Phosphonium Fluoride Salts

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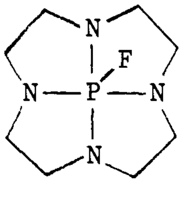
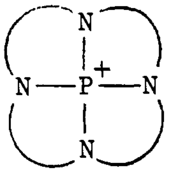
We wish to report the characterization of compounds that we believe represent the first examples of phosphonium salts containing *ionic fluoride*.[2] Phosphonium salts with complexed fluoride ion (e.g., PF_6^-) have been reported.[3]

In previous communications in this series we reported the synthesis of cyclenfluorophosphorane (**1**)[4] and the chloride salts of the cyclic phosphonium ions represented by structure **2**.[5]



1



2

(Curved lines in structure **2** represent ethylene or trimethylene bridges.) The chloride salts of **2** show increasing stability as the periphery is expanded. Models suggest that with a 16-membered periphery (four trimethylene bridges) the phosphonium center in **2** can achieve a tetrahedral geometry buried within the macrocyclic shell.[6] We have prepared the fluoro derivatives of **2** with the expectation that the larger members of this series would also be ionic. This expectation has been realized.

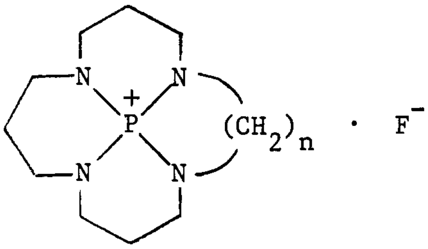
The original synthesis of **1** involved the reaction of PF_5 with the silylated derivatives of cyclen (the peripheral ring of **1**).[4] Attempts to extend this synthesis to higher homologues of **1** have not succeeded. However, ion exchange of the chloride salts of **2** by stirring overnight with AgF in anhydrous acetonitrile produces the fluoro compounds in good yields. Filtration or centrifugation of the resulting slurries followed by vacuum removal of the solvent gives about a 50% yield of the hygroscopic fluoro derivatives (see Table I).[7]

Table I. Physical and Spectrosopic Properties of the Chloro and Fluoro Derivatives of 2

		fluoro derivatives					chloro derivative[b]
compd[a]	peripheral ring size	$\delta\,^{31}$P	$\delta\,^{19}$F	J_{PF}, Hz	mp, °C	bp, °C (pressure, torr)	$\delta\,^{31}$P
2,2,2,2 (1)[c]	12	−14.2	−75.4	793	87–92	100 (0.1)	
3,2,2,2	13	−32.2	−82.6	872	liq.	70–80/0.05	+65.6
3,3,2,2	14	−42.8	−67.2	872	51.5–53.5	80/0.05	+43.2
3,2,3,2	14	−46.3	−93.3	927	63.5–66.5	80/0.1	+31.4
3,3,3,2 (3)	15	+25.2	−126.7	0	97–105	*d*	+25.4
3,3,3,3 (4)	16	+15.1	−127.4	0	120–128	*e*	+15.0

[a] Numbers represent the bridging sequences in structure 2. [b] In $CDCl_3$ solution.[5] [c] Reference 4. [d] An extremely weak molecular ion of 3 (covalent) was observed in the mass spectrum only at ca. 300 °C. [e] Not volatile.

The spectroscopic data in Table I offer convincing evidence that in acetonitrile solution both **3** and **4** exist as ionic salts.



3, n = 2
4, n = 3

The ^{31}P NMR spectra of the fluoro derivatives of **2** with 12- to 14-membered peripheries show doublets that exhibit a monotonic shift to higher field as ring size increases. Table I shows a similar effect for ring expansion on the ^{31}P chemical shifts of the tetravalent phosphonium chloride salts.[8] The ^{31}P chemical shifts of both **3** and **4** fall completely out of the sequence shown by the lower homologues and agree with the ionic chloride salts. The ^{19}F NMR spectra of **2** also show doublets for the covalent PF compounds but singlets for the ionic compounds **3** and **4** at a chemical shift characteristic of ionic fluoride.[9]

Weakly solvated ionic fluoride compounds are of interest as sources of nucleophilic and basic fluoride ion. Addition of benzyl bromide to a dilute solution (ca. 0.1 M) of **3** in acetonitrile at ambient temperature cleanly produced benzyl fluoride. The rate of this reaction followed by ^{19}F NMR is estimated to be approximately 100 times that for the reaction of "naked" fluoride[10] (KF·18-crown-6 in acetonitrile) with benzyl bromide. This observation supports the ionic nature of **3** and suggests that there is only a weak interaction of the phosphonium center with the fluoride ion.

Other tests of the reactivity of the fluoride ion in **3** and **4** are under way. A report on the structures of the oxides derived by hydrolysis of **2** is forthcoming.[11]

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[2] Kloditz (Kloditz, L. *Z. Anorg. Allg. Chem.* **1956**, *286*, 307–316) has previously reported the ionic phosphonium fluoride $PCl_4^+F^-$. The structure of this salt is questionable; $PFCl_3^+Cl^-$ would appear more likely.

[3] For closely related examples, see: (a) Schlak, O.; Schmutzler, R.; Schiebel, H.-M.; Wazeer, M. I. M.; Harris, R. K. *J. Chem. Soc., Dalton Trans.* **1974**, 2153–2157. (b) Peake, S. C.; Fild, M.; Hewson, M. J. C.; Schmutzler, R. *Inorg. Chem.* **1971**, *10*, 2723–2727. (c) Jeanneaux, F.; Riess, J. G. *Nouv. J. Chim.* **1979**, *3*, 263–268.

[4] Richman, J. E. *Tetrahedron Lett.* **1977**, 559–562.

[5] Richman, J. E.; Gupta, O. D.; Flay, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1291–1292.

[6] The faces of the P$^+$ center not covered by the bridges are protected by the lone pair electrons of the four sp^3 hybridized nitrogens.

[7] The fluoro derivatives of 2 all give acceptable C, H, and N elemental analyses. The volatile fluoro derivatives show molecular ions in their mass spectra.

[8] A similar relationship between phosphorus chemical shifts and O–P–O bond angles in phosphate esters has been reported by: Gorenstein, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 898–900.

[9] Connick, R. E.; Poulson, R. E. *J. Phys. Chem.* **1959**, *63*, 568–569.

[10] Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250–2252.

[11] Richman, J. E.; Flay, R. B.; Gupta, O. D. *ACS Symp. Ser.*, in press.

Gas-Phase Nitration of Aromatic Radical Cations

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The possibility that radical cations may be intermediates in aromatic nitrations is a subject of current debate. For aromatics

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