ChemPubSoc Europe

DOI: 10.1002/ejic.201701402

EurJIC European Journal of Inorganic Chemistry

Full Paper

Fluorinated Phosphorus Compounds

Bis(diethylamino)pentafluorophenylphosphane as Valuable Precursor for the Design of Tetrafluorophenylphosphanes, Tetrafluorophenylphosphinic and -phosphonic Acids

Christian Alter,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] and Berthold Hoge*[a]

Abstract: Facile replacement of the *p*-fluorine atom in bis(diethylamino)pentafluorophenylphosphane [$(Et_2N)_2PC_6F_5$] by organolithium derivatives LiR (R = CH_3, *n*-Bu, Ph), lithium alkoxides (R = OMe, OEt) and amides (NMe_2, NEt_2) is described. The obtained phosphanes *p*-R-C_6F_4-$P(NEt_2)_2$ are fully characterized. Their acid-catalyzed hydrolysis affords the corresponding phosphinic acids *p*-R-C_6F_4-P(O)(H)OH, which are smoothly oxidized by treatment with a mixture of DMSO/I_2 to phosphonic acids *p*-R-C_6F_4-$P(O)(OH)_2$.

Introduction

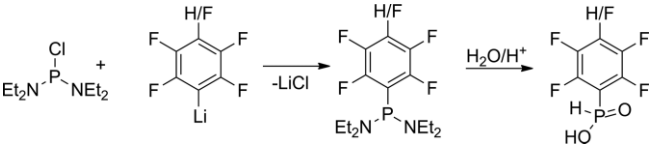
In recent years considerable interest has been spent on arylphosphinic and arylphosphonic acids. This is mainly due to the widespread applications of such species for the fabrication of functional polymers and membranes,[1] or for surface modificators and self-assembling materials.[2] Moreover they function as important ligands[3] and ingredients for rare earth metal extraction,[4] as well as for the manufacturing of flame retardants,[5] agrochemicals[6] and pharmaceuticals.[7]

In this context fluorinated derivatives are of particular importance as organofluorine functionalities significantly influence the properties of drugs or agrochemicals.[8] Polymers bearing fluorinated arylphosphonic acids as substituents are promising as materials of high stability for proton conducting membranes in fuel cells.[9] In surface modification studies, fluorinated phosphonic acids exhibit pronounced bidentate binding affinities.[10]

Despite these challenging perspectives and the vast scope of applications, protocols for the synthesis of functionalized, highly fluorinated arylphosphinic- and phosphonic acids are only rare.

Fluorinated arylphosphinic acids are generally accessible by the reaction of lithium aryls with phosphorus(III) halides or protected derivatives thereof, for example, $ClP(NEt_2)_2$. Hydrolysis of bis(amino)arylphosphanes leads to fluoroarylphosphinic acids (Scheme 1).[11] In addition to this multistep synthesis, fluoroarylphosphinic acids are accessible via several transition metal catalyzed procedures.[12]

To the best of our knowledge no widely applicable protocols are known for the synthesis of *para* substituted tetrafluoro-



Scheme 1. Syntheses of fluorinated arylphosphinic acids starting from protected chlorophosphanes.

phenylphosphinic acids. Derivatives of this type, as evidenced by the literature, are limited to pentafluorophenylphosphinic acid and 2,3,5,6-tetrafluorophenylphosphinic acid (Scheme 1).[11,13]

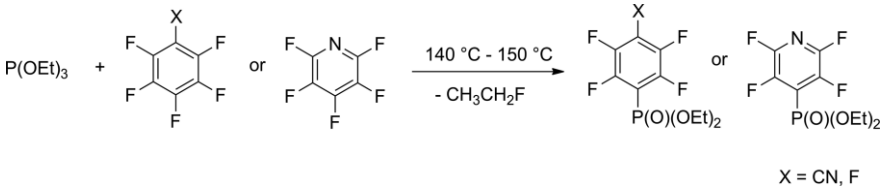
Highly fluorinated arylphosphonic acids are generally accessible by two classical synthetic routes, the Michaelis–Arbuzov and the Michaelis–Becker reaction. Both protocols yield dialkylphosphonates, which by subsequent dealkylation yield the corresponding phosphonic acid.

The Michaelis–Arbuzov reaction of trialkylphosphites with fluorinated aromatics requires very harsh conditions. This process is not selective and distillation is necessary to purify the products which are isolated in only low yields (25–30 %) (Scheme 2).[14]

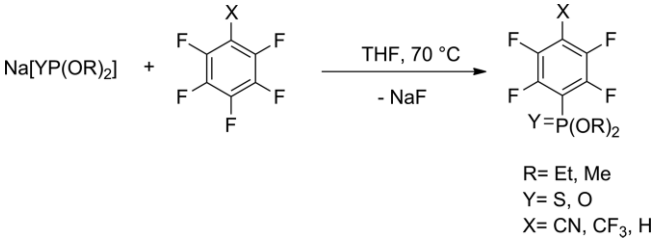
The Michaelis–Becker reaction, utilizing sodium diethylphosphites, operates under more moderate conditions (THF, 70 °C) and yields the arylphosphonates in low to good yields after distillation (10–65 %) (Scheme 3).[15]

Here we report on the functionalization of bis(diethylamino)pentafluorophenylphosphane simply by nucleophilic substitution of the *para* fluorine atom with lithium nucleophiles LiR. This discovery opens up a new avenue for the generation of *para* substituted tetrafluoroarylphosphinic and phosphonic acids. The starting material, $C_6F_5P(NEt_2)_2$, is readily available from the reaction of C_6F_5Li with $ClP(NEt_2)_2$. We improved this procedure essentially by the use of C_6F_5MgBr as the pentafluorophenyl transfer reagent, thus avoiding the labile C_6F_5Li, which tends to decompose violently at temperatures above

[a] *Universität Bielefeld, Fakultät für Chemie, Centrum für Molekulare Materialien, Universitätsstraße 25, 33615 Bielefeld, Germany*
E-mail: b.hoge@uni-bielefeld.de
https://www.uni-bielefeld.de/chemie/acii/hoge/
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.201701402.



Scheme 2. Michaelis–Arbuzov reaction of triethylphosphite with fluorinated benzene and pyridine derivatives.

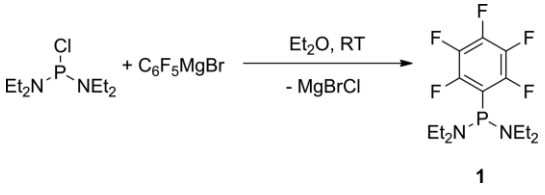


Scheme 3. Michaelis–Becker reaction of sodium diethylphosphites with fluorinated benzene derivatives.

–50 °C while C_6F_5MgBr is stable at room temperature in ethereal solution.[11] Thus $C_6F_5P(NEt_2)_2$ is now easily accessible on a multi-gram scale from cheap, commercially available precursors (PCl_3, $HNEt_2$, C_6F_5Br, Mg).[11,16]

Results and Discussion

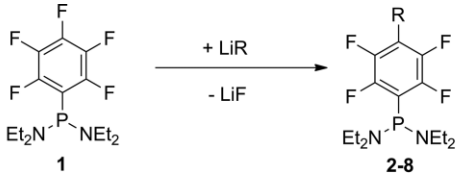
The starting material $C_6F_5P(NEt_2)_2$ (**1**) was prepared by the straightforward and cost-efficient reaction of in situ generated C_6F_5MgBr with $ClP(NEt_2)_2$ (Scheme 4).



Scheme 4. Synthesis of bis(diethylamino)pentafluorophenylphosphane **1**.

Synthesis of Tetrafluorophenylphosphane Derivatives

Bis(diethylamino)pentafluorophenylphosphane **1** is functionalized by nucleophilic replacement of the *para* fluorine atom at the ring with organolithium compounds, lithium dialkylamides and lithium alcoholates (Scheme 5). Obviously, the elimination of LiF serves as a driving force of the reaction. In our studies



R: Me (**2**), *n*Bu (**3**), OMe (**4**), OEt (**5**), NMe_2 (**6**), NEt_2 (**7**), Ph (**8**)

Scheme 5. Nucleophilic substitution of bis(diethylamino)pentafluorophenylphosphane **1**.

nucleophilic substitution with Grignard reagents failed. The results of the substitution reactions are presented in Table 1.

Table 1. Isolated yields, ^{31}P and ^{19}F NMR chemical shifts of phosphanes **1**–**8**.[a]

R	^{19}F (*ortho*) [ppm]	^{19}F (*meta*) [ppm]	^{31}P [ppm]	Yield [%]
F (**1**)	–136.4	–162.3	78.6	–
Me (**2**)	–138.5	–144.6	79.2	81
*n*Bu (**3**)	–138.3	–145.8	79.4	67
OMe (**4**)	–138.0	–158.2	78.9	66
OEt (**5**)	–138.2	–157.6	78.9	58
NMe_2 (**6**)	–138.8	–151.9	79.3	70
NEt_2 (**7**)	–138.9	–149.7	79.3	75
Ph (**8**)	–137.2	–144.9	79.5	89

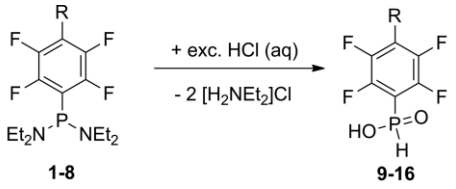
[a] Solvent: $CDCl_3$.

Lithium dialkylamides react readily with $C_6F_5P(NEt_2)_2$ at 0 °C within minutes. The reaction of alkyllithium species or LiPh takes two hours to complete, and use of LiOEt requires heating of the THF solution at 66 °C for 19 hours. All nucleophiles, except LiOMe, react selectively by substitution of the *para* fluorine atom, leaving $C_6F_5P(NEt_2)_2$ as the only impurity after separation from LiF. As with LiOMe, no reaction is observed in THF at room temperature or 66 °C. The expected substitution, however, proceeds in boiling methanol as a solvent. Prolonged reaction times lead to the cleavage of the carbon phosphorus bond and should be avoided. All newly prepared phosphanes were purified by vacuum distillation and fully characterized by means of NMR spectroscopy, IR spectroscopy and mass spectrometry. As presented in Table 1 the nature of the substituent has a dramatic influence on the ^{19}F NMR chemical shift of the adjacent *m*-fluorine atoms ranging from –162.3 ppm in phosphane **1** to –144.6 ppm in phosphane **2**.

Aminophosphanes **1**–**8** are moisture sensitive and contact with water leads to hydrolysis.

Synthesis of Tetrafluorophenylphosphinic Acids

The hydrolysis of the bis(diethylamino)phosphanes **1**–**8** with aqueous HCl to produce phosphinic acids **9**–**16** was completed within hours. After phase separation, extraction with diethyl ether and drying in vacuo the analytically pure acids were obtained in excellent yields (80–97 %) (Scheme 6). Phosphinic acid **16**, resulting from hydrolysis of phosphane **8**, is only poorly soluble in Et_2O and water and precipitates during the hydrolysis. The ^{31}P NMR resonances of the phosphinic acids **9**–**16** are observed as doublets in the range of δ = –1.0 to 10.4 ppm with a $^1J_{PH}$ coupling constant of 600 to 635 Hz, and are thus high field shifted by ca. 70 ppm in comparison to the corresponding aminophosphanes **1**–**8** (Table 2).



R: F (**9**), Me (**10**), *n*Bu (**11**), OMe (**12**), OEt (**13**) NMe_2 (**14**), NEt_2 (**15**), Ph (**16**)

Scheme 6. Hydrolysis of bis(diethylamino)phosphanes **1**–**8** with hydrochloric acid.

Table 2. Isolated yields, ^{31}P and ^{19}F NMR chemical shifts of the obtained phosphinic acids **9**–**16**.[a]

R	^{19}F (*ortho*) [ppm]	^{19}F (*meta*) [ppm]	^{31}P [ppm]	Yield [%]
F (**9**)	–135.3	–158.9	6.9 $^1J(P,H)$ = 635 Hz	80
Me (**10**)	–138.1	–141.4	9.5 $^1J(P,H)$ = 630 Hz	81
*n*Bu (**11**)	–137.7	–142.7	8.4 $^1J(P,H)$ = 627 Hz	92
OMe (**12**)	–137.3	–156.3	9.1 $^1J(P,H)$ = 627 Hz	97
OEt (**13**)	–137.4	–155.7	8.2 $^1J(P,H)$ = 627 Hz	93
NMe_2 (**14**)	–138.3	–151.6	10.2 $^1J(P,H)$ = 622 Hz	83
NEt_2 (**15**)	–138.4	–149.8	10.4 $^1J(P,H)$ = 624 Hz	96
Ph (**16**)	–138.5	–142.8	–1.0 $^1J(P,H)$ = 600 Hz	80

[a] Solvent: $CDCl_3$,**16**: $[D_6]$DMSO.

Compounds **9**–**16** are air stable and, with exception of **16**, well soluble in acetonitrile, chloroform and dichloromethane. Single crystals of phosphinic acid **12** are grown from a dichloromethane solution and subjected to an X-ray diffraction analysis (Figure 1). The phosphinic acid crystallizes in the orthorhombic space group $P2_12_12_1$. The crystal structure reveals a molecular unit with one short PO bond [d(P1–O1) = 149.5(1) pm] and one long PO bond [d(P1–O2) = 152.9(1) pm]. Intermolecular hydrogen bonding between O1 and O2′ constitutes a chain structure, similar to the one observed for pentafluorophenylphosphinic acid.[11b] The O1–O2′ distance amounts to 243.9(2) pm.

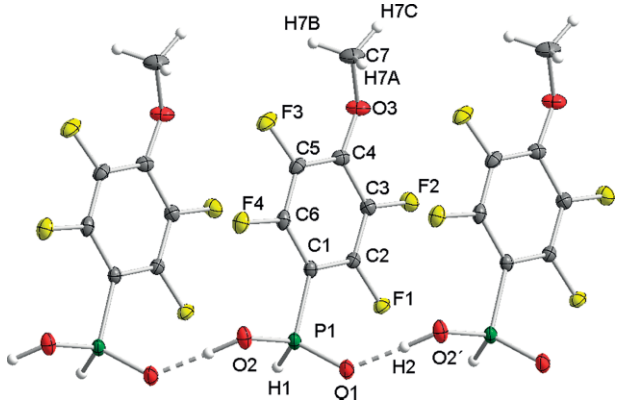
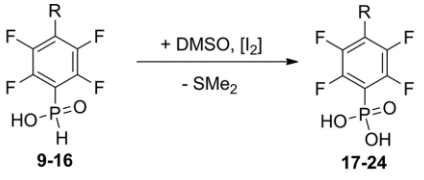


Figure 1. Molecular structure of *p*-$(CH_3O)C_6F_4P(O)(OH)H$ (**12**) in the crystal (thermal ellipsoids are set to 50 % probability).

Synthesis of Tetrafluorophenylphosphonic Acids

Mild oxidation of the phosphinic acids **9**–**16** to the corresponding phosphonic acids **17**–**24**[18] was performed by an equimolar amount of DMSO and catalytic quantities of iodine in methyl-*tert*-butyl ether (MTBE) (Scheme 7). After evaporation of the solvent and drying in vacuo analytically pure phosphonic acids are obtained in 78–99 % yield. The oxidation of phosphinic acid **16** to **24** in MTBE is very sluggish and takes more than seven days. Changing the solvent to toluene accelerates this process significantly so that completion was reached after 24 hours (Table 3). All of the presented tetrafluorophenylphosphonic acids represent hitherto unknown compounds. Alkyl esters of **20** are described in the literature and accessible by the Michaelis–Arbuzov reaction in 24 % yield.[15] The isolated compounds are not hygroscopic and well soluble in acetonitrile, methanol and DMSO. All compounds except phosphonic acid **24** are also soluble in water.



R: F (**17**), Me (**18**), *n*Bu (**19**), OMe (**20**), OEt (**21**), NMe_2 (**22**), NEt_2 (**23**), Ph (**24**)

Scheme 7. Oxidation of the phosphinic acids **9**–**16** to the phosphonic acids **17**–**24**.

Table 3. Isolated yields, ^{31}P and ^{19}F NMR chemical shifts of phosphonic acids **17**–**24** in $[D_6]$DMSO.

R	^{19}F (*ortho*) [ppm]	^{19}F (*meta*) [ppm]	^{31}P [ppm]	Yield [%]
F (**17**)	–133.0	–161.6	–2.0	95
Me (**18**)	–134.8	–143.2	–1.2	89
*n*Bu (**19**)	–133.7	–143.9	–0.7	98
OMe (**20**)	–134.5	–157.7	–1.1	99
OEt (**21**)	–134.4	–157.0	–1.0	96
NMe_2 (**22**)	–135.3	–152.1	–0.0	98
NEt_2 (**23**)	–135.1	–150.3	–0.3	94
Ph (**24**)	–133.5	–143.6	–1.5	78

Single crystals of phosphonic acid **21** were grown from toluene at –80 °C and were subjected to an X-ray diffraction study (Figure 2). The molecule displays the geometry of a distorted tetrahedron about the phosphorus atom [O3–P1–C1 = 108.3(1)°; O1–P1–O3 = 113.5(1)°; O1–P1–O2 = 114.5(1)°; O1–P1–C1 = 109.6(1)°]. For the P1–C1 distance 179.9(2) pm and for the C4–O4 distance 134.0(2) pm were measured.

Single crystals of phosphonic acid **24** were obtained from a methanol solution by slow evaporation of the solvent (Figure 3). An X-ray structural analysis exhibits two crystallographically independent molecules per asymmetric unit and one equivalent methanol per molecule. The biphenyl substituent is twisted at the phosphorus atom with P–C bond lengths of 180.7(1) pm

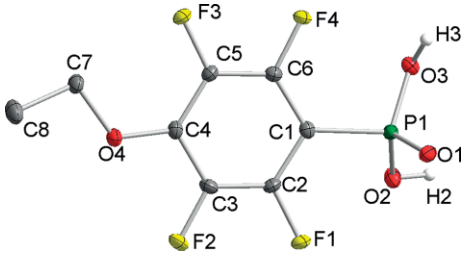


Figure 2. Molecular structure of *p*-(EtO)$C_6F_4P(O)(OH)_2$ (**21**) in the crystal (thermal ellipsoids are set to 50 % probability, aliphatic hydrogen atoms omitted).

resp. 180.5(1) pm and encloses an interplanar angle of about 53° with the tetrafluorophenylene unit. The phosphonic acid is involved in a complex system of hydrogen bridging in the solid state under participation of methanol.

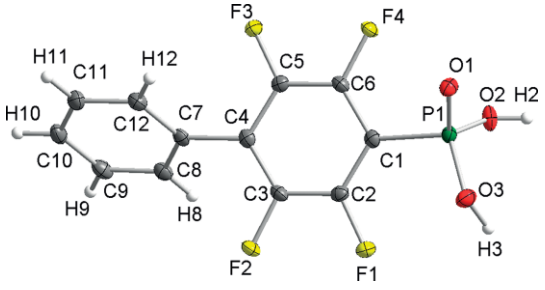


Figure 3. Molecular structure of *p*-$(C_6H_5)C_6F_4P(O)(OH)_2$ (**24**) in the crystal (thermal ellipsoids are set to 50 % probability).

Single crystals of **17** were grown from toluene, and its crystal structure was ascertained by X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/n$ (Figure 4). Similar to phenylphosphonic acid, pentafluorophenylphosphonic acid exhibits a network of hydrogen bridges in the solid state.[17] The tetra coordinated phosphorus atom unveils one short {d[P1–O1 = 149.9(1) pm]} and two long [d(P1–O2) = 154.2(1) pm, d(P1–O3) = 154.6(1) pm] PO bonds. O1 is bridged by two hydrogen atoms (H2′, H3#) from two adjacent molecules

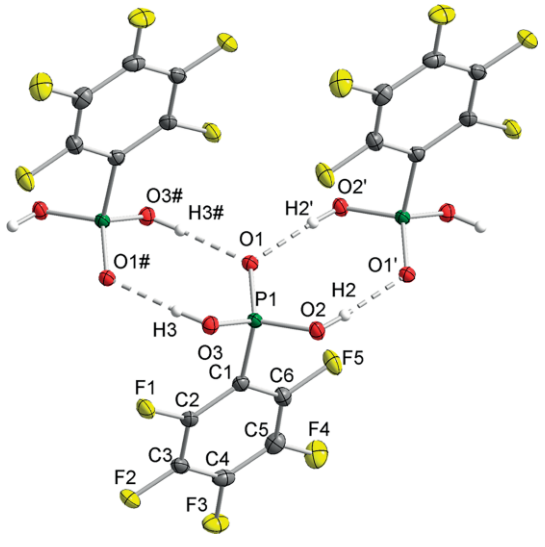


Figure 4. Molecular structure of pentafluorophenylphosphonic acid (**17**) in the crystal (thermal ellipsoids are set to 50 % probability).

whilst O2 and O3 are bridged to the oxygen atoms O1# and O1′ of the adjacent molecules. X-ray studies on crystals of phosphonic acid **19** reveal a similar hydrogen bonding network (Figure 5).

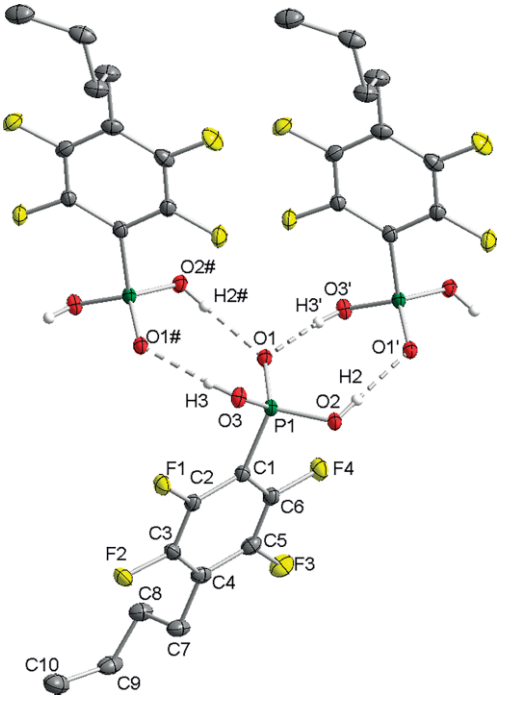


Figure 5. Molecular structure of *p*-(*n*Bu)$C_6F_4P(O)(OH)_2$ (**19**) in the crystal (thermal ellipsoids are set to 50 % probability, aliphatic hydrogen atoms omitted).

The X-ray structure of phosphonic acid **23** reveals two different molecules in the asymmetric unit (Figure 6). The nitrogen N1 is tetrahedrally coordinated by two ethyl groups, one aryl moiety and hydrogen atom H1 [C4–N1–C7 = 112.6(1)°; C4–N1–C9 = 113.1(1)°; C7–N1–C9 = 110.0(1)°]. Thereby, protons H2 and H3 have an atomic occupancy of 50 % each. In contrast to this zwitterionic ammonium hydrogenphosphonate structure, N2 of the second molecule remained nonprotonated [C14–N2–C17 = 114.8(1)°; C14–N2–C19 = 119.5(1)°; C19–N2–C17 = 116.0(1)°].

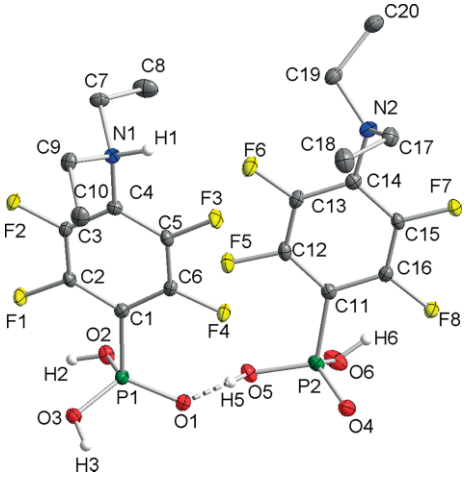


Figure 6. Molecular structure of *p*-$(Et_2N)C_6F_4P(O)(OH)_2$ (**23**) in the crystal (thermal ellipsoids are set to 50 % probability, aliphatic hydrogen atoms omitted).

Conclusions

We reported a straightforward synthesis for novel tetrafluorophenylphosphanes, phosphinic acids and phosphonic acids. The starting material $C_6F_5P(NEt_2)_2$ was prepared by the reaction of C_6F_5MgBr with $ClP(NEt_2)_2$. Nucleophilic substitution of the *para* fluorine atom was achieved with seven different lithium nucleophiles (MeLi, *n*BuLi, MeOLi, EtOLi, Me_2NLi, Et_2NLi and PhLi) to furnish novel functionalized tetrafluorophenylphosphanes **1**–**8**. The corresponding phosphinic acids **9**–**16** are easily accessible via hydrolysis with hydrochloric acid. Subsequent oxidation affords the corresponding phosphonic acids **17**–**24**.

Experimental Section

The starting material $ClP(NEt_2)_2$[16] was synthesized as described in the literature. All other chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed throughout all experiments. Non-volatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. The crystal data were collected on a Rigaku Supernova diffractometer at 100 K using Mo-K_α or Cu-K_α radiation. All non-hydrogen atoms were refined anisotropically, all donor hydrogen atoms were refined isotropically. Details of the X-ray investigation are given in the Supporting Information. IR spectra were recorded with a Bruker Alpha FTIR spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with an ATR unit with a diamond crystal for liquids and solids. The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer (^{31}P 121.5 MHz; ^{19}F 282.4 MHz; ^{13}C 75.5 MHz; ^{1}H 300.1 MHz) with positive shifts being downfield from the external standards [TMS (^{13}C;^{1}H), CCl_3F (^{19}F); 85 % H_3PO_4 (^{31}P)]. 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. EI mass spectra were recorded using an Autospec Xmagnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI or CI source. Melting points were measured on a Mettler Toledo Mp70 Melting Point System.

CCDC 1586050 [for *p*-$(CH_3O)C_6F_4P(O)(OH)H$], 1586051 [for $C_6F_5P(O)(OH)_2$], 1586052 [for *p*-$(nBu)C_6F_4P(O)(OH)_2$], 1586053 [for *p*-$(C_2H_5O)C_6F_4P(O)(OH)_2$], 1586054 [for $(Et_2N)C_6F_4P(O)(OH)_2$·*p*-$(Et_2NH)C_6F_4P(O)_2(OH)$·$3H_2O$], and 1586055 [for *p*-$(C_6H_5)C_6F_4P(O)(OH)_2$·MeOH] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of Bis(diethylamino)phosphanes

$C_6F_5P(NEt_2)_2$ (1): A sample of magnesium turnings (8.00 g; 330 mmol) was suspended in diethyl ether (400 mL). The suspension was stirred and C_6F_5Br (43.0 g; 175 mmol), dissolved in diethyl ether (100 mL), was slowly added and the resulting suspension refluxed for two hours. After the solution was cooled to room temperature $ClP(NEt_2)_2$ (36.8 g; 175 mmol), dissolved in diethyl ether (200 mL), was added dropwise at 0 °C. The solution was stirred at room temperature for 18 h. After filtration and removal of the solvent the raw product was distilled in dynamic vacuo to yield 46.5 g of $C_6F_5P(NEt_2)_2$ (b.p. = 78.0 °C; 136 mmol; 80 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.06 [t, ^{3}J(H,H) = 7 Hz, 12 H, CH_3], 3.06 [dq, ^{3}J(P,H) = 10, ^{3}J(H,H) = 7 Hz, 8 H, CH_2] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –136.4 [m, ^{3}J(P,F) = 26, J(F,F) = 13 Hz, 2 F, CF-*ortho*], –155.5 (m, 1 F, CF-*para*), –162.3 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 78.6 (m, 1 P, P) ppm.

***p*-$(CH_3)C_6F_4P(NEt_2)_2$ (2):** A sample of bis(diethylamino)pentafluorophenylphosphane (5.00 g; 14.6 mmol) was dissolved in THF (50 mL) and methyllithium (9.1 mL; 1.6 M in Et_2O, 14.6 mmol) was added dropwise at –80 °C. After stirring for two hours the solvent was evaporated and the crude product condensed off in dynamic vacuo at 350 °C. Distillation in dynamic vacuo yielded 4.00 g of the product (b.p. = 65.0 °C; 11.8 mmol; 81 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.06 [t, ^{3}J(H,H) = 7 Hz, 12 H, CH_3], 2.24 [pseudo q, J(H,F/P) = 2 Hz, 3 H, CH_3], 3.07 [dq, ^{3}J(P,H) = 10, ^{3}J(H,H) = 7 Hz, 8 H, CH_2] ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, r.t.): δ = 7.7 (m, CH_3), 14.9 [d, ^{3}J(P,C) = 3 Hz, CH_3], 44.3 [dt, ^{2}J(P,C) = 19, ^{5}J(F,C) = 1 Hz, CH_2] ppm. $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, r.t.): δ = 7.7 [qd, ^{1}J(C,H) = 132, ^{5}J(P,C) = 1 Hz, CH_3], 115.3 [qd, ^{2}J(C,H) = 6, ^{4}J(P,C) = 2 Hz, C-CH_3], 119.0 [d, ^{1}J(P,C) = 46 Hz, C-P], 145.1 [dq, ^{3}J(P,C) = 4, ^{3}J(C,H) = 2 Hz, CF], 145.4 [dm, ^{2}J(P,C) = 12 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.5 (m, 2 F, CF-*ortho*), –144.6 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 79.2 (m, 1 P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2968 (w), 2931 (w), 2864 (w), 1580 (w), 1441 (s), 1375 (m), 1360 (shoulder, w), 1292 (m), 1253 (m), 1198 (m), 1115 (m), 1098 (w), 1060 (m), 1027 (m), 1014 (s), 974 (w), 927 (m), 904 (s), 787 (m), 722 (w), 668 (m), 642 (w), 605 (w), 580 (w), 502 (w), 478 (w), 440 (w), 418 (w) cm^{-1}. MS (EI, 70 eV, pos.): *m/z* (%) = 338.0 (17) $[M]^{\cdot+}$, 266.9 (13) $[C_{11}H_{14}F_4NP]^{\cdot+}$, 265.9 (100) $[C_{11}H_{13}F_4NP]^{+}$, 194.9 (17) $[C_7H_4F_4P]^{+}$, 103.9 (10) $[C_4H_{11}NP]^{+}$. HRMS (ESI): calcd. for $C_{15}H_{23}F_4N_2PH^{+}$ 339.1613, found 339.1621.

***p*-$(C_4H_9)C_6F_4P(NEt_2)_2$ (3):** A sample of bis(diethylamino)pentafluorophenylphosphane (8.54 g; 25.0 mmol) was dissolved in THF (50 mL) and *n*-butyllithium (16.25 mL; 1.6 M in *n*-hexane, 26.0 mmol) was added dropwise at 0 °C. After stirring for two hours the solvent was evaporated and the crude product condensed off in dynamic vacuo at 350 °C. Distillation in dynamic vacuo yielded 6.43 g of the product (b.p. = 84.7 °C; 16.4 mmol; 67 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$, r.t.): δ = 0.96 [t, ^{3}J(H,H) = 7 Hz, 3 H, CH_3], 1.09 [t, ^{3}J(H,H) = 7 Hz, 12 H, CH_3], 1.39 (m, 2 H, CH_2), 1.60 (m, 2 H, CH_2), 2.72 (m, 2 H, CH_2), 3.10 [dq, ^{3}J(P,H) = 10, ^{3}J(H,H) = 7 Hz, 8 H, CH_2] ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, r.t.): δ = 13.7 (s, CH_3), 14.8 [d, ^{3}J(P,C) = 3 Hz, CH_3], 22.3 (s, CH_2), 22.6 (m, CH_2), 31.4 (s, CH_2), 44.1 [dt, ^{2}J(P,C) = 19, ^{5}J(F,C) = 1 Hz, CH_2] ppm. $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, r.t.): δ = 119.0 [d, ^{1}J(P,C) = 46 Hz, C-P], 120.0 (m, *C*-CH_2), 144.8 [td, ^{3}J(C,H) = 5, ^{3}J(P,C) = 2 Hz, CF], 145.3 [d, ^{2}J(P,C) = 12 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.3 (m, 2 F, CF-*ortho*), –145.8 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 79.4 (m, 1 P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2965 (w), 2931 (w), 2864 (w), 1512 (w), 1441 (m), 1401 (w), 1375 (m), 1293 (w), 1247 (m), 1198 (m), 1183 (m), 1123 (w), 1095 (w), 1077 (w), 1059 (w), 1014 (s), 972 (m), 963 (m), 927 (m), 909 (m), 787 (m), 754 (w), 737 (w), 712 (w), 669 (m), 639 (m), 604 (w), 579 (w), 503 (w), 419 (w) cm^{-1}. MS (EI, 70 eV, pos.): *m/z* (%) = 380.1 (20) $[M]^{\cdot+}$, 308.1 (100) $[C_{14}H_{19}F_4NP]^{+}$, 270.0 (18), 175.1 (10) $[C_8H_{20}N_2P]^{+}$, 104 (19) $[C_4H_{11}NP]^{+}$, 72.1 (36) $[C_4H_{10}N]^{+}$. HRMS: calcd. for $C_{18}H_{29}F_4N_2P^{\cdot+}$ 380.19990, found 380.20177.

***p*-$(CH_3O)C_6F_4P(NEt_2)_2$ (4):** A sample of *n*-butyllithium (27.4 mL; 1.6 M in *n*-hexane, 24.4 mmol) was added to dry methanol (100 mL) and stirred for 10 min at room temperature. A sample of bis(diethylamino)pentafluorophenylphosphane (10.0 g; 29.2 mmol) was added and the reaction mixture was refluxed for 48 h. The solvent was evaporated and the crude product dissolved in *n*-pentane (50 mL) and filtered. Separation from the solvent and distillation in dynamic vacuo yielded 6.49 g of the product (b.p. = 81.7 °C; 19.3 mmol; 66 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.06 [t, ^{3}J(H,H) = 10 Hz, 12 H, CH_3], 3.06 [dq, ^{3}J(P,H) = 10, ^{3}J(H,H) = 7 Hz, 8 H, NCH_2], 4.06 [t, ^{5}J(F,H) = 1 Hz, 3 H, OCH_3] ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, r.t.): δ = 14.9 [d, ^{3}J(P,C) = 3 Hz, CH_3], 44.2 [dt, ^{2}J(P,C) = 19, ^{5}J(F,C) = 1 Hz, NCH_2], 62.0 [td, ^{4}J(F,C) = 4, ^{7}J(P,C) = 2 Hz, OCH_3] ppm. $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, r.t.): δ = 114.7 [d, ^{1}J(P,C) = 47 Hz, C-P], 137.7 [dq, ^{4}J(P,C) = 4,

^3J(C,H) = 2 Hz, *C*-O], 140.8 [d, ^3J(P,C) = 2 Hz, CF], 146.1 [d, ^2J(P,C) = 12 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.0 (m, 2 F, CF-*ortho*), –158.2 (m, 2 F, CF-*meta*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 78.9 (m, 1 P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2968 (w), 2932 (w), 2864 (w), 1635 (w), 1496 (m), 1448 (s), 1375 (m), 1360 (m), 1292 (w), 1269 (w), 1197 (m), 1182 (s), 1100 (s), 1058 (w), 1014 (s), 975 (s), 926 (s), 911 (m), 787 (m), 733 (w), 670 (m), 638 (m), 576 (w), 505 (w), 477 (w), 447 (w), 422 (w) cm^{-1}. MS (EI, 70 eV, pos.): *m*/*z* (%) = 354.2 (23) $[M]^{+\cdot}$, 283.1 (13) $[C_{11}H_{14}F_4NOP]^{+\cdot}$, 282.1 (100) $[C_{11}H_{13}F_4NOP]^+$, 211.0 (67) $[C_7H_4F_4OP]^+$. HRMS: calcd. for $C_{15}H_{23}F_4N_2OP^{+\cdot}$ 354.14787, found 354.14876.

***p*-$(C_2H_5O)C_6F_4P(NEt_2)_2$ (5):** A sample of ethanol (1.22 g; 26.6 mmol) was dissolved in THF (50 mL) and *n*-butyllithium (16.6 mL; 1.6 M in *n*-hexane, 26.6 mmol) was added dropwise at 0 °C. After stirring for 30 min at room temperature bis(diethylamino)pentafluorophenylphosphane (7.00 g; 20.5 mmol) was added. The reaction mixture was refluxed for 19 h. The solvent was evaporated and the crude product condensed off in dynamic vacuo at 350 °C. Destillation in dynamic vacuo yielded 4.38 g of the product (b.p. = 66.9 °C; 11.9 mmol; 58 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.05 [t, ^3J(H,H) = 10 Hz, 12 H, CH_3], 1.40 [t, ^3J(H,H) = 7 Hz, 3 H, CH_3], 3.06 [dq, ^3J(P,H) = 10, ^3J(H,H) = 7 Hz, 8 H, NCH_2], 4.27 [qt, ^3J(H,H) = 7, ^5J(F,H) = 1 Hz, 2 H, OCH_2] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 14.8 [d, ^3J(P,C) = 3 Hz, CH_3], 15.4 (s, CH_3), 44.1 [dt, ^2J(P,C) = 19, ^5J(F,C) = 1 Hz, NCH_2], 70.6 [tm, ^4J(F,C) = 3 Hz, OCH_2] ppm. $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, r.t.): δ = 114.6 [d, ^1J(P,C) = 47 Hz, C-P], 136.5 [pseudo q, ^3J(H,C)/^4J(P,C) = 3 Hz, *C*-O], 141.0 [d, ^3J(P,C) = 2 Hz, CF], 145.9 [d, ^2J(P,C) = 12 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.2 (m, 2 F, CF-*ortho*), –157.6 (m, 2 F, CF-*meta*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 78.9 (m, 1 P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2969 (w), 2932 (w), 2866 (w), 1634 (w), 1493 (m), 1477 (s), 1375 (m), 1360 (m), 1292 (w), 1264 (w), 1198 (m), 1183 (m), 1094 (s), 1055 (w), 1014 (s), 968 (s), 927 (m), 911 (m), 870 (m), 788 (m), 735 (w), 670 (m), 639 (w), 505 (w), 479 (w), 453 (w) cm^{-1}. MS (EI, 70 eV, pos.): *m*/*z* (%) = 368.1 (25) $[M]^{+\cdot}$, 297.0 (14) $[C_{12}H_{16}F_4NOP]^{+\cdot}$, 296.0 (100) $[C_{12}H_{15}F_4NOP]^+$, 224.9 (10) $[C_8H_6F_4OP]^+$, 196.9 (48) $[C_6H_2F_4OP]^+$. HRMS: calcd. for $C_{16}H_{25}F_4N_2OP^{+\cdot}$ 368.16352, found 368.16569.

***p*-$[(CH_3)_2N]C_6F_4P(NEt_2)_2$ (6):** A sample of *n*-butyllithium (12 mL; 1.6 M in *n*-hexane, 19.3 mmol) was dissolved in THF (40 mL). The solution was degassed at –80 °C in dynamic vacuo and dimethylamine (19.3 mmol) was condensed onto the solution. After stirring for 30 min the mixture was warmed to room temperature and stirred for 10 min. The reaction mixture was cooled to –60 °C and bis(diethylamino)pentafluorophenylphosphane (6.00 g; 17.5 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 30 min. The solvent was evaporated and the crude product condensed off in dynamic vacuo at 350 °C. Distillation in dynamic vacuo yielded 4.52 g of the product (b.p. = 90.4 °C; 12.3 mmol; 70 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.05 [t, ^3J(H,H) = 7 Hz, 12 H, CH_3], 2.94 [t, ^5J(F,H) = 2 Hz, 6 H, NCH_3], 3.06 [dq, ^3J(P,H) = 10, ^3J(H,H) = 7 Hz, 8 H, NCH_2] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 14.9 [d, ^3J(P,C) = 3 Hz, CH_3], 43.4 [td, ^4J(P,C) = 4, ^6J(P,C) = 1 Hz, NCH_3], 44.1 [dt, ^2J(P,C) = 19, ^5J(F,C) = 1 Hz, NCH_2] ppm. $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, r.t.): δ = 112.8 [d, ^1J(P,C) = 44 Hz, C-P], 130.6 (m, C-N), 142.1 [d, ^3J(P,C) = 2 Hz, CF], 146.4 [d, ^2J(P,C) = 12 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.8 (m, 2 F, CF-*ortho*), –151.9 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 79.3 (m, 1 P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2967 (w), 2931 (w), 2863 (w), 2810 (w), 1631 (w), 1506 (w), 1436 (s), 1374 (m), 1362 (w), 1345 (w), 1292 (w), 1226 (m), 1197 (m), 1097 (w), 1059 (s), 1013 (s), 959 (s), 926 (m), 910 (m), 787 (m), 731 (w), 669 (m), 637 (w), 563 (w), 497 (w), 475 (w), 452 (w), 420 (w), 383 (w) cm^{-1}. MS (ESI, pos.): *m*/*z* (%) = 368.3 (100) $[M + H]^+$, 295.1 (32). HRMS: calcd. for $C_{16}H_{26}F_4N_3PH^+$ 368.18732, found 368.1879.

***p*-$[(C_2H_5)_2N]C_6F_4P(NEt_2)_2$ (7):** A sample of *n*-butyllithium (15.3 mL; 1.6 M in *n*-hexane, 24.4 mmol) was dissolved in THF (50 mL). The solution was degassed at –80 °C and diethylamine (24.4 mmol) was condensed onto the solution. The reaction mixture was stirred for 30 min and allowed to reach 0 °C. At 0 °C bis(diethylamino)pentafluorophenylphosphane (8.00 g; 23.4 mmol) was added dropwise. The reaction mixture was stirred for 20 min at room temperature. The solvent was evaporated and the crude product condensed off in dynamic vacuo at 350 °C. Distillation in dynamic vacuo yielded 6.90 g of the product (b.p. = 73.0 °C; 17.5 mmol; 75 %) as a colorless liquid. ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.07 [t, ^3J(H,H) = 7 Hz, 18 H, CH_3], 3.08 [dq, ^3J(P,H) = 10, ^3J(H,H) = 7 Hz, 8 H, NCH_2], 3.21 [qt, ^3J(H,H) = 7, ^5J(F,H) = 1 Hz, 2 H, C-NCH_2] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 13.3 (s, CH_3), 14.8 [d, ^3J(P,C) = 3 Hz, CH_3], 44.1 [dt, ^2J(P,C) = 19, ^5J(F,C) = 1 Hz, NCH_2], 47.1 [tm, ^4J(F,C) = 3 Hz, $CNCH_2$] ppm. $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, r.t.): δ = 114.6 [d, ^1J(P,C) = 44 Hz, C-P], 127.9 (m, C-N), 144.0 [d, ^3J(P,C) = 2 Hz, CF], 146.0 [d, ^2J(P,C) = 12 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.9 (m, 2 F, CF-*ortho*), –149.7 (m, 2 F, CF-*meta*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 79.3 (m, 1 P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2968 (m), 2932 (w), 2867 (w), 1629 (w), 1488 (w), 1439 (s), 1375 (m), 1361 (m), 1344 (w), 1293 (w), 1264 (w), 1196 (s), 1183 (s), 1072 (m), 1014 (s), 963 (s), 925 (s), 853 (w), 787 (m), 756 (w), 670 (m), 638 (w), 552 (w), 499 (w), 420 (w) cm^{-1}. MS (EI, 70 eV, pos.): *m*/*z* (%) = 395.1 (32) $[M]^{+\cdot}$, 324.1 (14) $[C_{14}H_{21}F_4N_2P]^{+\cdot}$, 323.0 (78) $[C_{14}H_{20}F_4N_2P]^+$, 237.0 (23), 208.0 (10). HRMS: calcd. for $C_{18}H_{30}F_4N_3P^{+\cdot}$ 395.21080, found 395.21203.

***p*-$(C_6H_5)C_6F_4P(NEt_2)_2$ (8):** A sample of bromobenzene (4.45 g; 28.3 mmol) was dissolved in THF (50 mL) and *n*-butyllithium (16.25 mL; 1.6 M in *n*-hexane, 26.0 mmol) was added dropwise at –78 °C. After stirring for two hours bis(diethylamino)pentafluorophenylphosphane (8.00 g; 23.4 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature and the solvent evaporated. The raw product was condensed off in dynamic vacuo at 450 °C. Distillation in dynamic vacuo yielded 8.37 g of the product (b.p. = 102.4 °C; 20.9 mmol; 89 %) as a yellow oil. ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.11 [t, ^3J(H,H) = 7 Hz, 12 H, CH_3], 3.13 [dq, ^3J(P,H) = 10, ^3J(H,H) = 7 Hz, 8 H, CH_2], 7.42–7.54 (m, 5 H, Ar-C-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 15.0 [d, ^3J(P,C) = 3 Hz, CH_3], 44.4 [dt, ^2J(P,C) = 19, ^5J(F,C) = 1 Hz, CH_2], 128.1 (m, C_6F_4-*C*), 128.6 (s, C-*meta*), 129.0 (s, C-*para*), 130.3 (m, C-*ortho*) ppm. $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, r.t.): δ = 119.7 (m, *C*-C_6H_5), 121.2 [d, ^1J(P,C) = 47 Hz, C-P], 143.8 [d, ^3J(P,C) = 2 Hz, CF], 146.0 [d, ^2J(P,C) = 11 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –137.2 (m, 2 F, CF-*ortho*), –144.9 (m, 2 F, CF-*meta*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, r.t.): δ = 79.5 (m, 1 P, P) ppm. IR (ATR): $\tilde{\nu}$ = 3062 (w), 3023 (w), 2967 (w), 2930 (w), 2863 (w), 1603 (w), 1584 (w), 1504 (w), 1459 (m), 1428 (s), 1408 (w), 1375 (m), 1343 (w), 1284 (w), 1198 (m), 1182 (m), 1155 (m), 1097 (w), 1074 (w), 1058 (w), 1014 (s), 961 (s), 927 (m), 914 (m), 841 (w), 778 (m), 748 (w), 723 (m), 694 (m), 670 (m), 647 (m), 635 (w), 615 (w), 498 (w), 457 (w), 415 (w), 403 (w), 379 (w) cm^{-1}. MS (EI, 70 eV, pos.): *m*/*z* (%) = 400.2 (20) $[M]^{+\cdot}$, 329.1 (19) $[C_{16}H_{16}F_4NP]^{+\cdot}$, 328.1 (100) $[C_{16}H_{15}F_4NP]^+$, 257.0 (34) $[C_{12}H_6F_4P]^+$, 188.0 (26), 161.1 (10) $[C_7H_{18}N_2P]^+$, 104.1 (16) $[C_4H_{11}NP]^+$. HRMS: calcd. for $C_{20}H_{25}F_4N_2P^{+\cdot}$ 400.16860, found 400.16820.

General Procedure for the Preparation of Phosphinic Acids

$C_6F_5P(O)(OH)H$ (9): A solution of bis(diethylamino)pentafluorophenylphosphane (5.47 g; 16.0 mmol) in diethyl ether (20 mL) was charged with hydrochloric acid (18 %) at 0 °C and stirred for 1 h. The phases were separated and the aqueous phase extracted with diethyl ether (2 × 30 mL). The combined organic phases were dried

with Mg_2SO_4 and the solvent was evaporated. Drying in vacuo yielded 2.97 g of pentafluorophenylphosphinic acid (12.8 mmol; 80 %) as a colorless powder. ^{1}H NMR ($CDCl_3$, r.t.): δ = 7.82 [d, ^1J(P,H) = 635 Hz, 1 H, PH], 12.85 (s, 1 H, POH) ppm. ^{13}C{^{19}F} NMR ($CDCl_3$, r.t.): δ = 106.4 [dd, ^1J(P,C) = 124, ^2J(C,H) = 23 Hz, CP], 137.7 [dd, ^3J(P,C) = 11, ^4J(C,H) = 1 Hz, CF], 144.7 [d, ^2J(P,C) = 3 Hz, CF], 147.3 [dd, ^3J(P,C) = 1, ^4J(C,H) = 1 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –135.3 (m, 2 F, CF-*ortho*), –144.6 (m, 1 F, CF-*para*), –158.9 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 6.9 [dm, ^1J(P,H) = 635 Hz, 1 P] ppm.

***p*-$(CH_3)C_6F_4P(O)(OH)H$ (10):** (1.78 g; 7.79 mmol; 81 %; colorless crystals). M.p. 61.4 °C. ^{1}H NMR ($CDCl_3$, r.t.): δ = 2.33 [t, ^4J(F,H) = 2 Hz, 3 H, CH_3], 7.85 [d, ^1J(P,H) = 630 Hz, 1 H, PH], 11.28 (s, 1 H, POH) ppm. ^{13}C{^{19}F} NMR ($CDCl_3$, r.t.): δ = 8.3 [q, ^1J(C,H) = 133 Hz, CH_3], 108.8 [dd, ^1J(P,C) = 124, ^2J(C,H) = 23 Hz, CP], 122.2 [qm, ^2J(C,H) = 6 Hz, CCH_3], 145.0 (m, CF), 146.4 (s, CF) ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.1 (m, 2 F, CF-*ortho*), –141.4 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 9.5 [dm, ^1J(P,H) = 630 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2934 (w), 2856 (w), 2594 (w, broad), 2427 (w), 2283 (w, broad), 2127 (w, broad), 1650 (w), 1463 (s), 1391 (w), 1379 (w), 1275 (m), 1181 (m), 1125 (m), 1051 (m), 973 (s), 902 (s), 841 (m), 722 (m), 604 (m), 580 (m), 511 (m), 483 (w), 467 (m), 440 (m), 430 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 457.0 (100) [2M + H]$^+$, 270.0 (55) [M + H + ACN]$^+$, 246.0 (13), 228.9 (81) [M + H]$^+$. (ESI, neg.): *m/z* (%) = 226.7 (100) [M – H]$^-$. HRMS: calcd. for $C_7H_5F_4O_2PH^+$ 229.00361, found 229.00430.

***p*-$(C_4H_9)C_6F_4P(O)(OH)H$ (11):** (2.03 g; 7.52 mmol; 92 %; colorless crystals). M.p. 43.8 °C. ^{1}H NMR ($CDCl_3$, r.t.): δ = 0.94 [t, ^3J(H,H) = 7 Hz, 3 H, CH_3], 1.37 (m, 2 H, CH_2), 1.58 (m, 2 H, CH_2), 2.76 [tt, ^3J(H,H) = 8, ^4J(F,H) = 1 Hz, 2 H, CH_2], 7.84 [d, ^1J(P,H) = 627 Hz, 1 H, PH], 13.00 (s, 1 H, POH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, r.t.): δ = 13.8 (s, CH_3), 22.4 (m, CH_2), 23.2 (m, CH_2), 31.2 (s, CH_2) ppm. ^{13}C{^{19}F} NMR ($CDCl_3$, r.t.): δ = 108.6 [dd, ^1J(P,C) = 125, ^2J(C,H) = 22 Hz, C-P], 126.8 (m, *C*-CH_2), 144.8 [dt, ^3J(P,C) = 12, ^3J(C,H) = 6 Hz, CF], 146.3 (s, CF) ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –137.7 (m, 2 F, CF-*ortho*), –142.7 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 8.4 [d pseudo sept, ^1J(P,H) = 627, *J*(P,F) = 7 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2962 (w), 2934 (w), 2873 (w), 2432 (w, broad), 2278 (w, broad), 2125 (w, broad), 1649 (w), 1464 (s), 1407 (w), 1379 (w), 1333 (w), 1298 (w), 1273 (m), 1251 (w), 1183 (m), 1127 (w), 1105 (w), 1055 (m), 977 (s), 954 (s), 904 (s), 843 (m), 799 (w), 757 (w), 738 (w), 710 (w), 656 (w), 603 (w), 576 (w), 512 (m), 483 (w), 470 (m), 453 (m), 441 (m), 390 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 563.0 (37) [2M + Na]$^+$, 541.0 (24) [2M + H]$^+$, 470.3 (47), 397.2 (51), 344.2 (19), 334.1 (28) [M + Na + ACN]$^+$, 312.1 (36) [M + H + ACN]$^+$, 293.0 (90) [M + Na]$^+$, 271.1 (100) [M + H]$^+$. (ESI, neg.): *m/z* (%) = 268.8 (100) [M – H]$^-$. HRMS: calcd. for $C_{10}H_{11}F_4O_2PH^+$ 271.05056, found 271.05140.

***p*-$(CH_3O)C_6F_4P(O)(OH)H$ (12):** (11.8 g; 45.4 mmol; 97 %; colorless crystals). M.p. 60.5 °C. ^{1}H NMR ($CDCl_3$, r.t.): δ = 4.18 [t, ^5J(F,H) = 2 Hz, 3 H, OCH_3], 7.80 [d, ^1J(P,H) = 627 Hz, 1 H, PH], 10.25 (s, 1 H, POH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, r.t.): δ = 62.2 [t, ^4J(F,C) = 4 Hz, OCH_3] ppm. ^{13}C{^{19}F} NMR ($CDCl_3$, r.t.): δ = 103.5 [d, ^1J(P,C) = 128 Hz, C-P], 140.3 [d, ^2J(P,C) = 12 Hz, CF], 142.8 (m, CO), 147.6 (s, CF) ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –137.3 (m, 2 F, CF-*ortho*), –156.3 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 9.1 [dm, ^1J(P,H) = 627 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 3414 (w, broad), 3025 (w), 2966 (w), 2843 (w), 2790 (w), 2621 (w), 2571 (w), 2509 (w, broad), 2458 (w), 2404 (w, broad), 1692 (m), 1639 (w, shoulder), 1504 (m), 1465 (s), 1431 (m), 1389 (m), 1289 (w), 1190 (m), 1111 (s), 1027 (m, shoulder), 995 (s), 967 (s), 931 (s), 843 (s), 760 (m), 731 (m), 648 (m), 578 (m), 511 (s), 450 (s), 437 (s), 409 (s), 391 (s), 318 (19), 308 (13) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 511.0 (25) [2M + Na]$^+$, 489.0 (16) [2M + H]$^+$, 318.1 (19), 308.0 (13), 289.0 (27), 267.0 (100) [M + Na]$^+$, 245.0 (80) [M + H]$^+$. (ESI, neg.): *m/z* (%) = 242.7 (100) [M – H]$^-$. HRMS: calcd. for $C_7H_6F_4O_3P^+$ 244.99852, found 244.9985.

***p*-$(C_2H_5O)C_6F_4P(O)(OH)H$ (13):** (1.89 g; 7.31 mmol; 93 %; colorless oil). ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.44 [t, ^3J(H,H) = 7 Hz, 3 H, CH_3], 4.41 [qt, ^3J(H,H) = 7, ^5J(F,H) = 1 Hz, 2 H, OCH_2], 7.79 [d, ^1J(P,H) = 627 Hz, 1 H, PH], 12.28 (s, 1 H, POH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, r.t.): δ = 15.5 (s, CH_3), 71.1 [t, ^5J(F,C) = 4 Hz, OCH_2] ppm. ^{13}C{^{19}F} NMR ($CDCl_3$, r.t.): δ = 103.4 [dd, ^1J(P,C) = 105, ^2J(C,H) = 23 Hz, C-P], 140.5 [dd, ^2J(P,C) = 12, ^3J(C,H) = 1 Hz, CF], 141.8 [dt, ^4J(P,C) = 2, ^3J(C,H) = 2 Hz, $COCH_2$], 147.4 [t, ^5J(C,H) = 1 Hz, CF] ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –137.4 (m, 2 F, CF-*ortho*), –155.7 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 8.2 [d pseudo sept, ^1J(P,H) = 627, *J*(P,F) = 7 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2989 (w), 2939 (w), 2909 (w), 2872 (w), 2413 (w, broad), 2108 (w, broad), 1641 (w), 1499 (w), 1470 (s), 1388 (m), 1366 (w), 1284 (w), 1169 (w), 1103 (s), 955 (s), 878 (m), 835 (m), 761 (m), 731 (w), 663 (w), 606 (w), 576 (w), 509 (m), 451 (m), 439 (m), 386 (m) cm^{-1}. MS (ESI, neg.): *m/z* (%) = 514.8 (10) [2M – H]$^-$, 256.8 (100) [M – H]$^-$. HRMS: calcd. for $C_8H_7F_4O_3PH^+$ 259.01417, found 259.01462.

***p*-$[(CH_3)_2N]C_6F_4P(O)(OH)H$ (14):** (2.08 g, 8.11 mmol, 83 % colorless solid). M.p. 106.3 °C. ^{1}H NMR ($CDCl_3$, r.t.): δ = 3.07 [t, ^5J(F,H) = 3 Hz, 6 H, NCH_3], 7.80 [d, ^1J(P,H) = 622 Hz, 1 H, PH], 12.43 (s, 1 H, POH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, r.t.): δ = 42.9 [t, ^4J(F,C) = 5 Hz, NCH_3] ppm. ^{13}C{^{19}F} NMR ($CDCl_3$, r.t.): δ = 99.4 [dd, ^1J(P,C) = 133, ^2J(C,H) = 23 Hz, C-P], 136.0 (m, *C*-N), 140.3 [d, ^2J(P,C) = 11 Hz, CF], 147.9 (s, CF) ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.3 (m, 2 F, CF-*ortho*), –151.6 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 10.2 [d, ^1J(P,H) = 622 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2932 (w), 2886 (w), 2853 (w), 2813 (w), 2597 (w, broad), 2398 (w), 2274 (w, broad), 2142 (w, broad), 1634 (w), 1521 (w), 1471 (s), 1435 (m), 1393 (w), 1316 (w), 1303 (w), 1247 (w), 1219 (w), 1175 (m), 1079 (m), 975 (s), 949 (s), 908 (m), 816 (m), 763 (m), 728 (w), 650 (w), 565 (w), 504 (m), 476 (m), 453 (m), 441 (m), 386 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 537.0 (21), 515.0 (47), 321.1 (14) [M + Na + ACN]$^+$, 299.0 (24) [M + H + ACN]$^+$, 280.0 (27) [M + Na]$^+$, 275.0 (14), 258.0 (100) [M + H]$^+$. (ESI, neg.): *m/z* (%) = 255.7 (100) [M – H]$^-$. HRMS: calcd. for $C_8H_8NF_4O_2PH^+$ 258.03016, found 258.0300.

***p*-$[(C_2H_5)_2N]C_6F_4P(O)(OH)H$ (15):** (2.09 g; 7.32 mmol; 96 %; colorless crystals). M.p. 67.2 °C. ^{1}H NMR ($CDCl_3$, r.t.): δ = 1.14 [t, ^3J(H,H) = 7 Hz, 6 H, CH_3], 3.33 [qt, ^3J(H,H) = 7, ^5J(H,H) = 1 Hz, 4 H, CH_2], 7.80 [d, ^1J(P,H) = 624 Hz, 1 H, PH], 9.61 (s, 1 H, POH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, r.t.): δ = 13.7 [t, ^5J(F,C) = 1 Hz, CH_3], 46.8 [t, ^4J(F,C) = 4 Hz, NCH_2] ppm. ^{13}C{^{19}F} NMR ($CDCl_3$, r.t.): δ = 100.8 [dd, ^1J(P,C) = 130, ^2J(C,H) = 22 Hz, C-P], 134.3 (s, *C*-CH_2), 141.7 [d, ^2J(P,C) = 11 Hz, CF], 147.8 (s, CF) ppm. ^{19}F NMR ($CDCl_3$, r.t.): δ = –138.4 (m, 2 F, CF-*ortho*), –149.8 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($CDCl_3$, r.t.): δ = 10.4 [d pseudo sept, ^1J(P,H) = 624, *J*(P,F) = 7 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2988 (w), 2965 (w), 2933 (w), 2900 (w), 2875 (w), 2593 (w, broad), 2442 (w), 2407 (w), 2286 (w, broad), 2125 (w, broad), 1988 (w, broad), 1636 (w), 1519 (w), 1467 (s), 1405 (w), 1381 (w), 1364 (w), 1278 (w), 1191 (m), 1134 (m), 1092 (s), 1019 (m), 972 (s), 953 (s), 915 (s), 884 (m), 808 (w), 793 (w), 776 (w), 758 (w), 725 (w), 650 (w), 567 (w), 506 (m), 470 (m), 434 (m), 420 (m), 406 (m), 395 (m), 380 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 437.2 (45), 393.4 (94), 381.4 (100), 353.4 (90), 330.1 (20). (ESI, neg.): *m/z* (%) = 283.8 (100) [M – H]$^-$. HRMS: calcd. for $C_{10}H_{12}F_4O_2NPH^+$ 286.06146, found 286.06229.

***p*-$(C_6H_5)C_6F_4P(O)(OH)H$ (16):** A sample of **8** (3.32 g; 8.30 mmol) was dissolved in diethyl ether (20 mL) and charged with hydrochloric acid (18 %) at 0 °C. The resulting white precipitate was filtered off and washed with diethyl ether (30 mL) and water (3 × 30 mL). Drying in vacuo yielded 1.94 g of *p*-$(C_6H_5)C_6F_4P(O)(OH)H$ (**16**) (6.68 mmol; 80 %) as a colorless powder. M.p. 285.0 °C. ^{1}H NMR

([D$_6$]DMSO, r.t.): δ = 7.55 (m, 5 H, C$_6$H$_5$), 7.79 [d, ^1J(P,H) = 600 Hz, 1 H, PH], 8.16 (s, broad, 1 H, POH) ppm. ^{13}C{^{1}H}APT NMR ([D$_6$]DMSO, r.t.): δ = 126.8 [t, ^3J(F,C) = 2 Hz, C], 129.3 (s, CH), 130.2 (s, CH), 130.4 [t, ^4J(F,C) = 2 Hz, CH] ppm. ^{13}C{^{19}F} NMR ([D$_6$]DMSO, r.t.): δ = 113.9 [dd, ^1J(P,C) = 108, ^2J(C,H) = 24 Hz, C-P], 124.0 (m, *C*-C$_6$H$_5$), 143.6 [d, ^2J(P,C) = 10 Hz, CF], 146.3 (s, CF) ppm. ^{19}F NMR ([D$_6$]DMSO, r.t.): δ = –138.5 (m, 2 F, CF-*ortho*), –142.8 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ([D$_6$]DMSO, r.t.): δ = –1.0 [dm, ^1J(P,H) = 600 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 3061 (w), 2644 (w, broad), 2446 (w, broad), 2244 (w, broad), 2143 (w, broad), 1643 (w), 1571 (w), 1501 (w), 1471 (s), 1434 (s), 1409 (w), 1387 (w), 1318 (w), 1299 (w), 1233 (w), 1162 (m), 1151 (m), 1023 (w), 986 (s), 959 (s), 921 (m), 865 (m), 809 (w), 781 (m), 749 (w), 726 (m), 693 (m), 659 (w), 643 (w), 613 (w), 518 (m), 475 (w), 461 (m), 414 (w), 382 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 408.4 (78), 360.4 (100); (ESI, neg.): *m/z* (%) = 288.8 (100) [M – H]$^-$. HRMS: calcd. for C$_{12}$H$_7$O$_2$F$_4$N$_2$PH$^+$ 291.01926, found 291.0197.

General Procedure for the Preparation of Phosphonic Acids

C$_6$F$_5$P(O)(OH)$_2$ (17): A solution of pentafluorophenylphosphinic acid (3.50 g; 10.2 mmol) in MTBE (20 mL) was charged with DMSO (622 mg; 7.96 mmol) and a catalytical amount of iodine (10 mg; 0.05 mol-%) at 0 °C and stirred for 24 h. Evaporation of the solvent and drying in dynamic vacuo yielded 1.88 g of pentafluorophenylphosphonic acid (**17**) (7.58 mmol; 95 %) as colorless crystals. ^{1}H NMR ([D$_6$]DMSO, r.t.): δ = 10.26 (s, 2 H, POH) ppm. ^{13}C{^{19}F} NMR ([D$_6$]DMSO, r.t.): δ = 109.5 [d, ^1J(P,C) = 166 Hz, CP], 137.5 [d, ^3J(P,C) = 14 Hz, CF], 142.6 [d, ^2J(P,C) = 3 Hz, CF], 146.5 [d, ^3J(P,C) = 1 Hz, CF] ppm. ^{19}F NMR ([D$_6$]DMSO, r.t.): δ = –133.0 (m, 2 F, CF-*ortho*), –150.5 (m, 1 F, CF-*para*), –161.6 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ([D$_6$]DMSO, r.t.): δ = –2.0 (m, 1 P, P) ppm.

***p*-(CH$_3$)C$_6$F$_4$P(O)(OH)$_2$ (18):** (1.70 g; 6.94 mmol; 89 %; colorless powder). M.p. 193.1 °C (dec). ^{1}H NMR ([D$_6$]DMSO, r.t.): δ = 2.26 (m, 3 H, CH$_3$), 10.46 (s, broad, 2 H, POH) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, r.t.): δ = 7.8 (m, CH$_3$) ppm. ^{13}C{^{19}F} NMR ([D$_6$]DMSO, r.t.): δ = 111.5 [d, ^1J(P,C) = 169 Hz, C-P], 119.7 [qm, ^2J(C,H) = 6 Hz, *C*-CH$_3$], 144.9 [dq, ^3J(P,C) = 14, ^3J(C,H) = 4 Hz, CF], 145.8 [d, ^2J(P,C) = 2 Hz, CF] ppm. ^{19}F NMR ([D$_6$]DMSO, r.t.): δ = –134.8 (m, 2 F, CF-*ortho*), –143.2 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ([D$_6$]DMSO, r.t.): δ = –1.2 [t, ^3J(P,F) = 8 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2754 (w), 2307 (w), 2165 (w), 1689 (w), 1655 (w), 1463 (s), 1394 (w), 1383 (w), 1277 (m), 1202 (w), 1161 (w), 1130 (w), 1066 (m), 1052 (m), 981 (m), 942 (s), 912 (s), 840 (w), 809 (w), 725 (m), 609 (w), 586 (m), 558 (m), 550 (m), 483 (m), 459 (s), 444 (s) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 685.5 (31), 554.9 (16), 437.2 (100), 379.4 (19), 330.0 (19), 289.0 (28). (ESI, neg.): *m/z* (%) = 242.8 (100) [M – H]$^-$. HRMS: calcd. for C$_7$H$_5$F$_4$O$_3$PH$^+$ 244.99852, found 244.9980.

***p*-(C$_4$H$_9$)C$_6$F$_4$P(O)(OH)$_2$ (19):** (630 mg; 2.20 mmol; 98 %; colorless crystals recrystallized from toluene). M.p. 116.1 °C. ^{1}H NMR ([D$_6$]DMSO, r.t.): δ = 0.89 [t, ^3J(H,H) = 7 Hz, 3 H, CH$_3$], 1.31 (m, 2 H, CH$_2$), 1.53 (m, 2 H, CH$_2$), 2.72 [tm, ^3J(H,H) = 7 Hz, 2 H, CH$_2$], 8.96 (s, 2 H, POH) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, r.t.): δ = 13.5 (s, CH$_3$), 21.7 (s, CH$_2$), 22.3 (m, CH$_2$), 30.6 (s, CH$_2$) ppm. ^{13}C{^{19}F} NMR ([D$_6$]DMSO, r.t.): δ = 111.5 [d, ^1J(P,C) = 168 Hz, C-P], 123.4 (m, *C*-CH$_2$), 144.4 [dt, ^3J(P,C) = 13, ^3J(C,H) = 5 Hz, CF], 145.4 [d, ^2J(P,C) = 2 Hz, CF] ppm. ^{19}F NMR ([D$_6$]DMSO, r.t.): δ = –133.7 (m, 2 F, CF-*ortho*), –143.9 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ([D$_6$]DMSO, r.t.): δ = –0.7 [tm, ^3J(P,F) = 8 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2963 (w), 2935 (w), 2868 (w), 2727 (w, broad), 2317 (w, broad), 2172 (w, broad), 1694 (w), 1650 (w), 1458 (s), 1407 (w), 1386 (w), 1341 (w), 1329 (w), 1302 (w), 1273 (m), 1248 (w), 1178 (m), 1124 (w), 1099 (w), 1052 (m), 1031 (s), 974 (s), 959 (s), 939 (s), 915 (w), 879 (w), 846 (w), 812 (w), 758 (m), 663 (w), 603 (w), 577 (w), 557 (s), 505 (w), 475 (s), 443 (m), 398 (w) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 372.1 (47), 360.4 (15), 350.1 (23) [M + Na + ACN]$^+$, 331.1 (100), 316.3 (29), 309.1 (18) [M + Na]$^+$, 202.1 (32). (ESI, neg.): *m/z* (%) = 284.8 (100) [M – H]$^-$. HRMS: calcd. for C$_{10}$H$_{10}$O$_3$F$_4$P$^-$ 285.03092, found 285.0314.

***p*-(CH$_3$O)C$_6$F$_4$P(O)(OH)$_2$ (20):** (4.14 g; 15.9 mmol; 99 %; colorless crystals). M.p. 191.6 °C. ^{1}H NMR ([D$_6$]DMSO, r.t.): δ = 4.10 [t, ^5J(F,H) = 2 Hz, 3 H, OCH$_3$], 9.61 (s, broad, 2 H, POH) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, r.t.): δ = 62.4 [t, ^5J(F,C) = 4 Hz, OCH$_3$] ppm. ^{13}C{^{19}F} NMR ([D$_6$]DMSO, r.t.): δ = 106.6 [d, ^1J(P,C) = 170 Hz, CP], 139.9 (m, *C*OMe), 140.0 [d, ^2J(P,C) = 14 Hz, CF], 146.3 [d, ^3J(P,C) = 2 Hz, CF] ppm. ^{19}F NMR ([D$_6$]DMSO, r.t.): δ = –134.5 (m, 2 F, CF-*ortho*), –157.7 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ([D$_6$]DMSO, r.t.): δ = –1.1 [tt, ^3J(P,F) = 7, ^4J(P,F) = 2 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2962 (w), 2841 (w, broad), 2199 (w, broad), 1699 (w), 1643 (w), 1504 (m), 1470 (s), 1438 (m), 1391 (m), 1297 (w), 1186 (m), 1119 (s), 1086 (s), 1027 (s), 964 (s), 928 (s), 717 (m), 669 (m), 584 (m), 552 (s), 479 (m), 430 (m), 421 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 339.1 (10), 283.0 (83) [M + Na]$^+$, 261.0 (100) [M + H]$^+$. (ESI, neg.): *m/z* (%) = 258.8 (100) [M – H]$^-$. HRMS: calcd. for C$_7$H$_5$F$_4$O$_4$PH$^+$ 260.99344, found 260.9930.

***p*-(C$_2$H$_5$O)C$_6$F$_4$P(O)(OH)$_2$ (21):** (1.52 g; 5.58 mmol; 96 %; colorless crystals). M.p. 112.6 °C. ^{1}H NMR ([D$_6$]DMSO, r.t.): δ = 1.33 [t, ^3J(H,H) = 7 Hz, 3 H, CH$_3$], 4.36 [qt, ^3J(H,H) = 7, ^5J(F,H) = 1 Hz, 2 H, OCH$_2$], 9.81 (s, broad, 2 H, POH) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, r.t.): δ = 15.3 (s, CH$_3$), 70.9 [t, ^5J(F,C) = 4 Hz, OCH$_2$] ppm. ^{13}C{^{19}F} NMR ([D$_6$]DMSO, r.t.): δ = 106.7 [d, ^1J(P,C) = 171 Hz, C-P], 139.0 [q, ^3J(C,H) = 3 Hz, C-O], 140.4 [d, ^2J(P,C) = 14 Hz, CF], 146.3 [d, ^3J(P,C) = 2 Hz, CF] ppm. ^{19}F NMR ([D$_6$]DMSO, r.t.): δ = –134.4 (m, 2 F, CF-*ortho*), –157.0 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ([D$_6$]DMSO, r.t.): δ = –1.0 [tt, ^3J(P,F) = 7, ^4J(P,F) = 2 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 3369 (w), 2988 (w), 2939 (w), 2903 (w), 2773 (w, broad), 2122 (w, broad), 1721 (w), 1644 (w), 1501 (m), 1472 (s), 1388 (m), 1368 (w), 1268 (w), 1202 (w), 1104 (s), 1010 (s), 978 (s), 944 (s), 883 (m), 810 (m), 763 (m), 727 (m), 654 (w), 643 (w), 615 (w), 553 (s), 476 (s), 459 (s), 441 (m), 429 (m), 403 (s) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 548.9 (67) [2M + H]$^+$, 372.2 (96), 316.1 (66) [M + H + ACN]$^+$, 275.0 (62) [M + H]$^+$, 251.1 (100), 192.0 (42). (ESI, neg.): *m/z* (%) = 272.8 (100) [M – H]$^-$. HRMS: calcd. for C$_8$H$_7$F$_4$O$_4$PH$^+$ 275.00909, found 275.0086.

***p*-[(CH$_3$)$_2$N]C$_6$F$_4$P(O)(OH)$_2$ (22):** (2.17 g; 7.94 mmol; 98 %; yellow oil). ^{1}H NMR ([D$_6$]DMSO, r.t.): δ = 2.95 [t, ^5J(F,H) = 3 Hz, 6 H, NCH$_3$], 10.06 (s broad, 2 H, POH) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, r.t.): δ = 42.7 [t, ^4J(F,C) = 5 Hz, CH$_3$] ppm. ^{13}C{^{19}F} NMR ([D$_6$]DMSO, r.t.): δ = 103.1 [d, ^1J(P,C) = 176 Hz, C-P], 133.5 (m, C-N), 140.5 [td, ^3J(P,F) = 14 Hz, CF], 146.7 [d, ^4J(P,F) = 2 Hz, CF] ppm. ^{19}F NMR ([D$_6$]DMSO, r.t.): δ = –135.3 (m, 2 F, CF-*ortho*), –152.1 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ([D$_6$]DMSO, r.t.): δ = –0.0 (m, 1 P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2925 (w), 2893 (w), 2858 (w), 2815 (w), 2676 (w), 2264 (w), 1632 (m), 1521 (w), 1465 (s), 1436 (m), 1398 (w), 1244 (m), 1219 (m), 1075 (m), 1075 (m), 964 (s), 937 (s), 898 (s), 804 (m), 765 (m), 730 (m), 696 (w), 655 (w), 571 (s), 546 (s), 473 (m), 434 (m), 401 (m), 386 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 360.4 (100). MS (ESI, neg.): *m/z* (%) = 271.8 (100) [M – H]$^-$. HRMS: calcd. for C$_8$H$_8$F$_4$O$_3$N$_2$PH$^+$ 274.02507, found 274.0244.

***p*-[(C$_2$H$_5$)$_2$N]C$_6$F$_4$P(O)(OH)$_2$ (23):** (1.85 g; 6.14 mmol; 94 %; colorless crystals recrystallized from toluene). M.p. 90.4 °C. ^{1}H NMR ([D$_6$]DMSO, r.t.): δ = 1.04 [t, ^3J(H,H) = 7 Hz, 6 H, CH$_3$], 3.24 [qm, ^3J(H,H) = 7 Hz, 4 H, CH$_2$], 10.34 (s, 2 H, POH) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, r.t.): δ = 13.2 (s, CH$_3$), 46.2 [t, ^5J(F,C) = 4 Hz, CH$_2$] ppm. ^{13}C{^{19}F} NMR ([D$_6$]DMSO, r.t.): δ = 105.0 [d, ^1J(P,C) = 174 Hz, C-P], 131.3 (m, C-N), 142.2 [d, ^2J(C,H) = 13 Hz, CF], 146.5 [d, ^3J(P,C) = 2 Hz, CF] ppm. ^{19}F NMR ([D$_6$]DMSO, r.t.): δ = –135.1 (m, 2 F, CF-*ortho*), –150.3 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ([D$_6$]DMSO, r.t.): δ = –0.3 [tm, ^3J(P,F) = 4 Hz, 1 P, P] ppm. IR (ATR): $\tilde{\nu}$ = 2974 (w), 2935 (w), 2875 (w), 2612 (w, broad), 2302 (w, broad), 1636 (w), 1462 (s), 1407

(w), 1379 (w), 1349 (w), 1303 (w), 1275 (m), 1242 (m), 1202 (m), 1179 (m), 1144 (m), 1083 (m), 1006 (m), 968 (s), 930 (s), 841 (m), 801 (m), 759 (m), 735 (m), 695 (w), 656 (w), 587 (m), 560 (s), 517 (s), 501 (m), 493 (m), 465 (s), 446 (m), 434 (m), 391 (s) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 437.3 (100), 413.4 (19), 406.2 (69), 393.4 (22), 335.2 (23), 316.3 (12), 302.2 (7) $[M + H]^+$. MS (ESI, neg.): *m/z* (%) = 327.0 (27), 314.0 (75), 300.0 (100) $[M - H]^-$, 281.3 (16), 255.3 (13). HRMS: calcd. for $C_{10}H_{12}O_3F_4NPH^+$ 302.05637, found 302.0563.

***p*-$(C_6H_5)C_6F_4P(O)(OH)_2$ (24):** A sample of phosphinic acid **16** (1.94 g; 6.68 mmol) was suspended in toluene (30 mL) and charged with DMSO (521 mg; 6.68 mmol) and a catalytical amount of iodine (10 mg; 0.06 mol-%). The resulting suspension was stirred for 24 h. The product was filtered off and washed with toluene (30 mL) and MTBE (30 mL). Drying in vacuo yielded 1.60 g of the pure phosphonic acid **24** (5.21 mmol; 78 %) as a colorless powder. M.p. 165.5 °C. ^1H NMR ($[D_6]$DMSO, r.t.): δ = 7.55 (m, 5 H, C_6H_5), 9.42 (s, 2 H, POH) ppm. $^{13}C\{^1H\}$ NMR ($[D_6]$DMSO, r.t.): δ = 126.6 (m, 1 C), 128.8 (s, CH), 129.7 (s, CH), 130.0 (s, CH) ppm. $^{13}C\{^{19}F\}$ NMR ($[D_6]$DMSO, r.t.): δ = 113.0 [d, ^1J(P,C) = 168 Hz, C-P], 122.6 (m, *C*-C_6H_5), 143.3 [d, ^2J(P,C) = 14 Hz, CF], 145.8 [d, ^3J(P,C) = 2 Hz, CF] ppm. ^{19}F NMR ($[D_6]$DMSO, r.t.): δ = –133.5 (m, 2 F, CF-*ortho*), –143.6 (m, 2 F, CF-*meta*) ppm. ^{31}P NMR ($[D_6]$DMSO, r.t.): δ = –1.5 [t, ^3J(P,F) = 7 Hz, 1 P, P] ppm. IR (KBr): $\tilde{\nu}$ = 3417 (w, broad), 3060 (w), 3020 (w), 2922 (w), 2851 (w), 2720 (w, broad), 2263 (w, broad), 1649 (w), 1572 (w), 1507 (w), 1469 (s), 1436 (s), 1410 (w), 1318 (w), 1300 (w), 1234 (w), 1172 (w), 1114 (w), 1077 (w), 967 (s), 928 (m), 806 (w), 783 (w), 751 (w), 724 (w), 691 (m), 648 (w), 614 (w), 571 (w), 498 (w), 456 (w), 435 (w), 420 (w) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 685.5 (30), 437.3 (100), 393.2 (29), 316.3 (31). (ESI, neg.): *m/z* (%) = 304.9 (100) $[M - H]^-$. HRMS: calcd. for $C_{12}H_6F_4O_3P^-$ 304.99962, found 305.0001.

Acknowledgments

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

Keywords: Phosphonic acid · Phosphinic acid · Phosphorus · Fluorine · Phosphanes

[1] a) H. Allcock, *J. Membr. Sci.* **2002**, *201*, 47–54; b) F. Hacıvelioğlu, E. Okutan, S. Ü. Çelik, S. Yeşilot, A. Bozkurt, A. Kılıç, *Polymer* **2012**, *53*, 3659–3668; c) S. D. Alexandratos, M. A. Strand, D. R. Quillen, A. J. Walder, *Macromolecules* **1985**, *18*, 829–835.

[2] a) E. S. Skibinski, W. J. I. DeBenedetti, M. A. Hines, *J. Phys. Chem. C* **2017**, *121*, 14213–14221; b) A. Ostapenko, T. Klöffel, J. Eußner, K. Harms, S. Dehnen, B. Meyer, G. Witte, *ACS Appl. Mater. Interfaces* **2016**, *8*, 13472–13483; c) S. A. Paniagua, A. J. Giordano, O. L. Smith, S. Barlow, H. Li, N. R. Armstrong, J. E. Pemberton, J.-L. Brédas, D. Ginger, S. R. Marder, *Chem. Rev.* **2016**, *116*, 7117–7158; d) C. Quefféléc, M. Petit, P. Janvier, D. A. Knight, B. Bujoli, *Chem. Rev.* **2012**, *112*, 3777–3807; e) Y. Zheng, A. J. Giordano, R. C. Shallcross, S. R. Fleming, S. Barlow, N. R. Armstrong, S. R. Marder, S. S. Saavedra, *J. Phys. Chem. C* **2016**, *120*, 20040–20048.

[3] a) D. Yakhvarov, E. Trofimova, O. Sinyashin, O. Kataeva, Y. Budnikova, P. Lönnecke, E. Hey-Hawkins, A. Petr, Y. Krupskaya, V. Kataev, R. Klingeler, B. Büchner, *Inorg. Chem.* **2011**, *50*, 4553–4558; b) S. Richeter, J. Larionova, J. Long, A. van der Lee, D. Leclercq, *Eur. J. Inorg. Chem.* **2013**, 3206–3216; c) J. Ai, X. Min, C.-Y. Gao, H.-R. Tian, S. Dang, Z.-M. Sun, *Dalton Trans.* **2017**, *46*, 6756–6761; d) R. Zhang, P. A. Russo, M. Feist, P. Amsalem, N. Koch, N. Pinna, *ACS Appl. Mater. Interfaces* **2017**, *9*, 14013–14022; e) M. Wilke, A. Kabelitz, T. E. Gorelik, A. G. Buzanich, U. Reinholz, U. Kolb, K. Rademann, F. Emmerling, *Dalton Trans.* **2016**, *45*, 17453–17463.

[4] a) C. Yuan, H. Ma. (Cytec Technology Corp., Wilmington, Del.), US 5.639.433 **1996**; b) V. Luca, J. J. Tejada, D. Vega, G. Arrachart, C. Rey, *Inorg. Chem.* **2016**, *55*, 7928–7943.

[5] a) S. V. Levchik, E. D. Weil, *J. Fire Sci.* **2016**, *24*, 345–364; b) S. Hörold, H. Bauer (Clariant International LTD, Muttenz), WO **2012**/113520 A1 **2011**; c) X.-B. Lin, S.-L. Du, J.-W. Long, L. Chen, Y.-Z. Wang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 881–890; d) J. Wang, B. Yuan, X. Mu, X. Feng, Q. Tai, Y. Hu, *Ind. Eng. Chem. Res.* **2017**, *56*, 7192–7206; e) L.-S. Wang, H.-B. Kang, S.-B. Wang, Y. Liu, R. Wang, *Fluid Phase Equilib.* **2007**, *258*, 99–107.

[6] a) W. Wielkopolski, R. Śmieszek, S. Witek, A. Dabrowski, P. Wieczorek, B. Lejczak, P. Kafarski, *Pestic. Sci.* **1994**, *40*, 107–112; b) L. Maier, D. Duerr, H. Rempfler, *Phoshorus Sulfur Silicon Relat. Elem.* **1987**, *32*, 19–36; c) E. G. Williams, *Nature* **1970**, *227*, 84–85.

[7] a) Y. Yang, J. K. Coward, *J. Org. Chem.* **2007**, *72*, 5748–5758; b) J.-N. Volle, D. Filippini, B. Krawczy, N. Kaloyanov, A. van der Lee, T. Maurice, J.-L. Pirat, D. Virieux, *Org. Biomol. Chem.* **2010**, *8*, 1438–1444; c) W. Jahnke, G. Bold, A. L. Marzinzik, S. Ofner, X. Pellé, S. Cotesta, E. Bourgier, S. Lehmann, C. Henry, R. Hemmig, F. Stauffer, J. C. D. Hartwieg, J. R. Green, J.-M. Rondeau, *Angew. Chem. Int. Ed.* **2015**, *54*, 14575–14579; *Angew. Chem.* **2015**, *127*, 14783; d) N. Venkatramaiah, P. M. R. Pereira, F. A. Almeida Paz, C. A. F. Ribeiro, R. Fernandes, J. P. C. Tomé, *Chem. Commun.* **2015**, *51*, 15550–15553.

[8] For selected reviews see: a) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok, H. Liu, *Chem. Rev.* **2014**, *114*, 2432–2506; b) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; c) E. A. Ilardi, E. Vitaku, J. T. Njardarson, *J. Med. Chem.* **2014**, *57*, 2832–2842; d) Y. Zhou, J. Wang, Z. Gu, S. Wang, W. Zhu, J. L. Aceña, V. A. Soloshonok, K. Izawa, H. Liu, *Chem. Rev.* **2016**, *116*, 422–518; e) V. D. Romanenko, V. P. Kukhar, *Chem. Rev.* **2006**, *106*, 3868–3935.

[9] a) V. Atanasov, D. Gudat, B. Ruffmann, J. Kerres, *Eur. Polym. J.* **2013**, *49*, 3977–3985; b) V. Atanasov, J. Kerres, *Macromolecules* **2011**, *44*, 6416–6423.

[10] a) L. Sang, A. Mudalige, A. K. Sigdel, A. J. Giordano, S. R. Marder, J. J. Berry, J. E. Pemberton, *Langmuir* **2015**, *31*, 5603–5613; b) H. Li, E. L. Ratcliff, A. K. Sigdel, A. J. Giordano, S. R. Marder, J. J. Berry, J.-L. Brédas, *Adv. Funct. Mater.* **2014**, *24*, 3593–3603.

[11] a) N. Allefeld, B. Kurscheid, B. Neumann, H.-G. Stammler, N. Ignat'ev, B. Hoge, *Chem. Eur. J.* **2015**, *21*, 13666–13675; b) N. Allefeld, B. Neumann, H.-G. Stammler, N. Ignat'ev, B. Hoge, *Chem. Eur. J.* **2015**, *21*, 12326–12336; c) A. Orthaber, M. Fuchs, F. Belaj, G. N. Rechberger, C. O. Kappe, R. Pietschnig, *Eur. J. Inorg. Chem.* **2011**, 2588–2596; d) G. G. Furin, A. I. Rezvukhin, M. A. Fedotov, G. G. Yakobson, *J. Fluorine Chem.* **1983**, *22*, 231–252.

[12] a) J.-L. Montchamp, Y. R. Dumond, *J. Am. Chem. Soc.* **2001**, *123*, 510–511; b) M. Kalek, J. Stawinski, *Tetrahedron* **2009**, *65*, 10406–10412.

[13] A. Orthaber, J. H. Albering, F. Belaj, R. Pietschnig, *J. Fluorine Chem.* **2010**, *131*, 1025–1031.

[14] L. N. Markovskii, G. G. Furin, Y. G. Shermolovich, G. G. Yakobson, *Russ. Chem. Bull.* **1977**, *26*, 2628–2629.

[15] L. N. Markovskii, G. G. Furin, Y. G. Shermolovich, G. G. Yakobson, *Russ. Chem. Bull.* **1981**, *30*, 646–648.

[16] E. E. Coyle, B. J. Doonan, A. J. Holohan, K. A. Walsh, F. Lavigne, E. H. Krenske, C. J. O'Brien, *Angew. Chem. Int. Ed.* **2014**, *53*, 12907–12911; *Angew. Chem.* **2014**, *126*, 13121.

[17] A. H. Mahmoudkhani, V. Langer, *J. Mol. Struct.* **2002**, *609*, 97–108.

[18] Y. Kinoshita, S. Kubota, S. Hashimoto, H. Ishikawa, *Agric. Biol. Chem.* **1973**, *37*, 701–702.

Received: November 30, 2017