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FOURIER TRANSFORM HETERONUCLEAR MAGNETIC TRIPLE RESONANCE IN COMPLEX SPIN SYSTEMS—III†

SYMMETRICAL DITERTIARY PHOSPHINE COMPLEXES OF GROUP VI METAL CARBONYLS

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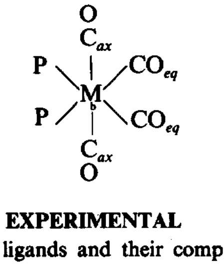
Abstract—Magnetic multiple resonance experiments of the types ^{13}C-$\{^{31}P, ^{1}H\}$, ^{13}C–$\{^{1}H\}$ and ^{31}P–$\{^{183}W, ^{1}H\}$ have been used to determine the magnitudes and signs of P–C and P–P coupling constants in the symmetrical complexes $LM(CO)_4$ ($L = Ph_2P(CH_2)_nPPh_2$, $Ph_2PN(H)PPh_2$, $(Ph_2P)_2C{=}CH_2$, *cis*-$Ph_2PCH{=}CHPPh_2$; M = Cr, Mo, W; n = 1–4). A knowledge of the signs of the couplings shows that they display a systematic pattern of behaviour according to metal atom and ring size and this may have diagnostic value. ^{13}C, ^{31}P and ^{183}W chemical shifts are also reported.

INTRODUCTION

Proton and more recently ^{13}C and ^{31}P NMR spectroscopy has played an important part in the development of the chemistry of phosphine complexes of metal carbonyls. Not only can the technique be used to establish molecular structure and stereochemistry, it can also in principle be used to probe intimate details of electronic distribution and the factors which determine this. For this latter purpose ^{13}C and ^{31}P are probably more valuable than proton NMR, since the shieldings and coupling constants for these two nuclei are more directly affected by the metal atom and are also less subject to external influences such as changes of solvent. However, ordinary proton-decoupled spectra seldom yield all the information necessary for a proper assessment of the relationship between the NMR parameters and electronic structure, and in this paper we describe the results of multiple resonance experiments upon a series of chelating tertiary biphosphine complexes of group VI metal carbonyls which resolve this difficulty. In particular, the magnitudes of the two-bond coupling constants between ^{31}P and the ^{13}C nuclei of the carbonyl groups show a complex pattern of variation[1–4] whose dependence upon the metal and upon the stereochemical relationships can be understood only if the *signs* of the couplings are also known. Additionally, the important homonuclear phosphorus–phosphorus couplings are not normally available directly from simple ^{31}P spectra when the ligands are chemically symmetrical. In order to get the signs of the ^{31}P–^{13}C coupling constants it is necessary to perform ^{31}P–$\{^{13}C\}$ or ^{13}C–$\{^{31}P\}$ selective multiple resonance experiments,[5] the latter being generally the more convenient,[6] but neither type of experiment has been usual in previous work. For the ^{31}P–^{31}P couplings considerable effort[7,8] in the past has gone into making complexes with unsymmetrical ligands such as $R_2P(CH_2)_nPR'_2$ where R and R′ are sufficiently different (e.g. Et and Ph) for there to be a substantial chemical shift difference between the two kinds of phosphorus so as to allow $^{2}J(PP)$ to be read off directly from the essentially first-order spectra. This method is synthetically demanding and does not give the sign of $J(PP)$. The multiple resonance approach used here is easier synthetically and gives the sign of $J(PP)$ in complexes of symmetrical ligands of possibly greater fundamental importance; it is based upon using spin-tickling experiments[9] for the indirect detection of weak transitions in the spectra from species which are chemically but not magnetically symmetric.[5,6] All of the complexes studied are of the type *cis*-$LM(CO)_4$ with M = Cr, Mo, or W, and $L = (Ph_2P)_2CH_2$ (*dppm*), $(Ph_2P)_2C{=}CH_2$ (*gem-pp*), $(Ph_2P)_2NH$ (*dpnp*), $Ph_2P(CH_2)_2PPh_2$ (*dppe*), *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis-vpp*), $Ph_2P(CH_2)_3PPh_2$ (*dppp*), or $Ph_2P(CH_2)_4PPh_2$ (*dppb*). They have octahedral co-ordination at the metal and thus contain two types of CO group—axial and equatorial as in (**I**). With the exception of [**4**] and the three *dpnp* derivatives all have been previously reported.[10–13]



(I)

EXPERIMENTAL

All solutions of ligands and their complexes were prepared and manipulated under an atomsphere of gaseous dry dinitrogen. The ligands were made as described elsewhere[6] and were purified by recrystallization; the complexes[10–13] were made by refluxing together stoichiometric amounts of ligand and the appropriate metal hexacarbonyl in diglyme for 12 hr, followed by removal of the diglyme *in vacuo* and recrystallization from $CHCl_3$/MeOH (1:1). New complexes were: ***gem-pp***$Cr(CO)_4$ [**4**]: Found: C 64.1; H 3.9; $C_{30}H_{22}CrO_4P_2$ requires: C 64.3; H 3.9%. m.p. 197–198°. *dpnp*

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† For Part II see Ref. 6.

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$Cr(CO)_4$ [7]: Found: C 61.1; H 3.8; $C_{28}H_{21}CrO_4P_2$ requires: C 61.2; H 3.8%. m.p. 194°. *dpnp*$Mo(CO)_4$ [8]: Found: C 56.5; H 3.6; $C_{28}H_{21}MoO_4P_2$ requires: C 56.7; H 3.5%. m.p. 216°. *dpnp*$W(CO)_4$ [9]: Found: C 49.1; H 3.1; $C_{28}H_{21}WO_4P_2$ requires: C 49.4; H 3.1%. m.p. 205°. The others had properties identical to those previously reported.

The NMR measurements were performed at 22°C upon concentrated solutions in dichloromethane containing *ca.* 10% C_6D_6 to provide a locking signal for the spectrometer. This was a JEOL FX-60 Fourier transform instrument operating at measuring frequencies of 59.8, 15.0 and 24.2 MHz for ^1H, ^{13}C and ^{31}P respectively. The probes of the spectrometer were modified[5] to permit $^1H-\{^{31}P\}$, $^{13}C-\{^{31}P, ^1H\}$ and $^{31}P-\{^{183}W, ^1H\}$ multiple resonance experiments, the additional radio frequency being provided by a GenRad model 1061 frequency synthesizer which was locked to the master oscillator of the spectrometer. $Cr(acac)_3$ was added to the solutions to facilitate observations of the ^{13}CO signals. Samples were examined in 10 mm o.d. tubes, and prior to Fourier transformation the f.i.d. was weighted so as to maximise the signal-to-noise ratio while retaining sufficient resolution for the purpose in hand.

METHODS AND RESULTS

The proton-decoupled ^{31}P NMR spectra of the complexes (**I**) consist of a single line due to an A_2 spin system from which it is not possible to derive a value of $J(PP)$ when the two phosphorus atoms are *chemically* equivalent, as is the case with all the molecules studied here. However, the presence of ^{13}C ($I = \frac{1}{2}$, natural abundance 1.1%) at a particular site can lower the *magnetic* symmetry so that the relevant spin system becomes $AA'X$ ($A, A' = {}^{31}P$, $X = {}^{13}C$) and more information is available.[14] It is convenient to distinguish three general cases.

(i) *J(PP) is zero or very small.* The main ^{31}P peak (from molecules containing ^{12}C) is flanked by ^{13}C satellites whose positions give the magnitudes of the two $^{31}P-^{13}C$ coupling constants, and the ^{13}C spectrum is a doublet of doublets. Neither spectrum gives the relative signs of the two $^{31}P-^{13}C$ coupling constants.

(ii) *J(PP) is of moderate size.* The magnitude of $J(PP)$ can be obtained from the positions of the ^{13}C satellites in the ^{31}P spectrum, and their intensity pattern normally makes it possible to get the relative signs of the two $^{31}P-^{13}C$ coupling constants. The ^{13}C spectrum is a symmetrical five-line pattern having half its intensity in two lines separated by N, the algebraic sum of the two $^{31}P-^{13}C$ coupling constants, and the remainder in a central ine and two weaker outer lines whose positions depend upon $J(PP)$ and the $^{31}P-^{13}C$ couplings. Analysis of this pattern can also give a good indication of the magnitude of $J(PP)$.

(iii) *J(PP) is large.* The ^{13}C satellites in the ^{31}P spectrum are again in positions which give the values of the various coupling constants, but four of them are too weak to be detected and the other four are close to the central main peak and may be obscured by its wings. The ^{13}C spectrum is a triplet with almost a 1:2:1 intensity distribution, the small amount of intensity missing from the central line being in two outer lines at approx. $\pm J(PP)$, but which are too weak to be detected by normal observation.

The transition between cases (ii) and (iii) depends upon the relative values of the three coupling constants involved, and also upon the capabilities of the spectrometer, but as a very rough guide $|J(PP)| = 50$ Hz usually represents the maximum value that can be measured from a normal spectrum.

For case (ii) it is possible to use straightforward selective heteronuclear double resonance experiments[15] (under conditions of complete proton decoupling) to compare the sign of $J(PP)$ with that of either of the two $^{31}P-^{13}C$ couplings. Either $^{31}P-\{^{13}C, ^1H_{noise}\}$ or $^{13}C-\{^{31}P, H_{noise}\}$ experiments can be used, but the latter are generally more convenient since they avoid the severe dynamic range problems associated with detecting the weak ^{13}C satellites in the presence of a strong ^{31}P signal from molecules containing no ^{13}C. An important feature of this approach is that it can also be applied to case (iii) and used to determine the positions of *all* of the lines including the very weak ones even though only the strong ones are detected directly. This is because no matter how weak a particular line is, it is possible to increase the amplitude of the heteronuclear irradiating field to such a level that tickling effects will be transferred to a strong observed line, and a systematic search over a suitable range of trial frequencies will than give the position of the normally unobservable weak line.[5]

In the complexes studied in the present work the sites where the presence of ^{13}C can lead to the above kind of magnetic inequivalence are the equatorial CO groups, any of the positions in the phenyl groups, and certain of the backbone carbons of the bidentate phosphine ligands. However, a ^{13}C in an axial CO group or a symmetric central position in the backbone (i.e. in *dppm*, *gem-pp*, or *dppp*) leads to an A_2X spin system from which it is not possible to determine either $J(AA)[= J(PP)]$ or the sign of $J(AX)[= J(PC)]$. However, this latter parameter can often be inferred by comparison with another similar coupling.

The experiments involving the aromatic carbons are particularly valuable because they permit almost all of the signs of the coupling constants to be put onto an absolute basis. In practice, the signals from the non-protonated carbons bound to phosphorus were too weak (owing to the long relaxation times and absence of any n.O.e.) to be used conveniently in this way, whilst the couplings to the *para*-carbons were too small. However, in the case of the *ortho*-carbons the determination of $J(PP)$ also gave its sign relative to $N(PC)[= {}^2J(PC) + {}^4J(PC)]$. Since ${}^4J(PC) \ll {}^2J(PC)$ the sign of $N(PC)$ is also that of ${}^2J(PC)$ which was found to be positive by comparison with ${}^3J(PH)$ [itself known[16] to be positive] in a selective $^{13}C-\{^1H\}$ decoupling experiment. Similar considerations apply to the *meta*-carbons with the added security that ${}^5J(PC)$ is even smaller. The signs of the various other $^{31}P-^{13}C$ couplings were then related to that of $J(PP)$ in each complex. At high power levels the ^{31}P irradiation gives complete decoupling in the ^{13}C spectra, and the simplification achieved in this way can be a valuable aid to assignment in certain cases, although this was not really necessary in the present work.

The peaks of the ^{31}P spectra of the tungsten complexes are flanked by satellites arising from coupling to ^{183}W ($I = \frac{1}{2}$, natural abundance = 14%); $^{31}P-\{^{183}W, ^1H_{noise}\}$ experiments gave the tungsten resonance frequency and hence $\delta(^{183}W)$. The sign of ${}^1J(PW)$ can be reliably taken as positive in this type

Table 1. Coupling constants in group VI metal carbonyl complexes[a]

No.	Complex(j)		^2J(PP)	$J(PC_{b\text{-}bone})$(c)	$^2J(P-CO_{ax})$(h) cis	$^2J(P-CO_{eq})$ cis	$^2J(P-CO_{eq})$ trans	^1J(PW)
1	dppm	$Cr(CO)_4$	-13.0	18.3	12.8	-12.1	- 7.7	-
2	"	$Mo(CO)_4$	+25.5	19.2	8.7	- 8.4	+23.2	-
3	"	$W(CO)_4$	+30.5	24.4	6.8	- 7.4	+21.6	+201.2
4	gem-pp	$Cr(CO)_4$	+47 (b)	13.7,7.8	12.2	(∓)17.1(i)		-
5	"	$Mo(CO)_4$	+76 (b)	14.6,6.1	8.3	(±)16.6(i)		-
6	"	$W(CO)_4$	+84 (b)	20.9,6.1	6.8	(±)16.6(i)		+210.9
7	dpnp	$Cr(CO)_4$	-38 (b)	-	13.1	(∓)18.3(i)		-
8	"	$Mo(CO)_4$	0 (b)	-	8.9	(∓) 9.8	(±)25.1	-
9	"	$W(CO)_4$	+ 2.9	-	7.0	(∓) 8.0	(±)23.4	+207.5
10	dppe	$Cr(CO)_4$	-10.8	N=40.0 (d)	13.4	-12.7	-4.7	-
11	"	$Mo(CO)_4$	- 4.0	23.8,16.1(f)	8.9	- 9.1	+25.3	-
12	"	$W(CO)_4$	+ 5.5	27.3,14.5(f)	6.8	- 6.7	+23.9	+229 (b)
13	cis-vpp	$Cr(CO)_4$	0 (b)	34.7,29.8(f)	13.2	(∓)12.7	(∓) 3.4	-
14	"	$Mo(CO)_4$	+ 8.7	N=62.5 (d)	8.8	- 8.2	+26.3	-
15	"	$W(CO)_4$	+19.8	$\bar{N}$=64.5 (d)	6.6	- 5.8	+24.4	+233 (b)
16	dppp	$Cr(CO)_4$	-33.7	N=22.8(e),5.8	13.4	-12.1	- 6.9	-
17	"	$Mo(CO)_4$	-28.6	21.5,5.8,0.9 (g)	9.0	- 9.4	+23.5	-
18	"	$W(CO)_4$	-21.5	24.3,4.8,2.1 (g)	7.0	- 7.7	+22.6	222.2
19	dppb	$Cr(CO)_4$	-27.0	15.7,4.9,2.0 (g)	13.2	(∓)17.6(i)		-
20	"	$Mo(CO)_4$	-21.5	17.1,7.8,1.0 (g)	8.3	(±)16.6(i)		-
21	"	$W(CO)_4$	-15.0	22.2,6.3,0.4 (g)	7.0	- 6.4	+24.2	+230.7

Notes:

(a) In Hz, ±0.2Hz unless otherwise noted. Signs without parentheses are absolute, those with parentheses have been assigned by comparison with a closely related coupling.

(b) ±0.5Hz

(c) ^nJ listed for increasing values of n.

(d) $N = {}^1J + {}^2J$.

(e) $\bar{N} = {}^1J + {}^3J$.

(f) ^1J and ^2J of like sign, but their assignment is uncertain.

(g) ^1J and ^3J are of like sign.

(h) All are probably negative.

(i) Sum of cis and trans couplings.

(j) See text for meanings of abbreviations.

Table 2. ^{13}C chemical shifts[(a)] in phosphine ligands of group VI metal carbonyl complexes

No.	Complex[(b)]		Phenyl Groups				$C_{b\text{-bone}}$[(c)]
			C_1	C_2	C_3	C_4	
1	dppm	$Cr(CO)_4$	136.9	131.5	129.1	130.6	47.3
2	"	$Mo(CO)_4$	137.0	131.5	129.1	130.6	48.7
3	"	$W(CO)_4$	135.9	131.9	128.9	130.6	51.4
4	*gem*-pp	$Cr(CO)_4$	133.7	132.8	129.0	130.7	152.1,127.5
5	"	$Mo(CO)_4$	133.5	133.2	129.0	130.8	154.1,130.3
6	"	$W(CO)_4$	132.9	133.0	128.9	130.8	156.3,132.4
7	dpnp	$Cr(CO)_4$	138.7	129.9	128.4	130.2	-
8	"	$Mo(CO)_4$	138.8	130.5	128.6	130.4	-
9	"	$W(CO)_4$	137.8	130.3	128.5	130.5	-
10	dppe	$Cr(CO)_4$	138.2	132.1	129.5	130.4	28.4
11	"	$Mo(CO)_4$	137.8	132.5	129.5	130.7	27.9
12	"	$W(CO)_4$	135.6	131.8	128.9	130.2	29.7
13	*cis*-vpp	$Cr(CO)_4$	136.9	131.6	129.0	130.3	148.9
14	"	$Mo(CO)_4$	137.1	132.1	129.1	130.4	148.0
15	"	$W(CO)_4$	136.4	132.0	129.0	130.5	149.4
16	dppp	$Cr(CO)_4$	138.1	132.1	129.4	129.7	30.9,20.0
17	"	$Mo(CO)_4$	138.2	132.2	128.7	129.9	31.6,20.1
18	"	$W(CO)_4$	137.6	132.3	130.1	130.2	31.2,20.5
19	dppb	$Cr(CO)_4$	139.0	131.8	128.3	129.4	32.1,23.6
20	"	$Mo(CO)_4$	138.5	131.9	128.4	129.4	30.3,23.6
21	"	$W(CO)_4$	138.3	132.0	128.4	129.6	31.1,23.5

Notes:

(a) In ppm (±0.1 ppm) to high frequency of Me_4Si.

(b) See text for meanings of abbreviations.

(c) When two figures are given the first refers to carbon bound to phosphorus.

of compound.[17] Tables 1–4 list the NMR parameters of these complexes.

DISCUSSION

(a) *Coupling constants*

The main factors which are known to affect nuclear spin-coupling constants involving phosphorus are the effective nuclear charge and hybridization of phosphorus and of the other nucleus, and the geometry of the coupling path.[18] With the possible exception of the three derivatives [7–9] of *dpnp* all of the complexes examined here must have very comparable effective nuclear charges at phosphorus since in each case the phosphorus is bound to the metal atom, to two phenyl groups, and to a carbon atom which may be either sp^3 or sp^2 hybridized. The phosphorus hybridization will be between p^3 and sp^3 in all of the compounds, and although it will be affected by changes in the interbond angles at phosphorus brought about by different ring sizes, this effect is likely to be relatively unimportant. Support for this contention is provided by the narrow range of variation for any particular metal atom of the coupling $^2J(P\text{–}CO_{ax})$ for which the relevant PMC interbond angle is 90° and should be little affected by alterations in the size of the chelate ring. It thus seems reasonable to attribute the major trends in the phosphorus-phosphorus and phosphorus-carbonyl couplings to

Table 3. Carbonyl ^{13}C, ^{31}P and ^{183}W chemical shifts in group VI metal complexes

No	Complex(a)	CO_{ax} (b)(c)	CO_{eq} (b)(d)	$\delta(^{31}P)$(e)	$\Delta\delta(^{31}P)$(f)	$\delta(^{183}W)$(g)
1	dppm $Cr(CO)_4$	222.6	229.7	26.0	49.6	-
2	" $Mo(CO)_4$	211.0	219.5	1.5	25.1	-
3	" $W(CO)_4$	203.6	211.0	-23.5	0.1	527
4	gem-pp $Cr(CO)_4$	222.9	229.7	50.1	54.0	-
5	" $Mo(CO)_4$	211.4	219.1	26.4	30.3	-
6	" $W(CO)_4$	203.9	210.4	7.8	11.7	477
7	dpnp $Cr(CO)_4$	220.7	228.2	96.2	53.6	-
8	" $Mo(CO)_4$	209.6	218.2	69.6	27.0	-
9	" $W(CO)_4$	201.9	209.6	45.7	3.1	482
10	dppe $Cr(CO)_4$	221.5	230.4	79.4	91.9	-
11	" $Mo(CO)_4$	209.9	218.0	54.7	67.2	-
12	" $W(CO)_4$	201.9	208.8	40.1	52.6	192
13	cis-vpp $Cr(CO)_4$	219.3	229.0	88.0	111.1	-
14	" $Mo(CO)_4$	208.4	217.2	63.9	87.0	-
15	" $W(CO)_4$	200.4	208.1	49.8	72.9	150
16	dppp $Cr(CO)_4$	222.0	226.9	41.0	58.3	-
17	" $Mo(CO)_4$	208.6	213.2	20.4	37.3	-
18	" $W(CO)_4$	203.2	206.0	-0.1	17.2	326
19	dppb $Cr(CO)_4$	221.9	225.9	48.0	63.0	-
20	" $Mo(CO)_4$	210.4	214.9	29.2	44.2	-
21	" $W(CO)_4$	203.0	205.6	11.3	26.3	367

Notes:

(a) See text for meaning of abbreviations.
(b) In ppm (±0.1 ppm) to high frequency of Me_4Si.
(c) Carbonyl trans to carbonyl.
(d) Carbonyl trans to phosphorus.
(e) In ppm (±0.1 ppm) to high frequency of external 85% H_3PO_4.
(f) Coordination chemical shift (see ref. 10) in ppm.
(g) In ppm (±2 ppm) to high frequency of $W(CO)_6$, for which $\Xi(^{183}W)$ = 4.151878 MHz.

geometrical and electronic changes in the through-bond coupling path(s).

(i) $^2J(PP)$. This coupling can be regarded as being the sum of through-metal and "backbone" contributions as suggested by Grim *et al.*[7] For the complexes of *dppb* the backbone contribution will be over five sigma bonds and can probably be ignored, so that the observed coupling is a good measure of the through-metal component. Furthermore, for these complexes and those of *dppp* there is likely to be little or no distortion of the interbond angle at the metal atom due to the constraints of the chelate ring. The uniform difference in ^2J(PP) between the three complexes of *dppb* and the corresponding ones of *dppp*, which is essentially independent of the metal atom, may thus be ascribed to a backbone contribution of − 6.8 ± 0.3 Hz in the latter complexes. This may be compared with a value of ± 1.0 Hz in the free ligand *dppp* itself[6] where there is no special rigid stereochemical relationship between the two phosphorus atoms. In *cis*-$(Me_3P)_2M(CO)_4$ where the PMP interbond angles are likely to be close to 90° and there can be no backbone contribution J(PP) has values of − 36, − 29.7 and − 25.0 Hz for M = Cr, Mo and W respectively.[19]

By contrast, a comparison of the complexes having a five-membered chelate ring with those of *dppb* does show a significant dependence upon the metal atom,

Table 4. Coupling constants between ^{31}P and ^{13}C in phenyl groups of group VI metal carbonyl complexes[a]

No.	Complex (b)	^1J(PC), ^3J(PC) (c)	^2J(PC) (c), ^4J(PC) (c)	^3J(PC) (c), ^5J(PC) (c)	^4J(PC) (d)
1	dppm $Cr(CO)_4$	36.7	+12.7,-0.6	9.8	<2.0
2	dppm $Mo(CO)_4$	37.0	+14.9,-0.9	10.0	<2.0
3	dppm $W(CO)_4$	42.3	13.4	10.2	<2.0
4	gem-pp $Cr(CO)_4$	39.0	11.7	9.8	<1.5
5	gem-pp $Mo(CO)_4$	37.8	14.0	11.0	<1.5
6	gem-pp $W(CO)_4$	44.0	13.2	10.3	<1.5
7	dpnp $Cr(CO)_4$	43.1,-3.4	13.4	10.4	2
8	dpnp $Mo(CO)_4$	32.4,$(\mp)$6.8	15.3,0	10.4,0	1.8
9	dpnp $W(CO)_4$	38.5,-6.9	15.3,-0.7	10.7,0	2.2
10	dppe $Cr(CO)_4$	36.6	+9.7,-0.1	8.8	1.8
11	dppe $Mo(CO)_4$	35.0	+12.5,-0.3	9.2	1.7
12	dppe $W(CO)_4$	39.0	+9.7,-0.1	12.2	1.8
13	cis-vpp $Cr(CO)_4$	37.4,2.9	11.2,<0.5	9.5,<0.5	1.9
14	cis-vpp $Mo(CO)_4$	35.5,2.6	12.2,0.5	9.3,0.5	<1.5
15	cis-vpp $W(CO)_4$	41.5,2.5	11.2,0.5	10.3,<0.5	<1.5
16	dppp $Cr(CO)_4$	37.3	8.8	10.6	<3.5
17	dppp $Mo(CO)_4$	34.8	12.0	9.1	<2.0
18	dppp $W(CO)_4$	38.5,2.5	+11.9,-0.5	9.2	<3.0
19	dppb $Cr(CO)_4$	32.8,3.3	9.3,0.5	8.8,0	<1.5
20	dppb $Mo(CO)_4$	31.3,2.4	11.2,0.2	8.8,0	<1.5
21	dppb $W(CO)_4$	37.9,1.9	11.2,0	9.0,0	<1.5

Notes: (a) In Hz, ± 0.2 Hz. Signs are given only when definitely known.

(b) For meanings of abbreviations see text.

(c) When there is only one entry it refers to N(PC), the algebraic sum of the two coupling constants.

(d) Strictly N(PC), but it is reasonable to assume ^6J(PC) = 0.

the changes of *dppb*→*dppe* being + 16.2, + 17.5 and + 20.5 Hz for Cr, Mo, and W respectively, while for *dppb*→*cis-vpp* the corresponding changes are + 27.0, + 30.2 and + 34.8 Hz. This is certainly consistent with there being significant (different) backbone contributions in the complexes of *dppe* and *cis-vpp*, but it should also be noted that the presence of two sp^2 hybridized carbon atoms in the chelate ring formed by *cis-vpp* will seriously affect the conformational mobility of its complexes and hence will produce greater constraints upon the PMP interbond angle than in the case of *dppe*. For the complexes with a four-membered ring the differences are even greater, the chromium complex being the most discrepant, as is to be expected if through-metal interactions are beginning to play a major role.

Although it can hardly be doubted that there are two separate paths available for the coupling mechanism, a problem with this type of analysis is that changes in the geometry of the ring are likely to affect both paths. Thus the smaller size of chromium compared with molybdenum and tungsten will affect the conformation of the chelate ring and hence of the ligand backbone—values of J(PP) are known to be very sensitive to such conformational effects. Nonetheless, it does emerge clearly from this study that in the sequence chromium, molybdenum, tungsten there is a progressive positive increment in ^2J(PP) for all types of complex studied. In view of the diversity of types of backbone involved it seems reasonable to attribute the major part of this change to the through-metal contribution. For the four-membered chelate rings the difference between ^2J(PP) for the chromium and molybdenum complexes is much greater than for the molybdenum and tungsten: this is reasonable since in these complexes the PMP interbond angle is constrained to be substantially less (typically it is 70°) than its "normal" value of 90° and is very sensitive to the PM bond lengths which are quite similar for molybdenum and tungsten.[20] It is of course well-known that ^2J(PP) is strongly dependent upon the hybridization of an intermediate carbon atom, and on theoretical grounds it is believed that differences in the energies of the various metal electronic excitations will affect this coupling and may cause it to change sign. It is also clear from our results that it is essential to determine the sign of ^2J(PP) *experimentally*. Previously, it has been usual[3] simply to rely upon the expected algebraic increase in the sequence Cr, Mo, W, to estimate the signs, but evidently this would not necessarily have predicted the negative sign in compound [**1**].

(ii) $^2J(^{31}P-^{13}CO)$. The symmetry of the complexes is such that it was possible to obtain only the magnitude of $^2J(P-CO_{ax})$ and not its sign. However, comparison with the other similar *cis* couplings $^2J(P-CO_{eq})$ of known sign in these complexes makes it obvious that in all cases the sign is actually negative. Indeed, the magnitudes of the two kinds of *cis* P–CO coupling run so closely parallel that it is feasible to use the value of $^2J(P-CO_{ax})$ to estimate $^2J(P-CO_{eq})$ in those complexes where it was possible to measure only the sum of the *cis* and *trans* $P-CO_{eq}$ couplings and hence to obtain a good estimate of the *trans* $^2J(P-CO_{eq})$. For the six complexes to which this applies the calculated values are: [**4**], −4.9; [**5**], +24.9; [**6**], +23.4; [**7**], −5.2; [**19**], −4.4; [**20**], +24.9 Hz; all probably correct to within 1 Hz.

Our results demonstrate that for all the chromium complexes the *cis*- and *trans* P–CO couplings are negative, while for the molybdenum and tungsten complexes the *cis*-couplings are still negative but the *trans* are positive. This could constitute a useful assignment aid. It had been previously observed that in *cis*-$(PH_3)_2Cr(CO)_4$ the *cis* and *trans* P–CO couplings are of opposite sign although their absolute signs were unknown.[2] It is perhaps worth noting that for the complexes with a four-membered chelate ring two paths are in principle available for the P–CO coupling: the two-bond P–M–C one, and the four-bond P–C–P–M–C route which is not necessarily negligible, especially when there is a fixed geometry. However, the relative insensitivity of the P–CO coupling to chelate ring size suggests that in fact the four-bond route is unimportant. The most striking feature of the behaviour of J(P–CO) is that in the sequence Cr, Mo, W there are algebraic increases of *ca.* 4 and 2 Hz respectively for the *cis* relationship, whereas the changes are *ca.* +30 and −2 Hz for the *trans*. These changes are much more consistent throughout the series of complexes than the changes in J(PP), suggesting that the previously observed correlation between the two types of coupling may not be of very great generality.[3] It has been proposed elsewhere[21] that geminal coupling constants can be represented by an expression which for our complexes will take the form

$$^2J(P\text{–}M\text{–}C) = S \cdot {}^1J(PM) \cdot {}^1J(MC) \qquad (1)$$

where S depends upon the hybridization and electronic excitations of the intermediary atom M. In the tungsten complexes there is a rough correlation between the *trans* $^2J(P-CO_{eq})$ coupling and ^1J(PW) which is in agreement with eqn (1), but not for the *cis* ^2J(P–CO) couplings. Thus it is probably reasonable to apply the mean electronic excitation energy approximation to the *trans* couplings, which are relatively large and positive, but not to the *cis*, which are smaller and negative. In this context it would be very interesting to know the signs and magntidues of the geminal $^{13}C-^{13}C$ couplings between the carbonyl groups.

(iii) $^1J(^{183}W-^{31}P)$. This coupling increases with increasing size of the chelate ring, i.e. with increasing PWP interbond angle, and as pointed out above is broadly paralleled by *trans* $^2J(^{31}P-CO)$.

(iv) $J(^{31}P-^{13}C)_{backbone}$. The most striking feature of the one-bond couplings is that the differences between the tungsten and molybdenum complexes are greater than those between the molybdenum and chronium ones. For sp^3 hybridized phosphorus one-bond P–C couplings are normally positive and fairly large, while for p^3 they are negative and fairly small. Thus ^1J(PC) can be regarded as indicative of phosphorus hydribization, and shows it to be intermediate between p^3 and sp^3 in these complexes as expected. However, it is surprising that the phosphorus hybridizations in the molybdenum and tungsten complexes differ sufficiently to produce the observed differences in ^1J(PC). In this connection it must be realized that particularly for the complexes with smaller rings the nominally one-bond P–C couplings will in fact be made up of contributions from the true one-bond pathway and also from a route *via* the metal atom. This latter contribution will depend upon the electronic excitations involving the metal atom which may well differ significantly for molybdenum and tungsten.

The longer-range $P-C_{backbone}$ couplings will depend upon the above factors and also upon the stereochemical constraints of the ring; further discussion is not warranted at present. In principle the P–C couplings of the phenyl groups can also provide a guide to phosphorus hybridization and again provide evidence for significant differences between the phosphorus hybridizations in the molybdenum and tungsten (and also the chromium complexes).

(b) *Chemical shifts*

As has been discussed elsewhere[11] the tungsten chemical shifts in these complexes are sensitive to the size of the chelate ring, but the precise nature of the relationship is complex. Thus a four-membered ring experiences a large shift to high frequency, and a five-membered ring a large shift to low frequency, compared with an unstrained ring or no ring at all. This feature may be of diagnostic value, since it should be possible to use $\delta(^{183}W)$ to distinguish between small-ring monomers and large-ring dimers which might otherwise have very similar NMR parameters. The newly reported phosphorus coordination shifts, $\Delta\delta(^{31}P)$, also show the same marked dependence upon ring size and metal atom that was previously noted by Grim for *dppm*, *dppe* and *dppp* complexes.[10]

For any particular metal atom the ^{13}C chemical shifts of the axial carbonyl groups are quite insensitive to the size of the chelate ring, whilst those of the equatorial carbonyls do show some effect. This is reasonable, since for an axial CO group the P–M–C interbond angle will always be very close to 90° and hence any through-space shielding effect will be essentially constant, whilst for an equatorial CO group this interbond angle and the concomitant shielding effect will be much more variable, according to the size of the chelate ring.

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