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 $^1J(\mathrm{CH}) > 0$ were investigated by heteronuclear INDOR-technique in the series $\mathrm{Me}_n\mathrm{PF}_{5-n}$ ($n = 1, 2, 3$) and in $[\mathrm{MePF}_5]^-$ showing that $^1J(\mathrm{PF}_a) < 0$, $^1J(\mathrm{PF}_e) < 0$, and $^1J(\mathrm{PC}) > 0$.

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(PH) and ^1J(PC) increase from relatively small positive or negative values, respectively, to relatively large positive values,[2,3,4d] while ^1J(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] $\mathrm{Me}_n\mathrm{PF}_{5-n}$ ($n = 1, 2, 3$), and the anion $[\mathrm{MePF}_5]^-$ [6] were investigated by heteronuclear INDOR-spectroscopy, using the equipment previously described.[4d,7]

Spectra of MePF_4 and $\mathrm{Me}_2\mathrm{PF}_3$ 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(PF) and ^3J(HF) could be observed while ^2J(FF) remained undetected. INDOR-spectra of molecules containing ^{13}C in natural abundance could only be obtained for $\mathrm{Me}_3\mathrm{PF}_2$ and $[\mathrm{MePF}_5]^-$ 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 ^{1}H resonance of $\mathrm{Me}_4\mathrm{Si}$ 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 $^1J(\mathrm{CH}) > 0$,[1] ^2J(PH) was found to be negative and ^1J(PC) to be positive in $\mathrm{Me}_3\mathrm{PF}_2$ and $[\mathrm{MePF}_5]^-$. Since there is only a small change of $|^2J(\mathrm{PH})|$ in all four compounds investigated, a negative sign of ^2J(PH) in MePF_4 and $\mathrm{Me}_2\mathrm{PF}_3$ was assumed and, relative to this, signs of the other coupling constants were determined. ^1J(PF) was found to be negative for both axial and equatorial positions. In view of the earlier observation of a negative sign of ^1J(PF)[4] and since $|^1J(\mathrm{PF})|$ is always large[9] a negative sign of ^1J(PF) is likely in all cases. The increase of ^1J(PC) from +56·5 Hz in $[\mathrm{Me}_4\mathrm{P}]^+$ [3] to +128 Hz in $\mathrm{Me}_3\mathrm{PF}_2$ is consistent with the assumption of a dominating contact mechanism and sp^3-character of the four P-orbitals in $[\mathrm{PMe}_4]^+$ and nearly sp^2-character of the three equatorial P-orbitals in $\mathrm{Me}_3\mathrm{PF}_2$. The agreement is even more convincing if the s-character of the carbon orbitals making the P–C bond, as deduced from ^1J(CH), is taken into account.[3] Going to the six-co-ordinate anion a further increase of ^1J(PC) is observed. This seems to be analogous to the trends observed for ^1J(CH) in the fluoromethane series, $\mathrm{CH}_n\mathrm{F}_{4-n}$.[10] Also, according to Bent's rule[11] the s-character of a bond to an electropositive substituent increases at the expense of s-character in bonds to electronegative groups. Since in $[\mathrm{MePF}_5]^-$ one methyl group competes with five highly

MePF_4 (25%; 25% $\mathrm{Me}_4\mathrm{Si}$; 50% CFCl_3; −70°)

^1J(PF)	= −967·7 ± 1·0	{F}; ^2J(PH)
^2J(PH)	= −20·3 ± 0·2	
^3J(HF)	= +7·0 ± 0·1	{P}; ^1J(PF)
ν(^{1}H)	= 1·00000194	
ν(^{19}F)	= 0·94089783	
ν(^{31}P)	= 0·40479544	

$\mathrm{Me}_2\mathrm{PF}_3$ (5%; 25% $\mathrm{Me}_4\mathrm{Si}$; 70% CFCl_3; −40°)

$^1J(\mathrm{PF}_a)$*	= −781·6 ± 1·0	{F}; ^2J(PH)
$^1J(\mathrm{PF}_e)$	= −976·2 ± 1·0	{F}; ^2J(PH)
^2J(PH)	= −17·0 ± 0·2	
$^2J(\mathrm{F}_a\mathrm{F}_e)$	= −28·1 ± 0·5	{F}; $^3J(\mathrm{HF}_a)$, $^3J(\mathrm{HF}_e)$
$^3J(\mathrm{HF}_a)$	= +12·6 ± 0·2	{P}; $^1J(\mathrm{PF}_a)$, $^1J(\mathrm{PF}_e)$
$^3J(\mathrm{HF}_e)$	= +3·05 ± 0·1	{P}; $^1J(\mathrm{PF}_a)$, $^1J(\mathrm{PF}_e)$
ν(^{1}H)	= 1·00000176	
ν($^{19}\mathrm{F}_e$)	= 0·94085755	
ν($^{19}\mathrm{F}_a$)	= 0·94093787	
ν(^{31}P)	= 0·40480960	

$\mathrm{Me}_3\mathrm{PF}_2$† (5%; 25% $\mathrm{Me}_4\mathrm{Si}$; 70% CFCl_3)

^1J(CH)	= +129·3 ± 0·1	
^1J(PC)	= +128·1 ± 0·5	{P}; ^1J(CH)
^1J(PF)	= −552·2 ± 1·0	{F}; ^2J(PH)
^2J(PH)	= −17·54 ± 0·05	{C}; ^1J(PC)
^2J(CF)	= +30·9 ± 0·5	{C}; ^3J(HF)
^3J(HF)	= +12·17 ± 0·05	{P}; ^1J(PF)
ν(^{1}H)	= 1·00000161	
ν(^{13}C)	= 0·25145501	
ν(^{19}F)	= 0·94093578	
ν(^{31}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% $\mathrm{Me}_3\mathrm{PF}_2$ and 65% $\mathrm{Me}_4\mathrm{Si}$.

$[\mathrm{MePF}_5]^-$ {*ca.* 40% $[\mathrm{MePF(NMe}_2)_2]^+[\mathrm{MePF}_5]^-$; 20% $\mathrm{C}_6\mathrm{H}_6$; 40% MeCN}

^1J(CH)	= +124·6 ± 0·5	
^1J(PC)	= +262 ± 3	{P}; ^1J(CH)
$^1J(\mathrm{PF}_a)$	= −675·7 ± 1·0	by analogy with $\mathrm{Me}_2\mathrm{PF}_3$
$^1J(\mathrm{PF}_e)$	= −832·4 ± 1·0	{F}; ^2J(PH)
^2J(PH)	= −20·5 ± 0·5	{C}; ^1J(PC)
$^2J(\mathrm{F}_a\mathrm{F}_e)$	= −35·9 ± 1·0	by analogy with $\mathrm{Me}_2\mathrm{PF}_3$
$^3J(\mathrm{HF}_a)$	= 0·0 ± 0·5	
$^3J(\mathrm{HF}_e)$	= +8·9 ± 0·5	{P}; ^1J(PF)
ν(^{1}H)	= 1·00000115	
ν(^{13}C)	= 0·25145761	
ν(^{19}F)	= 0·94089622	
ν(^{31}P)	= 0·40475690	

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

Assuming the same mechanism to be responsible for ^{1}J(PC) and ^{2}J(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 $|^{2}J(\mathrm{PH})|$ increases as ^{1}J(PC) increases.

The vicinal coupling constants ^{3}J(FH) were found to be positive as has recently been shown[7] for all reduced vicinal coupling constants ^{3}K(XH) in ethyl- and vinyl-fragments.

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