Determination of the Relative Signs of $^2J(^{31}P-^{31}P)$ in Complexes of Tungsten(0) and Molybdenum(0) using Two-dimensional [$^{31}P-^{31}P$]-COSY-45 Nuclear Magnetic Resonance Chemical Shift Correlation

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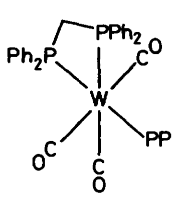
Two-dimensional [$^{31}P-^{31}P$]-COSY-45 n.m.r. spectroscopy has been used to determine the magnitudes and relative signs of $J(^{31}P-^{31}P)$ in three- and four-spin systems. The complexes studied are of molybdenum(0) and tungsten(0) with CO and $Ph_2PC(=CH_2)PPh_2$ (vdpp), $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH(CH_2CH_3)PPh_2$ (1,1-dppp), PEt_3, or $PPhEt_2$ as ligands. It is found that $^2J(^{31}P-^{31}P)$ (*cis*) when the P atoms are coupled *via* both P–M–P and P–C–P linkages and $^2J(^{31}P-^{31}P)$ (*trans*) are of the same sign, presumably positive, and both are of opposite sign to $J(^{31}P-^{31}P)$ (*cis*) when the P atoms are linked *via* the P–M–P pathway only. This suggests a dominant positive contribution to cisoid $^{31}P-^{31}P$ coupling *via* the P–C–P pathway.

The magnitudes and signs of internuclear spin–spin coupling constants ^2J(PP)† are important in determining the stereochemistry of metal–phosphine complexes, and, ultimately, in assessing the chemical bonding. In such complexes the general rule $|^2J(PP)(trans)| > |^2J(PP)(cis)|$ normally holds[1] but the magnitude of ^2J(PP) depends on factors such as (*i*) the nature of the metal and its valence state, (*ii*) the P–M–P bond angle, which may differ from 90 or 180° in formally *cis* or *trans* arrangements, (*iii*) the nature of the other ligands, and (*iv*) the organyl substituents on the phosphorus.[2] However, in most cases ^2J(PP)(*trans*) is large and positive and ^2J(PP)(*cis*) is smaller (sometimes much smaller) and is negative.[3]

Indirect observations of ^{31}P resonances, *e.g.* $^1H-\{^{31}P\}$ or $^{19}F-\{^{31}P\}$ INDOR experiments, were first used to determine the relative signs and magnitudes of J(PP).[4–6] With the introduction of Fourier-transform n.m.r. spectroscopy, many determinations of the magnitudes of J(PP) have been made but in simple first-order systems the one-dimensional ^{31}P n.m.r. spectrum does not give relative signs of J(PP). The development of two-dimensional n.m.r. techniques,[7–10] in particular homonuclear shift-correlated spectroscopy (COSY), makes possible the determination of relative signs of coupling constants in multispin systems. These COSY experiments have been used mainly for ^1H, relatively little for other nuclei.[11–15] Some applications of two-dimensional spectroscopy to ^{31}P n.m.r., principally biochemical, have been reviewed by Hutton[16] and by Bolton[17] and instances of its use in transition-metal complex chemistry have been reported.[15]

Here we present the results of [$^{31}P-^{31}P$]-COSY spectroscopy, carried out with {^1H(broad-band noise)} decoupling, on some previously unreported molybdenum(0) and tungsten(0) complexes, *mer*-[$W(CO)_3$(dppm-*PP′*)($PPhEt_2$)] (1), *mer*-[$Mo(CO)_3$(vdpp-*PP′*)(PEt_3)] (2), *mer*-[$W(CO)_3$(1,1-dppp-*PP′*)($PPhEt_2$)] (3), and *cis*-[$W(CO)_2$(dppm-*PP′*)(vdpp-*PP′*)] (4); dppm = bis(diphenylphosphino)methane, vdpp = vinylidenebis(diphenylphosphine), and 1,1-dppp = 1,1-bis(diphenylphosphino)propane.



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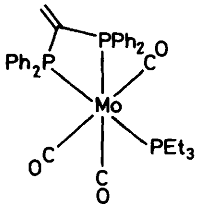

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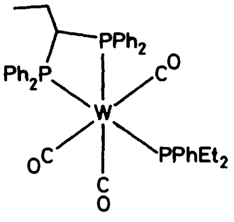

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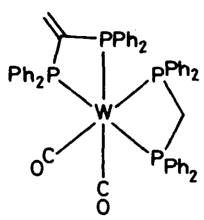

(4)

Results and Discussion

The complex *mer*-[$W(CO)_3$(dppm-*PP′*)($PPhEt_2$)] (1) was prepared by heating [$W(CO)_4$(dppm-*PP′*)] with $PPhEt_2$ in n-decane; compounds (2) and (4) were prepared similarly. Compound (3) was prepared by the conjugate addition of methyl-lithium to the co-ordinated vdpp of [$W(CO)_3$(vdpp-*PP′*)($PPhEt_2$)] followed by addition of a proton. This reaction is analogous to the addition of methyl-lithium to [$W(CO)_4$(vdpp-*PP′*)], which we have reported.[18] Details of the preparations with characterising data are in the Experimental section.

The magnitudes and relative signs of the couplings ^2J(PP) in compounds (1)—(4) are summarised in Tables 1 and 2 together with the ^{31}P chemical shifts.

Assignments of ^{31}P Resonances.—The stereochemical assignments of compounds (1)—(3) as the *mer* isomers and compound (4) as the *cis* isomer follow from the inequivalence of all the ^{31}P resonances. The assignments of the monodentate phosphine ^{31}P resonances in the tricarbonyl species (1)—(3) are readily inferred by comparison with other similar complexes[19] that differ in that they have different substituents on this phosphorus atom, *e.g.* diethylphenylphosphine *versus* triethylphosphine, the ^{31}P chemical shifts of vdpp, dppm, or 1,1-dppp being essentially unaffected. These assignments are con-

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† In this paper the shortened forms ^nJ(PP), ^nJ(PH), ^nJ(WP), *etc.* are employed to signify $^nJ(^{31}P-^{31}P)$, $^nJ(^{31}P-^1H)$, $^nJ(^{183}W-^{31}P)$, *etc.*

Table 1. ^{31}P N.m.r. data for compounds (**1**)—(**3**)

Compound	$\delta(P)^a$/p.p.m.			$^2J(PP)^b$/Hz		
	P_A	P_B	P_C	P_AP_B	P_AP_C	P_BP_C
(**1**)	13.1	−24.1	−11.9	−24.4	+62.5	+29.3
(**2**)	32.1	26.5	45.7	−24.1	+69.1	+79.1
(**3**)	13.0	11.4	0.2	−23.0	+62.3	+37.5

[a] To high frequency (low field) of external H_3PO_4; P_A = PR_3, P_B,P_C = vdpp, dppm, or 1,1-dppp (P_C *trans* to P_A). [b] Signs assigned on the basis of $^2J(P_AP_C)$(*trans*) being positive.

Table 2. ^{31}P N.m.r. data for compound (**4**)*

$\delta(P_A)$	$\delta(P_B)$	$\delta(P_C)$	$\delta(P_D)$
22.0	7.2	−14.7	−28.3

$J(P_AP_B)$	$J(P_AP_C)$	$J(P_AP_D)$
+86.9	+86.9	−19.8
$J(P_BP_C)$	$J(P_BP_D)$	$J(P_CP_D)$
−20.6	−19.0	+25.3

* P_A,P_B = vdpp, P_C,P_D = dppm, P_A *trans* to P_C. Chemical shifts in p.p.m. to high frequency (low field) of external H_3PO_4. Coupling constants in Hz; signs assigned on the basis of $J(P_AP_C)$(*trans*) being positive.

firmed by ^1H-{^{31}P(selective)} experiments in which the CH or CH_2 proton resonances of the vdpp, dppm, or 1,1-dppp ligands are directly related to their intraligand ^{31}P resonances. This selective {^{31}P} decoupling of protons also distinguishes between the vdpp and dppm phosphorus nuclei in compound (**4**), *i.e.* P_A and P_B are in the vdpp and P_C and P_D in the dppm. The ^{31}P resonances of the triorganyl monodentate phosphine ligands in the tricarbonyl compounds (**1**)—(**3**) show typical interphosphorus couplings of *ca.* 24 and 65 Hz. It is reasonable to assign these to $^2J(PP)$(*cis*) and $^2J(PP)$(*trans*) respectively, and to assume that the latter has positive sign. Similar reasoning leads to the positional assignments of all the ^{31}P resonances for the dicarbonyl compound (**4**).

Determination of the Relative Signs of Coupling Constants.—It is well known that, if the mixing pulse in the Jeener sequence[7] [P_1–t_1–P_2–acquire f.i.d. (free induction decay)] is shortened such as to provide a 45° flip angle (*i.e.* $P_2 = \pi/4$), spin–spin coupled transitions which are indirectly connected are suppressed. The diagonal in a two-dimensional COSY plot is thereby simplified and only the directly connected transitions appear in the cross-peaks.[10] In a system of three or more coupled spins, the resultant tilt of the cross-peak pairs with respect to the diagonal may be used to determine the relative signs of coupling constants. Thus if the high-frequency components of the multiplets associated with the resonances of two of the coupled spins correlate, the relative signs of the couplings* to a third coupled nuclide will be the same, whereas high-frequency to low-frequency correlations will imply an opposite sign. In this sense the basis of the method is the same as that of the selective decoupling experiments.

Figure 1 shows a high-resolution COSY-45 plot for compound (**2**). Each cross-peak is made up of two groups of four lines which form an exact square. It is the relative position of these two squares which determines the relative signs of the coupling constants. Assuming $^2J(P_AP_C)$(*trans*) to be positive, it can be seen that $^2J(P_BP_C)$(*cis*) is also positive, whilst $^2J(P_AP_B)$ (*cis*) is negative. The COSY-45 spectra for compounds (**1**) and (**3**) lead to similar conclusions.

The results of the COSY-45 experiment on compound (**4**) (Figure 2) are more complex. The ^{31}P n.m.r. spectrum of compound (**4**) represents a four-spin system in which each of the spins is coupled with all the other three spins. It follows that each cross-peak contains sign information about *two pairs* of spins, *e.g.* the $^2J(P_AP_B)$ correlation contains information about the relative signs of $^2J(P_AP_C)$ and $^2J(P_BP_C)$ and also about the relative signs of $^2J(P_AP_D)$ and $^2J(P_BP_D)$. These cross-peaks can, in an equiscalar contour plot, be visualised as defining four exact squares, pairs of which will represent pairs of couplings (see Figure 3). Knowledge of the magnitudes of the coupling constants is required to decide which pairs of squares represent which pairs of coupling constants, although in the general case detailed analysis of all the cross-peaks should not be necessary. The relative signs determined are summarised in Table 2.

An examination of Tables 1 and 2 reveals that in all cases $^2J(PP)$(*trans*) is of the same sign (presumably positive) as $^2J(PP)$(*cis*) when the latter coupling occurs between phosphorus atoms that are linked by both P–M–P and P–C–P paths, but is of opposite sign to a $^2J(PP)$(*cis*) coupling between phosphorus atoms linked by a P–M–P path only. The couplings of *ca.* −20 Hz for the non-carbon-bridged *cis* linkages $^2J(PMP)$ compared to the positive values for the carbon-bridged phosphorus atoms imply dominant positive contributions to the coupling constant *via* the P–C–P pathway. Assuming an approximately additive relationship,[20,21] this indicates contributions of *ca.* + 50 Hz *via* the alkylene bridges and *ca.* + 100 Hz *via* the vinylidene ones, although differences in bond-angle constraints at the metal centre arising from the different bite size of vdpp *versus* the other bidentate ligands might affect the P–M–P contributions.

For complexes of similar types to those studied in this work where ^2J(PCP, PMP)(*cis*) is positive and $^2J(PMP)$(*cis*) is negative, the two-dimensional [^{31}P–^{31}P]-COSY-45 technique could be used to assign ^{31}P resonances to individual P atoms. This will be important when ^1H-{^{31}P(selective)} experiments are not practicable or when substituent effects are not sufficiently clear cut. It is of interest that for the vdpp complex (**2**) $|^2J$(PCP, PMP)(*cis*)$|$ is larger than $|^2J(PMP)$(*trans*)$|$ so that the general rule $|^2J(PP)$(*trans*)$| > |^2J(PP)$(*cis*)$|$[1] does not hold in this case.

Experimental

N.M.R. Spectroscopy.—The one- and two-dimensional ^{31}P n.m.r. experiments were carried out on a Bruker AM-400 instrument operating at 162 MHz. The samples were examined at 298 K as $CDCl_3$ solutions contained in cylindrical tubes (outside diameter 5 mm) in a 10-mm tunable multinuclear (high-frequency range) probe head. Chemical shifts are reported in

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* This statement applies to the relative signs of the reduced coupling constant *K*, where $K(AB) = 4\pi^2J(AB)/h\gamma_A\gamma_B$: in a homonuclear system *K* will have the same sign as *J*.

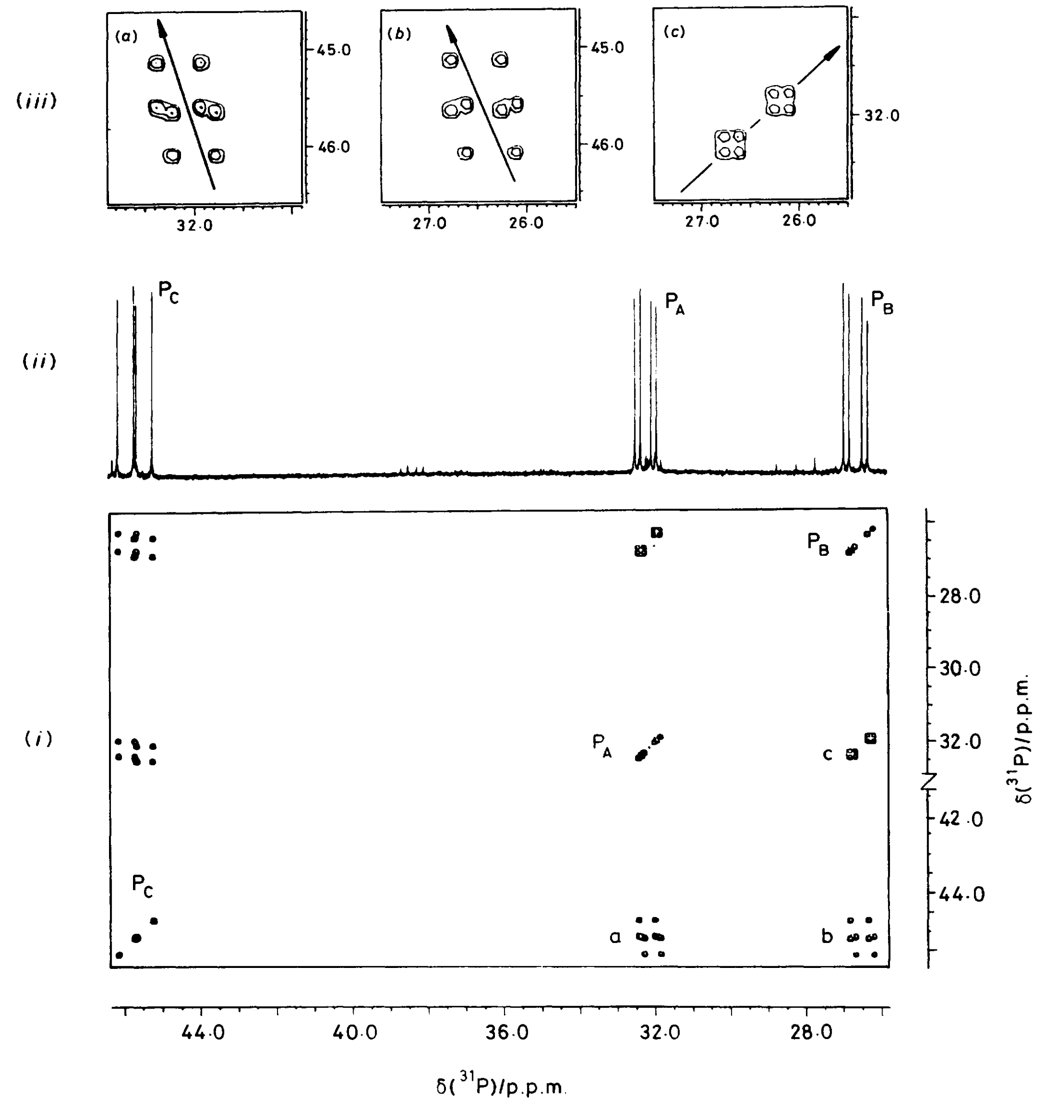

Figure 1. (*i*) A (symmetrised) absolute value contour plot of the high-resolution two-dimensional [^{31}P–^{31}P]-COSY-45 n.m.r. spectrum of compound (**2**). (*ii*) The corresponding one-dimensional ^{31}P–{^1H (broad-band noise)} spectrum. (*iii*) Expansions of the off-diagonal peaks of the two-dimensional spectrum: (*a*) $J(P_AP_C)$, (*b*) $J(P_BP_C)$, and (*c*) $J(P_AP_B)$. The tilts (indicated by the arrows) of the correlations with respect to the vertical indicate the relative signs of the couplings [arrows tilting to the right (*i.e.* making an angle smaller than 45° with the diagonal) indicate the same signs, those tilting to the left, opposite signs]

p.p.m. to high frequency (low field) of Ξ 48.480 730 MHz, *i.e.* nominally 85% H_3PO_4.

The high-resolution [^{31}P–^{31}P]-COSY-45 experiments were made with the sequence[10] (relaxation delay)—(90° pulse)—(evolution period)—(45° pulse)—(acquire f.i.d.), with negative (N) peak type selection and appropriate phase cycling to allow for quadrature detection in both dimensions. In the probe configuration used for these experiments the ^{31}P 90° pulse width was 17.3 μs. Uninterrupted {^1H (broad-band noise)} decoupling was applied throughout. Typically, a *ca.* 0.05 mol dm^{-3} sample required *ca.* 12 h of acquisition time. Data set sizes were generally chosen such as to achieve adequate digital resolution of the individual multiplet components of the one-dimensional spectra, although data storage and spectrometer time available precluded this in some cases. The time-domain matrices were weighted by a sine-bell-squared apodization function in both dimensions prior to Fourier transformation. Further experimental details are collated in Table 3.

Preparation of the Complexes.—All reactions were carried out in an atmosphere of dry dinitrogen in degassed solvents. Tetrahydrofuran (thf) was dried over sodium wire. Infrared spectra were recorded using dichloromethane solutions on a Perkin-Elmer 257 grating spectrometer.

mer-[W(CO)$_3$(dppm-*PP*′)(PPhEt$_2$)] (**1**). A solution of [W(CO)$_4$(dppm-*PP*′)] (0.460 g, 0.676 mmol) and PPhEt$_2$ (0.169 g, 1.014 mmol) in n-decane (20 cm^3) was heated under reflux for 8 h. The mixture was then allowed to cool to room temperature after which the product separated as a yellow solid; yield 0.34 g (61%) (Found: C, 55.8; H, 4.6. $C_{38}H_{37}O_3P_3W$ requires C, 55.8; H, 4.6%). Infrared data: ν(C≡O) 1 964s, 1 950s, and 1 840 (sh) cm^{-1}. N.m.r. data (in CDCl$_3$) for PCH_2P: δ 5.0 p.p.m. [^2J(PH) = 9.0, ^4J(PH) = 1.4 Hz].

mer-[Mo(CO)$_3$(vdpp-*PP*′)(PEt$_3$)] (**2**). A solution of [Mo(CO)$_4$(vdpp-*PP*′)] (0.300 g, 0.496 mmol) and PEt$_3$ (0.088 g, 0.745 mmol) in n-decane (20 cm^3) was heated under reflux for 24 h. The mixture was then allowed to cool to room

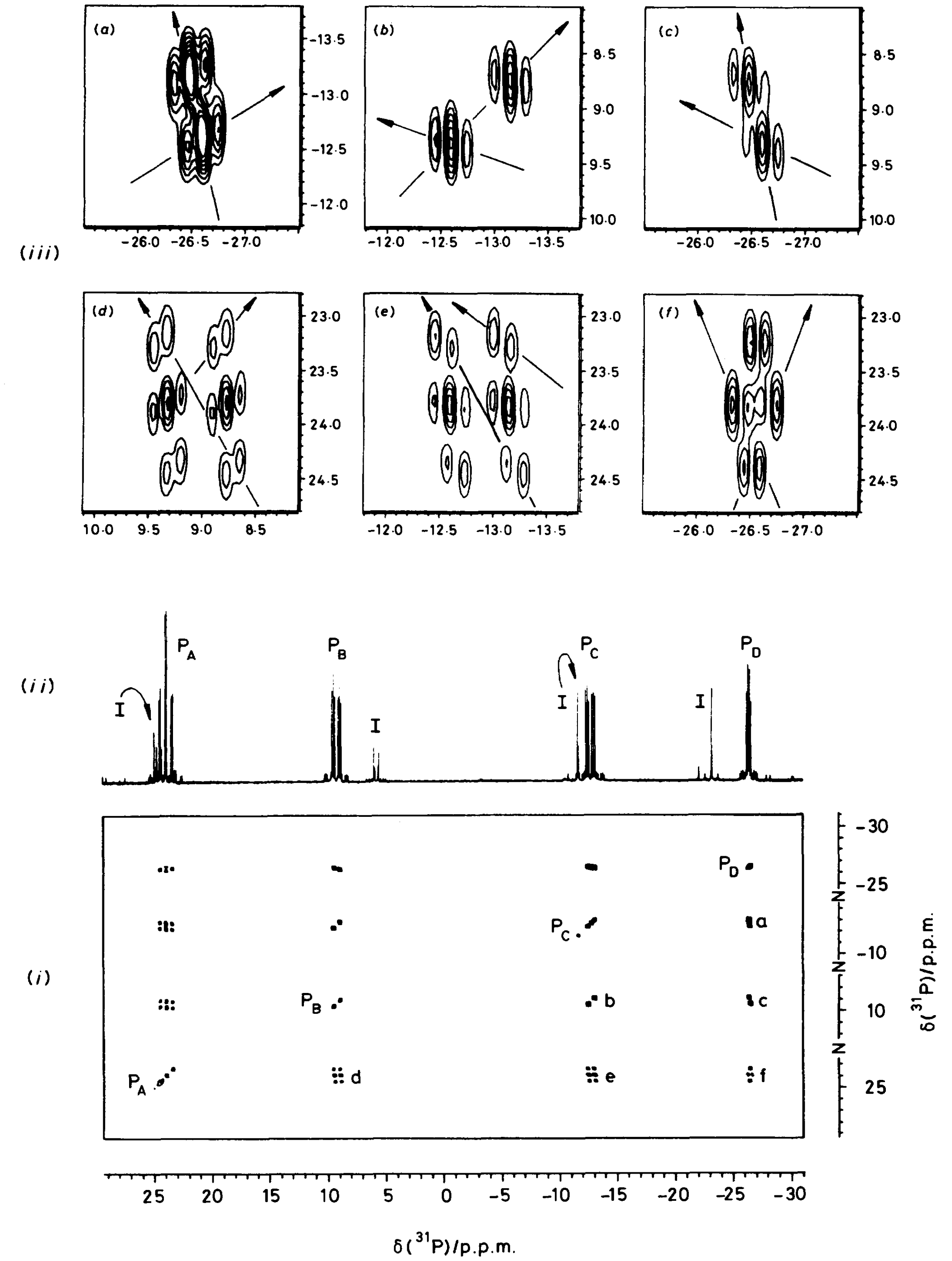

Figure 2. (*i*) An (unsymmetrised) absolute value contour plot of the high-resolution two-dimensional [^{31}P–^{31}P]-COSY-45 n.m.r. spectrum of compound (4). (*ii*) The corresponding one-dimensional ^{31}P–{^{1}H (broad-band noise)} spectrum (I denotes impurity). (*iii*) Expansions of the off-diagonal peaks of the two-dimensional spectrum: (*a*) $J(P_CP_D)$, (*b*) $J(P_BP_C)$, (*c*) $J(P_BP_D)$, (*d*) $J(P_AP_B)$, (*e*) $J(P_AP_C)$, and (*f*) $J(P_AP_D)$. Arrows indicate the relative signs of pairs of couplings as in Figure 1. See also Figure 3

temperature, after which the product separated as a red solid; yield 0.23 g (65%) (Found: C, 60.3; H, 5.1. $C_{35}H_{37}MoO_3P_3$ requires C, 60.5; H, 5.4%). Infrared data: ν(C≡O) 1 970m, 1 868s, and 1 844 (sh) cm^{-1}. N.m.r. data (in $CDCl_3$) for $PC(=CH_2)P$: ^{1}H-{^{31}P}, two singlets, δ 5.39 and 5.30 p.p.m.; ^{1}H, two doublets of doublets [$^{3}J(PH)$ 27.3, 19.1 and 28.6, 19.3 Hz respectively].

mer-[$W(CO)_3\{(Ph_2P)_2CHCH_2CH_3\}(PPhEt_2)$] (3). A solution of [$W(CO)_3$(vdpp-*PP'*)($PPhEt_2$)] (0.103 g, 0.124 mmol) in thf (5 cm^3) was treated with *N,N,N',N'*-tetramethylethylenediamine (28 μl, 0.185 mmol) followed by a solution of methyllithium in diethyl ether (0.132 cm^3, 0.185 mmol). The mixture was stirred at room temperature for 2 h then hydrolysed, and the solid product isolated and recrystallised from dichloromethane–methanol. Yield 0.079 g (76%) (Found: C, 57.0; H, 5.0. $C_{40}H_{41}O_3P_3W$ requires C, 56.8; H, 4.9%). Infrared data: ν(C≡O) 1 952m, 1 848s, and 1 832 (sh) cm^{-1}. N.m.r. data (in

Table 3. Experimental details for the two-dimensional [^{31}P–^{31}P]-COSY-45 experiments

	Compound			
	(1)	**(2)**	**(3)**	**(4)**
Data size (t_2, t_1/words)	1 024, 256	1 024, 256	512, 128	1 024, 256
Transform size (F_2, F_1/words)	2 048, 1 024	1 024, 512	1 024, 512	4 096, 1 024
t_2 sweep width (= $2t_1$ sweepwidth/Hz	7 812	4 032	2 890	4 804
Digital resolution (F_2, F_1/Hz per point)	(15.3/2), (15.3/2)	(7.9), (7.9)	(11.3/2), (11.3/2)	(9.6/4), (9.6/2)
No. of transients per increment	160	144	320	192
Recycling time/s	1.3	1.0	1.1	1.1

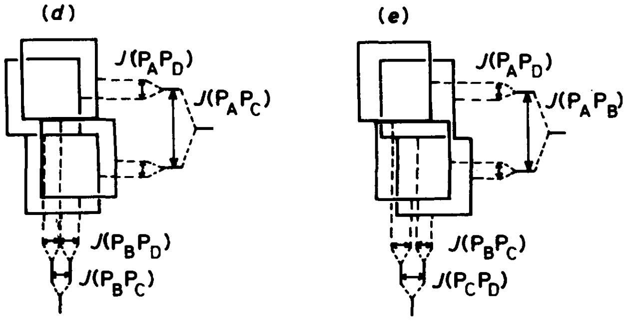

Figure 3. Diagrammatical illustration of the cross-peaks of Figure 2 arising from (*d*) $J(P_AP_B)$ and (*e*) $J(P_AP_C)$. In (*d*) the sides of each square represent $J(P_AP_B)$; $J(P_AP_D)$ and $J(P_BP_D)$ are of the same sign but $J(P_AP_C)$ and $J(P_BP_C)$ are of opposite signs. In (*e*) the sides of each square represent $J(P_AP_C)$; $J(P_AP_D)$ and $J(P_CP_D)$ are of mutually opposite signs and so are $J(P_AP_B)$ and $J(P_BP_C)$

CDCl$_3$) for PC*H*P: ^{1}H-{^{31}P}, a doublet of doublets, δ 4.68 p.p.m. [^3J(HH) 7.4 and 6.1 Hz]; ^{1}H, apparent triplet of doublet of doublets [^2J(PH)(mean) = 11.2 Hz].

cis-[W(CO)$_2$(dppm-*PP'*)(vdpp-*PP'*)] (**4**). A solution of [W(CO)$_4$(dppm-*PP'*)] (1 g, 1.470 mmol) and vdpp (0.583 g, 1.470 mmol) in n-decane (25 cm^3) was heated under reflux for 90 h. The mixture was then allowed to cool to room temperature after which the product separated as a red solid. Yield 1.35 g (90%) (Found: C, 62.4; H, 4.3. $C_{53}H_{44}O_2P_4W$ requires C, 62.4; H, 4.3%). Infrared data: ν(C≡O) 1 864s and 1 796s cm^{-1}. N.m.r. data (in CDCl$_3$): for PC*H*$_2$P, ^{1}H-{^{31}P}, an AB quartet, δ 5.15 and 5.13 ppm [^2J(HH) = 15.4]; ^{1}H, complex multiplet; for PC(=C*H*$_2$)P, ^{1}H-{^{31}P}, two singlets, δ 5.35 and 5.25 p.p.m.; ^{1}H, two doublets of doublets [^3J(PH) 29.4, 20.7 and 28.4, 20.3 Hz, respectively].

mer-[W(CO)$_3$(vdpp-*PP'*)(PPhEt$_2$)]. A solution of [W(CO)$_4$-(vdpp-*PP'*)] (0.604 g, 0.872 mmol) and PPhEt$_2$ (0.217 g, 1.305 mmol) in n-decane (20 cm^3) was heated under reflux for 24 h. The mixture was then allowed to cool to room temperature after which the product separated as a red solid; yield 0.64 g (88.3%) (Found: C, 56.4; H, 4.5. $C_{39}H_{37}O_3P_3W$ requires C, 56.4, H, 4.5%). Infrared data: ν(C≡O) 1 966m, 1 864s, and 1 840 (sh) cm^{-1}. N.m.r. data (in CDCl$_3$) for PC(=C*H*$_2$)P: ^{1}H-{^{31}P}, two singlets, δ 5.24 and 5.18; ^{1}H, two doublets of doublets [^3J(PH) 20.6, 20.3, and 28.3, 19.8 Hz, respectively]; ^{31}P-{^{1}H}, δ(P$_A$) (PPhEt$_2$) 12.2, δ(P$_B$) (vdpp, *cis* to P$_A$) 6.1, δ(P$_C$) (vdpp, *trans* to P$_A$) 21.0 p.p.m. [$^2J(P_AP_B) = 20$, $^2J(P_AP_C) = 65$, $^2J(P_BP_C) = 89$, $^1J(WP_A) = 284$, $^1J(WP_B) = 284$, and $^1J(WP_C) = 259$ Hz].

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