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Reaction of pentacarbonyl(η^2 -bis(trimethylsilyl)ethyne)tungsten(0) with tricyclohexylphosphine: X-ray structure of pentacarbonyltricyclohexylphosphinetungsten(0)

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Abstract

The pentacarbonyl(η^2 -bis(trimethylsilyl)ethyne)tungsten(0), $W(CO)_5(\eta^2\text{-btmse})$, reacts with tricyclohexylphosphine, PCy_3 , to yield two stable endproducts which could be isolated and fully characterized by using the single crystal X-ray diffractometry and the MS, IR, and NMR spectroscopy: $W(CO)_5(PCy_3)$ and *trans*- $W(CO)_4(PCy_3)_2$. The former complex is the alkyne substitution product, while the latter one is formed from the conversion of its labile *cis*-isomer, which is generated by further reaction of the CO substitution product, *cis*- $W(CO)_4(\eta^2\text{-btmse})(PCy_3)$, with a second PCy_3 molecule. The intermediate *cis*- $W(CO)_4(\eta^2\text{-btmse})(PCy_3)$ complex could not be detected even in the solution. The *cis*- $W(CO)_4(PCy_3)_2$ complex was observable, however, found to be unstable and rapidly isomerizes to *trans*- $W(CO)_4(PCy_3)_2$. The crystal and molecular structure of $W(CO)_5(PCy_3)$ was determined and compared with those of *trans*- $W(CO)_4(PCy_3)_2$. The coordination sphere around the W atom is a slightly distorted octahedron, involving five carbonyls and one phosphine. The W–C distances have values between 1.986(6) and 2.042(6) Å. The W–P distance is 2.5794(12) Å. Maximum deviation from an ideal octahedral coordination angle is observed to be 95.68(17)°. All three cyclohexyl rings are in chair configuration.

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1. Introduction

The UV photolysis of $W(CO)_6$ in alkane solution with bis(trimethylsilyl)ethyne (btmse) yields $W(CO)_5(\eta^2\text{-btmse})$ which is stable enough to be isolated as yellow crystals from the hydrocarbon solution and survives in solution even in the absence of btmse at room temperature [1]. However, it is labile towards ligand substitution at room temperature, giving alkyne and/or carbonyl substitution depending on the incoming ligand [2]. Thus, it can be used as starting material for the preparation of some metal-carbonyl derivatives, which are otherwise

inaccessible. Since the complexes of tricyclohexylphosphine have gained interest due to the agostic C–H \rightarrow M interaction of a cyclohexyl hydrogen [3] we decided to study the reaction of $W(CO)_5(\eta^2\text{-btmse})$ with tricyclohexylphosphine at ambient temperature. A CO substitution accompanied by an alkyne detachment might generate an 16-electron $W(CO)_4(PCy_3)$ complex with an agostic C–H \rightarrow W interaction of a cyclohexyl hydrogen. The 16-electron complexes of the type *trans*- $M(CO)_3(PCy_3)_2$ are known for all of the Group 6 metals, chromium [4], molybdenum, and tungsten [5]. These complexes are in fact 18-electron species due to an agostic C–H \rightarrow M interaction of a cyclohexyl hydrogen, which has been shown to be weak enough to allow replacement by Lewis bases [6]. $M(CO)_5(PCy_3)$ and $M(CO)_4(PCy_3)_2$ complexes have been known for a long time [7]. Here we report on the reaction of $W(CO)_5(\eta^2\text{-btmse})$ with tricyclohexylphosphine, the

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¹ D. Ülkü and L.T. Yildirim were responsible for the X-ray crystal-structure analysis.

isolation and characterization of possible substitution products: $W(CO)_5(PCy_3)$, $trans-W(CO)_4(PCy_3)_2$, and $cis-W(CO)_4(PCy_3)_2$. This is the first example of reactions involving both the CO and alkyne substitution in an alkyne complex. In the presence of tricyclohexylphosphine, $W(CO)_5(\eta^2\text{-btmse})$ undergoes both the CO and alkyne substitution at room temperature. This substitution indicates the labilization of CO groups *cis* to the alkyne ligand. It is exactly this unique ability of $W(CO)_5(\eta^2\text{-btmse})$ to give both the alkyne and CO substitution (from the position *cis* to the alkyne ligand), which enable us to observe, for the first time, the formation of $cis-W(CO)_4(PCy_3)_2$. The latter complex is a kinetic product and rapidly converted to the thermodynamically more stable $trans-W(CO)_4(PCy_3)_2$. All the complexes have also been prepared for verification by using the known procedure.

2. Experimental

2.1. General remarks

All of reactions and manipulations were carried out either in vacuum or under a dry and oxygen free nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days and stored under nitrogen until used.

Analytical grade and deuterated solvents, tricyclohexylphosphine, piperidine (pip), and hexacarbonyltungsten(0) were purchased from Aldrich Chemical Co. Ltd., Dorset, UK, and bis(trimethylsilyl)ethyne (btmse) was purchased from Fluka (Buchs, Switzerland), and used as received. The thermal reactions and other treatments of organometallic compounds such as purification and crystallisation were followed by taking IR spectra from solutions on a Perkin–Elmer 16 PC FT-IR spectrometer. NMR spectra were recorded on a Bruker Avance DPX 400 (400.1 MHz for 1H ; 161.3 MHz for ^{31}P ; and 100.6 MHz for ^{13}C). TMS was used as internal reference for 1H - and ^{13}C -NMR chemical shifts. H_2SO_4 (85%, in a glass capillary) was used as reference for ^{31}P -NMR chemical shifts. Mass spectra were taken on a Finnigan MAT 8400.

Photochemical reactions were carried out in an immersion-well apparatus [8] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high pressure mercury lamp, which was cooled by circulating water or cold methanol. $W(CO)_5(\eta^2\text{-btmse})$ [1] and $cis-W(CO)_4(\text{pip})_2$ [9] were prepared according to the literature procedures.

2.2. Reaction of $W(CO)_5(\eta^2\text{-btmse})$ with tricyclohexylphosphine

In a Schlenk tube, a certain amount of tricyclohexylphosphine ($P(c\text{-}C_6H_{11})_3$, PCy_3 ; 0.14–0.70 g, 0.50–2.5

mmol) was completely dissolved in 20 ml *n*-hexane at room temperature (r.t.). This solution was transferred into another Schlenk tube containing an *n*-hexane solution of 0.25 g (0.50 mmol) $W(CO)_5(\eta^2\text{-btmse})$ under stirring at r.t. The solution was stirred at r.t. The reaction was followed by recording the IR spectra of the samples taken from the solution. When the reaction was completed, the solution was left for one night over dry-ice for crystallization. The crystals separated from the mother liquor contains two compounds as determined by IR spectra: $W(CO)_5(PCy_3)$ and $trans-W(CO)_4(PCy_3)_2$. These two complexes were separated on a silica gel column (20 cm long, 3 cm diameter). $W(CO)_5(PCy_3)$ was first eluded with *n*-hexane and then crystallized from the same solution as pale yellow needle-like crystals. $trans-W(CO)_4(PCy_3)_2$ was eluded as the second fraction with a 1:3 mixture of dichloromethane and *n*-hexane, and then crystallized from *n*-hexane as colorless needle like crystals. $W(CO)_5(PCy_3)$: MS: m/z 604 [M^+]; IR (*n*-hexane) $\nu(CO) = 2065$ (w), 1968 (vw), 1938 (s), 1933 (vs), 1929 (s) cm^{-1} . ^{13}C -NMR (*d*-chloroform) $\delta = 199.31$ ppm (CO_{trans} , d, $J = 20.2$ Hz), 198.80 ppm (CO_{cis} , d, $J = 6.7$ Hz), 37.09 (C1, d, 18.1 Hz), 30.48 (C3 and C5, s), 27.94 (C2, C6, d, 10.6 Hz), and 26.61 (C4, s) ppm; ^{31}P -NMR (*d*-chloroform) $\delta = 33.41$ ppm (^{183}W satellites, $^{183}W\text{-}^{31}P$ coupling constant is 232 Hz); 1H -NMR (*d*-chloroform) $\delta = 1.85$, 1.67, 1.36, 1.22 ppm. $trans-W(CO)_4(PCy_3)_2$: MS: m/z 856 [M^+]; IR (*n*-hexane) $\nu(CO) = 1865$ (vs) cm^{-1} ; ^{13}C -NMR (*d*-chloroform) $\delta = 207.27$ ppm (CO, t, $J = 12.3$ Hz), 36.69 (C1, t, 9.8 Hz), 28.68 (C3 and C5, s), 26.82 (C2 and C6, t, 4.9 Hz), and 25.57 (C4, s) ppm; ^{31}P -NMR (*d*-chloroform) $\delta = 32.18$ ppm (^{183}W satellites, $^{183}W\text{-}^{31}P$ coupling constant is 256 Hz); 1H -NMR (*d*-chloroform) $\delta = 2.02$, 1.91, 1.79, 1.64, 1.45, 1.21 ppm.

2.3. X-ray diffraction structure analyses

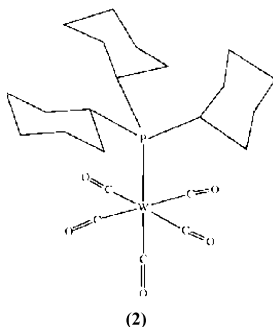
X-ray diffraction data were collected at r.t. with graphite-monochromated $Mo\text{-}K_\alpha$ radiation on an Enraf–Nonius CAD4 diffractometer [10] operating in $\omega\text{-}2\theta$ scan mode. The cell parameters were determined from a least-squares refinement of 15 centred reflections in the range of $10.09 \leq \theta \leq 11.29^\circ$. Cell refinement was carried out using CAD-4 EXPRESS. During data collection, three standard reflections were periodically measured every 120 min, showed no significant intensity variation. Absorption correction (ψ -scan) was applied ($T_{max} = 0.243$, $T_{min} = 0.175$). Data reduction was carried out using SHELXL-97 [11]. The structure was solved by direct methods using the program SHELXS-97 [11] in the WINGX package [12]. A full-matrix least-squares refinement on F^2 converged at $R = 0.03$. For all non-hydrogen atoms anisotropic displacement parameters were refined. Hydrogen atoms of the C6 and C12 were taken from a difference map, while the other hydrogen

atoms were placed geometrically. A riding model was used with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. A negative residual electron density of -1.502 is observed at a distance of 0.80 \AA from W atom. All three cyclohexyl rings are in chair form. In one of the rings which is composed of the C18–C23 atoms, the parapositioned C20 and C23 atoms show disorder evidenced by the larger displacement parameter values. An attempt to model the disorder indicated that it is an orientation disorder of the two components with a 40 to 60% ratio.

A chemical diagram of $\text{W}(\text{CO})_5(\text{PCy}_3)$ (**2**) is given in Scheme 1. The ORTEP drawing [13] of the molecule is shown in Fig. 2. Crystal and experimental data are given in Table 1, selected bond lengths and angles are given in Table 2.

3. Results and discussion

To a solution of $\text{W}(\text{CO})_5(\eta^2\text{-btmse})$ (**1**) in *n*-hexane was added the *n*-hexane solution of tricyclohexylphosphine, PCy_3 , in various amount (one to five equivalents) at room temperature. The solution was stirred at room temperature under argon atmosphere. The reaction was followed by monitoring the IR spectrum of the samples taken from the reaction solution. Some IR spectra taken during the reaction of **1** with two equivalents of PCy_3 in *n*-hexane at room temperature are depicted in Fig. 1 as an illustrating example. The IR spectrum of the solution just before the addition of PCy_3 shows five $\nu(\text{CO})$ bands at 2080 s , 1988 vw , 1960 s , 1953 s , 1938 s cm^{-1} and one $\nu(\text{C}\equiv\text{C})$ band at 1906 w cm^{-1} in the carbonyl stretching region (Fig. 1a). In the course of reaction these absorption features decrease gradually and new absorption bands grow in concomitantly. After two hours reaction the spectrum looks very rich in absorption bands for the CO stretching region. However, all the species present in the solution can be identified by comparing the spectrum with those of the corresponding substances in pure or almost pure state (Fig. 1a,d–f). The absorption bands at 2065 , 1938 , 1933 and 1929 cm^{-1} are readily assigned to $\text{W}(\text{CO})_5(\text{PCy}_3)$, the FTIR spectrum of which is given in Fig. 1d. The



Scheme 1.

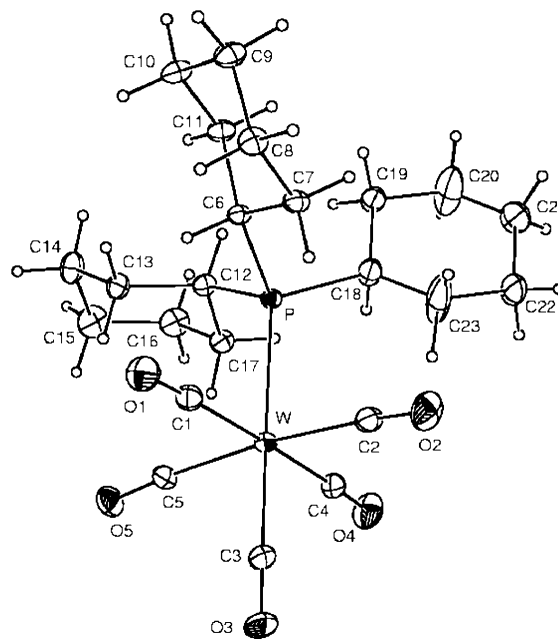


Fig. 2. ORTEP [13] drawing of the title molecule with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small circles with arbitrary radii.

Table 1

Crystal and experimental X-ray data for the $\text{W}(\text{CO})_5\text{P}(c\text{-C}_6\text{H}_{11})_3$ complex **2**

Empirical formula	$\text{C}_{23}\text{H}_{33}\text{O}_5\text{PW}$
Formula weight (g mol^{-1})	604.30
Crystal color	Colorless/prismatic
Temperature (K)	295(2)
Wavelength (\AA)	0.71073
Crystal system	Monoclinic
Space group [no.]	$P2_1/n$ [no.14]
Unit cell dimensions	
a (\AA)	11.7210(12)
b (\AA)	12.7055(14)
c (\AA)	17.688(3)
α ($^\circ$)	90
β ($^\circ$)	108.270(10)
γ ($^\circ$)	90
V (\AA^3)	2501.3(5)
Z	4
D_{calc} (Mg m^{-3})	1.605
μ (mm^{-1})	4.711
Crystal size (mm^3)	$0.4 \times 0.4 \times 0.3$
θ Range ($^\circ$)	2.43–26.3
Index ranges	$-13 \leq h \leq 14$, $0 \leq k \leq 15$, $-22 \leq l \leq 0$
Reflections collected/unique	5221/5069 [$R_{\text{int}} = 0.0422$]
Absorption correction	Psi-scan
Refinement method	Full-matrix least-squares refinement on F^2
Data/restraints/parameters	5069/2/279
Goodness-of-fit on F^2	1.03
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0329$, $wR_2 = 0.0847$
R indices (all data)	$R_1 = 0.0519$, $wR_2 = 0.0921$
Largest difference peak and hole (e \AA^{-3})	1.124 and -1.502

Table 2
Selected bond lengths (Å) and bond angles (°) of the $W(CO)_5P(c-C_6H_{11})_3$ complex **2** (esd's are given parentheses)

Bond lengths			
W–C3	1.986(6)	W–P	2.5794(12)
W–C4	2.032(6)	P–C18	1.848(6)
W–C5	2.037(6)	P–C6	1.862(5)
W–C1	2.041(6)	P–C12	1.865(5)
W–C2	2.042(6)		
Bond angles			
C3–W–C4	89.6(3)	C4–W–P	90.65(18)
C3–W–C5	85.5(3)	C5–W–P	95.68(17)
C4–W–C5	89.6(2)	C1–W–P	89.97(16)
C3–W–C1	89.8(3)	C2–W–P	91.81(16)
C4–W–C1	178.2(2)	C18–P–C6	107.8(3)
C5–W–C1	88.6(2)	C18–P–C12	104.0(3)
C3–W–C2	87.0(2)	C6–P–C12	102.7(2)
C4–W–C2	92.3(2)	C18–P–W	114.42(18)
C5–W–C2	172.2(2)	C6–P–W	111.31(15)
C1–W–C2	89.3(2)	C12–P–W	115.65(16)
C3–W–P	178.8(2)		

strong absorption band at 1865 cm^{-1} is attributed to the $trans\text{-}W(CO)_4(PCy_3)_2$ complex (Fig. 1e). The four absorption bands at 2006, 1900, 1880, and 1870 cm^{-1}

are attributed to the $cis\text{-}W(CO)_4(PCy_3)_2$ complex (Fig. 1f).

As the reaction further proceeds the absorption bands of the $cis\text{-}W(CO)_4(PCy_3)_2$ complex starts to decrease gradually and disappears completely after 12 h at room temperature, while the absorption bands for $W(CO)_5(PCy_3)$ and $trans\text{-}W(CO)_4(PCy_3)_2$ are increasing. After the reaction completed, the latter two complexes $W(CO)_5(PCy_3)$ and $trans\text{-}W(CO)_4(PCy_3)_2$ could be isolated from the reaction solution by column chromatography and crystallization. On a silica-gel column (20 cm length, 3 cm diameter), $W(CO)_5(PCy_3)$ was eluted with *n*-hexane and then $trans\text{-}W(CO)_4(PCy_3)_2$ with a 1:3 mixture of dichloromethane and *n*-hexane.

Pentacarbonyltricyclohexylphosphinetungsten(0), $W(CO)_5(PCy_3)$, **2** was also prepared by adding $P(c-C_6H_{11})_3$ to $W(CO)_5(THF)$, generated photochemically from the hexacarbonyltungsten(0) in tetrahydrofuran (THF) [14], for the purpose of comparison. Both samples of the complex give exactly the same spectral feature. The complex could be obtained in the form of needle like crystals by crystallizing from the *n*-hexane solution of the first eluent after the chromatography of

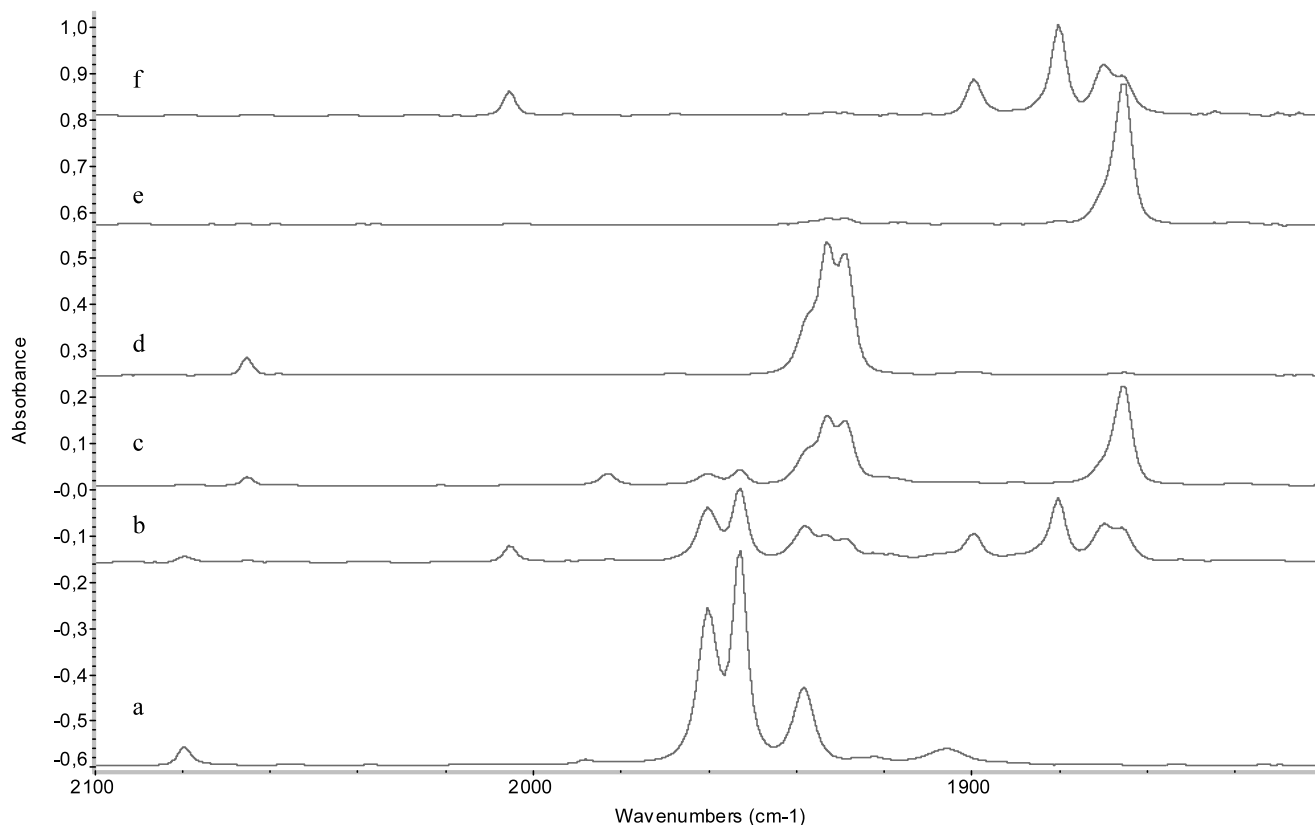


Fig. 1. IR spectra in the CO stretching region recorded during the reaction of $W(CO)_5(\eta^2\text{-btmse})$ (**1**) with two equivalents of PCy_3 in *n*-hexane at room temperature: (a) before reaction, just of $W(CO)_5(\eta^2\text{-btmse})$ (**1**), (b) after 2 h, (c) after 12 h, (d) of the $W(CO)_5P(c-C_6H_{11})_3$ complex **2** in *n*-hexane, (e) of the $trans\text{-}W(CO)_4(PCy_3)_2$ complex **5** in *n*-hexane, (f) of the $cis\text{-}W(CO)_4(PCy_3)_2$ complex **4** in *n*-hexane (small amount of $trans\text{-}W(CO)_4(PCy_3)_2$ present).

the products mixture of the reaction with $W(CO)_5(\eta^2\text{-btmse})$.

Inspection of the X-ray structural data in Table 2 reveals some important findings. In essence, the metal atom has a pseudooctahedral arrangement of six ligands, one phosphine and five carbonyls. The metal–carbon bond distance for CO in *trans*-position to the phosphine ligand [$W-C3 = 1.986(6)$ Å] is noticeably shorter than those for the four equatorial CO ligands, which are almost equivalent [$W-C4 = 2.032(6)$, $W-C5 = 2.037(6)$, $W-C1 = 2.041(6)$, and $W-C2 = 2.042(6)$ Å]. The small differences observed in the W–CO bond distances for the carbonyl groups *cis* to the phosphine ligand seemingly originate from crystal packing effects [15]. The difference in W–CO bond distances between *cis*- and *trans*-carbonyls in the complex **2** is in accord with the notion of an enhanced tungsten (d_{π}) → carbonyl (π^*) back-donation arising from the fact that the π -accepting ability of phosphine is less than that of carbon monoxide.

Concerning the P–W–CO bond angles, a noticeable deviation is observed only in the C5–W–P angle, $95.68(17)^\circ$, from the regular 90° . This may be attributed to the steric interaction between the carbonyl ligand and one cyclohexyl group of $P(c\text{-}C_6H_{11})_3$, which is oriented toward this CO. All the other P–W–CO bond angles are more or less close to the values expected for a regular octahedral geometry [$C1-W-P = 89.97(16)$, $C2-W-P = 91.81(16)$, $C3-W-P = 178.8(2)$, and $C4-W-P = 90.65(18)^\circ$].

The IR spectrum of $W(CO)_5(PCy_3)$ exhibits four prominent absorption bands at 2065, 1938, 1933 and 1929 cm^{-1} in the CO stretching vibrational region, along with a weak feature at 1968 cm^{-1} . The five-band $\nu(CO)$ pattern indicates that the C_{4v} symmetry of $W(CO)_5$ skeleton, commonly observed for $M(CO)_5L$ complexes [$\nu(CO)$ modes: $2A_1$, E (IR active) and A_2 (IR inactive)] [16], is reduced to C_{2v} symmetry by the bulky phosphine ligand: the degeneracy of the very intense E mode is lifted ($\rightarrow B_1$, B_2) and the A_2 becomes IR active ($\rightarrow B_1$), albeit with intrinsically low intensity, such that the assignments of bands in Fig. 1d is straightforward. A_1 : 2065, A_1 : 1968, B_1 : 1938, B_2 : 1933 and A_1 : 1929 cm^{-1} .

The ^{13}C -NMR spectrum of $W(CO)_5(PCy_3)$ shows two doublets for the carbonyl groups at 199.31 ($J = 20.2$ Hz) and 198.8 ppm ($J = 6.7$ Hz) in approximately 1:4 intensity ratio [17]. The appearance of only one signal for the four equatorial CO groups indicates that the molecule is fluxional with respect to rotation about the metal–phosphine bond axis. The ^{13}C – ^{31}P coupling is stronger for *trans* CO than for *cis* CO groups as observed in the $W(CO)_5PR_3$ complexes [18]. In the ^{13}C – $\{^1H\}$ -NMR spectrum, the complex $W(CO)_5P(c\text{-}C_6H_{11})_3$ shows four signals for the cyclohexyl carbons of

$P(c\text{-}C_6H_{11})_3$: 37.09 (d, $J(^{13}C\text{-}^{31}P) = 18.1$ Hz), 30.48 (s), 27.94 (d, $J(^{13}C\text{-}^{31}P) = 10.6$ Hz), and 26.61 (s) ppm.

In the ^{31}P -NMR spectrum of $W(CO)_5(PCy_3)$, one observes a signal at 33.43 ppm, accompanied by the ^{183}W satellites (the ^{183}W – ^{31}P coupling constant is 232 Hz, similar to the values observed for the $W(CO)_5(PR_3)$ complexes [19]).

The second fraction eluted with a 1:3 mixture of dichloromethane and *n*-hexane on the silica-gel column of the solution obtained from the reaction of $W(CO)_5(\eta^2\text{-btmse})$ with $P(c\text{-}C_6H_{11})_3$ contains *trans*- $W(CO)_4(PCy_3)_2$. This latter complex could be crystallized from the *n*-hexane solution and characterized by using the IR, MS and NMR spectroscopy.

The molecular structure of *trans*- $W(CO)_4(PCy_3)_2$ has already been reported in a recent paper [20]. It is noteworthy to compare the W–P and W–CO bond distances and bond angles in these two complexes, $W(CO)_5(PCy_3)$ (**2**) and *trans*- $W(CO)_4(PCy_3)_2$ (**5**). The complex **2** has a W–P bond distance of 2.5794(12) Å, which is slightly longer than those in the complex **5** [$W-P = 2.525(3)$, 2.506(3) Å]. The W–C bond distances in **5** [$W-C = 2.129(13)$, 2.064(13), 2.018(14), and 1.99(2) Å] compare well with the metal–carbon bonds for the four equatorial CO ligands in **2** [$W-C4 = 2.032(6)$, $W-C5 = 2.037(6)$, $W-C1 = 2.041(6)$, and $W-C2 = 2.042(6)$ Å]. All of them are slightly longer than the metal–carbon bond distance for CO *trans* to the phosphine ligand in $W(CO)_5P(c\text{-}C_6H_{11})_3$ [$W-C3 = 1.986(6)$ Å]. The *trans*- $W(CO)_4(PCy_3)_2$ complex shows more distortion from the regular octahedral geometry than $W(CO)_5(PCy_3)$, as seen from the P–W–P bond angle of $170.93(8)^\circ$, for example.

The appearance of one single strong $\nu(CO)$ band at 1865 cm^{-1} in the IR spectrum is indicative of a square-planar structure of the $W(CO)_4$ skeleton in *trans*- $W(CO)_4(PCy_3)_2$, which implies that in the presumed octahedral coordination geometry the phosphine ligands are in mutual *trans*-positions.

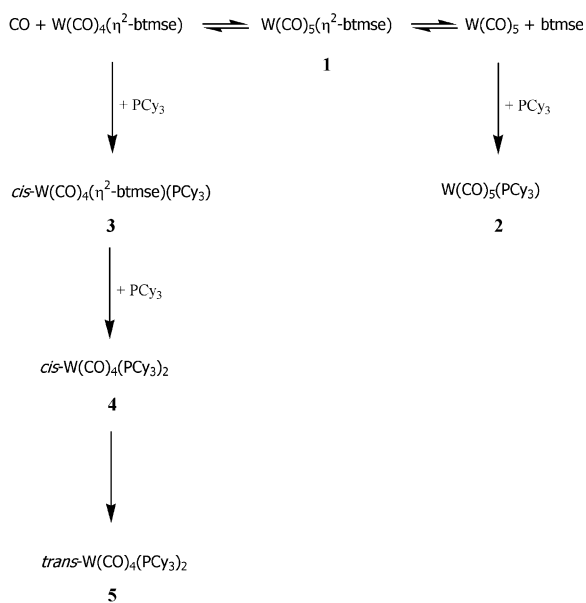
The ^{13}C -NMR spectrum of *trans*- $W(CO)_4(PCy_3)_2$ shows one signal at 207.27 ppm, which is split to a triplet due to the ^{13}C – ^{31}P coupling ($J = 12.3$ Hz). The appearance of only one signal for the four equatorial CO groups indicates that the molecule is fluxional with respect to rotation about the metal–phosphine bond axis. In the ^{13}C – $\{^1H\}$ -NMR spectrum, the complex **5** shows four signals for the cyclohexyl carbons of $P(c\text{-}C_6H_{11})_3$: 36.69 (t, $J(^{13}C\text{-}^{31}P) = 9.8$ Hz), 28.68 (s), 26.82 (t, $J(^{13}C\text{-}^{31}P) = 4.9$ Hz), and 25.57 (s) ppm.

The ^{31}P -NMR spectrum of *trans*- $W(CO)_4(PCy_3)_2$ exhibits one signal at 32.18 ppm, accompanied by the ^{183}W satellites (the ^{183}W – ^{31}P coupling constant is 256 Hz, similar to the values observed for the *trans*- $W(CO)_4(PR_3)_2$ complexes [21]. The larger ^{183}W – ^{31}P coupling constant in *trans*- $W(CO)_4(PCy_3)_2$ than that in

$W(CO)_5(PCy_3)$ is consistent with the stronger (shorter) W–P bond in the former than that in the latter complex.

In the reaction of $W(CO)_5(\eta^2\text{-btmse})$ with of $P(c\text{-}C_6H_{11})_3$ at room temperature, four $\nu(CO)$ bands at 2006, 1900, 1880 and 1870 cm^{-1} grow in first, then start to decrease and finally disappear at the end of the reaction. In a separate experiment, the reaction was ceased by cooling the solution down when these four bands have maximum intensity for the purpose of isolation of the species giving rise these absorption features in the IR spectra. By recrystallization from *n*-hexane solution we could get a sample which gave the IR spectrum in Fig. 1f, which shows, in addition to the four strong absorption bands of this species, a $\nu(CO)$ band at 1865 cm^{-1} for $trans\text{-}W(CO)_4(PCy_3)_2$. On standing the sample at room temperature, these four absorption bands lose intensity while the band at 1865 cm^{-1} grows in concomitantly, indicating that the species giving rise the four absorption bands is converted to $trans\text{-}W(CO)_4(PCy_3)_2$. Thus, this species is concluded to be the $cis\text{-}W(CO)_4(PCy_3)_2$ complex, which is thermodynamically not stable and rapidly converted to the trans isomer.

The mechanism in Scheme 2 can be proposed for the reaction of the complex $W(CO)_5(\eta^2\text{-btmse})$ (**1**) with PCy_3 at room temperature. It has already been shown that $W(CO)_5(\eta^2\text{-btmse})$ can undergo both the alkyne and CO dissociations, resulting in the reversible formation of the five-coordinate, 16-electron intermediates, $W(CO)_5$ and $cis\text{-}W(CO)_4(\eta^2\text{-btmse})$, which can be attacked by any potential ligands [1]. In the presence of tricyclohexylphosphine, the five-coordinate, 16-electron intermediate $W(CO)_5$ forms the stable complex



Scheme 2. The reaction of pentacarbonyl(η^2 -bis(trimethylsilyl)ethyne)tungsten(0), $W(CO)_5(\eta^2\text{-btmse})$, with tricyclohexylphosphine, PCy_3 .

$W(CO)_5(PCy_3)$ (**2**). The other five-coordinate, 16-electron intermediate $cis\text{-}W(CO)_4(\eta^2\text{-btmse})$ may be attacked by of $P(c\text{-}C_6H_{11})_3$ forming the complex **3**, $cis\text{-}W(CO)_4(\eta^2\text{-btmse})(PCy_3)$. The latter complex **3** is not stable because of the presence of bulky trimethylsilyl and cyclohexyl groups close to each other. The labile alkyne ligand in **3** is easily replaced by another PCy_3 molecule forming the complex **4** $cis\text{-}W(CO)_4(PCy_3)_2$. This complex **4** is the kinetic product, however, is thermodynamically not stable because of the bulky tricyclohexylphosphine ligand. The large cone angle of 170° for the tricyclohexylphosphine [22] may account for the difficulty in the preparation of the complex **4** $cis\text{-}W(CO)_4(PCy_3)_2$ as reported previously [23]. The instable complex **4** $cis\text{-}W(CO)_4(PCy_3)_2$ is converted to the thermodynamically stable isomer **5** $trans\text{-}W(CO)_4(PCy_3)_2$.

A recent paper [24] has interestingly reported the preparation of the analogous molybdenum complex, $cis\text{-}Mo(CO)_4(PCy_3)_2$, from cis -tetracarbonylbis(piperidine) molybdenum(0) following the procedure of Darsenbourg and Kump [9]. In a similar experiment with cis -tetracarbonylbis(piperidine)tungsten(0), the $cis\text{-}W(CO)_4(PCy_3)_2$ complex was generated as an intermediate which rapidly isomerized to the stable $trans$ -product as followed by IR spectroscopy.

Although the reaction of $W(CO)_5(\eta^2\text{-btmse})$ with PF_3 yields isolable CO substitution products [1], the complex **3**, $cis\text{-}W(CO)_4(\eta^2\text{-btmse})(PCy_3)$ could not be detected in the solution by IR spectroscopy. Neither it could be obtained from the reaction of the photochemically generated $cis\text{-}W(CO)_4(PCy_3)(THF)$ with of $P(c\text{-}C_6H_{11})_3$, a procedure used for the preparation of $cis\text{-}W(CO)_4(\eta^2\text{-alkene})(PR_3)$ complexes [25]. The instability of $cis\text{-}W(CO)_4(\eta^2\text{-alkyne})(PCy_3)$ may be arising from the mutual steric and/or electronic effects of two bulky ligands.

The reaction of $W(CO)_5(\eta^2\text{-btmse})$ with of $P(c\text{-}C_6H_{11})_3$ was carried out with various initial proportion of tricyclohexylphosphine to the alkyne complex. It was found that the reaction of $W(CO)_5(\eta^2\text{-btmse})$ with of $P(c\text{-}C_6H_{11})_3$ in different ligand to complex ratio between 1 and 5 yields always the same products, $W(CO)_5(PCy_3)$ and $trans\text{-}W(CO)_4(PCy_3)_2$, however, in varying relative amount. Increasing the ligand to complex ratio causes the relative amount of the alkyne substitution product $W(CO)_5(PCy_3)$ to decrease while the relative amount of $trans\text{-}W(CO)_4(PCy_3)_2$ increases. This can be rationalised by considering the reaction mechanism given in Scheme 1.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the

Cambridge Crystallographic Data Centre, CCDC no. 212613. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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