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ARTICLE

Fluorotrimethyl[(*Z*)-pentafluoropropen-1-yl]phosphorane: Structure, Bonding, and Reactivity

Mira Keßler,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] and Berthold Hoge*[a]

Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract. In this contribution we report on fluorotrimethyl[(*Z*)-pentafluoropropen-1-yl]phosphorane as a phosphorus based fluorinating reagent. Its solid state structure can be described as a trigonal bipyramid featuring elongated axial bonds due to the formation of a 3-center 4-electron bond. Abstraction of the fluoride ion leads to a shortening of the axial P–C bond. Thus the title compound can be utilized for substitution of bromine with fluorine and for the transfer of fluoride ions onto electrophilic compounds. Reaction with $Sn(C_2F_5)_2Br_2$ afforded salt $[P(CH_3)_3(C_3F_5)]_2[Sn(C_2F_5)_2F_4]$. When fluorotrimethyl[(*Z*)-pentafluoropropen-1-yl]phosphorane was treated with $P(C_2F_5)_2F$ the primarily produced anion is sufficiently nucleophilic to attack the propenyl group of the cation in β-position to the phosphorus atom to yield zwitterionic $[Me_3PCF{=}C(CF_3){-}PF_3(C_2F_5)_2]$.

Introduction

Metal fluorides are commonly used fluorinating agents although their application is limited due to their low solubility in most organic solvents, often requiring high temperatures and long reaction times, and the hardly avoidable formation of by-products.[1] In some cases the solubility can be enhanced by addition of crown ethers, especially 18-crown-6 when the size of the respective cations match the cavity of the crown ether.[2] To overcome the obstacle of low solubility saline fluorides with organic cations were designed. Thus tetraalkylammonium fluorides represent a widely used member of this class. Unfortunately, they are hygroscopic and decompose upon drying.[1] Furthermore tetramethylammonium fluoride reacts at room temperature with some solvents such as acetonitrile and dichloromethane forming $[HF_2]^-$ salts.[3]

Today various reasonably stable and easy to handle fluorinating reagents for different applications are commercially available, as depicted in Figure 1.

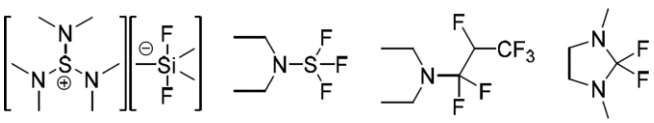
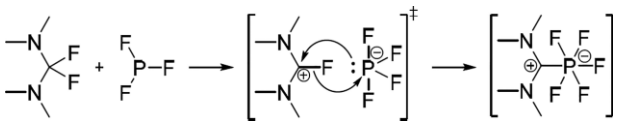


Figure 1. TASF, DAST, Ishikawa's reagent, and DFI from left to right.

Tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) as well as diethylaminosulfur trifluoride (DAST) are relatively mild fluorinating reagents both prepared from sulfur tetrafluoride.[4–6] TASF has mainly been employed for the substitution of other halogen atoms and the cleavage of Si–O bonds. As this salt can be prepared under anhydrous conditions it is suitable for fluorinating moisture-sensitive compounds.[4,7] DAST, as well as diethyl(1,1,2,3,3,3,-hexafluoropropyl)amine (Ishikawa's reagent) and 2,2-difluoro-1,3-dimethylimidazolidine (DFI) have been successfully used for the deoxyfluorination of organic molecules.[5,8] DFI and bis(dimethylamino)-difluoromethane have been deployed for fluorination of various inorganic species.[9,10] Bis(dimethylamino)difluoromethane reacts with trifluorophosphane with formation of $[(Me_2N)_2C\text{-}PF_5]$. It was assumed that this process involved a carbenium tetrafluorophosphate(III) (Scheme 1).



Scheme 1. Reaction of bis(dimethylamino)difluoromethane with trifluorophosphane.[10]

There are some phosphorus based fluorinating agents as well. Due to the high nucleophilicity of the naked fluoride anion a covalent bond can commonly be observed in phosphonium fluorides, such as those shown in Figure 2.

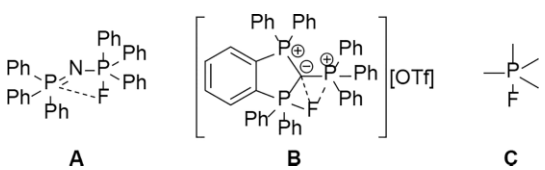


Figure 2. Phosphorus based fluorinating reagents **A**–**C**.[11–13]

Although the fluorine atoms in **A** and **B** display a relatively short P–C bond length (182.0 and 177.6 pm), weak contacts to a second P atom (264.6 and 251.8 pm) were observed. The

* 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

arrangement at those phosphorus atoms is distorted trigonal bipyramidal, whereby the axial P–C bonds are significantly longer than the equatorial bonds due to a 3-center 4-electron bonding.[11,12] Although tetramethylphosphonium fluoride (**C**) shows a salt structure in the solid state with a tetrahedral arrangement at the phosphorus atom, its gas phase structure resembles a trigonal bipyramid with a distinct P–F bond.[13]

Fluorotrimethyl[(*Z*)-pentafluoropropen-1-yl]phosphorane (**1**) is reported to act as a fluorinating agent in the transformation of acyl chlorides into acyl fluorides.[14] Hexafluoroacetone inserts into the P–F bond and is released again by treatment with trifluoroborane, leading to the formation of trimethyl[(*Z*)-pentafluoropropen-1-yl]phosphonium tetrafluoroborate.[14] Phosphorane **1** contains three electron donating methyl substituents and contrary to the previously mentioned phosphorus based fluorinating reagents (**A**–**C**) one electron deficient pentafluoropropenyl substituent. The introduction of an electron withdrawing group should lead to a more stable P–F bond and therefore to more selective reactions as well. The aim of this research was to further elucidate the fluorinating abilities of phosphorane **1** as well as the structural characterization in the solid state and its corresponding phosphonium salts.

Results and Discussion

Fluorotrimethyl[(*Z*)-pentafluoropropen-1-yl]phosphorane (**1**) was prepared by treatment of trimethylphosphane with hexafluoropropene according to literature procedures.[14,15] A suitable crystal for X-ray diffraction was obtained through in situ crystallization. Phosphorane **1** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure is shown in Figure 3.

As expected the arrangement can be regarded as a slightly distorted trigonal bipyramid, the τ_5 value[16] is 0.9. The fluorine atom and the propenyl group occupy the axial positions. The P–C bond between the phosphorus atom and the propenyl group is significantly longer than the P–C bonds between the phosphorus atom and the methyl groups, which well agrees with structural details of similar phosphoranes previously mentioned (**A**–**C**) (Table 1).

The P–F bond in phosphorane **1** is shorter than in phosphoranes **A**–**C**. This structural characteristic clearly underlines the prominent electron withdrawing activity of the perfluoropropenyl group and the stability of the P–F bond. In accordance to this the P–C bond to the axial substituent is significantly longer than in the other phosphoranes which indicates a higher sensitivity towards substitution. This is convincingly illustrated by the reaction of **1** with chlorine affording chloropentafluoropropene.[14] Phosphorane **1** readily hydrolyzes in the presence of water yielding pentafluoropropene whereas tetramethylphosphonium fluoride forms hydrates under these conditions.[13] Besides pentafluoropropene, trimethylphosphane oxide and difluorotrimethylphosphorane, all volatile compounds, are formed upon hydrolysis. Because of the reluctance to hydrate formation phosphorane **1** is an attractive fluorinating agent for moisture sensitive substrates.

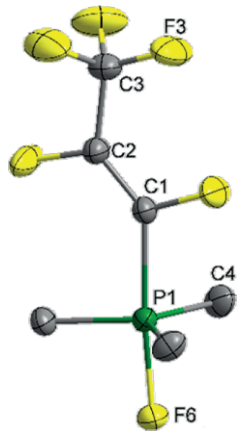
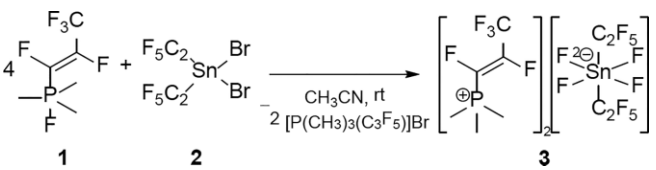


Figure 3. Molecular structure of $P(CH_3)_3(C_3F_5)F$ (**1**). Thermal ellipsoids are shown at 50 % probability. Hydrogen atoms are omitted. The asymmetric unit contains three molecules, two of these are disordered (ratio 59:41 and 95:5). Only the non-disordered molecule is shown for clarity. Selected bond lengths /pm and angles /°: P1–F6 173.30(6), P1–C1 194.50(8), P1–C4 180.97(9), C1–C2 132.7(1), C2–C3 150.0(1), C3–F3 131.0(1), C4–P1–C1 89.84(4).

The reaction of an excess of phosphorane **1** with dibromobis(pentafluoroethyl)stannane (**2**) led to the substitution of both bromine atoms by fluorine accompanied by the addition of two extra fluoride ions. Bis{trimethyl[(*Z*)-pentafluoropropen-1-yl]phosphonium} tetrafluorobis(pentafluoroethyl)stannate (**3**) was formed in addition to trimethyl[(*Z*)-pentafluoropropen-1-yl]phosphonium bromide as a byproduct (Scheme 2). The latter is easily removed by washing and recrystallizing from acetonitrile.



Scheme 2. Reaction of phosphorane **1** with stannane **2** to stannate **3**.

Suitable crystals for an X-ray diffraction study were grown from acetonitrile. Stannate **3** crystallizes with one molecule of acetonitrile per sum formula in the monoclinic space group *C*2/*c*. The molecular structure is shown in Figure 4.

Table 1. Selected bond lengths *d* in $P(CH_3)_3(C_3F_5)F$ (**1**), $Ph_3P{=}N{-}PPh_3F$ (**A**), **B**, and $P(CH_3)_4F$ (**C**).

	1	**A** [12]	**B** [11]	**C** [13] a)
d(P–C_{ax}) /pm	194.50(8)	188.7(2)	187.8(2)	188.4(8)
d(P–C_{eq}) /pm	180.97(9)	183.8(2)	179.1(3)	182.6(4)
	181.36(9)	184.0(2)		
	180.35(9)			
d(P–F) /pm	173.30(6)	181.98(13)	176.6(1)	175.3(6)

a) Gas phase structure.

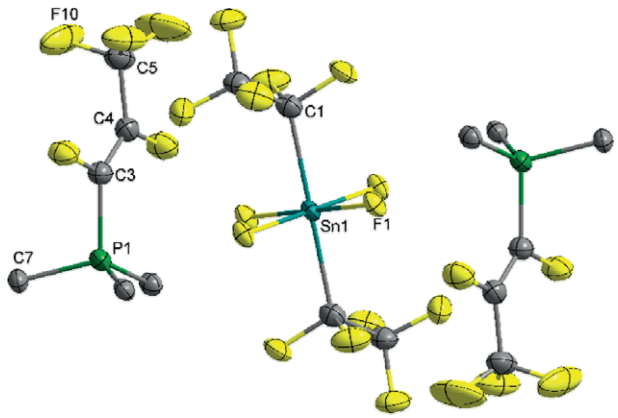
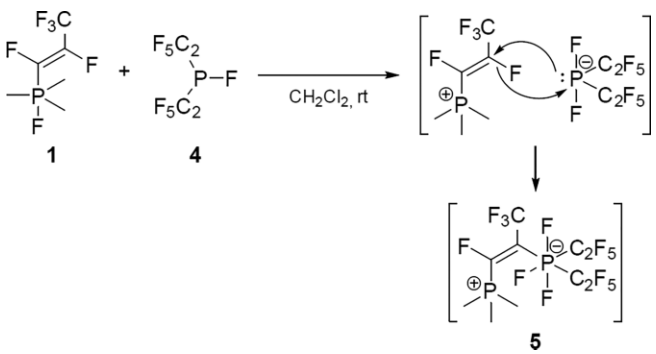


Figure 4. Molecular structure of $[P(CH_3)_3(C_3F_5)]_2[Sn(C_2F_5)_2F_4]\cdot CH_3CN$ (**3**). Thermal ellipsoids are shown at 50 % probability. Hydrogen atoms and acetonitrile are omitted. Selected bond lengths / pm and angles /°: P1–C7 179.0(3), P1–C3 182.1(4), C3–C4 130.6(5), C4–C5 149.9(5), C5–F10 132.0(5), Sn1–F1 199.5(2), Sn1–C1 223.1(4), C7–P1–C3 104.7(2).

The structural details of the anion are virtually identical to those found in the Cs salt.[17] The two pentafluoroethyl groups are in *trans* position although according to NMR spectra both *trans* and *cis* isomers are present in solution.

The reaction of phosphorane **1** with fluorobis(pentafluoroethyl)phosphane (**4**) takes a different course resulting in the formation of a zwitterion composed by a phosphonium and a phosphate(V) ion. It is reasonable to assume that after an initial fluoride transfer from phosphorane **1** to phosphane **4** the transiently formed phosphate(III) salt undergoes a nucleophilic substitution in β-position to the phosphorus atom of the cation (Scheme 3). This is similar to the reaction of 2,2-difluorobis-(dialkylamines) with phosphanes mentioned earlier.



Scheme 3. Reaction of phosphorane **1** and phosphane **4** to zwitterion **5**.

The phosphorus atom of the phosphate moiety gives rise to a multiplet at –149.9 ppm in the ^{31}P NMR spectrum which was simulated using the fluorine phosphorus coupling constants determined via ^{19}F NMR spectroscopy (Figure 5).

Suitable crystals for an X-ray diffraction study were grown in dichloromethane. Three molecules of phosphate **5** crystallize with one molecule of dichloromethane in the triclinic space group $P\bar{1}$. The molecular structure is shown in Figure 6.

While in the solid state structure only the *Z* isomer was observed, an NMR spectroscopic investigation of the crude product in acetonitrile revealed the formation of the corresponding *E* isomer to an amount of 9 %. This points to the formation of an intermediate species where free rotation along the C–C bond is possible.

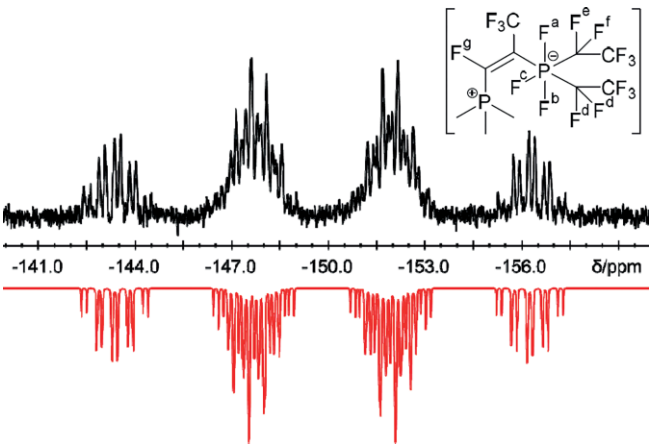


Figure 5. Section of the ^{31}P NMR spectrum highlighting the signal of the phosphate unit of **5** in CD_3CN (experimental above, simulation[18] below). $^1J(F^{a,b,c},P)$ = 860, 829, 916, $^2J(F^{d,e,f},P)$ = 93, 98, 101, $^3J(F^g,P)$ = 33 Hz.

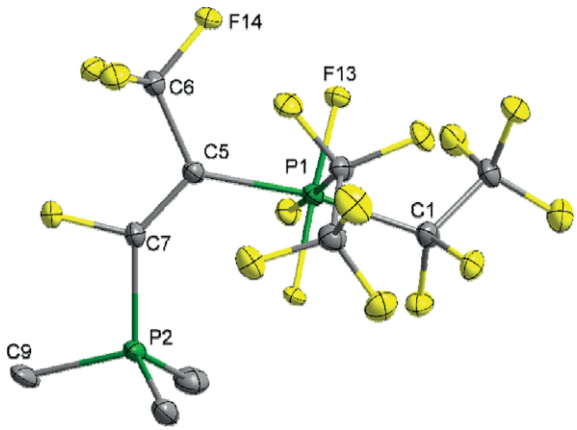


Figure 6. Molecular structure of $[Me_3PCF{=}C(CF_3)\text{-}PF_3(C_2F_5)_2]\cdot 1/3\ CH_2Cl_2$ (**5**). Thermal ellipsoids are shown at 50 % probability. Hydrogen atoms and dichloromethane are omitted. The asymmetric unit contains three molecules of which only one is shown for clarity. Selected bond lengths /pm and angles /°: P2–C9 177.6(4), P2–C7 184.4(4), C7–C5 132.8(4), C5–C6 152.8(5), C6–F14 132.3(4), C5–P1 191.1(3), P1–F13 160.5(2), P1–C1 194.5(3), C9–P2–C7 104.5(2).

The P–C bond between phosphorus and propenyl group is significantly shorter in both of the phosphonium salts, **3** [182.1(4) pm] and **5** [184.4(4) pm], than in phosphorane **1** [194.50(8) pm]. When the fluoride ion of the F–P–C 3-center 4-electron bond in **1** is removed an increase of the P–C bond order occurs.

Conclusions

The electron withdrawing character of the pentafluoropropenyl group strengthens the P–F bond of phosphorane **1** which mitigates its reactivity in comparison to other phosphoranes.

On the other hand the P–C bond to the propenyl group is more labile towards substitution than non-electron withdrawing substituents. Therefore phosphorane **1** hydrolyzes upon contact with water to volatile compounds instead of forming hydrates. It proved to be a valuable reagent for substitution of bromine with fluorine and for transfer of fluoride ions to electrophilic centers as demonstrated by the reaction with stannane **2**. In cases where the primarily generated anion is sufficiently nucleophilic an additional reaction was observed. The anion attacked the propenyl group in β-position to the phosphorus atom, inserting into the C–F bond as illustrated for the reaction between phosphorane **1** and phosphane **4** which led to the formation of zwitterionic phosphonium phosphate **5**.

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 N_2 atmosphere using Schlenk techniques. NMR spectra were recorded on a Bruker Model Avance III 500 HD spectrometer (^{1}H 500.0 MHz; ^{13}C 125.8 MHz; ^{19}F 470.7 MHz; ^{31}P 202.5 MHz) and a Bruker Model Avance 600 (^{13}C 150.9 MHz; ^{119}Sn 223.8 MHz). Positive shifts are downfield from the external standards $Si(CH_3)_4$ (^{1}H, ^{13}C), CCl_3F (^{19}F), H_3PO_4 (^{31}P), $Sn(CH_3)_4$ (^{119}Sn). The NMR spectra were recorded in the indicated deuterated solvent. 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 Supernova diffractometer using Mo-K_α (λ = 0.71073 Å) radiation. The crystals were kept at 100.0(1) K during data collection if not mentioned otherwise. Using Olex2,[19] the structures were solved with the ShelXT[20] structure solution program using Intrinsic Phasing and refined with the ShelXL[21] refinement package using Least Squares minimization. Dibromobis(pentafluoroethyl)stannane (**2**)[22] and fluorobis(pentafluoroethyl)phosphane (**4**)[23] were prepared as described in the literature. Crystallographic data and structure refinement results are summarized in Table 2.

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-1980903 (phosphorane **1**), CCDC-1980904 (stannate **3**), and CCDC-1980905 (phosphate **5**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Table 2. Crystal data and refinement characteristics for phosphorane **1**, stannate **3** and phosphate **5**.

	$P(CH_3)_3(C_3F_5)F$ [a]	$[P(CH_3)_3(C_3F_5)]_2[SnF_4(C_2F_5)_2]\cdot CH_3CN$ [b]	$3[Me_3PC{=}C(CF_3){-}PF_3(C_2F_5)_2]\cdot CH_2Cl_2$ [c]
Empirical formula	$C_6H_9F_6P$	$C_{18}H_{21}F_{24}NP_2Sn$	$C_{31}H_{29}F_{51}P_6Cl_2$
M /g·mol^{-1}	226.10	887.99	1627.26
T /K	94.0(5)	100.0(1)	100.0(1)
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a /pm	895.154(11)	2450.71(11)	926.46(4)
b /pm	1119.705(14)	892.74(4)	1574.51(12)
c /pm	1499.68(2)	1406.98(5)	2035.31(12)
α /°	80.4025(11)	90	69.344(6)
β /°	88.6259(10)	95.677(4)	89.942(4)
γ /°	69.4826(11)	90	75.825(5)
V /10^6·pm^3)	1387.12(3)	3036.2(2)	2681.6(3)
Z	6	4	2
ρ_{calc} /g·cm^{-3}	1.624	1.925	2.015
μ /mm^{-1}	0.343	1.098	0.508
F(000)	684.0	1728.0	1596.0
Crystal size /mm^3	0.59 × 0.34 × 0.28	0.15 × 0.09 × 0.03	0.34 × 0.1 × 0.08
Radiation /Å	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)
2Θ range for data coll. /°	5.5 to 72.93	5.8 to 65.46	4.16 to 65.01
Index range	$-14 \le h \le 14$ $-18 \le k \le 18$ $-24 \le l \le 24$	$-35 \le h \le 35$ $-13 \le k \le 12$ $-20 \le l \le 21$	$-13 \le h \le 13$ $-23 \le k \le 23$ $-30 \le l \le 30$
Total data collection	108036	23694	66734
Unique data	13136 [R_{int} = 0.0284, R_{sigma} = 0.0158]	5250 [R_{int} = 0.0615, R_{sigma} = 0.0661]	22201 [R_{int} = 0.0539, R_{sigma} = 0.0748]
Observed data [$I > 2\sigma(I)$]	11156	3701	14109
Data / restraints / parameters	13136 / 442 / 600	5250 / 0 / 223	22201 / 0 / 821
Goodness of fit on F^2	1.028	1.037	0.982
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0350 / 0.0941	0.0502 / 0.1029	0.0504 / 0.1276
R_1 / wR_2 [all data]	0.0432 / 0.0989	0.0843 / 0.1181	0.0865 / 0.1388
$\Delta\rho_{max/min}$ /e·Å^{-3}	0.53 / –0.46	1.51 / –0.84	1.09 / –0.80

a) Crystal was grown in situ by generating manually a crystal seed inside of a sealed capillary and subsequent slow chilling. Two of the three crystallographic independent molecules are disordered in ratios 59:41 and 95:5, respectively, by a rotation around the P–C bond, rigid bond restraints were applied. b) CH_3CN is disordered on a twofold axis. c) Crystal was a pseudo-merohedral twin, component 2 rotated by 180° around [100], ratio 1:1. Both domains were taken into account during data integration and refinement.

Synthesis of Phosphorane 1:[14,15] Trimethylphosphane (1.48 g, 19.4 mmol) was stirred under an atmosphere of hexafluoropropene (30 mmol) for 20 h. During this period of time the colorless solution was gently warmed from –70 °C to room temperature. All volatile compounds with a vapor pressure above 5 mbar were removed in vacuo. The crude product was purified by vacuum distillation. Phosphorane **1** (4.20 g, 18.6 mmol, 96 %) was obtained as a colorless liquid. To obtain a crystal suitable for X-ray diffraction it was sealed in a capillary and chilled to 223 K with 1 K·h^{-1} and afterwards to 94 K with 50 K·h^{-1}. **^{1}H NMR** (CD_2Cl_2, 298 K): δ = 2.0 [dd, ^2J(H,P) = 17, ^3J(H,F) = 6 Hz, 9 H]. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 298 K) : δ = 18.6 [dddd, ^1J(C,P) = 121, ^2J(C,F) = 41, ^3J(C,F) = 4, ^4J(C,F) = 4 Hz, 3 C, CH_3], 119.3 [qd, ^1J(C,F) = 273, ^3J(C,P) = 39 Hz, 1 C, CF_3], 141.2 [dm, ^1J(C,F) = 232 Hz, 1 C, PC**C**], 172.9 [dm, ^1J(C,F) = 306, ^1J(C,P) = 96 Hz, 1 C, PCF]. **^{19}F NMR** (CD_2Cl_2, 298 K): δ = –168.5 [ddq, ^3J(F,F) = 130, ^3J(F,P) = 10, ^3J(F,F) = 10 Hz, 1 F, PCCF], –143.0 [dqd, ^3J(F,F) = 130, ^4J(F,F) = 23, ^2J(F,P) = 14 Hz, 1 F, PCF], –67.6 [dd, ^4J(F,F) = 23, ^3J(F,F) = 10 Hz, 3 F, CF_3], 20.1 [d, ^1J(F,P) = 539 Hz, 1 F, PF]. **^{31}P NMR** (CD_2Cl_2, 298 K): δ = –76.2 [dm, ^1J(F,P) = 539 Hz, 1 P] ppm.

Synthesis of Stannate 3: Phosphorane **1** (913 mg, 4.04 mmol), stannane **2** (413 mg, 0.80 mmol) and acetonitrile (20 mL) were combined via condensation. After thawing of the reaction mixture a colorless solid was formed immediately. After 2 h the orange supernatant was removed and the residue was washed with acetonitrile (3 × 3 mL). After recrystallization from acetonitrile (30 mL) stannate **3** (511 mg, 603 µmol, 75 %) was obtained as a colorless solid. Suitable crystals for X-ray diffraction were obtained by recrystallization from acetonitrile. Two isomers in a ratio of 1.0:2.5 (*cis*:*trans* for the anion) were observed. Note: due to low solubility in acetonitrile the least intense signals could not be observed or resolved in the ^{13}C and ^{119}Sn NMR spectra. **$[P(CH_3)_3(C_3F_5)]^+$ cation**: **^{1}H NMR** (CD_3CN, 298 K): δ = 2.3 [d, ^2J(H,P) = 16 Hz, 9 H]. **^{13}C{^{1}H} NMR** (CD_3CN, 298 K): δ = 7.2 [dd, ^1J(C,P) = 54, ^3J(C,F) = 3 Hz, 3 C, CH_3], 117.8 [overlap with solvent signal, ^1J(C,F) = 274 Hz, 1 C, CF_3], 145.3 [ddd, ^1J(C,F) = 282, ^1J(C,P) = 97, ^2J(C,F) = 50 Hz, 1 C, PCF], 149.3 [dm, ^1J(C,F) = 262 Hz, 1 C, PC**C**]. **^{19}F NMR** (CD_3CN, 298 K): δ = –156.8 [ddq, ^3J(F,F) = 142, ^2J(F,P) = 62, ^4J(F,F) = 21 Hz, 1 F, PCF], –151.6 [ddq, ^3J(F,F) = 142, ^3J(F,P) = 9, ^3J(F,F) = 9 Hz, 1 F, PCCF], -69.7 [dd, ^4J(F,F) = 21, ^3J(F,F) = 9 Hz, 3 F, CF_3]. **^{31}P NMR** (CD_3CN, 298 K): δ = 30.8 (m, 1 P). ***cis*-$[Sn(C_2F_5)_2F_4]^{2-}$ anion**: **^{13}C NMR** (CD_3CN, 298 K): δ = –122.8 [qm, ^1J(C,F) = 284 Hz, 2 C, CF_3]. **^{19}F NMR** (CD_3CN, 298 K): δ = –146.9 [t, ^2J(F,F) = 33 Hz, 2 F, Sn-F], –137.9 [t, ^2J(F,F) = 33 Hz, 2 F, Sn-F], –124.1 (s, 4 F, CF_2), –83.4 (s, 6 F, CF_3, overlap with *trans* isomer). **^{119}Sn NMR** (CD_3CN, 298 K): δ = ca. –680 (overlap with *trans* isomer). ***trans*-$[Sn(C_2F_5)_2F_4]^{2-}$ anion**: **^{13}C NMR** (CD_3CN, 298 K): δ = –122.8 [qm, ^1J(C,F) = 284 Hz, 2 C, CF_3]. **^{19}F NMR** (CD_3CN, 298 K): δ = –143.1 [s, ^1J(F,Sn) = 2545/2670 Hz, 4 F, Sn-F], –124.2 [quin, ^3J(F,F) = 7, ^2J(F,Sn) = 419/436 Hz, 4 F, CF_2], –83.4 (s, 6 F, CF_3, overlap with *cis* isomer). **^{119}Sn NMR** (CD_3CN, 298 K): δ = –678.8 [quinquinm, ^1J(F, Sn) = 2670, ^2J(F, Sn) = 436 Hz, 1 Sn] ppm. **MS** (ESI, neg) *m*/*z* = 414.8 ($[Sn(C_2F_5)_2F_3]^-$, 100 %). **MS** (ESI, pos) *m*/*z* = 207.0 ($[P(CH_3)_3(C_3F_5)]^+$, 100 %), 227.0 ($[P(CH_3)_3(C_3F_5)\cdot HF]^+$, 30 %). Melting point: 200–206 °C (decomposition). **EA**: $C_{16}H_{18}F_{24}P_2Sn$: C 22.68 (calcd. 22.69), H 2.10 (calcd. 2.14) %.

Synthesis of Phosphate 5: Phosphorane **1** (600 mg, 2.65 mmol), phosphane **4** (450 mg, 1.56 mmol) and dichloromethane (10 mL) were combined via condensation. After thawing of the reaction mixture a colorless solid was formed immediately. After 1 h the colorless supernatant was removed and the residue was dried in vacuo. Phosphate **5** (742 mg, 1.44 mmol, 93 %) was obtained as a colorless solid. Suitable crystals for X-ray diffraction were obtained by recrystallization from dichloromethane. Two isomers in a ratio of 10.2:1.0 (*Z*:*E*) were observed. ***Z* isomer: ^{1}H NMR** (CD_3CN, 298 K): δ = 2.1 [d, ^1J(H,P) = 14 Hz, 9 H]. **^{13}C{^{1}H} NMR** (CD_3CN, 298 K): δ = 10.8 [qm, ^1J(C,F) = 135 Hz, 1 C, C=C**C**F_3], 54.9 [d, ^1J(C,P) = 169 Hz, 3 C, CH_3], 120.2 (m, 6 C, CF_2**C**F_3), 124.2 (m, 4 C, CF_2), 139.9 [d(broad), ^1J(C,P) ≈ 230 Hz, 1 C, C=**C**PF], 157.0 [ddm, ^1J(C,F) = 295, ^1J(C,P) = 115 Hz, 1 C, P(CH_3)$_3$**C**]. **^{19}F NMR** (CD_3CN, 298 K): δ = –118.3/–116.4 [AB spin system, ^2J(F,F) = 295, ^2J(F,P) = 101/98 Hz, 2 F, PCF_2], –115.8 [d, ^2J(F,P) = 93 Hz, 2 F, PCF_2], –83.4 [dddq, ^2J(F,P) = 105, ^3J(F,P) = 33, ^4J(F,F) = 25, ^4J(F,F) = 25 Hz, 1 F, C=CF], –82.7 (m, 3 F, CF_2C**F$_3$**), –80.3 (m, 3 F, CF_2C**F$_3$**), –79.1 (dqm, ^1J(F,P) = 916, ^4J(F,F) = 45 Hz, 1 F, PF), –61.0 [ddm, ^1J(F,P) = 829, ^4J(F,P) ≈ 37 Hz, 1 F, PF], –55.3 [dd, ^4J(F,F) = 25, ^4J(F,F) = 45 Hz, 3 F, C=CC**F$_3$**], –16.2 [dm, ^1J(F,P) = 860 Hz, 1 F, PF]. **^{19}F{^{31}P} NMR** (CD_3CN, 298 K, selective decoupling of ^{31}P phosphate moiety): δ = –118.3/–116.4 [AB spin system, ^2J(F,F) = 295 Hz, 2 F, PCF_2], –115.8 (s, 2 F, PCF_2), –83.4 [ddq, ^2J(F,P) = 105, ^4J(F,F) = 25, ^4J(F,F) = 25 Hz, 1 F, C=CF], –82.7 (m, 3 F, CF_2C**F$_3$**), –80.3 (m, 3 F, CF_2C**F$_3$**), –79.1 [qm, ^4J(F,F) = 45 Hz, 1 F, PF], –61.0 [dm, ^4J(F,P) ≈ 37 Hz, 1 F, PF], –55.3 [dd, ^4J(F,F) = 25, ^4J(F,F) = 45 Hz, 3 F, C=CC**F$_3$**], –16.2 (m, 1 F, PF). **^{19}F{^{31}P} NMR** (CD_3CN, 298 K, selective decoupling of ^{31}P phosphonium moiety): δ = –118.3/–116.4 [AB spin system, ^2J(F,F) = 295, ^2J(F,P) = 101/98 Hz, 2 F, PCF_2], –115.8 [d, ^2J(F,P) = 93 Hz, 2 F, PCF_2], –83.4 [ddq, ^3J(F,P) = 33, ^4J(F,F) = 25, ^4J(F,F) = 25 Hz, 1 F, C=CF], –82.7 (m, 3 F, CF_2C**F$_3$**), –80.3 (m, 3 F, CF_2C**F$_3$**), –79.1 [dqm, ^1J(F,P) = 916, ^4J(F,F) = 45 Hz, 1 F, PF], –61.0 [dm, ^1J(F,P) = 829 Hz, 1 F, PF], –55.3 [dd, ^4J(F,F) = 25, ^4J(F,F) = 45 Hz, 3 F, C=CC**F$_3$**], –16.2 [dm, ^1J(F,P) = 860 Hz, 1 F, PF]. **^{31}P NMR** (CD_3CN, 298 K): δ = –149.9 (m, 1 P, PF_3), 39.0 [ddez, ^2J(F,P) = 105, ^2J(H,P) = 14 Hz, 1 P, P(CH_3)$_3$]. ***E* isomer**: Due to a small proportion of the *E* isomer and overlap of the signals with those of the *Z* isomer no ^{13}C data are given. **^{1}H NMR** (CD_3CN, 298 K): δ = 2.1 (overlap with *Z* isomer, 9 H). **^{19}F NMR** (CD_3CN, 298 K): δ = –117.5 [d, ^2J(F,P) = 95 Hz, 2 F, PCF_2], –116 (overlap with *Z* isomer, 2 F, PCF_2), –84.7 [dd, ^2J(F,P) = 109, ^4J(F,F) = 132 Hz, 1 F, C=CF], –82.7 (overlap with *Z* isomer, 3 F, CF_2C**F$_3$**), –80.9 (m, 3 F, CF_2C**F$_3$**), –77.7 [d(broad), ^1J(F,P) = 886 Hz, 1 F, PF], –68.8 [ddm, ^1J(F,P) = 927, ^4J(F,F) = 132 Hz, 1 F, PF], –52.1 [d, ^4J(F,F) = 26 Hz, 3 F, C=CC**F$_3$**], –27.7 [dm, ^1J(F,P) = 863 Hz, 1 F, PF]. **^{19}F{^{31}P} NMR** (CD_3CN, 298 K, selective decoupling of ^{31}P phosphate moiety): δ = –117.5 (s, 2 F, PCF_2), –116 (overlap with *Z* isomer, 2 F, PCF_2), –84.7 [dd, ^2J(F,P) = 109, ^4J(F,F) = 132 Hz, 1 F, C=CF], –82.7 (overlap with *Z* isomer, 3 F, CF_2C**F$_3$**), 80.9 (m, 3 F, CF_2C**F$_3$**), –77.7 [s(broad), 1 F, PF], –68.8 [dm, ^4J(F,F) = 132 Hz, 1 F, PF], –52.1 [d, ^4J(F,F) = 26 Hz, 3 F, C=CC**F$_3$**], –27.7 (m, 1 F, PF). **^{19}F{^{31}P} NMR** (CD_3CN, 298 K, selective decoupling of ^{31}P phosphonium moiety): δ = –117.5 [d, ^2J(F,P) = 95 Hz, 2 F, PCF_2], –116 (overlap with *Z* isomer, 2 F, PCF_2), –84.7 [d, ^4J(F,F) = 132 Hz, 1 F, C=CF], –82.7 (overlap with *Z* isomer, 3 F, CF_2C**F$_3$**), –80.9 (m, 3 F, CF_2C**F$_3$**), –77.7 [d(broad), ^1J(F,P) = 886 Hz, 1 F, PF], –68.8 [ddm, ^1J(F,P) = 927, ^4J(F,F) = 132 Hz, 1 F, PF], –52.1 [d, ^4J(F,F) = 26 Hz, 3 F, C=CC**F$_3$**], –27.7 [dm, ^1J(F,P) = 863 Hz, 1 F, PF]. **^{31}P NMR** (CD_3CN, 298 K): δ = ca. –150 (overlap with *Z* isomer), 37.5 [dm, ^2J(F,P) = 109 Hz, 1 P, P(CH_3)$_3$] ppm. Melting point: 125–133 °C. **EA**: $C_{10}H_9F_{17}P_2$: C 23.41 (calcd. 23.36), H 1.78 (calcd. 1.76) %.

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