Measurement of P–P Coupling Constants in *cis*- and *trans*-Square Planar Complexes

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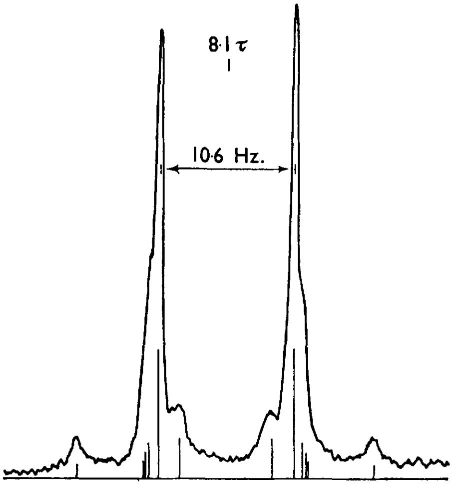
WHEN two phosphine ligands such as $MePh_2P$ are co-ordinated to one acceptor, the ^1H n.m.r. spectrum should be of the $X_nAA'X'_n$ type[1] ($X = {}^1H$, $A = {}^{31}P$) from which $J_{AA'}$ can be found in favourable circumstances. Unfortunately, hitherto[2] all *cis*-isomers have shown simple doublets ($J_{PP} \sim 0$, $J_{PH'} \sim 0$) whilst *trans*-isomers usually give triplets ($J_{PP} >> J_{PH}$) allowing only an estimate of J_{PP} to be obtained from the shape of the central line. Here the measurement of a *cis* P–P coupling from the ^1H n.m.r. spectrum of $PdCl_2(Me_3P)_2$ and of a *trans* P–P coupling from the ^{31}P resonance spectrum of $PdI_2(Me_3P)(Et_3P)$ is reported.

The ^1H n.m.r. spectrum of $PdCl_2(MeP_3)_2$ in both dichloromethane and nitrobenzene shows, in addition to the triplet due to the *trans*-isomer, the set of lines (see Figure) assignable to the *cis*-isomer. Whilst the main feature of the latter is a sharp doublet, other lines expected of an $X_9AA'X'_9$ system are observable. The spectrum was analysed by the method of Harris[1] to obtain $|J_{AA'}| = 8{\cdot}0$ and $|J_{AX} - J_{AX'}| = 12{\cdot}9$ Hz. As the second is greater than $|J_{AX} + J_{AX'}|$—the separation of the strong doublet—these two couplings must be of opposite sign. The values $|J_{P\text{-}Pd\text{-}P}| = 8{\cdot}0$, $J_{P\text{-}C\text{-}H} = \pm\, 11{\cdot}7_5$ and $J_{P\text{-}Pd\text{-}P\text{-}C\text{-}H} = \pm\, 1{\cdot}1_5$ Hz. gave the calculated lines shown in the Figure. Qualitatively similar results were obtained for other Pd^{II} and Pt^{II} complexes.

The methyl resonances of the *trans*-isomers investigated were triplets, the width of the central line suggesting that J_{PP} was several hundreds. To evaluate a *trans* P–P coupling, the ^{31}P spectrum of an equimolar mixture of $PdI_2(Me_3P)_2$ and $PdI_2(Et_3P)_2$ was measured. After a day, the four lines typical of an AB system had appeared in addition to those of the starting materials. Analysis of the AB system gave $|J| = 565 \pm 10$ Hz. and shifts the same as those due to $PdI_2(Et_3P)_2$ and $PdI_2(Me_3P)_2$ respectively. In the ^1H n.m.r. spectrum, extra Me_3P resonances appeared as a doublet of doublets, $|J_{PH}| = 10{\cdot}1$ and $|J_{P'H}| = 2{\cdot}7$ Hz. Clearly the new spectrum is due to *trans*-$PdI_2(Me_3P)(Et_3P)$. The very small change in shifts and closeness of $|J_{PH} + J_{P'H}|$ (7·4 Hz.) to that observed for *trans*-$PdI_2(Me_3P)_2$ (7·2 Hz.) suggests that there is little difference in bonding between the two complexes and, therefore, that J_{PP} must be about 565 Hz. for *trans*-$PdI_2(Me_3P)_2$ [and *trans*-$PdI_2(Et_3P)_2$].



FIGURE

100 MHz. ^1H *n.m.r. spectrum of* cis-$PdCl_2(Me_3P)_2$

The assignment of the larger P–H coupling to the nearer phosphorus atom was confirmed by the methyl resonances of *trans*-$PdI_2(Me_3P)(Et_3P)$ [present in a mixture of $PdI_2(Me_3P)_2$ and $PdI_2(Me_3As)_2$] which has the wider doublet at the shift expected of the phosphine and the narrower doublet at the shift expected of the arsine.

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