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Tetracarbonyl Tungsten Complexes Containing Two Different Donor Ligands. III. [1] ^{31}P-NMR Spectra

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^{31}P-NMR spectral data of 38 complexes of the type cis- *and* trans-*$W(CO)_4(PR_3)(L)$ are presented. The much larger chemical shift range for a particular phosphine in* cis *compounds is shown to arise mainly from steric interactions. $^1J(W-P)$ depends on the electronegativity of the substituents at phosphorus and the nature of the* trans *ligand. A* trans *influence series for octahedral tungsten(0) is derived: $SbPh_3 < AsPh_3 < PPh_3 \cong P(OPh)_3 < CO$.*

Introduction

Organic derivatives of trivalent phosphorus are probably the most important ligands employed in transition metal organic chemistry. One of the reasons for their widespread use is their easy characterization by ^{31}P-NMR spectroscopy [2–4]. Apart from chemical shift values, information is obtained from spin–spin coupling of other nuclei to phosphorus. This includes $^nJ(P-X)$ of various nuclei situated in the organic groups as well as $^2J(P-P)$ if the species in question contains more than one phosphine ligand, and $^1J(M-P)$ if the metal has a stable isotope with a nuclear spin of ½ (*e.g.* ^{103}Rh, $^{107/109}$Ag, ^{183}W, ^{195}Pt, ^{199}Hg). $^2J(P-P)$ may be observed directly only if the phosphines are chemically different, *i.e.* bear different substituents or occupy non-equivalent positions at the coordination polyhedron.

In the majority of cases information on $^2J(P-P)$ in octahedral transition metal phosphine complexes came from an observation of ^{1}H or ^{19}F-NMR spectra which are of the $A_nXX'A'_n$ type [5–7], yielding $J(XX')$ directly if $|J(AX) - J(AX')| > J(XX')$. For the common phosphorus ligands $|J(AX) - J(AX')|$ is usually much smaller than $J(XX')$; in this case the A part of the spectrum is an apparent triplet with a set of very weak outer lines. If these cannot be observed, a rough estimate of $J(XX')$ may still be obtained from an analysis of the shape of the broad central peak [8].

There are a few reports on unsymmetrical complexes $M(CO)_4(PR_3)(PR'_3)$ (M = Cr, Mo, W) in the literature for which $^2J(P-P)$ has been observed directly [9–11]. Complexes of chelating unsymmetrical *bis*(phosphine) ligands have also been obtained. In derivatives of this type $^2J(P-P)$ is the sum of two contributions, one being transmitted through the organic backbone of the ligand and one being transmitted through the metal [12]. Since there is also a 'chelate effect' on the chemical shift and possibly even on $^1J(M-P)$ [13], one must be cautious in generalizing results from those studies.

Recently a synthetic method for the successive introduction of two different ligands into carbonyl complexes of chromium, molybdenum, and tungsten has been developed in our laboratory. This method rests on (a) the lability of the *cis*-CO's in halide complexes $[M(CO)_5X]^-$ and (b) the pronounced solvent dependence of the lability of the M–X bond (eqn. 1) [14]. A variety of *cis*-disubstituted derivatives of

$$[M(CO)_5(X)]^- \xrightarrow[-CO]{+L,\ THF} [M(CO)_4(L)(X)]^- \xrightarrow[-X^-]{+L',\ EtOH} M(CO)_4(L)(L') \qquad (1)$$

the group 6b metal carbonyls have thus been prepared with L = phosphines and L′ = amines [14], phosphines, $AsPh_3$, $SbPh_3$ [15], and olefins [16]. If L′ is a P-, As-, or Sb-donor, *trans* isomers have also been obtained. The ^{31}P-NMR spectra of the tungsten derivatives are the subject of this work.

Results

In Table I the phosphorus NMR data of pentacarbonyl tungsten derivatives of various phosphines

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TABLE I. ^{31}P NMR Data of the Complexes $W(CO)_5(PR_3)$.

PR_3	δ (free ligand) (ppm)	δ (complex) (ppm)	Δ (ppm)	$^1J(W-P)$ (Hz)
$P(iPr)_3$	19.4	41.5	22.1	233
PPh_3	−6.0	20.9	26.9	243
$P(NMe_2)_3$[a]	122.3	127.4	5.1	313
$P(OiPr)_3$	139.1	130.4	−8.7	381
$P(OPh)_3$[a]	128.0	130.8	2.8	416

[a] Ref. [4].

TABLE II. ^{31}P NMR Data of the Complexes *cis*-$W(CO)_4(PR_3)(L)$.

PR_3	δ (ppm)	$^1J(W-P)$ (Hz)	L	δ (ppm)	$^1J(W-P)$ (Hz)	$^2J(P-P)$ (Hz)
$P(iPr)_3$	28.0	219	$P(iPr)_3$	28.0	219	
$P(iPr)_3$	33.1	224	PPh_3	18.4	229	24
$P(iPr)_3$	36.9	225	$P(OiPr)_3$	134.2	380	31
$P(iPr)_3$	38.3	227	$P(OPh)_3$	125.4	413	29
$P(iPr)_3$	37.1	227	$AsPh_3$			
$P(iPr)_3$	40.4	229	$SbPh_3$			
$P(iPr)_3$	40.1	229	NC_5H_5			
$P(iPr)_3$	25.7	201	dmf[a]			
$P(iPr)_3$	24.3	217	C_2H_4			
$P(iPr)_3$	38.5	218	Cl^-			
$P(iPr)_3$	35.3	221	Br^-			
$P(iPr)_3$	29.8	223	I^-			
PPh_3	22.1	225	$P(OiPr)_3$	137.0	375	34
PPh_3	22.9	238	$P(OPh)_3$	130.0	414	30
$P(OiPr)_3$	136.1	374	$P(OiPr)_3$	136.1	374	
$P(OiPr)_3$	134.1	376	$P(OPh)_3$	129.6	410	41
$P(OiPr)_3$	138.2	377	$AsPh_3$			
$P(OPh)_3$[b]	125.9	416	$P(OPh)_3$	125.9	416	
$P(OPh)_3$	133.2	410	$SbPh_3$			

[a] Dimethyl fumarate. [b] Ref. [4].

are presented, together with the shift values of the free ligand and the coordination chemical shift $\Delta = \delta(\text{complex}) - \delta(\text{free ligand})$. Positive δ's are downfield from ext. H_3PO_4 (85%): a positive Δ therefore means a downfield shift of the phosphorus resonance upon coordination to tungsten. Tables II and III contain the pertinent data of the *cis* and *trans* disubstituted derivatives. The coordination shift Δ decreases with decreasing shielding of the phosphorus nucleus in the free phosphine, even becoming negative for some complexes of triisopropyl phosphite. With few exceptions Δ is larger for *trans* compounds than for the corresponding *cis* isomers.

$^2J(P-P)$ (*cis*) is usually quite small (20 to 50 Hz) whereas the values for the *trans* analogues fall in a range of 50 to 200 Hz. Thus, apart from theoretical considerations, $^2J(P-P)$ provides useful information for structural assignments. In complexes with *cis* stereochemistry $^1J(W-P)$ for a given phosphine is only slightly smaller than the value in the pentacarbonyl derivative. From the large body of data we have at hand, a derivative of the strongly π-accepting olefin dimethyl fumarate emerges as the

TABLE III. ^{31}P NMR Data of the Complexes *trans*-$W(CO)_4(PR_3)(L)$.

PR_3	δ (ppm)	$^1J(W-P)$ (Hz)	L	δ (ppm)	$^1J(W-P)$ (Hz)	$^2J(P-P)$ (Hz)
$P(iPr)_3$	40.8	262	$P(iPr)_3$	40.8	262	
$P(iPr)_3$	43.3	268	PPh_3	27.4	277	53
$P(iPr)_3$	42.0	258	$P(NMe_2)_3$	133.3	353	68
$P(iPr)_3$	43.8	259	$P(OiPr)_3$	137.0	434	89
$P(iPr)_3$	40.8	250	$P(OPh)_3$	131.3	480	108
$P(iPr)_3$	44.1	298	$AsPh_3$			
$P(iPr)_3$	43.8	317	$SbPh_3$			
PPh_3	27.4	282	PPh_3	27.4	282	
PPh_3	27.8	274	$P(NMe_2)_3$	133.1	360	73
PPh_3	27.3	272	$P(OiPr)_3$	138.2	441	95
PPh_3	24.3	263	$P(OPh)_3$	133.8	480	115
$P(NMe_2)_3$	134.6	347	$P(NMe_2)_3$	134.6	347	81[a]
$P(NMe_2)_3$	134.7	354	$P(OiPr)_3$	138.5	417	122
$P(NMe_2)_3$	130.3	353	$P(OPh)_3$	133.6	457	147
$P(OiPr)_3$	140.0	423	$P(OiPr)_3$	140.0	423	
$P(OiPr)_3$	134.7	432	$P(OPh)_3$	136.6	449	188
$P(OiPr)_3$	137.4	486	$AsPh_3$			
$P(OPh)_3$[b]	132.7	446	$P(OPh)_3$	132.7	446	
$P(OPh)_3$	132.4	562	$SbPh_3$			

[a] $^2J(P-P)$ determined from ^{1}H-NMR: Ref. [4]. [b] Ref. [4].

only exception. For *trans* disubstituted carbonyl derivatives *trans*-$W(CO)_4(PR_3)(ER'_3)$ (E = P, As, Sb) $^1J(W-P)$ of PR_3 is found considerably larger than in either the *cis* isomers or the pentacarbonyls $W(CO)_5(PR_3)$. For E = P there is an increase of approx. 13%, for E = As 28%, and for E = Sb 36% over the values in the pentacarbonyls. On the other hand $^1J(W-P)$ turns out to be almost independent of the nature of the groups R′, at least for the 15 derivatives with E = P in this study.

Discussion

Chemical Shifts

The screening constant for a particular nucleus may be expressed as the sum of three contributions (eqn. 2) [2–4, 17].

$$\sigma = \sigma(\text{dia}) + \sigma(\text{para}) + \sigma(\text{other atoms}) \qquad (2)$$

For protons, changes in the diamagnetic shielding (σ(dia)) and contributions from the magnetic anisotropy of neighboring atoms or groups (σ(other atoms)) are responsible for variations of the chemical shift. The much larger shift range of heavier nuclei is thought to arise from changes in σ(para). A detailed treatment of this term (including d orbitals) within the framework of LCAO MO theory has been presented by Jameson and Gutowsky [18] and applied to PR_3 and XPR_3 molecules by Letcher and Van Wazer [19]. The following expression for the phosphorus chemical shift relative to a standard was obtained (eqn. 3), where ΔE is an average excitation

$$\delta - \delta_o = + \frac{2e^2\hbar^2}{3m^2c^2\Delta E}\left(\langle r^{-3}\rangle_p\zeta_1 + \langle r^{-3}\rangle_d\zeta_2\right) \qquad (3)$$

energy, $\langle r^{-3}\rangle$ is the mean inverse cube of the distance from the nucleus of the phosphorus p and d electrons, respectively, and ζ_i are determined by the p and d orbital occupations [20]. Changes in ΔE and $\langle r^{-3}\rangle$ were considered to be of minor importance. ζ_1 could be calculated from bond angle and electronegativity data yielding phosphorus chemical shifts for various PR_3 molecules which agreed reasonably well with observed ones [19]. Phosphites and phosphorus halides gave resonances at lower field than expected, and this was attributed to electron donation from the hetero atom's p orbitals into the d orbitals of phosphorus, *i.e.* a contribution from the $\langle r^{-3}\rangle_d\zeta_2$ term to the chemical shift.

In discussions of the ^{31}P chemical shift of transition metal phosphine complexes the coordination chemical shift Δ has received much attention [4]. Its near linear dependence on the shift value of the uncoordinated ligand has been noted frequently [21]. The shift range for three coordinate phosphorus compounds is considerably larger than that for molecules containing phosphorus in a tetrahedral and thus more symmetrical environment [19]. This means that Δ reflects primarily a property of the uncoordinated ligand. The coordination chemical shift should not, therefore, be used to discuss any properties of the metal–phosphorus bond.

The question of π bonding between metal and phosphorus is still a matter of dispute [22]. Our recent discussion of M–CO bonding and ^{13}C chemical shifts [23] suggests that a (d–p)π bond order term should also be considered as contributing to the ^{31}P chemical shifts whenever this type of bonding occurs. A considerable degree of π back donation in phosphine complexes $M(CO)_5(PX_3)$ (M = Cr, Mo, W) has been inferred from the observation that analogous adducts $BCl_3 \cdot PX_3$ have resonances at higher field [24]. It has been argued that such a shift difference might be due to the higher electronegativity of boron [25]. On the other hand, in our series of tungsten compounds replacement of the good π acceptor CO by a donor L *trans* to a phosphine causes a downfield shift of several ppm, in accord with the π bonding hypothesis. Nevertheless, in view of the pronounced dependence of σ(para) on bond angles and the electronegativities of the groups attached to phosphorus (including the metal) [19] it seems not appropriate to single out one or two parameters as being entirely responsible for shift changes, even in a series of related compounds. Attempts to ascribe trends in the phosphorus chemical shift in coordination compounds to changes in any single term of eqn. 3 should thus be viewed with caution. Nevertheless, one trend of the shift values in Table II deserves to be mentioned. In general, displacement of a *cis* carbonyl group in $W(CO)_5(PR_3)$ by any other ligand causes an upfield shift of the phosphorus resonance of PR_3. Apart from the *cis*-phosphine/olefin and phosphine/halide derivatives, which will be discussed below, this upfield shift is largest (a) when the incoming ligand is sterically demanding, and (b) when PR_3 itself is a bulky ligand, *e.g.* triisopropyl phosphine. Thus it seems that steric interactions, which may influence the chemical shift through a distortion of the bond angles both at the metal and at phosphorus [19, 26], are largely responsible for this upfield shift. This view has been expressed by early workers in this field [27], and may be substantiated by the following observations:

In *cis*-$Mo(CO)_4(PPh_3)_2$ the strain between the bulky triphenyl phosphine ligands (cone angle θ = 145° [26]) results in a substantial distortion of both the octahedral geometry around molybdenum and the local C_{3v} symmetry around phosphorus [28]. Such a distortion of the environment around phosphorus is known to result in large changes of the chemical shift [29]. The cone angle of triisopropyl phosphine is even larger (θ = 160° [26]). Thus it is not surprising that *cis*-$W(CO)_4(P(iPr)_3)_2$ has the highest field ^{31}P resonance of all *bis*(phosphine) complexes containing this ligand [30]. The steric argument might even hold for the olefin derivatives. From extensive ^{1}H-NMR investigations it is known that olefins in compounds of the type *cis*-$M(CO)_4(PR_3)$(olefin) align themselves in such a way that the C–C bond is parallel to the M–P bond [31]. This has been confirmed by an X-ray study of *cis*-$W(CO)_4(PMe_3)$(dimethyl fumarate), which also shows a sizeable distortion of the octahedral geometry around tungsten due to steric interactions between the phosphine and olefin ligands [32]. Other series of closely related compounds such as *cis*-$[W(CO)_4P(iPr)_3(X)]^-$ (X = Cl, Br, I) and *cis*-$W(CO)_4(P(iPr)_3)(EPh_3)$ (E = P, As, Sb) show a similar upfield shift of the $P(iPr)_3$ resonance with increasing cone angles of the *cis* ligand (note that the cone angle of X^- *increases* with increasing atomic number of X whereas that of EPh_3 *decreases* with increasing atomic number of E [26]). Most remarkably, no such effect is seen in the *trans* series, lending further credit to the interpretation of these shift differences as arising from steric interactions.

One-bond Coupling Constants $^1J(^{183}W-^{31}P)$

Although the theory of spin–spin coupling across one bond was developed more than 20 years ago [33–36], there has been much dispute about the factors that contribute to $^1J(M-P)$ in transition metal phosphine complexes [37–41]. There is now a general consensus that this value is dominated by the Fermi contact term, which may be given in its simplified form [42] (eqn. 4), where ζ is a normalizing factor

$$J_{AB} = \frac{64h\beta^2}{9^3\Delta E}\gamma_A\gamma_B\zeta^2\alpha_A^2\alpha_B^2S_A^2(0)S_B^2(0) \qquad (4)$$

for the valence bond function describing the A–B bond using hybrid orbitals and allowing, if necessary, for the polarity of the bond. For two given nuclei A and B with their respective γ values, the quantities that can vary in a series of compounds are the s-electron densities at the nuclei, $S^2(0)$, the s-character of the hybrid orbitals involved in A–B-bonding, α^2, and the average triplet excitation energy $^3\Delta E$.

The s-character of the orbital at phosphorus used for M–P bonding and, to a lesser extent, $S^2{}_P(0)$

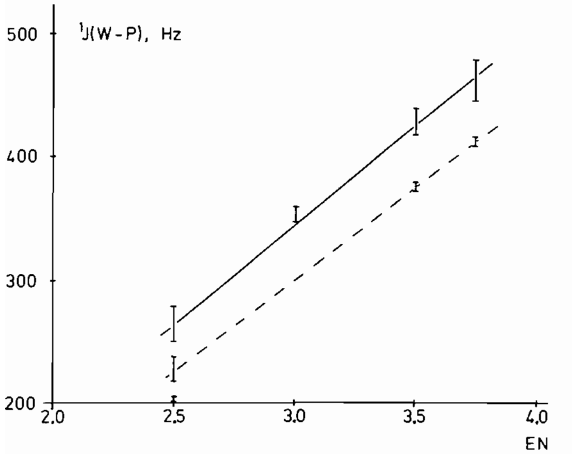


Fig. 1. $^1J(W-P)$ of the complexes *cis*-$W(CO)_4(PR_3)(L)$ (-----) and *trans*-$W(CO)_4(PR_3)(L)$ (———) *vs.* electronegativity (EN) of R.

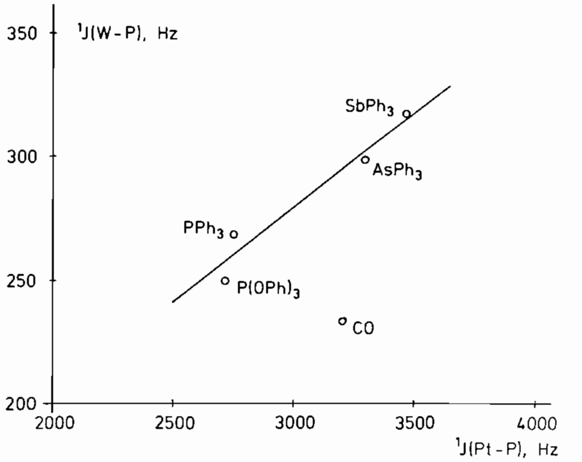
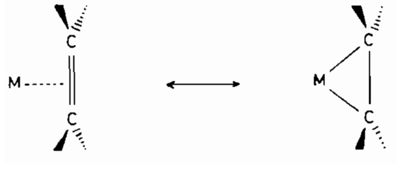


Fig. 2. $^1J(W-P)$ of the complexes *trans*-$W(CO)_4(P(iPr)_3)$(L) *vs.* $^1J(Pt-P)$ of $Pt(CH_3)$(diphos) (L).

are known to increase with increasing electronegativity of the groups R. Thus in a series of related compounds one usually finds a good correlation between $^1J(M-P)$ and the electronegativity of the α-atoms of the substituents R [41]. Such a plot for the phosphine complexes employed in this study is shown in Fig. 1. *Trans* disubstituted derivatives with arsine and stibine ligands are not included and will be discussed separately.

The correlation is reasonably good, with only a few exceptions. The triphenylphosphite complexes show higher values of $^1J(W-P)$ than would be expected if 3.5 were used as EN of the PhO groups. This cannot be ascribed to a change in $S^2_W(0)$ or $^3\Delta E$, since $^1J(W-P)$ of the other phosphine is approximately the same as in the rest of the compounds. In other words, the effective electronegativity of a phenoxy group is significantly underestimated by simply taking the value of oxygen. Indeed oxygen is known to be a good π donor towards the phenyl ring, and the resulting electron demand might well be propagated to the phosphorus atom. To account for this effect we chose to use an empirical electronegativity value of 3.75 for the phenoxy group in this study.

The very small tungsten–phosphorus coupling constant of *cis*-$W(CO)_4(P(iPr)_3)$(dimethyl fumarate) deserves extra attention. The metal–olefin bond in olefin complexes may be described by two resonance structures symbolizing the donor and acceptor contributions of the olefin [43], the latter increasing in importance with increasing electron density at the metal and increasing electron demand of the substituents at the double bond. Thus *cis*-$W(CO)_4(P(iPr)_3)$-(dimethyl fumarate) may be labelled a metallacyclopropane derivative, the effective coordination number of tungsten being 7 instead of 6. If we look at this in a very naive way it would mean that the tungsten 6 s orbital is now involved in 7 bonds instead of 6, thus reducing α^2_W to 6/7 of the value in normal 6 coordinate compounds. Along similar lines the difference between $^1J(Pt-P)$ in square planar Pt(II) and octahedral Pt(IV) compounds has been explained [2]. Although this approach is certainly crude, it predicts a value of 200 Hz for $^1J(W-P)$ in *cis*-$W(CO)_4(P(iPr)_3)$(dimethyl fumarate) based on 233 Hz for the reference compound $W(CO)_5(P(iPr)_3)$.



Certainly the most interesting feature of the entries in Table III are the unusually large values of $^1J(W-P)$ found in complexes containing an arsenic or antimony donor *trans* to a phosphine. The *trans* influence, including its measurement by crystallographic as well as IR and NMR spectroscopic methods, has been discussed extensively [44]. It is usually interpreted in terms of Syrkin's rehybridisation theory [45]: A ligand forming a strong bond to the metal also demands more s and d character for this bond, leaving less s and d and more p character for the bond to the *trans* ligand. Since $^1J(W-P)$ directly reflects the contribution of the tungsten 6 s orbital to the tungsten–phosphorus bond (*vide supra*), $^1J(W-P)$ is a measure of the *trans* influence of the ligand opposite to phosphorus. A high value of $^1J(W-P)$ in a compound *trans*-$W(CO)_4(PR_3)(L)$ in the above mentioned definition means a low *trans* influence of L. Thus the following ligands may be arranged according to their increasing *trans* influence towards tungsten:

$SbPh_3 < AsPh_3 < PPh_3 \cong P(OPh)_3 < CO$

A similar dependence of a one-bond coupling constant on the nature of the *trans* ligand has been found in various square planar complexes of rhodium and platinum [46–51]. A plot of $^1J(W–P)$ of the compounds *trans*-$W(CO)_4(P(iPr)_3)$ (L) *versus* $^1J(Pt–P)$ of $Pt(CH_3)(diphos)(L)$ [47] (Fig. 2) indicates that the ligands EPh_3 (E = P, As, Sb) and $P(OPh)_3$ are similar in their *trans* influence towards both tungsten(0) and platinum(II). Carbon monoxide, however, which so far has been taken as a not particularly good *trans* influence ligand [52], turns out to have a high *trans* influence in octahedral tungsten(0) complexes. Unfortunately the range of ligands that can be accomodated *trans* to a phosphorus donor in tungsten complexes of the type $W(CO)_4(PR_3)(L)$ is rather limited. A more complete study of the *trans* influence in octahedral tungsten(0) complexes has, therefore, been undertaken using the ^{13}C resonance of the *trans* CO in compounds $W(CO)_5$-L as a probe [53].

Two-bond Coupling Constants $^2J(^{31}P–^{31}P)$

Two-bond coupling constants for the *bis*(phosphine) tungsten complexes are included in Tables II and III. No attempts have been made to determine their signs. Whenever this has been done *cis* couplings turned out to be negative whereas *trans* couplings are positive [7], and this is certainly also true for the compounds in this study. Apart from its dependence on the metal orbitals [7, 8] the absolute value of $^2J(P–P)$ is governed by the electronegativity of the groups R at both phosphorus atoms in much the same way as $^1J(W–P)$. Consequently plots of $^2J(P–P)$ *vs.* the average electronegativity of the α-atoms of the groups R and R′ should be roughly linear (Fig. 3). In view of this dependence of both $^1J(M–P)$ and $^2J(P–P)$ on EN it is not surprising that empirical correlations can be constructed between $^1J(M–P)$ and $^2J(P–P)$ [54]. While the correlation in the *trans* series is quite good, larger deviations occur in the *cis* series. This is perhaps not unexpected. The sign change between *cis* and *trans* stereochemistry indicates that there is a pronounced dependence of $^2J(P–P)$ on the angle P–W–P, which in turn is affected by both the steric and electronic properties of the phosphine ligands R_3P and R'_3P.

Conclusions

From the work presented here we are able to draw the following conclusions. Unexpected high field resonances for a particular phosphorus ligand as compared to the pentacarbonyl derivative $W(CO)_5$-(PR_3) are indicative of steric strain between this phosphine and ligands *cis* to it. $^1J(W–P)$ is determined by the electronegativity of the groups R as well as by the *trans* influence of the ligand *trans* to PR_3. A *trans* influence series for octahedral tungsten(0) complexes has thus been established. Finally the value of $^2J(P–P)$ allows one to clearly distinguish between *cis* and *trans* stereochemistry.

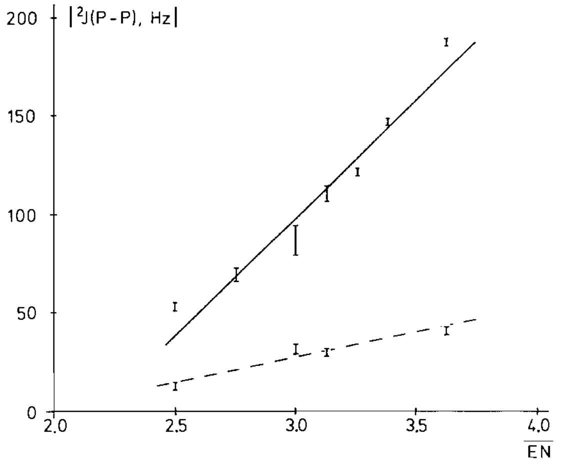


Fig. 3. $|^2J(P–P)|$ of the complexes *cis*-$W(CO)_4(PR_3)(PR'_3)$ (------) and *trans*-$W(CO)_4(PR_3)(PR'_3)$ (———) *vs.* average electronegativity ($\overline{EN}$) of R and R′.

Acknowledgement

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Experimental

^{31}P NMR spectra were recorded from solutions in $CDCl_3$ in standard 5 mm tubes. The spectrometer (Bruker WH 90) operated in the Fourier transform mode at 36.44 MHz with proton noise decoupling. The deuterium signal of the solvent was used as internal lock, chemical shifts (in ppm) downfield from ext. H_3PO_4 are positive. A digital resolution of 0.75 Hz was employed, the coupling data in Tables I–III should thus be accurate to ±2 Hz.

The pentacarbonyls were prepared following standard procedures. The preparation of phosphine–halide, phosphine–amine, phosphine–olefin, and phosphine–phosphine′ complexes has been reported earlier [14–16].

Tetracarbonyl-triisopropylphosphite-triphenylphosphite-tungsten

0.55 g $W(CO)_4(P(OiPr)_3)(NCCH_3)$ [14] and 0.5 ml triphenylphosphite are heated together at 80 °C (1 h). The resulting colourless oil is dissolved in 5 ml ethanol and cooled to −20 °C to precipitate the *cis* isomer (yield 0.1 g ≙ 12%) which may be recrystallized from dichloromethane/ethanol. ν(CO) 2035(m), 1946(s), 1921(vs) (pentane). To the mother liquor an equal volume of water is added. The resulting colourless oil is washed with water, dried *in vacuo* and dissolved in 10 ml pentane. Cooling to −20 °C causes the *trans* isomer to crystallize in large cubes. A second batch of equal quality is obtained by evaporating the mother liquor to 4 ml and cooling to −20 °C. Combined yield 375 mg (46%) m.p. 80 °C, ν(CO) 2043(vw), 1971(w), 1924(vs) (pentane).

Tetracarbonyl-triisopropylphosphite-triphenylarsine-tungsten

1.34 g $Et_4N[W(CO)_4(P(OiPr)_3)Cl]$ [14] and 0.8 g triphenylarsine are dissolved in 50 ml ethanol and allowed to react overnight at room temperature. The white precipitate is filtered off, washed with ethanol and dried *in vacuo*. Yield 1.41 g (87%) of analytically pure *cis* isomer, m.p. 102 °C. ν(CO) 2022(m), 1934(m), 1907(vs), 1894(s). 0.8 g of the *cis* isomer are fused together with 0.1 g triphenylarsine at 120 °C (1 h). The resulting white solid is dissolved in a minimum amount of methylcyclohexane. Upon cooling to −20 °C most of the remaining *cis* isomer crystallizes. The mother liquor is evaporated to dryness leaving a white solid which according to its IR and ^{31}P NMR spectra is a 1:2 mixture of *cis* and *trans* isomers.

Tetracarbonyl-triphenylphosphite-triphenylstibine-tungsten

1.54 g $Et_4N[W(CO)_4(P(OPh)_3)Cl]$ [14] and 0.9 g triphenylantimony are dissolved in 50 ml ethanol and allowed to react overnight at room temperature. The white precipitate is filtered off, washed with ethanol and dried *in vacuo*. Yield 1.55 g (81%) of analytically pure *cis* isomer, m.p. 128 °C, ν(CO) 2032(m), 1945(s), 1924(vs), 1919(sh) (pentane). 0.96 g of the *cis* isomer are fused together with 0.1 g triphenylantimony at 130 °C (1 h). The white solid is dissolved in a minimum amount of methylcyclohexane. Upon cooling to 0 °C most of the remaining *cis* isomer crystallizes. Further cooling to −20 °C causes the *trans* isomer to separate in large colourless crystals. Yield 0.32 g (33%), m.p. 118 °C. ν(CO) 2036(vw), 1965(w), 1922(vs) (pentane).

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