Nuclear Magnetic Resonance Spectra of Complexes of Platinum(II), Palladium(II), Platinum(IV), Rhodium(III), and Iridium(III) containing Three or Four Trimethylphosphine Ligands

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The ^{1}H n.m.r. spectra of $[MX(PMe_3)_3][NO_3]$ (M = Pd or Pt), *mer*-$[PtX_3(PMe_3)_3][NO_3]$, *mer*- and *fac*-$MX_3(PMe_3)_3$, *trans*-$[MX_2(PMe_3)_4]^+$ (M = Rh or Ir, X = Cl or Br), $[PtI(PMe_3)_3][NO_3]$, and $[Pt(PMe_3)_4][BF_4]_2$ are reported and discussed, together with data from $^1H\{^{31}P\}$ INDOR measurements. The signs of several of the couplings have been determined by heteronuclear double resonance. A partial analysis is presented for the spectra of the $[AX_n]_4$ (planar) systems.

WE have discussed the ^{1}H n.m.r. spectra of trimethylphosphine and trimethylarsine complexes of platinum(II) and palladium(II) [1] and those of the analogous platinum(IV) complexes will be included in a future paper.[2] We now consider some complexes in which there are three or four phosphine ligands. In addition to ^{1}H n.m.r. measurements, we have obtained ^{31}P information from $^1H\{^{31}P\}$ INDOR measurements. Vibrational data for the complexes are reported elsewhere.[3,4] The increased

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[1] 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.

[2] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, and B. F. Taylor, *J.C.S. Dalton*, submitted for publication.

[3] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc. (A)*, 1970, 545.

[4] P. L. Goggin and J. R. Knight, *J.C.S. Dalton*, 1973, 1489.

number of phosphines in these compounds adds to the possible complexity of the spectra and they will be considered according to their spin system.

RESULTS

Complexes with Spin System $[AX_9]_2BY_9$.—The complex cations $[MX(PMe_3)_3]^+$ (M = Pd or Pt, X = Cl, Br, or I) belong to this group as do the meridional isomers $MX_3(PMe_3)_3$ (M = Rh^{III}, Ir^{III}, or Pt^{IV}). Poorly resolved ^1H n.m.r. spectra of *mer*-$RhCl_3(PMe_3)_3$ have been reported [5,6] and the spectra of the similar systems *mer*-$RhX_3(PMe_2Ph)_3$ and *mer*-$IrX_3(PMe_2Ph)_3$ are known.[7,8] The spectrum of $[PdCl(PMe_3)_3][NO_3]$ is shown in Figure 1. The main features agree with those of the PMe_2Ph spectra, namely a triplet due to the *trans*-pair of phosphines which have a large P–P coupling between them and a doublet of half the intensity for the remaining phosphine. However, the latter doublet has each line split into a triplet by the *trans*-pair of phosphorus atoms. For *mer*-$RhCl_3(PMe_3)_3$ in dichloromethane solution (Figure 2) the two parts of the spectrum are superimposed. This complication is removed in benzene when the doublet is moved to high field. Rhodium–hydrogen coupling is clearly visible and since, for the single phosphine, $^4J_{PH}$ is similar in magnitude to $^3J_{RhH}$ the lines of the doublet appear as quartets. The platinum complexes show the expected satellites due to ^{195}Pt. All the spectra in this group show the same basic pattern except for $[PtCl(PMe_3)_3][NO_3]$ (Figure 3) where the low-field satellite of the single phosphine appears as a doublet of doublets instead of the doublet of triplets shown by the main lines.

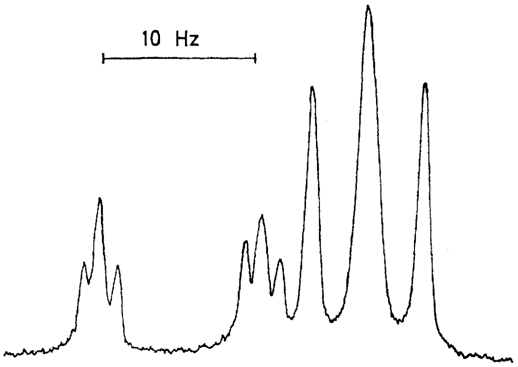

FIGURE 1 ^1H N.m.r. spectrum of $[PdCl(PMe_3)_3][NO_3]$

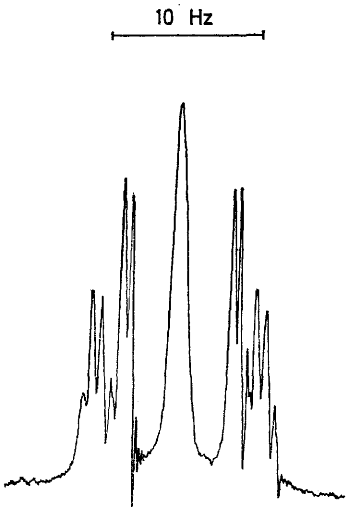

FIGURE 2 ^1H N.m.r. spectrum of *mer*-$RhCl_3(PMe_3)_3$

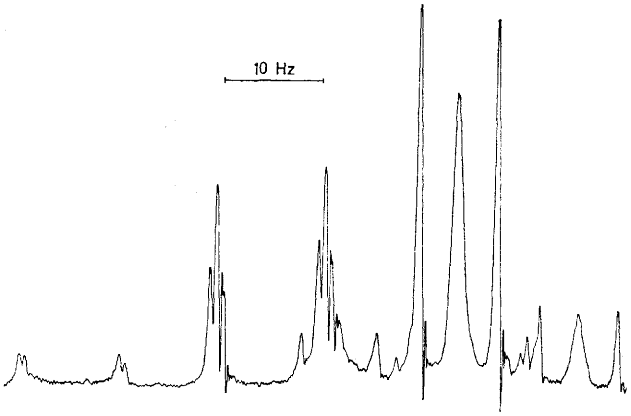

FIGURE 3 ^1H N.m.r. spectrum of $[PtCl(PMe_3)_3][NO_3]$

This long distance phosphorus–hydrogen coupling has not been reported for the analogous complexes of other phosphines and the previous spectra of *mer*-$RhCl_3(PMe_3)_3$ have too great a line width for it to have been observed.[5,6] There is no indication of analogous $^4J_{PH}$ from the single phosphorus to the protons of the *trans*-pair, *i.e.*, as a fine doublet splitting on the triplet. Lest the absence of this splitting on the triplet could be due to the spin system rather than because $J_{BX} = ca.\ 0$, we have considered the $[AX_9]BY_9$ system in more detail. Since no proton–proton splitting is observed in complexes such as *trans*-$MX_2(PMe_3)(AsMe_3)$ [1] it is safe to assume that $^6J_{XX} = {}^6J_{XY} = 0$. The smallest separation between the main resonances of A and B, $|\nu_A - \nu_B|$, is 2·9 p.p.m. or 117 Hz which is over four times J_{AB}. Further, the spectra of the main resonances are unaffected by the relative values of J_{AB} and $|\nu_A - \nu_B|$ and show long-distance phosphorus–hydrogen coupling on the doublet but not on the triplet when $|\nu_A - \nu_B| \gg J_{AB}$. Thus, for our purpose, we may make the approximation that there is no mixing between states differing in the spin of B, *e.g.*, between $\alpha\alpha\beta$ and $\alpha\beta\alpha$ where these refer to the spin states of A, A′, and B respectively. The Y spectrum is then a doublet of width J_{BY} which is further split by J_{AY} into triplets. The X spectrum will be two $[ax_9]_2$ subspectra [9] with separation J_{BX} between them. As $J_{AA'}$ will be similar in value to that in *trans*-$MX_2(PMe_3)_2$, the $[ax_9]_2$ subspectra will be triplets with broad central bands but the other two components should be sharp and show the splitting J_{BX}. On this basis, the conclusion that J_{AY} is finite whilst J_{BX} is too small to be observed is inescapable. In fact, $^1H\{^{195}Pt\}$ INDOR runs show that the low-field line of the relevant doublet in the platinum spectrum (due to coupling to the single phosphorus) is stronger when the monitoring point is slightly to low-field of the centre of either of the sharp lines of the triplet and *vice versa*. This

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[5] G. M. Intille, *Inorg. Chem.*, 1972, **11**, 695.

[6] S. O. Grim and R. A. Ference, *Inorg. Chim. Acta*, 1970, **4**, 277.

[7] P. R. Brookes and B. L. Shaw, *J. Chem. Soc. (A)*, 1967, 1079.

[8] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 1407.

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

implies that J_{BX} is positive and of the order of 0·1 Hz. In all other respects, the ^1H spectra agree with those predicted.

A doublet of doublets as observed for [PtCl(PMe$_3$)$_3$][NO$_3$] *could* be caused by J_{AB} having similar magnitude to $|\nu_A - \nu_B|$. Evaluating the ($\alpha\alpha\beta$, $\alpha\beta\alpha$, $\beta\alpha\alpha$) matrices for the more important proton configurations, using typical values of coupling constants, we found that a doublet of broad doublets would be produced when $|\nu_A - \nu_B|$ is about twice J_{AB}. From the $^1H\{^{31}P\}$ INDOR measurements J_{AB} is 25 Hz and the low-field satellites of the two types of phosphorus atom are 29 Hz apart. This is therefore a satisfactory explanation of these anomalous satellites. For *mer*-[PtCl$_3$(PMe$_3$)$_3$][NO$_3$], the high-field satellites in the ^{31}P spectrum are only *ca.* 10 Hz shifted with respect to one another. The upfield satellites of the single phosphine in the proton spectrum are rather obscured by other resonances but seem to be broad humps. The upfield satellites of the *trans*-pair of phosphines are also affected, at least a third of the intensity of the typical three lines now occurring as a featureless contribution to the area between them {this is also true of the low-field satellites in the spectrum of [PtCl(PMe$_3$)$_3$][NO$_3$] (Figure 3)}. The resulting pattern is not dissimilar to that of a system with a much lower $^2J_{PP}(trans)$ and emphasises the dangers of making deductions from partial analyses of these complex systems.

TABLE 1

N.m.r. parameters of complexes with meridional configuration †

	L *trans to* L					L *trans to* X						
	τ_{Me}	$^3J_{MH}$	$^2J_{PH} + {}^4J_{PH}$	δ_P	J_{MP}	τ_{Me}	$^3J_{MH}$	$^2J_{PH}$	$^4J_{PH}$	δ_P	J_{MP}	$^2J_{PP}$
[PdCl(PMe$_3$)$_3$][NO$_3$]	8·33		−7·4	7·0		8·19		−11·1	+1·2	4·1		−25
[PdBr(PMe$_3$)$_3$][NO$_3$]	8·27		−7·5	8·6		8·20		−11·2	+1·3	5·4		−23
[PtCl(PMe$_3$)$_3$][NO$_3$]	8·26	+23·8	−7·8	12·6	+2266	8·07	+40·6	−10·9	+0·6	27·5	+3402	−25
[PtBr(PMe$_3$)$_3$][NO$_3$]	8·19	+24·2	−7·8	16·6	+2255	8·06	+41·2	−10·9	+0·5	25·6	+3412	−23
[PtI(PMe$_3$)$_3$][NO$_3$]	8·09	+24·6	−7·8	20·5	+2248	8·10	*ca.* 41	−10·9		26·1	+3349	*ca.* 27
[PdCl(AsMe$_3$)$_3$][NO$_3$]	8·36					8·22						
[PdBr(AsMe$_3$)$_3$][NO$_3$]	8·30					8·24						
[PtCl(AsMe$_3$)$_3$][NO$_3$]	8·33	18·0				8·15	26·5					
[PtBr(AsMe$_3$)$_3$][NO$_3$]	8·27	18·2				8·14	26·8					
[PtI(AsMe$_3$)$_3$][NO$_3$]	8·17	19·0				8·13	26·2					
[PtCl$_3$(PMe$_3$)$_3$][NO$_3$]	8·08	+13·9	−8·0	9·6	+1454	7·81	+22·1	−12·1	+0·5	2·0	+2054	−12
[PtBr$_3$(PMe$_3$)$_3$][NO$_3$]	7·90	+15·3	−7·8	26·0	+1461	7·74	+23·0	−11·9	0·4	13·6	+1975	−13
[PtCl$_3$(AsMe$_3$)$_3$][NO$_3$]	8·14	11·4				7·90	17·0					
[PtBr$_3$(AsMe$_3$)$_3$][NO$_3$]	8·00	12·3				7·87	17·2					
[RhCl$_3$(PMe$_3$)$_3$]	8·38	−0·4	−7·4	8·9	−84	8·37	−0·7	−11·0	+0·7	−7·2	−110	−29
[RhBr$_3$(PMe$_3$)$_3$]	8·20	−0·4	−7·2	18·5	−85	8·25	−0·7	−10·7	0·5	−3·7	−108	28
[IrCl$_3$(PMe$_3$)$_3$]	8·40		−7·8	42·4		8·34		−10·5	0·4	47·1		−22
[IrBr$_3$(PMe$_3$)$_3$]	8·23		7·7			8·23		10·2	0·3			

† In these Tables, signs are only included for coupling constants in those cases where they were actually determined relative to J_{PtP} as positive or $^2J_{PH}$ as negative (see text). However, the other couplings of the same type probably have the same sign.

The relevant parameters are recorded in Table 1 together with those of the phosphorus part of the spectrum obtained from the INDOR measurements. Monitoring each of the three lines of either part of the doublet in turn produces ^{31}P resonances for the single phosphine which are shifted with respect to one another by $^2J_{PP}(cis)$. The values obtained are not, however, as accurate as those obtained by Mann *et al.*[10] by direct ^{31}P n.m.r. measurements using random noise decoupling of protons. The composite spectra are similar to those previously published for this type of system and for MCl$_3$(PMe$_3$)$_3$ (M = Rh or Ir) agree with the reported values [6,10] within the limits of error. As the shift between the phosphorus resonances was never less than $4J_{PP}$, it was not necessary to treat the system as AB$_2$ to extract the ^{31}P parameters. We have investigated the relative signs of the coupling constants by $^1H\{^{31}P\}$, $^1H\{^{195}Pt\}$, and $^1H\{^{103}Rh\}$ double resonance experiments. McFarlane [11] has shown that J_{PtP} is positive in both *cis*- and *trans*-PtCl$_2$(PEt$_3$)$_2$. It is reasonable to assume that it has the same sign in these trimethylphosphine complexes as it has similar magnitude and in view of its large value is very unlikely to have changed sign. For the platinum complexes, $^3J_{PtH}$ has the same sign as J_{PtP} and is therefore positive whilst both types of $^2J_{PH}$ are of opposite sign and hence negative in agreement with previous suggestions.[1,12] On account of the coupling between the *trans*-pair of phosphorus nuclei and the protons of the single phosphine, when the resonances of the latter are monitored, lines of both phosphorus resonances are picked up and the sign of $^2J_{PP}(cis)$ can be determined as negative. Thence we find that $^4J_{PH}$ is positive in agreement with our previous observations [1] on its sign relative to that of $^2J_{PH}$. In order to obtain signs for the rhodium and palladium complexes, we have assumed that $^2J_{PH}$ has the same sign as in the platinum compounds since its value is similar. On this basis, $^3J_{RhH}$ and J_{RhP} are negative, the latter as previously suggested,[13] and the other couplings have the same signs as in the platinum complexes, further justifying the assumption.

Data for some trimethylarsine complexes are in Table 1. These spectra are much simpler than those of the phosphine complexes, consisting of two lines in ratio 1 : 2 with platinum satellites where relevant.

Complexes with Spin System [AX$_9$]$_3$.—This type of spin system has been analysed by Finer and Harris.[14] The only examples we have examined are four facial isomers of MX$_3$(PMe$_3$)$_3$ (M = Rh or Ir, X = Cl or Br). The proton spectrum of *fac*-IrCl$_3$(PMe$_3$)$_3$ is shown in Figure 4. Four small features are visible on the otherwise unresolved absorptions forming a ' washing line ' between the two sharp

[10] B. E. Mann, C. Masters, and B. L. Shaw, *J.C.S. Dalton*, 1972, 704.

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

[12] A. R. Cullingworth, A Pidcock, and J. D. Smith, *Chem. Comm.*, 1966, 89.

[13] T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, 1969, **91**, 3378.

[14] E. G. Finer and R. K. Harris, *J. Chem. Soc.* (*A*), 1969, 1972.

lines (which have separation $|^2J_{PH} + 2^4J_{PH}|$). Only about half the 'complex' transitions have explicit expressions for their energies so a definite analysis is not possible. The general form of the spectrum is most probably consistent with the $^2J_{PP}$ in the range 5—25 Hz. The spectra of the rhodium compounds show coupling to ^{103}Rh on the sharp lines. There are no obvious features on the region between the sharp lines, but this region is curved upwards instead of downwards, implying a greater phosphorus–phosphorus coupling constant than in the iridium complexes. The results are in Table 2.

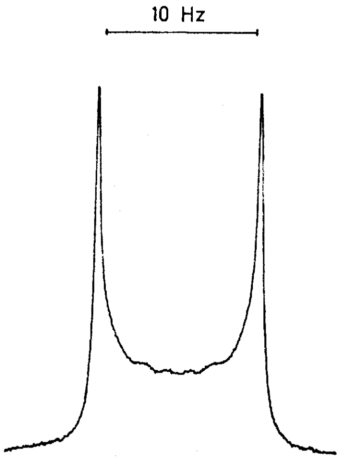

FIGURE 4 ^1H N.m.r. spectrum of *fac*-$IrCl_3(PMe_3)_3$ (CD_3NO_2 solution)

TABLE 2

N.m.r. parameters of *fac*-$[MX_3(PMe_3)_3]$ (M = Rh or Ir; X = Cl or Br)

	τ_{Me}	$^3J_{MH}$	$(^2J_{PH} + 2^4J_{PH})$	δ_P	J_{MP}
$RhCl_3(PMe_3)_3$	8·26	−0·8	−10·4	−5·4	−110
$RhBr_3(PMe_3)_3$	8·15	−0·7	−10·2	1·8	−105
$IrCl_3(PMe_3)_3$	8·24		10·3	42·9	
$IrBr_3(PMe_3)_3$	8·12		10·5	47·3	

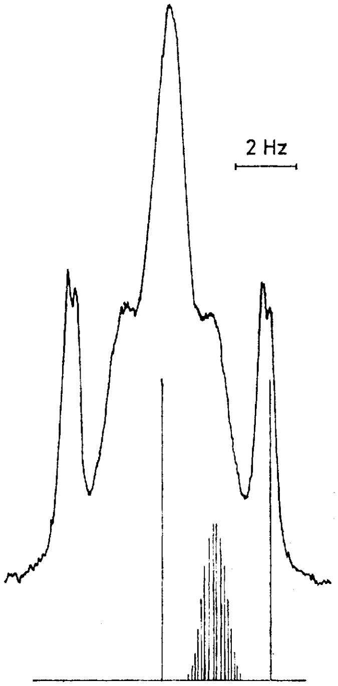

FIGURE 5 ^1H N.m.r. spectrum of *trans*-$[IrCl_2(PMe_3)_4][NO_3]$ together with lines calculated for the $m_T(A) = +1$ submatrices

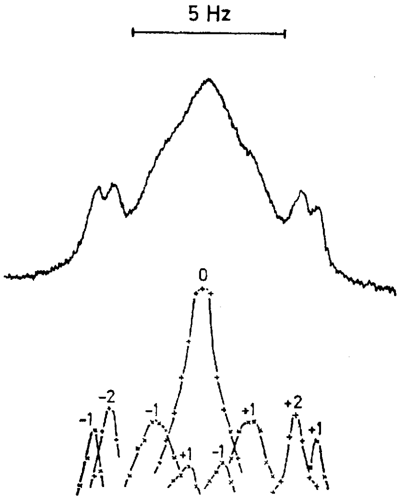

FIGURE 6 ^1H N.m.r. spectrum of $[Pt(PMe_3)_4][BF_4]_2$ (D_2O solution, main resonance only) with (below) plot of height of each line in the $^1H\{^{195}Pt\}$ INDOR spectrum against proton frequency. The numbers are the values of $m_T(A)$ for the various lines

Complexes with Spin System $[AX_9]_4$ (*planar*).—The complex cations $[Pt(PMe_3)_4]^{2+}$ and *trans*-$[MX_2(PMe_3)_4]^+$ (M = Rh or Ir; X = Cl or Br) are of this type. A well resolved example is *trans*-$[IrCl_2(PMe_2)_4]^+$ (Figure 5). The spectra of $RhBr_2[P(OMe)_3]_4^+$ and several related species of rhodium [15] and iridium [16] are similar except that the two outer lines coincide. Surprisingly, the spectrum of $[IrX_2(PMe_2Ph)_4][ClO_4]$ is reported as a single broad resonance, width at half-height *ca.* 6 Hz, and exchange was ruled out by the effect of addition of excess of phosphine.[17] The broadening might be caused by impurities since we have frequently obtained poorly resolved spectra from impure samples, *e.g.*, of $PdCl_2(PMe_3)_2$. (It is usually cured by recrystallisation from methanol.) An analysis of the tetrahedral spin system $[AX]_4$ has been given [18] but there does not seem to be one of a planar $[AX_n]_4$ type. Finer and Harris [19] have emphasised the spectral complexity of such systems but the fact that Figure 5 shows four well resolved lines suggests that some parameters can be extracted from it. To this end and also to give some account of the origins of the other features, we have attempted a partial analysis of the spin system. To assist the analysis, we have used $^1H\{^{195}Pt\}$ INDOR to relate the phosphorus spin states to the proton spectrum of $[Pt(PMe_3)_4]^{2+}$. The ^{195}Pt spectrum consists of five bands corresponding to the sum of the phosphorus spin eigenvalues, $m_T(A)$, having values ±2, ±1, and 0. These bands are well separated as J_{PtP} is 2230 Hz. The $^1H\{^{195}Pt\}$ INDOR spectrum was drawn out for a series of points in the proton spectrum,

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[15] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1693.

[16] L. M. Haines and E. Singleton, *J.C.S. Dalton*, 1972, 1891.

[17] B. L. Shaw and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 1184.

[18] R. M. Lynden-Bell, *Mol. Phys.*, 1968, **15**, 523.

[19] E. G. Finer and R. K. Harris, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 61.

0·24 Hz apart. The height of a particular ^{195}Pt band was then plotted against the proton frequency (Figure 6). The process clearly identifies the values of $m_T(A)$ for the various parts of the spectrum and the sum agrees well with the normal proton spectrum.

We follow the procedure of Finer and Harris [14] and as above assume that coupling between protons on different phosphines is zero. The nuclei are assumed as having spin $I = \frac{1}{2}$ and the sum of the spin eigenvalues for a X_n group is written $m(X_n)$. Because there is no mixing between states (i) of different $m_T(A)$ and (ii) of different $m(X_n)$ if $J_{XX}(cis) = J_{XX}(trans) = 0$, the spin Hamiltonian will break down into a series of five matrices of order 1, 4, 6, 4, and 1 corresponding to the value of $m_T(A)$. If the basis functions are described by expressions of the form $\alpha\beta\alpha\beta(x,x',x'',x''')$ where α or β refer to the spin function of the four A nuclei and the x's are the values of $m(X_n)$ for the four groups of X_n in the same cyclic order as the A nuclei, then the submatrices have basis functions (i)—(v). The sub-

(i) $\alpha\alpha\alpha\alpha(x,x',x'',x''')$

(ii) $\alpha\alpha\alpha\beta(x,x',x'',x''')$; $\alpha\alpha\beta\alpha(x,x',x'',x''')$;
$\alpha\beta\alpha\alpha(x,x',x'',x''')$; $\beta\alpha\alpha\alpha(x,x',x'',x''')$

(iii) $\alpha\alpha\beta\beta(x,x',x'',x''')$; $\alpha\beta\alpha\beta(x,x',x'',x''')$;
$\beta\alpha\alpha\beta(x,x',x'',x''')$; $\alpha\beta\beta\alpha(x,x',x'',x''')$;
$\beta\alpha\beta\alpha(x,x',x'',x''')$; $\beta\beta\alpha\alpha(x,x',x'',x''')$

(iv) $\alpha\beta\beta\beta(x,x',x'',x''')$; $\beta\alpha\beta\beta(x,x',x'',x''')$;
$\beta\beta\alpha\beta(x,x',x'',x''')$; $\beta\beta\beta\alpha(x,x',x'',x''')$

(v) $\beta\beta\beta\beta(x,x',x'',x''')$

matrices (i) and (v) have eigenvalues $2\nu_A + J_{AA'} + \frac{1}{2}J_{AA''} + (x + x' + x'' + x''')(\nu_X + \frac{1}{2}J_{AX} + J_{AX'} + \frac{1}{2}J_{AX''})$ and $-2\nu_A + J_{AA'} + \frac{1}{2}J_{AA''} - (x + x' + x'' + x''')(-\nu_X + \frac{1}{2}J_{AX} + J_{AX'} + \frac{1}{2}J_{AX''})$ respectively where $A''X''_n$ refers to the group *trans* to AX_n. In the X spectrum, these states will give rise to a doublet, width $|J_{AX} + 2J_{AX'} + J_{AX''}|$, comprising one-eighth of the X intensity. This is identified as the inner pair of the four sharp lines in Figure 6 and, as expected, $(J_{AX} + 2J_{AX'} + J_{AX''})$ is negative with respect to J_{PtP}.

The basis functions of submatrix (ii) have eigenvalues (a)—(d) in addition to the common term $\nu_A + (x + x' +$

(a) $\frac{1}{2}(x + x' + x'' - x''')J_{AX} + (x' + x''')J_{AX'} + \frac{1}{2}(x - x' + x'' + x''')J_{AX''}$

(b) $\frac{1}{2}(x + x' - x'' + x''')J_{AX} + (x + x'')J_{AX'} + \frac{1}{2}(- x + x' + x'' + x''')J_{AX''}$

(c) $\frac{1}{2}(x - x' + x'' + x''')J_{AX} + (x' + x''')J_{AX'} + \frac{1}{2}(x + x' + x'' - x''')J_{AX''}$

(d) $\frac{1}{2}(- x + x' + x'' + x''')J_{AX} + (x + x'')J_{AX'} + \frac{1}{2}(x + x' - x'' + x''')J_{AX''}$

$x'' + x''')\nu_X$. The off-diagonal terms are all $\frac{1}{2}J_{AA'}$ (the *cis*-$^2J_{PP}$) except for those between (a) and (c) and between (b) and (d) which are $\frac{1}{2}J_{AA''}$. The latter are removed by using the functions $(1/\sqrt{2})(a + c)$, $(1/\sqrt{2})(b + d)$, $(1/\sqrt{2})(a - c)$, and $(1/\sqrt{2})(b - d)$. If we now mix the first and second of these with the third and fourth respectively to get rid of the off-diagonal term between them, we obtain the diagonal terms (e)—(h) with off-diagonal

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

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

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

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

terms (1,2), $\cos\theta\cos\phi\, J_{AA'}$; (1,4), $-\sin\phi\cos\theta\, J_{AA'}$; (2,3), $-\sin\theta\cos\phi\, J_{AA'}$; and (3,4), $\sin\theta\sin\phi\, J_{AA'}$ where $\tan 2\theta = (x' - x''')(J_{AX} - J_{AX''})/J_{AA''}$ and $\tan 2\phi = (x - x'')(J_{AX} - J_{AX''})/J_{AA''}$. Assuming typical values, we expect $J_{AA''}$ to be large compared with $J_{AA'}$ or $(J_{AX} - J_{AX''})$ and hence that any off-diagonal term involving $\sin\theta$ or $\sin\phi$ will be sufficiently small to be ignored. Thus the last two diagonal terms approximate to eigenvalues and will result in lines centred on $\frac{1}{2}(J_{AX} + J_{AX''})$ and $J_{AX'}$ each comprising one-sixteenth of the total X intensity. The line at $\frac{1}{2}(J_{AX} + J_{AX''})$ will be sharp because it does not involve a change in the square-root term. It is identified as the outermost line in Figure 6 implying that $J_{AX'}$ has opposite sign to $(J_{AX} + J_{AX''})$ as expected. In the trimethyl phosphite complexes [15,16] the two outer sharp lines no doubt coincide because $J_{AX'}(^5J_{PH})$ is zero whereas $^4J_{PH}$ in the trimethylphosphine complexes is not. The line at $J_{AX'}$ involves changes in the square-root term and since this term is identical with that for *trans*-$MX_2(PMe_3)_2$ complexes, the line should be broadened to a similar extent. This is found by the $^1H\{^{195}Pt\}$ INDOR measurements on the opposite side of ν_X to the other $m_T(A) = 1$ transitions in agreement with the relative signs. The other two diagonal terms will mix under the action of $\cos\theta\cos\phi\, J_{AA'}$. To get some idea of the resulting spectrum we will approximate $\cos\theta\cos\phi\, J_{AA'}$ to $J_{AA'}$ and ignore the square-root terms. The eigenvalues are then $\frac{1}{4}(x + x' + x'' + x''')(J_{AX} + 2J_{AX'} + J_{AX''}) \pm \frac{1}{4}[(x - x' + x'' - x''')^2(J_{AX} - 2J_{AX'} + J_{AX''})^2 + 16J_{AA'}{}^2]^{\frac{1}{2}}$ so that X transitions occur at $\frac{1}{4}(J_{AX} + 2J_{AX'} + J_{AX''}) \pm \frac{1}{4}[\chi^2(J_{AX} - 2J_{AX'} + J_{AX''})^2 + 16J_{AA'}{}^2]^{\frac{1}{2}} \pm \frac{1}{4}[(\chi - 1)^2(J_{AX} - 2J_{AX'} + J_{AX''})^2 + 16J_{AA'}{}^2]^{\frac{1}{2}}$ where χ has integral values from 1 to $2n$. The total intensity for lines of a particular value of χ is given by function (1) (relative to a total

$$8 \sum_{r=\chi}^{2n} r\,{}^{2n}C_r\,{}^{2n}C_{r-\chi} \qquad (1)$$

X intensity of $n2^{(4n+5)}$) and is split between lines where the square-root terms have different signs and those where they have the same sign in the ratio $(1 + g) : (1 - g)$ where $g = [\chi(\chi - 1)(J_{AX} - 2J_{AX'} + J_{AX''})^2 + 16J_{AA'}{}^2]/\{[\chi^2(J_{AX} - 2J_{AX} + J_{AX''})^2 + 16J_{AA'}{}^2]^{\frac{1}{2}}[(\chi - 1)^2(J_{AX} - 2J_{AX'} + J_{AX''})^2 + 16J_{AA'}{}^2]^{\frac{1}{2}}\}$. For a value of 25 Hz for $J_{AA'}$ (typical of *cis*-$^2J_{PP}$ in the *mer*-complexes) this results in a broad line about $\frac{1}{4}(J_{AX} + 2J_{AX'} + J_{AX''})$ in good agreement with that observed (see Figure 5). In view of the approximations made and the uncertainty on the line widths of the component lines it is not practicable to try to evaluate $J_{AA'}$ (see ref. 19). The lines corresponding to the sum of square-root terms are much too weak to contribute to the spectrum.

The submatrices (iv) will give lines on the opposite side of ν_X to those of submatrices (ii). The four sharp, outer lines integrate as approximately one-quarter of the total intensity as required by this analysis. From the $^1H\{^{195}Pt\}$ INDOR experiments, the submatrices (iii) only give lines belonging to the central, broad feature. In view of the complexity of these 6 × 6 matrices and the improbability of deriving any parameters from such a band, we have not attempted to solve these submatrices in detail. However, for $J_{AA'} = 0$ the transitions of $\alpha\beta\alpha\beta(x,x',x'',x''')$ and $\beta\alpha\beta\alpha(x,x',x'',x''')$ would occur at $\pm\frac{1}{2}(J_{AX} - 2J_{AX'} + J_{AX''})$. As this is not so in our examples, it is clear that these states are mixed with the other four by a significant $J_{AA'}$ [*i.e.*, $^2J_{PP}(cis)$].

Thus the evaluatable parameters are $(J_{AX} + J_{AX''})$ and $J_{AX'}$. We have obtained the phosphorus shifts and metal–phosphorus coupling constants from $^1H\{^{31}P\}$ INDOR measurements and all these data are in Table 3.

TABLE 3

N.m.r. parameters of $[Pt(PMe_3)_4]^{2+}$ and *trans*-$[MX_2(PMe_3)_4]^+$

	τ_{Me}	$^3J_{MH}$	$[^2J_{PH} + {}^4J_{PH}$ (*trans*)]	$^4J_{PH}$ (*cis*)	δ_P	J_{MP}
$[Pt(PMe_3)_4][BF_4]_2$	8·11	+26·0	−7·3	+0·5	21·5	+2230
$[RhCl_2(PMe_3)_4][BF_4]$	8·21	−0·4	−6·4	0·4	10·3	−83
$[RhBr_2(PMe_3)_4][BF_4]$	8·32	−0·4	−6·6	0·4	16·6	−80
$[IrCl_2(PMe_3)_4][NO_3]$	8·28		6·7	0·3	47·3	
$[IrBr_2(PMe_3)_4][NO_3]$	8·17		6·8	0·2	54·7	

DISCUSSION

We will leave discussion of the relationship between metal–phosphorus bonding and M–P coupling constants to later [2] when the results here can be compared with the vibrational frequencies for the same molecules.

$^2J_{PP}(cis)$ of *mer*-$[PtX_3(PMe_3)_3]^+$ is approximately half the value found for the rest of the meridional complexes. $^2J_{PP}(cis)$ decreases from rhodium to iridium paralleling the behaviour in *cis*-$M(CO)_4(PMe_3)_2$ (M = Cr, Mo, or W) [20] but does not show any significant difference between Pd^{II} and Pt^{II} or much sensitivity to halide. This contrasts with the behaviour of *cis*-$MX_2(PMe_3)_2$ where the values are much larger for platinum than palladium and decrease in the order Cl > Br > I. A possible explanation is that the latter complexes are less rigid and the P–M–P angles alter more between the complexes [∠PMP is 96° rather than 90° in *cis*-$PtCl_2(PMe_3)_2$ [21]]. $^2J_{PP}(cis)$ is negative in all cases where we have determined it, similar to $^2J_{PP}$ in other Rh^I and Rh^{III} complexes [22] and in *cis*-$M(CO)_4(PMe_3)_2$ (M = Cr, Mo, or W) [23] but in contrast to the positive sign in *cis*-$PdCl_2[P(OMe)_3]_2$.[24]

We have observed [1] that a halide in the *cis*-position has a marked effect on the shift of the protons of the PMe_3 ligand and that it is more reasonable to ascribe this to the 'through-space' effects of magnetic anisotropy and electric dipole of the M–X bond than chemically significant changes in the bonding. The proton shifts of the present complexes behave in the same way, *e.g.*, for $[PtX(PMe_3)_3]^+$ the mutually *trans*-phosphines change by 0·17 p.p.m. from chloride to iodide whilst the phosphine *trans* to halide changes by only 0·03 p.p.m. It is clear that the phosphorus shift is also affected by the *cis*-halide but in this case the changes are in the opposite direction and are much greater, *e.g.*, 7·9 p.p.m. for the *trans*-phosphorus atoms but only 1·4 p.p.m. for the phosphorus *trans* to halide when chloride is replaced by iodide. It is more difficult to explain this magnitude of change by magnetic anisotropy or electric dipole effects but chemical explanations seem equally unreasonable. Previously [1] we found that $^3J_{PtH}$ was affected by the halides present and, particularly for $[PtX_3(PMe_3)_3]^+$, it becomes obvious that $^3J_{PtH}$ is much more affected by the *cis*-halide than the *trans*-halide. This is not so for the much smaller $^3J_{RhH}$ in *mer*-$RhX_3(PMe_3)_3$, so it appears that the effect is proportional to $^3J_{MH}$ rather than an additional contribution to it. In contrast, there does not seem to be any abnormal behaviour of J_{PtP} (or J_{RhP}) with change of halide and hence this parameter is much more suitable as a basis for chemical discussion than $^3J_{PtH}$.

EXPERIMENTAL

The ^1H n.m.r. spectra were measured on a Varian Associates HA 100 spectrometer in 'HA' mode with 2% tetramethylsilane as internal reference. Chemical shifts and the larger coupling constants were measured with the aid of a frequency counter (±0·1 Hz) and are given on the τ scale and in Hz respectively. The temperature was ambient magnet temperature (*ca.* 300 K) except for $[PdX(PMe_3)_3]^+$ which were measured at *ca.* 260 K to slow the exchange of phosphine groups. To the same end, a little $M_2X_4(PMe_3)_2$ was added to the solution of both these complexes and their platinum analogues. Samples were normally run as 0·1M-solutions in dichloromethane except that the facial isomers and the $[MX_2(PMe_3)_4]^+$ (M = Rh or Ir) salts were not soluble to this extent. $[Pt(PMe_3)_4][BF_4]_2$ was run in D_2O with $Me_3Si{\cdot}(CH_2)_3{\cdot}SO_3Na$ as reference (but HDO as lock).

The second frequency for heteronuclear INDOR was provided by a Schomandl ND 100M frequency synthesiser, the swept frequency generator of which is coupled to the *X*-axis of the recorder of the HA 100 instrument. The two radio frequencies were applied to the probe transmitter coil by the double-tuned network described by Burton and Hall.[24] The observed frequencies and the operating frequency of the HA 100 instrument were measured with the frequency counter and the results corrected to tetramethylsilane resonating at 100 MHz exactly. The relevant frequency for external 85% H_3PO_4 was found to be 40,480,754 Hz by measuring the frequency of neat trimethyl phosphite and then determining the latter's shift from H_3PO_4 as −140·2 p.p.m. by direct ^{31}P n.m.r. measurement in 'HR' mode. In all cases the peak

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maximum was monitored and relatively low irradiating powers (H_2) used. The amount of detail visible in the INDOR spectra varied with the type of complex. Thus phosphorus proton coupling was 'resolved' for the phosphorus *trans* to halide in *mer*-complexes but not for the mutually *trans*-pair of nuclei or the phosphorus nuclei in the *fac*- or tetrakis-complexes. The results are accurate to $\pm 0{\cdot}1$ p.p.m. or ± 2 Hz for coupling constants. The values for J_{RhP} are from ^{1}H{^{103}Rh} measurements since the lines are narrower and give more accurate values than for ^{1}H{^{31}P}. The INDOR measurements on the facial isomers and tetrakis-complexes of rhodium and iridium were done on saturated solutions in CD_3NO_2 in which they are more soluble than in dichloromethane. The preparation and characterisation of the complexes is described elsewhere [3,4] except for *mer*-$[PtX_3L_3][NO_3]$ (L = PMe_3 or $AsMe_3$, X = Cl or Br) which were obtained by oxidation of the solutions of $[PtXL_3][NO_3]$ with the respective halogen and were not isolated. The action of chlorine on $[PtCl(PMe_3)_3][NO_3]$ produced two complexes in the approximate ratio 2 : 1. ^{1}H{^{31}P} and ^{1}H{^{195}Pt} INDOR measurements show that both are of the meridional type, the proton resonances of the single phosphines being almost coincident. Oxidation of $[PtCl(PMe_3)_3][BF_4]$ gives only one species which corresponds to the major component of the nitrate salt. For consistency with the other systems, the values for $[PtCl_3(PMe_3)_3][NO_3]$ are given in Table 1. The parameters of $[PtCl_3(PMe_3)_3][BF_4]$ are: (*trans*-pair of phosphines) τ_{Me} 8·11; $^3J_{\text{PtH}}$, +13·9; $^2J_{\text{PH}} + {}^4J_{\text{PH}}$, −8·0; δ_{P}, +9·5; J_{PtP}, +1450: (single phosphine) τ_{Me}, 7·91; $^3J_{\text{PtH}}$, +22·5; $^2J_{\text{PH}}$, −12·3; $^4J_{\text{PH}}$, +0·5; δ_{P}, +1·9; J_{PtP}, +2045, $^2J_{\text{PP}}(cis)$, −12 whilst the additional species has parameters: (*trans*-pair of phosphines) τ_{Me}, 8·07; $^3J_{\text{PtH}}$, +12·5; $^2J_{\text{PH}} + {}^4J_{\text{PH}}$, −7·8; δ_{P}, 0·0; J_{PtP}, +1480: (single phosphine) δ_{P}, −2·8; J_{PtP}, +2184 (proton resonances obscured by other species). From these, it is likely that the additional species is *mer*-$[PtCl_2(NO_3)(PMe_3)_3]^+$ with nitrate *trans* to the single phosphine. It is probably formed by insertion of the nitrate anion as the ion-pair undergoes oxidation; a reaction which is less likely with the very poor ligand $[BF_4]^-$ or in competition with the bromide ion.

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