Determination of the Magnitudes and Signs of Phosphorus–Phosphorus Coupling ($^2J_{PP}$) by Hydrogen-1{Phosphorus-31} Internuclear Double-resonance Measurements on some Gold(I), Iridium(III), Mercury(II), Palladium(II), Platinum-(II) and -(IV), and Rhodium(III) Complexes containing Two, Three, or Four Trialkylphosphine Ligands

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The application of $^1H\{^{31}P\}$ INDOR spectroscopy to the evaluation of P–P coupling in a number of complexes has been investigated. The sign of $^2J_{PP}$ (*cis*) for the complexes *cis*-$[MX_2(PMe_3)_2]$, *cis*-$[MX_2\{P(OMe)_3\}_2]$ (M = Pd or Pt; X = Cl, Br, or I), and *cis*-$[PtMe_2(PMe_3)_2]$ has been determined by comparison of observed and calculated $^1H\{^{31}P\}$ INDOR spectra. The sign and magnitude of $^2J_{PP}$(*trans*) in the complexes *trans*-$[MX_2(PMe_3)_2]$ (M = Pd or Pt; X = Cl, Br, I, or CN), *trans*-$[MX_2(PEt_3)_2]$ (M = Pd or Pt; X = Cl, Br, or I), *trans*-$[PtX_4(PMe_3)_2]$, $[MX(PMe_3)_3]^+$ (M = Pd or Pt), *mer*-$[PtX_3(PMe_3)_3]^+$, *mer*-$[RhX_3(PMe_3)_3]$, and *trans*-$[PtX_4(PEt_3)_2]$ (X = Cl or Br), *trans*-$[IrCl_4(PMe_3)_2]^-$, *mer*-$[IrCl_3(PMe_3)_3]$, $[Hg(PMe_3)_2]^{2+}$, $[Au(PMe_3)_2]^+$, *trans*-$[PtBr_2(PPr^n_3)_2]$, and *trans*-$[PdI_2\{P(OMe)_3\}_2]$ have been obtained using increased irradiating powers. Signs and magnitudes of both $^2J_{PP}$(*cis*) and $^2J_{PP}$(*trans*) have similarly been determined for the complexes *trans*-$[RhX_2(PMe_3)_4]^+$ and *trans*-$[IrX_2(PMe_3)_4]^+$ (X = Cl or Br), $[Pt(PMe_3)_4]^{2+}$, and $[Pt\{P(OMe)_3\}_4]^{2+}$. All the *trans*-couplings are positive and greater than 250 Hz, whilst the *cis*-couplings are much smaller and negative except for those of the complex *cis*-$[PdX_2\{P(OMe)_3\}_2]$. Vibrational spectra of the latter complexes have been recorded and it is suggested that there may be something abnormal about their structure. The difference between the values of $^2J_{PP}$ in corresponding PMe_3 and PEt_3 complexes is discussed.

NIXON and PIDCOCK have emphasized the importance of the sign in comparisons of $^2J_{PP}$ in phosphine complexes of metal ions.[1] We have determined the sign of $^2J_{PP}(cis)$ in some meridional complexes by heteronuclear double resonance,[2] but the same approach is not possible for *cis*-$[MX_2(PMe_3)_2]$ (M = Pt or Pd; X = Cl, Br, or I) as the phosphine ligands are chemically equivalent. Finer and Harris [3] have described an elegant double-resonance method of determining the sign of $^2J_{PP}$ in $[AX_n]_2$ systems involving the use of ^{13}C satellites, and this has been used by Bertrand *et al.*[4] to determine the signs in a number of bis(phosphine) complexes. The method cannot be safely applied unless $^2J_{PP}$ is fairly large compared to J_{PP}, since the inner and outer lines of the ^{31}P[ab] sub-spectra are in fact multiplets (due to P–H coupling) which will overlap for smaller values of $^2J_{PP}$ especially if n is as large as nine. For this reason, and also because of their relatively low solubility, the Finer and Harris method is not suitable for *cis*-complexes of trimethylphosphine which we have previously studied.[5,6]

More recently, McFarlane has pointed out that, since weak transitions in a ^{31}P spectrum may be detected by $^1H\{^{31}P\}$ experiments using strong lines in the proton spectrum, the sign and magnitude of J_{PP} may be found for dilute solutions.[7] This is clearly applicable to systems where J_{PP} is large compared with J_{PH}, *etc.* so that the ' outer ' lines in the phosphorus spectrum are clear of the inner lines, *e.g.* Ph(Me)PP(Me)Ph,[8] but he has also applied $^1H\{^{31}P\}$ tickling experiments to the pyrophosphite ion [9] where $J_{PH} \gg J_{PP}$. The ^{31}P spectrum of the latter $[AX_2]$ system consists of only six lines so identification and irradiation of specific lines is relatively simple. The ^{31}P spectrum of the complexes *cis*-$[MX_2(PMe_3)_2]$ is much more complicated (*cf.* the spectrum of tetramethyl pyrophosphate [10] which has similar parameters) precluding such a process. During $^1H\{^{31}P\}$ INDOR measurements on these complexes, we observed that the INDOR spectra are not symmetric and that spectra obtained by monitoring the two ' sharp ' lines were mirror images.[6] The $^1H\{^{31}P\}$ INDOR spectra of simple phosphine complexes such as $[MX_3(PMe_3)]^-$ (M = Pt or Pd; X = Cl, Br, or I) are essentially inverted images of directly measured ^{31}P spectra (*cf.* Baker *et al.*[11]), suggesting that spin-population transfer effects are not important.

Here we investigate the possibility that the relative signs of $^2J_{PP}$ and J_{PH} are related to asymmetry of the ^{31}P INDOR spectra of these *cis*-complexes. From a consideration of the expected ^{31}P spectra for *trans*-$[MX_2(PMe_3)_2]$ (M = Pd or Pt; X = Cl, Br, I, or CN) and complexes containing three or four PMe_3 groups (whose ^1H spectra we have recently discussed [2]), we have investigated the application of $^1H\{^{31}P\}$ INDOR spectroscopy to the determination of $^2J_{PP}$ in such systems (*cf.* McFarlane [7]).

THEORY AND RESULTS

$X\{A\}$ INDOR Spectrum of the $[AX_n]_2$ Spin System.—A full calculation of the INDOR spectrum would include the

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[1] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

[2] P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2220.

[3] E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **13**, 65.

[4] R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1908.

[5] D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc.* (*A*), 1969, 2134.

[6] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, and B. F. Taylor, *J.C.S. Dalton*, 1974, 523.

[7] W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1972, **A5**, 353.

[8] H. C. E. McFarlane and W. McFarlane, *Chem. Comm.*, 1971, 1589.

[9] W. McFarlane, *J. Chem. Soc.* (*A*), 1968, 1715.

[10] D. J. Mowthorpe and A. C. Chapman, *Spectrochim. Acta*, 1967, **23**, 451.

[11] E. B. Baker, L. W. Burd, and C. V. Root, *Rev. Sci. Instr.*, 1963, **34**, 238, 243.

irradiating field and be a complicated problem. For the present purpose we merely regarded the X{A} INDOR spectrum as the part of the A spectrum related to a particular X transition. This drastic assumption is partially justified by the low power of the irradiating field (H_2) used (*i.e.* similar to that of 'tickling' experiments) and the agreement between observed spectra and those predicted on this basis. The X spectrum of $[AX_n]_2$ has been described by Harris [12] for $J_{XX'} = 0$ (which is valid for our complexes) and the related A spectrum by Mowthorpe and Chapman.[10] Unfortunately, the latter do not relate the A transitions to the X transitions as we require.

The problem breaks down into a series of four submatrices [12] which have eigenvalues (1)—(3), where α or β refer to spin functions of the A nuclei, m and p are sums of spin eigenvalues for the X_n and X_n' groups respectively,

$$\alpha\alpha(m,p):\quad \nu_A + (m+p)\nu_X + \tfrac{1}{4}J + \tfrac{1}{2}(m+p)N \qquad (1)$$

$$\left.\begin{matrix}\alpha\beta(m,p):\\ \beta\alpha(m,p):\end{matrix}\right\} \quad (m+p)\nu_X - \tfrac{1}{4}J \pm \tfrac{1}{2}[(m-p)^2L^2 + J^2]^{\frac{1}{2}} \qquad (2)$$

$$\beta\beta(m,p):\quad -\nu_A + (m+p)\nu_X + \tfrac{1}{4}J - \tfrac{1}{2}(m+p)N \qquad (3)$$

$J = J_{AA'}$, $N = J_{AX} + J_{AX'}$, and $L = J_{AX} - J_{AX'}$. We were particularly interested in A transitions related to the strong doublet in the X spectrum, *i.e.* X transitions of the $\alpha\alpha(m,p)$ and $\beta\beta(m,p)$ states. These will be as in (4) and (5),

$$\alpha\alpha(m,p):\ \nu_A + \tfrac{1}{2}\{J + (m+p)N \pm [(m-p)^2L^2 + J^2]^{\frac{1}{2}}\} \qquad (4)$$

$$\beta\beta(m,p):\ \nu_A + \tfrac{1}{2}\{-J + (m+p)N \pm [(m-p)^2L^2 + J^2]^{\frac{1}{2}}\} \qquad (5)$$

where m and p take values $(n/2)$, $(n/2) - 1 \ldots -(n/2)$. By a similar argument to that used by Harris [12] for the X part, intensities of the A lines were found to be $(1 \pm \sin 2\theta)\text{-}{}^nC_{[(n/2)+m]}{}^nC_{[(n/2)+p]}$ where $\sin 2\theta = J/[(m-p)^2L^2 + J^2]^{\frac{1}{2}}$ and the positive sign refers to transitions where the J and square-root terms have opposite signs. The total A intensity on this scale is $2^{(2n+2)}$ and the complete set of transitions agree with those of ref. 10.

If we consider the transitions to $\alpha\alpha(m,p)$, there is a set of 'inner' lines where the J and square-root terms have opposite signs, and a set of 'outer' lines, J away from the 'inner' lines, on *one side only*. Thus, if J is sufficiently large the sign can be determined immediately. In fact, the rule is similar to that for the more usual determination of signs by double resonance; namely, if the 'outer' A line observed lies to the same side of ν_A as the X line monitored does of ν_X, then $J_{AA'}$ and $(J_{AX} + J_{AX'})$ have the same sign and *vice versa*. This assumes γ_A and γ_X have the same sign; if they have opposite signs, then the reverse of the above rule is true. However, for lower values of J, inner and outer lines overlap and the best way of obtaining the sign of J is comparison of observed spectra with those calculated from the formulae above using appropriate parameters.

cis-*Bis(phosphine) Complexes.*—^{31}P Spectra of the complexes *cis*-$[MX_2(PMe_3)_2]$ (M = Pd or Pt; X = Cl, Br, or I), which originally aroused our interest, should have overlapping inner and outer lines. Since *cis*-$[PtCl_2\{P(OMe)_3\}_2]$ is more soluble than the analogous PMe_3 complex and has a similar value for $^2J_{PP}$, we use this to illustrate the type of spectra obtained (Figure 1). ^1H N.m.r. spectra of the complexes $[PtX_2\{P(OMe)_3\}_2]$ have been studied by Church and Mays,[13] who found the lines of $(m - p) = 1$ resolved for X = Cl and Br. By irradiating the three areas of ^{195}Pt resonances rapidly in turn, we removed the interference due to platinum satellites and hence obtained more accurate values of $^2J_{PP}$ (Table 1). Even with platinum decoupling the di-iodo-complex did not show resolved inner and outer lines, only shoulders on either side of lines of the strong doublet giving a value of *ca.* 1·9 Hz for $^2J_{PP}$. It is possible, however, that these are merely residual platinum satellites in which case $^2J_{PP}$ must be less than 1·9 Hz. $^1H\{^{195}Pt\}$ Measurements showed N to be positive (by comparison with J_{PtP}[6]) as in other trimethyl phosphite complexes.[4] In Figure 1, the $^1H\{^{31}P\}$ INDOR spectrum obtained by monitoring the high-frequency strong line, $\alpha\alpha(m,p)$, is compared with that calculated for transitions to $\alpha\alpha(m,p)$ for $^2J_{PP}$ having negative sign. When the low-frequency line, $\beta\beta(m,p)$, was monitored the observed spectrum was the mirror image, whilst if $^2J_{PP}$ was taken as positive, the calculated spectrum was the mirror image. (In the Figures the vertical axis is inverted, *i.e.* the decreasing output of the signal being monitored is upwards so as to be comparable with directly observed spectra.) The separate plots of the inner and outer lines in Figure 1 show how the INDOR

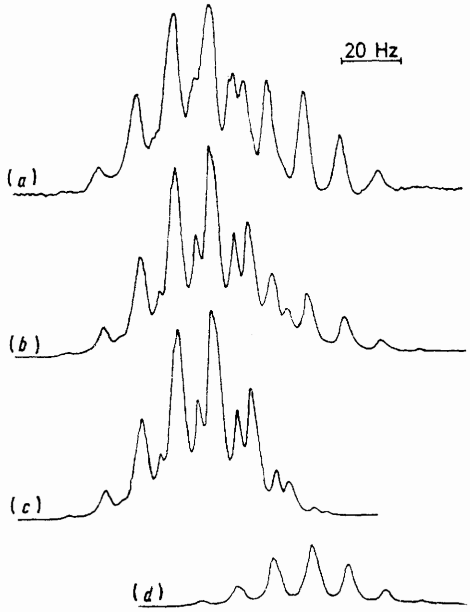

FIGURE 1 $^1H\{^{31}P\}$ INDOR Spectrum of the complex *cis*-$[PtCl_2\{P(OMe)_3\}_2]$: (*a*) spectrum observed, monitoring high-frequency line $\alpha\alpha(m,p)$; (*b*) total calculated spectrum of transitions to $\alpha\alpha(m,p)$ for $^2J_{PP}$ negative; (*c*) calculated inner lines; and (*d*) calculated outer lines

TABLE 1

Values of $^2J_{PP}$ (Hz) for the complexes *cis*-$[MX_2L_2]$ [M = Pd or Pt; L = PMe_3 or $P(OMe)_3$]

Complex	X = Cl	Br	I	Me
$[PdX_2(PMe_3)_2]$	−8·0	*ca.* −1 [a]		
$[PdX_2\{P(OMe)_3\}_2]$	+77·9	+84·8	+61·9 [b]	
$[PtX_2(PMe_3)_2]$	−18·9 [a]	−16·2 [a]	−14·0 [b]	−12·0
$[PtX_2\{P(OMe)_3\}_2]$	−17·8	−8·4	*ca.* −1·9	

[a] In CH_2Cl_2 solution; sign determined in CD_3NO_2. [b] At *ca.* 240 K.

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[12] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[13] M. J. Church and M. J. Mays, *J. Inorg. Nuclear Chem.*, 1971, **33**, 253.

spectrum is made up. In particular, this shows that, under the conditions used to obtain the best defined INDOR spectrum, the outer lines are enhanced compared to the inner lines (about two fold).

By the same process of comparison of observed and calculated $^1H\{^{31}P\}$ INDOR spectra, we established $^2J_{PP}$ to be negative in the complexes *cis*-$[PtBr_2\{P(OMe)_3\}_2]$, *cis*-$[PdCl_2(PMe_3)_2]$, and *cis*-$[PtX_2(PMe_3)_2]$ (X = Cl, Br, and I). From $^1H\{^{195}Pt\}$ measurements, N for the PMe_3 complexes was negative, *i.e.* $\alpha\alpha(m,p)$ is to low frequency, and values of the parameters used for the calculated spectra were those of ref. 5. As $^2J_{PP}$ decreases, the inner and outer lines are more nearly superimposed and the asymmetry of the spectrum decreases, the limit being a multiplet of splitting J_{AX} each line of which is a multiplet of separation $J_{AX'}$. The platinum(IV) complexes, *cis*-$[PtX_4(PMe_3)_2]$ (X = Cl or Br), have low values of $^2J_{PP}$ (*ca.* 4 Hz [6]) which partly accounts for our inability to be certain of the sign. The real problem was the low solubility of these complexes, even in CD_3NO_2, which resulted in poor INDOR spectra in which the differences due to the sign of $^2J_{PP}$ were not discernible. INDOR Spectra of the complexes *cis*-$[PtI_2\{P(OMe)_3\}_2]$ and *cis*-$[PdBr_2(PMe_3)_2]$, which have a lower value of $^2J_{PP}$ still, did indicate that $^2J_{PP}$ was negative. The complex *cis*-$[PtI_2\{P(OMe)_3\}_2]$ gave a simple multiplet since $J_{AX'} \approx 0$, but asymmetry in the intensities of the lines was sufficient to establish the sign (Figure 2), whilst for *cis*-$[PdBr_2(PMe_3)_2]$ the relatively large value of $J_{AX'}$ probably assisted the determination.

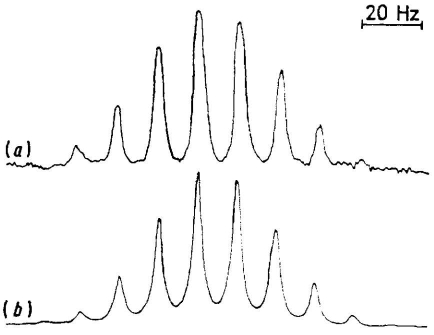

FIGURE 2 $^1H\{^{31}P\}$ INDOR Spectrum of the complex *cis*-$[PtI_2\{P(OMe)_3\}_2]$: (*a*) observed, monitoring high-frequency line $\alpha\alpha(m,p)$; and (*b*) calculated for transitions to $\alpha\alpha(m,p)$ states

We applied this method to the complex *cis*-$[PtMe_2(PMe_3)_2]$ which is an example of the spin system $[AR_tX_n]_2$ with $^2J_{PP}$ 12·0 Hz.[14] The R and X parts of the spectrum of this system have been described by Hägele *et al.* with the restrictions $J_{RR'} = J_{XX'} = J_{RX} = J_{RX'} = 0$.[15] The significant difference between the $[AX_n]_2$ and $[AR_tX_n]_2$ system is that the X spectrum (and R spectrum) depends on the parameters and spins of both R and X nuclei. Following ref. 15, A transitions to the $\alpha\alpha(q,s,p,m)$ states have energies given by (6), where $J = J_{AA'}$, $N_{AR} = J_{AR} + J_{AR'}$, $L_{AR} =$

$$\nu_A + \tfrac{1}{2}J + \tfrac{1}{2}(q + s)N_{AR} + \tfrac{1}{2}(m + p)N_{AX} \pm \tfrac{1}{2}\{[(q - s)L_{AR} + (m - p)L_{AX}]^2 + J^2\}^{\frac{1}{2}} \quad (6)$$

$J_{AR} - J_{AR'}$, $N_{AX} = J_{AX} + J_{AX'}$ and $L_{AX} = J_{AX} - J_{AX'}$; q and s take values $(t/2)$, $(t/2) - 1 \ldots -(t/2)$, and m and p take values $(n/2)$, $(n/2) - 1, \ldots -(n/2)$. The intensities are as in (7), where $\sin 2\theta = J/\{[(q - s)L_{AR} + (m - p)L_{AX}]^2 + J^2\}^{\frac{1}{2}}$. Taking the platinum-bonded methyl groups as R nuclei, N_{AR} is positive [14] and the $\alpha\alpha(q,s,m,p)$ line is to high

$$(1 \pm \sin 2\theta)\,{}^tC_{[(t/2)+q]}\,{}^tC_{[(t/2)+s]}\,{}^nC_{[(n/2)+m]}\,{}^nC_{[(n/2)+p)]}/2^{(2t+2n+1)} \quad (7)$$

frequency. The observed $^1H\{^{31}P\}$ INDOR spectrum is compared, in Figure 3, with that calculated from data of ref. 14. Despite the large number of transitions involved, a well resolved spectrum was obtained which confirms that $^2J_{PP}$ is negative. The spectrum was less complicated than that of the general $[AR_tX_n]_2$ system because L_{AR} is *ca.* $2L_{AX}$. Similar spectra were obtained from the PMe_3 part, except that the $\alpha\alpha(q,s,m,p)$ line was to low frequency as N_{AX} is negative. In fact, using Figure 1 as a guide, it can be seen that the outer lines lie to low frequency in the observed INDOR spectrum of the complex *cis*-$[PtMe_2(PMe_3)_2]$ so $^2J_{PP}$ could be deduced to be negative even without a calculated spectrum.

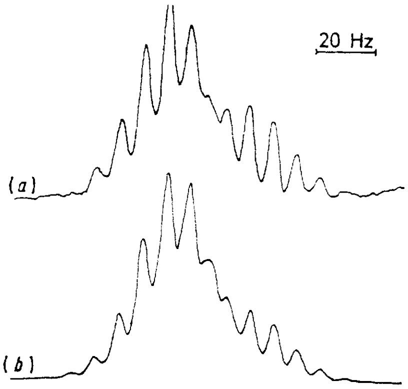

FIGURE 3 $^1H\{^{31}P\}$ INDOR Spectrum of the complex *cis*-$[PtMe_2(PMe_3)_2]$: (*a*) observed, monitoring high-frequency ($\alpha\alpha$) line of $PtMe_2$ resonance; and (*b*) calculated for transitions to ($\alpha\alpha$) states

The reported value of $^2J_{PP}$ for the complex *cis*-$[PdCl_2\{P(OMe)_3\}_2]$ is 79·9 Hz [4] which would put the outer lines clear of the main resonance in the $^1H\{^{31}P\}$ INDOR spectrum. As the sign of $^2J_{PP}$ is reported as positive,[4] in contrast to that found for the *cis*-complexes above, we felt it worthwhile to examine *cis*-$[PdX_2\{P(OMe)_3\}_2]$ (X = Cl, Br, and I) in detail. Although the inner lines of the proton n.m.r. spectrum crowded together in the middle of the strong doublet, the lines due to $(m - p) = 1$—3 were visible as shoulders. The outer lines were not easily detected in 0·1M-solution under normal conditions, but, following the suggestion of Finer and Harris,[16] much higher radio-frequency power was used without saturating these weakly allowed transitions. In this way lines corresponding to $(m - p) = 1$—3 were found and their behaviour with increasing radio-frequency power contrasted with that of ^{13}C satellites which occurred in the same region. It was not possible to get an accurate value of L from either the inner or outer lines. As $^5J_{PH}$ must be small, we assumed it to be zero in order to calculate $^2J_{PP}$ and the values obtained (Table 1) reproduce the inner and outer lines within experimental error. The spectrum of $[PdI_2\{P(OMe)_3\}_2]$ showed only a broad featureless hump between the lines of the strong doublet at room temperature, but on cooling to *ca.*

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[14] R. J. Goodfellow, M. J. Hardy, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2450.

[15] G. Hägele, R. K. Harris, and J. M. Nichols, *J.C.S. Dalton*, 1973, 79.

[16] E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **12**, 457.

240 K it resembled spectra of the other *cis* palladium phosphite complexes, together with additional features that can be assigned to the *trans*-isomer (*ca.* 10%).

Monitoring the high-frequency strong line, $\alpha\alpha(m,p)$, the main resonances in the $^1H\{^{31}P\}$ INDOR spectra of these complexes had some asymmetry (Figure 4) but this was barely enough to distinguish the sign. However, when more irradiating power (*ca.* 15 dB) was used, outer lines appeared *ca.* $^2J_{PP}$ on the high-frequency side only, indicating that $^2J_{PP}$ is indeed positive. The pattern observed differs from the main band but agrees well with that calculated (Figure 4). The middle of the pattern of outer lines was a line where $(m + p) = 0$, but was not $m = \frac{1}{2}$, $p = -\frac{1}{2}$ (as might have been expected) but $m = \frac{3}{2}$, $p = -\frac{3}{2}$. Thus the separation between the middle of the groups of outer lines obtained from $\alpha\alpha(m,p)$ and $\beta\beta(m,p)$ respectively was $J + [9L^2 + J^2]^{\frac{1}{2}}$, which for these phosphite complexes is some 8—13 Hz greater than $2J$. When corrected in this way, values of J agreed with those from proton spectra within experimental error (±1 Hz for the INDOR measurements).

trans-*Bis(phosphine) Complexes*.—Following the results for the *cis* palladium phosphite species, we expected to find outer lines in the $^1H\{^{31}P\}$ INDOR spectrum of a *trans*-complex if even more irradiating power was used to compensate for the greater value of $^2J_{PP}$. Figure 5 illustrates the effect of scanning through the ^{31}P spectrum of the complex *trans*-$[Pd(CN)_2(PMe_3)_2]$ with increasing irradiating powers whilst monitoring the lowest-frequency proton line, $\alpha\alpha(m,p)$. As the power increased, the central resonance broadened and then the outer line on the high-frequency side appeared (additional features on the central resonance are due to 50 Hz interference). The larger the value of $^2J_{PP}$, the more power was required to bring up the outer line (*ca.* 30 dB for $^2J_{PP}$ 400 Hz and *ca.* 35 dB for $^2J_{PP}$ 1 100 Hz referred to the power used for the central resonance). Although this increased the width of the central resonance, the two processes seemed to be balanced such that the central resonance did not interfere too seriously with the weak outer resonance. The outer lines were not particularly broadened at this power level since the effective irradiating power is proportional to the transition moment as well as the power of the irradiating field [17] and hence is much smaller for these weakly allowed transitions than for the central resonance.*

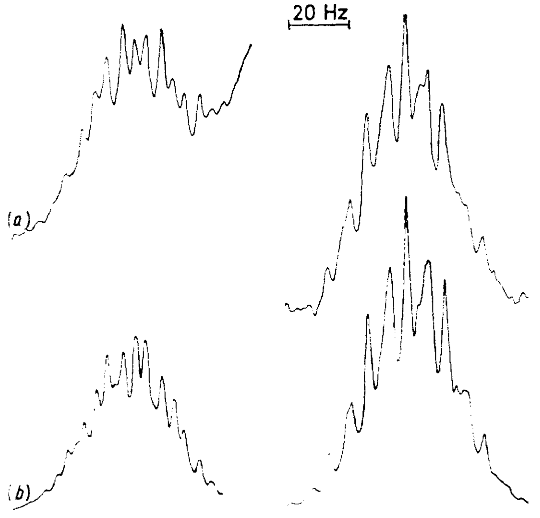

FIGURE 4 $^1H\{^{31}P\}$ INDOR Spectrum of the complex *cis*-$[PdBr_2\{P(OMe)_3\}_2]$: (*a*) observed, monitoring high-frequency $\alpha\alpha(m,p)$ line (16 dB more irradiating power for high-frequency part); and (*b*) calculated for transitions to $\alpha\alpha(m,p)$ states (×80 for high-frequency part)

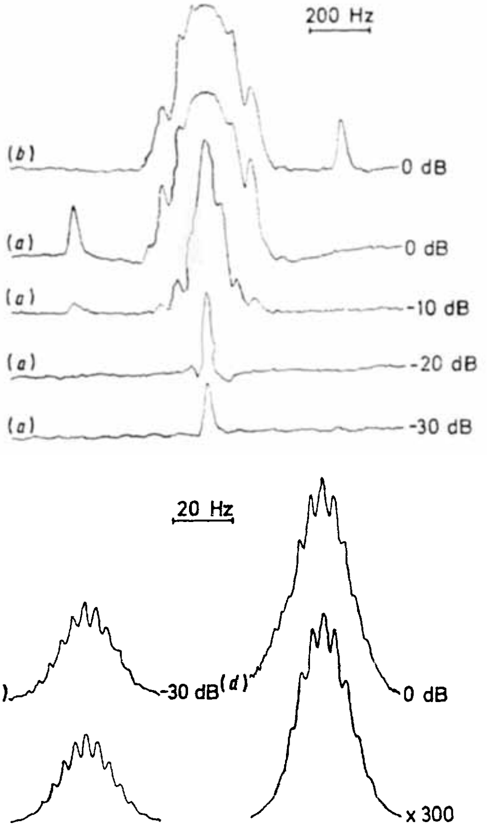

FIGURE 5 $^1H\{^{31}P\}$ INDOR Spectrum of the complex *trans*-$[Pd(CN)_2(PMe_3)_2]$: (*a*) observing $\alpha\alpha(m,p)$ line using various power levels of the irradiating field (dB below a nominal 1 V into 50 Ω); (*b*) observing $\beta\beta(m,p)$ line; (*c*) expansion of central multiplet with (below) calculated spectrum; and (*d*) expansion of outer low-frequency multiplet with (below) calculated spectrum

Using the highest-frequency line of the proton spectrum gave the outer line on the other side of ν_P in the phosphorus spectrum, *i.e.* at $-^2J_{PP}$. The positions of the outer lines were most reliably found by running a series of spectra at increasing irradiating powers as in Figure 5. When expanded, the outer and inner lines were similar regular multiplets with splitting $\frac{1}{2}N$ (Figure 5). The central line of an outer resonance had $(p + m) = 0$, but the most significant components were $(\frac{3}{2}, -\frac{3}{2})$, $(\frac{5}{2}, -\frac{5}{2})$, and $(\frac{1}{2}, -\frac{1}{2})$ in the ratio 4 : 2 : 1. Thus the distance between the central lines of the two outer resonances was a little greater than twice $^2J_{PP}$. Taking a weighted average, the excess over 2 $^2J_{PP}$ was *ca.* 2 Hz when $^2J_{PP}$ was 300 Hz, and 1 Hz when it was 600 Hz. The results in Table 2 have been corrected in this way. Spectra were run at several power levels of the irradiating field to reduce the possibility of selecting the wrong line as centre.

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* We thank a referee for pointing this out.

[17] R. Freeman and W. A. Anderson, *J. Chem. Phys.*, 1962, **37**, 2053.

In general, it was not practicable to check values of $^2J_{PP}$ from INDOR measurements against those obtained from the ^1H spectrum, because for such large values of $^2J_{PP}$ the outer lines in the ^1H spectrum were exceedingly weak and difficult to find. However, for $[Hg(PMe_3)_2]^{2+}$, which had the lowest value of $^2J_{PP}$ amongst the *trans*-complexes, we were able to identify an outer line in the proton spectrum after accumulation. This gave a value of 250·1 Hz for $^2J_{PP}$ which agrees with the INDOR value of 250 ± 1 Hz. The discrepancy between our value for the complex *trans*-$[PdI_2(PMe_3)_2]$ and that previously reported[4] may arise because it is more difficult to identify the middle lines of the outer multiplets in a normal heteronuclear-decoupling experiment than in an INDOR experiment. The proportion of the *trans*-isomer of $[PdI_2\{P(OMe)_3\}_2]$ present is increased on going to $CDCl_3$ solution, and when cooled to *ca.* 240 K a well resolved spectrum of both isomers was obtained. Despite the large value of $^2J_{PP}$, there was no difficulty in measuring it by this method. In carbon tetrachloride solution, $[PdI_2\{P(OMe)_3\}_2]$ is almost entirely in the *trans*-form, but we were unable to obtain any definite evidence of the *trans*-isomer of any of the other phosphite complexes in this or any other solvent. The sensitivity of this method of determining $^2J_{PP}$ is illustrated by the ability to determine a value for *trans*-$[PtBr_2(PMe_3)_2]$ which is present as the minor component in a saturated (but still dilute) solution of the *cis*-isomer in nitrobenzene when the temperature is raised to *ca.* 430 K.

TABLE 2

Values of $^2J_{PP}$ (Hz) for some *trans*-bis(phosphine) complexes

Complex	X = Cl	Br	I	CN
$[PdX_2(PMe_3)_2]$	+610	+612	+604	+441
$[PdX_2(PEt_3)_2]$	+541	+537	+520	
$[PdX_2\{P(OMe)_3\}_2]$			+1 145 [a]	
$[PtX_2(PMe_3)_2]$	+510	+514 [b]	+498	+383
$[PtX_2(PEt_3)_2]$	+436	+449	+438	
$[PtX_2(PPr^n_3)_2]$		451		
$[PtX_4(PMe_3)_2]$	+660	+645		
$[PtX_4(PEt_3)_2]$	+587	+574		
$(Pr^n_4N)[IrX_4(PMe_3)_2]$	+539			
$[Hg(PMe_3)_2](NO_3)_2$		+250 [c]		
$[Au(PMe_3)_2][Au(CN)_2]$		+353		

[a] In $CDCl_3$ at *ca.* 240 K. [b] In nitrobenzene at *ca.* 430 K. [c] In D_2O.

The spectra of bis(triethylphosphine) complexes are much more complicated since they belong to the $[AR_6X_9]_2$ spin system with $J_{RX} \neq 0$. However, for relatively large values of $^2J_{PP}$, outer lines in the ^{31}P spectrum would be expected with a separation of *ca.* 2 $^2J_{PP}$ and hence estimates of $^2J_{PP}$ should be obtainable from $^1H\{^{31}P\}$ INDOR experiments on the *trans*-isomers. We consider only the less-complex and more-intense methyl resonances which, in *trans*-isomers, approximate to a five-line pattern since splitting of the triplet due to coupling with phosphorus is similar to $^2J_{HH}$. As $^3J_{PH}$ is positive,[18] the highest-frequency line is related to the αα-phosphorus spin state. However we found that the next line, which has a larger component related to the αα-phosphorus spin state, gave similar results but with better sensitivity. Using the latter line and the equivalent one for the ββ-phosphorus spin state, we obtained satisfactory results for a range of *trans*-triethylphosphine complexes (Table 2). Due to the complex spin system, ^{31}P INDOR resonances were broad and without fine structure (width at half height *ca.* 50 Hz), resulting in an error of ±5 Hz in values of $^2J_{PP}$. Proton n.m.r. spectra of PPr^n_3 complexes are yet more complicated making INDOR measurements difficult. We were able to pick up outer lines in the ^{31}P spectrum of the complex *trans*-$[PtBr_2(PPr^n_3)_2]$ using the α-CH_2 group, but ^{31}P resonances were very weak and not easily identified. The proton peaks used related to both αα- and ββ-phosphorus spin states so that outer lines in the INDOR spectrum appeared simultaneously on both sides of the main ^{31}P resonance and no information on the sign of $^2J_{PP}$ was obtained.

Meridional Tris(phosphine) Complexes.—We have previously considered[2] proton spectra of the complexes $[MX(PMe_3)_3]$ (M = Pt or Pd; X = Cl, Br, or I) and *mer*-$[MX_3(PMe_3)_3]$ (M = Pt, Rh, or Ir; X = Cl or Br) which have the spin system $[AX_9]_2BY_9$. Approximate values of $^2J_{PP}$ (*cis*) were obtained from $^1H\{^{31}P\}$ INDOR measurements at normal power levels, but the value of $^2J_{PP}$ (*trans*) could not be obtained in this way. The proton spectrum of the *trans* pair of phosphines was similar to that of a *trans*-bis(phosphine) complex suggesting that $^2J_{PP}$ (*trans*) might be found by $^1H\{^{31}P\}$ INDOR at higher power levels as for the latter complex. For the systems studied, $J_{AB} = {}^2J_{PP}$ (*cis*) is small compared to δ_{AB} (the shift between the two types of phosphorus resonance) and $J_{XY} = 0$, so that the X part can be considered as that of two $[ax_9]_2$ sub-spectra with splitting J_{BX}. Similarly, the A spectrum should be a series of $[ax_9]_2$ sub-spectra with separations due to $^2J_{PP}$ (*cis*) and long-range coupling to the nine Y protons. Because the coupling J_{BX} is too small to be resolved, the lowest-frequency X line corresponds to the phosphorus spin state ααβ as well as ααα (for ^{31}P nuclei in the order AA′B). Accordingly, monitoring this line will pick up sets of sub-spectra related to both spin states of the ^{31}P nucleus B, *i.e.* inner and outer features will be found as for the *trans*-complexes but each will be a doublet of separation $^2J_{PP}$ (*cis*). The additional long-range coupling from the Y protons will greatly reduce the possibility of resolving the band further and we did not find fine structure for any of the complexes listed in Table 3. Apart from the J_{AB} and J_{AY} terms (which occur only outside the square root), the transition energies are the same as for the complexes *trans*-$[MX_2(PMe_3)_2]$ so we corrected the values observed on the same basis. The sign of $^2J_{PP}$ (*trans*) found by this method was always positive as in the *trans*-complexes [the values and sign of $^2J_{PP}$(*cis*) are from the previous study[2]].

TABLE 3

Values of $^2J_{PP}$ (Hz) for some tris- and tetrakis-(phosphine) complexes

	X = Cl		X = Br	
Complex	$^2J_{PP}$ (*cis*)	$^2J_{PP}$ (*trans*)	$^2J_{PP}$ (*cis*)	$^2J_{PP}$ (*trans*)
$[PdX(PMe_3)_3]NO_3$ [a]	−25	+461	−23	+469
$[PtX(PMe_3)_3]^+$ [b]	−25	+414	−23	+415
mer-$[PtX_3(PMe_3)_3]^+$ [b]	−12	+556	−13	+547
mer-$[RhX_3(PMe_3)_3]$	−29	+567	28	+555
mer-$[IrX_3(PMe_3)_3]$	−22	+452		
trans-$[RhX_2(PMe_3)_4]BF_4$	−35	+469	−35	+461
trans-$[IrX_2(PMe_3)_4]NO_3$	−28	+374	−27	+362
	$^2J_{PP}$ (*cis*)		$^2J_{PP}$ (*trans*)	
$[Pt(PMe_3)_4](NO_3)_2$ [c]	−30		+335	
$[Pt\{P(OMe)_3\}_4]I_2$	−44		+689	

[a] At *ca.* 230 K. [b] Chloride as BF_4^- salt, bromide as NO_3^- salt. [c] In D_2O.

trans *Tetrakis(phosphine) Complexes.*—The species *trans*-$[MX_2(PMe_3)_4]^+$ (M = Rh or Ir) and $[Pt(PMe_3)_4]^{2+}$ have the

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[18] W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1922.

spin system $[AX_9]_4(D_{4h})$. In order to explain the proton spectrum, we derived analytical solutions for those states where the sum of the A spin eigenvalues, $m_T(A)$, is ± 2 or ± 1, but no attempt was made to analyse the 6×6 sub-matrices of the $m_T(A) = 0$ states.[2] Proton features relevant to the various values of $m_T(A)$ were established by $^1H\{^{195}Pt\}$ INDOR spectroscopy and $m_T(A) = 0$ states correspond to the broad central feature. No values of $^2J_{PP}$ (*cis*) or $^2J_{PP}$(*trans*) were obtained but the results above suggest that these might be evaluated if weak features in the ^{31}P spectrum could be found by $^1H\{^{31}P\}$ INDOR spectroscopy.

From the solutions for the $m_T(A) = +2$ and $+1$ states we may evaluate A transitions to the $\alpha\alpha\alpha\alpha(x,x',x'',x''')$ state (where α or β refer to spin functions of the four A nuclei and x's are sums of spin eigenvalues for the X_n groups in the same cyclic order as the A nuclei). The $m_T(A) = +2$ sub-matrices have eigenvalues (8). After some manipulation of the original basis functions of the $m_T(A) = +1$ sub-matrices, the diagonal terms (9)—(12), with the common

$$2\nu_A + J_{AA'} + \tfrac{1}{2}J_{AA''} + (x + x' + x'' + x''')(\nu_X + \tfrac{1}{2}J_{AX} + J_{AX'} + \tfrac{1}{2}J_{AX''}) \quad (8)$$

$$\tfrac{1}{2}(x + x'')(J_{AX} + J_{AX''}) + (x' + x''')J_{AX'} + \tfrac{1}{2}[(x' - x''')^2(J_{AX} - J_{AX''})^2 + J_{AA''}{}^2]^{\frac{1}{2}} \quad (9)$$

$$\tfrac{1}{2}(x' + x''')(J_{AX} + J_{AX''}) + (x + x'')J_{AX'} + \tfrac{1}{2}[(x - x'')^2(J_{AX} - J_{AX''})^2 + J_{AA''}{}^2]^{\frac{1}{2}} \quad (10)$$

$$\tfrac{1}{2}(x + x'')(J_{AX} + J_{AX''}) + (x' + x''')J_{AX'} - \tfrac{1}{2}[(x' - x''')^2(J_{AX} - J_{AX''})^2 + J_{AA''}{}^2]^{\frac{1}{2}} \quad (11)$$

$$\tfrac{1}{2}(x' + x''')(J_{AX} + J_{AX''}) + (x + x'')J_{AX'} - \tfrac{1}{2}[(x - x'')^2(J_{AX} - J_{AX''})^2 + J_{AA''}{}^2]^{\frac{1}{2}} \quad (12)$$

term $\nu_A - (x + x' + x'' + x''')\nu_X$, were obtained. The off-diagonal terms involve the sines and cosines of the angles θ and ϕ, where $\tan 2\theta = (x' - x''')(J_{AX} - J_{AX''})/J_{AA''}$ and $\tan 2\phi = (x - x'')(J_{AX} - J_{AX''})/J_{AA''}$. Using the values of $J_{AA''}$ found, θ or ϕ were small even for the relatively rare states where $(x - x'')$ or $(x' - x''') = 9$, and hence the off-diagonal terms involving sines may be safely ignored and the remaining one, relating the first two diagonal terms, approximated to $J_{AA'}$. Thus the last two diagonal terms are effectively eigenvalues and give rise to A transitions to the $m_T(A) = 2$ states with frequencies (13). (Here, and

$$\nu_A + J_{AA'} - \tfrac{1}{2}J_{AA''} + \tfrac{1}{2}(x' + x''')(J_{AX} + J_{AX''}) + (x + x'')J_{AX'} + \tfrac{1}{2}[(x' - x''')^2(J_{AX} - J_{AX''})^2 + J_{AA''}{}^2]^{\frac{1}{2}} \quad (13)$$

below, identical frequencies result from interchange of x and x'' with x' and x''' respectively.) From the similarity of expression (13) to that for the complexes *trans*-$[MX_2(PMe_3)_2]$, we expect these lines to occur as a broad envelope at $\nu_A + J_{AA'} - J_{AA''}$ when high irradiation levels are used to record the $^1H\{^{31}P\}$ INDOR spectrum. As might be anticipated in view of the additional term $(x + x'')J_{AX'}$, no fine structure was seen but otherwise the observation of these lines paralleled that of the complexes *trans*-$[MX_2(PMe_3)_2]$.

The mixing of the first two diagonal terms, caused by the off-diagonal term of *ca.* $J_{AA'}$, results in a rather complicated expression. This becomes much simpler if $[(x - x'')^2(J_{AX} - J_{AX''})^2 + J_{AA''}{}^2]^{\frac{1}{2}}$ is replaced by $J_{AA''}$, giving (14) which has A transitions to the $m_T(A) = +2$ states with frequencies (15). These will occur as an envelope of lines at ν_A and a weaker one at *ca.* $+2J_{AA'}$. Since the maximum difference between $[(x - x'')^2(J_{AX} - J_{AX''})^2 + J_{AA''}{}^2]^{\frac{1}{2}}$ and $J_{AA''}$ is 16 Hz, and then for relatively rare states, the effect of including the $[(x - x'')^2(J_{AX} - J_{AX''})^2 + J_{AX''}{}^2]^{\frac{1}{2}}$ terms

$$\tfrac{1}{2}(x + x' + x'' + x''')(\tfrac{1}{2}J_{AX} + J_{AX'} + \tfrac{1}{2}J_{AX''}) + \tfrac{1}{2}J_{AA''} \pm \tfrac{1}{2}[(x - x' + x'' - x''')^2(\tfrac{1}{2}J_{AX} - J_{AX'} + \tfrac{1}{2}J_{AX''})^2 + 4J_{AA'}{}^2]^{\frac{1}{2}} \quad (14)$$

$$\nu_A + J_{AA'} + \tfrac{1}{2}(x + x' + x'' + x''')(\tfrac{1}{2}J_{AX} + J_{AX'} + \tfrac{1}{2}J_{AX''}) \pm \tfrac{1}{2}[(x - x' + x'' - x''')^2(\tfrac{1}{2}J_{AX} - J_{AX'} + \tfrac{1}{2}J_{AX''})^2 + 4J_{AA'}{}^2]^{\frac{1}{2}} \quad (15)$$

would only be additional broadening of the envelopes. Thus when the $m_T(A) = +2$ proton line was monitored while scanning over the ^{31}P INDOR resonance at ν_A, a weak feature appeared on the low-frequency side of the main peak when the irradiating power was increased by *ca.* 10 dB, *i.e.* $^2J_{PP}$ (*cis*) is negative.

Because of the complexity of the calculation, we did not attempt to evaluate the intensities of these transitions and hence did not know what correction to apply in deriving the values of $^2J_{PP}$ (*cis*) and (*trans*). It is probable that the correction to $J_{AA'} + J_{AA''}$ is similar to that for the complexes *trans*-$[MX_2(PMe_3)_2]$. For the band at $2J_{AA'}$, it might be argued that the correction would be similar to that of an $[AX_n]_2$ system with a value of $J_{AA} = 2\ ^2J_{PP}$ (*cis*). However, these bands were similar in form and, particularly, width to those at $J_{AA'} + J_{AA''}$, and much narrower than those of *cis*-$[PdX_2\{P(OMe)_3\}_2]$ which have a value of $^2J_{PP}$ approximately the same as 2 $^2J_{PP}$ (*cis*) of the tetrakis(phosphine) complexes. In view of this uncertainty, we did not make any corrections when extracting values of $^2J_{PP}$ for the tetrakis(phosphine) complexes given in Table 3, but we do not think that the resulting error is likely to be significantly greater than that inherent in the measurements themselves.

A sharp X peak belonging to $m_T(A) = +1$ occurs only $J_{AX'}$ away from the $m_T(A) = +2$ peak and since $J_{AX'}$ may be very small coincidence of the two peaks may occur. Thus some knowledge of the A transitions linked to this $m_T(A) = +1$ line is desirable. The X line results from the last two diagonal terms when one of the x values not involved in the square-root term alters.[2] We did not attempt to find a general solution to the 6×6 sub-matrices of the $m_T(A) = 0$ states, but an idea of the positions of the A transitions can be gained from the special case $x = x' = x'' = x'''$. These sub-matrices were readily solved and gave the eigenvalues $\tfrac{1}{2}J_{AA''} + J_{AA'}$, $\tfrac{1}{2}J_{AA''} - J_{AA'}$, $\tfrac{1}{2}J_{AA''} - 2J_{AA'}$, $-\tfrac{1}{2}J_{AA''}$ (twice), and $-\tfrac{3}{2}J_{AA''}$ in addition to the common term $(x + x' + x'' + x''')\nu_X$. Although for $x = x' = x'' = x'''$ all the A transitions linked to the sharp X line are totally forbidden except that at ν_A, it is reasonable to expect them to be weakly allowed for $x \neq x'$, *etc.*, and occur near those predicted for the $x = x' = x'' = x'''$ case. Thus, weak features are anticipated at $+J_{AA''}$, $-J_{AA''} - J_{AA'}$, $-J_{AA''} + J_{AA'}$, and $-J_{AA''} + 2J_{AA'}$.

For the complexes *trans*-$[IrCl_2(PMe_3)_4]^+$ and $[Pt(PMe_3)_4]^{2+}$, where the appropriate X transition was easily identified, we found $^1H\{^{31}P\}$ INDOR features at all the above positions [and the set related to $m_T(A) = -1$] in agreement with the values of $J_{AA'}$ and $J_{AA''}$ derived from measurements on $m_T(A) = \pm 2$ states. In fact, we found the estimate of $J_{AA'}$ which was obtained from measurements using the $m_T(A) = \pm 1$ states, made adjustment of the power required to observe the lines at 2 $^2J_{PP}$ (*cis*) much easier. Particular care was necessary for the rhodium complexes because $^4J_{PH}$

(*cis*) was close in value to $^3J_{\mathrm{RhH}}$ so that sharp lines of the $m_{\mathrm{T}}(\mathrm{A}) = +2$ and $+1$ states appeared as a triplet. Further, when looking for the weak lines at 2 $^2J_{\mathrm{AA'}}$, interference occurred from the central resonance related to the other ^{103}Rh spin state as J_{RhP} and 2 $^2J_{\mathrm{PP}}$ (*cis*) were of similar magnitude. This was avoided when the centre line of the triplet was used, since the weak feature then fell on the opposite side to the line of opposite ^{103}Rh spin. For the complex $[\mathrm{Pt\{P(OMe)_3\}_4}]^{2+}$, $J_{\mathrm{AX'}}$ was very small and sharp features related to $m_{\mathrm{T}}(\mathrm{A}) = +2$ and $+1$ occurred as a single line. Monitoring this gave weak features at 645 and -88 Hz relative to ν_{A}, from which it seems that this line behaves as $m_{\mathrm{T}}(\mathrm{A}) = +2$ only and we assumed that the feature at $+645$ Hz was $J_{\mathrm{AA''}} - J_{\mathrm{AA'}}$ (rather than $J_{\mathrm{AA''}}$).

DISCUSSION

For the trimethylphosphine complexes examined here, phosphorus–phosphorus coupling constants are clearly distinguished according to type, $^2J_{\mathrm{PP}}$ (*cis*) being relatively small (<40 Hz) and negative whilst $^2J_{\mathrm{PP}}$ (*trans*) is large (>250 Hz) and positive, in keeping with previous reports on phosphine complexes of these metal ions. The trimethyl phosphite complexes of platinum also fit this pattern but the *cis* palladium phosphite complexes seem anomalous, $^2J_{\mathrm{PP}}$ (*cis*) being positive and about twice the magnitude expected. Indeed, the only other cases of $^2J_{\mathrm{PP}}$ being positive for a square-planar or octahedral complex seem to be *cis*-$[\mathrm{M(CO)_4\{EtN(PF_2)_2\}}]$ (M = Cr, Mo, and W) where it is postulated that a positive contribution from the P–N–P link dominates a negative term through the metal atom.[1] We therefore wondered if there was something abnormal about the structure of these palladium complexes and have made a comparison of the vibrational spectra of the equivalent platinum and palladium complexes.

As Raman spectra obtained for bromo- and iodo-derivatives were not of sufficient quality to provide a distinction between the platinum and palladium complexes, they have not been included amongst the results given in Table 4. They do, however, identify the $\mathrm{MX_2}$ stretching vibrations as 188 and 179 ($\mathrm{PdBr_2}$), 202 ($\mathrm{PtBr_2}$), 157 and 143(sh) ($\mathrm{PdI_2}$), and 165 and 154 cm^{-1} ($\mathrm{PtI_2}$). The spectra all have the same general pattern of bands in the region 1 100—350 cm^{-1} which relates to vibrations of the neutral ligand. The correspondence is very good between platinum and palladium complexes of the same halide, especially when compared with differences between spectra of different halogeno-complexes of the same metal ion. This implies that there are no changes in the internal configuration of the ligand or of the symmetry relation between different phosphite ligands in the unit cell for the two complexes of the same halide.

TABLE 4

Vibrational spectra (1 100—70 cm^{-1}) of the complexes *cis*-$[\mathrm{MX_2\{P(OMe)_3\}_2}]$ (M = Pt and Pd; X = Cl, Br, and I)

$[\mathrm{PtCl_2\{P(OMe)_3\}_2}]$			$[\mathrm{PdCl_2\{P(OMe)_3\}_2}]$			$[\mathrm{PtBr_2\{P(OMe)_3\}_2}]$	$[\mathrm{PdBr_2\{P(OMe)_3\}_2}]$	$[\mathrm{PtI_2\{P(OMe)_3\}_2}]$	$[\mathrm{PdI_2\{P(OMe)_3\}_2}]$
I.r. (mull)	Raman (solid) [a]	Raman ($\mathrm{CH_2Br_2}$) [a]	I.r. (mull)	Raman (solid)	Raman ($\mathrm{CH_2Br_2}$) [a]	I.r. (mull)	I.r. (mull)	I.r. (mull)	I.r. (mull)
1 040 (sh)						1 067 (sh)	1 069 (sh)	1 066w	1 062w
						1 055 (sh)	1 048 (sh)		
1 018vs			1 017vs	1 014 (sh)		1 020vs	1 015vs	1 018vs	1 015vs
				1 006m					
830s			829s	828w		836s	829s	825s	820s
816s			818s	822m		820s	814s	809s	805s
794s			788s	784s		794s	783s	787s	786s
761s			758s	756vw		760s	753s	750s	746s
560m			553m	553m		563ms	554ms	560ms	552ms
539s			534s			543s	537s	541ms	534ms
452m			446m	448w		458w	447wm	428w	428w
						444w	435m		
402m			399ms	401w		388m	384m	383wm	378wm
								362(sh)	361 (sh)
321m	322s	327s, p	327m	327s	332s, p	316w		320w, bd	313w, bd
306s			307s	305 (sh)			309m		
297 (sh)						297ms	298m		
290s	292ms	298wm, dp,	293 (sh)	290m	303wm, dp		287m	286m	284m
	270m	276w, p	273ms	273w		268w	263s	266 (sh)	
249w			256 (sh)	256s	257s, p	257w	256 (sh)	251w	251m
218w	219m		236 (sh)	222s		227m	231w	218w	227 (sh)
			213w		215m, p	203w	194w		
165w, vbd			155w, v, bd	173 (sh)					178vw
				143s		147w	142w	146m	141w
						123w	120w		
96w			97w			112w	107w		110w

[a] For the region 350—200 cm^{-1} only.

Spectra of the two iodo-complexes are completely comparable below 350 cm^{-1}, as would be those of the bromo-complexes but for the strong band observed at 263 cm^{-1} for palladium which has no counterpart in the spectrum of the platinum complex. The $\mathrm{MCl_2}$ stretching vibrations form part of a broad multicomponent feature in i.r. spectra of both of the chloro-complexes, but the Raman spectrum of solid $[\mathrm{PdCl_2\{P(OMe)_3\}_2}]$ is distinctly more complicated than that of its platinum analogue, the strong bands at 256 and 222 cm^{-1} being particularly notable.

To avoid complications due to the solid state, we have made a limited study of these two complexes in dibromomethane solution. The Raman spectrum of the complex $[PtCl_2\{P(OMe)_3\}_2]$ now clearly identifies the Pt–Cl stretching vibrations as 327 (sym) and 298 cm^{-1} (asym) which occur at 326m and 298s cm^{-1} in the i.r. spectrum. The corresponding bands for the palladium complex are at 332 and 303 cm^{-1} (i.r., 331m and 305s cm^{-1}). The platinum complex only shows one other feature in this region, a weak band at 276 cm^{-1}, but the palladium complex shows a rather broad, polarised, band at 257 cm^{-1} which is the strongest in the spectrum and a weaker feature at 215 cm^{-1} both, presumably, related to the two extra bands in the spectrum of the solid. The i.r. spectrum of this solution shows a broad shoulder in the region of 270 cm^{-1} which is absent for the platinum complex. Changing the solvent to nitromethane increases the intensity of the Raman band at 257 cm^{-1} relative to that at 332 cm^{-1}. There is a parallel small increase in $^2J_{PP}$ from 77·9 Hz in dichloromethane solution to 79·1 Hz in CD_3NO_2 solution. There does not seem to be any significant change in $^2J_{PP}$ on lowering the temperature to 180 K.

The vibrational results suggest that a second species may be present, and the value of $^2J_{PP}$ observed would be explained if the *cis*-square-planar form was in rapid intramolecular equilibrium with another structure which had a large positive phosphorus–phosphorus coupling constant. The second species cannot be the *trans*-square-planar isomer as the *cis*-iodo-complex shows a positive coupling in the presence of the *trans*-isomer. Likewise, dissociation of halide to an ionic species would be expected to be more affected by the change to a more polar solvent such as nitromethane. Other possible forms are tetrahedral and trigonal bipyramidal. The highly polarised nature of the Raman band at 257 cm^{-1} would fit the linear MCl_2 unit of the latter, but there is no obvious choice for the fifth ligand. It is unfortunate that the vibrational measurements do not definitely prove that a second species is present, but they do give sufficient grounds to doubt whether the values of $^2J_{PP}$ observed for these *cis*-palladium complexes truly relate to the *cis*-square-planar structure alone.

The difference in $^2J_{PP}$ (*trans*) for PMe_3 and $P(OMe)_3$ complexes can be readily explained in terms of the electronegativity of the substituents on phosphorus,[19] which increases the *s*-electron density at the nucleus, and the *s*-orbital contribution to the M–P bond (the latter is probably more significant). In particular, the ratio of $^2J_{PP}$ (*trans*) in the complexes $[Pt(PR_3)_4]^{2+}$ for the two ligands compares well with the square of the ratio of J_{PtP}, as would be expected since the same terms affect only one of the two nuclei in the second case. These terms affect the magnitude of $^2J_{PP}$ regardless of sign and accordingly $^2J_{PP}$ (*cis*) also increases (in a negative sense) from the complex $[Pt(PMe_3)_4]^{2+}$ to $[Pt\{P(OMe)_3\}_4]^{2+}$.

There is a decrease of *ca.* 70 Hz in $^2J_{PP}$ (*trans*) between equivalent PMe_3 and PEt_3 complexes. For the trimethylphosphine derivatives, *trans*-$[PtX_2(PMe_3)_2]$, J_{PtP} (2 379, 2 336, and 2 230 Hz for X = Cl, Br, and I respectively [6]) is, if anything, slightly less than in the corresponding triethylphosphine complexes (2 408, 2 336, and 2 269 Hz), which suggests that changes in hybridisation at phosphorus cannot be responsible for the decrease in $^2J_{PP}$. The electronic transitions involved in $^2J_{PP}$ are unlikely to be very different between PMe_3 and PEt_3 complexes since *trans*-$[PtCl_2(PEt_3)_2]$ shows visible–u.v. absorption bands at 45 500, 40 200, 37 200, 32 900, and 29 300 cm^{-1} in methanol, which are close to those of *trans*-$[PtCl_2(PMe_3)_2]$ (45 900, 40 800, 38 100, 32 800, and 29 100 cm^{-1}).

The only possibility that occurs to us is that the longer alkyl chain results in a different distribution of rotational positions of the PC_3 group and that $^2J_{PP}$ is dependent on the relative orientation of the PC_3 groups. If this is the case, then consideration of such effects adds a further complication to the theoretical interpretation of P–P coupling. The effect on the rotation of PEt_3 should be rather different in the octahedral platinum(IV) complexes yet there is a drop of *ca.* 70 Hz here also. For these complexes, however, there is a significant drop in J_{PtP} from 1 516 and 1 550 Hz for *trans*-$[PtX_4(PMe_3)_2]$ (X = Cl and Br respectively [6]) to 1 461 and 1 471 Hz for *trans*-$[PtX_4(PEt_3)_2]$, which may indicate that because of the difficulties of accommodating the ethyl groups there is an actual weakening of the metal–phosphorus bond. Indeed, a relatively weak M–P bond in the complex *trans*-$[PtCl_4(PEt_3)_2]$ is suggested by the M–P bond length compared with those in the series *trans*-$[MCl_4(PMe_2Ph)_2]$ (M = W, Re, Os, and Ir).[20]

When the number of phosphine ligands in a complex is increased, there is a marked decrease in $^2J_{PP}$ (*trans*) (*ca.* 20% per PR_3 added). Change in the *s*-orbital distribution at phosphorus, due to the increased positive charge on the metal atom, cannot be the main cause since the decreases in J_{MP} are much smaller and $^2J_{PP}$ (*cis*) increases in magnitude by *ca.* 20%. It is presumably due to changes in triplet excitation energies and the nature of the orbitals involved on the metal atom. Thus comparison of $^2J_{PP}$ values will involve uncertainties if the overall charge on the species is not always the same. There may be related objections to the comparison by Bright *et al.*[21] of *trans*-$[PdX_2(PHBu^t_2)_2]$ with *trans*-$[RhX(CO)(PHBu^t_2)_2]$ (X = Cl, Br, or I), but from our results, whether one compares complexes with the same number of phosphines or the same overall charge, $^2J_{PP}$ is greater for Pt^{IV} than for Ir^{III}, paralleling their observations for Pd^{II} and Rh^I. Like Bright *et al.*, we find that the lighter metal atom in a Group gives rise to the larger value of $^2J_{PP}$ (*trans*). This also applies to $^2J_{PP}$ (*cis*), with the exception of *cis*-$[PdX_2(PMe_3)_2]$ where the values seem abnormally low possibly because of a rather different P–M–P angle compared to the rest of the complexes. The difference between *cis*- and *trans*-couplings in the tetrakis(phosphine) systems, where all the phosphines

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are chemically equivalent and there is a common overall set of orbitals, emphasises the fact that any attempt to explain $^2J_{\mathrm{PP}}$ on the basis of the Pople and Santry molecular-orbital theory must combine each triplet excitation-energy term with its related LCAO coefficients.

Comparison of the complexes $[\mathrm{PtCl_2(PMe_3)_2}]$, $[\mathrm{PtMe_2(PMe_3)_2}]$, and $[\mathrm{Pt(PMe_3)_4}]^{2+}$ allows us to gauge the effect of the *trans*-group on $^2J_{\mathrm{PP}}$ (*cis*). The large *trans*-influence of Me and $\mathrm{PMe_3}$ is illustrated by the low value of J_{PtP} opposite them (1 790 [14] and 2 230 Hz [2] respectively compared to 3 480 Hz for the chloro-complex [6]). The decrease in $^2J_{\mathrm{PP}}$ on going from $[\mathrm{PtCl_2(PMe_3)_2}]$ to the methyl complex no doubt does reflect the *trans*-influence of the methyl group, but changes of this magnitude are easily outweighed by others which have much less chemical significance. Thus, although the M–P bond should be weaker in the complex $[\mathrm{Pt(PMe_3)_4}]^{2+}$ than in *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$, $^2J_{\mathrm{PP}}$ (*cis*) is larger. Similarly, oxidation to the complex *cis*-$[\mathrm{PtCl_4(PMe_3)_2}]$ causes a reduction in $^2J_{\mathrm{PP}}$ (to 4·5 Hz) which must greatly exceed any change in bond strengths.

From our results and those of previous studies [19,22] it is clear that, whilst some *trans*-complexes result in relatively low values of $^2J_{\mathrm{PP}}$, a value greater than +250 Hz can only be due to a linear P–M–P arrangement. Hence obtaining a value of $^2J_{\mathrm{PP}}$ greater than 250 Hz by $^{31}\mathrm{P}$ double-resonance experiments is a much more reliable proof of a *trans*-configuration than the form or bandwidths of the $^1\mathrm{H}$ spectrum, *e.g.* compare the value of 90 Hz estimated [18] from the proton spectrum of the complex *trans*-$[\mathrm{PtCl_2(PEt_3)_2}]$ with that in Table 2. Proton resonances of methyl groups of *trans*-complexes of $\mathrm{PMe_2Ph}$ and $\mathrm{PMePh_2}$ are triplets [23] similar to those of the $\mathrm{PMe_3}$ complexes and thus should be amenable to $^1\mathrm{H}\{^{31}\mathrm{P}\}$ determination of $^2J_{\mathrm{PP}}$. Trimethylphosphine is, unfortunately, a relatively little used phosphine but the applicability of this technique to complexes of $\mathrm{PEt_3}$, $\mathrm{PMe_2Ph}$, and $\mathrm{PMePh_2}$ should be of general usefulness. Two examples are the complexes $[\mathrm{PtCl}\{\overline{\mathrm{C{:}N{\cdot}CH{:}C(Me)S}}\}(\mathrm{PEt_3})_2]$ and $[\mathrm{PtCl}\{\overline{\mathrm{C{:}N(Me){\cdot}CH{:}C(Me)S}}\}(\mathrm{PMePh_2})_2]\mathrm{BF_4}$ prepared by Fraser *et al.*[24] for which values of $^2J_{\mathrm{PP}}$ of 407 and 417 Hz respectively were readily obtained by $^1\mathrm{H}\{^{31}\mathrm{P}\}$ INDOR, clearly showing both to have a *trans*-structure.

EXPERIMENTAL

INDOR Spectra were recorded as previously described.[2] Except where otherwise indicated, the samples were 0·1M-solutions in dichloromethane and were examined at ambient magnet temperature (*ca.* 300 K). The trialkylphosphine complexes were samples used in our previous studies,[6,25] except for $[\mathrm{PtX_4(PEt_3)_2}]$ (X = Cl and Br) which were prepared from platinum(II) complexes by oxidation with the halogen *in situ*. Preparation of the complex *cis*-$[\mathrm{PdCl_2\{P(OMe)_3\}_2}]$ has been reported by Jenkins and Verkade; [26] our sample had the same m.p. and satisfactory analysis.

Dibromobis(trimethyl phosphite)palladium(II).—Trimethyl phosphite (0·5 cm³) was added to the salt $\mathrm{K_2[PdBr_4]}$ (1 g) in water (20 cm³) and stirred for 0·5 h. The water was then decanted off and the residue dissolved in dichloromethane, dried with dry $\mathrm{MgSO_4}$, and reprecipitated by addition of diethyl ether. The product was recrystallised from hot methanol as yellow plates (0·5 g, 51% yield), m.p. 133—134 °C (Found: C, 14·25; H, 3·55. Calc. for $\mathrm{C_6H_{18}Br_2O_6P_2Pd}$: C, 13·95; H, 3·5%).

Di-iodobis(trimethyl phosphite)palladium(II).—Trimethyl phosphite (0·7 cm³) and palladium(II) iodide in acetone (20 cm³) were stirred for 1 h. After evaporating to dryness, the resulting dark residue was recrystallised from hot methanol to give red crystals (1·1 g, 66% yield), m.p. 128—129 °C (Found: C, 12·0; H, 3·05. Calc. for $\mathrm{C_6H_{18}I_2O_6P_2Pd}$: C, 11·85; H, 3·0%).

As our samples of the complexes $[\mathrm{PtX_2\{P(OMe)_3\}_2}]$ (X = Cl, Br, and I) were prepared by a different route to that described previously,[13] we include a brief description here.

Dichlorobis(trimethyl phosphite)platinum(II).—Trimethyl phosphite (1 cm³) and platinum(II) chloride (1 g) were stirred in acetone until all the solid had dissolved. After evaporation of the solvent, the residue was recrystallised from benzene on addition of light petroleum to give the product as colourless plates (0·4 g, 25% yield), m.p. 140—142 °C (Found: C, 14·05; H, 3·55. Calc. for $\mathrm{C_6H_{18}Cl_2O_6P_2Pt}$: C, 14·0; H, 3·5%). Dibromobis(trimethyl phosphite)platinum(II) was prepared in the same manner from $\mathrm{PtBr_2}$, and recrystallised from methanol as colourless crystals (27% yield), m.p. 143—144 °C (Found: C, 12·15; H, 3·1. Calc. for $\mathrm{C_6H_{18}Br_2O_6P_2Pt}$: C, 11·9; H, 3·0%).

Di-iodobis(trimethyl phosphite)platinum(II).—A solution of the salt $\mathrm{K_2[PtI_4]}$ was prepared by stirring $\mathrm{K_2[PtCl_4]}$ (2 g) and potassium iodide (6 g) in water (50 cm³) for 3 h. Trimethyl phosphite (1 cm³) was added and the mixture set aside overnight. After decanting off the aqueous layer, the resulting residue was dissolved in dichloromethane treated with dry $\mathrm{MgSO_4}$ and animal charcoal. After removal of the solvent, the product was recrystallised from hot methanol as lime-green blocks (1·2 g, 68% yield), m.p. 141—143 °C (Found: C, 10·4; H, 2·65. Calc. for $\mathrm{C_6H_{18}I_2O_6P_2Pt}$: C, 10·35; H, 2·6%).

Tetrakis(trimethyl phosphite)platinum(II) *Di-iodide*.—Trimethyl phosphite (2 cm³) was stirred with the complex $[\mathrm{PtI_2\{P(OMe)_3\}_2}]$ (0·4 g) in water (8 cm³) for 4 h when all the starting material had reacted. The water was decanted from the colourless product, which was washed with more water and then dissolved in dichloromethane. After drying with dry $\mathrm{MgSO_4}$ and evaporation of the solvent, the residue was recrystallised from hot methanol to give colourless crystals (0·15 g, 27% yield), m.p. 177—178 °C (Found: C, 15·1; H, 3·95. Calc. for $\mathrm{C_{12}H_{36}I_2O_{12}P_4Pt}$: C, 15·25; H, 3·8%).

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