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Reaction of Perfluoroalkyl Grignard Reagents with Phosphorus Trihalides: A New Route to Perfluoroalkyl-phosphonous and -phosphonic Acids

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The reaction of perfluoroalkyl Grignard reagents with phosphorus(III) halides was explored. In the process a new convenient, one-pot, high yield method for the synthesis of (perfluoroalkyl)phosphonic acids has been developed. Perfluoroalkyl Grignard reagents react with phosphorus trichloride or phosphorus tribromide to form (perfluoroalkyl)-phosphonous dihalides. Hydrolysis gives the corresponding (perfluoroalkyl)phosphonous acids. Oxidation of the phosphonous acids with H_2O_2 produces (perfluoroalkyl)phosphonic acids in 60−78% overall yields, based on the corresponding perfluoroalkyl iodide. The X-ray crystal structures of the toluidinium salts, $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$ and $[MeC_6H_4NH_3][C_8F_{17}P(O)_2OH]$, are reported.

Introduction

(Perfluoroalkyl)phosphonic acids have proved to be of interest in several diverse applications including use as anti-foaming agents,[1] as alumina HPLC stationary phases,[2] as sublimation-type thermal transfer sheets,[3] as ligand components for optical gain media,[4] as etchants of transparent In−Sn oxide electrode films,[5] as fluorinated ion-exchange membranes in fuel cells[6] and recently as lubricants for micro/nano-optoelectromechanical systems.[7] Despite this interest, (perfluoroalkyl)phosphonic acids (and indeed other perfluoroalkyl-substituted phosphorus compounds) have historically proved difficult to make. Generally, modifications of the original procedure are still used for the synthesis of (perfluoroalkyl)phosphonic acids. Emeléus and co-workers seminal discovery that white phosphorus reacts with trifluoromethyl iodide in an autoclave, to provide a mixture of trifluoromethyl-substituted phosphorus(III) compounds opened up the chemistry of perfluoroalkylphosphorus compounds (Scheme 1).[8−10] The simplest perfluoroalkylphosphonic acid $CF_3P(O)(OH)_2$ was thus synthesized by oxidative hydrolysis of CF_3PX_2, $(CF_3)_2PX$, (X = Cl, I), $P(CF_3)_3$, or CF_3PH_2, compounds which in turn were synthesized, directly or indirectly, from the phosphorus/CF_3I reaction.[10,11]

The higher analogues of perfluoroalkylphosphonic acids have been synthesized using similar methodology.[12,13] For example, Shreeve and Mahmood reported the synthesis of $C_2F_5P(O)(OH)_2$ by the Emeléus method (Scheme 2).[14] The major problems with this methodology stem from the initial Emeléus method. While the final oxidation and hydrolysis steps proceed in high yield, the initial Emeléus procedure does not. Initial conversions are often modest and thus unreacted perfluoroalkyl iodide needs to be recovered and recycled for optimum efficiency. Separation of the light-sensitive

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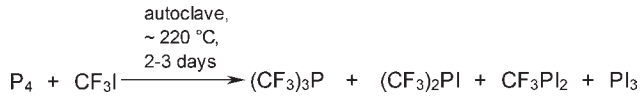
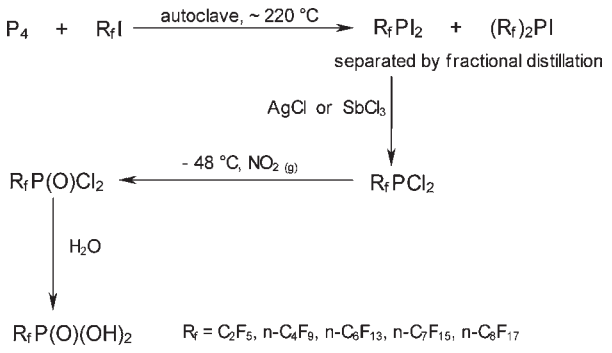
Scheme 1



Scheme 2



perfluoroalkylphosphonous diiodides from the bis(perfluoroalkyl)phosphinous iodides, phosphorus triiodide, perfluoroalkyliodides, and other materials is required. This results in reduced yields and can be problematic (for example, co-distillation of $C_4F_9PI_2/(C_4F_9)_2PI$ as well as $C_6F_{13}PI_2/(C_6F_{13})_2PI$ is a particular problem).[13] In addition, direct hydrolysis of the isolated iodides results in trace iodine contamination. This issue can be circumvented on a small scale by metathesis of the iodides to chlorides; however, stoichiometric AgCl or $SbCl_3$ are required.[14,15] Ultimately these methods lead to maximum overall yields of the final perfluoroalkylphosphonic acid of 30% or less based on the corresponding perfluoroalkyl iodide.

Recently, progress has been made in the development of improved syntheses of other perfluoroalkyl substituted phosphorus compounds. For example, tris(perfluoroalkyl)difluorophosphoranes, $(R_f)_3PF_2$ ($R_f = C_nF_{2n+1}$), have been made from trialkylphosphines via either electrochemical fluorination in anhydrous HF,[16] or direct fluorination with F_2.[17] Tris(perfluoroalkyl)phosphines, $P(R_f)_3$, are produced by the fluoride mediated reaction of Me_3SiR_f with $P(OR)_3$ (R = Ph, *p*-C_6H_4CN),[18] and metathesis procedures have been used for the synthesis of perfluoroalkyl substituted aryl- and alkylphosphines.[19] In the case of $(R_f)_3PF_2$ and $P(R_f)_3$, alkaline hydrolysis generates the corresponding perfluoroalkylphosphonic acids.[16] This synthetic strategy, however, is not "atom efficient" with respect to perfluoroalkyl groups.

The main reason that perfluoroalkyl phosphorus derivatives have proved more difficult to make than their corresponding alkyl derivatives is a relative lack of effective perfluoroalkyl carbanion organometallic reagents. It is well-known that perfluoroalkyl derivatives (particularly trifluoromethyl) of the more electropositive metals are thermally unstable.[20−22] Although perfluoroalkyl derivatives of less electropositive metals exhibit better thermal stability, they tend to be markedly less nucleophilic than their alkyl counterparts. Thus, to date, attempts to synthesize (perfluoroalkyl)phosphorus compounds from the reactions of main group perfluoroalkyl organometallics with phosphorus trihalides have met with mixed success. Reaction of pentafluoroethyl lithium with phosphorus trichloride at low temperature gave $P(C_2F_5)_3$ in 41% yield.[23] Caution must be exercised, however, as the authors have warned of the risk of explosive decomposition in closely related procedures.[24] Less nucleophilic bis(trifluoromethyl) cadmium, mercury and tellurium reagents[25] have produced small to moderate yields of $P(CF_3)_3$, the latter two under forcing conditions. Interestingly the reactivity of perfluoroalkyl Grignards with PX_3 (X = Cl, Br) does not appear to have been previously investigated. This is despite the fact that Grignard treatment of PCl_3 has been studied for over a century[26] and is established as the preferred method for the synthesis of trialkyl and many triarylphosphines.[27−30] This therefore was the subject of our study reported here. In the course of our investigation we have developed a convenient, atom efficient, one-pot synthesis of (perfluoroalkyl)phosphonic and (perfluoroalkyl)-phosphonous acids in 60−78% overall yields.

Reaction of Perfluoroalkyl Grignard Reagents with PCl_3 and PBr_3

Equimolar amounts of C_2F_5MgCl (generated *in situ* from C_2F_5I and C_2H_5MgCl in ether)[31] and PCl_3 were reacted at −78 °C in ether solution for 6 h. After warming to room temperature, a triplet of quartets was observed in the ^{31}P NMR spectrum, at δ 142.4, indicating formation of $C_2F_5PCl_2$ (lit.[14] δ 141.7). This was confirmed by the observation of doublets at δ −80.0 ($^3J_{PF}$ = 15 Hz) and δ −123.8 ($^2J_{PF}$ = 68 Hz) in the ^{19}F NMR spectrum [lit.[14] δ −78.5 ($^3J_{PF}$ = 14.65 Hz), −122.5 ($^2J_{PF}$ = 68.36 Hz)]. Quenching of the mixture with water led to formation of crude phosphonous acid $C_2F_5PH(O)OH$ [^{31}P NMR δ 7.4 (dt, $^1J_{PH}$ = 588 Hz,

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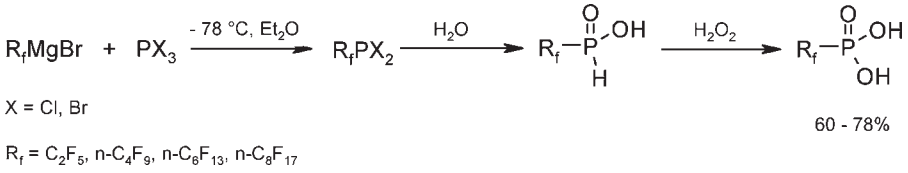
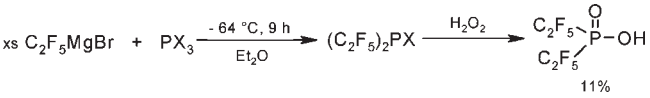
Scheme 3



$^2J_{PF}$ = 80 Hz); ^{19}F NMR δ −81.1 (s, CF_3), −132.0 (d, CF_2)]. Oxidation of the solution with aqueous 35% H_2O_2 produced the crude phosphonic acid $C_2F_5P(O)(OH)_2$ (Scheme 3). It was subsequently found that use of PBr_3 in place of PCl_3 and the bromo-Grignard, C_2F_5MgBr, instead of the chloro-Grignard, C_2F_5MgCl, led to a cleaner reaction and slightly increased yields of these acids. Thus, reaction at −78 °C of equimolar amounts of C_2F_5MgBr (generated from C_2F_5I and C_2F_5MgBr),[31] and PBr_3 led to the formation of a species tentatively proposed to be $C_2F_5PBr_2$. This assignment was based on the observation of a triplet of quartets at δ 128.1 in the ^{31}P NMR spectrum, and the observation of doublets at δ −79.2 ($^3J_{PF}$ = 18 Hz) and δ −117.7 ($^2J_{PF}$ = 53 Hz) in the ^{19}F NMR spectrum of the mixture. No attempt was made to isolate $C_2F_5PBr_2$. Oxidative quenching with 35% H_2O_2 led to crude $C_2F_5P(O)(OH)_2$ as before. Other species present are magnesium salts, C_2H_5I and small amounts of H_3PO_4 originating from unreacted PBr_3. The H_3PO_4 was removed from the aqueous mixture by addition of ammonia, which resulted in the precipitation of NH_4MgPO_4. After filtration, treatment with Amberlyst (IR 120) cation exchange resin in the H^+ form removed remaining NH_4^+ and Mg^{2+} ions. The phosphonic acid could then be conveniently isolated by ether extraction, followed by addition of two equivalents of *p*-toluidine. This resulted in selective precipitation of the corresponding bis(*p*-toluidinium) salt, $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$ in 60% overall yield based on C_2F_5I. In an analogous manner, using C_4F_9MgBr, the perfluorobutyl-substituted phosphonic acid salt, $[MeC_6H_4NH_3]_2[C_4F_9PO_3]$ could be isolated in 60% yield. Quantitative isolation of the corresponding pure phosphonic acid, $C_4F_9P(O)(OH)_2$, could be achieved by eluting an aqueous Na_2CO_3 solution of $[MeC_6H_4NH_3]_2[C_4F_9PO_3]$ through the H^+ form of the cation exchange resin. Using R_fMgBr (R_f = C_6F_{13}, C_8F_{17}), the corresponding longer chain (perfluoroalkyl)phosphonic acids could be made. In the case of these longer chain acids, however, after treatment of ether solutions of the crude acids with *p*-toluidine, the mono-*p*-toluidinium salts crystallized, thus for example, $[MeC_6H_4NH_3][C_6F_{13}P(O)_2OH]$ was isolated as white crystals in 78% overall yield based on $C_6F_{13}I$.

The intermediate free phosphonous acid, $C_2F_5PH(O)OH$, decomposed on attempted distillation. Addition of aniline or *p*-toluidine to the reaction mixture led to the formation of intractable oils. Since the parent free acid, $CF_3PH(O)OH$ has proved thermally sensitive, and difficult to obtain in analytically pure form,[10,11,32] no further attempts were made to isolate the pure acid. For the longer chain perfluoroalkyl derivates, however, it was found that after washing the residual reaction mixture with water, the intermediate phosphonous acids can be precipitated from the organic layer as anilinium or *p*-toluidinium salts by addition of $RC_6H_4NH_2$

Scheme 4



(R = H, Me). In the case of R_f = C_6F_{13}, for example, evaporation of solvent and recrysallization from dichloromethane/methanol gave crystalline $[C_6H_5NH_3][C_6F_{13}PH(O)_2]$ in 70% yield based on $C_6F_{13}I$. As far as we are aware, with the exception of R_f = CF_3, perfluoroalkylphosphonous acids and their salts have not been isolated before. Attempts to thermally decompose solutions of $[C_6H_5NH_3][C_6F_{13}PH(O)_2]$ were successful, $[C_6H_5NH_3][H_2PO_3]$ and 1H-perfluorohexane being produced quantitatively. Oxidation of the phosphonous acid *in situ*, as before gives the corresponding phosphonic acid derivatives.

During reactions using a slight excess of C_2F_5MgCl with PCl_3, in addition to the $C_2F_5PCl_2$ resonance, a faint multiplet at δ 61.3 in the ^{31}P NMR spectrum of the reaction mixture was observed. In the ^{19}F NMR spectrum doublets at δ −82.0 ($^3J_{PF}$ = 15 Hz) and δ −117.5 ($^2J_{PF}$ = 60 Hz) were observed. This suggested formation of traces of $(C_2F_5)_2PCl$ [lit:[14] ^{31}P NMR; δ 61.17; ^{19}F NMR δ −81.63 (d, $^3J_{PF}$ = 14.56 Hz) and δ −117.2 (d, $^2J_{PF}$ = 58.59 Hz)], but upon work up no $(C_2F_5)_2P(O)OH$ was isolated. Subsequent optimization, using a 6 fold excess of C_2F_5MgBr and longer reaction time at −64 °C (9 h), led to observation of a 3:1 ratio of $(C_2F_5)_2PCl$ to $C_2F_5PCl_2$ (Scheme 4). Oxidative hydrolysis with 35% H_2O_2 allowed isolation bis(perfluoroethyl)phosphinic acid, $(C_2F_5)_2P(O)OH$ in 11% yield based on C_2F_5I.

No evidence of formation of tris(perfluoroalkyl)phosphines was observed. It appears that substitution of a third perfluoroalkyl group is so slow at reduced temperature that perfluoroalkyl Grignard decomposition sets in before it can occur. It is well established that perfluoroalkyl Grignard reagents must be prepared and used at low temperature. Above −20 °C, decomposition is rapid in ether (and even faster in other solvents), to give the reduced perfluoroalkane, R_fH, or a fluoroolefin via β-elimination.[33,34]

Attempts to react $^iC_3F_7MgBr$[35] with PBr_3 lead to predominantly unreacted PBr_3, even after 12 h at −78 °C. ^{31}P NMR monitoring of the reaction mixture indicated a trace of a species, tentatively assigned as $^iC_3F_7PBr_2$ on the basis of a doublet of septets at δ 131 ($^2J_{PF}$ = 80, $^3J_{PF}$ = 17 Hz). Upon workup, however, no perfluoroisopropyl-phosphonous or -phosphonic acid could be recovered. It should be further noted that this method cannot be extended to the synthesis of

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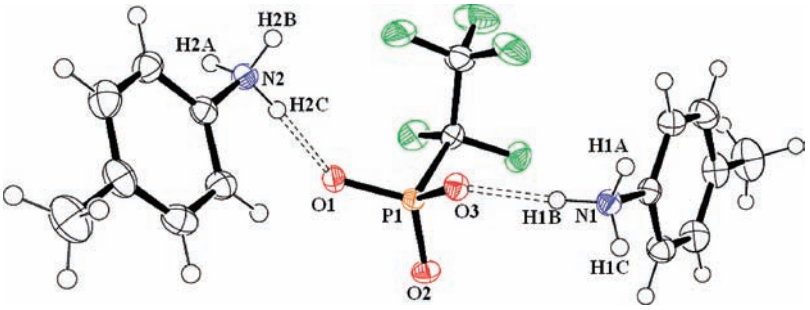

Figure 1. Molecular structure of $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$. Ellipsoids drawn at 50% probability.

the trifluoromethyl-substituted phosphorus acids, since CF_3MgBr is thermally unstable and known to decompose below −78 °C.[20−22,36]

To help establish the scope of the reactivity of perfluoroalkyl Grignard reagents toward basic phosphorus reagents, treatment with phosphorus(III) iodide was examined. No reaction was observed, however, between PI_3 and C_2F_5MgBr after 12 h at −78 °C. The low solubility of PI_3 in ether (the preferred solvent for the formation and use of perfluoroalkyl Grignard reagents)[20,34] may explain this lack of reactivity.

The reaction of conventional alkyl and aryl Grignard reagents with triphenylphosphite in refluxing ether has been established as an alternative route to tertiary phosphines.[37] In light of this procedure, we also tested the low temperature treatment of the perfluoroalkyl Grignard, C_4F_9MgBr, with triphenylphosphite in ether. After 6 h at −78 °C, however, no substitution of perfluoroalkyl groups on to phosphorus was detected by ^{31}P and ^{19}F NMR. Thermal decomposition of C_4F_9MgBr was observed upon warming to room temperature.

X-ray Structure of the Perfluoroalkylphosphonates, $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$ and $[MeC_6H_4NH_3][C_8F_{17}P(O)_2OH]$

Alkyl phosphonate salts are of interest because of their potential utility as sorbents, catalysts and because of the ease with which layered, pillared and intercalated structures can be obtained.[38] Structures of extended alkyl chain phosphonates have thus been intensely studied recently.[39,40] Shreeve et al., in reporting the first crystal structures of bis(*n*-perfluoroalkyl)phosphinic acids, noted that in general it is difficult to crystallize compounds having long perfluoroalkyl chains.[41]

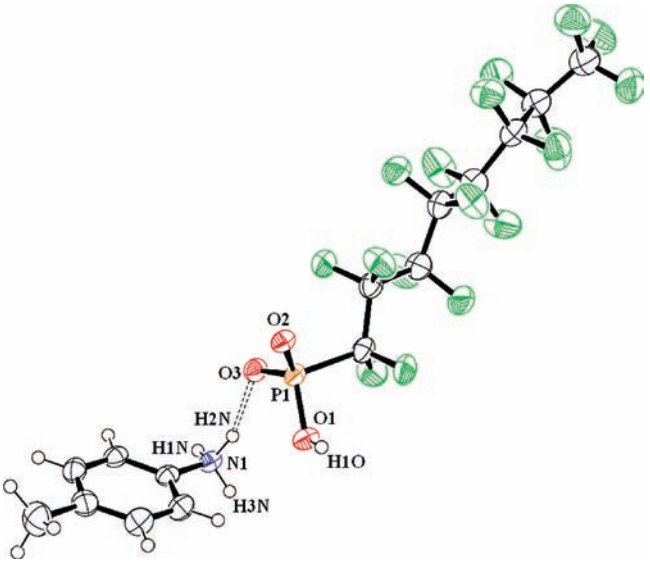

Figure 2. Molecular structure of $[MeC_6H_4NH_3][C_8F_{17}P(O)_2OH]$. Ellipsoids are drawn at 50% probability.

Although the structure of a trifluoromethyl-susbtituted phosphonate has been determined,[42] no phosphonates substituted with a longer perfluoroalkyl chain have yet been described. We report here the first crystal and molecular structures of extended chain perfluoroalkyl phosphonates.

$[MeC_6H_4NH_3]_2[C_2F_5PO_3]$ was crystallized from methanol, the molecular structure is shown in Figure 1. The phosphorus configuration is approximately tetrahedral. Each of the phosphonate oxygens are hydrogen bonded to two different *p*-toluidinium cations. Each *p*-toluidinium cation is hydrogen bonded to three phosphonate dianions. All three P−O bond distances are similar (1.507(1), 1.510(1) and 1.513(1) Å). The average O−P−O bond angle is 114.3° and the P−C bond length is 1.868(1) Å. It has previously been noted that the structures of bis(perfluoroalkyl)phosphinates exhibit longer P−C bonds, shorter P−O bonds and more obtuse O−P−O angles than found for dialkylphosphinates.[41] Comparison of structural data of $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$ with that reported for *n*-alkylphosphonates,[39,40] suggests that these same trends seem to also apply to perfluoroalkylphosphonates, albeit that the differences are relatively subtle.

$[MeC_6H_4NH_3][C_8F_{17}P(O)_2OH]$ was crystallized from chloroform/acetone (9:1). The molecular structure is shown in Figure 2. The hydrogenphosphonate groups are situated adjacent to the *p*-toluidinium ions forming neutral sheets

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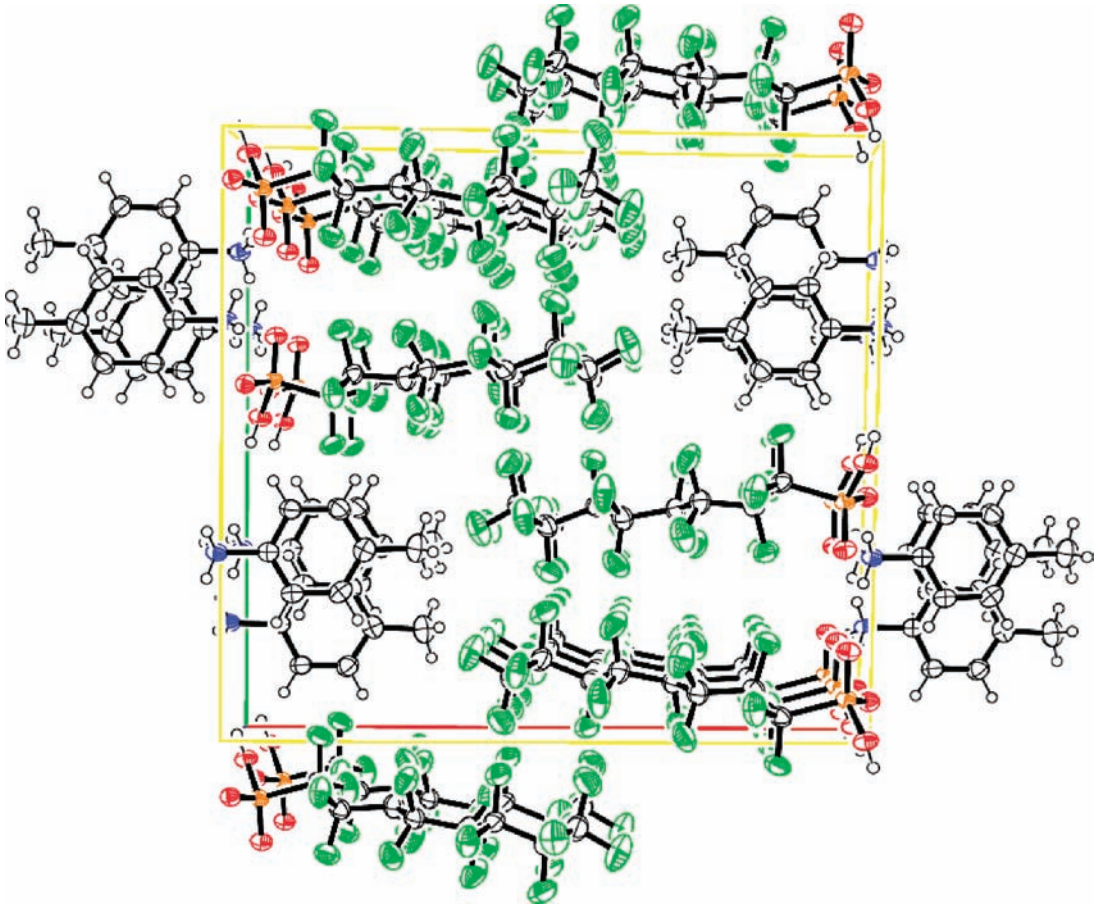

Figure 3. Unit cell packing of $[MeC_6H_4NH_3][C_8F_{17}P(O)_2OH]$. Ellipsoids are drawn at 50% probability.

(Figure 3). The perfluorooctyl groups point away from this plane. As has been observed for other hydrogenphosphonates,[40,42] there is a large difference in phosphorus−oxygen bond distances; the P−OH distance (1.553(1) Å) being considerably longer than the two other P−O distances (1.486(1) and 1.498(1) Å). The hydrogenphosphonate OH's are hydrogen bonded, to a phosphonate oxygen of an adjacent hydrogenphosphonate group in a pairwise fashion forming an eight membered ring (such eight membered rings have been observed in the structures of other hydrogenphosphonate salts).[42] This phosphonate oxygen is also hydrogen bonded to a *p*-toluidinium cation, with the remaining phosphonate oxygen hydrogen bonded to two *p*-toluidinium cations.

Conclusion

In this study we have shown that when PCl_3 or PBr_3 are reacted stoichiometrically with perfluoroalkyl Grignards, (perfluoroalkyl)phosphonous dihalides are formed exclusively. By contrast, although a few alkylphosphonous dihalides have been prepared by replacement of one halide of PX_3 by reaction with a Grignard reagent, the simplest and commonest conventional alkyl or aryl Grignards are generally too reactive for this purpose and give high yields of trialkyl- or triaryl-phosphines. This method is therefore widely used for the synthesis of trialkylphosphines and triarylphosphines. It has been described as "difficult or impossible" to limit the reaction to monosubstitution.[43] Thus the Grignard method is not generally applicable to the synthesis of alkylphosphonous dihalides except in cases where sterically bulky phosphonous dihalides are targeted and thus where overalkylation is avoided.[44] Another reaction, where selective mono-, di- and trisubstitution are possible, is the dropwise addition of C_6F_5MgBr to PCl_3.[45]

The specific production of (perfluoroalkyl)phosphonous dihalides from perfluoroalkyl Grignard treatment of phosphorus trihalides means that a selective and convenient new route to (perfluoroalkyl)phosphonous and (perfluoroalkyl)-phosphonic acids has been established through aqueous quenching or oxidation with aqueous H_2O_2 respectively.

Experimental Section

General Experimental Procedures. Perfluoroalkyliodides $C_nF_{2n+1}I$ (n = 2, 4, 6, 8) were purchased from Apollo Scientific. PCl_3, PBr_3, $P(OPh)_3$, aniline, and *p*-toluidine were purchased from Sigma-Aldrich and used as received. C_2H_5MgBr and C_2H_5MgCl were prepared in ether and standardized by literature methods. All organic solvents used were distilled and degassed. Ether was dried and distilled from sodium/benzophenone and stored over 4 Å molecular sieves. Reactions were carried out in Schlenk tubes and under an inert atmosphere of dry argon using standard Schlenk line techniques.

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^{31}P, ^{19}F, ^{13}C, and ^{1}H NMR spectra were recorded by an Avance Bruker 400 MHz FT NMR spectrometer with 85% H_3PO_4, CCl_3F, and $Si(CH_3)_4$ as external references, respectively. Elemental analyses were performed by Medac Ltd.. Yields are based on perfluoroalkyl iodides unless otherwise stated.

Synthesis of $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$. C_2F_5I (13.0 g, 52.9 mmol) and C_2H_5MgBr (28 mL, 60 mmol in 80 mL ether) were stirred at −78 °C in a Schlenk tube under argon. The Grignard exchange reaction was allowed to proceed for 1 h, after which PBr_3 (14.3 g, 52.8 mmol) was added. The mixture was then stirred at −78 °C for 6 h and then allowed to warm to room temperature overnight. The reaction was then quenched with water at 0 °C and washed with ether. H_2O_2 (35%, 12 mL) was then added, and the mixture stirred for 3 h and then boiled for 1 h to destroy the excess H_2O_2. An excess of concentrated aqueous ammonia was then added dropwise until precipitation of NH_4MgPO_4 ceased. After filtration, the solution was boiled to remove excess ammonia and treated with Amberlyst (IR120) cation exchange resin in the H^+ form to remove residual NH_4^+ and Mg^{2+} ions. The aqueous solution was then concentrated and extracted with ether until no phosphonic acid was detected in the water layer by ^{31}P NMR. The ether extracts were combined and pumped down under vacuum to constant mass to give crude $C_2F_5P(O)(OH)_2$ as a slightly yellow, viscous liquid (6.2 g, 60% yield). A portion of the crude acid (0.50 g, 2.5 mmol) was analyzed by quantitative conversion to the bis(*p*-toluidinium) salt, by treatment with *p*-toluidine (0.55 g, 5.1 mmol) in methanol at room temperature. After 2 days, colorless, crystalline platelets of $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$ (1.0 g, 97%) were obtained, which were recrystallized from methanol. ^{31}P NMR (dmso-d_6): δ −4.3 (t, $^2J_{PF}$ = 69.7 Hz). ^{19}F NMR (dmso-d_6): δ −80.9 (s, 3F, CF_3), −125.8 (d, 2F, CF_2−P). ^{1}H NMR (dmso-d_6): δ 7.49 (s, br, 6H, $2ArNH_3^+$), 6.95 (m, 8H, Ar), 2.21 (s, 6H, $2CH_3$). Mp: 246 °C (dec). Anal. Calcd for $C_{16}H_{20}F_5N_2O_3P$: C, 46.38; H, 4.87; N, 6.76. Found: C, 46.41; H, 5.11; N, 6.79.

Synthesis of $[MeC_6H_4NH_3]_2[C_4F_9PO_3]$. (a). From PBr_3. C_4F_9I, (4.02 g, 11.7 mmol), C_2H_5MgBr (11.7 mmol in 40 mL of ether), PBr_3 (3.16 g, 11.7 mmol), and *p*-toluidine (0.40 g, 3.7 mmol) were used in an analogous procedure to give crude $C_4F_9P(O)(OH)_2$ (2.10 g, 60%). Treatment of the crude acid (0.50 g, 1.7 mmol) with *p*-toluidine (0.40 g, 3.7 mmol) in methanol gave after 2 days crystalline $[MeC_6H_4NH_3]_2[C_4F_9PO_3]$ (0.84 g, 98%) which was recrystallized from methanol. ^{31}P NMR (dmso-d_6): δ −3.8 (t, $^2J_{PF}$ = 71 Hz.). ^{19}F NMR (dmso-d_6): δ −81.1 (s, 3F, CF_3), −121.6 (s, 2F, CF_2), −122.7 (d, 2F,CF_2−P), −126.0 (s, 2F, CF_2). ^{1}H NMR (dmso-d_6): δ 8.5 (s, br, 6H, $2ArNH_3^+$), 7.0 (m, 8H, Ar), 2.3 (s, 6H, $2CH_3$). Mp: 269 °C (dec). Anal. Calcd for $C_{18}H_{20}F_9N_2O_3P$: C, 42.04; H, 3.92; N, 5.44; P, 6.02. Found: C, 41.87; H, 4.04; N, 5.37; P, 5.55.

(b). From PCl_3. C_4F_9I (4.02 g, 11.7 mmol), C_2H_5MgBr (11.7 mmol in 40 mL of ether), PCl_3 (1.61 g, 11.7 mmol) were used in an analogous procedure to give crude $C_4F_9P(O)(OH)_2$ (1.9 g, 55%).

Synthesis of $C_4F_9P(O)(OH)_2$. Crystalline $[MeC_6H_4NH_3]_2[C_4F_9PO_3]$ (0.20 g, 0.40 mmol) was dissolved in 20 mL aqueous Na_2CO_3 (0.05 M). A 0.04 mL portion of this solution was used to obtain initial NMR spectra. The remaining solution was passed through freshly activated Amberlyst IR120 cation exchange resin (10 g) in the H^+ form to give a solution of pure $C_4F_9P(O)(OH)_2$ which was concentrated and made up to 2 mL in a volumetric flask. The ^{31}P and ^{19}F NMR spectra of this aqueous solution of $C_4F_9P(O)(OH)_2$ were in agreement with the literature.[14] Peaks for the *p*-toluidine group were absent in the ^{13}C NMR spectrum. The concentration of the phosphonic acid solution was determined by a 1 scan ^{31}P NMR experiment and spiking with triphenyl phosphate. Conversion to the free acid was achieved in 98%.

Synthesis of $[RC_6H_4NH_3][n\text{-}C_6F_{13}PH(O)_2]$ (R = H, Me). $C_6F_{13}I$ (4.13 g, 9.25 mmol) and C_2H_5MgBr (9.25 mmol in 35 mL of ether) were reacted while stirring at −78 °C in a 100 mL Schlenk tube under argon. The Grignard exchange reaction was allowed to proceed for 1 h after which PBr_3 (2.42 g, 8.95 mmol) was added dropwise to the cold Grignard mixture. After the addition was complete, the reaction mixture was allowed to stir at −78 °C for 6 h and then warmed to room temperature over 1 h. The mixture was then cooled to 0 °C, and 25 mL water was added dropwise while stirring. The mixture was washed with water (3 × 100 mL), and $RC_6H_4NH_2$ (R = H, Me), (10 mmol), in 50 mL of ether was added dropwise to the washed ether solution. The ether was evaporated to leave behind a yellowish residue. The residue was then washed with hot $CHCl_3$ followed by recrystallization from chloroform/acetone (9:1) to obtain fine, sticky, white crystals of $[RC_6H_4NH_3][n\text{-}C_6F_{13}PH(O)_2]$. $[C_6H_5NH_3][n\text{-}C_6F_{13}PH(O)_2]$ (3.0 g, 70%): ^{31}P NMR (dmso-d_6): δ 2.3 (dt, $^1J_{PH}$ = 549 Hz, $^2J_{PF}$ = 72 Hz). ^{19}F NMR (dmso-d_6): δ −79.7 (s, 3F, CF_3); −121.9 (br s, 4F, 2 × CF_2), − 122.0 (s, 2F, CF_2), −126.0 (s, 2F, CF_2), −128.1(d, 2F, CF_2−P). ^{1}H NMR (dmso-d_6): δ 10.1 (s, br, 3H, $ArNH_3^+$), 7.29 (m, 5H, Ar), 6.9 (d, 1H, P−H). [*p*-$MeC_6H_4NH_3$][*n*-$C_6F_{13}PH(O)_2$] (2.6 g, 59%): ^{31}P NMR (dmso-d_6): δ 1.7 (dt, $^1J_{PH}$ = 542 Hz, $^2J_{PF}$ = 71.2 Hz). ^{19}F NMR (dmso-d_6): δ −80.9 (s, 3F, CF_3, 3F), −122.2 (br s, 2 × CF_2, 4F), −122.3 (s, CF_2, 2F), −126.4 (s, CF_2, 2F), −128.8 (d, CF_2−P, 2F). ^{1}H NMR (dmso-d_6): δ 9.93 (s, br, $ArNH_3^+$, 3H), 7.25 (m, Ar, 4H), 7.0 (d, P−H, 1H), 2.31 (s, CH_3, 3H). Anal. Calcd for $C_{13}H_{11}F_{13}NO_2P$: C, 31.79; H, 2.25; N, 2.85. Found: C, 31.66; H, 2.26; N, 2.94.

Synthesis of $[C_6H_5NH_3][n\text{-}C_8F_{17}PH(O)_2]$. The anilinium salt was prepared in a similar procedure using $C_8F_{17}I$ (8.10 g, 14.8 mmol), C_2H_5MgBr (16.0 mmol in 58 mL ether), PBr_3(4.02 g, 14.8 mmol) and aniline (1.40 g, 15.0 mmol). The crude salt was then recrystallized from chloroform/acetone, (9:1). Yield, 6.30 g, 72%. ^{31}P NMR (dmso-d_6): δ 0.81 (dt, $^1J_{PH}$ = 548.0 Hz, $^2J_{PF}$ = 72.8 Hz). ^{19}F NMR (dmso-d_6): δ −82.6 (s, 3F, CF_3), −122.7 (s, 2F, CF_2), −123.1 (s, 2F, CF_2),−123.3 (s, 4F, $2CF_2$), −124.1 (s, 2F, CF_2), −127.6 (s, 2F, CF_2), −130.2 (d, 2F, CF_2−P). ^{1}H NMR (dmso-d_6): δ 9.8 (s, br, 3H, $PhNH_3^+$), 7.3 (m, 5H, Ar), 6.9 (d, 1H, P−H). Mp: 155 °C (dec). Anal. Calcd for $C_{14}H_9F_{17}NO_2P$: C, 29.13; H, 1.57; N, 2.43. Found: C, 28.82; H, 1.51; N, 2.73.

Synthesis of $[MeC_6H_4NH_3][n\text{-}C_6F_{13}P(O)_2OH]$. $C_6F_{13}I$ (3.09 g, 6.93 mmol) and C_2H_5MgBr (7.3 mmol in 40 mL of ether), were reacted while stirring at −78 °C in a 100 mL Schlenk tube under argon. The Grignard exchange reaction was allowed to proceed for 1 h after which PBr_3 (1.88 g, 6.95 mmol) was added dropwise to the cold Grignard mixture. After the addition was complete, the reaction mixture was allowed to stir at −78 °C for 6 h and then warmed to room temperature over 1 h. The mixture then cooled to 0 °C, and 25 mL water was added dropwise while stirring. The mixture was washed with water (3 × 100 mL). The washed ether layer was then vigorously shaken with 50 mL of 35% H_2O_2 and the layers allowed to separate overnight. The ether layer was then washed free of peroxide with water (5 × 50 mL or until the solution did not bleach red litmus paper). The ether solution was added dropwise to a stirring solution of *p*-toluidine, (1.51 g, 14.1 mmol), in 50 mL of ether, upon which an immediate precipitate was observed. The precipitate was filtered and washed with 10 mL of ether followed by 10 mL of CH_2Cl_2, then recrystallized from H_2O/methanol (1:1) to obtain white needle like crystals of $[MeC_6H_4NH_3][C_6F_{13}P(O)_2OH]$ (3.1 g, 78%). ^{31}P NMR (dmso-d_6): δ −3.58 (t, $^2J_{PF}$ = 74.4 Hz). ^{19}F NMR (dmso-d_6): δ −80.9 (s, 3F, CF_3), −120.7 (s, 2F, CF_2), −122.2 (s, 2F, CF_2), −122.6 (d, 2F, CF_2−P), −123.2 (s, 2F, CF_2), −126.4 (s, 2F, CF_2). ^{1}H NMR (dmso-d_6): δ 8.64 (s, br, 3H, $ArNH_3^+$), 7.17 (m, 4H, Ar), 2.28 (s, 3H, CH_3). Anal. Calcd for $C_{13}H_{11}F_{13}NO_3P$: C, 30.78; H, 2.19; N, 2.76. Found: C, 30.69; H, 2.19; N, 2.82.

Synthesis of $[MeC_6H_4NH_3][n\text{-}C_8F_{17}P(O)_2OH]$. $C_8F_{17}I$ (2.99 g, 5.47 mmol), C_2H_5MgBr (5.85 mmol), PBr_3 (1.48 g, 5.47 mmol),

50 mL of 35% H_2O_2 and *p*-toluidine (1.34 g, 12.5 mmol) were used in an analogous procedure to obtain white needle like crystals of $[MeC_6H_4NH_3][C_8F_{17}P(O)_2OH]$ (3.0 g, 76%). ^{31}P NMR (dmso-d_6): δ −3.6 (t, J_{PF} = 72.3 Hz). ^{19}F NMR (dmso-d_6): δ −81.2 (s, 3F, CF_3), −120.7 (s, 2F, CF_2), −122.1 (s, 2F, CF_2), −122.5 (s, 2F, CF_2), −122.6 (d, 2F, CF_2−P), −122.8 (s, 2F, CF_2), −123.3 (s, 2F, CF_2), −126.6 (s, 2F, CF_2). ^1H NMR (dmso-d_6): δ 8.0 (s, br, 3H, $ArNH_3^+$), 7.1 (m, 4H, Ar), 2.27 (s, 3H, CH_3), Mp: 233 °C (dec). Anal. Calcd for $C_{15}H_{11}F_{17}NO_3P$: C, 29.67; H, 1.83; N, 2.31. Found: C, 29.27; H, 1.73; N, 2.74.

Thermal Decomposition of $[C_6H_5NH_3][C_6F_{13}PH(O)_2]$. $[C_6H_5NH_3][C_6F_{13}PH(O)_2]$ (0.042 g, 0.088 mmol) was dissolved in diglyme (0.4 mL), and dmso-d_6 (0.1 mL) and water (0.1 mL) were added to an NMR tube. To determine the yields, the NMR sample was spiked with triphenyl phosphate (0.175 g, 0.536 mmol) and 1,2-trichlorotrifluoroethane (0.0570 g, 0.302 mmol). The tube was sealed and heated using an oil bath, decomposition of the salt begins at 115 °C and after 4 h at this temperature ^{31}P and ^{19}F NMR indicated full decomposition yielding $[C_6H_5NH_3][H_2PO_3]$ (98%) and $C_6F_{13}H$ (95%). ^{31}P NMR (dmso-d_6) δ 2.8, (d, J_{PH} = 640 Hz.). ^{19}F NMR (dmso-d_6) δ −82.1 (s, 3F, CF_3), −124.1 (s, 2F, CF_2), −124.4 (s, 2F, CF_2), −127.3 (s, 2F, CF_2), −130.0 (s, 2F, CF_2), −139.4 (d, 2F, CF_2−H, J_{FH} = 52.7 Hz.). This procedure was repeated yielding $[C_6H_5NH_3][H_2PO_3]$ (96%) and $C_6F_{13}H$ (95%).

Synthesis of $[C_6H_5NH_3][(C_2F_5)_2PO_2]$. C_2F_5I (17.0 g, 69.1 mmol) and C_2H_5MgCl (69.0 mmol in 30 mL of ether), were reacted while stirring at −78 °C in a 100 mL Schlenk tube under argon. The Grignard exchange reaction was allowed to proceed for 1 h after which PCl_3 (1.58 g, 11.5 mmol) was added dropwise to the cold Grignard mixture. After the addition was complete, the reaction mixture was allowed to stir at −78 °C for 20 min, then the Schlenk tube was quickly transferred to a bath at −64 °C ($CHCl_3$/dry ice), where it was maintained at that temperature for 9 h and left to gradually warm to room temperature overnight. The mixture was immersed in an ice bath and shaken thoroughly with 35% H_2O_2 (10 mL). The aqueous layer was removed, and the ether layer washed with distilled water (3 × 10 mL). The washed ether layer was then added dropwise to a solution of aniline (0.80 g, 8.6 mmol in 40 mL ether). The mixture was stirred for 1 h, and the ether was pumped off leaving behind a yellow solid which was recrystallized from chloroform/acetone (9:1) to give white needles of $[C_6H_5NH_3][(C_2F_5)_2PO_2]$ (3.0 g, 11% based on C_2F_5I). ^{31}P NMR (dmso-d_6): δ −1.3, (pentet, $^2J_{PF}$ = 65.4 Hz). ^{19}F NMR (dmso-d_6): δ −80.5, (s, CF_3); −125.6, (d, CF_2). ^1H NMR (dmso-d_6): δ 9.75, (s, br, NH_3^+); 7.49 (m, 2H, *meta*); 7.41 (m, 1H, *para*); 7.34 (m, 2H, *ortho*). ^{13}C NMR (dmso-d_6): δ 112.5, (tdq, CF_2, $^1J_{CF}$ = 287 Hz, $^1J_{CP}$ = 126 Hz, $^2J_{CF}$ = 35 Hz.), 119.6, (qtd, CF_3, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 32 Hz, $^2J_{CP}$ = 16 Hz.), 123.5, 128.6, 130.4, 132.4. Calcd for $C_{10}H_8F_{10}NO_2P$: C, 30.40; H, 2.04; N, 3.54. Found: C, 30.88; H, 2.04; N, 3.37.

Crystal Structure Determinations. $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$ was dissolved in hot methanol in a conical flask, and the solution was left to crystallize by slow evaporation. Colorless crystalline platelets were obtained after 2 days. $[MeC_6H_4NH_3][n\text{-}C_8F_{17}P(O)_2OH]$ was dissolved in water/methanol (1:1), and colorless needles were obtained by slow evaporation. Crystals were mounted on fiberglass using paraton oil and immediately cooled to 150 K in a cold stream of nitrogen. All data were collected on a Nonius Kappa CCD diffractometer at 150(1) K using Mo K_α (λ = 0.71073 Å) X-ray source and a graphite monochromator. The cell parameters were initially determined using more than 50 reflections. Experimental details are described in Table 1. The crystal structures were solved in SIR 97[46] and refined in SHELXL-97[47] by full-matrix least-squares using anisotropic thermal displacement parameters for all non-carbon and non-hydrogen atoms. Ortep drawings were made with ORTEP3-v2.[48]

Table 1. Selected Crystallographic Data of $[p\text{-}H_3CC_6H_4NH_3]_2[C_2F_5PO_3]$ and $[p\text{-}H_3CC_6H_4NH_3][C_8F_{17}P(OH)O_2]$

	$[p\text{-}H_3CC_6H_4NH_3]_2$-$[C_2F_5PO_3]$	$[p\text{-}H_3CC_6H_4NH_3]$-$[C_8F_{17}P(OH)O_2]$
empirical formula	$C_{16}H_{20}F_5N_2O_3P$	$C_{15}H_{11}F_{17}NO_3P$
formula weight	414.31	607.22
temperature/K	150.0(1)	150.0(1)
crystal habit	colorless block	colorless block
crystal size/mm	0.22 × 0.20 × 0.16	0.20 × 0.20 × 0.10
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a/Å	12.922(1)	18.909(1)
b/Å	21.573(1)	17.485(1)
c/Å	6.666(1)	6.732(1)
β/deg	91.285(1)	98.397(1)
V/Å^3	1857.8(3)	2201.9(4)
Z	4	4
D_{calc} /g cm^{-3}	1.481	1.832
μ/cm^{-1}	0.215	0.287
λ(Mo Kα)/Å	0.71069	0.71069
F(000)	856	1200
maximum θ/deg	30.03	30.03
reflections measured	18634	18846
unique data	5437	6437
R_{int}	0.0219	0.0321
reflections used	4324	3877
refln/param ratio	16	11
goodness of fit	1.066	0.970
R_1 (all data)	0.0384 (0.0511)	0.0469 (0.0894)
wR_2 (all data)	0.1078 (0.1153)	0.1251 (0.1434)

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Supporting Information Available: CIF files giving X-ray diffraction data for $[MeC_6H_4NH_3]_2[C_2F_5PO_3]$ and $[MeC_6H_4NH_3][n\text{-}C_8F_{17}P(O)_2OH]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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