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^{183}W NMR study of alkenylcarbyne– and alkenylvinylidene–tungsten complexes

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ABSTRACT: ^{183}W NMR data are reported for a series of alkenylvinylidene– and alkenylcarbyne–tungsten complexes of the type [(dppe)(CO)$_3$W=C=CHR], [(dppe)(CO)$_3$W≡C—CH=CR$_2$]$^+$BF$_4^-$ and [(dppe)(CO)$_2$LW≡C—CH=CR$_2$] [dppe = 1,2-bis(diphenylphosphino)ethane]. Spectra were recorded using inverse 2D ^{1}H,^{183}W- and ^{31}P,^{183}W{^{1}H}-HMQC NMR spectroscopy without ^{183}W decoupling. In some examples of the alkenylcarbyne series minor amounts of the propenylcarbyne isomer were present and the corresponding ^{183}W chemical shifts could also be characterized. For a given complex and measuring time the proton-detected correlation spectra based on the existing long-range coupling to the metal affords a higher signal-to-noise ratio than the phosphorus-detected correlation via $^1J(^{183}\mathrm{W},^{31}\mathrm{P})$. Additionally, the tilt of cross peaks in the ^{1}H,^{183}W HMQC spectra reveals the relative sign of the coupling of these nuclei with phosphorus. ^{183}W chemical shift variations for compounds [(dppe)(CO)$_2$LW≡C—CH=CR$_2$] (L = CO, PMe$_3$, CH$_3$CN or halogen) are rationalized in terms of the π-acceptor ability of the ligand. Halogen derivatives show shielding decreases in the order F < Cl < Br < I. For carbyne complexes a deshielding of the metal is observed with increase in the size of the carbocyclic ring substituent as a result of steric effects. For complexes [(dppe)(CO)$_2$LW≡C—CH=CR$_2$] (L = CO, PMe$_3$, CH$_3$CN) the phosphorus–tungsten scalar coupling is also determined by the σ-donor/π-acceptor ability and bulkiness of the ligands. © 1998 John Wiley & Sons, Ltd.

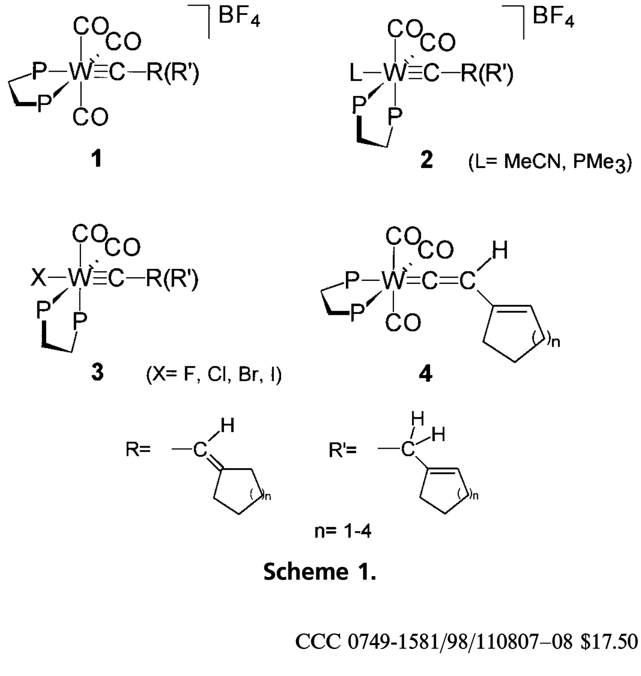
KEYWORDS: NMR; ^{183}W NMR; ^{1}H-, ^{31}P-indirect detection; carbynes; vinylidenes

INTRODUCTION

Transition metal complexes in which the metal is multiply bonded to carbon represent a research area of great interest because of the synthetic applications of this compound class. Comparatively, functionalized carbyne complexes have received less attention than the corresponding carbenes and the number of studies about their reactivity is still small.[1]

Transition metal NMR spectroscopy has been successfully used to study electronic[2] and steric[3] effects in coordination compounds, and also to correlate the metal chemical shift variations with reactivity.[4] However, the number of ^{183}W NMR data is relatively limited.[5] At the start of this project the ^{183}W chemical shifts of only nine carbyne compounds were known, corresponding to three Schrock-type[6] W(≡CR)(L)$_3$ (R = SiMe$_3$, ^{t}Bu, Ph; L = CH$_2$SiMe$_3$, CH$_2$CMe$_3$, OCMe$_3$) and six Fischer-type[7] W(Cl)(dppf)(≡CR)(CO)$_2$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene; R = Me, Ph, thienyl, furyl], W(Cp)(≡CR)(CO)$_2$ (R = C$_5$H$_7$, *p*-tolyl) tungsten–carbyne complexes. For the cyclopentadienyl derivatives indirect detection techniques through protons were used to extract the ^{183}W NMR parameters. Recently, we have reported the preliminary results on the ^{183}W NMR characterization of alkenylcarbyne–tungsten complexes **1**–**3** and alkenylvinylidene–tungsten complexes **4** (Scheme 1).[8]

Here we report the full data obtained in the ^{183}W NMR study of the previously described tungsten complexes **1**–**4** (Scheme 1). Series **3** of halogen compounds has been completed to include examples where X = F. To overcome the problem of the low receptivity of ^{183}W ($R^C = 5.89 \times 10^{-2}$), the indirect detection schemes ^{1}H,^{183}W-[9] and ^{31}P,^{183}W{^{1}H}-HMQC[10] were



Scheme 1.

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used. The expected increase in sensitivity over the direct detection experiment would be a factor of $(\gamma_x/\gamma_w)^{5/2}$ ($X = {}^1H$ or ${}^{31}P$), which corresponds to gains of 2830- and 295-fold using ^1H and ^{31}P detection, respectively. They are compared in the light of the signal-to-noise ratio they afford and the information they provide. Metal chemical shift variations are interpreted in terms of the electronic changes induced by the ligands. The carbocyclic substituents on vinylidene and carbyne ligands cause a deshielding of $\delta\ {}^{183}W$ with increasing size of the ring, an effect that is explained by a combination of electronic and steric factors.

RESULTS AND DISCUSSION

First, we will compare the performance of the long-range coupling correlation $^1H,^{183}W$-HMQC[11] *vs.* $^{31}P,^{183}W\{^1H\}$-HMQC based on $^1J(^{183}W,^{31}P)$ for ^{183}W NMR characterization. We will then analyze the trends observed in $\delta\ {}^{183}W$ along the series of structurally related complexes. The pulse sequences used in this work are shown in Fig. 1.

Indirect HMQC spectroscopy based on $^nJ(^{183}W,^1H)$ ($n > 1$) *vs.* $^1J(^{183}W,^{31}P)$

Numerous examples are known where the ^{183}W NMR parameters have been obtained using indirect $^1H,^{183}W$ correlation spectroscopy based on long-range $^1H,^{183}W$ couplings because of the lack of an alternative sensitive nucleus directly bonded to tungsten.[12] $^1H,^{183}W$ correlations up to six[13] and seven[7b] bonds have recently been reported. Ideally, proton detection would afford a higher signal-to-noise ratio than phosphorus detection by a factor $(\gamma_H/\gamma_P)^{5/2} \approx 9.6$. However, some factors may contribute to a decrease in this figure. The first concerns to the relaxation problem. In principle, a similar order of magnitude of $T_1(^1H)$ and $T_1(^{31}P)$ can be assumed for ligands coordinated to transition metals. [Generally, $T_1(^1H)$ is shorter than $T_1(^{31}P)$, but it is well known that phosphorus T_1s of phosphines became much shorter when they are complexed; see, for example, Ref. 14.] Therefore, the same repetition delay Δ_1 may be adequate for both NMR experiments. However, the dephasing delay Δ_2 is much shorter for ^{31}P detection [*ca.* 2 ms, average $^1J(^{183}W,^{31}P) \approx 230$ Hz] than for ^1H detection (*ca.* 60 ms for couplings in the range 1–10 Hz)[12] and during this time a substantial loss of magnetization via relaxation takes place.

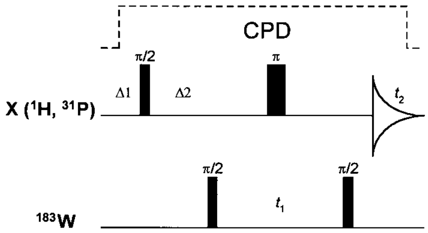

Figure 1. Pulse sequences used in this work, where Δ_1 is the repetition delay and $\Delta_2 = [(2\,{}^nJ(^{183}W,Y)]^{-1}$ ($Y = {}^1H$, ^{31}P, $n \geqslant 1$). ^1H, ^{183}W correlation spectra were obtained by using the standard 2D HMQC pulse sequence. Δ_2 was set to allow the dephasing out of the long-range $^{183}W,^1H$ scalar coupling constants typically 50–100 ms. For $^{183}W,^{31}P$, correlation spectroscopy the pulse sequence included simultaneous proton decoupling (indicated with dashed lines) during the whole experiment. In this case the average $^{183}W,^{31}P$ coupling of 235 Hz affords a Δ_2 value of 2 ms.

On the other hand, the 180° pulse applied during t_1 removes the heteronuclear coupling ^{183}W,X. However, all other possible couplings act as passive couplings,[15] modulating the quantum coherences evolving during this time period, which will produce an additional splitting of the tungsten signal along F_1 and, therefore, a loss of sensitivity. This drawback affects particularly the proton detection scheme because protons show homonuclear $^1H,^1H$ in addition to coupling to phosphorus. Moreover, the ^{183}W will also exhibit a $^{183}W,^{31}P$ passive coupling. Instead, by observing phosphorus the scalar coupling to protons is permanently removed, so that only the homonuclear $^{31}P,^{31}P$ coupling remains, if it exists.

Another limitation of the long-range couplings correlation experiment is in obtaining spectra retaining the metal coupling in F_2. To achieve ^{183}W decoupling during t_2 a refocusing period Δ_2 should be included after the last 90° pulse and the losses of signal intensity may become excessive. Moreover, the refocusing will not be perfect for all coupling constants because the Δ_2 time used is an average value, and therefore signal cancellation may occur. (Recently, it has been claimed[16] that long-range $^1H,^{13}C$ correlation spectroscopy including ^{13}C decoupling during acquisition afford spectra with improved sensitivity respect to the undecoupled experiment.) Consequently, an intensity increase by a factor of *ca.* 2 can be gained with the $^{31}P,^{183}W\{^1H\}$ HMQC pulse sequence *vs.* the $^1H,^{183}W$ HMQC by applying ^{183}W decoupling in the former experiment.

The 2D $^1H,^{183}W$- and $^{31}P,^{183}W\{^1H\}$-HMQC spectra of **3j** acquired in the TPPI[17] mode are given in Fig. 2. The measuring time was 15 min in both cases. Figure 2 also shows the slices taken along the ^{183}W chemical shift for the low-field phosphorus and the olefinic proton in the respective spectra. The calculated signal-to-noise ratio (S/N) from these slices is 32 and 21 for proton and phosphorus-31 observation, respectively. Clearly, without including a ^{183}W decoupling step during acquisition, the sensitivity gain afforded by the $^1H,^{183}W$ long-range correlation is larger by a factor of *ca.* $2^{1/2}$ than that obtained with the phosphorus detection sequence. In any case, the S/N difference between the two detection methods is much less than the approximated factor of 10 predicted by the magnitude of gyromagnetic ratios. Interestingly, the correlation between protons and ^{183}W extends up to the α-protons of the carbocyclic ring, i.e. through $^5J(^{183}W,^1H)$ as deduced by the cross peaks at 2.25 ppm [Fig. 2(a)]. For complex spin systems such as those found in the ^1H

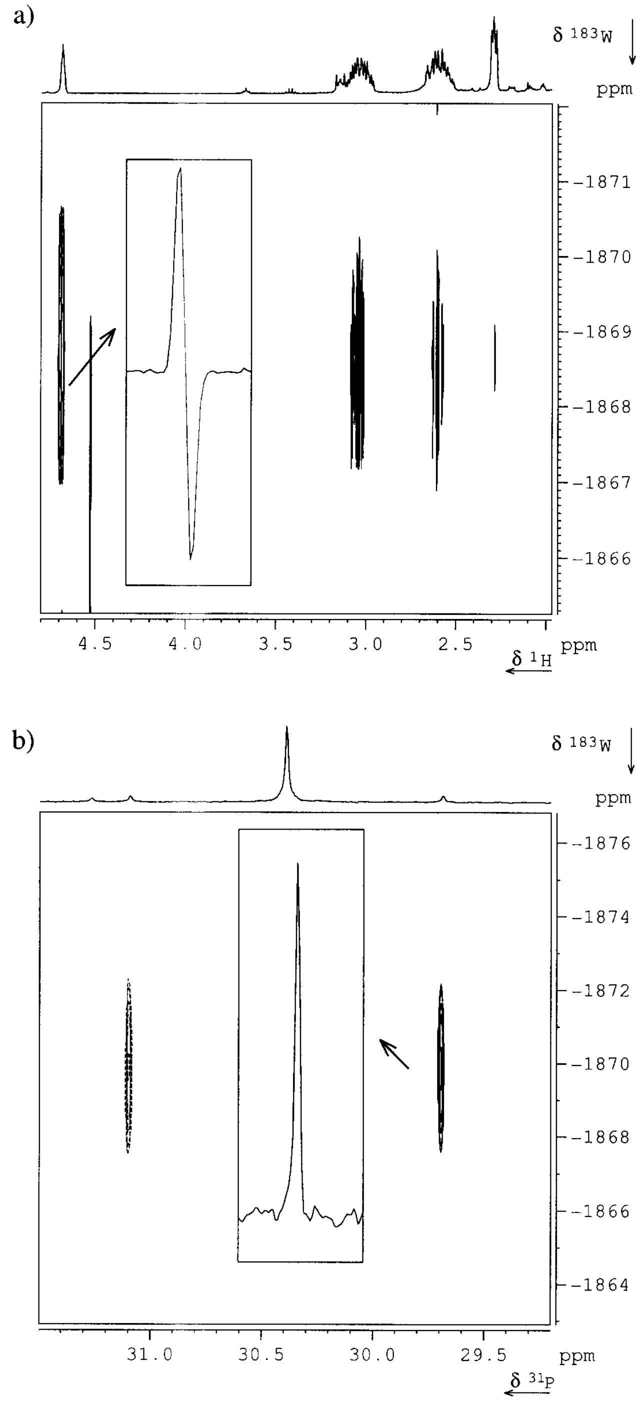

Figure 2. Phase-sensitive (TPPI) 2D (a) ^{1}H,^{183}W- and (b) ^{31}P,^{183}W{^{1}H}-HMQC spectrum of complex **3j**. Negative cross peaks are indicated by dotted lines. In both cases 64 increments of eight scans each were recorded. The sweep widths used were 1600 (^{1}H), 4500 Hz (^{31}P) and 1250 Hz (^{183}W). Final data matrix after zero filling, 1024 × 256. Qsine apodization of factor $\pi/2$ was applied in both dimensions prior to Fourier transformation. The threshold used to observe the cross peak at 2.25 ppm in spectrum (a) is close to the noise level as deduced from the artifact appearing at about 4.5 ppm. The insets are an expansion of the respective rows taken along the ^{183}W chemical shift. From these rows an S/N ratio of 32 and 21 is measured for the proton and phosphorus detected experiments, respectively. F_2 traces show the corresponding one-dimensional ^{1}H and ^{31}P{^{1}H} spectra.

NMR spectrum of **3j**, it may be difficult to correct the phase of the 2D absorption spectrum. One alternative is to obtain the magnitude spectrum. Under these circumstances, the sensitivity of the ^{31}P,^{183}W{^{1}H} experiment recorded in the absorption mode is slightly larger than that observed in the magnitude mode ^{1}H,^{183}W spectrum.

However, the ^{1}H,^{183}W spectrum contains additional information concerning the relative sign of the passive couplings involved in each set of cross peaks (Fig. 3).[10a] Thus, the position of the cross peaks of the olefinic proton at δ 4.68 ppm [Fig. 3(a)] indicates that the ^{1}H low-field cross peak correlates with the ^{183}W high field. Since ^{1}H, ^{31}P and ^{183}W all have a positive gyromagnetic ratio, it follows that $^{4}J(^{31}\mathrm{P},^{1}\mathrm{H})$ is of opposite sign to $^{1}J(^{183}\mathrm{W},^{31}\mathrm{P})$. Taking into account that $^{1}J(^{183}\mathrm{W},^{31}\mathrm{P})$ can be assumed to be positive,[18] then the sign of both passive couplings is determined, i.e. $^{4}J(^{31}\mathrm{P},^{1}\mathrm{H},) < 0$. The passive ^{1}H,^{1}H long-range couplings acting during t_1 are not resolved. Similar arguments apply to the methylene protons α to the phosphorus [Fig. 3(b)], and we again obtain that $^{2}J(^{31}\mathrm{P},^{1}\mathrm{H},) < 0$.[19]

^{183}W NMR spectroscopy of complexes 1–4

^{183}W NMR data for **1**–**4** were obtained by inverse 2D ^{1}H,^{183}W- and/or ^{31}P,^{183}W{^{1}H}-HMQC experiments and are collected in Table 1. We have previously reported ^{183}W chemical shifts for **1a**, **2a**, **2c**, **3c**, **3g**, **3i** and **4a**, and also $^{1}J(^{183}\mathrm{W},^{31}\mathrm{P})$ for complexes **1**–**4**.[8] They have also been included in Table 1 for the sake of comparison. Some complexes present a minor amount of a propenylcarbyne isomer, which is indicated with a prime. The measurements were carried out in CD_2Cl_2 as solvent except for compounds **4**, where benzene was used instead. Solvent effects were analyzed in only two cases. Complex **3c** is deshielded by 10 ppm when the solvent changes from methylene dichloride to benzene. In contrast, **4d** is deshielded by 22 ppm when using methylene dichloride instead of benzene as solvent.

For heavy nuclei the nuclear shielding is determined by the paramagnetic σ_{P} contribution,[20] which in a rough approximation can be expressed by

$$\sigma_{\mathrm{p}} = -\langle r^{-3}\rangle(\Delta E)^{-1}\Sigma Q_{\mathrm{N}} \tag{1}$$

where r represents the distance to the valence d electrons from the ^{183}W nucleus, ΔE is the average electronic excitation energy and ΣQ_{N} is the angular imbalance of charge. For complexes having the same d-electron configuration and symmetry the chemical shift variations can be analyzed in terms of fluctuations in r and/or ΔE. Either a decrease in the d-orbital radius (nephelauxetic effect) or in ΔE (ligand-field effect) will produce a high-frequency shift of δ ^{183}W.

For the series of compounds studied the ^{183}W chemical shift variations are related to: (i) the different type of ligands in the first coordination sphere of the metal (complexes **2** and **3**) and (ii) the effect of the ring size of the carbocyclic moiety in the carbyne and vinylidene

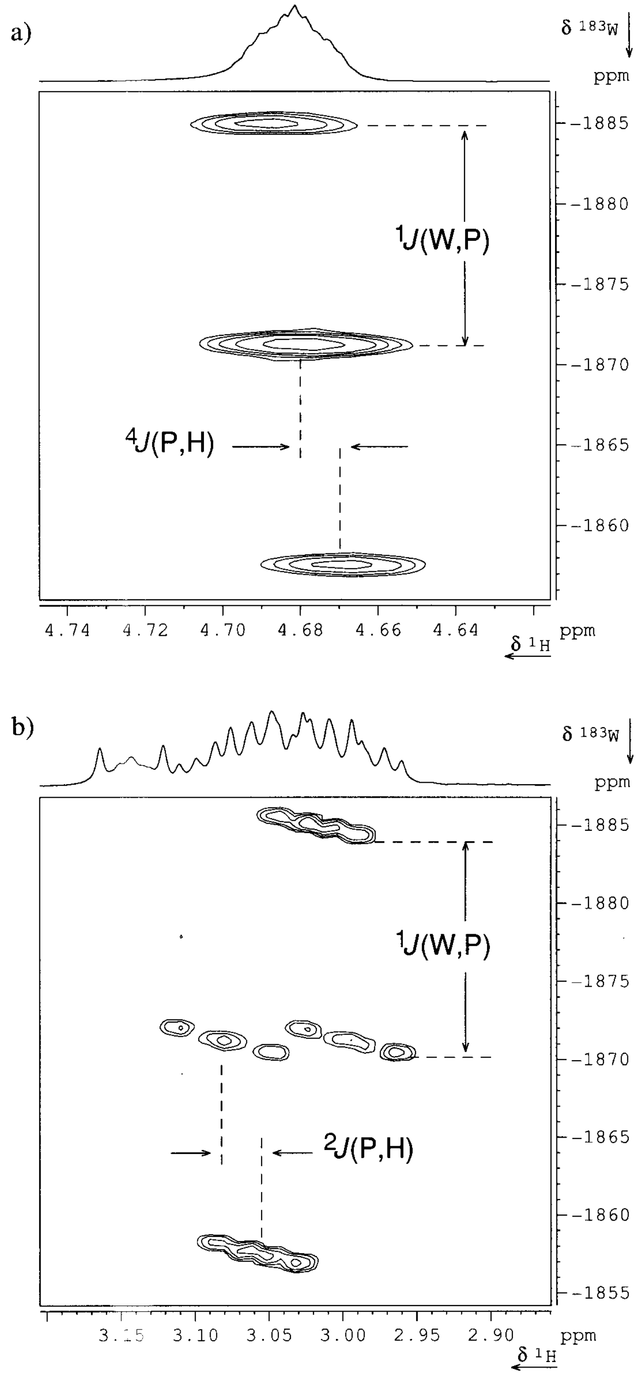

Figure 3. Expansions of the 2D ^{1}H,^{183}W HMQC spectrum of **3j** showing the correlations of (a) the olefinic proton and (b) a pair of methylene protons of the diphosphine ligand. The arrangement of the cross peaks allows to obtain the relative sign of the passive coupling constant involved (see text).

ligands. The first case will be an electronic effect, while the size of the ring may have both steric and electronic influences.

The chemical shifts of complexes **1**–**4** span 1029 ppm. Compounds **3** show a normal halogen dependence, i.e. a decrease in metal shielding with increasing electronegativity I < Br < Cl < F. The effect of the four halogens can be observed for complexes with an alkenylcarbyne ligand containing a eight-membered ring and is shown graphically in Fig. 4. Thus, the replacement of fluorine by chlorine is accompanied by a low-frequency shift of the metal by 156 ppm, the substitution of chlorine by bromine results in a shielding of 47 ppm, while using iodine instead of bromine as ligand promotes an additional displacement of 103 ppm to lower frequencies. The same trends are found in the other series of halogen derivatives with different ring sizes in the carbyne moiety (Table 1). The normal halogen dependence of δ ^{183}W is a common effect in metal NMR, explained by the nephelauxetic effect and, therefore, the dominance of $\langle r^{-3} \rangle$ on σ_p [Eqn (1)].[21] Additionally, it must be kept in mind that the nuclear shielding will also be affected by relativistic effects for the heaviest halogens.[22] The presence of ^{19}F in **3a** and **3b** introduces a passive spin which produces a tilt of the cross peaks. From the negative slope of the line connecting the cross signals, it is concluded that the signs of $^1J(^{183}\mathrm{W},^{19}\mathrm{F})$ and $^2J(^{31}\mathrm{P},^{19}\mathrm{F})$ are opposite.

For the cationic complexes **1** and **2**, ^{183}W shielding increases in the series CH_3CN < PMe_3 < CO (Table 1), correlated with the increasing π-acceptor ability of the ligands, thus implying that σ_p is governed by the ΔE term. A better π-acceptor will increase the HOMO–LUMO gap by lowering the energy of the HOMO via back-bonding. Consequently, ΔE increases and a shift of the metal to low frequencies results (Fig. 5).

In some cases the synthesis of **1**–**3** afforded mixtures of alkenyl- and propenylcarbyne complexes. Generally, the propenyl isomer is the minor component of the mixture. They are marked by adding a prime to the label of the corresponding major compound (Table 1). Their δ ^{183}W show the same type of ligand effects as mentioned for the alkenylcarbyne isomers and are rationalized in the same way.

Finally, we studied the ^{183}W NMR of alkenylvinylidene complexes **4**. The tungsten is found at the high-field edge of the shielding measured for **1**–**4**. Interestingly, the replacement of the conjugated alkenylcarbyne ligand in **1** by a cumulene-type alkenylvinylidene ligand in **4** is accompanied by an average ^{183}W shielding of 384 ppm. According to the above com-

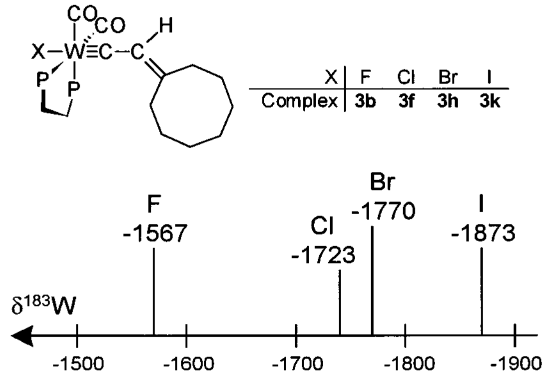

Figure 4. Graphical representation of the 'normal' halogen dependence of δ ^{183}W for selected complexes **3** having an eight-membered ring substituent on the alkenylcarbyne ligand.

Table 1. δ ^{183}W (ppm), δ ^{31}P (ppm) and $^{1}J(^{183}W,^{31}P)$ (Hz) from compounds **1–4**[a]

Compound	L, X	n[b]	δ ^{183}W[c]	δ ^{31}P	$^{1}J(^{183}W,^{31}P)$
1a[d]	—	1	−2218	24.0,[e] 39.8	97.6,[e] 240.0
1a′[d]	—	1	−2262	22.9,[e] 39.9	92.3,[e] 241.0
1b	—	3	−2196	24.1,[e] 39.6	98.5,[e] 240.2
1c	—	4	−2197	24.2,[e] 39.8	98.4,[e] 239.7
1c′	—	4	−2258	22.9,[e] 39.8	91.6,[e] 240.2
2a[d]	MeCN	1	−1786	47.5	233.2
2b	MeCN	4	−1775	47.4	233.1
2b′	MeCN	4	−1872	48.0	238.4
2c[d]	PMe_3	1	−2018	39.8, −55.6[f]	89.6,[f] 228.3
2c′	PMe_3	1	−1944	—[g]	—[g]
2d	PMe_3	4	−2003	39.4, −55.7[f]	91.6,[f] 227.3
2d′	PMe_3	4	−1930	—[g]	—[g]
3a	F	1	−1580	38.6	229.8
3b	F	4	−1567	38.6	228.9
3c[d]	Cl	1	−1739 −1729[h]	39.9	228.1
3c′	Cl	1	−1722	39.8	226.7
3d	Cl	2	−1733	40.0	228.4
3d′	Cl	2	−1694	38.9	—[i]
3e	Cl	3	−1725	39.8	228.1
3f	Cl	4	−1723	39.9	227.8
3g[d]	Br	1	−1786	36.8	228.8
3h	Br	4	−1770	36.7	228.7
3h′	Br	4	−1884	37.4	229.7
3i[d]	I	1	−1891	30.6	228.7
3j	I	3	−1875	30.4	228.6
3k	I	4	−1873	30.3	228.5
4a[d,h]	—	1	−2596	36.9,[j] 46.7	158.5,[j] 241.9
4b[h]	—	3	−2580	37.5,[j] 46.8	160.2,[j] 243.3
4c[h]	—	4	−2589	37.5,[j] 47.2	159.9,[j] 242.7
4d[h]	—	Ph[k]	−2570 −2548[l]	36.5,[j] 46.2	156.0,[j] 242.6

[a] Spectra recorded in CD_2Cl_2 unless stated otherwise.
[b] Carbocyclic ring size (see Scheme 1).
[c] Referred to Na_2WO_4.
[d] Previously published data in Ref. 14.
[e] ^{31}P *trans* to carbyne.
[f] ^{31}P from PMe_3.
[g] Not resolved because signals overlap.
[h] Recorded in C_6D_6.
[i] ^{183}W satellites not visible.
[j] ^{31}P *trans* to vinylidene.
[k] Carbocyclic ring substituted by a phenyl group.
[l] Recorded in CD_2Cl_2.

ments, a better π-acceptor causes a shift to lower δ values by increasing ΔE. Therefore, the low-frequency shift observed reveals a stronger π-acceptor character of the alkenylvinylidene *vs.* the alkenylcarbyne moiety. However, it is worth mentioning that we are comparing a neutral complex with a cationic analogue and consequently the chemical shift differences may vary significantly for complexes with the same charge.

The chemical shift effects discussed so far have been induced by the different electronic properties of the coordinating atom of the ligands used. A second source of ^{183}W chemical shift variations is associated with the size of the carbocyclic ring present in the vinylidene and carbyne ligands. For **2** and **3**, a high-frequency shift takes place with increasing size of the ring. Thus, the series of chloro derivatives **3c**–**f** show an almost steady deshielding of *ca.* 7 ppm per unit of ring size increase [$\Delta\delta$(**3d**–**3c**) = 6 ppm; $\Delta\delta$(**3e**–**3d**) = 8 ppm]. However, the ^{183}W shift differences between the complexes with a ligand of seven- (**3e**) and eight-membered ring (**3f**) are only 2 ppm (Fig. 6). Similar shift differences are found for the bromo **3g** and **h** ($\Delta\delta$ 16 ppm) and iodo compounds **3i**–**k** [$\Delta\delta$(**3j**–**3i**) = 16 ppm; $\Delta\delta$(**3k**–**3j**) = 2 ppm], and also for the cationic complexes **2c** and **d** ($\Delta\delta$ = 15 ppm). Compounds **2a** and **b** are the exception, with a chemical shift increment of only 11 ppm on going from $n = 1$ to 4.

For complexes **1** and **4** the derivatives containing an eight-membered ring are more shielded than the corresponding seven-membered analogues, whereas the

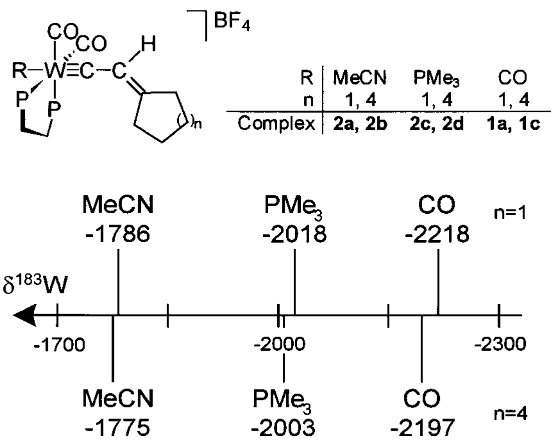

Figure 5. Graphical representation of the ^{183}W shift to lower frequencies with increasing π-acceptor power of the coordinating atom of the ligands.

lowest δ ^{183}W is again observed for the compounds with $n = 1$. The shielding effect of the carbocycle with $n = 1$ *vs.* $n = 4$ is also observed in the series of propenylcarbyne complexes [$\Delta\delta$(**1c**′–**1a**′) = 4 ppm; $\Delta\delta$(**2d**′–**2c**′) = 14 ppm].

The correlation between the tungsten chemical shift and the ring size of the alkenylcarbyne ligand may be explained in terms of electronic and/or steric effects. From the electronic point of view, the empty p-orbitals of the carbyne atom will receive electronic density from two competing sources: the π-electron donation of the substituents on the carbyne and the π-back-donation coming from the metal. A decrease in the π-electron donation ability of a substituent on the carbyne may produce an increase in the metal π-back-donation to the carbyne and, consequently, a shift of δ ^{183}W to lower values should be observed because of the increase in the ΔE term in Eqn (1). In complexes **1**, **2** and **3** the carbyne carbon is conjugated with an exocyclic double bond connected to rings of different size and this may affect the π-electron donation to the carbyne. However, this argument can not be applied to the propenylcarbyne complexes **1a**′, **1c**′ and **2c**′, **2d**′. Here the conjugation is disrupted, but δ ^{183}W shifts again to higher values with increasing size of the ring. These facts suggest that the ^{183}W chemical shift variations as a function of the ring size substituent on the alkenylcarbyne is governed by steric effects. A similar reasoning may be applied to the alkenylvinylidene complexes **4**.

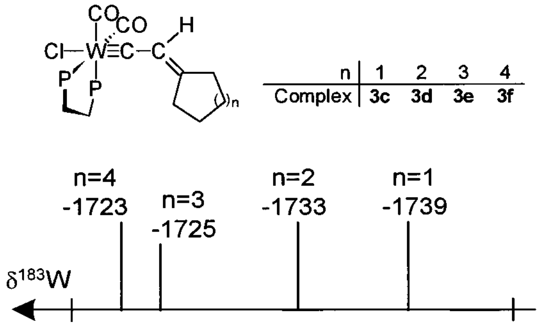

Figure 6. Graphical representation of the ^{183}W shift to higher frequencies with increasing size of the ring substituent on the alkenylcarbyne ligand for the chloro complexes studies.

Steric effects are well documented in the metal NMR bibliography.[3,23] They cause a deshielding of the metal nucleus which may be explained by a larger value of the $\langle r^{-3} \rangle$ term or a lower HOMO–LUMO gap.[24]

Substituents effect on $^1J(^{183}\text{W},^{31}\text{P})$

The ^{183}W,^{31}P scalar coupling in complexes **1**–**4** is insensitive to changes outside the first coordination sphere. Generally, the $^1J(^{183}\text{W},^{31}\text{P})$ variation with increasing size of the carbocyclic moiety of the carbyne and carbene ligands is less than 1 Hz (Table 1). For compounds **1** and **2a** and **b** $^1J(^{183}\text{W},^{31}\text{P})$ increases with increasing shielding of the metal nucleus, which corresponds to an increase in the π-acceptor ability of the coordinating atom of the ligand. However, this effect seems to be reversed within the series of compounds **2** because the higher π-acceptor ligand (PMe$_3$) exhibits lower ^{183}W,^{31}P coupling.

The scalar phosphorus–tungsten coupling constants are dominated by the Fermi contact term:

$$^1J(^{183}\text{W},\ ^{31}\text{P}) \propto \gamma_P \gamma_W \Delta E^1 \,|S(0)|^2{}_P |S(0)|^2_W \,\pi_{PW} \qquad (2)$$

where ΔE is the mean triplet excitation energy, $|S(0)|^2$ represents the s-electron density at the nucleus and π_{PW} denotes the mutual polarizability of the orbitals on phosphorus and tungsten.[25]

An increase in the electron density on the metal will cause (i) a reduction in ΔE and (ii) a reduced affinity of the metal for the remaining ligands leading to a reduction in the Fermi contact term (we thank a referee for suggesting this explanation). The first effect will tend to increase $^1J(^{183}\text{W},^{31}\text{P})$, whereas the second will do the opposite. Because the electron density on the metal is fairly low, ΔE will be large and changes in ΔE caused by exchange of ligands will be relatively small when expressed as a fraction of ΔE. In such a case the overall effect will be dominated by the decrease in the Fermi contact term leading to a decrease in $^1J(^{183}\text{W},^{31}\text{P})$ in the sequence CO > CH$_3$CN > PMe$_3$ (CH$_3$CN is a good σ-donor, CO is a good π-acceptor, PMe$_3$ exhibits both characters), as is observed experimentally. Additionally, the larger size of the trimethylphosphine ligand[23b,c] compared with acetonitrile would also produce a weakening of the phosphorus–metal bond, so that a contribution of the steric crowding to the decrease in $^1J(^{183}\text{W},^{31}\text{P})$ in **2c** and **d** *vs.* **2a** and **b** cannot be excluded.

CONCLUSIONS

We have shown that proton detection of ^{183}W through long-range coupling affords a S/N slightly superior to that of phosphorus detection of the metal via $^1J(^{183}\text{W},^{31}\text{P})$. Additionally ^{1}H,^{183}W correlation spectra of tungsten complexes containing phosphine and fluorine ligands also allow one to extract the relative sign of couplings to passive spins. Thus, $^1J(^{183}\text{W},^{31}\text{P})$ is of opposite sign to $^2J(^{31}\text{P},^1\text{H})$ and $^4J(^{31}\text{P},^1\text{H})$. For complexes **3a** and **b**, $^1J(^{183}\text{W},^{19}\text{F})$ and $^2J(^{31}\text{P},^{19}\text{F})$ are also of opposite sign. Metal chemical shift variations measured within series of structurally related complexes are explained by the influence on σ_p of the ligands coordinated to the metal: δ ^{183}W shift to larger (less negative) values with decreasing π-acceptor power of the ligand L ($\text{CO} < \text{PMe}_3 < \text{CH}_3\text{CN}$) for complexes $[(\text{dppe})(\text{CO})_2\text{LW}{\equiv}\text{C}{-}\text{CH}{=}\text{CR}_2]$ **1** and **2** (ΔE dominance), and with increasing electronegativity for the halogen derivatives **3** (nephelauxetic effect, radial term dominance). The increase in the size of the carbocyclic ring bonded to the carbyne and vinylidene moieties produces a deshielding of the metal nucleus, an effect ascribed to steric crowding. However, for complexes **1b** and **c** and **4b** and **c** this trend is reversed. The differences in ^{183}W,^{31}P couplings for the dppe ligand in complexes **1** and **2** have been explained by a combination of electronic and steric effects.

EXPERIMENTAL

Compounds

Samples were prepared using previously dried and degassed CD_2Cl_2 as solvent (unless stated otherwise) and working under a nitrogen atmosphere to prevent decomposition of the organometallic complexes. The average sample concentration was *ca.* 40–160 mg ml^{-1}, depending on availability. The measurement temperature was 298 K. Compounds **1**–**4** were prepared according to previously described methods and the conventional spectral data have been reported,[8] except for complexes **3a** and **b**, $[(\text{dppe})(\text{CO})_2\text{FW}{\equiv}\text{C}{-}\text{CH}{=}\text{C}{-}\overline{\text{CH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2}]$, which are as follows.

***n* = 1 (3a).** Yield 75%. IR [CH_2Cl_2, cm^{-1}, ν(CO)]: 1991 (vs), 1919 (vs). ^{1}H NMR (δ, ppm): 1.34 (m, 4H, 2CH_2), 1.72 (m, 2H, CH_2), 1.81 (m, 2H, CH_2), 2.61 (m, 2H, $\text{P}(\text{C}H_a\text{H}_b)_2\text{P}$), 2.67 [m, 2H, $\text{P}(\text{CH}_a H_b)_2\text{P}$], 4.69 (s, 1H, C_βH), 7.36–7.77 (m, 20H, PPh_2). ^{13}C NMR (δ, ppm): 25.6 (s, CH_2), 26.1 (s, CH_2), 27.8 [m, $\text{P}(\text{CH}_2)_2\text{P}$], 30.6 (s, CH_2), 33.7 (s, CH_2), 128.2–135.5 (m, PPh_2), 129.9 [d, $^3J(\text{F,C}) = 5.8$ Hz, C_β], 159.6 (m, C_γ), 215.3 (m, 2 *cis* CO), 274.4 [dt, $^2J(\text{F,C}) = 106.8$, $^2J(\text{P,C}) = 8.1$ Hz, C_α]. ^{19}F NMR (δ, ppm): −294.4 [t, $^2J(\text{P,F}) = 47.5$, $^1J(\text{W,F}) = 44.8$ Hz]. ^{31}P NMR (δ, ppm): 38.2 [d, $^2J(\text{P,F}) = 47.5$, $^1J(\text{W,P}) = 229.8$ Hz].

***n* = 4 (3d).** Yield 87%. IR [CH_2Cl_2, cm^{-1}, ν(CO)]: 1990 (vs), 1919 (vs). ^{1}H NMR (δ, ppm): 1.30 (m, 6H, 2CH_2), 1.37 (m, 2H, CH_2), 1.54 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 2.06 (m, 2H, CH_2), 2.61 [m, 2H, $\text{P}(\text{C}H_a\text{H}_b)_2\text{P}$], 2.67 [m, 2H, $\text{P}(\text{CH}_a H_b)_2\text{P}$], 4.43 (s, 1H, C_βH), 7.36–7.78 (m, 20H, PPh_2). ^{13}C NMR (δ, ppm): 25.6 (s, CH_2), 26.5 (s, CH_2), 26.7 (s, CH_2), 27.0 (s, CH_2), 27.2 (s, CH_2), 27.8 [m, $\text{P}(\text{CH}_2)_2\text{P}$], 30.9 (s, CH_2), 35.4 (s, CH_2), 128.3–135.4 (m, PPh_2), 135.1 [d, $^3J(\text{F,C}) = 6.4$ Hz, C_β], 157.5 (m, C_γ), 215.5 (m, 2 *cis* CO), 274.4 [dt, $^2J(\text{F,C}) = 109.0$, $^2J(\text{P,C}) = 9.0$ Hz, C_α]. ^{19}F NMR (δ, ppm): −294.7 [t, $^2J(\text{P,F}) = 47.5$, $^1J(\text{W,F}) = 52.0$ Hz]. ^{31}P NMR (δ, ppm): 38.7 [d, $^2J(\text{P,F}) = 47.5$, $^1J(\text{W,P}) = 228.9$ Hz].

NMR spectra

NMR spectra were measured on a Bruker AMX 400 spectrometer. The instrument was equipped with a third radiofrequency channel. A 5 mm reverse triple probe head was used. The inner coil was doubly tuned for ^{1}H and ^{31}P and the outer coil was tunable in the frequency range 18–162 MHz. The ^{183}W nucleus lies outside this frequency range, but it could be tuned without major difficulties. The pulse widths for the 90° pulses and operating frequencies were as follows: 10.4 μs (^{1}H, 400.13 MHz), 14.5 μs (^{31}P, 161.98 MHz) and 53 μs (^{183}W, 16.65 MHz). The attenuation levels used were 5 dB for the proton channel and 3 dB for the heteronuclei. The spectral references used were tetramethylsilane for ^{1}H, 85% H_3PO_4 for ^{31}P and Na_2WO_4 for ^{183}W.

Selected spectral parameters in the AMX 400 spectrometer were as follows. One-dimensional ^{1}H NMR: 32K data points; spectral width 4000 Hz. ^{31}P NMR: 32K data points; spectral width, 3500 Hz; exponential line broadening of 1 Hz. ^{1}H,^{183}W 2D HMQC: spectral width, 4000 Hz in F_2 and 1000 Hz in F_1; 96 increments recorded; final matrix after zero filling, 1024×256; evolution delay of $^nJ(^{183}\text{W},^1\text{H})$ ($n > 1$), 60 ms; 16 scans per increment in F_1. ^{31}P,^{183}W{^{1}H} 2D HMQC: spectral width, 3500 Hz in F_2 and 1000 Hz in F_1; 96 increments recorded; final matrix after zero filling, 1024×256; evolution delay of $^1J(^{183}\text{W},^{31}\text{P})$, 2.2 ms; 80 scans per increment in F_1. In both cases spectra were recorded in the TPPI mode and a qsine multiplication of $\pi/2$ was applied in both dimensions prior to transformation. The correct ^{183}W chemical shift was found by acquiring a first experiment with a large sweep width in F_1 and a short number of t_1 increments. Subsequently, the spectral window of the tungsten nucleus was shifted and reduced to 1000 Hz according to the first value observed to ensure that no folding in the F_1 dimension occurred and to improve the accuracy of the chemical shift obtained.

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