The Difluorodimethylphosphorus(V) Cation $[Me_2PF_2]^+$

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Summary Complexes of Me_2PF_3 with PF_5 or AsF_5 were shown to have the structure $[Me_2PF_2]^+[MF_6]^-$ in MeCN solution; n.m.r. data for the series $[Me_2PF_2]^+$, Me_2PF_3 and $[Me_2PF_4]^-$ have been compared.

COMPLEXES between fluorophosphoranes and Lewis acids have been reported by Muetterties and Mahler[1] but evidence on the structures of the complexes was not presented, although it was speculated that, at least in the solid state, the complexes were ionic, *e,g.* $[RPF_3]^+$ (or $[R_2PF_2]^+$) $[MF_n]^-$. ^{19}F n.m.r. spectroscopy has been of great value in elucidating the nature of fluoro-complexes with Lewis acid fluorides, both ionic[2] and covalent.[3] The wealth of spin 1/2 nuclei in fluorophosphoranes makes n.m.r. especially useful and allowed confirmation of the $[Me_2PF_2]^+$ ion in $Me_2PF_3{\cdot}PF_5$ and $Me_2PF_3{\cdot}AsF_5$.

Complexes were prepared by direct combination, either of the neat constituent compounds, or in acetonitrile solvent. At room temperature ^{19}F resonances from the $[Me_2PF_2]^+$ cation were broad, due to temperature-dependent exchange processes of the type previously encountered in the n.m.r. investigation of fluoro cations.[2b,4] The ^{19}F resonances due to the anions $[PF_6]^-$ and $[AsF_6]^-$ (the latter appearing as a fully resolved quartet[5]) were observed in the room temperature spectra. N.m.r. data for the $[Me_2PF_2]^+$ cation are summarized in the Table.

N.m.r. data for the series, $[Me_2PF_2]^+$, Me_2PF_3, and $[Me_2PF_4]^-$,[6] are now available (for data on Me_2PF_3 and $[Me_2PF_4]^-$, see refs 6 and 7). A smooth increase in δ_P by increments of 147 and 145 p.p.m., respectively in going from $[Me_2PF_2]^+$ *via* Me_2PF_3 to $[Me_2PF_4]^-$ ($\delta_P = -155$, $-8{\cdot}0$, and $+137{\cdot}0$ p.p.m., respectively) is noteworthy.

TABLE

N.m.r. parameters for the $[Me_2PF_2]^+$ Ion[a]

	$[Me_2PF_2]^+[PF_6]^-$	$[Me_2PF_2]^+[AsF_6]^-$
$\delta(CFCl_3)$	+ 83·5 p.p.m.	+83·3 p.p.m.
$^1J_{P-F}$	1145 Hz	1147 Hz
$^3J_{F-H}$	11 Hz	
$\delta(Me_4Si)$	−2·6 p.p.m.	−2·7 p.p.m.
$^2J_{P-H}$	15 Hz	15 Hz
$\delta(H_3PO_4)$	−155 p.p.m.	

[a] All n.m.r. measurements were conducted on saturated solutions of the complexes in acetonitrile.

Confirmation of the existence of $[Me_2PF_2]^+$, as well as $[Me_2PF_4]^-$ suggests that fluoride ion transfer might contribute to intermolecular fluorine exchange in Me_2PF_3.[8] It emphasizes the necessity of eliminating both fluoride ion acceptors as well as donors when studying exchange processes in fluorophosphoranes.

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