The same reaction pattern is observed in the reaction of enamines with inorganic tetrahalides [7].

The highly Lewis acidic phosphorane $(C_2F_5)_3PF_2$ gives rise to octahedral adducts, $[P(C_2F_5)_3F_2(D)]$, with Lewis bases (D) [8]. $(C_2F_5)_3PF_2$ adds a hydride in the reaction with $LiAlH_4$, yielding the hydridophosphate anion, $[P(C_2F_5)_3F_2H]^-$, which is stable towards water and air at room temperature [9].

2. Results and discussion

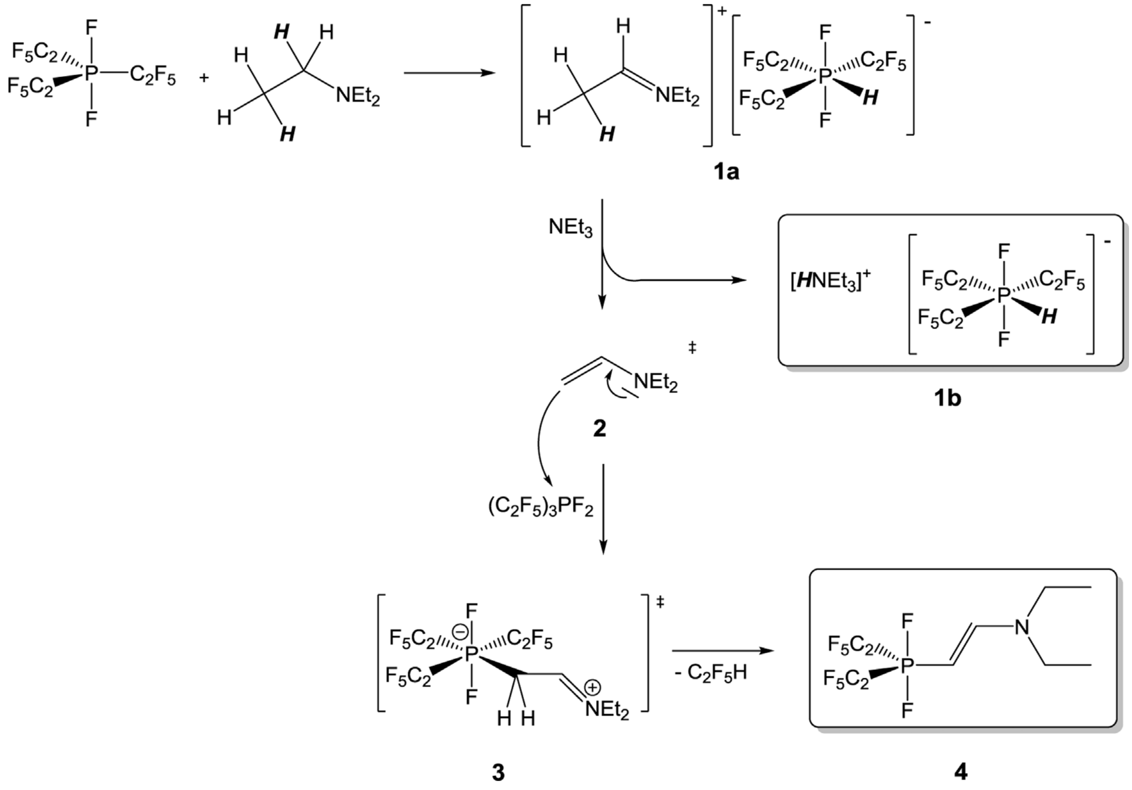
We were interested in a deeper insight in the scope and limitations for hydride abstractions from alkylamines by Lewis acidic phosphoranes. Treatment of $(C_2F_5)_3PF_2$ with an equimolar amount of neat triethylamine during 4 days at room temperature led to the formation of the ammonium hydridophosphate $[HNEt_3][P(C_2F_5)_3F_2H]$ (**1b**) and the liquid phosphorane derivative $(C_2F_5)_2PF_2C_2H_2NEt_2$ (**4**). The latter was separated from the salt **1b** and isolated as a colourless liquid by vacuum distillation (60% yield). These products may be rationalized by the initial α-hydride abstraction from NEt_3 by $(C_2F_5)_3PF_2$ under the formation of an iminium hydridophosphate, $[Et_2N = CHCH_3][P(C_2F_5)_3F_2H]$ (**1a**). This proposed reaction mechanism generally follows the one formulated for the dehydrogenation of *N,N*-diethylaniline with $B(C_6F_5)_3$ [4]. The cation of **1a** was deprotonated by a second equivalent of NEt_3 affording the triethylammonium ion, which remained as its phosphate **1b** and was identified by NMR spectroscopy, and vinyldiethylamine **2**. The sequence of hydride abstraction and deprotonation corresponds to a net dehydrogenation of triethylamine by means of the powerful Lewis acid $(C_2F_5)_3PF_2$. As a strong nucleophile, enamine **2** was trapped by the Lewis acid $(C_2F_5)_3PF_2$ to the transient zwitterionic phosphate **3**. **3** was in contrast to the analogous $B(C_6F_5)_3$ derivative[4] not stable and rapidly underwent β-elimination of pentafluoroethane, affording the second isolated product **4** (Scheme 1).

In view of these findings, a study of the reactivity between $(C_2F_5)_3PF_2$ and a secondary amine, e.g. $HNEt_2$, was intriguing. Equimolar amounts of $(C_2F_5)_3PF_2$ and $HNEt_2$ were combined and the mixture was stirred for 2 days at room temperature. Liberated C_2F_5H was removed in vacuo and the residue was subjected to a fractional distillation to separate colourless liquid $(C_2F_5)_2PF_2(NEtH)$ (**8**) (57 %) from the colourless liquid $(C_2F_5)_2PF_2C_2H_2NEt_2$ (**4**) (15 %). The solid residue was identified as $[H_2NEt_2][P(C_2F_5)_3F_2H]$ (**1d**). Again the product pattern finds a rationale in a commencing α-hydride transfer from the amine to the Lewis acid (Scheme 2). The iminium cation of the resulting intermediate **1c** is intercepted by $HNEt_2$ to give ammonium

---

* Corresponding author.
E-mail address: b.hoge@uni-bielefeld.de (B. Hoge).
[1] http://www.uni-bielefeld.de/chemie/acii/hoge.

https://doi.org/10.1016/j.jfluchem.2017.12.015
Received 8 December 2017; Received in revised form 20 December 2017; Accepted 20 December 2017



Scheme 1. Proposed mechanism of the reaction between $(C_2F_5)_3PF_2$ and NEt_3.

ion **5a**. For the progress of the ongoing reaction a proton exchange between the two nitrogen atoms to furnish **5b** is conceivable, which allows the fragmentation of the cation into ethylamine and iminium ion **6**. The latter suffers from deprotonation by $HNEt_2$ with formation of a diethylammonium ion, which ends up in the saline product $[H_2NEt_2][P(C_2F_5)_3F_2H]$ (**1d**). The also generated vinyldiethylamine **2** combines with $(C_2F_5)_3PF_2$, as already described for the reaction of $(C_2F_5)_3PF_2$ with NEt_3, to give the phosphorane derivative $(C_2F_5)_2PF_2C_2H_2NEt_2$, **4**. In a second pathway, the Lewis acid $(C_2F_5)_3PF_2$ adds the in situ formed ethylamine to give the transient zwitterionic phosphate **7**, which spontaneously eliminates C_2F_5H to afford phosphorane **8**. The ^{31}P NMR spectrum of the aminophosphorane **8** exhibits a triplet of quintets of pseudo quartets at $\delta(^{31}P) = -60.4$ ppm. The pseudo quartet splitting results from ^2J and $^3J(PH)$ couplings of 14 Hz to the NHEt substituent. Due to overlaps in the ^1H NMR spectrum, the exact splitting pattern of the resonances could not be resolved.

In addition to the ^1J and $^2J(PF)$ couplings, the ^{31}P NMR spectrum of the β-aminovinylphosphorane **4** discloses the coupling of the phosphorus atom to the olefinic protons as a doublet of doublets with ^2J and $^3J(PH)$ coupling constants of 15 and 20 Hz, respectively. The resonances of the two sp^2 carbon atoms in the ^{13}C NMR spectrum of **4** at $\delta = 60.5$ and 160.5 ppm show couplings to the phosphorus atom of 218 Hz (^1J) and 25 Hz (^2J), respectively. Additionally, ^2J and $^3J(CF)$ couplings of 28 and 20 Hz, respectively, are observed. There are two sets of signals for the ethyl groups, indicating a hindered rotation due to a conjugation of the electron pair at the nitrogen atom and the CC double bond. Quantum chemical calculations (B3LYP/aug-cc-pvtz) predict significant double-bond character for the CC and CN bonds, a planar nitrogen atom and a significantly shortened PC bond length (Table 1).

The β-aminovinylphosphorane **4** reacts with [Cs{[18]crown-6}]F to the corresponding trifluorophosphate derivative **9** in a 40% yield (Scheme 3).

$[Cs\{[18]crown\text{-}6\}_2][P(C_2F_5)_2F_3C_2H_2NEt_2]$, **9a**, crystallizes in the monoclinic space group $C2/c$ with one molecule in the asymmetric unit.[10] The structure of the anion of **9a** and characteristic bond lengths and angles are given in Fig. 1.

The C5A-C6A bond length of 133.0(5) pm reflects a classical CC double bond. The P1-C5A bond of 184.5(4) pm is significantly shortened with respect to the PC bonds of the pentafluoroethyl groups. Bond length C6A-N1A of 138.9(4) pm lies between a CN single and double bond. Additionally, the angular sum at the nitrogen atom of 348° points to some conjugation within the P-C-C-N unit.

A cation exchange with $[PPh_4]Cl$ in a THF/CH_2Cl_2 mixture furnished $[PPh_4][P(C_2F_5)_2F_3C_2H_2NEt_2]$ (**9b**) as a colourless oil. After a prolonged contact with air, colourless crystals of $[PPh_4][P(C_2F_5)_2F_3CH_2CHO]$, **10**, were obtained, which obviously originate from hydrolysis of the precursor (Scheme 4).

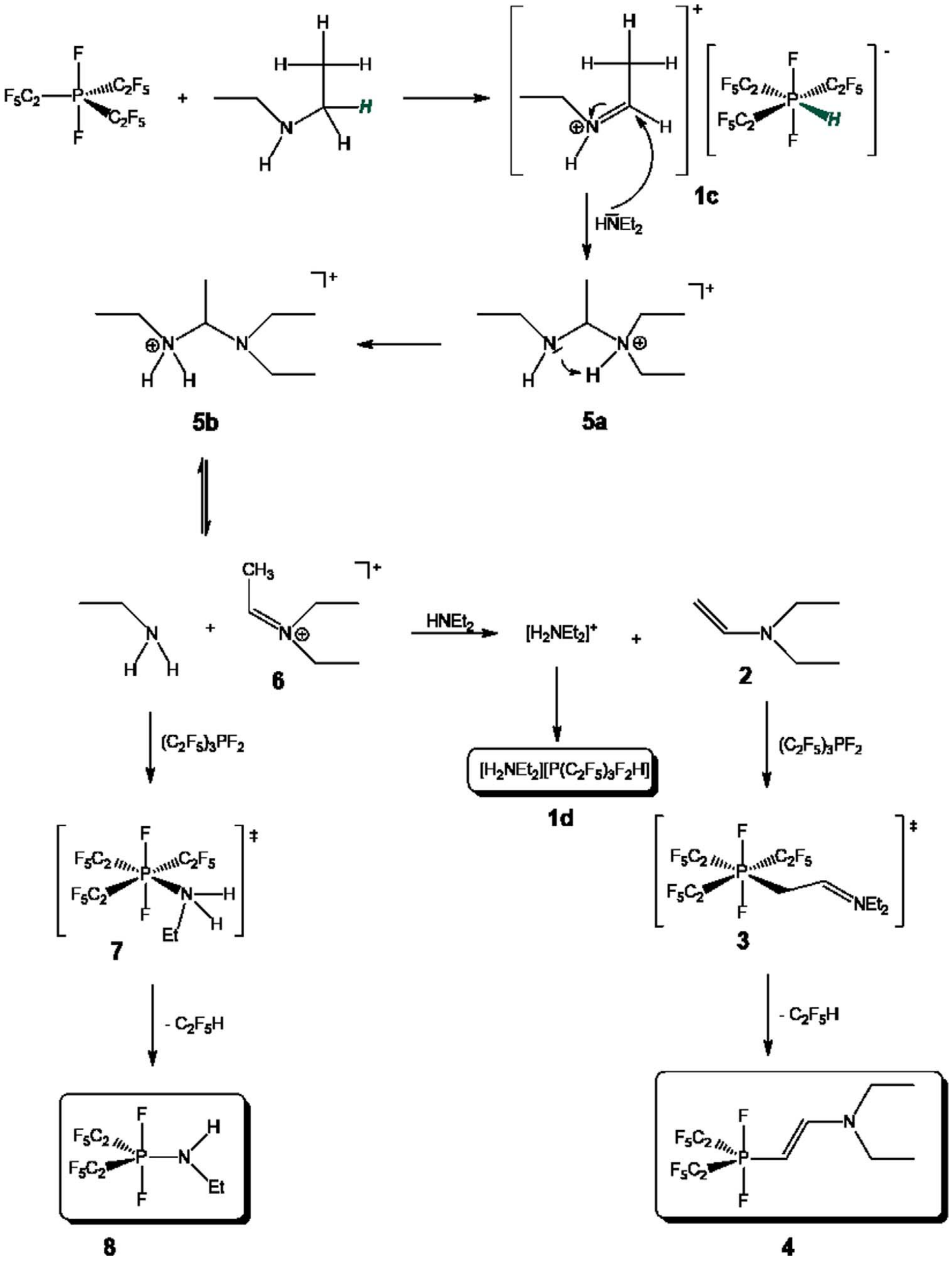
10 crystallizes in the monoclinic space group $C2/c$ with one molecule in the asymmetric unit (Fig. 2) [10]. The observed CO bond length of 121.0(2) pm is in good agreement with the expected value of a typical $C = O$ double bond.

Reaction of the β-aminovinylphosphorane **4** with anhydrous HF gave rise to the formation of the zwitterionic iminium phosphate $[P(C_2F_5)_2F_3C_2H_3NEt_2]$ (**11**) as a colourless solid. Most likely the formation of **11** starts with fluoride addition to the pentacoordinate phosphorus centre to afford transient **9**. Subsequent protonation of **9** at the carbon atom of the double bond adjacent to the phosphorus atom led to the final product **11** (Scheme 5).

The zwitterionic salt **11** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit [10]. The C6-N1 bond length of 128.5(2) pm lies in the range of a typical CN double bond and, together with the angular sum of 359.8° at the nitrogen atom, confirms the structural feature of an iminium moiety (Fig. 3).

3. Conclusions

The reaction of the strong Lewis acid $(C_2F_5)_3PF_2$ with triethylamine is dominated by a hydride abstraction, resulting in the formation of the hydridophosphate anion $[P(C_2F_5)_3F_2H]^-$ and the iminium ion



Scheme 2. Proposed mechanism of the reaction between $(C_2F_5)_3PF_2$ and $HNEt_2$.

Table 1

Comparison of selected experimental and calculated[a] bond lengths [pm] of $[P(C_2F_5)_2F_3X]$ derivatives (X = $C_2H_3NEt_2$ (**11**), $C_2H_2NEt_2$ (**9**), C_2H_3O (**10**)) and $P(C_2F_5)_2C_2H_2NEt_2$ (**4**)

		X = $C_2H_3NEt_2$, 11		X = $C_2H_2NEt_2$, 9		X = C_2H_3O, 10		4
		exp.	calc.	exp.	calc.	exp.	calc.	calc.
P1	F1	162.7(1)	164.1	163.0(1)	166.0	163.2(1)	165.9	166.1
	F2	163.2(1)	162.0	163.5(1)	166.0	164.1(1)	165.8	167.0
	F3	164.0(1)	166.8	163.8(1)	167.1	164.3(1)	167.2	
	C1	193.3(1)	196.2	194.1(2)	196.1	192.8(2)	197.0	192.6
	C3	193.6(1)	195.7	194.0(2)[b]	196.1	193.2(2)	196.3	192.5
	C5	191.0(1)	203.8	184.5(4)[b]	186.6	188.3(2)	192.0	174.7
C5	C6	147.5(2)	143.8	133.0(5)[b]	132.4	149.8(2)	149.3	136.6
C6	N1	128.5(2)	129.7	138.9(4)[b]	144.2	121.0(2)[c]	121.3[c]	133.9
$\Sigma_{<N}$		359.8	360.0	348.7	332.7			360.0

[a] B3LYP/aug-cc-pvtz; CF_3 derivative.

[b] disorder; main compound.

[c] C6-O1.

4 **9**

Scheme 3. Reaction of **4** to the trifluorophosphate $[P(C_2F_5)_2F_3C_2H_2NEt_2]^-$ **9**.

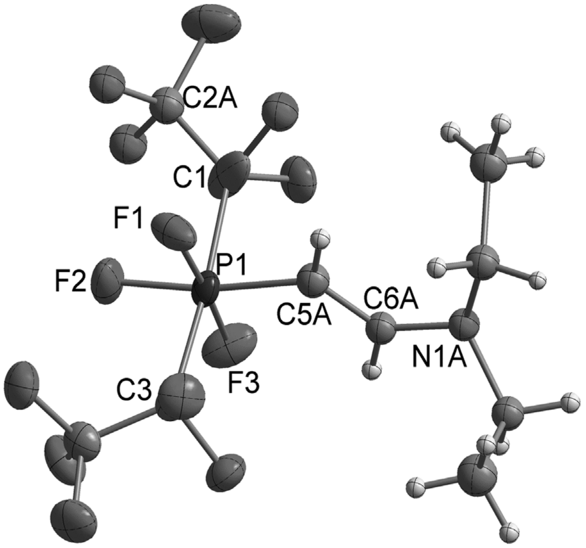
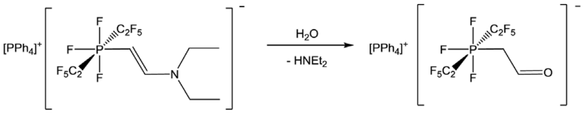


Fig. 1. Molecular structure of the β-aminovinylphosphate anion of **9a**. 50 % probability amplitude displacement ellipsoids are shown. Disorder of one trifluoromethyl unit (C2) and the enamine ligand (C5) on two positions (52:48). Selected bond lengths [pm] and angles [°]: conformer A (depicted): P1-F1 163.0(1), P1-F2 163.5(1), P1-F3 163.8(1), P1-C1 194.1(2), P1-C3 194.0(2), P1-C5A 184.5(4), C5A-C6A 133.0(5), C6A-N1A 138.9(4), Σ(< N) 348.7; conformer B: P1-C5 B 181.6(4), C5B-C6 B 134.9(5), C6B-N1 B 138.8(5), Σ(< N) 347.9.



9 **10**

Scheme 4. Reaction of **9b** to the aldehyde $[P(C_2F_5)_2F_3CH_2CHO]^-$ **10**.

$[CH_3CH = NEt_2]^+$. The iminium ion was subject to deprotonation by excess NEt_3 which formally corresponds to the abstraction of dihydrogen.

4. Experimental section

$(C_2F_5)_3PF_2$ was provided by the Merck company, Germany. All other chemicals were obtained from commercial sources. NEt_3 and $HNEt_2$ were dried over CaH_2. All other chemicals were used without further purification. Standard high-vacuum techniques were employed throughout all preparative procedures. Non-volatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. NMR spectra were recorded with a Bruker 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)]. EI mass spectra were recorded with a Finnigan MAT 95 spectrometer (20 eV). Intensities are referenced to the most intense peak of a group. 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. Melting and visible decomposition points were determined using a HWS Mainz 2000 apparatus. Data collection at 100.0(1) K for X-Ray structure determination of $[Cs\{18crown\text{-}6\}][P(C_2F_5)_2F_2C_2H_2NEt_2]$ and $[P(C_2F_5)_2F_3C_2H_3NEt_2]$ was performed on a Bruker Nonius KappaCCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 71.073 pm). Data collection for $[PPh_4][P(C_2F_5)_2F_3C_2H_3O]$ was performed on a Bruker AXS X8 Prospector Ultra diffractometer at 100.0(1) K using $Cu_{K\alpha}$ radiation (λ = 154.178 pm). The structures were solved by direct methods and refined by full-matrix least-squares cycles [11]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically for **10**, for **9** and **11** a riding model was used.

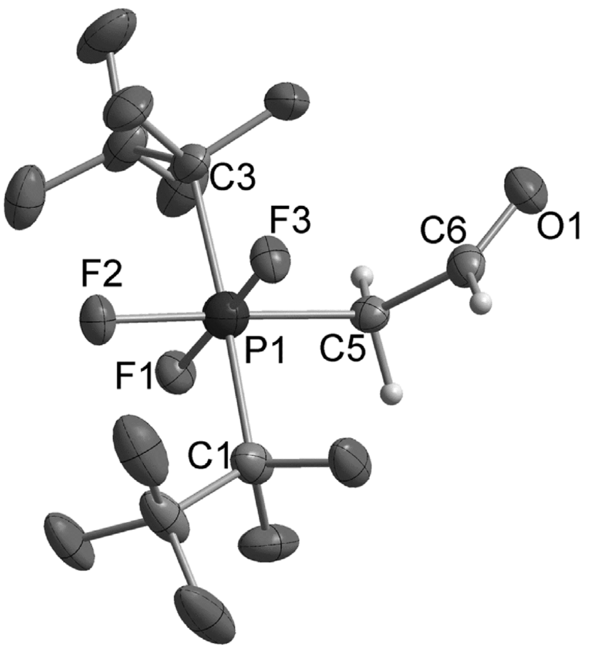
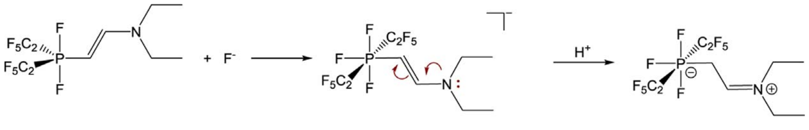


Fig. 2. Structure of the phosphate anion of **10**. 50 % probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm]: P1-F1 163.2(1), P1-F2 164.1(1), P1-F3 164.3(1), P1-C1 193.2(2), P1-C3 192.8(2), P1-C5 188.3(2), C5-C6 149.8(2), C6-O1 121.0(2).

Synthesis of $(C_2F_5)_2PF_2C_2H_2NEt_2$, 4: $(C_2F_5)_3PF_2$ (45.01 g, 0.11 mol) was combined with NEt_3 (10.85 g, 0.11 mol) and the mixture was stirred for 4 days. Volatile compounds were removed in vacuo at room temperature. The intense red reaction mixture was distilled in vacuo. A colourless liquid was collected (12.41 g, 60%) and identified as $(C_2F_5)_2PF_2C_2H_2NEt_2$. b.p. 59 °C/$1{\cdot}10^{-3}$ mbar. ^{1}H NMR (CD_2Cl_2): δ = 0.5 (t, ^3J(HH) = 7, 3H, CH_3), 0.6 (t, ^3J(HH) = 7, 3H, CH_3), 2.3 (quar, ^3J(HH) = 7, 2H, CH_2), 2.4 (quar, ^3J(HH) = 7, 2H, CH_2), 3.2 (d, d, t, ^2J(PH) = 20, ^3J(HH) = 14, ^3J(FH) = 14, 1H, PC*H*), 7.0 ppm (d, d, ^3J(PH) = 14, ^3J(HH) = 14, 1H, NC*H*); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 10.6 (s, CH_3), 14.0 (s, CH_3), 42.7 (s, CH_2), 51.4 (s, CH_2), 60.5 (d, t, ^1J(PC) = 218, ^2J(CF) = 28, P*C*H), 160.5 ppm (d, t, ^2J(PC) = 25, ^3J(CF) = 20, N*C*H); ^{19}F NMR (CD_2Cl_2): δ = -56.5 (d, d, m, ^1J(PF) = 763, ^{2}J(FF) = 67, 1F, PF_A), −71.5 (d, d, m, ^1J(PF) = 791, ^2J(FF) = 67, 1F, PF_B), −81.8 (t, ^3J(FF) = 10, 6F, CF_3), −119.2 ppm (d, t, ^2J(PF) = 107, ^3J(FF) = 13, 4F, CF_2); ^{31}P NMR (CD_2Cl_2): δ = −48.8 ppm (t, quin, d, d, ^1J(PF) = 792, ^2J(PF) = 107, ^2J(PH) = 15, ^3J(PH) = 20, $(C_2F_5)_2PF_2C_2H_2NEt_2$). Mass spectrum (EI, 20 eV) {*m/z* (%) [assignment]}: 406 (4) $[M]^{\cdot +}$, 386 (29) $[M\text{-}F]^+$, 286 (88) $[M\text{-}C_2F_5]^+$, 198 (17) $[M\text{-}C_2F_5\text{-}C_2F_4]^+$, 186 (13) $[F_3PC_2H_2NEt_2]^+$, 166 (5) $[M\text{-}2C_2F_5]^+$, 119 (55) $[C_2F_5]^+$, 98 (33) $[C_2H_2NEt_2]^+$, 69 (58) $[CF_3]^+$, 29 (100) $[C_2H_5]^+$. IR (ATR): = 3100 (vw), 2988 (w), 2946 (w), 2887 (vw), 1605 (vs), 1473 (w), 1451 (w), 1387 (w), 1363 (w), 1311 (m), 1293 (m), 1198 (vs), 1143 (vs), 1001 (m), 949 (s), 905 (s), 818 (w), 757 (s), 745 (s), 641 (m), 600 (s), 577 (s), 520 (s), 467 (w), 429 (m) cm^{-1}. The distillation



Scheme 5. Addition of one molecule HF to the β-aminovinylphosphorane **4** yielding the zwitterionic iminium phosphate **11**.

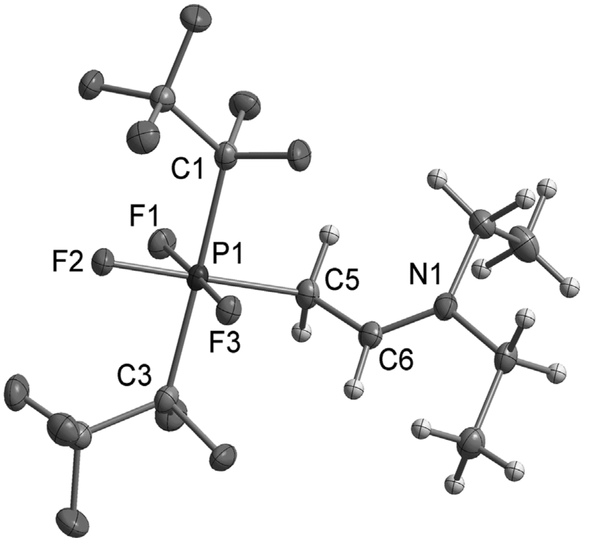


Fig. 3. Molecular structure of the iminium phosphate **11**. 50 % probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm] and angles [°]: P1-F1 162.7(1), P1-F2 163.2(1), P1-F3 164.0(1), P1-C1 193.3(1), P1-C3 193.6(1), P1-C5 191.0(1), C5-C6 147.5(2), C6-N1 128.5(2), Σ(< N) 359.8.

residue consists of $[HNEt_3][P(C_2F_5)_3F_2H]$ which was identified by its known NMR data.[9]

Reaction of $(C_2F_5)_3PF_2$ with $HNEt_2$: $HNEt_2$ (9.6 mmol) was condensed onto $(C_2F_5)_3PF_2$ (4.07 g, 9.5 mmol) and the mixture was stirred for 2 days at room temperature. By cooling the reaction mixture to −78 °C, C_2F_5H was removed in vacuo. At room temperature, a volatile product was separated via trap to trap distillation into a liquid N_2 trap. The obtained colourless liquid (1.90 g, 57%) was identified as $(C_2F_5)_2PF_2NEtH$. The residue was distilled in vacuo. The colourless liquid with a boiling point of 90 °C (0.57 g, 15%) was identified as $(C_2F_5)_2PF_2C_2H_2NEt_2$. The distillation residue consists of $[H_2NEt_2][P(C_2F_5)_3F_2H]$.

$(C_2F_5)_2PF_2NEtH$, **8**: ^1H NMR ($CDCl_3$): δ = 1.2 (m, 3H, $C\mathit{H}_3$), 2.7 (s (broad), NH), 3.1 ppm (m, 2H, $C\mathit{H}_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 16.4 (t, $^3J(PC)$ = 5, $\mathit{C}H_3$), 36.8 ppm (t, $^3J(FC)$ = 9, $\mathit{C}H_2$); ^{19}F NMR ($CDCl_3$): δ = −55.7 (d (broad), $^1J(PF)$ = 851, 1F, $P\mathit{F}_A$), −64.3 (d (broad), $^1J(PF)$ = 859, 1F, $P\mathit{F}_B$), −81.9 (t, $^3J(FF)$ = 9, 6F, $C\mathit{F}_3$), −119.8 ppm (d, t, $^2J(PF)$ = 114, $^3J(FF)$ = 13, 4F, $C\mathit{F}_2$); ^{31}P NMR ($CDCl_3$): δ = −60.4 ppm (t, quin, pseudo-quar, $^1J(PF)$ = 866, $^2J(PF)$ = 114, $^{2/3}J(PH)$ = 14, $(C_2F_5)_2\mathit{P}F_2NEtH$).

$[H_2NEt_2][P(C_2F_5)_3F_2H]$, **1d**: ^1H NMR ($CDCl_3$): δ = 1.2 (m, 6H, $C\mathit{H}_3$), 2.9 (m, 4H, $C\mathit{H}_2$), 6.1 ppm (s(br), NH_2); ^{19}F NMR ($CDCl_3$): δ = −81.3 (m, 3F, $C\mathit{F}_3$), −82.5 (m, 6F, $C\mathit{F}_3$), −114.4 (d, d, m, $^1J(PF)$ = 734, $^2J(FH)$ = 63, 2F, $P\mathit{F}_2$), −119.9 (d, m, $^2J(PF)$ = 104, 2F, $C\mathit{F}_2$), −126.5 ppm (d, m, $^2J(PF)$ = 93, 4F, $C\mathit{F}_2$); ^{31}P NMR ($CDCl_3$): δ = −154.4 ppm (d, t, quin, t, $^1J(PH)$ = 675, $^1J(PF)$ = 734, $^2J(PF)$ = 93, $^2J(PF)$ = 104, $[\mathit{P}(C_2F_5)_3F_2H]^-$).

Synthesis of $[Cs\{[18]crown\text{-}6\}][P(C_2F_5)_2F_3C_2H_2NEt_2]$, 9a: A solution of **4** (0.72 g, 1.77 mmol) in CH_2Cl_2 was treated with $[Cs\{[18]crown\text{-}6\}]F$ (0.57 g, 1.37 mmol). After stirring for 45 min, diethyl ether was added to the clear solution. The resulting precipitate was washed with diethyl ether (3 ×) and subsequently dried in vacuo. A colourless solid remained (0.45 g, 40%). m.p. 94 °C. ^1H NMR (CD_2Cl_2): δ = 1.1 (t, $^3J(HH)$ = 7, 6H, $C\mathit{H}_3$), 3.0 (t, 4H, $^3J(HH)$ = 7, $C\mathit{H}_2$), 3.6 (s, 24H, [18]crown-6), 4.2 (m, $^3J(HH)$ = 15, 1H, PCH), 6.4 ppm (d, d, $^3J(HH)$ = 15, $^3J(PH)$ = 15, 1H, NCH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 12.7 (s, CH_3), 44.6 (s, CH_2), 69.6 (s, [18]crown-6), 97.6 (d, m, $^1J(PC)$ = 186, PCH), 144.7 ppm (m, NCH); ^{19}F NMR (CD_2Cl_2): δ = −31.7 (d, m, $^1J(PF)$ = 780, 1F, $P\mathit{F}_A$), −81.8 (d, t, J = 16, J = 5, 6F, $C\mathit{F}_3$), −84.4 (d, d, m, $^1J(PF)$ = 784, $^2J(FF)$ = 41, 2F, $P\mathit{F}_B$), −116.5 ppm (d, d, t, $^2J(PF)$ = 90, $^3J(FF)$ = 17, $^3J(FF)$ = 6, 4F, $C\mathit{F}_2$); ^{31}P NMR (CD_2Cl_2): δ = −154.8 ppm (quar, quin, d, d, $^1J(PF)$ = 786, $^2J(PF)$ = 91, $^3J(PH)$ = 18, $^2J(PH)$ = 14, $[\mathit{P}(C_2F_5)_2F_3C_2H_2NEt_2]^-$). ESI mass (pos.) {*m/z* (%) [assignment]}: 303 (12) $[K\{C_{12}H_{24}O_6\}]^+$, 287 (100) $[Na\{C_{12}H_{24}O_6\}]^+$. ESI mass (neg.) {*m/z* (%) [assignment]}: 423.8 (100) $[M]^-$.

NMR spectroscopical data of $[PPh_4][P(C_2F_5)_2F_3CH_2CHO]$, 10: Cation exchange of **9a** with $[PPh_4]Cl$ in a solvent mixture of THF and CH_2Cl_2 afforded $[PPh_4][P(C_2F_5)_2F_3C_2H_2NEt_2]$, **9b,** as a colourless oil. The product hydrolysed slowly on contact with air yielding colourless crystals, which were identified as $[PPh_4][P(C_2F_5)_2F_3CH_2CHO]$ by multinuclear NMR spectroscopy and X-ray structure analysis. ^1H NMR (CD_2Cl_2): δ = 2.7 (d, m, 2H, $^2J(PH)$ = 17, H1), 7.7-8.0 (m, 20H, $[PPh_4]^+$), 9.7 ppm (m, 1H, CHO); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 50.3 (d, m, $^1J(PC)$ = 97, PCH_2), 130.3 (d, $^2J(PC)$ = 13, ortho-C), 134.7 (d, $^3J(PC)$ = 10, meta-C), 135.4 (d, $^4J(PC)$ = 3, para-C), 201.0 ppm (m, CHO); ^{19}F NMR (CD_2Cl_2): δ = −40.7 (d, m, $^1J(PF)$ = 822, 1F, $P\mathit{F}_A$), −78.5 (d, d, m, $^1J(PF)$ = 816, $^2J(FF)$ = 33, 2F, $P\mathit{F}_B$), −82.4 (d, t, $^3J(FF)$ = 15, $^4J(FF)$ = 6, 6F, $C\mathit{F}_3$), −118.4 ppm (d, d, t, $^2J(PF)$ = 93, $^3J(FF)$ = 17, $^3J(FF)$ = 9, 4F, $C\mathit{F}_2$); ^{31}P NMR (CD_2Cl_2): δ = −150.5 ppm (d, t, quin, t, d, $^1J(PF)$ = 819, $^1J(PF)$ = 815, $^2J(PF)$ = 93, $^2J(PH)$ = 17, $^3J(PH)$ = 4, $[P(C_2F_5)_2F_3CH_2CHO]^-$).

Synthesis of $[P(C_2F_5)_2F_3CH_2CHNEt_2]$, 11: Excess anhydrous HF was condensed onto a solution of **4** in diethyl ether. The reaction mixture was stirred for 10 min. Volatile compounds were removed in vacuo and the colourless residue was washed with diethyl ether (2x). The product was dried in vacuo. A colourless solid remained. m.p. 85 °C. ^1H NMR (CD_2Cl_2): δ = 1.4 (t, $^3J(HH)$ = 7, 3H, CH_3), 1.5 (t, $^3J(HH)$ = 7, 3H, CH_3), 3.1 (d, d, $^2J(PH)$ = 16, $^3J(HH)$ = 7, 2H, PCH_2), 3.8 (quar, $^3J(HH)$ = 7, 2H, CH_2), 3.9 (quar, $^3J(HH)$ = 7, 2H, CH_2), 8.3 ppm (d, t, $^3J(HH)$ = 7, $^3J(PH)$ = 3, 1H, NCH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 12.2 (s, CH_3), 13.2 (s, CH_3), 38.4 (d, m, $^1J(PC)$ = 86, PCH_2), 46.8 (s, CH_2), 55.6 (s, CH_2), 180.3 ppm (m, NCH); ^{19}F NMR (CD_2Cl_2): δ = −44.4 (d, m, $^1J(PF)$ = 859, 1F, $P\mathit{F}_A$), −76.4 (d, d, m, $^1J(PF)$ = 842, $^2J(FF)$ = 36, 2F, $P\mathit{F}_B$), −82.6 (d, t, $^3J(FF)$ = 17, $^4J(FF)$ = 6, 6F, $C\mathit{F}_3$), −118.5 ppm (d, d, t, $^2J(PF)$ = 97, $^3J(FF)$ = 17, $^3J(FF)$ = 10, 4F, $C\mathit{F}_2$); ^{31}P NMR (CD_2Cl_2): δ = −152.2 ppm (d, t, quin, m, $^1J(PF)$ = 865, $^1J(PF)$ = 845, $^2J(PF)$ = 97, $[P(C_2F_5)_2F_3CH_2CHNEt_2]$). Mass spectrum (EI, 20 eV) {*m/z* (%) [assignment]}: 405 (2) $[M\text{-}HF]^{\cdot +}$, 386 (5) $[M\text{-}2HF]^{\cdot +}$, 307 (5) $[M\text{-}C_2F_5]^+$, 286 (38) $[M\text{-}HF\text{-}C_2F_5]^+$, 207 (29) $[M\text{-}C_2F_5\text{-}C_2F_4]^+$, 186 (7) $[M\text{-}C_2F_5{-}C_2F_5H]^+$, 119 (100) $[C_2F_5]^+$, 84 (27), 69 (32) $[CF_3]^+$.

Acknowledgements

This work was financially supported by Merck KGaA (Darmstadt, Germany). Solvay (Hannover, Germany) is gratefully acknowledged for donating chemicals. We acknowledge the support by the Deutsche Forschungsgemeinschaft (Core Facility GED@BI, Mi477/21-1) and we thank Prof. Dr. Lothar Weber for helpful discussions.

References

[1] A.H. Éll, J.S.M. Samec, C. Brasse, J.-E. Bäckvall, Chem. Commun. (2002) 1144–1145.

[2] X. Zhang, A. Fried, S. Knapp, A.S. Goldman, Chem. Commun. (2003) 2060–2061.

[3] V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo, B. Rieger, Angew. Chem. 120 (2008) 6090–6092 (Angew. Chem. Int. Ed. 2008, 47, 6001–6003).

[4] N. Millot, C.C. Santini, B. Fenet, J.M. Basset, Eur. J. Inorg. Chem. (2002) 3328–3335.

[5] C. Jiang, O. Blacque, T. Fox, H. Berke, Organometallics 30 (2011) 2117–2124.

[6] A. Di Saverio, F. Focante, I. Camurati, L. Resconi, T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli, A. Sironi, Inorg. Chem. 44 (2005) 5030–5041.

[7] H. Weingarten, J.S. Wagner, J. Chem. Soc. (1970) 854a.

[8] (a) J. Bader, N. Ignat'ev, B. Hoge, Inorg. Chem. 53 (2014) 7547–7553;
(b) J. Bader, B. Hoge, N. Ignatyev, M. Schulte, EP 2 621 940 B1, Merck Patent GmbH, Darmstadt, Germany, 2017;
(c) B. Hoge, J. Bader, N. Ignatyev, M. Schulte, W. Hierse, W. Wiebe, H. Willner, EP 2 621 939 B1, Merck Patent GmbH, Darmstadt, 2017.

[9] (a) B. Hoge, J. Bader, M. Schulte, N. Ignatyev, EP 2 513 123 B1, Merck Patent GmbH, Darmstadt, Germany, 2011;
(b) J. Bader, N. Ignat’ev, B. Hoge, Eur. J. Inorg. Chem. (2017), http://dx.doi.org/10.1002/ejic.201701375.

[10] Data for [Cs{[18]crown-6}][$P(C_2F_5)_2F_3C_2H_2NEt_2$]: colourless crystal, M_r = 1085.71 g mol^{-1}, monoclinic space group C2/c, a = 2697.2(1) pm, b = 1945.0(1) pm, c = 1914.3(1) pm, β = 114.60(1)°, V = 9130.9(1) × 10^8 pm^3, Z = 8, ρ_{calcd} = 1.580 g cm^{-3}, F(000) = 4432; 196131 reflections up to Θ = 30 collected, 13309 independent reflections, thereof 11190 with $I > 2\sigma(I)$, 550 parameters. R-values: R_1 = 0.028 for refl. with $I > 2\sigma(I)$, wR_2 = 0.070 for all data.

[11] SHELX-97: G. M. Sheldrick, Acta Cryst. 2008 A64, 112–122.