Photochemical Synthesis and Reactivity of New Chloro-Bridged Complexes with Tungstenocene (η^5-C_5H_5)(η^5-$C_5H_4PPh_2$)WClX (X = H, Cl) and Tetracarbonylmetal (Cr, W) Units

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Chloro-bridged bimetallic complexes (η^5-C_5H_5)[η^5-$C_5H_4PPh_2M'(CO)_4$]W(μ-Cl)X [X = Cl (**3**), X = H (**4**); M′ = Cr, W] were prepared by photochemical irradiation of (η^5-C_5H_5)[η^5-$C_5H_4PPh_2M'(CO)_5$]WClX [X = Cl (**1**), X = H (**2**); M′ = Cr, W]. The reactivity of the chloro-bridged complexes towards Lewis bases was studied; by exposure to CO or phosphanes, a facile cleavage of the chloro bridge accompanied by regio- and stereospecific coordination at M′ occurs. The X-ray structure of complex **3** (M′ = W) is reported.

Introduction

We have recently reported that on treatment of the bent molybdocene and tungstenocene dichlorides with the metallophosphide anions $[PPh_2M'(CO)_x]^-$ (M′ = Cr, Mo, W), nucleophilic S_N2' substitution on one cyclopentadienyl Cp ring occurs.[1] This unexpected reaction offers the possibility of synthesizing various heterobimetallic systems by changing either the metal of the metallophosphide anion (M′) or that of the metallocene dichloride (M = Mo, W). Also in this field, we have observed that compounds with some interesting structures may be obtained by linking the two metallic units by an orthometallation reaction or by the formation of a hydride bridge.[2] The latter μ-H bimetallic cyclic complexes are prepared by UV irradiation of the corresponding terminal dihydrido precursors. They react with CO and phosphanes with concomitant cleavage of the hydride bridge.[3] Our ongoing interest in this area has led us to investigate the behavior of related chloro-hydrido complexes, with emphasis on the nature of the products obtained upon their photolysis. The present paper deals with the tungstenocene derivatives.

Results and Discussion

Chloro-Bridged Complexes

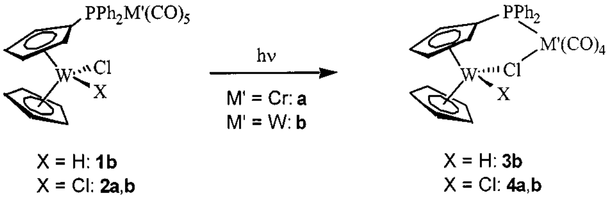
The two starting complexes **1** and **2** (Scheme 1) were prepared as reported previously.[2a] Thus, **1a**,**b** were prepared from Cp_2WCl_2 and $[PPh_2M'(CO)_5]^-$ (M′ = Cr, W) while the corresponding dichloro derivatives **2** were obtained by treatment of **1** with CCl_4.

UV irradiation of **1b** results in the formation of the chloro-bridged complex **3b** (Scheme 2). However, analogous treatment of the chromium derivative **1a** does not allow the isolation of defined products.

$$Cp_2WCl_2 \xrightarrow{[PPh_2M'(CO)_5]^-} \underset{\mathbf{1}}{CpCp'WHCl} \xrightarrow{CCl_4} \underset{\mathbf{2}}{CpCp'WCl_2}$$

$Cp' = C_5H_4PPh_2M'(CO)_5$ M′ = Cr: **a**
M′ = W: **b**

Scheme 1



Scheme 2

Spectroscopic data for the tungsten complex are supportive of the μ-chloro structure **3b**. The CO absorption pattern is typical of an $M'(CO)_4$ fragment (four CO stretching bands), while the ^{1}H-NMR spectrum features a hydride resonance at $\delta = -12.3$ (the signal is found at $\delta = -10.7$ in the precursor **1b**). This suggests that the tungstenocene hydride does not interact with the $W(CO)_4$ fragment and therefore behaves as a terminal ligand. The ^{31}P resonance is shifted downfield with respect to that in **1b** ($\Delta\delta$ = 43 ppm). Such a deshielding may indicate some steric strain on the phosphorus atom due to the formation of the cyclic structure.[4]

Dichlorides **2** may also be transformed to chloro-bridged species by photochemical means (**4**). In contrast to compounds **1**, this reaction works for both M′ = Cr and W. The CO absorption pattern is consistent with an $M'(CO)_4$ chromophore with approximate C_{2v} symmetry. The absorptions are observed at nearly the same frequencies for **3b** and **4b** (mean values are only 5 cm^{-1} lower for **3b** than for **4b**), indicating that the substitution of the terminal H by Cl has little or no effect on the electron density within the $W(CO)_4$ fragment. It is worth noting that $\tilde{\nu}$(CO) frequencies re-

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corded for our $(P)(Cl)W(CO)_4$ units are lower than those reported for diphosphane derivatives $(P)_2W(CO)_4$.[5] In particular, the lowest energy B_2 band (assuming C_{2v} symmetry) is shifted by 40−50 cm^{-1}. This indicates that the chloride bridge behaves as a weaker π-acceptor than the phosphane ligand. Note, however, that the values observed for **3b** and **4b** are close to those reported for dibridged complexes $Cp_2M(\mu\text{-}PPh_2,H)M'(CO)_4$ ($MPPh_2$ instead of a $CpPPh_2$ bridge),[6] but are higher than those reported for a trinuclear complex with mono-bridged bimetallic units $[Cp_2MoH(\mu\text{-}PMe_2)]_2W(CO)_4$ (1976, 1901, 1859, and 1811 cm^{-1})[7] or for an electron-rich anion $[W(CO)_4(PPh\mathit{i}Pr_2)Cl]^-$ (1997, 1869, 1857, and 1812 cm^{-1}).[8] ^{31}P resonances for **4a** and **4b** are shifted to lower fields with respect to those of the parent compounds (Δδ = 30 ppm, M′ = Cr; Δδ = 48 ppm, M′ = W). Once again, the observed deshieldings can be attributed to steric strain on the phosphorus atom.

In order to unambiguously establish that complex **3b** contains a chloride bridge, its molecular structure was determined by X-ray diffraction analysis. Suitable crystals for this study were grown from acetone solution. The crystal structure of **3b** is built up by dinuclear organometallic molecules, in which each metal center retains its typical pseudo-tetrahedral (W2) and pseudo-octahedral (W1) geometry (Figure 1). The two metallic fragments are linked through $C_5H_4PPh_2$ and Cl bridges without direct metal−metal interaction, thus forming a formally five-membered ring. The W1−W2 separation amounts to 4.2611(8) Å (Table 1). Such a separation roughly corresponds to the metal−metal distances observed in mono-bridged one-atom μ-phosphido complexes, e.g. 4.39 Å in $Cp_2MoH(\mu\text{-}PPh_2)Mn(CO)_2Cp$[9] and 4.56 Å in $[Cp_2MoH(\mu\text{-}PMe_2)]_2W(CO)_4$,[7] but is ca. 1 Å longer than the W−W distance (3.27 Å) reported for a dibridged $Cp_2W(\mu\text{-}PPh_2,\mu\text{-}H)W(CO)_4$ complex containing a four-membered central ring.[6] The longest metal−metal distance (4.78 Å) in complexes with a metallocene fragment has been reported for the dibridged compound $Cp_2Nb(\mu\text{-}PPh_2,dmpm)Mo(CO)_4$, which has a six-membered central ring.[10] Consequently, the size of the central bridging ring determines the metal−metal distance for complexes without a metal−metal bond.

The refined terminal hydride is found at a typical distance of 1.8(1) Å from the W2 atom. The W1−P bond length of 2.527(3) Å is of little diagnostic value as the W−P distances in $W(CO)_4P$ fragments fall in a rather large range from 2.49 to 2.60 Å.[11] The most similar W−P distances are found in the pentacarbonyl compounds $W(CO)_5PMe_3$ (2.52 Å)[12] and $W(CO)_5PPh_3$ (2.54 Å),[13] the tetracarbonyl compound $[W(CO)_4PEt_3]_2(\mu\text{-}NCC_6H_4CN)$ (2.53 Å),[14] as well as in the tetracarbonyl anions $[W(CO)_4(PR_3)X]^-$ (X = Cl, OAc, OPh and Me) where the W−P bond lengths are close to 2.53−2.54 Å.[15] It can be noted (Table 1) that the $W1^0$−Cl bond [2.593(3) Å] is longer than the $W2^{IV}$−Cl one [2.484(3) Å], a difference which is a priori due to the different covalent radii of W^0 and W^{IV}. The tungstenocene−chloride bond length is close to that reported for Cp_2MoCl_2 (2.47 Å),[16] but is larger than the values reported for the terminal M−Cl bonds in the related $[CpPPh_2Cr(CO)_5]_2W(H)Cl$ [structural model $Cp_2W(H)Cl$, W−Cl = 2.408(4) Å][3] and in *ortho*-metallated $Cp[CpPPh_2Cr(CO)_5]Mo(Cl)$ [structural model $Cp_2Mo(C)Cl$, Mo−Cl = 2.476(2) Å].[2c] Thus, the W2−Cl bond in **3b** may be considered as remaining strong with little perturbation resulting from coordination to the second W1 atom. Consequently, the W1−Cl bond [2.593(3) Å] has to be regarded as being rather long and weak. A search of the Cambridge Structural Database for $W(CO)_4Cl$ structures yielded only 8 entries. The structures of $(CO)_4W(\mu\text{-}Cl)_3W(CO)_3SnCl_3$ (heptacoordinated W, bridging chlorides) (W−Cl = 2.52 Å, W−Cl−W = 89°)[17] and $Cl(CO)_4WC(C_6H_5)Cr(CO)_3$ (W−Cl = 2.48 Å),[18] as well as those of the anionic species $[W(CO)_5Cl]^-$ (W−Cl = 2.56 Å)[19] and $[W(CO)_4(PMePh_2)Cl]^-$ (W−Cl = 2.58 Å)[15a] are indicative of a weak W1−Cl bond.

Table 1. Selected bond lengths [Å] and angles [°] for **3b**

	Bond length [Å]		Bond angle [°]
W(1)−W(2)	4.2611(8)	CP1−W(2)−CP2[a]	143.5
W(2)−Cl	2.484(3)	H−W(2)−Cl	79(5)
W(2)−H	1.78(15)	W(2)−Cl−W(1)	114.1(1)
W(2)−CP1	1.942	C(1)−W(1)−C(2)	87.2(6)
W(2)−CP2	1.950	C(1)−W(1)−C(4)	88.0(7)
W(1)−P	2.527(3)	C(2)−W(1)−C(4)	88.4(5)
W(1)−Cl	2.593(3)	C(1)−W(1)−C(3)	90.3(5)
W(1)−C(1)	1.919(13)	C(2)−W(1)−C(3)	87.7(5)
W(1)−C(2)	1.983(13)	C(4)−W(1)−C(3)	175.9(5)
W(1)−C(3)	2.036(12)	C(1)−W(1)−P	96.5(4)
W(1)−C(4)	2.004(14)	C(2)−W(1)−P	174.1(4)
P−C(5)	1.793(11)	C(4)−W(1)−P	96.3(4)
P−C(21)	1.832(10)	C(3)−W(1)−P	87.6(3)
P−C(15)	1.846(10)	C(1)−W(1)−Cl	176.2(4)
C(1)−O(1)	1.16(2)	C(2)−W(1)−Cl	89.0(4)
C(2)−O(2)	1.14(2)	C(4)−W(1)−Cl	92.4(5)
C(3)−O(3)	1.135(14)	C(3)−W(1)−Cl	89.0(3)
C(4)−O(4)	1.15(2)	P−W(1)−Cl	87.17(9)

[a] CP1 and CP2 are the centroïds of the C(5)−C(9) and C(10)−C(14) rings.

Reactions of Bridged Complexes with CO and Phosphanes

We have examined the reactivity of the two kinds of chloro-bridged compounds **3** and **4** towards CO and phosphanes, and, for a comparative study, we also carried out similar experiments with the previously reported μ-hydrido complex **5**.[2a] Addition of Lewis bases is regiospecific and occurs in all cases at the M′ metal center. Bubbling of CO through a THF solution of **3b**, **4b** or **5b** leads to the recovery of their precursors **1b**, **2b** and **6b** in high yields (Scheme 3).

Reactions of phosphanes with the chloro derivatives **3b** and **4b** proceed rapidly. With PMe_3 and PPhH, only the *cis* isomer is formed, whereas a *cis*/*trans* mixture (ratio 30:70) is obtained when the bulkier triphenylphosphane is used. Thus, the stereochemical course of the ring-opening reaction depends on steric hindrance to the incoming ligands (the cone angles for PMe_3, PPh_2H and PPh_3 are 118°, 126°

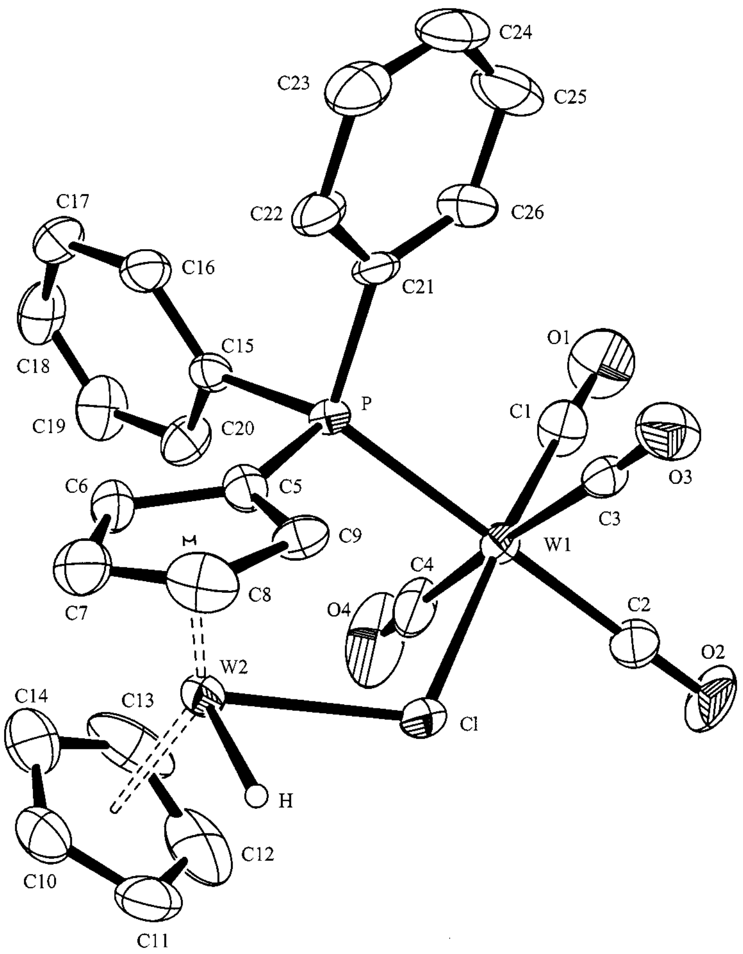
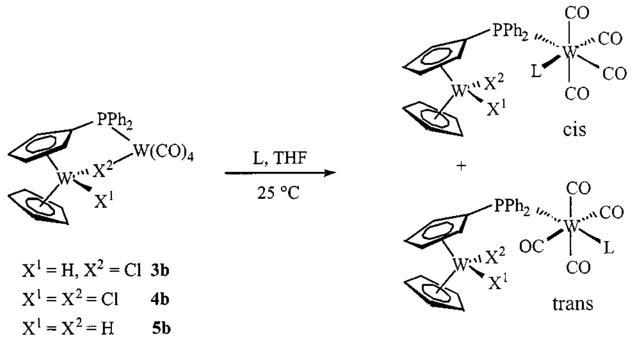


Figure 1. ORTEP view of **3b** (30% probability level)



$X^1 = H, X^2 = Cl$ **3b**
$X^1 = X^2 = Cl$ **4b**
$X^1 = X^2 = H$ **5b**

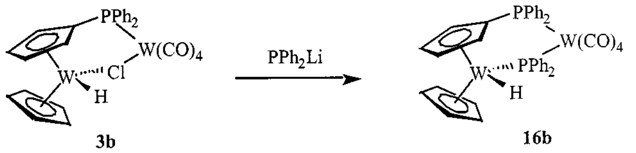
	$X^1 = H$ $X^2 = Cl$	$X^1 = Cl$ $X^2 = Cl$	$X^1 = H$ $X^2 = H$
CO	**1b**	**2b**	**6b**
PMe_3	**7b**	**10b**	**13b**
PPh_2H	**8b**	**11b**	**14b**
PPh_3	**9b**	**12b**	**15b**

Scheme 3

and 145°, respectively).[20] Moreover, the size of the M′ metal ion also seems to play a crucial role in determining the coordination site. The tungsten derivative **3b** furnishes exclusively the *cis* isomer when treated with PMe_3, whereas we have mentioned in a previous paper[3] that its chromium analogue **5a** gives a mixture of *trans* and *cis* isomers in an 80:20 ratio. We have also observed that a longer reaction time or heating is needed in order to achieve cleavage of the hydride bridge in **5b**. The more severe conditions required indicate a greater stability of the M−H−M′ linkage (stronger H−M′ bond) in the μ-H bridged compound **5b** compared to the M−Cl−M′ linkage (weaker Cl−M′ bond). The rather long W1−Cl bond found for **3b** (vide supra) supports this idea. The kinetic nature of the *cis* stereoisomer[21] is confirmed by the isomerization that occurs upon prolonged standing in solution. Thus, the *cis* complex **7b** gives a 70:30 *trans*/*cis* mixture, for example, after 4 h in THF solution. The *cis* and *trans* assignments were made on the basis of IR and ^{31}P-NMR data. Thus, the presence of one or four CO absorptions characterizes a *trans* (D_{4h}) or a *cis* (C_{2v}) arrangement about the M′ metal center. In ^{31}P-NMR spectroscopy, both the chemical shifts and the *J* values are indicative of the mutual position of the two phosphane ligands. A *cis* configuration results in a more shielded resonance of the bridging phosphido group, together with the observation of a smaller $^2J_{pp}$ value (*cis* $^2J_{pp} = 20$ Hz vs. *trans* $^2J_{pp} = 50$ Hz).[22]

Reactions of μ-Chloro Complexes with PPh_2^-

We envisaged that the bridge-opening reaction described above might allow a chloride substitution reaction by treating the μ-chloro complexes with the anionic species $[PPh_2]^-$. The reaction did not proceed starting from the dichloro compound **4b**, but proceeded as expected from the monochloride monohydride **3b** affording the diphosphido complex **16b** together with a small amount of **8b**. Chromatographic purification led to the isolation of **16b** in pure form (Scheme 4).



Scheme 4

The hydride resonance for **16b** is seen as a double doublet ($^2J_{PH}$ = 18.5 Hz and $^4J_{PH}$ = 5 Hz) at δ = −10.3, while the ^{31}P-NMR spectrum displays two well-defined doublets ($^2J_{PP}$ = 20 Hz) located at δ = 38.5 and −27.2, respectively. The *J* value is indicative of the *cis* configuration (vide supra) and the shielded resonance corresponds to the nucleus of a W−P−W phosphido bridge.

We have already discussed the dependence of the ^{31}P chemical shifts in phosphido-bridged bimetallic systems on the M−P−M′ angle.[6] The chemical shift observed for **16b** can be compared with those of related phosphido-bridged complexes, in particular with those displayed by monobridged M(μ-P)M′ and by dibridged M(μ-P, μ-H)M′ and M(μ-P, μ-Cl)M′ structures.[23] The former are structures with relatively open M−P−M′ angles (about 125°) and the ^{31}P resonance signals lie at high field in the range δ = −60 to −65 for tungsten compounds. The latter contain a bimetallic cyclic framework with a small M−P−M′ angle value (about 80°), which results in a ^{31}P resonance deshielding by more than 100 ppm.[24] In the complex **16b**, the W−P−W linkage forms part of a pseudo five-membered ring with relatively little angle strain, which accounts for the smaller deshielding compared to those seen in four-membered M(μ-P, μ-H)M′ or M(μ-P, μ-Cl)M′ cyclic frameworks.

Conclusion

In conclusion, chloro-bridged bimetallic complexes **3** and **4** have been synthesized by photochemical irradiation. It is interesting to note that the reaction proceeds equally well when dichloro compound **1** or monochloro-monohydrido compound **2** are used. We have also shown that the chloro bridges are cleaved in a regio- and stereospecific manner when the μ-chloro complexes are exposed to two-electron donor ligands.

Experimental Section

General Comments: All reactions were carried out under purified argon. The solvents and eluents were dried by appropriate procedures and distilled under argon from sodium/benzophenone immediately prior to use. Standard Schlenk techniques and conventional glass vessels were employed. − Column chromatography was performed under argon on silica gel (70−230 mesh). − Elemental analyses were carried out with a Fisons Instruments EA 1108 CHNS-O apparatus. − Electron ionization mass spectra were recorded with a Kratos Concept 32S spectrometer. − ^{1}H- and ^{31}P-NMR spectra were recorded with a Bruker AC 200 spectrometer. Chemical shifts are quoted relative to internal TMS (^{1}H) or external H_3PO_4 (^{31}P). − IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. − The complexes (η^5-C_5H_5)[η^5-C_5H_4-$PPh_2M'(CO)_5$]W(H)(Cl) (**1**), (η^5-C_5H_5)[η^5-C_5H_4-$PPh_2M'(CO)_5$]-WCl_2 (**2**), and (η^5-C_5H_5)[η^5-C_5H_4-$PPh_2M'(CO)_4$]W(H)(μ-H) (**5**) (M′ = Cr, W) were prepared according to literature procedures;[2a,3] PMe_3 and PPh_3 (Strem) were used as received. PPh_2H was prepared according to a literature method[25] and PPh_2Li was prepared from PPh_2H and butyllithium.

(η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_4$]W(H)(μ-Cl) (3b): A solution of (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_5$]W(H)(Cl) (**1b**) (1.7 g, 2 mmol) in THF (100 mL) was irradiated with a Hanau TQ 150 lamp for 2 h at room temperature. The solvent was then removed in vacuo, and the residue was washed with 40 mL of pentane and chromatographed (toluene/THF, 1:1). **3b** was obtained as red crystals by recrystallization from acetone; yield 1.0 g (60%). − IR (THF): $\tilde{\nu}_{CO}$ = 2013 (m), 1901 (s), 1882 (s), 1844 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = −12.35 (br., 1 H, W−H), 4.28 (m, 1 H, C_5H_4), 4.38 (m, 1 H, C_5H_4), 4.61 (m, 1 H, C_5H_4), 4.90 (s, 5 H, C_5H_5), 6.42 (m, 1 H, C_5H_4), 7.39−7.50 (m, 6 H, C_6H_5), 7.71−7.92 (m, 4 H, C_6H_5). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 55.5 (br.). − $C_{26}H_{20}ClO_4PW_2$ (830.6): calcd. C 37.60, H 2.43; found C 37.33, H 2.29.

(η^5-C_5H_5)[η^5-C_5H_4−$PPh_2M'(CO)_4$]W(Cl)(μ-Cl) (4): Complexes **4a** and **4b** were obtained according to the same procedure as described above for **3b**, except that (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2M'(CO)_5$]WCl_2 **2** (0.5 mmol) was used. The crude product was chromatographed on silanized silica (chloroform) to afford **4a** (220 mg, 60%) and **4b** (215 mg, 50%) as green crystals after recrystallization from chloroform. − (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2Cr(CO)_4$]W(Cl)(μ-Cl) (4a): IR (THF): ($\tilde{\nu}_{CO}$ = 2011 (m), 1913 (s), 1888 (s), 1854 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 4.07 (m, 1 H, C_5H_4), 5.45 (s, 5 H, C_5H_5), 5.51 (m, 2 H, C_5H_4), 6.61 (m, 1 H, C_5H_4), 7.35−7.50 (m, 6 H, C_6H_5), 7.56−7.88 (m, 4 H, C_6H_5). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 82 (s). − $C_{26}H_{19}Cl_2CrO_4PW$ (733.2): calcd. C 42.59, H 2.61; found C 42.14, H 2.73. − (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_4$]W(Cl)(μ-Cl) (4b): IR (THF): $\tilde{\nu}_{CO}$ = 2015 (m), 1909 (s), 1885 (s), 1849 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.99 (m, 1 H, C_5H_4), 5.43 (s, 5 H, C_5H_5), 5.51 (m, 1 H, C_5H_4), 5.87 (m, 1 H, C_5H_4), 6.63 (m, 1 H, C_5H_4), 7.41−7.64 (m, 6 H, C_6H_5), 7.70−7.88 (m, 4 H, C_6H_5). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 62.08 (s + d, J_{WP} = 262 Hz). − $C_{26}H_{19}Cl_2O_4PW_2$ (865.02): calcd. C 36.10, H 2.21; found C 36.01, H 2.22.

Synthesis of (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_5$]W(X^1)(X^2) (X^1 = H, X^2 = H, Cl; X^1 = X^2 = Cl): At 50°C, 0.5 mmol of (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_4$]W(X^1)(μ-X^2) (**3b**, **4b** or **5b**) was stirred in THF (20 mL) under carbon monoxide for 2 h. The solvent was then removed under reduced pressure, and the mono-bridged complex (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_5$]W(X_1)(X_2) (**1b**, **2b** or **6b**)[2a] was isolated.

Synthesis of (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_4$(L)]W(H)(Cl) (L = PMe_3, PPh_2H, PPh_3): To a solution of **3b** (200 mg, 0.25 mmol) in THF (20 mL) was added 1 equiv. of the appropriate phosphane and the resulting mixture was stirred at room temperature for 2 h. The solvent was then removed, and the crude product was washed with pentane (3 × 20 mL). All attempts to recrystallize the complexes resulted in their decomposition.

$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(PMe_3)]W(H)(Cl)$ (7b): The reaction afforded purely the *cis* isomer **7b**, which was obtained as an orange powder in 60% yield (140 mg). After redissolution of this product in THF and stirring at room temperature, small amounts of the *trans* isomer could be detected. − ***cis*** **Isomer 7b:** IR (THF): $\tilde{\nu}_{CO}$ = 2013 (m), 1906 (s), 1892 (s), 1872 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = −10.68 (s + d, $^1J_{WH}$ = 60 Hz, 1 H, W−H), 1.16 (d, $^2J_{PH}$ = 7.4 Hz, 9 H, Me), 4.19 (m, 1 H, C_5H_4), 4.58 (m, 1 H, C_5H_4), 4.79 (s, 5 H, C_5H_5), 5.09 (m, 1 H, C_5H_4), 5.75 (m, 1 H, C_5H_4), 7.29−7.43 (m, 6 H, C_6H_5), 7.53−7.62 (m, 4 H, C_6H_5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −41.9 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ = 216 Hz, PMe_3), 16.30 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ = 246 Hz, PPh_2). − $C_{29}H_{29}ClO_4P_2W_2$ (906.65): calcd. C 38.42, H 3.22; found C 38.86, H 3.60. − ***trans*** **Isomer 7b:** IR (THF): $\tilde{\nu}_{CO}$ = 1882 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = −10.66 (s + d, $^1J_{WH}$ = 60 Hz, 1 H, W−H), 1.27 (d, $^2J_{PH}$ = 7.4 Hz, 9 H, PMe), 3.25 (m, 1 H, C_5H_4), 4.15 (m, 1 H, C_5H_4), 4.72 (s, 5 H, C_5H_5), 5.19 (m, 1 H, C_5H_4), 6.03 (m, 1 H, C_5H_4), 7.20−7.60 (m, 10 H, C_6H_5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −34.1 (d + dd, $^2J_{PP}$ = 50 Hz, $^1J_{WP}$ masked, PMe_3), 16.30 (d + dd, $^2J_{PP}$ = 50 Hz, $^1J_{WP}$ masked, PPh_2).

$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(PPh_2H)]W(H)(Cl)$ (8b): The *cis* isomer **8b** was obtained as an orange powder in 50% yield (125 mg). When this product was redissolved in THF and stirred at room temperature, decomposition occurred. − IR (THF): $\tilde{\nu}_{CO}$ = 2019 (m), 1918 (s), 1904 (s), 1882 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = −10.75 (s + d, $^1J_{WH}$ = 59 Hz, 1 H, W−H), 4.26 (m, 1 H, C_5H_4), 4.55 (m, 1 H, C_5H_4), 4.77 (s, 5 H, C_5H_5), 5.05 (m, 1 H, C_5H_4), 5.58 (m, 1 H, C_5H_4), 5.49 (dd, $^3J_{PH}$ = 7.4 Hz, $^1J_{PH}$ = 327 Hz, 1 H, P−H), 7.26−7.57 (m, 20 H, C_6H_5). − ^{31}P NMR ($CDCl_3$): δ = 0.75 (d, $^1J_{PH}$ = 326 Hz, $^1J_{WP}$ = 261 Hz, $^2J_{PP}$ masked, PPhH). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 16.30 (d + dd, $^2J_{PP}$ = 15 Hz, $^1J_{WP}$ = 241 Hz, PPh_2). − MS; *m*/*z*: 1016 [M$^+$].

$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(PPh_3)]W(H)(Cl)$ (9b): The NMR spectra of the product indicated the presence of the *cis* and *trans* isomers in a 30:70 ratio; yield 160 mg (60%). − ***cis*/*trans* Mixture:** IR (THF): $\tilde{\nu}_{CO}$ = 2014 (m), 1913 (s), 1895 (s), 1890 (s), 1869 (s) cm^{-1}. − $C_{44}H_{35}ClO_4P_2W_2$ (1092.87): calcd. C 48.36, H 3.23; found C 48.80, H 3.58. − ***cis*** **Isomer 9b:** ^{1}H NMR ($CDCl_3$): δ = −10.97 (s + d, $^1J_{WH}$ = 60 Hz, 1 H, W−H), 4.19 (m, 1 H, C_5H_4), 4.22 (m, 1 H, C_5H_4), 4.61 (s, 5 H, C_5H_5), 4.98 (m, 1 H, C_5H_4), 5.5 (m, 1 H, C_5H_4), 7.19−7.61 (m, 25 H, C_6H_5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.7 (d + dd, $^2J_{PP}$ = 25 Hz, $^1J_{WP}$ = 236 Hz, PPh_3), 19.9 (d + dd, $^2J_{PP}$ = 25 Hz, $^1J_{WP}$ masked, PPh_2). − ***trans*** **Isomer 9b:** ^{1}H NMR ($CDCl_3$): δ = −10.67 (s + d, $^1J_{WH}$ = 61 Hz, 1 H, W−H), 4.43 (m, 1 H, C_5H_4), 4.60 (m, 1 H, C_5H_4), 4.69 (s, 5 H, C_5H_5), 5.03 (m, 1 H, C_5H_4), 5.86 (m, 1 H, C_5H_4), 7.19−7.61 (m, 25 H, C_6H_5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 19.20 (d + dd, $^2J_{PP}$ = 60 Hz, $^1J_{WP}$ = 291 Hz, PPh_3), 24.5 (d + dd, $^2J_{PP}$ = 60 Hz, $^1J_{WP}$ = 271 Hz, PPh_2).

Synthesis of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(L)]WCl_2$ (L = PMe_3, PPh_2H, PPh_3): “Open” structures could be isolated using the same procedure as above. All attempts to recrystallize the complexes resulted in their decomposition.

$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(PMe_3)]WCl_2$ (10b): The *cis* isomer **10b** was obtained in 60% yield as a grey powder (140 mg). When this product was redissolved in THF and stirred at room temperature, decomposition occurred. − IR (THF): $\tilde{\nu}_{CO}$ = 2013 (m), 1911 (s), 1892 (s), 1876 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.16 (d, $^2J_{PH}$ = 7.4 Hz, 9 H, PMe), 5.12 (m, 2 H, C_5H_4), 5.20 (s, 5 H, C_5H_5), 6.02 (m, 2 H, C_5H_4), 7.39−7.47 (m, 6 H, C_6H_5), 7.59−7.69 (m, 4 H, C_6H_5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −41.7 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ masked, PMe_3), 18.7 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ masked, PPh_2). − MS; *m*/*z*: 940 [M$^+$]. − $C_{29}H_{28}Cl_2O_4P_2W_2$ (941.09): calcd. C 37.01, H 3.00; found C 37.45, H 3.09.

$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(PPh_2H)]WCl_2$ (11b): The reaction afforded purely the *cis* isomer **11b**, which was obtained as a grey powder in 60% yield (160 mg). When this product was redissolved in THF and stirred at room temperature, decomposition occurred. − IR (THF): $\tilde{\nu}_{CO}$ = 2020 (m), 1920 (s), 1905 (s), 1884 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 5.08 (m, 2 H, C_5H_4), 5.20 (s, 5 H, C_5H_5), 5.99 (m, 2 H, C_5H_4), 5.38 (dd, $^4J_{PH}$ = 6.6 Hz, $^1J_{PH}$ = 338 Hz, 1 H, P−H), 7.29−7.55 (m, 20 H, C_6H_5). − ^{31}P NMR ($CDCl_3$): δ = 0.44 (d + dd, $^2J_{PP}$ masked, $^1J_{PH}$ = 338 Hz, $^1J_{WP}$ = 256 Hz, PPhH). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.90 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ = 230 Hz, PPh_2). − MS; *m*/*z*: 1050 [M$^+$]. − $C_{38}H_{30}Cl_2O_4P_2W_2$ (1051.21): calcd. C 43.42, H 2.88; found C 44.85, H 3.16.

$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(PPh_3)]WCl_2$ (12b): The NMR spectra of the product indicated the presence of the *cis* and *trans* isomers of **12b** in a 70:30 ratio; yield 200 mg (70%). − ***cis*/*trans* Mixture:** IR (THF): $\tilde{\nu}_{CO}$ = 2015 (m), 1907 (s), 1890 (s), 1885 (s), 1850 (s) cm^{-1}. − $C_{44}H_{34}Cl_2O_4P_2W_2$ (1127.31): calcd. C 46.88, H 3.04; found C 47.14, H 3.56. − ***cis*** **Isomer 12b:** ^{1}H NMR ($CDCl_3$): δ = 4.81 (m, 2 H, C_5H_4), 4.95 (s, 5 H, C_5H_5), 5.88 (m, 2 H, C_5H_4), 7.28−7.60 (m, 25 H, C_6H_5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.42 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ = 236 Hz, PPh_3), 20.5 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ masked, PPh_2). − ***trans*** **Isomer 12b:** ^{1}H NMR ($CDCl_3$): δ = 5.08 (s, 5 H, C_5H_5), 5.28 (m, 2 H, C_5H_4), 5.58 (m, 2 H, C_5H_4), 7.30−7.61 (m, 25 H, C_6H_5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 21.0 (d + dd, $^2J_{PP}$ = 60 Hz, $^1J_{WP}$ masked, PPh_3), 24.4 (d + dd, $^2J_{PP}$ = 60 Hz, $^1J_{WP}$ masked, PPh_2).

Synthesis of $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(L)]WH_2$ (L = PMe_3, PPhH, PPh_3): These complexes were isolated following the same procedure as above. All attempts to recrystallize the complexes resulted in their decomposition.

$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4$ $(PMe_3)]WH_2$ (13b): The *cis* isomer **13b** was obtained in 60% yield as an orange powder (200 mg). − IR (THF): $\tilde{\nu}_{CO}$ = 2010 (m), 1904 (s), 1889 (s), 1870 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = −12.18 (s + d, $^1J_{WH}$ = 71 Hz, 2 H, W−H), 1.12 (d, $^2J_{PH}$ = 7.4 Hz, 9 H, Me), 4.09 (m, 2 H, C_5H_4), 4.44 (s, 5 H, C_5H_5), 5.00 (m, 2 H, C_5H_4), 7.24−7.41 (m, 6 H, C_6H_5), 7.48−7.58 (m, 4 H, C_6H_5). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −41.7 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ = 220 Hz, PMe_3), 14.9 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ = 241 Hz, PPh_2). − MS; *m*/*z*: 872 [M$^+$]. − $C_{29}H_{30}O_4P_2W_2$ (872.2): calcd. C 39.94, H 3.47; found C 40.60, H 3.58.

$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4{-}PPh_2W(CO)_4(PPh_2H)]WH_2$ (14b): After stirring for 24 h, the pure *cis* isomer **14b** was obtained as an orange powder; yield 160 mg (40%). When this product was redissolved in THF and stirred at room temperature, decomposition occurred. −IR (THF): $\tilde{\nu}_{CO}$ = 2017 (m), 1914 (s), 1902 (s), 1877 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = −12.16 (s + d, $^1J_{WH}$ = 73 Hz, 2 H, W−H), 4.10 (m, 2 H, C_5H_4), 4.39 (s, 5 H, C_5H_5), 4.97 (m, 2 H, C_5H_4), 5.48 (dd, $^3J_{PH}$ = 6.6 Hz, $^1J_{PH}$ = 336 Hz, 1 H, P−H), 7.26−7.74 (m, 20 H, C_6H_5). − ^{31}P NMR ($CDCl_3$): δ = 1.44 (d, $^1J_{PH}$ = 336 Hz, $^1J_{WP}$ = 256 Hz, $^2J_{PP}$ masked, PPhH). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 15.4 (d + dd, $^2J_{PP}$ = 15 Hz, $^1J_{WP}$ = 236 Hz, PPh_2). − MS (*m*/*z*): 982 [M$^+$]. − $C_{38}H_{32}O_4P_2W_2$ (982.32): calcd. C 46.46, H 3.28; found C 47.95, H 3.96.

(η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_4(PPh_3)$]WH_2 (15b): A mixture of the *cis* and *trans* isomers of **15b** (*cis*/*trans* = 30:70) was obtained after stirring for 48 h at 50 °C. The isomers were invariably obtained accompanied by small amounts of the μ-hydrido complex **6b**. − ***cis*/*trans* Mixture:** IR (THF): $\tilde{\nu}_{CO}$ = 2017 (m), 1914 (s), 1889 (s), 1845 (s) cm^{-1}. − ***cis* Isomer 15b:** ^{1}H NMR ($CDCl_3$): δ = −12.29 (s + d, $^1J_{WH}$ = 71 Hz, 2 H, W−H), 4.03 (m, 2 H, C_5H_4), 4.39 (s, 5 H, C_5H_5), 4.96 (m, 2 H, C_5H_4), 7.26−7.82 (m, 25 H, C_6H_5). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 12.15 (d + dd, $^2J_{PP}$ = 25 Hz, $^1J_{WP}$ masked, PPh_3), 20.10 (d + dd, $^2J_{PP}$ = 25 Hz, $^1J_{WP}$ masked, PPh_2). − ***trans* Isomer 15b:** ^{1}H NMR ($CDCl_3$): δ = −12.19 (s + d, $^1J_{WH}$ = 72 Hz, 2 H, W−H), 4.24 (m, 2 H, C_5H_4), 4.32 (s, 5 H, C_5H_5), 5.00 (m, 2 H, C_5H_4), 7.25−7.82 (m, 25 H, C_6H_5). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 18.70 (d + dd, $^2J_{PP}$ = 60 Hz, $^1J_{WP}$ masked, PPh_3), 25.10 (d + dd, $^2J_{PP}$ = 60 Hz, $^1J_{WP}$ masked, PPh_2).

Synthesis of (η^5-C_5H_5)[η^5-C_5H_4−$PPh_2W(CO)_4$]W(H)(μ−PPh_2) (16b): A solution of PPh_2Li (100 mg, 0.5 mmol) in THF (5 mL) was added dropwise to a stirred solution of **3b** (400 mg, 0.5 mmol) in THF (20 mL) at −78 °C. The resulting mixture was allowed to warm to room temperature and then stirred for 3 h. Removal of the solvent afforded an orange residue. NMR spectra indicated the presence of two products, namely the complexes **8b** and **16b**. The crude residue was chromatographed (toluene/THF, 1:1). The first orange band contained **8b**, while **16b** was isolated in ca. 40% yield from the second yellow band (200 mg) as a yellow powder after recrystallization from acetone. − IR (THF): $\tilde{\nu}_{CO}$ = 2004 (m), 1905 (s), 1876 (s), 1860 (s) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = −10.36 (dd + ddd, $^4J_{PH}$ = 5 Hz, $^2J_{PH}$ = 18.5 Hz, $^1J_{WH}$ masked, 1 H, W−H), 4.28 (s, 5 H, C_5H_5), 4.66 (m, 1 H, C_5H_4), 5.04 (m, 1 H, C_5H_4), 5.19 (m, 1 H, C_5H_4), 5.67 (m, 1 H, C_5H_4), 7.18−7.81 (m, 20 H, C_6H_5). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −27.2 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ = 211 Hz, $^1J_{WP}$ masked, μ-PPh_2), 38.5 (d + dd, $^2J_{PP}$ = 20 Hz, $^1J_{WP}$ masked, PPh_2). − MS; *m*/*z*: 979 [M$^+$]. − $C_{38}H_{30}O_4P_2W_2$ (980.3): calcd. C 45.13, H 2.99; found C 45.99, H 3.16.

X-ray Crystallographic Study of 3b: An orange crystal of approximate dimensions 0.35 × 0.35 × 0.10 mm was used for unit cell measurements and intensity data collection, carried out at 296 K with an Enraf−Nonius CAD4 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The pertinent crystallographic data are given in Table 2. The unit cell was determined from 25 randomly selected reflections (CAD4-EXPRESS).[26] Intensity data were reduced with PROCESS as implemented in the MolEN package[27] with neutral-atom scattering factors taken from the usual source. An empirical absorption correction (ψ scan) was applied. The structure was solved by direct methods (SHELXS-97)[28] and refined by using the SHELXL-97 library.[29] The hydride ligand was located from a difference Fourier map. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-117399. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data and structure refinement for **3b**

Empirical formula	$C_{26}H_{20}ClO_4PW_2$
Molecular mass	830.54
T [K]	293(2)
Wavelength [Å]	0.71073
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	*a* = 16.048(3) Å, *b* = 10.148(2) Å, *c* = 15.728(2) Å β = 102.14(1)°
V [Å^3]	2504.1(8)
Z	4
Calculated density [Mg/m^3]	2.203
Absorption coefficient [mm^{-1}]	9.381
F(000)	1552
Crystal size [mm]	0.35 × 0.35 × 0.10
Theta range for data collection [°]	2.39 to 24.97
hkl range	0/19, 0/12, −18/18
Reflections collected/unique	4836/3562
EAC, ψ scan, min./max. transm.	25.54/99.99
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3562/0/311
Goodness-of-fit on F^2	1.094
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0426, $wR2$ = 0.1278
Largest diff. peak and hole [eÅ^{-3}]	2.850 and −2.457

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