Nuclear Magnetic Resonance Studies of Chelate-ring Effects in Tungsten(0) Carbonyl Complexes of Poly(tertiary phosphines)

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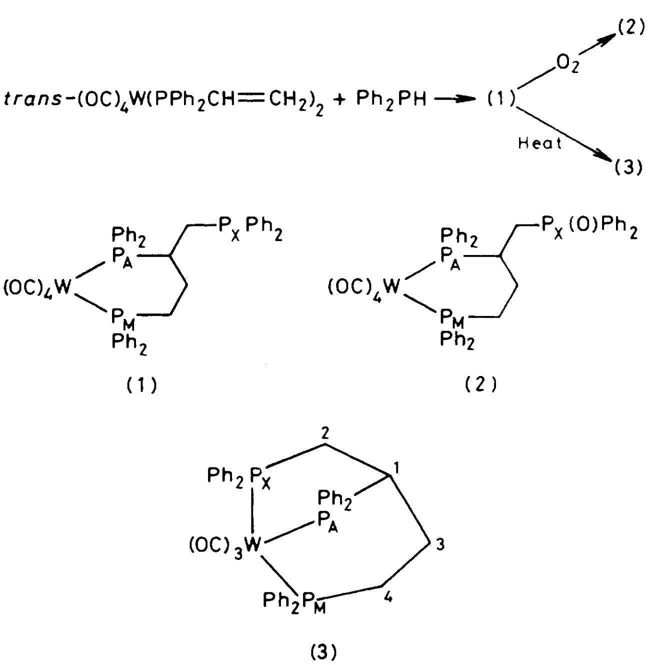
Magnetic multiple-resonance experiments have been used to determine the absolute signs of the various ^{31}P–^{31}P spin-coupling constants in tungsten carbonyl complexes of the ligand $Ph_2PCH(CH_2PPh_2)CH_2CH_2PPh_2$. Apparently anomalous values of these coupling constants may thereby be accounted for in simple terms and shown to be consistent with earlier ideas on the effects of chelate-ring formation on n.m.r. parameters.

Transition-metal complexes of polydentate phosphines have conventionally been prepared by reaction of the polyphosphorus ligand with an appropriate transition-metal starting compound. An alternative approach is to synthesize the ligand in complexed form using reactions of simpler phosphines which are already co-ordinated to the metal. An example of this second approach is shown in the Scheme.

In the unusual first reaction, free-radical catalyzed addition of the secondary phosphine is accompanied by *trans*→*cis* isomerization of the tungsten carbonyl derivative followed by a cyclization reaction.[1] The structure of compound (1) has been confirmed by *X*-ray crystallography.[2] The non-co-ordinated phosphorus atom (X) may readily be oxidized to give compound (2), or made to displace a further CO molecule from tungsten by refluxing in a high-boiling solvent [diglyme (2,5,8-trioxanonane), decalin (decahydronaphthalene)] under dinitrogen, to give the bicyclic complex (3). The structure of (3) was confirmed by its ^{31}P n.m.r. spectrum [three non-equivalent phosphorus atoms, all bonded to tungsten as evidenced by characteristic ^{183}W satellites with $^{1}J(^{183}W–^{31}P) \approx 200$ Hz] and by its i.r. spectrum in the carbonyl-stretching region, which is typical of that for a *fac* trisubstituted $M(CO)_3$ complex.

Much work has been done in recent years on ^{31}P–^{31}P coupling constants in transition-metal complexes, and this n.m.r. parameter has proved to be of great value, particularly in dealing with stereochemical problems.[3] We had previously determined the ^{31}P–^{31}P coupling constants in a series of molecules of the type *cis*-[M(CO)$_4$L] where L is a chelating ditertiary phosphine and M is one of the Group 6 metals.[4] Whilst the magnitudes of these couplings are erratic a knowledge of their signs enabled a regular pattern of behaviour to be uncovered, and the length of the ligand's carbon backbone was found to play an especially important role in determining this coupling constant. It was therefore of particular interest to examine the n.m.r. properties of compound (3) in some detail since this one molecule contains phosphorus atoms which are simultaneously part of five- and six-membered rings (A), six- and seven-membered rings (M), and five- and seven-membered rings (X). Thus the molecule provides a useful test case for the generalizations put forward in the earlier work.[4]



Scheme.

Results and Discussion

In the present instance two types of experiment were required to complete the sign determinations. (*a*) ^{31}P-{^{31}P,^{1}H$_{noise}$}: Since both compounds (1) and (3) possess three non-zero values of $J(^{31}P–^{31}P)$ it was possible to establish the *relative* signs of these by means of homonuclear phosphorus irradiation (tickling) experiments. (*b*) ^{31}P-{^{183}W, ^{1}H$_{noise}$}: The above relative sign determinations were then put onto an *absolute* basis by relating the sign of one of the ^{31}P–^{31}P coupling constants to that of $^{1}J(^{31}P–^{183}W)$ which is known to be positive in this type of molecule.[5] This experiment involved irradiation at the ^{183}W frequency and observation of the ^{183}W satellites in the ^{31}P spectrum, and therefore also provided $\delta(^{183}W)$ for the complexes.

Clearly the foregoing experiments require a correct assignment of the ^{31}P spectra of compounds (1)—(3), and with one exception, this proved to be straightforward. The resonances at −20.4 p.p.m. of (1) and at +31.2 p.p.m. of (2) may be assigned to the unco-ordinated phosphine and to the phosphine oxide respectively, by virtue both of their characteristic chemical shifts and the absence of ^{183}W satellites [$^{4}J(^{31}P–^{183}W) \approx 0$]. For (2) the resonance at +18.2 p.p.m. has a 30 Hz coupling to the phosphine oxide, typical of a three-bond ^{31}P–^{31}P coupling between two P^{V} atoms,[6] whereas the resonance at 2.3 p.p.m. has a zero coupling to P$_X$. The resonance at 18.2 p.p.m. is therefore assigned to P$_A$ and that at 2.3 p.p.m. to P$_M$. The ^{31}P chemical shifts of the phosphorus atoms in the ring in compounds (1) and (2) are so similar that

Table. ^{31}P and ^{183}W n.m.r. parameters

Compound [a]	$\delta(^{31}P)$ [b]			$\delta(^{183}W)$ [c]	$^1J(^{31}P-^{183}W)$ [d]			$J(^{31}P-^{31}P)$ [d]		
	A	M	X		A	M	X	AM	AX	MX
(1)	17.7	4.3	−20.4	347	221.1	226.5	*ca.* 0	−21.4	+9.3	+3.5
(2)	18.2	2.3	31.2	344	223.5	225.6	*ca.* 0	−21.8	(+)30.2 [e]	0
(3) [f]	41.0	−9.4	44.8	381	215.7	210.9	212.4	−18.3	+17.6	−17.2
[W(CO)$_4$(dppe)] [g]	40.1			192	229.0			+5.5		
[W(CO)$_4$(dppp)] [g]	−0.1			326	222.2			−21.5		
[W(CO)$_4$(dppb)] [g]	11.3			367	230.7			−15.0		

[a] dppe = $Ph_2P(CH_2)_2PPh_2$; dppp = $Ph_2P(CH_2)_3PPh_2$; dppb = $Ph_2P(CH_2)_4PPh_2$. [b] In p.p.m. (±0.1 p.p.m.) to high frequency of H_3PO_4. [c] In p.p.m. (±1 p.p.m.) to high frequency of [W(CO)$_6$] for which $\Xi(^{183}W)$ = 4.151 878 MHz. [d] In Hz(±0.2 Hz). [e] Since both J(MX) and $J(X-^{183}W)$ = 0 Hz for (2) the sign of J(AX) was not determined experimentally; as a three-bond coupling between two P^V atoms it is however very likely to be positive. [f] The alternative assignment δ(X) = 41.0 p.p.m., δ(A) = 44.8 p.p.m. may be the correct one (see text). [g] Data from refs. 4 and 10.

the additional assignments shown in the Table may also be made in the case of (1). A noteworthy feature here is the existence of the long-range coupling in (1) [J(MX) = 3.5 Hz] over five sigma bonds. These assignments are in agreement with those made previously by one of the present authors.[1]

It is now well established that when phosphorus is coordinated to a metal as part of a five-membered chelate ring there is an unusually large high-frequency change in the phosphorus chemical shift.[3,7] The pair of resonances at 41.0 and 44.8 p.p.m. in the spectrum of compound (3) may therefore be assigned to phosphorus atoms A and X {compare the value for [W(CO)$_4$(dppe)] given in the Table} since both these atoms are part of a five-membered ring. It is not possible, however, to say which resonance should be assigned to A and which to X. Although it should be borne in mind that the assignment given in the Table is only one of two alternatives, the reader will find below that this ambiguity does not adversely affect our argument. The third phosphorus atom (M) experiences an appreciable (14 p.p.m.) shift to lower frequency when compound (1) is converted into (3) indicating that its environment is somewhat perturbed by formation of the second ring. Remarkably, all three $^{31}P-^{31}P$ coupling constants of (3) are very nearly equal in magnitude so that, except under conditions of very high resolution, the AMX spectrum appears to consist of three triplets. However, the situation is dramatically changed when their signs are taken into consideration.

The two types of multiple-resonance experiment we have employed in order to establish these signs are illustrated in Figures 1 and 2. Figure 1(*a*) shows the unperturbed A and X resonances of (3) whilst 1(*b*) and (*c*) show the effect on A and X of homonuclear irradiation at the highest and lowest frequencies respectively of the M triplet. The coupling constants J(AM) and J(MX) are found to have the same sign, this being opposite to that of J(AX). The determination of absolute signs by a $^{31}P-\{^{183}W, {}^1H_{noise}\}$ experiment is shown in Figure 2, in this case for compound (1). For simplicity, only the ^{183}W satellites of A and M are shown. The pattern of perturbations shows that J(AM) is of opposite sign to $J(A-^{183}W)$[or $^1J(M-^{183}W)$] and is therefore negative. A further homonuclear $^{31}P-\{^{31}P, {}^1H_{noise}\}$ experiment then completed the sign determination by showing J(AM) to be of opposite sign to J(AX) and J(MX). The results are summarized in the last three columns of the Table.

The finding that one of the $^{31}P-^{31}P$ coupling constants is positive in compound (3), whilst the other two are negative, provides considerable support for the suggestion of Grim *et al.*[8] that each of these couplings may be thought of as the algebraic sum of through-metal and backbone contributions. The one positive coupling constant is between the two phosphorus atoms (A and X) which are linked by the shortest backbone path (two carbon atoms). It is important to note that the uncertainty over the assignments mentioned earlier does not in any way affect this conclusion since the assignment of M is unambiguous. In *cis* disubstituted complexes of unidentate phosphines where there is no question of a backbone route it has been established that $^2J(^{31}P-^{31}P)$ is negative,[9] but it appears that in four- or five-membered rings the additional presence of a positive backbone contribution can lead to a sign change, *e.g.* as found in the case of [W(CO)$_4$(dppe)].[4]

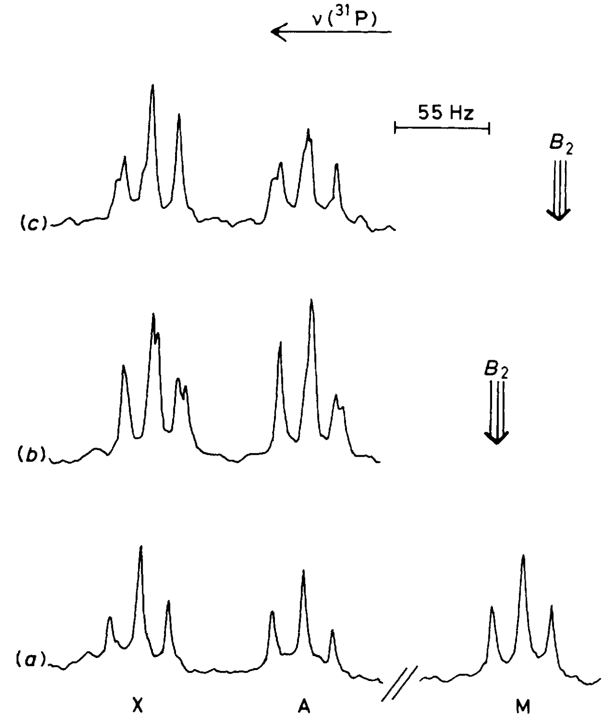


Figure 1. $^{31}P-\{^{31}P, {}^1H_{noise}\}$ n.m.r. spectra of compound (3), ^{31}P irradiation field strength, $\gamma B_2/2\pi \approx$ 4 Hz: (*a*) ν(^{31}P) off resonance; (*b*) ν(^{31}P) set at line 3 of the M multiplet; (*c*) ν(^{31}P) set at line 1 of the M multiplet

The crystal structure of compound (1) showed that the six-membered ring adopted the chair conformation with the CH_2PPh_2 substituent occupying an equatorial position.[2] In order for a third CO to be displaced to form (3) the substituent must either move to an axial position prior to reaction (in which case the six-membered ring can retain the chair

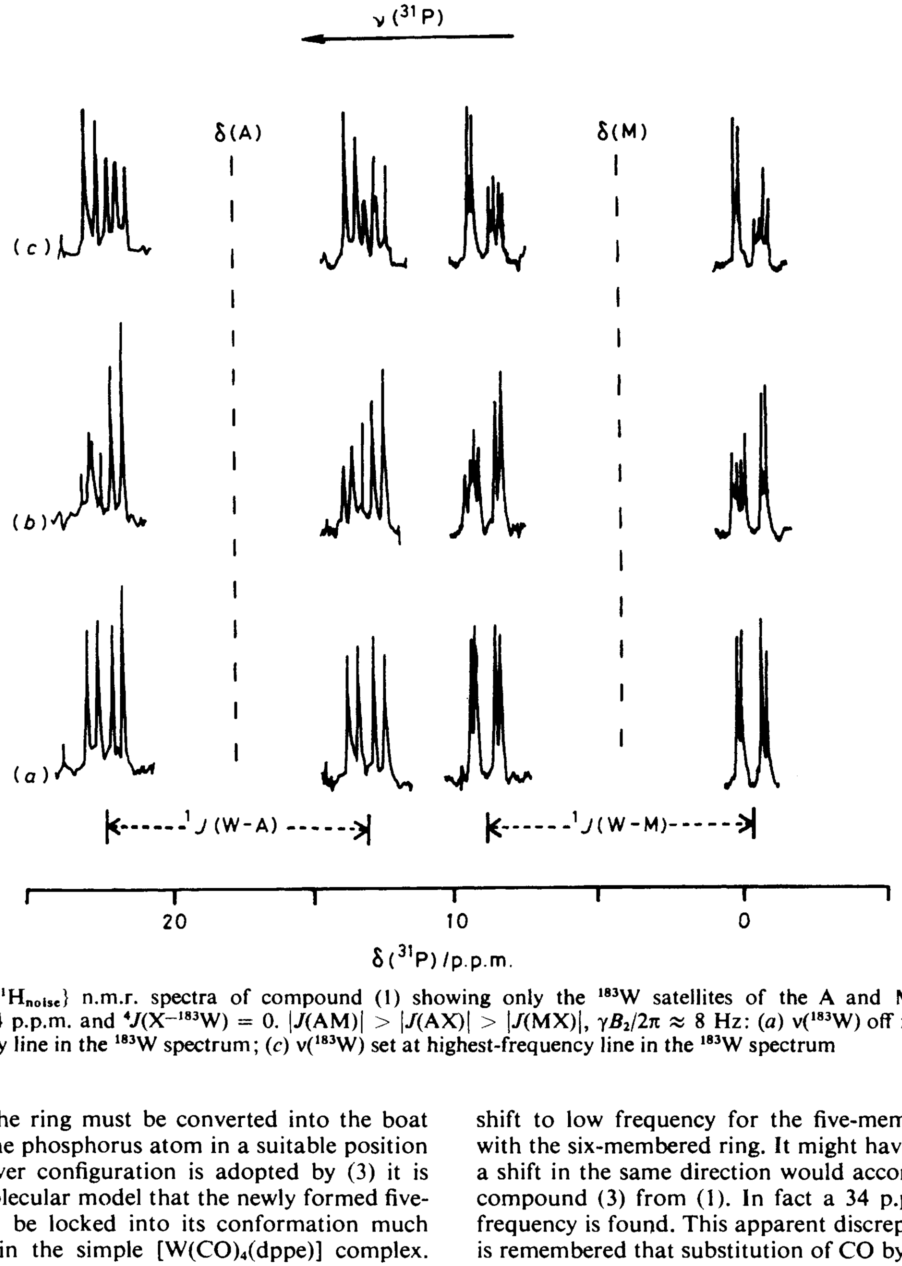


Figure 2. ^{31}P-{^{183}W, $^{1}H_{noise}$} n.m.r. spectra of compound (1) showing only the ^{183}W satellites of the A and M resonances. The X resonance is at -20.4 p.p.m. and $^{4}J(X-^{183}W) = 0$. $|J(AM)| > |J(AX)| > |J(MX)|$, $\gamma B_2/2\pi \approx 8$ Hz: (*a*) $\nu(^{183}W)$ off resonance; (*b*) $\nu(^{183}W)$ set at lowest-frequency line in the ^{183}W spectrum; (*c*) $\nu(^{183}W)$ set at highest-frequency line in the ^{183}W spectrum

configuration), or the ring must be converted into the boat form thus placing the phosphorus atom in a suitable position for attack. Whichever configuration is adopted by (3) it is apparent from a molecular model that the newly formed five-membered ring will be locked into its conformation much more rigidly than in the simple [W(CO)$_4$(dppe)] complex. When comparing J(AX) in compound (3) with J(PP) in [W(CO)$_4$(dppe)] it seems probable that reduced conformational mobility in (3) leads to an increased positive backbone contribution to J(AX) whilst the through-metal component remains about the same in the two compounds. The two negative coupling constants J(AM) and J(MX) are very nearly equal and have values lying halfway between those for a six-membered ring, [W(CO)$_4$(dppp)], and a seven-membered ring, [W(CO)$_4$(dppb)]. It has usually been assumed[8] that if the backbone linkage comprises four or more bonds then it makes a zero contribution to the coupling constant. The difference in J(PP) found for [W(CO)$_4$(dppp)] and [W(CO)$_4$(dppb)] together with the observation of a value of +3.5 Hz for ^{5}J(PP) in the present work suggest that this view may need some modification, although it is undoubtedly true that in these cases the two-bond contribution *via* the metal is the dominant one.

^{183}W *Chemical Shifts.*—The values of $\delta(^{183}W)$ given in the Table for [W(CO)$_4$L] (L = dppp or dppe) show a 134 p.p.m. shift to low frequency for the five-membered as compared with the six-membered ring. It might have been expected that a shift in the same direction would accompany formation of compound (3) from (1). In fact a 34 p.p.m. change to *high* frequency is found. This apparent discrepancy is resolved if it is remembered that substitution of CO by a phosphorus atom results in a high-frequency shift,[10] *e.g.* there is a 112 p.p.m. change in this direction between *fac*-[W(CO)$_3${P(OMe)$_3$}$_2$] and *cis*-[W(CO)$_4${P(OMe)$_3$}$_2$]. The difference between the chemical shifts of compounds (1) and (3) therefore appears to be the consequence of two factors of similar magnitude acting in opposition to each other.

^{13}C *Chemical Shifts.*—An attempt to resolve the remaining doubt about the assignment of the two high-frequency ^{31}P resonances of compound (3) was made by studying the ^{13}C spectrum of the aliphatic carbons in (3). ^{13}C-{^{31}P, $^{1}H_{noise}$} selective phosphorus-decoupling experiments were used to assist the assignment of the ^{13}C spectrum with the following results: $\delta(^{13}C)$ 37.0 [J(PC) = 23.9 [41.0], 15.1 [44.8]]; 32.2 [J(PC) = 18.1 [44.8], 16.6 [41.0]]; 26.6 [J(PC) = 4.4 [41.0] 4.4 [−9.4]]; 22.9 [J(PC) = 22.5 [−9.4], 4.2 Hz [44.8]].

Each ^{13}C resonance showed coupling to only two phosphorus nuclei. The figures in square brackets above indicate that irradiation at this value of $\delta(^{31}P)$ caused the associated $J(^{13}C-^{31}P)$ to be removed. The ^{13}C multiplet at 37.0 p.p.m.

was clearly shown to arise from C^1 by an off-resonance ^{1}H-decoupling experiment. Unfortunately it was still not possible to assign the two ^{31}P resonances at 41.0 and 44.8 p.p.m. without making some unwarranted assumptions regarding the relative magnitudes of $^1J(^{13}C-^{31}P)$ and $^2J(^{13}C-^{31}P)$ in the ring system, but the experiments did support the following ^{13}C spectral assignment: $\delta(^{13}C)$ 37.0 (C^1); 32.2 (C^2); 26.6 (C^3); 22.9 (C^4).

Experimental

Proton-decoupled ^{31}P spectra were recorded at 24.2 MHz (JEOL FX60) in the pulsed Fourier-transform mode using saturated CH_2Cl_2 [compounds (1) and (2)] or $CDCl_3$ (3) solutions contained in 10 mm outside diameter spinning tubes. A GenRad (model 1061) frequency synthesizer provided the second ^{31}P irradiation frequency for the homonuclear $^{31}P-\{^{31}P, ^1H_{noise}\}$ experiments. The time-sharing system of the spectrometer, normally used for $^1H-\{^1H\}$ decoupling experiments, was adapted to provide a means of gating the second ^{31}P frequency thereby preventing excessive receiver interference. The gated radio frequency (r.f.) was connected to the normal proton-decoupling coil *via* a tuned amplifier and matching network. The same frequency synthesiser was used to provide the ^{183}W frequency (2.48 MHz) which was applied *via* the amplifier and a matching network to an extra coil wound in the ^{31}P probe. Several hundred transients were required to obtain the ^{183}W satellites of compound (3) at a satisfactory signal-to-noise ratio so the automatic frequency-search procedure previously described [10] was employed to locate the ^{183}W frequencies.

Preparation of fac-[W(CO)$_3${Ph$_2$PCH(CH$_2$PPh$_2$)CH$_2$CH$_2$PPh$_2$}] (3).—A decalin solution of [W(CO)$_4${Ph$_2$PCH(CH$_2$PPh$_2$)CH$_2$CH$_2$PPh$_2$}] (1) (0.50 g, 5.5 mmol) was heated under dinitrogen at 180 °C for 2 h. Removal of solvent *in vacuo*, followed by crystallization of the resulting residue from a dichloromethane–methanol (1 : 4) solution, gave *fac*-[W(CO)$_3${Ph$_2$PCH(CH$_2$PPh$_2$)CH$_2$CH$_2$PPh$_2$}] (3) (0.43 g, 91%) (decomp. ≈ 240 °C); $\nu_{max.}$(CO) (CH$_2$Cl$_2$) at 1 841s and 2 000s cm^{-1}.

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