

# Chelated $\eta^5$ -cyclopentadienyl- $\eta$ -ethyl complexes of molybdenum and tungsten; molecular structure of $W(\eta^5-C_5H_4CH_2-\eta-CH_2)(CO)_3$

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Received 17 January 2000; accepted 3 April 2000

## Abstract

Molybdenum and tungsten complexes  $M(\eta^5-C_5H_4CH_2-\eta-CH_2)(CO)_3$  ( $M = Mo, W$ ) containing the bidentate ethyl-functionalized cyclopentadienyl ligand  $C_5H_4CH_2CH_2$  have been synthesized by the reaction of spiro[2.4]hepta-4,6-diene with  $M(CO)_3L_3$  ( $M = Mo$ ;  $L_3 = 1,3,5-C_6H_3Me_3$ ;  $M = W$ ;  $L = NCMe$ ). Reaction of the more stable tungsten complex with  $C_6H_5ICl_2$  and  $HBF_4$  gave complexes of the type  $W(\eta^5-C_5H_4CH_2CH_2Cl)(CO)_3Cl$ ,  $W(\eta^5-C_5H_4CH_2CH_3)(CO)_3Cl$  and  $W(\eta^5-C_5H_4CH_2CH_3)(CO)_3(FBF_3)$ , respectively. The crystal structure of the tungsten tricarbonyl complex  $W(\eta^5-C_5H_4CH_2-\eta-CH_2)(CO)_3$  has been determined by X-ray crystal diffraction on a single crystal and shows a four-legged piano stool structure. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Molybdenum; Tungsten; Cyclopentadienyl–ethyl ligand

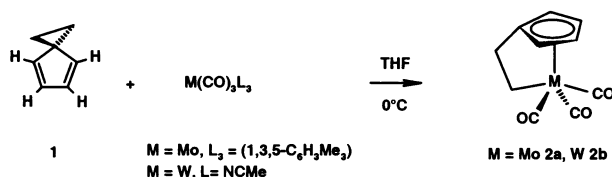
## 1. Introduction

Cyclopentadiene C–H activation followed by transfer of the hydrogen to the metal center has been extensively used to synthesize Group 6 metal–cyclopentadienyl complexes [1]. A similar descriptive model can be used for the so-called ‘tucked-in’ complexes [2], in which a distal methyl group of the substituted cyclopentadienyl ligand can undergo a cyclometallation reaction to produce metallacyclic compounds, where the metal center is coordinated to both the  $\eta^5$ -cyclopentadienyl and the  $\eta$ -alkyl group.

Although similar cyclopentadienyl C–C activations are much more rare, some examples with Group 6 and 9 metals have been reported [3] and Eilbracht has described many examples of this kind of reaction for a wide variety of spiro-dienes [4]. The resulting ligand can be considered as chelate where the cyclopentadienyl group and the alkyl group are both interacting with the metal center [5]. Herein we have studied the formation of some molybdenum and tungsten complexes containing a linked cyclopentadienyl–ethyl ligand and the stability of their metal–alkyl bond.

## 2. Results and discussion

Reaction of THF solutions of the spiro[2.4]hepta-4,6-diene (**1**) with the tricarbonyl complexes  $M(CO)_3L_3$  ( $M = Mo, L_3 = 1,3,5-C_6H_3Me_3$ ;  $M = W, L = NCMe$ ) takes place, as reported by Eilbracht [4] for related spiro-dienes, by coordination followed by activation of one  $C_{diene}-CH_2$  bond and ring opening with aromatization of the cyclopentadienyl ring and transfer of the terminal  $CH_2$  group to the metal center. In this way the  $L_3$  ligands are easily replaced by the resulting difunctionalized  $\eta^5$ -cyclopentadienyl- $\eta$ -alkyl ligand to give the metallacyclic complexes  $M(\eta^5-C_5H_4CH_2-\eta-CH_2)(CO)_3$  ( $M = Mo$  (**2a**),  $M = W$  (**2b**)), which were isolated as orange–red crystals in 30 and 72% yields, respectively (Eq. (1)) and characterized by elemental analyses, IR and NMR spectroscopy.



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<sup>1</sup> X-ray diffraction studies

After extraction of complexes **2**, brown solid residues initially thought to be polynuclear isomers of **2** were obtained. However their  $^1\text{H-NMR}$  spectra in  $\text{THF-}d_8$  showed them to be an unidentifiable mixture of components containing different residues from the starting materials.

Table 1  
Crystallographic data for  $\text{W}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{-}\eta\text{-CH}_2)(\text{CO})_3$  (**2b**)

Crystal data	
Empirical formula	$\text{C}_{10}\text{H}_8\text{O}_3\text{W}$
$f_w$	360.01
Crystal colour	Orange
Crystal size (mm)	$0.30 \times 0.13 \times 0.10$
Crystal system	Orthorhombic
Space group	$Pca2_1$ (no. 29)
$a$ (Å)	10.9949(7)
$b$ (Å)	7.4827(5)
$c$ (Å)	11.6549(7)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	958.9(1)
$Z$	4
$D_{\text{calc}}$ (mg m <sup>-3</sup> )	2.494
Absorption coefficient (mm <sup>-1</sup> )	12.021
$F(000)$	664
Data collection	
Temperature (K)	193(2)
Radiation	$\text{Mo-K}\alpha$ ( $\lambda = 0.71070$ Å)
$\theta$ range (°)	3–28
Reflections measured	$-14 \leq h \leq 14$ ; $-9 \leq k \leq 9$ ; $-15 \leq l \leq 15$
Refinement	
Reflections measured	8147
Independent reflections	2327 [ $R_{\text{int}} = 0.0364$ ]
Observed reflections	2101
Goodness-of-fit	1.096
$R$	0.0273
$wR_2$	0.0735
Largest $e_{\text{max}}$ , $e_{\text{min}}$ (e Å <sup>-3</sup> )	+1.428 and -1.283

Table 2  
Fractional coordinates (Å  $\times 10^4$ ) and temperature factors (Å<sup>2</sup>  $\times 10^3$ )<sup>a</sup> for  $\text{W}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{-}\eta\text{-CH}_2)(\text{CO})_3$  (**2b**)

Atom	$x$	$y$	$z$	$U(\text{eq})$
W	1529.7(2)	6732.1(3)	7700.5(7)	20.57(9)
O(1)	852(9)	3520(12)	9365(8)	60(2)
O(2)	1774(7)	3666(11)	5897(6)	40(2)
O(3)	3976(9)	6677(11)	8998(8)	53(2)
C(1)	1155(11)	4738(14)	8745(9)	37(2)
C(2)	1684(9)	4766(13)	6585(8)	32(2)
C(3)	3088(9)	6654(11)	8587(8)	28(2)
C(4)	1034(9)	9396(13)	6852(9)	32(2)
C(5)	87(10)	8264(13)	6656(9)	27(2)
C(6)	-461(7)	7779(9)	7582(11)	27(2)
C(7)	184(12)	8691(19)	8554(11)	46(3)
C(8)	1104(8)	9711(13)	8079(8)	29(2)
C(9)	2141(9)	9623(13)	6059(8)	38(2)
C(10)	2904(9)	8019(12)	6387(8)	32(2)

<sup>a</sup> For W, the equivalent isotropic temperature factor is given.

Table 3  
Selected bond lengths (Å) and angles (°) for  $\text{W}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{-}\eta\text{-CH}_2)(\text{CO})_3$  (**2b**)

Bond lengths		Angles	
W–C(1)	1.97(1)	C(1)–W–C(2)	82.0(4)
W–C(2)	1.97(1)	C(1)–W–C(3)	80.7(4)
W–C(3)	2.002(9)	C(1)–W–C(10)	147.7(4)
W–C(4)	2.29(1)	C(2)–W–C(3)	104.2(4)
W–C(5)	2.31(1)	C(2)–W–C(10)	79.7(4)
W–C(6)	2.329(7)	C(3)–W–C(10)	78.4(4)
W–C(7)	2.31(1)	O(1)–C(1)–W	176(1)
W–C(8)	2.320(9)	O(2)–C(2)–W	177.2(9)
W–C(9)	2.97(7)	O(3)–C(3)–W	174.5(9)
W–C(10)	2.36(1)	C(10)–C(9)–C(4)	101.5(8)
O(1)–C(1)	1.21(1)	C(9)–C(10)–W	97.7(6)
O(2)–C(2)	1.15(1)		
O(3)–C(3)	1.09(1)		
C(4)–C(9)	1.54(1)		
C(9)–C(10)	1.51(1)		

Both complexes **2** are moisture sensitive and thermally unstable and are readily decomposed to a mixture of uncharacterized products, although the slightly higher stability of the tungsten derivative **2b** allowed the X-ray diffraction study to be carried out at low temperature.

In an attempt to carry out the synthesis of titanium complexes similar to complexes **2**, we tested the reaction of **1** with titanium (II) precursors:  $\text{TiCl}_2$  [6],  $\text{TiPh}_2$  [7] and  $\text{TiBz}_2$  [8]. However, we have not as yet obtained the expected titanium (IV) complexes.

The  $^1\text{H-NMR}$  spectra of complexes **2** (see Section 3) show two multiplets corresponding to an AA'BB' spin system for the substituted cyclopentadienyl ring, and demonstrate the  $C_s$  symmetry of the distorted four-legged piano stool structure of these compounds. The protons of both bridging methylene groups appear as two pseudo-triplets of a typical AA'XX' system, those bound to the metal center being shifted to high field. This behavior is also confirmed by the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra which show three resonance signals for the cyclopentadienyl carbon atoms and two resonance signals for the bridging ethylene group, one of which (W–CH<sub>2</sub>) is significantly shifted to high field. The carbonyl ligand *trans* to the alkyl substituent in complexes **2** is easily distinguished by its higher field resonance signal in the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra compared with those observed for both equivalent mutually *trans* CO ligands. The  $\nu(\text{CO})$  wave numbers in complexes **2** are in the expected range for terminal carbonyl groups.

This molecular disposition was confirmed from the X-ray diffraction study of complex **2b**. The crystal structure was solved and refined in the space group  $Pca2_1$ . Crystallographic details are summarized in Table 1. Fractional coordinates and temperature factors are listed in Table 2 and selected bond distances and angles are summarized in Table 3.

The molecular structure is depicted in Fig. 1. The ligands are disposed in a distorted four-legged piano stool fashion similar to that established for analogous tricarbonyl cyclopentadienyl Group 6 metal complexes [1e, 9]. The angles between contiguous legs range from 78.4 to 82.0(4)°, typical values for this type of structure. The cyclopentadienyl ligand is bound in a pentahapto fashion, as inferred from the total value of the angles at the ring (540°) and the metal ring–carbon distances which range from 2.29(1) to 2.329(7) Å. The carbonyl ligands have a lineal arrangement, with W–C–O angles ranging from 174.5(9) to 177.2(9)°. The C–O bond lengths of between 1.09(1) and 1.21(1) Å and the averaged W–C(CO) bond length of 1.98 Å (with bond lengths ranging from 1.97(1) to 2.002(9) Å) are normal for terminal CO groups. A slightly long W–Csp<sup>3</sup> bond distance of 2.36(1) Å is in the range for a methyl group bound to a d<sup>4</sup>-tungsten center, as reported for W(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CMe<sub>2</sub>C<sub>9</sub>H<sub>7</sub>)(CO)<sub>3</sub>Me (2.293(9) Å) [10], W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>(C<sub>5</sub>H<sub>9</sub>) (2.343(9) Å) [11] and [W(CO)<sub>3</sub>Me]<sub>2</sub>{μ:η<sup>5</sup>-(C<sub>9</sub>H<sub>6</sub>CH<sub>2</sub>)<sub>2</sub>} (2.44(1) Å) [12], suggesting an electronically relatively saturated metal center due to the presence of the carbonyl groups. The bond angles at the lateral C<sub>2</sub>H<sub>4</sub> chain are rather different than the expected values for normal tetrahedral angles showing that W–C(10)–C(9)–C(4) is a strained four members ring with a precarious stability.

However complex **2b** remains unaltered when treated with CCl<sub>4</sub> at room temperature (r.t.).

It has been reported that oxidation of low valent Group 6 metal carbonyl complexes with phosphorous pentachloride [13] is a convenient route to high valent metal (V) and (VI) chloro complexes, whereas oxidation using iodobenzene dichloride [14] is a more convenient route to chloro complexes in lower oxidation states.

While a 1:1 reaction of **2b** with PCl<sub>5</sub> gives a mixture of unidentified materials it reacts with excess C<sub>6</sub>H<sub>5</sub>ICl<sub>2</sub> in chlorinated solvents to give different products de-

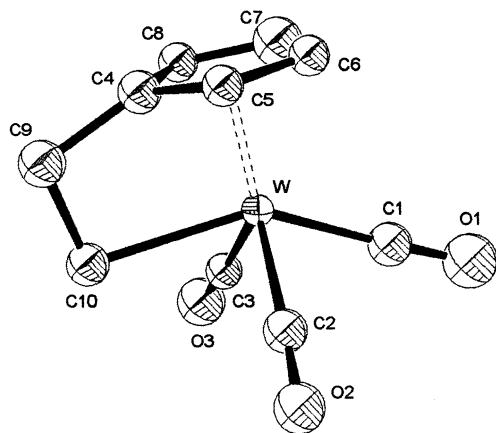
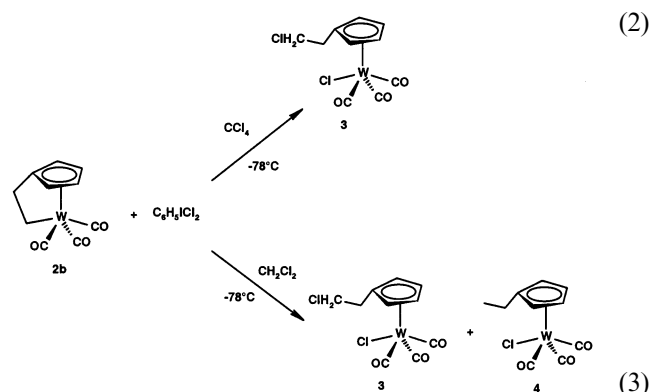


Fig. 1. ORTEP diagram of the molecular structure of W(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>-η-CH<sub>2</sub>)(CO)<sub>3</sub> (**2b**). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

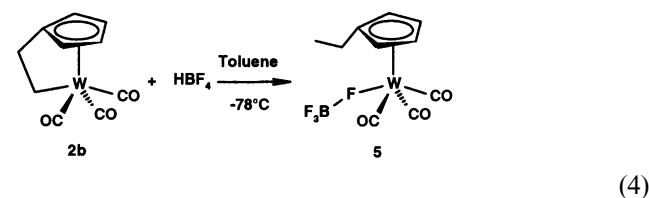
pending on the solvent. Addition of excess C<sub>6</sub>H<sub>5</sub>ICl<sub>2</sub> in CCl<sub>4</sub> yields a green precipitate of unknown composition, insoluble in all common solvents, and a red solution. Evaporation of the solvent in vacuo gave an orange oil which was a spectroscopically pure mixture containing variable proportions of the starting complex **2b** and the new chloro compound W(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-CH<sub>2</sub>CH<sub>2</sub>Cl)(CO)<sub>3</sub>Cl (**3**) (Eq. (2)). When the same reaction of **2b** was carried out in CH<sub>2</sub>Cl<sub>2</sub> instead of CCl<sub>4</sub>, a similar transformation took place to afford an orange oil which according to the NMR data (see Section 3) contained a mixture with a 6:1 molar ratio of complex **3** and the new η<sup>5</sup>-cyclopentadienyl-ethyl chloro complex W(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>)(CO)<sub>3</sub>Cl (**4**) (Eq. (3)).



Formation of different products cannot be explained as an addition to a polarized W–C bond because, beside this, **2b** does not react with ethyl–ether solutions of HCl. The formation of different products can be understood considering that C<sub>6</sub>H<sub>5</sub>ICl<sub>2</sub> causes the formation of radicals in both solvents. In this way, when the solvent is CCl<sub>4</sub> only Cl is transferred to both metal and ethyl terminals of the broken W–C bond of the cyclic system, whereas Cl and H are transferred when CH<sub>2</sub>Cl<sub>2</sub> is used as solvent.

The mixture of **2b** and **3** was separated by chromatography through a Silica-gel column, complex **3** was extracted into dichloromethane to give an orange oil in 50% yield. Chromatographic separation of complexes **3** and **4** was not achieved efficiently because their solubilities are similar and for this reason complex **4** was only identified by NMR spectroscopy.

Reaction of **2b** with tetrafluoroboric acid in toluene cleanly gives the tungsten complex W(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C-H<sub>3</sub>)(CO)<sub>3</sub>(F<sub>3</sub>B<sub>3</sub>) (**5**) which was isolated as oily brown crystals in 55% yield (Eq. (4)).



The  $\nu(\text{CO})$  wave numbers for **3** and **5** are in the expected range for terminal carbonyl groups. The  $^1\text{H-NMR}$  spectra of complexes **3–5** show the two expected multiplets for the ring protons of an AA'BB' spin system. The methylene groups in **3** appear as two pseudo-triplets while for complexes **4** and **5** the ethyl groups bound to the cyclopentadienyl ring appear as the expected  $\text{A}_2\text{B}_3$  spin system. The  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of complexes **3–5** show singlets for the carbon atoms of the cyclopentadienyl ring where the resonance signals of the *ipso* carbon atoms are the higher field signals. The resonance signals of the carbon atoms at the lateral chain of the cyclopentadienyl ring and those of the carbonyl carbon atoms appear as singlets in the appropriate range for all of these complexes. For complex **5** two resonance signals corresponding to carbonyl groups are observed due to the coordination of tetrafluoroborate to the highly electrophilic metal center [15], the r.t.  $^{19}\text{F-NMR}$  showing broad signals for one and three fluorine atoms respectively. No  $^{13}\text{C}$ – $^{19}\text{F}$  coupling was observed even at low temperature.

### 3. Experimental

All experiments were performed under argon using standard Schlenk or glove box techniques. All solvents were purified by distillation: THF from sodium–benzophenone ketyl, pentane and hexanes from sodium–potassium alloy, toluene from sodium sand, carbon tetrachloride from calcium dichloride and methylene dichloride from phosphorous pentoxide.  $\text{Mo}(\text{CO})_3$ –(1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ ) [16],  $\text{W}(\text{CO})_3(\text{NCMe})_3$  [17] and  $\text{C}_6\text{H}_5\text{ICl}_2$  [18] were synthesized according to published procedures. NaH (Aldrich), cyclopentadiene (Aldrich), 1,2-dibromoethane (Aldrich), tetrafluoroboric acid–ether complex (Aldrich) and Silica-gel (Fluka) were used as received. IR spectra were recorded in  $\text{CaF}_2$  cells for solutions, over the range 2500–1500  $\text{cm}^{-1}$  on a Perkin–Elmer 583 spectrophotometer. IR data are given in  $\text{cm}^{-1}$ . NMR spectra were recorded on a Varian Unity 300 spectrometer ( $^1\text{H}$ , 299.95 MHz;  $^{13}\text{C}$ , 75.43 MHz;  $^{19}\text{F}$ , 282.20 MHz) in  $\text{C}_6\text{D}_6$  or  $\text{CDCl}_3$  at 298 K. Chemical shifts (in ppm) for  $^1\text{H}$  and  $^{13}\text{C}$  were referenced internally using the residual solvent resonance signals and reported relative to tetramethylsilane.  $^{19}\text{F}$  spectra were referenced externally to  $\text{CFCl}_3$ . Mass spectra were recorded on a Finigan 8230 spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 CHNO instrument.

#### 3.1. Spiro[2.4]hepta-4,6-diene (**1**)

The procedure to obtain spiro[2.4]hepta-4,6-diene is a modification of the procedure published by Graig and

co-workers [19] using NaH instead of  $\text{NaNH}_2$ . Freshly distilled cyclopentadiene (47.32 ml, 0.57 mol) was added to a suspension of NaH (27.6 g, 1.15 mol) in 200 ml THF at  $0^\circ\text{C}$ . The flask was then cooled again to  $0^\circ\text{C}$  and 1,2-dibromoethane (40 ml, 0.46 mol) was added dropwise to maintain reflux for 3 h. The mixture was stirred overnight at r.t. and 100 ml water was added to destroy the unreacted NaH. The THF layer was separated and the aqueous layer was washed with hexanes ( $3 \times 50$  ml). The combined organic layers were washed with 100 ml water, 100 ml HCl (10%) and 100 ml water to obtain a yellow solution. All the organic solvents were distilled off and the spiro ligand **1** was obtained as a colorless oil distillable at  $70^\circ\text{C}$ : yield 12.6 g (30%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.68 (s, 4H,  $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ), 6.15, 6.54 (AA' and BB' parts of an AA'BB' system, 2H,  $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  12.5 ( $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ), 37.7 ( $C_{ipso}$   $\text{C}_5\text{H}_4$ ), 129.1, 139.2 ( $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ).

#### 3.2. $M(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{-}\eta\text{-CH}_2)(\text{CO})_3$ ( $M = \text{Mo}$ (**2a**), $\text{W}$ (**2b**))

The addition of a THF (ca. 20 ml) solution of the spiro ligand **1** (0.12 g, 1.28 mmol) to  $\text{Mo}(\text{CO})_3(1,3,5\text{-C}_6\text{H}_3\text{Me}_3)$  (0.38 g, 1.28 mmol) or  $\text{W}(\text{CO})_3(\text{NCMe})_3$  (0.5 g, 1.28 mmol) at  $0^\circ\text{C}$  produced orange solutions which were stirred overnight at r.t. All volatiles were removed in vacuo, and the residues were extracted into pentane (15 ml) and filtered. The filtrates were concentrated and cooled to  $-30^\circ\text{C}$  to afford thermally unstable orange–red needles of **2a** (yield 0.1 g, 30%) and **2b** (yield 0.33 g, 72%).

##### 3.2.1. Complex **2a**

IR (THF)  $\nu$  2012 s, 1920 vs.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  –0.58 (t, 2H,  $\text{Mo-CH}_2$ ), 2.31 (t, 2H,  $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ), 4.37, 4.50 (AA' and BB' parts of an AA'BB' system, 2H,  $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  –49.7 ( $\text{Mo-CH}_2$ ), 21.8 ( $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ), 67.0 ( $C_{ipso}$   $\text{C}_5\text{H}_4$ ), 88.1, 89.8 ( $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ), 229.6 ( $\text{CO}_{cis}$  to  $\text{CH}_2$ ), 237.9 ( $\text{CO}_{trans}$  to  $\text{CH}_2$ ). Anal. Calc. for  $\text{C}_{10}\text{H}_8\text{O}_3\text{Mo}$ : C, 44.13; H, 2.94. Found: C, 44.46; H, 2.84%.

##### 3.2.2. Complex **2b**

IR (THF)  $\nu$  2008 s, 1910 vs.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  –0.25 (t, 2H,  $\text{W-CH}_2$ ), 2.91 (t, 2H,  $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ), 5.19, 5.38 (AA' and BB' parts of an AA'BB' system, 2H,  $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  –61.7 ( $\text{W-CH}_2$ ), 21.9 ( $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ), 70.9 ( $C_{ipso}$   $\text{C}_5\text{H}_4$ ), 86.6, 87.6 ( $\text{CH}_2$ – $\text{C}_5\text{H}_4$ ), 218 ( $\text{CO}_{cis}$  to  $\text{CH}_2$ ), 226 ( $\text{CO}_{trans}$  to  $\text{CH}_2$ ). EIMS:  $m/z$  (%) 360 (21) [ $\text{M}^+$ ], 333 (22) [ $\text{M}^+ - \text{CO}$ ], 303 (36) [ $\text{M}^+ - 2\text{CO}$ ], 276 (8) [ $\text{M}^+ - 3\text{CO}$ ]. Anal. Calc. for  $\text{C}_{10}\text{H}_8\text{O}_3\text{W}$ : C, 33.35; H, 2.22. Found: C, 33.45; H, 2.12%.

### 3.3. $W(\eta^5-C_5H_4CH_2CH_2Cl)(CO)_3Cl$ (**3**)

Carbon tetrachloride (ca. 30 ml) was added over a solid mixture of **2b** (0.72 g, 2 mmol) and iodobenzene dichloride (0.82 g, 3 mmol) at  $-78^\circ\text{C}$  and the mixture was stirred overnight at r.t. A red solution was separated from a green gummy material and all solvents were removed to obtain a red oil that was dissolved in pentane (ca. 20 ml). The pentane solution was added to a Silica-gel column ( $10 \times 0.5$  cm) followed by 50 ml of pentane and 50 ml of  $\text{CH}_2\text{Cl}_2$  to obtain an orange solution. All volatiles were completely removed to obtain **3** as a spectroscopically pure orange oil: yield 0.4 g (50%). IR (THF)  $\nu$  2048 s, 1956 vs.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.75 (t, 2H,  $\text{CH}_2\text{-C}_5\text{H}_4$ ), 3.69 (t, 2H,  $\text{CH}_2\text{-Cl}$ ), 5.34, 5.83 (AA' and BB' parts of an AA'BB' system, 2H,  $\text{CH}_2\text{-C}_5\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  31.9 ( $\text{CH}_2\text{-C}_5\text{H}_4$ ), 43.5 ( $\text{CH}_2\text{-Cl}$ ), 77.2 ( $C_{\text{ipso}}$   $\text{C}_5\text{H}_4$ ), 86.9, 93.2 ( $\text{CH}_2\text{-C}_5\text{H}_4$ ), 215.1 ( $\text{CO}_{\text{cis}}$  to Cl), 230.5 ( $\text{CO}_{\text{trans}}$  to Cl).

### 3.4. $W(\eta^5-C_5H_4CH_2CH_3)(CO)_3Cl$ (**4**)

Following a similar procedure to that used to obtain **3**, iodobenzene dichloride (0.38 g, 1.39 mmol) was reacted with **2b** (0.5 g, 1.39 mmol) at  $-78^\circ\text{C}$  to obtain a red oil which comprised of a spectroscopically pure 6:1 mixture of **3** and  $W(\eta^5-C_5H_4CH_2CH_3)(CO)_3Cl$  (**4**).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.16 (t,  $^3J_{\text{HH}} = 7\text{Hz}$ , 3H,  $\text{CH}_3$ ), 2.36 (q,  $^3J_{\text{HH}} = 7\text{Hz}$ , 2H,  $\text{CH}_2\text{-C}_5\text{H}_4$ ), 5.36, 5.66 (AA' and BB' parts of an AA'BB' system, 2H,  $\text{CH}_2\text{-C}_5\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  13.5 ( $\text{CH}_3$ ), 21.7 ( $\text{CH}_2\text{-C}_5\text{H}_4$ ), 88.2, 91.8 ( $\text{CH}_2\text{-C}_5\text{H}_4$ ), 215.9 ( $\text{CO}_{\text{cis}}$  to Cl), 231.4 ( $\text{CO}_{\text{trans}}$  to Cl).

### 3.5. $W(\eta^5-C_5H_4CH_2CH_3)(CO)_3(\text{FBF}_3)$ (**5**)

Tetrafluoroboric acid–diethyl ether complex (0.6 ml, 3.33 mmol) was added via syringe to a solution of **2b** (1 g, 2.7 mmol) in toluene (ca. 20 ml) at  $-78^\circ\text{C}$ . The mixture was stirred at r.t. overnight. All volatiles were completely removed and the residue dissolved in hexane to give a red solution (ca. 15 ml). The solution was filtrated, concentrated and cooled to  $-30^\circ\text{C}$  to afford **5** as brown oily crystals: yield 0.65 g (55%). IR (THF)  $\nu$  2052 s, 1948 vs.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.18 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 3H,  $\text{CH}_3$ ), 2.26 (q,  $^3J_{\text{HH}} = 7.5$  Hz, 2H,  $\text{CH}_2\text{-C}_5\text{H}_4$ ), 5.75, 5.92 (AA' and BB' parts of an AA'BB' system, 2H,  $\text{CH}_2\text{-C}_5\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  14.2 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_2\text{-C}_5\text{H}_4$ ), 77.2 ( $C_{\text{ipso}}$   $\text{C}_5\text{H}_4$ ), 91.7, 92.9 ( $\text{CH}_2\text{-C}_5\text{H}_4$ ), 220.5 ( $\text{CO}_{\text{cis}}$  to  $\text{CH}_2$ ), 227.4 ( $\text{CO}_{\text{trans}}$  to  $\text{CH}_2$ ).  $^{19}\text{F-NMR}$  ( $\text{CDCl}_3$ )  $\delta$   $-151.78$  (3F,  $\text{FBF}_3$ ),  $-149.40$  (1F,  $\text{FBF}_3$ ). Anal. Calc. for  $\text{C}_{10}\text{H}_9\text{O}_3\text{BF}_4\text{W}$ : C, 26.81; H, 2.01. Found: C, 26.85; H, 2.25%.

### 3.6. X-ray crystal structure analysis of **2b**

Relevant crystallographic data for **2b** are summarized in Table 1. Single red–orange crystals suitable for X-ray crystal structure analysis were obtained by slow cooling of concentrated pentane solutions. Data were collected using  $\omega$ -scans on a Bruker AXS diffractometer with CCD detector and graphite-monochromated  $\text{Mo-K}_\alpha$  radiation. Data correction for Lorentz polarization and absorption was carried out using the program system SAINT [20a]. From 8147 measured reflections, all 2327 independent reflections were used and 62 parameters were refined by full-matrix least-squares against all  $F_o^2$  data (SHELXL-93) [20b]. The structure was solved using direct methods (SHELXS-86) [20c] and difference-Fourier syntheses and refined with anisotropic thermal parameters for the metal atom and isotropic thermal parameters for all other non-hydrogen atoms. Hydrogen atoms were calculated at their idealized positions. The refinement converged with  $R = 0.0273$ ,  $wR_2 = 0.0735$  for all observed  $F_o$  data, goodness-of-fit, 1.096.

## 4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141215. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## Acknowledgements

We thank Dirección General de Investigación Científica y Técnica (Project PB97-0776) and Universidad de Alcalá (E021/99) for financial support. We also thank Ms S. Stauf for collecting the X-ray data.

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