The Absolute Signs of the $^{1}J(P-^{13}C)$ and $^{2}J(P-C-H)$ Spin Coupling Constants in Dichloromethylphosphine

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Summary Relative to $^{1}J(C-H) > 0$, $^{1}J(P-C)$ is negative and $^{2}J(P-H)$ positive in $MePCl_2$, contrary to previous assumptions.

IN recent years a number of n.m.r. studies[1] concerned with the absolute signs of coupling constants involving phosphorus, have revealed that both magnitudes and signs of the $^{2}J(P-H)$ and $^{1}J(P-^{13}C)$ spin couplings vary in an opposite way with the co-ordination state of the phosphorus atom and therefore with its hybridisation state.

Changes in the signs of these coupling constants, as the result of substituent effects, have not been experimentally reported but in some instances such a change has been predicted by extending to phosphorus the rule suggested by Bent[2] to describe the rehybridisation effect of substituents on first-row elements. Thus Mavel and Green have assumed a negative $^{2}J(P-H)$ [3a] and a positive $^{1}J(P-^{13}C)$ [3b] for methyldichlorophosphine $MePCl_2$ in contrast with Me_3P for which these couplings are respectively positive and negative.[1] In order to show the unreliability of this generalisation in the case of P^{III} compounds, we report here the results of a magnetic double-resonance study of $MePCl_2$ which reveal that both $^{2}J(P-H)$ and $^{1}J(P-C)$ have signs opposite to the assumed ones.

Heteronuclear double-resonance experiments† were performed at 100 MHz by observing the proton spectrum of the 1% naturally abundant $^{13}CH_3PCl_2$ molecules and simultaneously irradiating at either the ^{31}P (*ca.* 40·5 MHz) or the ^{13}C (*ca.* 25·1 MHz) resonance frequency. The frequency response of the 40 MHz RF emitter was not sharp enough to permit tickling experiments but as $^{2}J(P-C-H)$ is smaller than $^{1}J(P-C)$, selective decoupling experiments[4] were adequate to provide the required information about the

† The spectra were run on a Varian HA. 100 instrument operating in the frequency-swept-locked mode and using a neat sample of $MePCl_2$ with *ca.* 5% Me_4Si. The probe of the spectrometer was fitted with appropriate double frequency probe-adapters (NMR Specialties). The ^{31}P irradiating frequency was provided by an NMR Specialties spin decoupler model HD 60 B modulated by an audio-frequency synthesiser Rhode and Schwarz ND 99 K. The ^{13}C irradiating frequency was provided by a Rhode and Schwarz frequency synthesiser model XUA.

relative signs. Tickling experiments in the ^{13}C region were performed as described elsewhere.[1] In this way, the signs of $^{1}J(P-^{13}C)$ and of $^{2}J(P-H)$ were related to the known[5] positive sign of the $^{1}J(^{13}C-H)$ coupling constant. The results of these two sets of decoupling experiments are given in the Table.

Values and signs of the coupling constants (in Hz) in $MePCl_2$

		Type of n.m.d.r.[c] experiment
$^{1}J(^{13}C-^{1}H)$	$+132 \pm 0{\cdot}5(133)$[a]	
$^{1}J(^{13}C-^{31}P)$	$-45 \pm 1(45)$[a]	{P} (C) H
$^{2}J(^{31}P-C-^{1}H)$	$+17{\cdot}6 \pm 0{\cdot}1(17{\cdot}6)$[b]	{C} (P) H

[a] Values quoted in ref. 3.
[b] Value quoted in ref. 7.
[c] The notation {A} (M) X means that one sweeps the resonance of X while irradiating one or all the transitions of A in a given spin state of M. Such an experiment gives the relative signs of the A–M and M–X coupling constants.

The $^{1}J(P-^{13}C)$ value in $MePCl_2$ appears to be the largest negative value observed for a phosphine but more negative values are perhaps not to be excluded for fluorophosphines‡ and strained cyclic phosphines. Large positive values of $^{2}J(P-C-H)$ are not unknown but they were observed in cyclic compounds and explained by a dihedral geometrical dependence[6] of this coupling in phosphines. In the case of $MePCl_2$ the free rotation about the P–C bond normally averages this effect, hence it is difficult to distinguish the influence of this dependence from that of the electronegativity of the chlorine substituent. Difficulties in the understanding of the $^{2}J(P-C-H)$ values in P^{III} compounds including halogenophosphines have already been reported.[7]

Recently, the sign of $^{1}J(P-P)$ has been found to be negative in P_2F_4 contrary to theoretical and qualitative predictions.[8] The present results indicate similar failures in predicting the signs of $^{1}J(P-^{13}C)$ and $^{2}J(P-H)$ in $MePCl_2$ and show that caution should be exercised when applying Bent's rule to three-co-ordinate phosphorus, even though this rule has proved useful to describe the variation of the $^{1}J(P-H)$ coupling constants in tetraco-ordinate phosphorus compounds.[9]

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‡ After completion of this work, we were informed that $^{1}J(P-^{13}C)$ is negative ($-34{\cdot}6$ Hz) in $(Me_3C)_2PF$ (ref. 10). We thank Dr. Dreeskamp (Stuttgart University) for giving us this information prior to publication.

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