Two-dimensional δ/*J*-Resolved ^{31}P n.m.r. Spectroscopy of [Bis(diphenylphosphino)methane](trimethylphosphine)chlororhodium(I)

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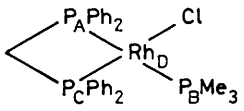
The two-dimensional δ/*J*-resolved n.m.r. method has been used to determine the spectral parameters in the $^{31}P\{^1H\}$-spectrum of the title compound.

Whilst the two-dimensional δ/*J*-resolved method[1] has frequently been applied in the analysis of complex ^1H and ^{13}C n.m.r. spectra, it has rarely been applied to the study of other nuclei.[2] Here we describe the use of this technique as an aid to the interpretation of the $^{31}P\{^1H\}$ spectrum of the complex $RhCl(PMe_3)(Ph_2PCH_2PPh_2)$ (**1**), prepared[3] by reacting



(1)

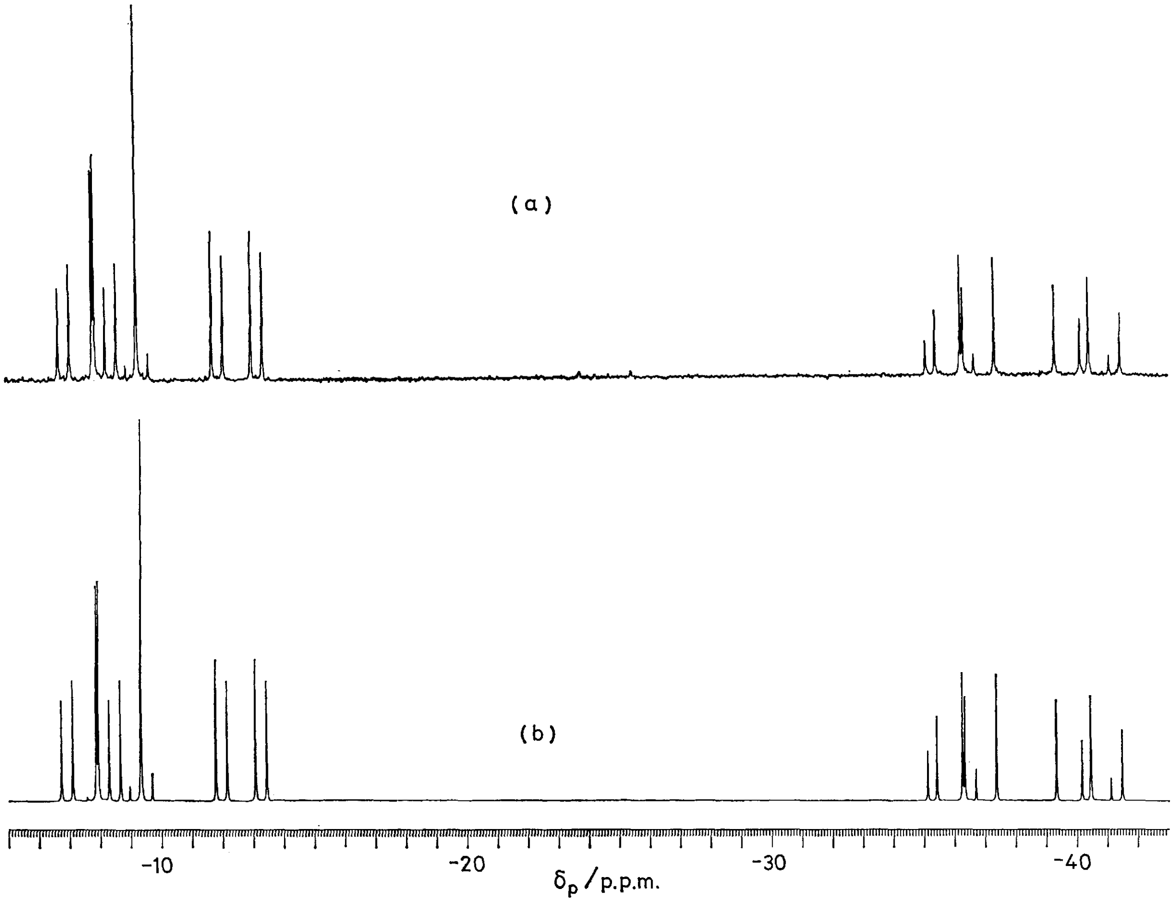


Figure 1. (a) One-dimensional 101 MHz $^{31}P\{^1H\}$ spectrum of (**1**) in benzene; (b) calculated spectrum, using a resolution of 2.0 Hz and the spectral parameters reported in the text.

$RhCl(PMe_3)_4$ with excess of bis(diphenylphosphino)methane (dpm) in toluene under reflux.†

The conventional one-dimensional $^{31}P\{^1H\}$ spectrum of this compound (Figure 1a) is rendered complex by the presence of $^{103}Rh,^{31}P$ coupling and analysis of the coupling constants and chemical shifts of the nuclei involved is not straightforward. A contour representation of the 101 MHz $^{31}P\{^1H\}$ δ/J-correlated spectrum, which has been tilted[4] by 45°, is shown in Figure 2.‡ To a first approximation the horizontal, or 'δ' axis in this representation contains only phosphorus chemical shift and ^{31}P, heteroatom coupling information, whereas the vertical, or 'J' axis contains only ^{31}P homonuclear couplings. The separation of variables in this technique results in considerable spectral simplification. A projection of the δ axis contains essentially three doublets, each separated by approximately $J(^{31}P,^{103}Rh)$, and each representing a different phosphorus atom. The cross sections in the J dimension through these six projected peaks each show a characteristic double doublet pattern resulting from the coupling of each phosphorus atom with the other two, and these can be readily analysed for the approximate values of the J_{PP} coupling constants by assuming weak coupling.[4] Second order effects are in fact apparent in the δ/J-resolved spectrum (Figure 2), such as the tilting of the peaks due to the two low field phosphorus atoms (which results in a 'chevron'-like appearance) and the presence of extra weak peaks. These effects seem to be due to strong coupling in the ABCX spin system, and not to 180° pulse imperfections.[4b] A calculation of the ABC sub-spectra using the program 'Son of LAOCOON'[4] and the spectral parameters reported below quantitatively reproduced these effects.

Although the assumption of weak coupling, and also the resolution in the two-dimensional spectrum imposed by the storage limitations of the computer system (2.9 Hz pt^{-1} in the F_2 dimension and 1.45 Hz pt^{-1} in the F_1 dimension), result in rather approximate initial values ($\pm$ 5 Hz) for the spectral constants, these are in fact more than adequate as starting values in a iterative analysis of the one-dimensional spectrum. The calculated (Figure 1b) and observed spectra are in almost exact agreement, with the following values obtained for: i, the homonuclear $^{31}P,^{31}P$ couplings, J_{AB} $\pm$ 407.7, J_{AC} $\pm$ 96.4, and J_{BC} $\mp$ 37.1 Hz; ii, the heteronuclear ^{31}P, ^{103}Rh couplings, J_{AD} $\pm$ 112.7, J_{BD} $\pm$ 131.1, and J_{CD} $\pm$ 158.2 Hz; iii, the phosphorus chemical shifts, δ_A -40.2, $\delta_B - 12.7$, and δ_C -10.2 p.p.m. relative to external H_3PO_4 in D_2O. The standard deviation in the calculated positions of the 24 observed transition frequencies was 0.11 Hz, and this fit could be obtained only by setting the relative values of J_{PP}^{trans} and J_{PP}^{cis} to be opposite in sign. Although the signs of J_{RhP} could not be determined by this approach, they are known to be negative in similar compounds,[5] owing to the negative magnetogyric ratio of rhodium. The calculated asymmetry in the $^{103}Rh\{^1H\}$ spectrum suggests that the relative signs of J_{RhP} and J_{PP}, and hence the absolute values of J_{PP}, could be assigned by observ-

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† This compound and other dpm compounds such as $Rh(dpm)_2Cl$ and $Rh(dpm)_2Me$, for which full analytical and spectroscopic data have been obtained, will be discussed separately.

‡ The spin-lattice relaxations times (T_1) of all the phosphorus atoms in (**1**) under these conditions were measured to be *ca.* 8 s. Acceptable two-dimensional spectra were only obtained if a delay between pulse cycles of at least $4T_1$ was used.

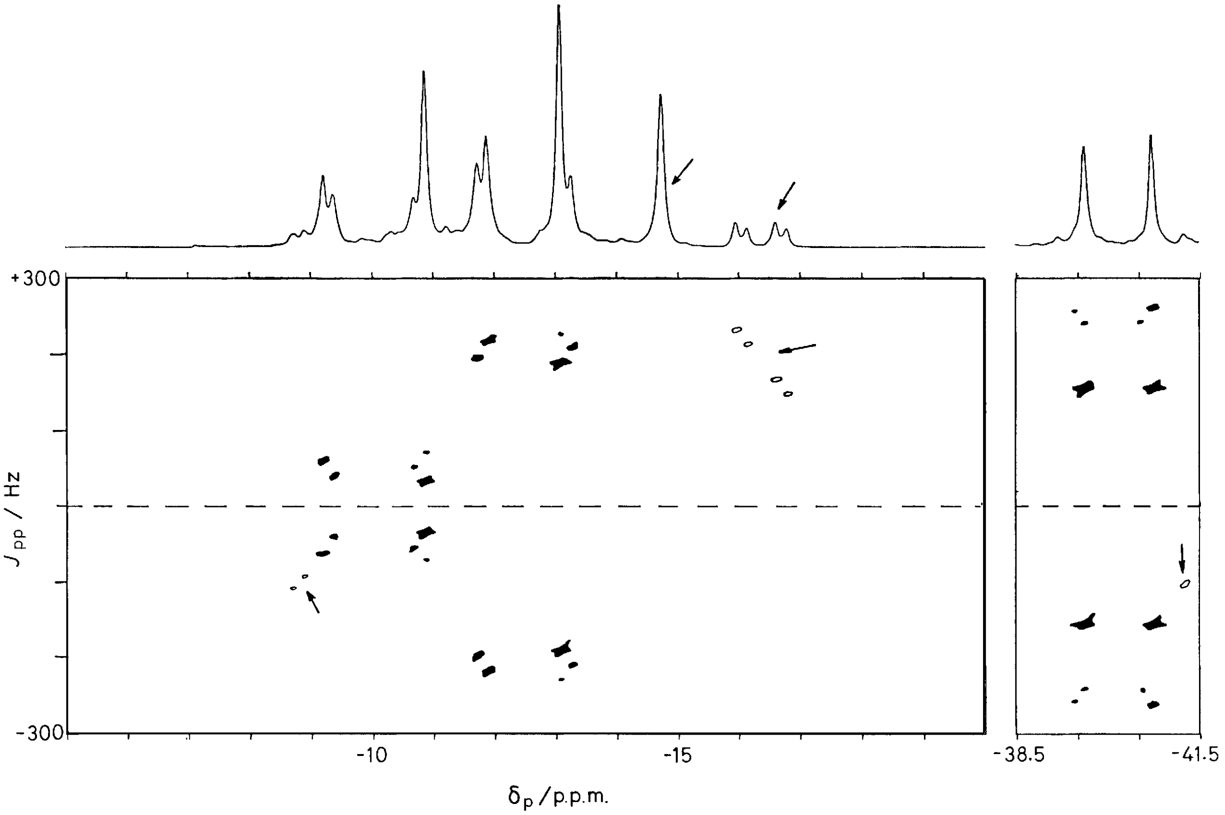

Figure 2. Two-dimensional 101 MHz $^{31}P\{^1H\}$ δ/J-resolved spectrum of a *ca.* 10 mM solution of (**1**) in benzene, recorded on a Bruker WM250 spectrometer in 17 h (this time was largely dictated by software limitations). The spectrum was tilted by 45° and is illustrated as a contour plot with a projection showing the ^{31}P chemical shift positions. Peaks marked with arrows are instrumental artifacts, and can be identified since they do not correctly reflect in the plane of symmetry in the J dimension (shown by a dashed line in the contour plot). Their positions and intensities also change according to the acquisition parameters, unlike the genuine peaks. Several such artifacts shown in the projection (*e.g.*, at δ −14.8 p.p.m.) are off the vertical scale in the contour representation.

ing this nucleus. These spectral constants are similar in magnitude to those previously reported for related rhodium complexes.[6]

These results suggest that the two-dimensional δ/J-resolved method can lead to a considerable simplification in the analysis of ^{31}P spectra which contain complex homo- and hetero-nuclear coupling, and should be readily applicable to other such nuclei.

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References

1 W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.*, 1976, **64**, 2229; W. P. Aue, J. Karhan, and R. R. Ernst, *J. Chem. Phys.*, 1976, **64**, 4226; R. Freeman and G. A. Morris, *Bull. Magn. Reson.*, 1979, **1**, 5.
2 W. McFarlane and D. S. Rycroft in 'Nuclear Magnetic Resonance,' ed. G. A. Webb (Specialist Periodical Reports), The Royal Society of Chemistry, London, 1981, Vol. 10, 162.
3 R. A. Jones, F. Mayor-Real, G. Wilkinson, M. B. Hursthouse, A. M. R. Galas, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 511.
4 (a) G. Bodenhausen, R. Freeman, G. A. Morris, and D. L. Turner, *J. Magn. Reson.*, 1978, **31**, 75; (b) A. Kumar, *J. Magn. Reson.*, 1978, **30**, 227.
5 E. M. Hyde, J. D. Kennedy, B. L. Shaw, and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1977, 1571; P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1973, 2220.
6 O. R. Hughes and D. A. Young, *J. Am. Chem. Soc.*, 1981, **103**, 6636.