^{1}H Nuclear Magnetic Resonance Spectra of *cis*-Dimethylbis(trimethylphosphine)platinum and Some Related Systems

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The ^{1}H n.m.r. spectrum of the platinum-bonded methyl groups of *cis*-$PtMe_2(PMe_3)_2$ is shown not to be of the $[AX_3]_2$ spin type but to be $[AR_3X_9]_2$ and the complete proton spectrum is analysed on this basis. ^{31}P Parameters are also given. The spectra of *cis*-$PtMe_2L_2$ (L = PPh_3 and PMe_2Ph) are also considered and it is suggested that all the phenyl protons must be included in the analysis. The lack of resolved features, other than the strong doublet, in the spectrum of *cis*-$PtCl_2(PMe_2Ph)_2$ is put down to the same cause.

THE methyl part of the ^{1}H n.m.r. spectrum of *cis*-$PtMe_2(PPh_3)_2$ has been reported by Greaves *et al.*[1] and described as an example of an $AA'MX_3X'_3$ spectrum ($M = {}^{195}Pt$) although no analysis was attempted. Allen and Pidcock[2] similarly describe the spectrum of the methyl groups of *cis*-$PtMe_2(PEt_3)_2$ as of the $X_3AA'X'_3$ type and extract values of $^2J_{PP}$, *etc.*, by matching a computed spectrum with that observed. The dimethylphenylphosphine complex is described[3] as having a similar spectrum for the platinum-bonded methyl groups to that of the triphenylphosphine analogue[1] although in a more recent paper[4] it is said to have $^2J_{PP}$ of *ca.* 0.

In the course of our studies on trimethylphosphine complexes of platinum metals[5,6] we prepared *cis*-$PtMe_2(PMe_3)_2$, first reported by Chatt and Shaw.[7] The ^{1}H n.m.r. spectrum (Figure 1) is similar to that of the triphenylphosphine complex for the platinum-bonded methyls whilst the phosphine part resembles that of *cis*-$PtBr_2(PMe_3)_2$ (Figure 2 of ref. 5) except that the ' inner ' doublet is only of about half the intensity. As lines in addition to the sharp doublet can be identified and are moderately resolved, we have attempted an analysis. However, it was soon apparent that an analysis of the platinum-bonded methyl spectrum on the basis of an $[AX_3]_2$ system[8] was not possible. For such a system where $J_{XX} = 0$, half the intensity appears as a

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[1] E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Comm.*, 1967, 860.

[2] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

[3] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

[4] A. J. Cheney, B. E. Mann, and B. L. Shaw, *Chem. Comm.*, 971, 431.

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

[7] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

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

sharp doublet of width $|J_{AX} + J_{AX'}|$, the rest occurring as a series of doublets of separation $[\chi^2L^2 + J_{AA'}{}^2]^{\frac{1}{2}} \pm [(\chi - 1)^2L^2 + J_{AA'}{}^2]^{\frac{1}{2}}$ where $L = |J_{AX} - J_{AX'}|$ and χ has values 1, 2, and 3. The ' outer ' lines, *i.e.*, those for the positive sign, are usually much weaker than the ' inner ' lines and as χ increases the total intensity of ' inner ' and ' outer ' lines decreases in the ratio 10 : 5 : 1. Thus it is not possible to explain why most of the intensity, other than the sharp lines, occurs outside the first and second inner lines (which should correspond to $\chi = 1$ and 2 respectively). The full description of the system is $[AR_3X_9]_2$ and we have been able to account for the observed spectrum on this basis. Whilst this work was in progress, an analysis of the system $[AR_tX_n]_2$ was published[9] and as this is essentially the same as our analysis, we shall use it here to discuss the spectrum of *cis*-$PtMe_2(PMe_3)_2$. The important difference between the predictions for the $[AX_n]_2$ and $[AR_tX_n]_2$ cases is that the complex lines in the X part depend on the parameters and spins of the R nuclei as well as of the X and A nuclei and *vice versa*. The complex lines for the R part are a series of doublets with separations given by expression (1) where $L_{AR} = J_{AR} - J_{AR'}$, $L_{AX} = J_{AX} - J_{AX'}$, Ω takes integral values from 1 to t, and χ takes integral values from $-n$ to n. As with $[AX_n]_2$, the ' outer ' lines where the square-root terms have the same sign are usually much weaker than the related ' inner ' lines where they have opposite signs.

$$[\{\Omega L_{AR} + \chi L_{AX}\}^2 + J_{AA'}{}^2]^{\frac{1}{2}} \pm [\{(\Omega - 1)L_{AR} + \chi L_{AX}\}^2 + J_{AA'}{}^2]^{\frac{1}{2}} \quad (1)$$

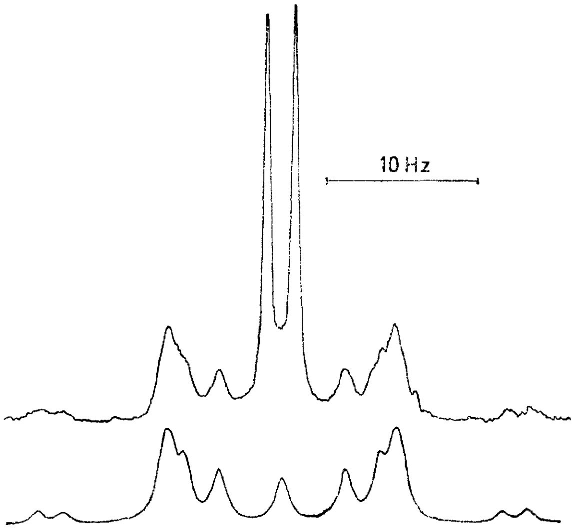

FIGURE 1 ^{1}H N.m.r. spectrum of the platinum-bonded methyl groups of *cis*-$PtMe_2(PMe_3)_2$ with (below) spectrum calculated for parameters given in the text (strong doublet omitted for clarity)

We will refer to the protons of the phosphine groups as X. The assumption that $J_{RX} = 0$ is clearly valid from the lack of any splitting on the sharp doublets (Figure 1). The other assumption, that $J_{RR} = 0$ (between the platinum-bonded methyl groups) is reasonable and, although it cannot be proved, is supported by the success of the analysis below. In the R part of the spectrum either of the features with doublet separations 29·4 and 32·3 Hz might be ' outer ' lines. The most intense R transitions are for $\Omega = 1$ and $\chi = 0$ and if they contribute to one of these ' outer ' lines and the doublet nearest the strong doublet then $^2J_{PP}$ is 10·5 or 12·0 Hz. The most likely assignment of the corresponding X transitions, $\Omega = 0$, $\chi = 1$, is to the only resolved pair of lines inside the strong doublet in which case the related outer lines will be under the ^{195}Pt satellites. However, ' tickling ' at a point 12·3 ± 0·5 Hz outside these resolved features perturbs them in a similar manner to ' tickling ' the outer lines of the spectrum of *cis*-$PtBr_2(PMe_3)_2$ (Figure 2 of ref. 5) favouring a value of 12·0 Hz for $^2J_{PP}$. On this basis, $L_{AR} = 16{\cdot}4$ and $L_{AX} = 8{\cdot}3$ Hz and the whole spectrum can be calculated. The strong doublet has been omitted from the calculated spectrum shown in Figure 1 so that the complex lines can be more easily seen. The excellent agreement with the observed spectrum shows that the correct set of parameters has been found. From the computed line positions it is clear that the reason for the reasonably intense lines observed is that several transitions coincide in each case. Thus the doublet of separation 8·3 Hz has significant contributions from (Ω,χ) values of (1,0), (1,2), (2,2), and (2,4) as has the outer doublet with separation 32·3 Hz; there is a significant intensity in between the sharp lines due to (1,1) and (2,3), and the features at ±6·6 Hz have main components (1,3), (1,−1), and (2,1). These coincidences are because L_{AR} is approximately twice L_{AX}. In the absence of such simplifying relationships, it is likely that there will be so many different, overlapping transitions that no resolved features are visible and analysis will not be possible.

$^2J_{PtH}$ was found to have negative sign (with respect to J_{PtP} taken as positive[10,11]) by ^{1}H{^{31}P} INDOR as expected. The signs of N_{AR} and N_{AX} were determined as positive and negative respectively by ^{1}H{^{195}Pt} INDOR and the *cis*- and *trans*-couplings to the platinum-bonded methyls can be identified by their signs.[12] We have determined the sign of $^2J_{PP}$ by comparing the asymmetric ^{1}H^3{^{1}P} INDOR spectra obtained from monitoring each of the strong lines with that calculated for the relevant part of the ^{31}P spectrum (see ref. 13 for details).

We thus obtain for *cis*-$PtMe_2(PMe_3)_2$, τ_{Me} 9·69, $^2J_{PtH}$ −65·4, $^3J_{PH}(cis)$ +9·1, $^3J_{PH}(trans)$ −7·3, $\tau_{Me}(PMe_3)$ 8·58, $^3J_{PtH}$ +20·1, $^2J_{PH}$ −8·1$_5$, $^4J_{PH}$ +0·1$_5$, δ_P 23·8 p.p.m., $^1J_{PtP}$ +1790, $^2J_{PP}$ −12·0. If the values of $^2J_{PP}$ and

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

[10] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, and B. F. Taylor, *J.C.S. Dalton*, in the press.

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

[12] M. A. Bennett, R. Bramley, and I. B. Tomkins, *J.C.S. Dalton*, 1973, 166.

[13] R. J. Goodfellow and B. F. Taylor, *J.C.S. Dalton*, submitted for publication.

$^1J_{PtP}$ are compared with those of *cis*-$PtX_2(PMe_3)_2$ (X = Cl, Br, and I),[5,10] it is apparent that whilst $^2J_{PP}$ decreases in almost equal steps Cl > Br > I > Me, the decrease in $^1J_{PtP}$ from iodide to methyl is an order of magnitude greater than that between the halides.

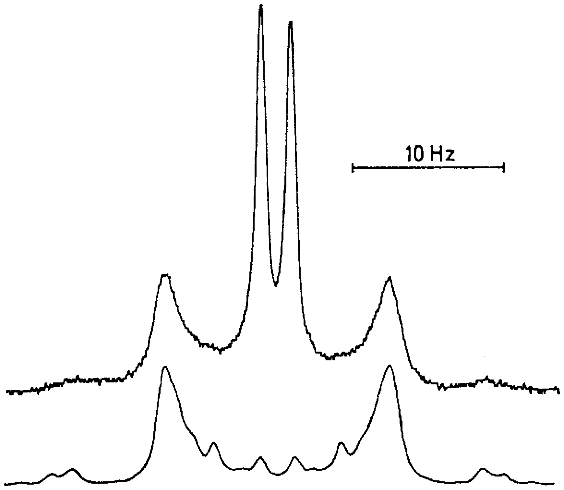

FIGURE 2 ^{1}H N.m.r. spectrum of the methyl groups of *cis*-$PtMe_2(PPh_3)_2$ with (below) spectrum calculated for parameters given in the text(strong doublet omitted for clarity)

Clearly, other complexes *cis*-$PtMe_2(PR_3)_2$ which have been described as $XAA'X'_3$ or $[AX_3]_2$ must be interpreted on the basis of $[AR_3X_n]_2$ at least. The triphenylphosphine complex might be described as $[AR_3X_6]_2$ if only the *ortho*-protons of the phenyl rings are included. The spectrum of the platinum-bonded methyls (Figure 2) is similar to that of the trimethylphosphine complex but lacks any resolved ' inner ' features and the ' outer ' lines are less distinct. Since $^5J_{PH}$ must be very small, L_{AX} and N_{AX} may be assumed to have the same value and this can be found from the phenyl part of the spectrum (the assignment was confirmed by irradiating the phosphorus nuclei). L_{AR} can be estimated from the ' wings ' of the methyl part of the spectrum and $^2J_{PP}$ from the position of the ' outer ' features. With small adjustments, the general envelope of the methyl spectrum can be reproduced with the parameters (Me)$^3J_{PH}$(*cis*) +8·9, $^3J_{PH}$(*trans*) −6·9, (*o*-Ph)$^3J_{PH}$ 9·8, $^5J_{PH}$ 0, and $^2J_{PP}$ 10·8 Hz. However, the calculated spectrum (Figure 2) has resolved ' inner ' lines corresponding to ($\Omega = 1$, $\chi = 0$) which, at best, appear as inflections in the observed spectrum. The most likely reason for these features not being properly resolved in the observed spectrum is the effect of the other phenyl protons. The spectrum of the *ortho*-protons is typical of an $[AB]_2$ system and the *meta*- and *para*-resonances are superimposed so this part of the spectrum alone is $[AB]_2C$ and the whole system should be described as $[AR_3([XY]_2Z)_3]_2$. Such a system is too complex for any attempt at analysis to be worthwhile particularly in view of the lack of resolved features. The other parameters obtained for this compound are τ_{Me} 9·67, $^2J_{PtH}$ −69·4 Hz, δ_P −27·0 p.p.m., and $^1J_{PtP}$ +1902 ± 10 Hz.

That the methyl part of the spectrum of the equivalent PMe_2Ph complex lacks resolved ' inner ' features, is hardly surprising since this complex has six methyl protons on the phosphine in addition to the phenyl ring protons. The spectrum resembles that of the PPh_3 complex implying that $^2J_{PP}$ is not zero. Indeed, broad ' outer ' features occur with much the same separation as the resolved features of the PMe_3 complex and the wings due to the larger values of (χ,Ω) are also of similar width to those of the PMe_3 complex so $^2J_{PP}$ must be similar, *i.e.*, in the region of 12 Hz in contrast to ref. 4. The results of $^1H\{^{31}P\}$ INDOR measurements agree with those of ref. 4 and the signs of the platinum–hydrogen coupling constants are the same as in the other compounds of this type.

We have long been puzzled why the proton spectra of the methyl groups in *cis*-$MCl_2(PMe_2Ph)_2$ (M = Pt and Pd) [14] which are described as simple doublets did not show resolved lines due to P–P coupling similar to those observed for the equivalent PMe_3 complexes.[5,15] We have remeasured these spectra and find that for the palladium complex the methyl doublet has shoulders on the outside suggesting that $^2J_{PP}$ is small but not zero (*cf.* Figure 1 of ref. 5) and that $|^2J_{PH} - {}^4J_{PH}|$ is *ca.* 1·2 Hz greater than $|^2J_{PH} + {}^4J_{PH}|$. In the case of the platinum compound, the area between the strong lines is raised above the baseline (Figure 3,A). This cannot be satisfactorily accounted for on the basis of an $[AX_6]_2$ system, *i.e.*, including methyl protons only. There is more hope

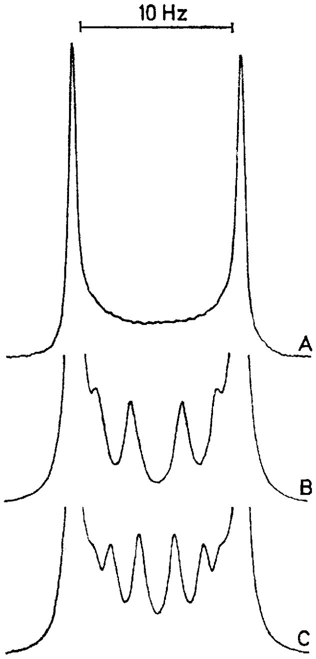

FIGURE 3

A, ^{1}H N.m.r. spectrum of methyl groups of *cis*-$PtCl_2(PMe_2Ph)_2$; B, spectrum calculated for $^2J_{PH}$ − 11·25, $^4J_{PH}$ 0·15, $^3J_{PH}$ 11·65, $^5J_{PH}$ 0, and $^2J_{PP}$ 18 Hz; and C, as curve B but with $^2J_{PP}$ 27 Hz

[14] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

[15] R. J. Goodfellow, *Chem. Comm.*, 1968, 114.

if the *ortho*-protons of the phenyl ring are included to make the system $[AR_2X_6]_2$. N_{AR} cannot be found from the phenyl region of this compound as all the phenyl protons overlap at 100 MHz, so we have used the value from $[Pr^n_4N][PtCl_3PMe_2Ph]$ for L_{AR}, assuming $^5J_{PH}$ to be zero and have estimated L_{AX} from N_{AX} and the palladium complex. The value of $^2J_{PP}$ in *cis*-$PtCl_2L_2$ is 18·9 Hz for L = PMe_3 and 17·8 Hz [13] for L = $P(OMe)_3$ so we made an initial calculation of the spectrum (L = PMe_2Ph) on the basis of $[AR_2X_6]_2$ with $^2J_{PP}$ equal to 18 Hz. The result (Figure 3,B) shows two well resolved lines inside the strong doublet. Increasing $^2J_{PP}$ brings these lines closer together and hence more likely to coalesce but the resulting envelope begins to curve upwards (*e.g.*, Figure 3,C where $^2J_{PP}$ = 27 Hz) instead of downwards as in the observed spectrum. Thus it seems impossible to account for the spectrum on the basis of $[AR_2X_6]_2$ and probably, as suggested for $PtMe_2(PPh_3)_2$, all the phenyl protons must be taken into account. If so, it is unlikely that any complex of PMe_2Ph or $PMePh_2$ will show resolved complex lines from which a value of $^2J_{PP}$ could be obtained. Certainly, the spectrum of *cis*-$PtCl_2(PMePh_2)_2$ resembles that of the PMe_2Ph complex, *i.e.*, Figure 3,A. When $^2J_{PP}$ is large, *e.g.*, in *trans*-isomers, a triplet is found [14] but any estimate of $^2J_{PP}$ from the width of the central band will be even more inaccurate than for a true $[AX_n]_2$ system as Hägele *et al.*[9] have pointed out that the conditions are different and more complicated for an $[AR_tX_n]_2$ system. Reliable results for $^2J_{PP}$ can be found by $^1H\{^{31}P\}$ INDOR measurements.[13] In a recent paper [16] Lynden-Bell *et al.* have considered the effect of the shift between the phosphorus resonances of *cis-mer*-$MX_2Y(PMe_2Ph)_3$ on the basis of the $[AM_3S_3]_2BX_6$ spin system. Thus they have included the non-equivalence of the methyl groups on the *trans*-pair of phosphines but taken no account of the phenyl protons which must greatly reduce the value of these calculations.

Conclusions.—The main result of this work is to emphasize that description and more especially analysis of spin systems ' by parts ' is not, in general, valid. (If all the couplings for one part of a system are very much greater than the rest, then consideration of this part alone may not involve very significant errors.)

That only Whitesides and Gaasch [17] have noted any difficulty in interpreting spectra of *cis*-$PtR_2(PR'_3)_2$ is probably because most authors have not given the spectra detailed consideration on account of the lack of resolved features, itself a consequence of the complex spin systems involved. These authors were concerned with *cis*-$Pt(CH_2{\cdot}CD_2{\cdot}CH_2{\cdot}CH_3)_2(PPh_3)_2$ and were forced to postulate a coupling of 7·3 Hz for H–C–Pt–C–H to achieve any sort of agreement between the observed spectrum of the platinum-bonded methylene groups and that calculated on the basis of $[AX_2]_2$. In fact, the spectrum looks much like that of *cis*-$PtMe_2(PPh_3)_2$ and can, no doubt, be explained in the same way. A significant HH′ coupling does not seem justified in view of the *cis*-disposition of the groups and the satisfactory explanation of the spectrum without it for $PtMe_2(PMe_3)_2$. Thus their value of 21 Hz for $^2J_{PP}$ is not valid nor is that of *ca.* 2 Hz for *cis*-$PtMe_2(PEt_3)_2$,[2] calculated on the basis of $[AX_3]_2$. [We have already shown that the value [4] of *ca.* 0 for *cis*-$PtMe_2(PMe_2Ph)$ is incorrect.] If we ignore these results, the range of $^2J_{PP}$ in *cis*-platinum alkyl complexes (0—21 Hz) which concerned Whitesides and Gaasch [17] is reduced to 10—12 Hz in much better agreement with the narrow range of $^2J_{PtH}$ (65—72 Hz).

Although the spectra of many bis-phosphine complexes have been described as of the $[AX_n]_2$ type, relatively few of them strictly belong to this spin system and it might be expected that the literature would contain a number of incorrect values of $^2J_{PP}$ as a result. Fortunately, the inherent complexity of the spectra has discouraged evaluation of $^2J_{PP}$ and where analysis has been possible this is usually because the coupling to one group is very much larger than to the rest, *e.g.*, complexes of PRF_2 where R = CF_3, $ClCH_2$, NMe_2, *etc.*[18]

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Varian Associates HA 100 instrument as described.[19] Approximately 0·1M solutions in dichloromethane were used at ambient magnet temperature (*ca.* 300 K). *cis*-$PtMe_2(PMe_3)_2$ decomposes after a time in this solvent and although it is more stable in benzene solution, the two types of methyl resonance overlap. ^{31}P N.m.r. data are from $^1H\{^{31}P\}$ INDOR measurements performed as in ref. 19. δ_P is in p.p.m. upfield of 85% H_3PO_4 taken as resonating at 40 480 754 Hz. The compounds were prepared by literature methods,[3,7,14] and gave satisfactory analyses, *etc.*

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[17] G. M. Whitesides and J. F. Gaasch, *J. Organometallic Chem.*, 1971, **33**, 241.

[18] C. G. Barlow, J. F. Nixon, and J. R. Swain, *J. Chem. Soc.* (*A*), 1969, 1082.

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