

Indirect Spin Coupling Constants in Fluorine Compounds of Five- and Six-co-ordinate Phosphorus

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Summary Magnitudes and signs of indirect spin coupling constants relative to $^1J(\text{CH}) > 0$ were investigated by heteronuclear INDOR-technique in the series $\text{Me}_n\text{PF}_{5-n}$ ($n = 1, 2, 3$) and in $[\text{MePF}_5]^-$ showing that $^1J(\text{PF}_a) < 0$, $^1J(\text{PF}_e) < 0$, and $^1J(\text{PC}) > 0$.

Of the many factors influencing spin coupling constants the co-ordination number seems to be particularly important.¹ Thus, going from three- to four-co-ordinate phosphorus, both $^1J(\text{PH})$ and $^1J(\text{PC})$ increase from relatively small positive or negative values, respectively, to relatively large positive values,^{2,3,4d} while $^1J(\text{PF})$ was found to be large and negative for both three- and four-co-ordinate phosphorus.⁴ To supplement the available data with coupling constants for five- and six-co-ordinate phosphorus compounds, the series of methylfluorophosphoranes,⁵ $\text{Me}_n\text{PF}_{5-n}$ ($n = 1, 2, 3$), and the anion $[\text{MePF}_5]^-$ were investigated by heteronuclear INDOR-spectroscopy, using the equipment previously described.^{4d,7}

Spectra of MePF_4 and Me_2PF_3 were recorded at reduced temperatures and low concentration (see Table), in order to slow down intramolecular exchange of axial and equatorial fluorine atoms.⁸ This could not be achieved with MePF_4 , hence only averaged couplings $^1J(\text{PF})$ and $^3J(\text{HF})$ could be observed while $^2J(\text{FF})$ remained undetected. INDOR-spectra of molecules containing ^{13}C in natural abundance could only be obtained for Me_3PF_2 and $[\text{MePF}_5]^-$ which could be recorded at normal temperature and relatively high concentrations. Even then, spectra accumulation (Varian C-1024 CAT) over periods of up to three days had to be used.

Data of coupling constants and chemical shifts, relative to the ^1H resonance of Me_4Si in the same magnetic field, are given in the Table. The nuclei perturbed and the coupling constants relative to which a sign determination was made are listed in the second and third columns, respectively.

Assuming $^1J(\text{CH}) > 0$, $^2J(\text{PH})$ was found to be negative and $^1J(\text{PC})$ to be positive in Me_3PF_2 and $[\text{MePF}_5]^-$. Since there is only a small change of $|^2J(\text{PH})|$ in all four compounds investigated, a negative sign of $^2J(\text{PH})$ in MePF_4 and Me_2PF_3 was assumed and, relative to this, signs of the other coupling constants were determined. $^1J(\text{PF})$ was found to be negative for both axial and equatorial positions. In view of the earlier observation of a negative sign of $^1J(\text{PF})$ ⁴ and since $|^1J(\text{PF})|$ is always large⁹ a negative sign of $^1J(\text{PF})$ is likely in all cases. The increase of $^1J(\text{PC})$ from $+56.5$ Hz in $[\text{Me}_4\text{P}]^{+3}$ to $+128$ Hz in Me_3PF_2 is consistent with the assumption of a dominating contact mechanism and sp^3 -character of the four P-orbitals in $[\text{PMe}_4]^+$ and nearly sp^2 -character of the three equatorial P-orbitals in Me_3PF_2 . The agreement is even more convincing if the s -character of the carbon orbitals making the P-C bond, as deduced from $^1J(\text{CH})$, is taken into account.³ Going to the six-co-ordinate anion a further increase of $^1J(\text{PC})$ is

observed. This seems to be analogous to the trends observed for $^1J(\text{CH})$ in the fluoromethane series, $\text{CH}_n\text{F}_{4-n}$.¹⁰ Also, according to Bent's rule¹¹ the s -character of a bond

MePF_4 (25%; 25% Me_4Si ; 50% CFCl_3 ; -70°)

$^1J(\text{PF})$	$= -967.7 \pm 1.0$	{F}; $^2J(\text{PH})$
$^2J(\text{PH})$	$= -20.3 \pm 0.2$	
$^3J(\text{HF})$	$= +7.0 \pm 0.1$	{P}; $^1J(\text{PF})$

$\nu(^1\text{H})$	$= 1.00000194$
$\nu(^{19}\text{F})$	$= 0.94089783$
$\nu(^{31}\text{P})$	$= 0.40479544$

Me_2PF_3 (5%; 25% Me_4Si ; 70% CFCl_3 ; -40°)

$^1J(\text{PF}_a)^*$	$= -781.6 \pm 1.0$	{F}; $^2J(\text{PH})$
$^1J(\text{PF}_e)$	$= -976.2 \pm 1.0$	{F}; $^2J(\text{PH})$
$^2J(\text{PH})$	$= -17.0 \pm 0.2$	
$^2J(\text{F}_a\text{F}_e)$	$= -28.1 \pm 0.5$	{F}; $^3J(\text{HF}_a)$, $^3J(\text{HF}_e)$
$^3J(\text{HF}_a)$	$= +12.6 \pm 0.2$	{P}; $^1J(\text{PF}_a)$, $^1J(\text{PF}_e)$
$^3J(\text{HF}_e)$	$= +3.05 \pm 0.1$	{P}; $^1J(\text{PF}_a)$, $^1J(\text{PF}_e)$

$\nu(^1\text{H})$	$= 1.00000176$
$\nu(^{19}\text{F}_a)$	$= 0.94085755$
$\nu(^{19}\text{F}_e)$	$= 0.94093787$
$\nu(^{31}\text{P})$	$= 0.40480960$

$\text{Me}_3\text{PF}_2^\dagger$ (5%; 25% Me_4Si ; 70% CFCl_3)

$^1J(\text{CH})$	$= +129.3 \pm 0.1$	{P}; $^1J(\text{CH})$
$^1J(\text{PC})$	$= +128.1 \pm 0.5$	
$^1J(\text{PF})$	$= -552.2 \pm 1.0$	{F}; $^2J(\text{PH})$
$^2J(\text{PH})$	$= -17.54 \pm 0.05$	{C}; $^1J(\text{PC})$
$^2J(\text{CF})$	$= +30.9 \pm 0.5$	{C}; $^3J(\text{HF})$
$^3J(\text{HF})$	$= +12.17 \pm 0.05$	{P}; $^1J(\text{PF})$

$\nu(^1\text{H})$	$= 1.00000161$
$\nu(^{13}\text{C})$	$= 0.25145501$
$\nu(^{19}\text{F})$	$= 0.94093578$
$\nu(^{31}\text{P})$	$= 0.40480052$

* F_a, F_e refer to axial and equatorial fluorines within the trigonal bipyramid.

[†] Coupling constants involving ^{13}C were determined on a sample containing 35% Me_3PF_2 and 65% Me_4Si .

$[\text{MePF}_5]^-$ {ca. 40% $[\text{MePF}(\text{NMe}_2)_2]^+[\text{MePF}_5]^-$; 20% C_6H_6 ; 40% MeCN }

$^1J(\text{CH})$	$= +124.6 \pm 0.5$	{P}; $^1J(\text{CH})$
$^1J(\text{PC})$	$= +262 \pm 3$	
$^1J(\text{PF}_a)$	$= -675.7 \pm 1.0$	by analogy with Me_3PF_3
$^1J(\text{PF}_e)$	$= -832.4 \pm 1.0$	{F}; $^2J(\text{PH})$
$^2J(\text{PH})$	$= -20.5 \pm 0.5$	{C}; $^1J(\text{PC})$
$^2J(\text{F}_a\text{F}_e)$	$= -35.9 \pm 1.0$	by analogy with Me_3PF_3
$^3J(\text{HF}_a)$	$= 0.0 \pm 0.5$	
$^3J(\text{HF}_e)$	$= +8.9 \pm 0.5$	{P}; $^1J(\text{PF})$

$\nu(^1\text{H})$	$= 1.00000115$
$\nu(^{13}\text{C})$	$= 0.25145761$
$\nu(^{19}\text{F})$	$= 0.94089622$
$\nu(^{31}\text{P})$	$= 0.40475690$

to an electropositive substituent increases at the expense of s -character in bonds to electronegative groups. Since in $[\text{MePF}_5]^-$ one methyl group competes with five highly

electronegative fluorine atoms this could well account for the large value of $^1J(\text{PC})$.

Assuming the same mechanism to be responsible for $^1J(\text{PC})$ and $^2J(\text{PH})$ a proportionality between these two quantities might have been expected if the transmission of spin polarisation between P and C or P and H is independent

of the molecule.¹² This is clearly not the case though $|^2J(\text{PH})|$ increases as $^1J(\text{PC})$ increases.

The vicinal coupling constants $^3J(\text{FH})$ were found to be positive as has recently been shown⁷ for all reduced vicinal coupling constants $^3K(\text{XH})$ in ethyl- and vinyl-fragments.

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