J. CHEM. SOC., CHEM. COMMUN., 1982

## Two-dimensional $\delta/J$ -Resolved <sup>31</sup>P n.m.r. Spectroscopy of [Bis(diphenylphosphino)methane](trimethylphosphine)chlororhodium(I)

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

Whilst the two-dimensional  $\delta/J$ -resolved method<sup>1</sup> has frequently been applied in the analysis of complex <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra, it has rarely been applied to the study of other nuclei.<sup>2</sup> Here we describe the use of this technique as an aid to the interpretation of the <sup>31</sup>P {<sup>1</sup>H} spectrum of the complex RhCl(PMe<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) (1), prepared<sup>3</sup> by reacting





Figure 1. (a) One-dimensional 101 MHz <sup> $s_1P$ </sup> { $^{t}H$ } 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.<sup>†</sup>

The conventional one-dimensional  ${}^{31}P{}^{H}$  spectrum of this compound (Figure 1a) is rendered complex by the presence of <sup>103</sup>Rh,<sup>31</sup>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 <sup>31</sup>P {<sup>1</sup>H }  $\delta/J$ -correlated spectrum, which has been tilted<sup>4</sup> by 45°, is shown in Figure 2.<sup>‡</sup> To a first approximation the horizontal, or ' $\delta$ ' axis in this representation contains only phosphorus chemical shift and <sup>31</sup>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  $\delta$  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  $J_{\rm PP}$  coupling constants by assuming weak coupling.<sup>4</sup> Second order effects are in fact apparent in the  $\delta/J$ -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.<sup>4b</sup> A calculation of the ABC sub-spectra using the program 'Son of LAOCOON'<sup>4</sup> 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<sup>-1</sup> 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 <sup>31</sup>P,<sup>31</sup>P couplings,  $J_{AB} \pm 407.7$ ,  $J_{AC} \pm 96.4$ , and  $J_{\rm BC}$   $\mp$  37.1 Hz; ii, the heteronuclear <sup>31</sup>P, <sup>103</sup>Rh couplings,  $J_{\rm AD} \pm 112.7$ ,  $J_{\rm BD} \pm 131.1$ , and  $J_{\rm CD} \pm 158.2$  Hz; iii, the phosphorus chemical shifts,  $\delta_{\rm A} -40.2$ ,  $\delta_{\rm B}-12.7$ , and  $\delta_{\rm C}$ -10.2 p.p.m. relative to external H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O. 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  $J_{\rm PP}^{trans}$  and  $J_{\rm PP}^{cis}$  to be opposite in sign. Although the signs of  $J_{\rm RhP}$  could not be determined by this approach, they are known to be negative in similar compounds,<sup>5</sup> owing to the negative magnetogyric ratio of rhodium. The calculated asymmetry in the  ${}^{103}Rh{}^{1}H$ 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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<sup>&</sup>lt;sup>†</sup> This compound and other dpm compounds such as Rh(dpm)<sub>2</sub>Cl and Rh(dpm)<sub>2</sub>Me, for which full analytical and spectroscopic data have been obtained, will be discussed separately.

<sup>&</sup>lt;sup>‡</sup> 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.



δ<sub>p</sub>/p.p.m.

Figure 2. Two-dimensional 101 MHz <sup>31</sup>P {<sup>1</sup>H }  $\delta$ /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 <sup>31</sup>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  $\delta$  -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.<sup>6</sup>

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

We thank Dr W. McFarlane and Dr R. Freeman for helpful discussions, Dr Freeman for making available to us 'Son of LAOCOON', and the S.E.R.C. for support.

Received, 18th January 1982; Com. 041

## 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.