

Tetra-arylfluorophosphoranes

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A number of novel tetra-arylfluorophosphoranes have been synthesised. The most stable form of these compounds is the ionic form PR_4^+F^- ($\text{R} = \text{aryl}$) although various other forms have been shown to exist including a molecular monomer PR_4F and a dimer $\text{PR}_4^+\text{PR}_4\text{F}_2^-$. The i.r. spectra of the ionic forms reveal strong $\text{P}^+ \cdots \text{F}^-$ interactions. The fluorides are prepared *via* the hydrogendifluorides $\text{PR}_4^+\text{HF}_2^-$ which contain distorted HF_2^- ions.

Compounds of general formula PR_4F are of interest because they may exist in both ionic (phosphonium fluorides) and molecular (tetraorganofluorophosphoranes) forms. They are also of interest as potential sources of nucleophilic and basic fluoride ion.^{1,2}

In 1973 Schmidbaur and co-workers^{3,4} reported the synthesis and characterisation of a series of tetraorganofluorophosphoranes containing all alkyl groups or a mixture of alkyl and aryl groups. They were able to identify both ionic and molecular forms of these compounds, although the simple tetra-alkylfluorophosphoranes proved to be highly sensitive to moisture and were easily decomposed in solution. The compounds proved to be good fluorinating agents for halogenocarbons and -silanes. Apart from a few scattered references to PR_4F compounds, this work represented the first successful attempt to prepare and properly characterise such compounds. The surprising paucity of reports can at least partly be attributed to the difficulty in the preparation of these compounds. If we consider the normal routes employed for the preparation of quaternary ammonium fluorides (NR_4F) then neutralisation of the hydroxyphosphorane is inappropriate (due to the unavailability of simple hydroxyphosphoranes) and simple halogen exchange is reported to be unsuitable or at least unreliable.^{3,4} Schmidbaur developed a novel method based on the phosphorus ylides or silylated ylides as starting materials. In a preliminary communication we recently reported⁵ the use of an ion-exchange resin to prepare the hydrogendifluoride $\text{PPh}_4^+\text{HF}_2^-$ which can easily be converted into both the ionic fluoride PPh_4^+F^- and the molecular fluorophosphorane PPh_4F . We have also shown that $\text{PPh}_4^+\text{HF}_2^-$ is a surprisingly active source of nucleophilic and basic fluoride.^{6,7} In this article we describe the preparation and characterisation of a series of novel tetra-arylfluorophosphoranes and their hydrogendifluorides, $\text{PR}_4^+\text{HF}_2^-$ ($\text{R} = \text{aryl}$).

Experimental

Infrared spectra were recorded on a Perkin-Elmer 683 ratio recording spectrophotometer with an interfaced 64K data station for spectral processing. N.m.r. spectra were recorded on a JEOL FX 90 FTNMR spectrometer operating at 36.20 (³¹P) or 84.57 (¹⁹F) MHz or on a Bruker WP 80SY FTNMR spectrometer operating at 32.44 (³¹P) or 75.40 (¹⁹F) MHz. The samples were referenced externally to 85% H_3PO_4 (³¹P) or CFCl_3 (¹⁹F). Mass spectra were recorded on a Kratos MS-3074 instrument. Thermogravimetric analyses were carried out on a Stanton Redcroft TG-750 system.

The ion-exchange resins (Amberlite IRA 401, IRA 410, or Amberlyst A26 all proved effective) were purchased in their chloride forms and were first converted into their hydroxide forms by passing 0.5 mol dm⁻³ NaOH through packed columns of the resins until no chloride ions were detectable in the column

washings. The resins were then washed with distilled water to removed free hydroxide, and converted into their hydrogendifluoride forms by treatment with 1 mol dm⁻³ HF (equivalent to twice the calculated exchange capacity of the resin). Finally they were thoroughly washed with distilled water to remove any free HF. An alternative procedure involves the direct conversion of the chloride forms of the resins into the hydrogendifluoride forms by repeated treatment with 0.5 mol dm⁻³ aqueous solutions of NH_4HF_2 . The resins were activated by washing with three bed volumes of acetonitrile to remove the bulk of water present.

Preparation of Tetra-arylphosphonium Bromides and Iodides.—Tri(4-methylphenyl)phosphine and tri(4-methoxyphenyl)phosphine were prepared in 82–86% yields by reactions of the lithium aryls with PCl_3 at -20°C .⁸ We found that PCl_3 gave better results than $\text{P}(\text{OPh})_3$. The phosphines were quaternised by reaction with the appropriate aryl iodide in the presence of palladium acetate in refluxing xylene.⁹ The products tetra(4-methylphenyl)phosphonium iodide and tetra(4-methoxyphenyl)phosphonium iodide were obtained in yields of greater than 90% after 3 h. A similar method was employed in the attempted synthesis of tetra(2-methoxyphenyl)phosphonium iodide (*via* reaction of the phosphine). The quaternisation step was sluggish and gave a low yield of product after reaction for 48 h. The product was essentially insoluble in most solvents and was not used further.

4-Cyanophenyltriphenylphosphonium iodide was prepared in two steps starting from 4-cyanoaniline. The aniline (0.040 mol) in aqueous sodium nitrite (0.046 mol) was reacted with sodium iodide (0.1 mol) at 0°C to give 4-iodobenzonitrile (0.036 mol, 90%). Quaternisation by reaction with triphenylphosphine was again achieved with palladium acetate as the catalyst giving the product in 20% yield.

2,6-Dimethylphenyltriphenylphosphonium bromide was prepared by reaction of triphenylphosphine (0.016 mol) with the pre-formed Grignard reagent of 1-bromo-2,6-dimethylbenzene [from 1-bromo-2,6-dimethylbenzene (0.06 mol) and magnesium turnings (0.06 mol) reacted together under nitrogen in ethoxyethane] at 0°C . The reaction was extremely sluggish and a recovered yield of only 1% was obtained.

Tetraphenylphosphonium bromide was a commercial sample used without further treatment.

Conversion of Tetra-arylphosphonium Bromides or Iodides into Their Hydrogendifluorides.—The tetra-arylphosphonium salts were dissolved in acetonitrile (*ca.* 0.01 mol dm⁻³) and the resulting solutions passed through a resin column containing at least 5 equivalents of HF_2^- with respect to Br^- or I^- . Acetonitrile was used to wash all of the product hydrogendifluorides off the resin. After removal of the bulk of the acetonitrile by evaporation, diethyl ether was added to the

residues to precipitate the products (any traces of phosphine oxides formed in the preparation were left in solution at this stage). The tetra-arylphosphonium hydrogendifluorides were then isolated by filtration and dried under vacuum. Thus tetraphenylphosphonium hydrogendifluoride was prepared as the dihydrate $\text{PPh}_4^+\text{HF}_2^- \cdot 2\text{H}_2\text{O}$, in 99% yield from the bromide (Found: C, 70.2; H, 5.85; P, 6.90. $\text{C}_{24}\text{H}_{25}\text{F}_2\text{O}_2\text{P}$ requires C, 69.6; H, 6.05; P, 7.50%); potentiometric titration for HF showed $98 \pm 2\%$ purity.

Conversion of Tetra-arylphosphonium Hydrogendifluorides into the Fluorides.—The tetra-arylphosphonium hydrogendifluorides were converted into their fluoride forms by rapid reaction with an equimolar amount of dilute aqueous sodium hydrogencarbonate. The products were extracted into chloroform and the solutions dried over magnesium sulphate. Addition of diethyl ether resulted in precipitation of the hydrated fluorides. Thus tetraphenylphosphonium fluoride was prepared as the tetrahydrate $\text{PPh}_4^+\text{F}^- \cdot 4\text{H}_2\text{O}$, in 85% yield from the hydrogendifluoride (Found: F^- , 4.45. $\text{C}_{24}\text{H}_{28}\text{FO}_4\text{P}$ requires F^- , 4.45%).

Discussion

Our attempts to synthesise tetra-arylphosphonium fluorides directly from the bromides or iodides by ion exchange *via* a resin were unsuccessful. Incomplete treatment of the resin with HF resulted in formation of the phosphine oxide which was invariably the alternative product to the hydrogendifluoride (or higher polyfluorides) over a wide range of resin pH. Resins that were completely in the HF_2^- form consistently gave the tetra-arylphosphonium hydrogendifluorides in quantitative yields. We therefore concentrated our efforts on the use of the hydrogendifluorides as precursors for the corresponding ionic fluorides and the molecular fluorophosphoranes.

The tetra-arylphosphonium hydrogendifluorides themselves prove to be very interesting compounds. When they are prepared in the manner described earlier they are hydrated (typically containing about 2 mol equivalents of water) and their i.r. spectra in the solid state show bands characteristic of the normal HF_2^- ion,⁵ and in particular the strong bonding mode at *ca.* $1\,210\text{ cm}^{-1}$ as well as bands due to the tetrahedral phosphonium cation. All of the hydrogendifluorides lose their water at *ca.* 60°C under vacuum. The i.r. spectra of the anhydrous hydrogendifluorides show changes in the regions of the spectra characteristic of the HF_2^- ion and in particular the band at *ca.* $1\,210\text{ cm}^{-1}$ becomes broad and split. The spectral changes observed are reminiscent of those observed on going from a normal hydrogendifluoride such as KHF_2 to a distorted form such as $\text{NR}_3\text{H}^+\text{HF}_2^-$ (where $\text{NH} \cdots \text{F}$ hydrogen bonding disturbs the symmetry of the HF_2^- ion).¹⁰ We believe that our observations are consistent with a $\text{P}^+ \cdots [\text{F} \cdots \text{H}-\text{F}]^-$ type interaction resulting in some distortion of the HF_2^- ion. The i.r. spectra of dried and undried PPh_4HF_2 are shown in Figure 1 as an example. It is interesting that dissolving dry PPh_4HF_2 in chloroform results in a partial restoration of the spectrum of normal (undistorted) HF_2^- ion presumably indicating that the ion-ion interaction is weakened in solution. A similar effect is observed if the dry hydrogendifluoride is allowed to pick up water. All of the hydrogendifluorides prepared, PPh_4HF_2 , $\text{PPh}_3(\text{C}_6\text{H}_4\text{CN}-4)\text{HF}_2$, $\text{P}(\text{C}_6\text{H}_4\text{OMe}-4)_4\text{HF}_2$, $\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_4\text{HF}_2$, and $\text{PPh}_3(\text{C}_6\text{H}_3\text{Me}_2-2,6)\text{HF}_2$, show the same effects.

Further evidence for $\text{PR}_4^+ \cdots (\text{FHF})^-$ type interactions is provided by ^{19}F n.m.r. chemical shifts (Table). The anhydrous form of PPh_4HF_2 gives a ^{19}F chemical *ca.* 13 p.p.m. to higher field than the hydrated form, which is consistent with a weakening of the hydrogen bonding in the HF_2^- ion. It is also interesting that, of the hydrogendifluorides investigated,

Table. Fluorine-19 (CFCl_3) and ^{31}P (H_3PO_4) n.m.r. chemical shifts (p.p.m.) of CDCl_3 solutions of anhydrous fluorides and hydrogendifluorides

Cation	Hydrogendifluorides		Fluorides	
	^{19}F	^{31}P	^{19}F	^{31}P
PPh_4^+	-162	22.3	-154	21.3
$\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_4^+$	-155	22.2	-150	21.4
$\text{P}(\text{C}_6\text{H}_4\text{OMe}-4)_4^+$	-159	20.4	-150	19.8
$\text{PPh}_3(\text{C}_6\text{H}_4\text{CN}-4)^+$	-167	23.2	-150	22.7
$\text{PPh}_3(\text{C}_6\text{H}_3\text{Me}_2-2,6)^+$	-150	17.7		22.7

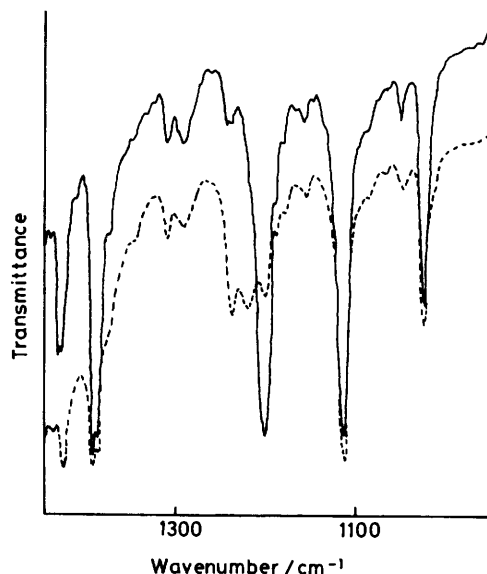


Figure 1. Infrared spectra ($1500\text{--}900\text{ cm}^{-1}$) of hydrated (—) and anhydrous (---) $\text{PPh}_4^+\text{HF}_2^-$

$\text{PPh}_3(\text{C}_6\text{H}_4\text{CN}-4)\text{HF}_2$ gives the highest-field ^{19}F n.m.r. signal which may be a result of the electron-withdrawing ability of the cyano group acting to enhance the $\text{P}^+ \cdots (\text{FHF})^-$ interaction. The lowest-field ^{19}F n.m.r. signal is observed for $\text{PPh}_3(\text{C}_6\text{H}_3\text{Me}_2-2,6)\text{HF}_2$ where steric crowding around the phosphorus is likely to reduce any interaction between the cation and the anion. Unfortunately we have as yet been unable to synthesise other tetra-arylphosphonium hydrogendifluorides that contain powerful electron-withdrawing groups such as NO_2 on one or more of the rings or those that contain other bulky *ortho* substituents on the ring(s).

Perhaps the most convincing evidence for $\text{P}^+ \cdots (\text{FHF})^-$ interactions leading to distortion of the anion is that PPh_4HF_2 is a surprisingly reactive source of both nucleophilic and basic F^- when hydrogendifluorides are normally unreactive. Our results from an investigation of the reactivity of PPh_4HF_2 have been presented,⁷ and those from a comparative study on the reactivity of ring-substituted tetra-arylphosphonium hydrogendifluorides will be reported elsewhere.

Several methods were considered for the conversion of the hydrogendifluorides into the fluorides. Thermal decomposition of PR_4HF_2 gave PR_4F but the presence of any residual water inevitably resulted in the formation of some PR_3O [$\nu(\text{P}=\text{O})$ at *ca.* $1\,200\text{ cm}^{-1}$] presumably as a result of activation of the water by F^- .² Chemical neutralisation methods involving strong bases such as H^- generally gave low yields of the products. Our preferred method is the rapid treatment of PR_4HF_2 with dilute

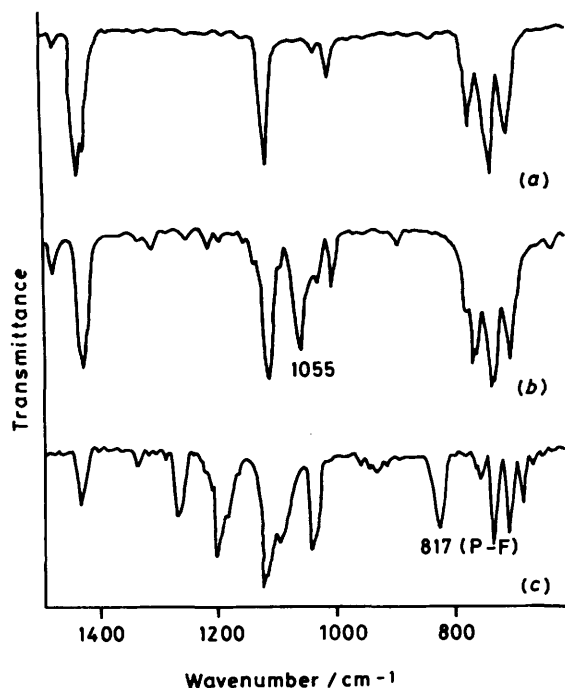


Figure 2. Infrared spectra ($1500\text{--}600\text{ cm}^{-1}$) of $\text{PPh}_4^+\text{Br}^-$ (a), PPh_4^+F^- (anhydrous) (b), and PPh_4F (gas phase) (c)

aqueous hydrogencarbonate followed by extraction of the product into chloroform.

The solid-state i.r. spectrum of PPh_4^+F^- shows a number of changes from that of the bromide or chloride and in particular the presence of an intense band at 1055 cm^{-1} (Figure 2). The solution (CDCl_3) i.r. spectrum shows a much weaker band at 1055 cm^{-1} . The changes are consistent with distortion of the tetrahedral symmetry about phosphorus,^{11,12} but not with a complete change to a trigonal-bipyramidal structure (as in molecular PPh_4F) which would be expected to result in the formation of more new bands (see later). A similar change in the i.r. spectrum is observed on going from $\text{P}(\text{C}_6\text{H}_4\text{Me-4})_4^+\text{Br}^-$ to anhydrous $\text{P}(\text{C}_6\text{H}_4\text{Me-4})_4^+\text{F}^-$ although the new activity at $ca. 1060\text{ cm}^{-1}$ is broader and more complex. Changes are also observed in the i.r. spectra of the other tetra-arylphosphonium salts on going from the bromides or iodides to the fluorides although they are less pronounced. We believe that these changes may be a result of a significant $\text{P}^+ \cdots \text{F}^-$ interaction. This is reminiscent of the suggested explanation for the changes observed in the spectra of wet and dry tetra-arylphosphonium hydrogendifluorides (see earlier) although the interactions in these cases are presumably weaker since little change in the i.r. spectra of the cations is observed.

Solutions of the fluorides in acetonitrile show single ^{19}F n.m.r. resonances at -150 to -154 p.p.m. (CFCl_3) indicative of a high degree of F^- character (Table). These values actually fall outside the normal range of ^{19}F chemical shifts for fluorides in solution ($ca. -130$ to $ca. -100$).¹³ They are also very different from those (-127 p.p.m.) reported by Richman and Flory¹ for the ionic forms of cyclofluorophosphoranes. We are not able to offer a satisfactory explanation for the unusually high-field ^{19}F chemical shifts of our fluorides although it has been suggested that shifts to high field may be a result of co-ordinative unsaturation of F^- .¹³

In an attempt to convert the ionic forms of PR_4F into their molecular forms we first studied the effects of heating on PPh_4^+F^- via thermogravimetric analysis (Figure 3). The first

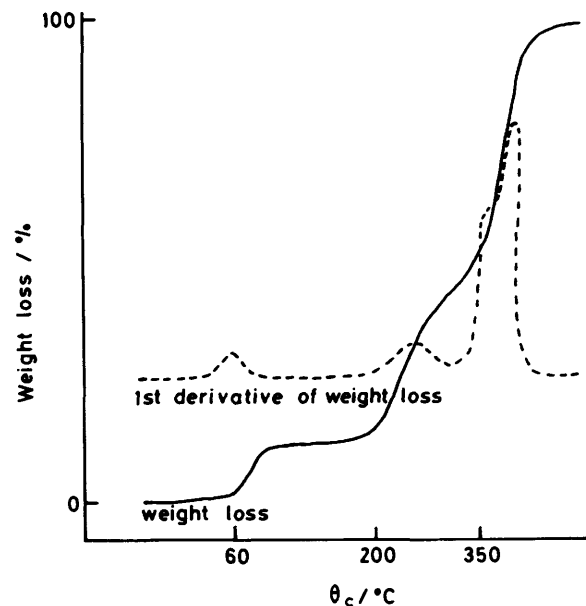


Figure 3. Plots of the weight loss (—) and its first derivative (---) against temperature for hydrated PPh_4^+F^-

weight loss from a sample of PPh_4^+F^- prepared in the normal way (see earlier) occurs at $ca. 60^\circ\text{C}$ (in flowing nitrogen) and is due to loss of part of the water of hydration. The only difference between a sample heated to $ca. 100^\circ\text{C}$ and the starting material is the strengthening of the i.r. band at $ca. 1055\text{ cm}^{-1}$ (see earlier). The next weight loss occurs at $ca. 220^\circ\text{C}$ followed by loss of the residual material at $ca. 350^\circ\text{C}$. The i.r. spectrum of a sample heated to 200°C shows bands characteristic of PPh_3O as well as PPh_4^+F^- and we believe that the weight loss at $ca. 220^\circ\text{C}$ corresponds to the vapourisation of PPh_3O which is presumably formed by F^- -catalysed hydrolysis of the phosphonium using the tightly held residual water that is not lost at 60°C . The i.r. spectrum of a sample heated to 350°C (i.e. at the commencement of the final weight loss) is identical to that of a normal tetraphenylphosphonium salt such as $\text{PPh}_4^+\text{Br}^-$, i.e. there is no band at $ca. 1055\text{ cm}^{-1}$. The material is soluble in CDCl_3 and the ^{19}F and ^{31}P n.m.r. spectra of this material are identical to those of the sample heated to $ca. 100^\circ\text{C}$. We believe that the solid formed on heating to 350°C is another form of the ionic fluoride which despite it being anhydrous does not involve significant $\text{P}^+ \cdots \text{F}^-$ interactions.

In an attempt to determine the nature of the species volatilising at $ca. 350^\circ\text{C}$ we used a heated i.r. gas cell to monitor directly the gases escaping from PPh_4^+F^- when heated. At lower temperatures the experiment confirmed our earlier observations in that water was first observed followed by PPh_3O (at $>200^\circ\text{C}$). At higher temperatures ($ca. 300^\circ\text{C}$ and above) the i.r. spectrum of the vapour changes (Figure 2). An intense band at 817 cm^{-1} is observed which is a typical P-F stretching frequency and this and other new bands observed are in excellent agreement with those reported for PMe_4F when studied as a five-co-ordinate phosphorane.³ Evidence for the molecular form is also provided by the mass spectrum of the fluoride in which the highest mass peak is at $m/z 358$. We were also able to observe weak gas-phase spectra at $ca. 300^\circ\text{C}$ for the phosphoranes $\text{P}(\text{C}_6\text{H}_4\text{OMe-4})_4\text{F}$ and $\text{PPh}_3(\text{C}_6\text{H}_4\text{CN-4})\text{F}$. Both of these compounds also showed a strong P-F stretching band at 817 cm^{-1} .

The i.r. spectra of the fluorophosphoranes persist on cooling the gas cell but we were unable actually to isolate any of them. Exposure of the fluorophosphoranes to air immediately resulted

in formation of the corresponding phosphine oxides. In a separate experiment we attempted to trap molecular PPh_4F by heating the ionic fluoride in a stream of nitrogen and passing the vapour through a cooled solvent. Rather than trap any product in the solvent we obtained a white powder from the unheated parts of the apparatus. Analysis of this material unambiguously showed it to be the dimeric species $\text{PPh}_4^+\text{PPh}_4\text{F}_2^-$. The i.r. spectrum of the material showed a strong P-F stretching band at 803 cm^{-1} , but more convincingly the ^{31}P n.m.r. spectrum showed a singlet at -22.5 p.p.m. (due to PPh_4^+) and a triplet at 15.2 p.p.m. with a $^{31}\text{P}-^{19}\text{F}$ coupling constant of 947 Hz (due to PPh_4F_2^-) while the ^{19}F n.m.r. spectrum showed a doublet at -80.6 p.p.m. ($J = 947\text{ Hz}$). The dimer, which is presumably formed by self-condensation of molecular PPh_4F , is very stable and no change was observed in its n.m.r. spectrum on heating to 150°C in dimethyl sulphoxide.

In summary, we have demonstrated that a variety of tetra-arylphosphonium hydrogendifluorides can be prepared by a simple and efficient one-stage reaction from their corresponding bromides or iodides. The anhydrous forms of these hydrogendifluorides show evidence for $\text{P}^+ \cdots (\text{FHF})^-$ interactions resulting in distortion of the normally symmetric HF_2^- ion. This distortion may well explain their high activity as sources of F^- . The hydrogendifluorides can be easily converted into the fluorides by treatment with hydrogencarbonate solution. The fluorides also appear to have $\text{P}^+ \cdots \text{F}^-$ interactions although they are weakened in solution and in at least one case a solid form of the fluoride which has no apparent $\text{P}^+ \cdots \text{F}^-$ interaction can be prepared. The fluorides show unusually high-field ^{19}F n.m.r. resonances. At high temperatures the ionic fluorides can be converted into their molecular fluorophosphorane forms

which are unstable. The stable dimeric species $\text{PPh}_4^+\text{PPh}_4\text{F}_2^-$ can also be prepared from the fluoride.

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