Tetraphenylfluorophosphorane

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Tetraphenylfluorophosphorane can exist in at least three different forms including an ionic monomer, a molecular monomer, and a dimer.

Compounds of the general formula R_4PF are of interest because they may exist in both ionic (phosphonium fluorides) and molecular (tetraorganofluorophosphoranes) forms.[1] They are also of interest as potential sources of nucleophilic and basic fluoride ion.[2] We report here the preparation of the first tetra-aryl form of this type of compound in ionic, molecular, and dimeric forms.

Attempted conversion of tetraphenylphosphonium bromide to the fluoride using an anion exchange resin leads to formation of triphenylphosphine oxide or polyfluorides, $Ph_4P^+F^-$-

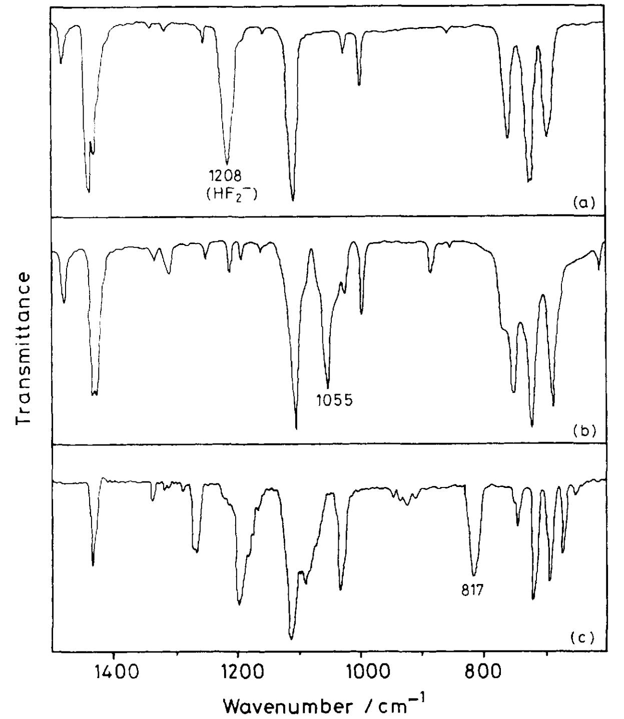


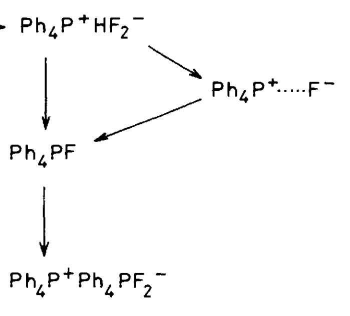
Figure 1. I.r. spectra (1500—600 cm^{-1}) of $Ph_4P^+HF_2^-$ (a), $Ph_4P^+F^-$ (b), and Ph_4PF (c).

Table 1. ^{31}P and ^{19}F N.m.r. chemical shifts and coupling constants.[a]

Compound	δ (^{31}P)[b]	δ (^{19}F)[c]	J_{PF}/Hz
$Ph_4P^+Br^-$	23.1	—	—
$Ph_4P^+HF_2^-$	22.3(s)	−150.5(s, br.)	0
$Ph_4P^+\cdots F^-$	22.5(s)	−151.0[d](s)	0
$Ph_4P^+Ph_4PF_2^-$	−15.2(t) 22.5(s)	−80.6(d)	947[e]

[a] Spectra were routinely run in CD_3CN. [b] P.p.m. with respect to H_3PO_4. [c] P.p.m. with respect to $CFCl_3$. [d] −154 P.p.m. in $CHCl_3$, −149 p.p.m. in Me_2SO. [e] No significant change in this value was observed on heating to 150 °C (in Me_2SO).

$(HF)_n$. Careful control of the resin pH and water content can lead to quantitative conversion of the bromide to the bifluoride $Ph_4P^+HF_2^-$. The n.m.r. (Table 1) and i.r. (Figure 1) spectra of the bifluoride are consistent with the presence of the HF_2^- anion[3] and a simple tetrahedral Ph_4P^+ cation[4] with no evidence of significant distortion of either ion resulting from P^+–F^- interaction. Treatment of the bifluoride with aqueous hydrogen carbonate followed by extraction into chloroform gives, on addition of ether, the solid fluoride $Ph_4P^+F^-$ in up to 60% yield. The solid-state i.r. spectrum of the fluoride shows a number of changes from that of the bromide and in particular the presence of an intense band at 1055 cm^{-1} (Figure 1). The solution ($CDCl_3$) i.r. spectrum shows only a weak band at 1055 cm^{-1}. The changes are consistent with distortion of the tetrahedral symmetry about phosphorus[4,5] in the solid state presumably resulting from significant P^+–F^- interaction. Solution n.m.r. spectra of the fluoride are consistent with an ionic fluoride and show no evidence of significant P^+–F^- interaction (Table 1).



Scheme 1

I.r. spectroscopic monitoring of the volatile products produced by heating a sample of the fluoride or the bifluoride to *ca.* 300 °C provides good evidence for the formation of the molecular tetraphenylfluorophosphorane (Figure 1). The strong band at 817 cm^{-1} is characteristic of a P–F stretching vibration and compares well with that reported for tetramethylfluorophosphorane at 808 cm^{-1} (ref. 1). The band at 817 cm^{-1} remains strong on cooling the cell but is immediately replaced by bands characteristic of triphenylphosphine oxide on exposure to the atmosphere.

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. In an attempt to crystallise the molecular tetraphenylfluorophosphorane, we cold-trapped the vapours escaping from a sample of the fluoride or bifluoride heated under reduced pressure. The solid-state i.r. spectrum of the resulting crystalline material was clearly different from anything observed previously although it did contain a strong band at 803 cm^{-1}. The ^{31}P and ^{19}F solution n.m.r. spectra of this material (Table 1) enable us to identify it as the dimer, $Ph_4P^+Ph_4PF_2^-$. The chemical shift of the ^{31}P singlet resonance is characteristic of the Ph_4P^+ group and the coupling in the ^{31}P triplet resonance and ^{19}F doublet resonance is typical for apical fluorines bonded to phosphorus. Variable temperature n.m.r. spectroscopy suggests that the dimer is stable in solution to over 150 °C. All of the proposed reaction pathways are summarised in Scheme 1.

In summary, we have demonstrated that Ph_4PF may exist in at least three different forms. In the solid state, the monomeric form contains a strong P^+–F^- interaction although it seems that this interaction is lost in solution. The molecular monomer is clearly very reactive and is readily hydrolysed in air or dimerised to $Ph_4P^+Ph_4PF_2^-$ on condensation in a vacuum.

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References

1 H. Schmidbaur and K.-H. Mitschke, *Chem. Ber.*, 1973, **106**, 1226.
2 J. E. Richman and R. B. Flay, *J. Am. Chem. Soc.*, 1981, **103**, 5265.
3 R. Newman and R. M. Badger, *J. Chem. Phys.*, 1951, **19**, 1207.
4 G. B. Deacon, R. A. Jones, and P. E. Ragasch, *Aust. J. Chem.*, 1963, **16**, 360.
5 J. B. Orenberg, M. D. Morris, and T. V. Long, *Inorg. Chem.*, 1971, **10**, 933.