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

WOLFDIETER A. SCHENK* and WOLFGANG BUCHNER

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, F.R.G.

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³¹P-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: SbPh₃ < AsPh₃ < PPh₃ \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 ${}^{n}J(P-X)$ of various nuclei situated in the organic groups as well as $^{2}J(P-P)$ if the species in question contains more than one phosphine ligand, and ${}^{1}J(M-P)$ if the metal has a stable isotope with a nuclear spin of ½ (e.g. ¹⁰³Rh, ^{107/109}Ag, ¹⁸³W, ¹⁹⁵Pt, ¹⁹⁹Hg). 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 ${}^{2}J(P-P)$ 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

$$[M(CO)_{5}(X)]^{-} \xrightarrow{+L, THF} [M(CO)_{4}(L)(X)]^{-} \xrightarrow{+L', EtOH} -X^{-}$$

$$M(CO)_4(L)(L')$$
 (1)

the group 6b metal carbonyls have thus been prepared with L = phosphines and L' = amines [14], phosphines, AsPh₃, SbPh₃ [15], and olefins [16]. If L' is a P-, As-, or Sb-donor, *trans* isomers have also been obtained. The ³¹P-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

^{*}Author to whom correspondence should be addressed.

PR ₃	δ (free ligand) (ppm)	δ (complex) (ppm)	∆ (ppm)	¹ J(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	

TABLE I. ³¹P NMR Data of the Complexes W(CO)₅(PR₃).

^aRef. [4].

TABLE II. ³¹P NMR Data of the Complexes cis-W(CO)₄(PR₃)(L).

PR ₃	δ (ppm)	¹ J(W-P) (Hz)	L	δ (ppm)	¹ J(W–P) (Hz)	² J(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	C1 ⁻			
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			

^aDimethyl fumarate. ^bRef. [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. H₃PO₄ (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

³¹P NMR of W(CO)₄(PR₃)(L) Type Complexes

PR ₃	δ (ppm)	¹ J(W–P) (Hz)	L	δ (ppm)	¹ J(W–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
P(iPr) ₃	42.0	258	$P(NMe_2)_3$	133.3	353
P(iPr) ₃	43.8	259	P(OiPr) ₃	137.0	434
P(iPr) ₃	40.8	250	P(OPh) ₃	131.3	480
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
PPh ₃	27.3	272	P(OiPr) ₃	138.2	441

P(OPh)₃

 $P(NMe_2)_3$

P(OiPr)₃

P(OPh)₃

P(OiPr)₃

P(OPh)₃

P(OPh)₃

AsPh₃

SbPh₃

133.8

134.6

138.5

133.6

140.0

136.6

132.7

263

347

354

353

423

432

486

446

562

TABLE III. ³¹P NMR Data of the Complexes trans-W(CO)₄(PR₃)(L).

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

24.3

134.6

134.7

130.3

140.0

134.7

137.4

132.7

132.4

only exception. For *trans* disubstituted carbonyl derivatives *trans*-W(CO)₄(PR₃)(ER'₃) (E = P, As, Sb) ¹J(W-P) of PR₃ is found considerably larger than in either the *cis* isomers or the pentacarbonyls W(CO)₅(PR₃). 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

PPh₃

 $P(NMe_2)_3$

 $P(NMe_2)_3$

 $P(NMe_2)_3$

P(OiPr)₃

P(OiPr)₃

P(OiPr)₃

P(OPh)3^b

P(OPh)₃

Chemical Shifts

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

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

For protons, changes in the diamagnetic shielding $(\sigma(dia))$ and contributions from the magnetic anisotropy of neighboring atoms or groups $(\sigma(other atoms))$ 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 PR₃ and XPR₃ 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

480

347

417

457

423

449

446

$$\delta - \delta_{\mathbf{o}} = + \frac{2e^{2}\hbar^{2}}{3m^{2}c^{2}\Delta E} \left(\langle \mathbf{r}^{-3} \rangle_{\mathbf{p}} \zeta_{1} + \langle \mathbf{r}^{-3} \rangle_{\mathbf{d}} \zeta_{2} \right)$$
(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 PR₃ 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.

²J(P-P) (Hz)

> 73 95

115

122

147

188

81^a

In discussions of the ³¹P 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 ¹³C chemical shifts [23] suggests that a $(d-p)\pi$ bond order term should also be considered as contributing to the ³¹P 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 BCl₃·PX₃ 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 $\sigma(\text{para})$ 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 PR₃. 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 ($\theta = 160^{\circ}$ [26]). Thus it is not surprising that $cis-W(CO)_4(P(iPr)_3)_2$ has the highest field ³¹P resonance of all bis(phosphine) complexes containing this ligand [30]. The steric argument might even hold for the olefin derivatives. From extensive ¹H-NMR investigations it is known that olefins in compounds of the type cis-M(CO)₄(PR₃)-(olefin) align themselves in such a way that the C-Cbond is parallel to the M-P bond [31]. This has been confirmed by an X-ray study of cis-W(CO)4-(PMe₃)(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)₄- $P(iPr)_3(X)$ [- (X = Cl, Br, I) and $cis-W(CO)_4(P (iPr)_3$ (EPh₃) (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 EPh₃ 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 ${}^{1}J({}^{183}W-{}^{31}P)$

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 ${}^{1}J(M-P)$ 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

$$\mathbf{J}_{\mathbf{A}\mathbf{B}} = \frac{64h\beta^2}{9^3\Delta E} \,\gamma_{\mathbf{A}}\gamma_{\mathbf{B}}\zeta^2 \,\alpha_{\mathbf{A}}^2 \alpha_{\mathbf{B}}^2 \mathbf{S}_{\mathbf{A}}^2(0) \mathbf{S}_{\mathbf{B}}^2(0) \tag{4}$$

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, S²(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. ${}^{1}J(W-P)$ of the complexes $cis W(CO)_4(PR_3)(L)$ (----) and $trans-W(CO)_4(PR_3)(L)$ (-----) vs. electronegativity (EN) of R.

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 ${}^{1}J(W-P)$ than would be expected if 3.5 were used as EN of the PhO groups. This cannot be ascribed to a change in $S_{W}^{2}(0)$ or ${}^{3}\Delta E$, since ${}^{1}J(W-P)$ 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 contri-





Fig. 2. ${}^{1}J(W-P)$ of the complexes *trans*-W(CO)₄(P(iPr)₃) (L) ν s. ${}^{1}J(Pt-P)$ of Pt(CH₃)(diphos) (L).

butions 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_w^2 to 6/7 of the value in normal 6 coordinate compounds. Along similar lines the difference between ${}^{1}J(Pt-P)$ 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 ${}^{1}J(W-P)$ 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 ${}^{1}J(W-P)$ in a compound trans-W(CO)₄(PR₃)(L) in the above mentioned definition means a low trans influence of L. Thus the following ligands may 194

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 ${}^{1}J(W-P)$ of the compounds trans-W(CO)₄(P(iPr)₃) (L) versus ¹J(Pt-P) of Pt(CH₃)(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 ¹³C resonance of the *trans* CO in compounds W(CO)₅-L as a probe [53].

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

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 ${}^{2}J(P-P)$ is governed by the electronegativity of the groups R at both phosphorus atoms in much the same way as ${}^{1}J(W-P)$. Consequently plots of ${}^{2}J(P-P)$ 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 ${}^{1}J(M-P)$ and ${}^{2}J(P-P)$ on EN it is not surprising that empirical correlations can be constructed between ${}^{1}J(M-P)$ and ${}^{2}J(P-P)$ [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 ${}^{2}J(P-P)$ 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 com-



Fig. 3. $|^{2}J(P-P)|$ of the complexes *cis*-W(CO)₄(PR₃)(PR'₃) (-----) and *trans*-W(CO)₄(PR₃)(PR'₃) (-----) *vs.* average electronegativity (EN) of R and R'.

pared to the pentacarbonyl derivative $W(CO)_{5}$ -(PR₃) 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 PR₃. 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.

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Experimental

³¹P NMR spectra were recorded from solutions in CDCl₃ 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. H₃PO₄ 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 phosphinehalide, 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)(NCCH₃) [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 \doteq 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-triphenylarsinetungsten

1.34 g Et₄N[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 ³¹P NMR spectra is a 1:2 mixture of *cis* and *trans* isomers.

Tetracarbonyl-triphenylphosphite-triphenylstibinetungsten

1.54 g Et₄N[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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