Direct Oxidation of Phosphines by the Bifluoride Ion

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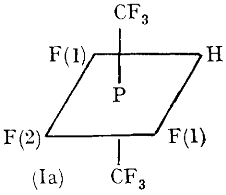
CURRENT interest[1-7] in pentaco-ordinate hydridofluorophosphoranes of the type $R_nPH_mF_{5-(n+m)}$, (R = alkyl, aryl), and RPF_2HX ($X = R_2N$, RO), prompts us to report the direct addition of potassium bifluoride to certain fluorophosphines (at 60—100°, sealed tube) to produce hexa-coordinate phosphorus salts containing phosphorus–hydrogen bonds.

$$(CF_3)_2PF + HF_2^- \rightarrow (CF_3)_2PF_3H^- \qquad \text{(I)}$$

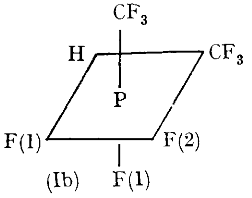
$$CF_3PF_2 + HF_2^- \rightarrow CF_3PF_4H^- \qquad \text{(II)}$$

The oxidation of trivalent to pentavalent phosphorus in these reactions is favoured by the formation of two additional strong phosphorus–fluorine bonds.

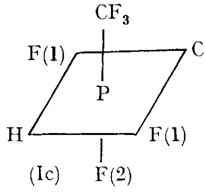
The ^{19}F n.m.r. spectrum (reproduced below) of an acetonitrile solution of (I) confirms the proposed formulation, and rules out (Ic) of the three possible stereoisomers, since (Ic) contains non-equivalent CF_3-groups. Isomer (Ia) containing *trans*-CF_3-groups would seem to be the most likely configuration since (Ib) would exhibit the observed spectrum only if $J_{F(1)CF_3}$ (*cis*) and $J_{F(1)CF_3}$ (*trans*) were equal. The spectrum can be interpreted on a first order basis owing to the surprisingly large chemical shift difference, (35·8 p.p.m.), between the two types of fluorine directly bonded to phosphorus, F(1) and F(2), which are respectively *cis*- and *trans*- to hydrogen in structures (Ia) and (Ib). The following assignments may be made:



(Ia)



(Ib)



(Ic)

(1) two widely spaced doublets at high field for the F(1) resonance, each split into two partially overlapping nine patterns of relative intensity 1 : 6 : 16 : 26 : 30 : 26 : 16 : 6 : 1 from spin coupling with phosphorus, hydrogen, single fluorine F(2) and six equivalent fluorines of the CF_3-groups. Each nine pattern arises from overlap of two septets since $J_{F(1)F(2)}$ is exactly twice $J_{CF_3-F(1)}$;

(2) a doublet, at intermediate field, for the CF_3-resonance split further into four overlapping 1 : 2 : 1 triplets from spin coupling with phosphorus, hydrogen, unique fluorine F(2), and two equivalent F(1) fluorines.

(3) A widely spaced doublet, at lower field, for the F(2) resonance, split into two overlapping 1 : 2 : 1 triplets of septets from coupling with phosphorus, hydrogen, two F(1) fluorines, and the six equivalent fluorines of the CF_3-groups.

The magnitude of the directly bonded J_{P-F} coupling constants are characteristic of hexa-coordinate species,[8,9] while further confirmation for (I) comes from the ^1H n.m.r. spectrum in which the resonance of the single proton shows the expected pattern of lines. Chemical shift and spin-coupling parameters are summarised in the Table.

The direct synthesis of (II) confirms our previous suggestion[10,11] that bifluoride ion is an intermediate in the unusual reaction between difluorotrifluoromethylphosphine and dimethylamine. We have also recently obtained (1) in the solid residue from the analogous fluorobistrifluoromethyl phosphine–amine reaction.[12] All the above reactions illustrate the ease of oxidation of these phosphines as do our recently described syntheses of platinum(0) complexes PtL_4 ($L = CF_3PF_2$, $(CF_3)_2PF$) by direct reaction between platinum(II) chloride and the phosphine.[13] No evidence has so far been obtained for the formation of the PF_5H^- ion from reactions between bifluoride ion and the parent trifluorophosphine.

TABLE

Nuclear spin-spin coupling constants for (I) [*in c./sec.*]

$J_{PF(1)}$	= 725	$J_{F(1)F(2)}$	= 25·0
$J_{PF(2)}$	= 834	$J_{F(1)H}$	= 69·5;[a] 70·2[b]
J_{PCF_3}	= 132	$J_{F(2)H}$	= 18·0[a]
$J_{F(1)CF_3}$	= 12·5	J_{HCF_3}	= 9·5;[a] 9·5[b]
$J_{F(2)CF_3}$	= 15·5	J_{PH}	= 622

Chemical shifts

ϕ_{F_1}†	= 94·3 p.p.m.	ϕ_{F_2}†	= 58·5 p.p.m.
ϕ_{CF_3}†	= 72·7 p.p.m.	τ_H‡	= 5·0 p.p.m.

[a] from ^{19}F spectrum; [b] from ^1H spectrum.

† Relative to CCl_3F; ‡ Relative to external Me_4Si.

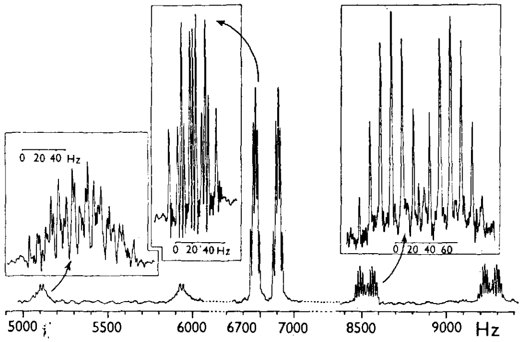


FIGURE. 94·1 *Mc./sec.* ^{19}F *n.m.r. spectrum of the* $(CF_3)_2PF_3H^-$ *anion* (I). *Figures are in c./sec., to high field of* CCl_3F.

Note added in proof: Recently we have been able to synthesise (I) and (II) at *room temperature* using MeCN as solvent.

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[1] R. A. Goodrich and P. M. Treichel, *Inorg. Chem.*, **1968**, **7**, 694.
[2] F. Seel, W. Gombler, and K. H. Rudolph, *Z. Naturforsch.*, 1968, **23**b, 387.
[3] S. Z. Ivin, K. V. Karavanov, and G. I. Drozd, U.S.S.R. Pat. 172,795, (*Chem. Abs.*, 1966, **64**, 756).
[4] G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, B. I. Tetel'baum, G. M. Luganskii and A. D. Varshavskii, *Zhur. obshchei Khim.*, 1967, **37**, 1343.
[5] R. R. Holmes and R. N. Storey, *Inorg. Chem.*, 1966, **5**, 2146.
[6] G. I. Drozd, S. Z. Ivin, V. N. Kulakova, and V. V. Sheluchenko, *J. Gen. Chem.* (*U.S.S.R.*), 1968, **38**, 576.
[7] Zh. M. Ivanova and A. V. Kirsanov, *Zhur. obshchei. Khim.*, 1961, **31**, 3991.
[8] R. Schmutzler and G. S. Reddy, *Angew. Chem.*, 1965, **77**, 530, and *Inorg. Chem.*, 1966, **5**, 164.
[9] E. L. Muetterties and W. Mahler, *Inorg. Chem.*, 1965, **4**, 119.
[10] R. G. Cavell and J. F. Nixon, *Proc. Chem. Soc.*, 1964, 229.
[11] J. F. Nixon and R. G. Cavell, *J. Chem. Soc.*, 1964, 5983.
[12] J. F. Nixon and J. R. Swain, unpublished results.
[13] J. F. Nixon and M. D. Sexton, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 275.