The Determination of the Sign of $^2J_{PP}$ in *cis*- and *trans*-$[(OC)_4Mo\{P(OMe)_3\}_2]$

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Summary The signs of $^2J_{PP}$ in *cis*- and *trans*-$[(OC)_4Mo\{P(OMe)_3\}_2]$ were found from double resonance experiments on the ^{13}C satellites in the ^1H spectra to be negative and positive, respectively.

THE discovery by Jenkins and Shaw[1] that ^{31}P–^{31}P coupling in complexes of second- and third-row transition metals containing identical phosphines is apparently larger in magnitude when the phosphorus ligands are *trans* than when they are *cis*, has been used as a method for confirming the stereochemistry of a wide variety of co-ordination compounds.[2] If the various values of $^2J_{PP}$ for different phosphorus ligands[3] are to have any promise of revealing the mechanism by which coupling is transferred between the phosphorus nuclei as well as providing additional information on the nature of the phosphorus–metal bond, it is necessary to obtain the sign of $^2J_{PP}$ for each configuration of the phosphorus nuclei with respect to the metal.

N.m.r. parameters (Hz.) relevant to the sign of $^2J_{PP}$ *in* cis- *and* trans-$[(OC)_4Mo\{P(OMe)_3\}_2]$

	N_C or $^2J_{PC}$[a]	N or $^3J_{PH}$[b]	$^2J_{PP}$	$^1J_{CH}$
$P(OMe)_3$[c]	$+10{\cdot}0\pm0{\cdot}2$	$+10{\cdot}0\pm0{\cdot}1$	—	$+146{\cdot}0\pm0{\cdot}2$
$[(OC)_5MoP(OMe)_3]$	$-\ 2{\cdot}3\pm0{\cdot}4$	$+11{\cdot}6\pm0{\cdot}1$	—	$+146{\cdot}8\pm0{\cdot}2$[d], $+146{\cdot}2\pm0{\cdot}4$[e]
cis-$[(OC)_4Mo\{P(OMe)_3\}_2]$	$-\ 3{\cdot}1\pm0{\cdot}4$[f]	$+11{\cdot}6\pm0{\cdot}1$[f]	$-40{\cdot}5\pm0{\cdot}1$[g]	$+144{\cdot}9\pm0{\cdot}4$[e]
trans-$[(OC)_4Mo\{P(OMe)_3\}_2]$	$-\ 1{\cdot}7\pm0{\cdot}4$[f]	$+11{\cdot}6\pm0{\cdot}1$[f]	$+162\pm5$[h]	$+145{\cdot}4\pm0{\cdot}4$[e]
$O{=}P(OMe)_3$[c]	$-\ 5{\cdot}8\pm0{\cdot}2$	$+10{\cdot}5\pm0{\cdot}1$	—	$+147{\cdot}0\pm0{\cdot}2$

[a] $N_C = {}^2J_{PC} + {}^4J_{PC}$ for the disubstituted complexes (see ref. 4); $^2J_{PC}$ refers to the remaining compounds. N_C and $^2J_{PC}$ are obtained from the ^{13}C INDOR spectra. [b] $N = {}^3J_{PH} + {}^5J_{PH}$ for the disubstituted complexes (see ref. 4); $^3J_{PH}$ refers to the remaining compounds, N and $^3J_{PH}$ are obtained directly from the ^1H spectra. [c] Values for this compound were taken from W. McFarlane, *Proc. Roy. Soc.*, 1968, *A*, **306**, 185. [d] From ^1H spectrum. [e] From ^{13}C INDOR spectrum. Sign assumed to be the same as in the nearly analogous $[(OC)_5MoP(OMe)_3]$. [g] Magnitude obtained directly from the separation of the first "inner" peak and the low-intensity absorption outside the main doublet in the ^1H spectrum (see ref. 4). [h] The separation corresponding to $^2J_{PP}$ in one of the AB quartets of the ^{13}C satellites in the ^{31}P spectrum was obtained by irradiation in the ^{31}P region while scanning one of the ^{13}C satellites in the ^1H spectrum (see ref. 4).

We now report the first example of such a sign determination. By employing double resonance experiments involving the ^{13}C satellites in the ^1H spectra[4] of $[(OC)_5MoP(OMe)_3]$ and of *cis*- and *trans*-$[(OC)_4Mo\{P(OMe)_3\}_2]$† it was concluded that $^2J_{PP}$ in the *cis*- and *trans*-complexes is negative and positive, respectively. The pertinent data set out in the Table were obtained on a Varian HR-60 instrument equipped with a field-frequency lock, frequency synthesizer and synthesizer driver, frequency counter and a digital analogue sweep unit for locating the ^{31}P and ^{13}C perturbing frequencies.

Because of the small value of $^2J_{PC} + {}^4J_{PC}$ (N_C) in both the *cis*- and *trans*-compounds, we were unable to distinguish between the centres of the frequency ranges used to tickle the outer lines of the two AB quartets of the ^{31}P spectrum corresponding to the two spin states of ^{13}C. Thus it was not possible to relate the sign of $^3J_{PH} + {}^5J_{PH}$ (N) to that of $^1J_{CH}$ (+). By irradiating selected transitions in one of the ^{31}P AB quartets corresponding to one of the ^{13}C spin states, the sign of $^2J_{PP}$ could be related to that of N.[4] Inasmuch as N is expected to be nearly equal to $^3J_{PH}$‡ and since this parameter is positive and of the same magnitude for $[(OC)_5MoP(OMe)_3]$, $P(OMe)_3$, and $O{=}P(OMe)_3$, we conclude that $^2J_{PP} < 0$ in the *cis*-compound and > 0 in the *trans*.

Although the reason for the sign inversion from the *cis*- to the *trans*-isomer is not obvious, it should be noted that a common p_σ metal orbital is shared between the *trans*-phosphorus nuclei which provides another route for coupling, whereas this is not the case in the *cis*-complex. Further experiments are under way to ascertain the sign of $^2J_{PP}$ for a variety of complexes containing phosphorus ligands whose substituents vary in electronegativity. In view of the recent observation by Finer and Harris that $^1J_{PP}$ undergoes a sign inversion in a series of diphosphorus compounds,[5] the possibility of a sign change in $^2J_{PP}$ in a given geometry (*cis* or *trans*) upon varying the phosphorus ligands in the metal complexes under study cannot be ruled out.

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† The preparations of the mono- and the *cis*- and the *trans*-trimethyl phosphite complexes were carried out according to the methods described by D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, 1968, **7**, 959; R. Mathieu and R. Poilblanc, *Compt. rend.*, 1967, **264**, *C*, 1053; and R. Poilblanc and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 1301, respectively.

‡ This assumption is made reasonable by our observations on mixed complexes of the type *cis*- and *trans*-$[(OC)_4MoP(OMe)_3P(OCH_2)_3CMe]$ in which no splitting of the main doublets attributed to $^3J_{PH}$ is observed due to $^5J_{PH}$ (F. B. Ogilvie, R. L. Keiter, G. Wulfsberg, and J. G. Verkade, to be published).

[1] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279.

[2] See for example M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 741; J. Powell and B. L. Shaw, *ibid.*, p. 211; and P. R. Brooks and B. L. Shaw, *ibid.*, 1967, 1079.

[3] F. Ogilvie, J. M. Jenkins, and J. G. Verkade, to be published.

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

[5] E. G. Finer and R. K. Harris, *Chem. Comm.*, 1968, 110.