Proton and Phosphorus-31 Nuclear Magnetic Resonance Spectra of Octahedral Trisdimethylphenylphosphine Complexes with Meridional Configurations

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Certain complexes of types *mer*-$[MoOX_2(Me_2PhP)_3]$ and *mer*-$[OsX_2L(Me_2PhP)_3]$ (X = anionic ligand, L = neutral ligand) give ^1H spectra that differ significantly from that expected from a virtually coupled pair of *trans*-phosphines with an isolated unique phosphine. Calculations of $[AM_3S_3]_2BX$- spectra indicate that the anomalies in the spectra of the unique phosphines could derive from near zero shift differences for the ^{31}P nuclei, and this interpretation is confirmed by measurement of the ^{31}P spectra at 24·29 MHz and ^1H spectra at 220 MHz.

THE stereochemistries of many transition-metal complexes of dimethylphenylphosphine have been determined from their ^1H nuclear resonance spectra by Shaw and his co-workers.[1,2] In octahedral complexes that have three of the phosphine ligands (P) in the meridional configuration, *mer*-$[MX_2YP_3]$, the protons of the methyl groups in each of the *trans* phosphines are non-equivalent when the groups X are *cis*. The ^1H-spectra of the methyl groups for such complexes are normally comprised of a doublet from the methyl groups of the unique phosphine ligand (corresponding to the spectrum of an essentially isolated PMe_2 group), and a triplet from each of the two types of methyl group on the *trans* phosphines.[2] The triplets correspond to a form of the $[AX_3]_2$ spectrum (in the notation of Haigh [3]) in the limiting case of large coupling between the A (phosphorus) nuclei, and the central component of each triplet is composed of a number of unresolved lines.[4] Consistent with

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[1] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279; *J. Chem. Soc.* (*A*), 1966, 770; J. M. Jenkins, J. R. Moss, and B. L. Shaw, *ibid.*, 1969, 2796; J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *ibid.*, 1966, 1787.

[2] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1407; B. L. Shaw and A. C. Smithies, *ibid.* 1968, 2784; J. R. Moss and B. L. Shaw, *ibid.*, 1966, 1793; P. R. Brookes and B. L. Shaw, *ibid.*, 1967, 1079.

[3] C. W. Haigh, *J. Chem. Soc.* (*A*), 1970, 1682.

[4] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275; R. K. Harris and C. M. Woodman, *Mol. Phys.*, 1965, **10**, 437.

this analysis, the coupling constant between the two *trans*-phosphorus nuclei has been shown to be usually very much greater than between *cis* phosphorus nuclei for transition-metal complexes,[5] although some exceptions are known.[6]

However, for some recently reported molybdenum(IV)[7] and osmium(II)[8] complexes, although meridional stereochemistries were assigned on the basis of the spectra of the methyl groups, it was noted that the patterns of doublet and triplet lines were somewhat indistinct, with additional structure between the expected lines. We have obtained ^1H spectra of these complexes at various field strengths and have recorded moderate-resolution ^{31}P spectra; results are given in the Table.

Description of ^1H (60 MHz) and ^{31}P (24·29 MHz) n.m.r. spectra of the methyl groups of some molybdenum(IV) and osmium(II) complexes with meridional configurations

Complex	Solvent	^1H Spectrum	^{31}P Spectrum [a]
$[MoOCl_2(Me_2PhP)_3]$	$CDCl_3$	Normal [b]	Resolved (111·7, 108·7)
	C_6D_6	Normal [b]	Resolved (111·5, 109·5)
$[MoOBr_2(Me_2PhP)_3]$	$CDCl_3$	Normal [b]	Decomposes
	C_6D_6	Anomalous [c]	Overlapping (116·1, 114·2)
$[MoOI_2(Me_2PhP)_3]$	$CDCl_3$	Anomalous [c]	Singlet (123·9)
	C_6D_6	Normal [b]	Resolved (124·5, 126·1)
$[OsCl_2(CO)(Me_2PhP)_3]$ [d]	$CDCl_3$	Normal [e]	Resolved (157·0, 159·0)
$[OsCl_2(CO)(Me_2PhP)_3]$ [f]	$CDCl_3$	Anomalous [c]	Singlet (144·4)
$[OsBr_2(CO)(Me_2PhP)_3]$ [d]	$CDCl_3$	Normal [e]	Resolved (163·4, 168·8)
$[OsCl_2(PhNC)(Me_2PhP)_3]$ [d]	$CDCl_3$	Normal [e]	Resolved (155·7, 159·0)
$[OsCl_2(MeNC)(Me_2PhP)_3]$ [d]	$CDCl_3$	Normal [e]	Resolved (154·0, 159·4)
$[OsCl_2(N_2)(Me_2PhP)_3]$ [f]	$CDCl_3$	Anomalous [c]	Singlet (148·5)

[a] Figures in parentheses are approximate chemical shifts from P_4O_6 external reference; positive shifts are to high field of the reference. The first value corresponds to the more intense peak of the 2 : 1 spectrum. [b] A spectrum composed of two triplets and one doublet. [c] A spectrum with perturbed triplets and significant absorption or an extra peak between the doublet lines. [d] Complex *mer*-$[OsX_2LP_3]$ has *trans* X ligands. [e] A spectrum composed of a triplet and a doublet. [f] Complex *mer*-$[OsX_2LP_3]$ has *cis* X ligands.

The ^1H spectra (60 MHz) for deuteriochloroform solutions of the complexes *mer*-$[MoOX_2(Me_2PhP)_3]$ (X = Cl, Br, I; X ligands *cis*) are illustrated in Figure 1. For X = Cl, Br the spectra are near normal, but there is significant absorption between the lines of the doublet. For X = I an additional broad peak is clearly evident between the doublet lines and the triplets are also noticeably perturbed. Some of the ^1H spectra are significantly affected by change of solvent to deuteriobenzene (Table), but not by the addition of small amounts of the phosphines to the solutions. From the ^{31}P spectra at the same field strength, it appears that normal ^1H spectra correlate with resolved ^{31}P lines from the *trans* and unique phosphine ligands, and that the intensity of absorption between the ^1H doublet lines increases as the separation between the ^{31}P lines decreases (see Table and Figure 2). We have therefore calculated ^1H spectra for the methyl doublet region of the spectrum for situations in which the chemical shift between the phosphorus nuclei is close to zero.

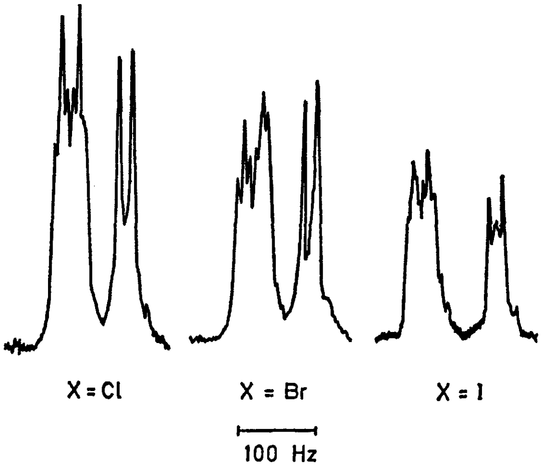

FIGURE 1 ^1H Spectra (60 MHz) of deuteriochloroform solutions of the complexes *mer*-$[MoOX_2(Me_2PhP)_3]$ (X = Cl, Br, I; X ligands *cis*)

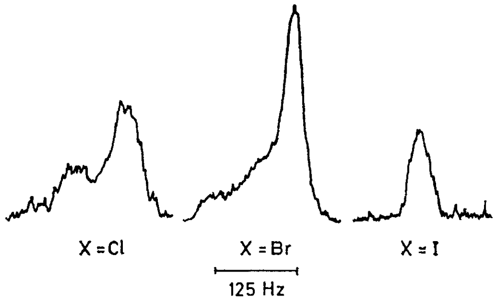

FIGURE 2 ^{31}P Spectra (24·29 MHz) of the complexes *mer*-$[MoOX_2(Me_2PhP)_3]$ (X = Cl, Br, I; X ligands *cis*). Solvents used were deuteriochloroform (X = Cl, I) and deuteriobenzene (X = Br)

Figures 3—5 show calculated X-spectra for the $[AM_3S_3]_2BX_6$ system for various values of J_{AB}/J_{BX} ($^2J_{PP'}/^2J_{P'H'}$ denoting the nuclei of the unique phosphorus ligand by P', H'), and δ_{AB}/J_{BX} ($\delta_{PP'}/^2J_{P'H'}$). These spectra are calculated by standard techniques[9] with the assumptions that there is no long range H $\cdots$ P

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[5] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **2**, 345.

[6] J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2796; F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1916; R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *ibid.*, 1970, **92**, 1908; T. R. Johnson, R. M. Lynden-Bell, and J. F. Nixon, *J. Organometallic Chem.*, 1970, **21**, P15; P. K. Maples and C. S. Kraihanzel, *Chem. Comm.*, 1968, 922.

[7] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

[8] D. P. Melville and R. L. Richards, unpublished results: D. P. Melville, D. Phil. Thesis, Sussex, 1970.

[9] R. M. Lynden-Bell and R. K. Harris, 'Nuclear Magnetic Resonance Spectroscopy,' Nelson, London, 1969, ch. 2.

or H · · · H coupling ($J_{XM} = J_{XS} = J_{AX} = 0$) and that the two chemically equivalent phosphorus nuclei are tightly coupled in the sense that $^2J_{PP} \gg {}^2J_{PH}$, $^2J_{PP'}$ ($J_{AA} \gg J_{AM}$, J_{AS}, J_{AB}). With these conditions the line positions can be written down immediately, as only 2×2 matrices are involved when factorisation due to symmetry is taken into account.

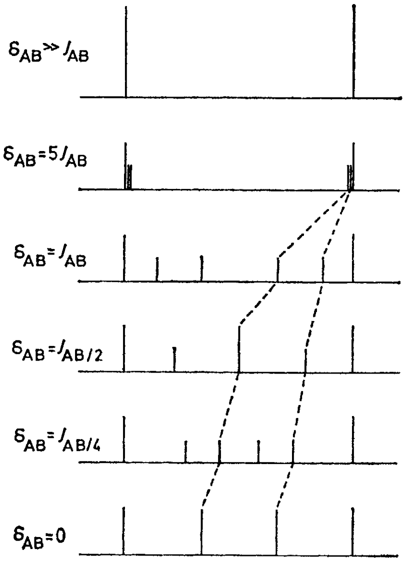

FIGURE 3 Calculated X-spectra of $[AM_3S_3]_2BX_6$ system under the conditions J_{AB} or $\delta_{AB} \gg J_{BX}$ ($^2J_{PP'}$ or $\delta_{PP} \gg {}^2J_{P'H'}$)

The general behaviour of the system can be understood from Figure 3. This represents the form the ^1H spectrum of the unique phosphine would take if $^2J_{PP'}$ were much larger than $^2J_{P'H'}$. In the top spectrum $\delta_{PP'}$ is large (there are no degeneracies), and the spectrum is identical to that of an isolated PMe_2 group, that is, there are two lines separated by $^2J_{P'H'}$. The subsequent spectra in the figure show the effect of reducing this chemical-shift difference but retaining the strong PP′ coupling. In the limit where $\delta_{PP'} = 0$, the H′ protons are virtually coupled to all the phosphorus nuclei, although as $^2J_{PP'}$ is assumed to remain small compared with $^2J_{PP}$ ($J_{AB} \ll J_{AA}$), the spectrum is not a 1 : 3 : 3 : 1 quartet, but has four lines of equal intensity. Between these limits the spectrum consists of two invariant outer lines with half the total intensity, and four inner lines of equal intensity. The effect of relaxing the condition that $^2J_{P'H'} \ll {}^2J_{PP'}$ ($J_{BX} \ll J_{AB}$) is shown in Figures 4 and 5. The basic pattern remains similar with two invariant outer lines with half the total intensity, but the four inner lines are split into many lines due to perturbation of the energy levels by the P′H′ coupling. The spectra were calculated with the assumption that all intraligand PH coupling constants are equal; small differences would increase the number of lines, but would not alter the form of the envelope of the substructure. In Figure 4 the basic pattern is still apparent when $^2J_{PP'} = 10^2 \ J_{P'H'}$ ($J_{AB} = 10J_{BX}$), whilst in Figure 5, calculated for $^2J_{PP'} = 2 \ {}^2J_{P'H'}$ ($J_{AB} = 2J_{BX}$), the basic pattern of four lines is lost in the substructure. A series of spectra calculated for $\delta_{PP'} = 0$ and various values of $J_{PP'}/{}^2J_{P'H'}$ is given in Figure 6. It demonstrates the change from the limit of large $^2J_{PP'}$ to the limit $J_{PP'} = 0$.

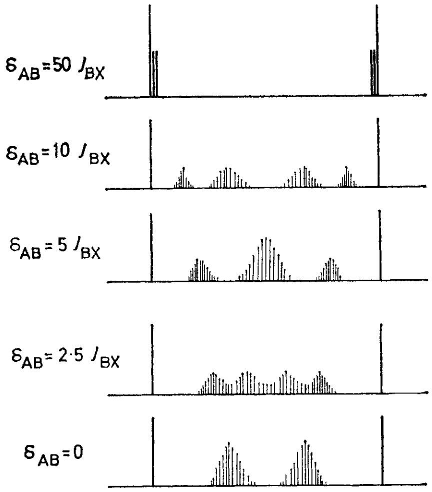

FIGURE 4 Calculated X-spectra of $[AM_3S_3]_2BX_6$ system under the condition $J_{AB} = 10 \ J_{BX}$ ($^2J_{PP'} = 10 \ {}^2J_{P'H'}$) for various values of δ_{AB}/J_{BX} ($\delta_{PP'}/{}^2J_{P'H'}$). (Because the lines are very close, the representation is not to be taken as strictly accurate.)

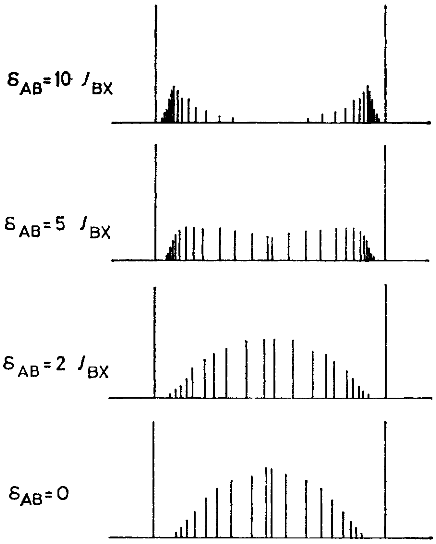

FIGURE 5 Calculated X-spectra of $[AM_3S_3]_2BX_6$ system under the condition that $J_{AB} = 2J_{BX}$ ($^2J_{PP'} = 2 \ {}^2J_{P'H'}$) for various values of δ_{AB} ($\delta_{PP'}$).

The implication of these calculations is clear. If the chemical-shift difference between the *cis* phosphorus nuclei in complexes such as $[MX_2YP_3]$ becomes comparable with the coupling between them, the ^1H spectrum will no longer be a simple doublet and triplet. The form of the additional structure depends on the ratio $^2J_{P'H'}/{}^2J_{PP'}$. For the complexes in the Table, this ratio is probably about 2,[5] so the form of the spectra should be as indicated by Figure 5. The ^1H spectra (60 MHz) in Figure 1 show the two invariant lines of separation $^2J_{P'H'}$ (8—10 Hz) and for X = Cl, Br and especially X = I there is further unresolved structure between these lines. The central maximum observed for *mer*-$[MoOI_2(Me_2PhP)_3]$ indicates that $\delta_{PP'} \leqslant 2{\cdot}5|{}^2J_{PP'}|$ (Figure 5). As $|{}^2J_{PP'}|$ is probably about 20 Hz, this implies that $\delta_{PP'} \leqslant 0{\cdot}5$ p.p.m., whilst for the bromo-complex $\delta_{PP'} \simeq 1$ p.p.m., and for the chloro-complex $\delta_{PP'} \geqslant 2$ p.p.m. These findings are supported by the ^{31}P spectra at 24·29 MHz (Table) and by ^1H spectra measured at higher field strengths;[10] for ^1H spectra at 220 MHz, the molybdenum complexes for X = Cl, Br, I in deuteriochloroform all give normal spectra in which, for example, the intensity of absorption between the doublet peaks is less than 25% of the peak height for the iodo-complex. At this field strength the frequency separation of the phosphorus resonances is evidently large enough to simplify the ^1H spectra.

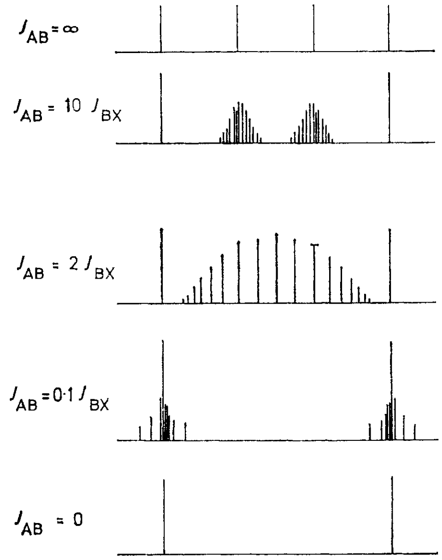

FIGURE 6 Calculated X-spectra of $[AM_3S_3]_2BX_6$ system for $\delta_{AB} = 0$ ($\delta_{PP} = 0$)

For the determination of complex stereochemistry, the perturbed spectra are just as useful as the normal simpler spectra, and when the coupling constants are similar to those for the molybdenum and osmium complexes discussed here, the calculations show that the phosphorus lines must be very close before perturbation of the simple ^1H spectra becomes significant. Phosphorus chemical shifts in co-ordination compounds are not well understood at present,[5] so it is not possible to predict where other perturbed spectra may be found.

EXPERIMENTAL

The osmium(II) complexes[8] were kindly provided by Dr. P. D. P. Melville, and the molybdenum(IV) complexes dichlorotris(dimethylphenylphosphine)oxomolybdenum(IV), m.p. 152—154° (dec.) (Found: C, 48·0; H, 5·4. Calc. for $C_{24}H_{33}Cl_2MoOP_3$: C, 48·3; H, 5·6%), dibromotris(dimethylphenylphosphine)oxomolybdenum(IV), m.p. 147—150° (dec.) (Found: C, 41·7; H, 5·1. Calc. for $C_{24}H_{33}Br_2MoOP_3$: C, 42·0; H, 4·9%), and di-iodotris(dimethylphenylphosphine)oxomolybdenum(IV), m.p. 141—144° (dec.) (Found: C, 37·0; H, 4·2. Calc. for $C_{24}H_{33}I_2MoOP_3$: C, 37·0; H, 4·2%) were prepared by the method of Butcher and Chatt.[7]

We thank the S.R.C. for a research studentship for G. G. M.

[2/1985 *Received*, 21*st August*, 1972]

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[10] G. G. Mather, D. Phil. Thesis, Sussex, 1971.