Coupling and "Virtual" Coupling in the Nuclear Magnetic Resonance Spectra of Phosphine Complexes

By A. PIDCOCK

(*The Chemical Laboratory, University of Sussex, Brighton*)

Two of the limiting forms of $X_nAA'X_n'$ n.m.r. spectra[1] are found for the ^1H-spectra of phenyldimethylphosphine complexes of transition metals.[2] When the phosphines are *trans*, the methyl resonance exhibits "virtual" coupling and is a triplet, because $|^2J(PMP')|$ is much larger than $|^2J(PCH) - {}^4J(PMPCH)|$.[1] When the phosphines are *cis*, the spectrum is a doublet because $|^2J(PMP')|$ and $|^4J(PMPCH)|$ are small. This behaviour is of great use in stereochemical determinations[2] and it shows that $|^2J(PMP')|$ depends strongly on the angle subtended at the metal atom by the two phosphorus atoms.

Careful examination of the ^1H spectra of some phosphite complexes has enabled lower limits to be placed on the magnitude of $|^2J(PMP')|$ in a number of situations,[3] but the data in the Table are believed to be the first actual measurements for phosphorus ligands placed *trans*.† The parameters were obtained by analysis of the AB-type ^{31}P-spectra at 24·29 Mc./sec. with a capillary tube containing phosphorus(III) oxide as the reference.

TABLE

	$\|^2J(PMP')\|$ (c./sec.)	δ (p.p.m. from P_4O_6)
trans-$[PdI_2(PhPMe_2)(PhO)_3P]$	829	127·2, 14·6
trans-$[PdI_2(Bu_3P)(PhO)_3P]$	758	102·7, 9·7
trans-$[PdI_2(PhPMe_2)(Bu_3P)]$	551	133·1, 111·4

The marked dependence of $|^2J(PMP'_{trans})|$ on the electronegativity of the groups bound to phosphorus occurs also for $|^2J(PMP'_{cis})|$, this being 21·9 c./sec. in *mer*-$[RhCl_3(Bu_3P)_3]$ and 30·3 c./sec. in *mer*-$[RhCl_3(Bu_3P)_2(PhO)_3P]$.[4] The direct couplings $|^1J(PM)|$ (M = ^{11}B, ^{103}Rh, and ^{195}Pt)[4,5] are similarly larger by a factor of *ca.* 1·5 in phosphite than in phosphine complexes, and the origin of the effect appears to be a larger value in the phosphite complexes of $|\psi_{(P3s)}(0)|^2$, on which all these coupling constants depend directly.[6]

The ^1H spectrum of *trans*-$[PdI_2(PhPMe_2)(PhO)_3P]$ in the methyl region is a 1 : 1 : 1 : 1-quartet (τ 7·87) from which the two phosphorus–hydrogen coupling constants may be obtained. They can be assigned as $|^2J(PCH)| = 10·2$ c./sec. and $|^4J(PMPCH)| = 4·5$ c./sec., since without exception $|^2J(PCH)| > 6$ c./sec. in a variety of phosphine co-ordination compounds.[7] In *trans*-bis(dimethylphenylphosphine)palladium complexes $|^2J(PCH)|$ will be very similar to the above value, and using the factor of 1·5 to allow for the difference between couplings involving phosphites and phosphines, we estimate $|^4J(PMPCH)|$ ~3 c./sec. However, the separation of the outer lines of the triplet in the spectra of the bis-phosphine complexes is given by $|^2J(PCH) + {}^4J(PMPCH)|$[1] and values of *ca.* 7—9 c./sec. have been obtained,[8] so it is evident that $^2J(PCH)$ and $^4J(PMPCH)$ have opposite signs in these compounds. It further follows that the absolute sign of $^4J(PMPCH)$ is positive, since $^2J(PCH)$ has been shown to be positive in the free phosphine[9] and to change sign on co-ordination.[7c]

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† In *trans*-$[Mo(CO)_4(Bu_3P)(Ph_3P)]$ direct observations have recently shown that $|^2J(PMP'_{trans})| = 50 \pm 10$ c./sec. (S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, 1967, **89**, 5573), and this indicates a strong dependence of the *trans*-coupling constant on the electronic structure of the complex.

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