ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 620 (2001) 106–112

Journal of Organometallic Chemistry

Reactivity and electronic property of decaphenylmetallocenes of Mo and W atoms

Ching-I Li [a], Wen-Yann Yeh [a,*], Shi-Ming Peng [b], Gene-Hsiang Lee [b]

[a] *Department of Chemistry, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, ROC*
[b] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, ROC*

Received 21 July 2000; received in revised form 11 September 2000; accepted 13 September 2000

Abstract

The perphenylmetallocene complexes $(\eta^5\text{-}C_5Ph_5)_2W$ (**1**), $[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1}^+\mathbf{I}_3$), $(\eta^5\text{-}C_5Ph_5)_2Mo$ (**2**) and $[(\eta^5\text{-}C_5Ph_5)_2Mo]^+I_3^-$ ($\mathbf{2}^+\mathbf{I}_3$) have been prepared. Hydrogenation of **1** in THF produces $(\eta^5\text{-}C_5Ph_5)_2WH_2$ (**4**), while $(\eta^5\text{-}C_5Ph_5)_2WHCl$ (**3**) is afforded in 1,2-dichloroethane solvent. Carbonylation of **1** produces $(\eta^5\text{-}C_5Ph_5)_2W(CO)$ (**5**). Treatment of **1** with the strong acid CF_3SO_3H leads to the dicationic species $[(\eta^5\text{-}C_5Ph_5)_2W]^{+2}[CF_3SO_3]_2^-$ ($\mathbf{1}^{+2}\mathbf{Tf}_2$) after crystallization. The structures of $\mathbf{2}^+\mathbf{I}_3$ and $\mathbf{1}^{+2}\mathbf{Tf}_2$ have been determined by an X-ray diffraction study. The magnetic susceptibility study indicates a $^3E_{2g}$ ground-state for **1** and **2**, and a $^4A_{2g}$ ground-state for $\mathbf{1}^+$ and $\mathbf{2}^+$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Perphenylmetallocene complexes; Neutral chromocene derivatives; Reactivity and magnetic property

1. Introduction

The neutral chromocene derivatives, Cp'_2Cr, are usually obtained by reaction of $CrCl_2$ or $Cr_2(\mu\text{-}OAc)_4$ with alkali metal cyclopentadienides [1,2]. The elusive molybdenocene and tungstenocene, however, have only been studied as transient species or trapped in inert argon matrix at low temperature on photolysis of $(C_5H_5)_2MH_2$ or $(C_5H_5)_2M(CO)$ [3–6]. One exception was $(C_5Ph_5)_2Mo$ [7] but without very extensive characterization. Recently, we reported the synthesis of $(\eta^5\text{-}C_5Ph_5)_2W$ from a stepwise alkyne–alkyne coupling reaction [8–10]. In this paper we wish to present reactivity and magnetic property of $(\eta^5\text{-}C_5Ph_5)_2W$ as well as its molybdenum analogs.

2. Results and discussion

2.1. Reactions

$(\eta^5\text{-}C_5Ph_5)_2W$ (**1**) can be obtained exclusively from thermal rearrangement of the metallocyclic complex $W(PhC{\equiv}CPh)(\eta^8\text{-}C_8Ph_8)$ or as a major product (30% yield) from co-thermolysis of $W(PhC{\equiv}CPh)_3(CO)$ and $PhC{\equiv}CPh$ [9,10]. The molybdenum analog $(\eta^5\text{-}C_5Ph_5)_2Mo$ (**2**) has been isolated previously as a side product (ca. 4%) from reaction of $PhC{\equiv}CPh$ with either $Mo(CO)_6$ or $Mo(CO)_3(diglyme)$ [7]. Alternatively, we prepare **2** by heating $Mo(CO)_3(NCMe)_3$ and $PhC{\equiv}CPh$ in THF solvent, but the reaction yields remain low (7%) (Scheme 1). The above reactions demonstrate a novel $[2+2+1]$ coupling feature [11] for the alkyne $C{\equiv}C$ units. On the contrary, thermal reaction of $Cr(CO)_3(NCMe)_3$ with $PhC{\equiv}CPh$ does not produce $(\eta^5\text{-}C_5Ph_5)_2Cr$ but results in several chromium hexaphenylbenzene complexes $(C_6Ph_6)[Cr(CO)_3]_n$, which are currently under investigation. The formation of even-numbered carbocycles, such as the cyclobutadiene, benzene and cyclooctatetraene derivatives, from alkyne coupling reactions with the transition metal catalysts is well-documented [12,13].

Other efforts to prepare $(\eta^5\text{-}C_5Ph_5)_2Cr$ were unsuccessful. Despite $(\eta^5\text{-}C_5H_5)_2Cr$ [14], $(\eta^5\text{-}C_5Me_5)_2Cr$ [15] and $(\eta^5\text{-}C_5HPh_4)_2Cr$ [16] have been obtained from nucleophilic substitution of $CrCl_2$ with $C_5H_5^-$, $C_5Me_5^-$ and $C_5HPh_4^-$ anions, respectively, treatment of $CrCl_2$ or $Cr_2(\mu\text{-}OAc)_4$ with $C_5Ph_5^-Na^+$ (or $C_5Ph_5^-Li^+$) leads only to reduction of the chromium salts and C_5HPh_5 is

---

* Corresponding author. Fax: +886-7-5253908.
E-mail address: wenyann@mail.nsysu.edu.tw (W.-Y. Yeh).

0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(00)00809-3

recovered after work-up. Apparently, the steric bulk of the $C_5Ph_5^-$ anion effectively reduces its nucleophillicity with respect to ligand substitution at metal centers, and consequently many synthetic pathways available in cyclopentadienyl chemistry, particularly the metallocenes, fail to give complexes when using $C_5Ph_5^-$ anion. Thus, only a few number of decaphenylmetallocene complexes are known so far [17–21], which have been prepared in quite different methods.

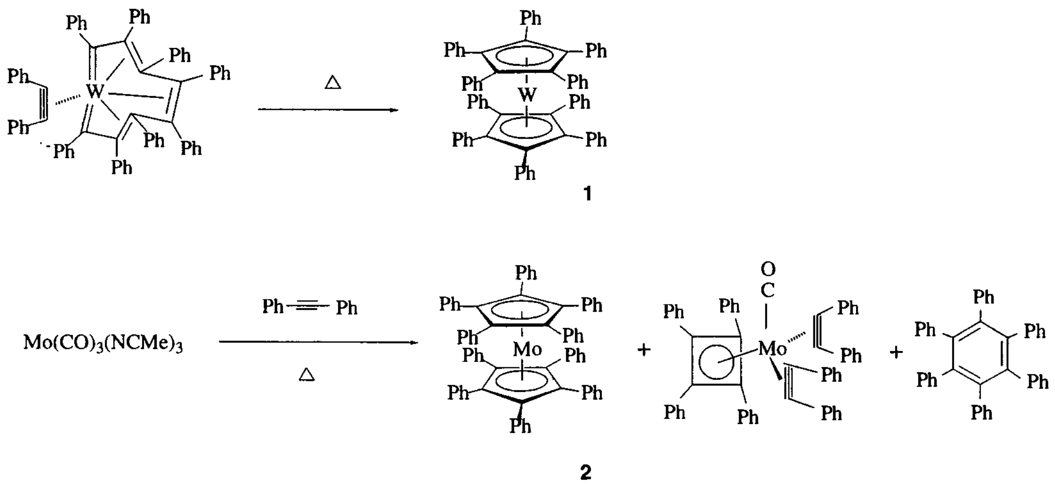
Oxidation of **1** with I_2 in hot benzene or with $AgBF_4$ in CH_2Cl_2 at room temperature affords the 15-electron cationic species $[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1^+I_3}$) [10] or $[(\eta^5\text{-}C_5Ph_5)_2W]^+BF_4^-$ ($\mathbf{1^+BF_4}$), and reduction of $\mathbf{1}^+$ with cobaltocene reforms **1**. The molybdenocene compound **2** presents an identical oxidation-reduction reaction fashion. Since **1** and **2** are closely resemblant, further investigation of their reactivity is focused on **1**; the results are summarized in Scheme 2. Heating **1** in THF at 110°C under 5 atm of H_2 produces $(\eta^5\text{-}C_5Ph_5)_2WH_2$ (**4**) in 73% yield, and carbonylation of **1** (5 atom CO) in 1,2-dichloroethane solvent at 110°C affords $(\eta^5\text{-}C_5Ph_5)_2W(CO)$ (**5**) in 80% yield. The high reaction temperature and long reaction time required are likely due to poor solubility of **1**, low molarity of H_2 and CO in solution, and energy needed to bent the bulky C_5Ph_5 groups for substrates to enter. In contrast, hydrogenation of **1** in chlorinated solvents, such as 1,2-dichloroethane, produces $(\eta^5\text{-}C_5Ph_5)_2WHCl$ (**3**; 83%). Bercaw [22] has shown that the dihydrido complex $(\eta^5\text{-}C_5Me_5)_2WH_2$ is converted sequentially to $(\eta^5\text{-}C_5Me_5)_2WHCl$ and $(\eta^5\text{-}C_5Me_5)_2WCl_2$ upon treatment with CCl_4. Presumably, compound **3** is derived from **4** via a similar transformation.

Attempts to protonate **1** with CF_3SO_3H does not produce $[(\eta^5\text{-}C_5Me_5)_2WH]^+$ or $[(\eta^5\text{-}C_5Me_5)_2WH_2]^{+2}$ but lead to the dicationic complex $[(\eta^5\text{-}C_5Ph_5)_2W]^{+2}[CF_3SO_3]_2^-$ ($\mathbf{1^{+2}Tf_2}$) after crystallization from dichloromethane–benzene. Moreover, treatment of $\mathbf{1^{+2}Tf_2}$ with $LiHBEt_3$ results in **1** without forming **4**. No intermediates are detected in these reactions. This suggests that the protonated species $[(\eta^5\text{-}C_5Ph_5)_2WH_2]^{+2}$, if formed, should be unstable and eliminate H_2 subsequently to give $\mathbf{1}^{+2}$. A process with direct electron-transfer from **1** to H^+ (as well as from H^- to $\mathbf{1}^{+2}$) is also plausible to account for the results.

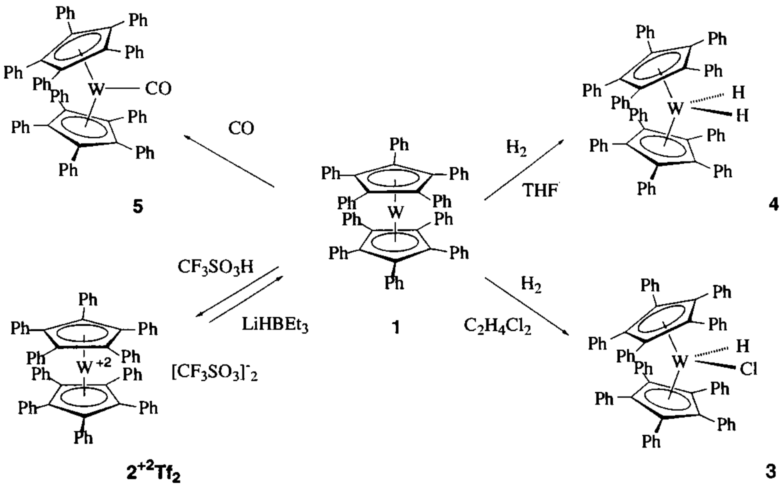
2.2. Characterization of compounds

Compounds **1** and **2** form orange–red, air-stable crystals and display identical IR spectra in KBr pellets. They are practically insoluble in all common solvents and were once thought to be polymeric [9]. Recent investigation on the molecular structures of $(\eta^5\text{-}C_5Ph_5)_2Fe$ [18], $(\eta^5\text{-}C_5Ph_5)_2Sn$ [17] and $[(\eta^5\text{-}C_5Ph_5)_2W]^+$ [10] has led to the conclusion that metallocenes of the general formula $(C_5Ph_5)_2M$ are expected to be highly insoluble due to very restricted rotation of the phenyl groups, which are canted to each Cp ring oppositely in a double-opposed paddlewheel fashion.

On the contrary, the cationic species $\mathbf{1}^+$ and $\mathbf{2}^+$ are quite soluble in polar solvent, such as dichloromethane, acetonitrile and acetone. They form slightly air-sensitive, dark green crystals. The crystal structure of $\mathbf{1^+I_3}$ has been recently reported [10]. The ORTEP diagram of $\mathbf{2^+I_3}$ (Fig. 1) shows a similar structure as $\mathbf{1^+I_3}$, where the formal Mo(III) atom is bonded to two pentaphenylcyclopentadienyl groups on a crystallographic center of symmetry. The two cyclopentadienyl rings are planar, staggered and exactly parallel. The phenyl *ipso* carbon atoms are bent away from the Cp rings by averaging 7.30°, apparently due to steric repulsions between the phenyl groups. The dihedral angles between the phenyl plane and the cyclopentadienyl plane are ranging from 48.15 to 52.70°. The averaged $Mo–C_{Cp}$ lengths of 2.37 Å (Table 1) is ca. 0.01 Å longer than that measured for $\mathbf{1^+I_3}$.



Scheme 1.



Scheme 2.

Compounds **3**–**5** are characteristic of 18-electron, bent metallocenes where the two Cp rings are not parallel [23]. Analogous Mo and W complexes with C_5H_5, C_5H_4Me and C_5Me_5 rings are known [22]. The ^{1}H-NMR spectra of **3** and **4** show the W–H resonance at −7.8 ppm, while no distinct IR absorptions near 1900 cm^{-1} for W–H stretching [22] are found, which might hide in the aromatic C–H bands between 2000 and 1700 cm^{-1}. The νCO absorption of **5** is recorded at 1956 cm^{-1}.

Compound $\mathbf{1^{+2}Tf_2}$ forms air-sensitive, dark green crystals; the ORTEP diagram of the cationic part is shown in Fig. 2. Selected bond distances and angles are collected in Table 1. The structure of $\mathbf{1}^{+2}$ closely resembles $\mathbf{1}^{+}$ and $\mathbf{2}^{+}$, where the formal W(IV) atom is bonded to two pentaphenylcyclopentadienyl groups on a crystallographic center of symmetry. The two cyclopentadienyl rings are planar, staggered and exactly parallel, with the phenyl *ipso* carbon atoms being bent away from the Cp ring by 5.15 (C6) to 10.00° (C30). The W–C_{Cp} lengths are averaged 2.37 Å, which is ca. 0.01 Å longer than that in $\mathbf{1}^{+}$. The dihedral angles between the phenyl plane and the cyclopentadienyl plane are in the range 44.00–55.56°.

2.3. Electrochemistry study of $\mathbf{1^{+}BF_4}$

The cyclic voltammogram study of $\mathbf{1^{+}BF_4}$ is taken in dry, oxygen-free dichloromethane at 28°C. It shows that $\mathbf{1^{+}BF_4}$ is reversibly reduced to **1** with the one-electron redox potential of −528 mV versus ferrocene | ferrocenium couple, and **1** is quasi-reversibly reduced to the anionic species $\mathbf{1}^{-}$ with the redox potential of −1890 mV, which is persistent on the electrochemical time scale. The $\mathbf{1}^{+}\leftrightarrow\mathbf{1}\leftrightarrow\mathbf{1}^{-}$ redox behavior is similar to that observed for the chromocene analogs [23]. Interestingly, a redox wave corresponding to the formation of the 14-electron compound $\mathbf{1}^{+2}$ is also observed at +53 mV, while the dicationic chromocenium species do not exist. Previous studies of (η^5-C_5Ph_5)$_2$Pd$_2$(μ-C_2Ph_2) have shown that the η^5-C_5Ph_5 ligand could stabilize various unusual oxidation states and the η^5-C_5Ph_5 complexes may frequently be markedly more stable than their η^5-C_5H_5 analogs [24,25].

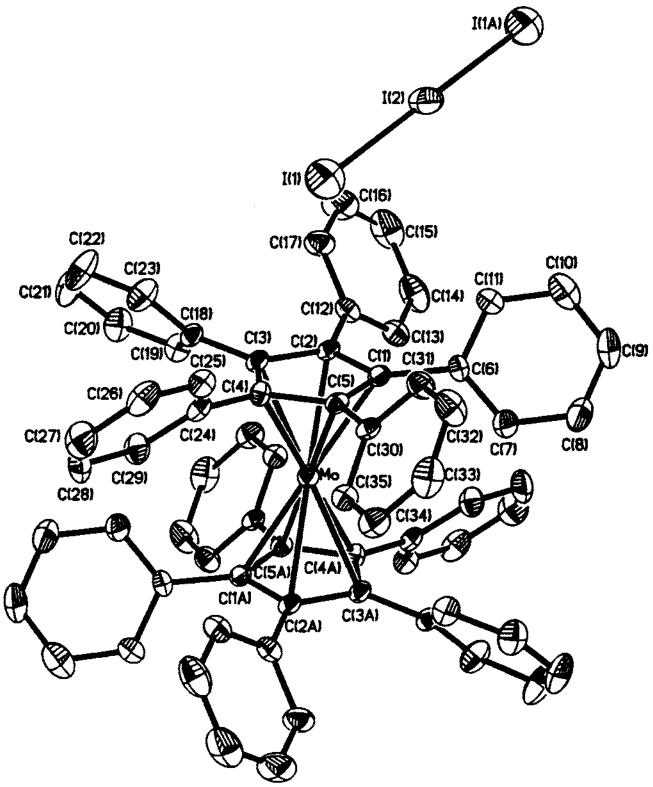


Fig. 1. ORTEP diagram of $\mathbf{2^{+}I_3}$ with thermal ellipsoids drawn at the 30% probability level.

Table 1
Selected bond lengths (Å) and bond angles (°) for $\mathbf{2^+I_3}$ and $\mathbf{1^{+2}Tf_2}$

	$\mathbf{2^+I_3}$ (M = Mo)	$\mathbf{1^{+2}Tf_2}$ (M = W)
Bond lengths		
M–C(1)	2.373(4)	2.371(3)
M–C(2)	2.375(4)	2.371(3)
M–C(3)	2.368(5)	2.369(3)
M–C(4)	2.365(5)	2.364(3)
M–C(5)	2.365(4)	2.367(3)
C(1)–C(2)	1.438(6)	1.449(5)
C(1)–C(5)	1.445(6)	1.440(4)
C(2)–C(3)	1.424(6)	1.442(5)
C(3)–C(4)	1.413(6)	1.435(4)
C(4)–C(5)	1.440(6)	1.445(5)
Bond angles		
C(1)–M–C(2)	35.3(1)	35.6(1)
C(1)–M–C(5)	35.5(2)	35.4(1)
C(2)–M–C(3)	35.0(1)	35.4(1)
C(3)–M–C(4)	34.8(1)	35.3(1)
C(4)–M–C(5)	35.5(1)	35.6(1)

2.4. Magnetic susceptibility and EPR studies

Variable temperatures magnetic susceptibility measurements were carried out on powdered samples of **1**, **2**, $\mathbf{1^+I_3}$ and $\mathbf{2^+I_3}$. The magnetic data, corrected for diamagnetism, are collected in Table 2. The 16-electron metallocenes 1 and 2 obey Curie law through the 5–300 K temperature range with θ near to zero. Two low-spin ground states are possible for the 16-electron metallocenes: the orbitally degenerate $e_{2g}^3a_{1g}^1$ ($^3E_{2g}$) configuration and the nondegenerate $e_{2g}^2a_{1g}^2$ ($^3A_{2g}$) configuration [15]. The magnetic moments of **1** (4.13 μ_B) and **2** (3.16 μ_B) are substantially larger than the spin-only value for $S = 1$ systems (2.87 μ_B), indicating a $^3E_{2g}$ ground-state assignment. The same ground-state has been assigned for $(C_5H_5)_2Mo$ and $(C_5H_5)_2W$ by Perutz [5] from a magnetic circular dichroism study in argon matrices. On the other hand, the 15-electron metallocenes $\mathbf{1^+}$ and $\mathbf{2^+}$ display the Curie–Weiss behavior through the 100–300 and 20–300 K temperature range with $\theta = -59$ and -7°, respectively, to indicate anti-ferromagnetic interactions between the metal centers. The magnetic moments of $\mathbf{1^+}$ (3.84 μ_B) and $\mathbf{2^+}$ (3.68 μ_B) are close to the spin-only value for an $S = 3/2$ system (3.87 μ_B). This suggests that $\mathbf{1^+}$ and $\mathbf{2^+}$ possess an orbitally nondegenerate $e_{2g}^2a_{1g}^1$ ($^4A_{2g}$) ground state. In comparison, Hübel has reported previously [7] the room temperature effective moments of **2** (2.75 and 3.17 μ_B) and

Table 2
Magnetic susceptibility data for **1**, **2**, $\mathbf{1^+I_3}$ and $\mathbf{2^+I_3}$

Complex	μ_{eff}, μ_B	θ (K)	Temperature range (K)
$(\eta^5\text{-}C_5Ph_5)_2W$ (**1**)	4.13	0	5–300
$(\eta^5\text{-}C_5Ph_5)_2Mo$ (**2**)	3.16	0	5–300
$[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1^+I_3}$)	3.84	−59	100–300
$[(\eta^5\text{-}C_5Ph_5)_2Mo]^+I_3^-$ ($\mathbf{2^+I_3}$)	3.68	−7	20–300

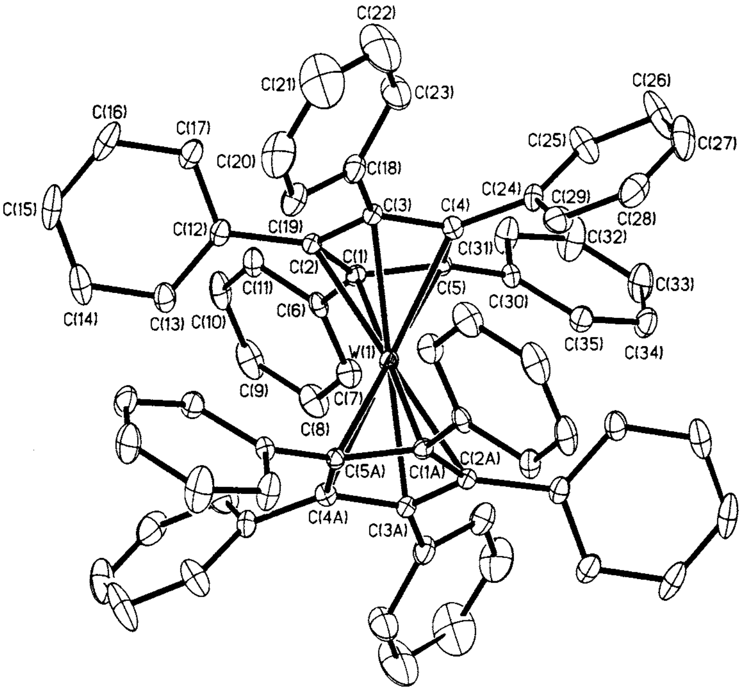


Fig. 2. ORTEP diagram of $\mathbf{1^{+2}Tf_2}$ with thermal ellipsoids drawn at the 30% probability level. The triflate anions have been artificially omitted for clarity.

Table 3
EPR data for **1**, **2**, $\mathbf{1^+I_3}$ and $\mathbf{2^+I_3}$

Complex	Host	Temperature (K)		$g_{\parallel}$	$g_{\perp}$
$(\eta^5\text{-}C_5Ph_5)_2W$ (**1**)		77	1.91	1.98	3.85
$(\eta^5\text{-}C_5Ph_5)_2Mo$ (**2**)		77	1.99		3.81
$[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1^+I_3}$)	CH_2Cl_2	77	2.03	2.19	3.83
$[(\eta^5\text{-}C_5Ph_5)_2Mo]^+I_3^-$ ($\mathbf{2^+I_3}$)	CH_2Cl_2	77	1.99	2.16	4.01

$\mathbf{2^+}Br_3^-$ (3.50 μ_B). We also note that it is 3.20 μ_B for $(C_5H_5)_2Cr$ [26], 3.01 μ_B for $(C_5Me_5)_2Cr$ [15], 3.87 μ_B for $[(C_5H_5)_2Cr]^+$ [27], and 3.73 μ_B for $[(C_5Me_5)_2Cr]^+$ [15].

The EPR spectra were measured on powdered samples of **1** and **2**, and in frozen dichloromethane for $\mathbf{1^+I_3}$ and $\mathbf{2^+I_3}$ at 77 K. Their g values are collected in Table 3. The spectra of $\mathbf{1^+}$ and $\mathbf{2^+}$ diluted in diamagnetic hosts consist of resonances near $g = 2$ ($g_{\parallel}$) and $g = 4$ ($g_{\perp}$), which are consistent with the EPR spectra recorded for $[(C_5H_5)_2Cr]^+$ [28] and $[(C_5Me_5)_2Cr]^+$ [15]. The EPR spectra of powdered **1** and **2** also display two resonances near $g = 2$ and 4, while no EPR spectra were reported previously for the 16-electron metallocenes, such as $(C_5H_5)_2Cr$, $(C_5Me_5)_2Cr$ and $[(C_5H_5)_2Mn]^+$, due to the large zero-field splitting parameters [15]. The results present in this paper, therefore, can fill in the missing link in the series of transition metallocenes.

3. Experimental

3.1. General methods

All the experimental manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques. $(\eta^5\text{-}C_5Ph_5)_2W$ (**1**) and $[(\eta^5\text{-}C_5Ph_5)_2W]^+I_3^-$ ($\mathbf{1^+I_3}$) were prepared as described in the literature [9,10]. $Mo(CO)_6$, PhC≡CPh, C_5Ph_5H, I_2, CF_3SO_3H and $LiHBEt_3$ (1.0 M in THF) were purchased from Aldrich and used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. IR spectra were taken on a Hitachi I-2001 spectrometer. MS spectra were obtained on a VG Blotch-5023 mass spectrometer. NMR spectra were recorded on a Varian VXR-300 spectrometer. Cyclic voltammetric measurements were taken with a CV 50W system, equipped with a Pt button working electrode, a Pt wire auxiliary electrode and a Ag/AgCl reference electrode, with 1 mM solution of sample in dry CH_2Cl_2 containing 0.1 M of $(n\text{-}C_4H_9)_4NPF_6$ as the supporting electrolyte. Electron paramagnetic resonance dada (X-band) were collected with a Bruker EMX-10 spectrometer at the National Tsing-Hua University, Hsinchu. Magnetic susceptibilities were measured with a SQUID magnetometer (Quantum Design) at the National Chen-Kung University, Tainan. Elemental analysis was performed at the National Chen-Kung University.

3.2. Alternative preparation of $(\eta^5\text{-}C_5Ph_5)_2Mo$ (**2**)

$Mo(CO)_6$ (500 mg, 1.9 mmol) and acetonitrile (20 ml) were introduced into an 100 ml Schlenk flask equipped with a magnetic stir bar and a reflux condenser connected to an oil bubble. The mixture was heated to reflux under dinitrogen for 5 h to result in a yellow solution, at which point the IR spectrum indicated $Mo(CO)_6$ was completely transformed to $Mo(CO)_3(NCMe)_3$. The acetonitrile solvent was removed under vacuum, and a THF (20 ml) solution of PhC≡CPh (1.81 g, 10.2 mmol) was added into the flask. The mixture was refluxed under N_2 for 45 h, cooled to ambient temperature, and filtered. The solid precipitate contained mainly $(\eta^5\text{-}C_5Ph_5)_2Mo$ (2; 136 mg, 7.3%). The filtrate was evaporated to dryness on a rotary evaporator. The residue was subjected to TLC, eluting with n-hexane–dichloromethane (4:1. v/v). The first band recovered the unreacted PhC≡CPh. The second pale yellow band yielded hexaphenylbenzene (65 mg). The third purple band afforded the known complex $Mo(CO)(\eta^4\text{-}C_4Ph_4)(PhC{\equiv}CPh)_2$ (631 mg, 40%) [7].

Analytically pure **2** in microcrystalline form can be obtained from reduction of $\mathbf{2^+I_3}$ (see below) with cobaltocene (Cp_2Co) in dichloromethane solvent at room temperature (r.t.).

3.3. Preparation of $[(\eta^5\text{-}C_5Ph_5)_2Mo]^+I_3^-$ ($\mathbf{2^+I_3}$)

Compound **2** (126 mg, 0.13 mmol) and iodine (54 mg, 0.21 mmol) were placed in a Schlenk flask under N_2 and dry benzene (15 ml) was introduced. The mixture was heated to reflux for 1 h, forming a dark green precipitate. The solid was filtered, washed with benzene, and crystallized from dichloromethane–benzene to give $[(\eta^5\text{-}C_5Ph_5)_2Mo]^+I_3^-$ ($\mathbf{2^+I_3}$) (119 mg, 68%). MS EI m/z: 989 ($\mathbf{2^+} + 1$, ^{98}Mo). IR (KBr): 3064, 1602, 1504, 1450, 1410, 1320, 1078, 1028, 928, 800, 778, 740, 712, 700, 556 cm^{-1}. Anal. for $C_{70}H_{50}I_3Mo$: Found C, 61.38; H, 3.64; Calc. C, 61.45; H, 3.66%.

3.4. Preparation of **4**

$(\eta^5\text{-}C_5Ph_5)_2W$ (**1**; 50 mg) and 30 ml of THF were placed in an oven-dried, 200 ml pressure bottle. The bottle was charged with 5 atm of H_2, and then heated at 110°C for 7 days. The bottle was then cooled to r.t., giving a yellow solution together with orange–yellow crystals. The slightly air-sensitive, orange–yellow crystals were characterized as $(\eta^5\text{-}C_5Ph_5)_2WH_2$ (**4**). The solution was dried, and the residue was crystallized from a small amount of hot THF to afford additional **4** in crystal form. Total **4** weighed 37 mg (73%). MS FAB *m*/*z*: 1076 ($[M^+]$, ^{184}W). IR (KBr): 3064, 1956, 1898, 1816, 1770, 1604, 1506, 1448, 1178, 1074, 1028, 800, 782, 738, 710, 700 cm^{-1}. ^1H-NMR (C_6D_6, 20°C): 6.74–7.31 (m, Ph), -7.76 (s, W–H) ppm.

3.5. Preparation of **3**

Reaction of $(\eta^5\text{-}C_5Ph_5)_2W$ (**1**; 200 mg) and H_2 (5 atm) were carried out in a fashion identical with that above, except that 1,2-dichloroethane (30 ml) was used as the solvent. The mixture was heated in an oil-bath at 110°C for 7 days and cooled to room temperature, resulting in an orange–yellow precipitate in the bottle. The supernatant was discarded and the residue was washed with fresh 1,2-dichloroethane twice. The crude product was recrystallized from hot benzene to afford an orange solid of $(\eta^5\text{-}C_5Ph_5)_2WHCl$ (3; 173 mg, 84%). MS EI *m*/*z*: 1076 ($[M^+ - Cl + H]$, ^{184}W). IR (KBr): 3064, 1958, 1894, 1814, 1774, 1604, 1506, 1448, 1178, 1074, 1028, 800, 782, 738, 710, 700 cm^{-1}. ^1H-NMR (C_6D_6, 20°C): 6.76–7.31 (m, Ph), -7.76 (s, W–H). Anal. for $C_{70}H_{51}ClW$: Found C, 76.16; H, 5.01; Calc. C, 75.64; H, 4.63%.

3.6. Preparation of **5**

$(\eta^5\text{-}C_5Ph_5)_2W$ (**1**; 136 mg) and 30 ml of 1,2-dichloroethane were placed in an oven-dried, 200 ml pressure bottle, equipped with a magnetic stir bar. The bottle was charged with 5 atm of CO, and then heated at 110°C for 14 days, forming a pale-yellow solution. The bottle was cooled to r.t. and opened in air. The reaction mixture was filtered and the filtrate was dried under vacuum. The residue was purified by crystallization from hot benzene, forming a pale-yellow solid of $(\eta^5\text{-}C_5Ph_5)_2W(CO)$ (**5**; 112 mg, 80%). MS FAB *m*/*z*: 1103 ($[M^+ + 1]$, ^{184}W), 1075 ($[M^+ + 1 - CO]$). IR (KBr): 3060, 3032, 2036, 1984, 1956 (CO), 1602, 1496, 1448, 1074, 1028, 976, 954, 914, 814, 770, 738, 696 cm^{-1}. ^1H-NMR (C_6D_6, 20°C): 7.07–6.85 (m, Ph).

3.7. Reaction of **1** with CF_3SO_3H

$(\eta^5\text{-}C_5Ph_5)_2W$ (**1**; 81 mg, 0.075 mmol) and CH_2Cl_2 (8 ml) were added into an oven-dried Schlenk tube under N_2. The tube was placed in a dry ice-acetone bath at -78°C and CF_3SO_3H (20 μl, 0.22 mmol) was added into the tube via a syringe. The tube was then removed from the cold bath and slowly warmed to ambient temperature. The mixture was stirred for another 2 h. resulting in a dark green clear solution. Freshly distilled Et_2O (30 ml) was then introduced to afford a solid precipitate. The solid was recrystallized from dichloromethane–benzene at 25°C to yield dark green crystals, characterized as $[(\eta^5\text{-}C_5Ph_5)_2W^{+2}][CF_3SO_3^-]_2$ ($\mathbf{1^{+2}Tf_2}$) (60 mg, 59%). MS FAB *m*/*z*: 1075 ($\mathbf{1}^+ + 1$, ^{184}W). IR (KBr): 3060, 1602, 1504, 1448, 1270, 1178, 1074, 1028, 904, 800, 780, 738, 712, 700 cm^{-1}.

3.8. Reaction of $\mathbf{1^{+2}Tf_2}$ with $LiHBEt_3$

$[(\eta^5\text{-}C_5Ph_5)_2W^{+2}][CF_3SO_3^-]_2$ ($\mathbf{1^{+2}Tf_2}$) (18 mg, 0.013 mmol) and freshly distilled THF (5 ml) was sequentially added into a oven-dried Schlenk tube under N_2. The resulting dark green solution was cooled to -78°C in a dry ice-acetone bath and $LiHBEt_3$ (28 μl, 0.028 mmol) was added via a syringe. The solution was then warmed to r.t. and stirred under N_2 for 8 h. At this point, the solution became almost colorless and a brick red precipitate was formed. The solid was characterized as $(\eta^5\text{-}C_5Ph_5)_2W$ (**1**) (12 mg, 86%).

3.9. Structure determination for $\mathbf{2^+I_3}$ and $\mathbf{1^{+2}Tf_2}$

The crystals of $[(\eta^5\text{-}C_5Ph_5)_2Mo]^+I_3^-$ ($\mathbf{2^+I_3}$) and $[(\eta^5\text{-}C_5Ph_5)_2W^{+2}][CF_3SO_3^-]_2$ ($\mathbf{1^{+2}Tf_2}$) found suitable for X-ray analysis were grown by slow diffusion of benzene into a concentrated dichloromethane solution at ambient temperature. A crystal of $\mathbf{2^+I_3}$ (ca. 0.40 × 0.40 ×

Table 4
Crystal data and refinement details for $\mathbf{2^+I_3}$ and $\mathbf{1^{+2}Tf_2}$

	$\mathbf{2^+I_3}$	$\mathbf{1^{+2}Tf_2}$
Formula	$C_{70}H_{50}I_3Mo$	$C_{72}H_{50}F_6O_6S_2W$
T (K)	293	150
Crystal system	Monoclinic	Triclinic
Crystal solvent	$4(C_6H_6)$	$C_6H_6+(H_2O)$
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	14.481(3)	13.1037(2)
b (Å)	18.602(4)	13.3458(2)
c (Å)	15.506(4)	19.1611(1)
α (°)		83.503(1)
β (°)	111.50(3)	80.645(1)
γ (°)		86.904(1)
V (Å^3)	3886(2)	3282.91(7)
Z	2	2
D_{calc} (g cm^{-1})	1.436	1.486
F(000)	1678	1484
Radiation λ (Å)	0.71073	0.71073
μ (mm^{-1})	1.406	1.897
θ range (°)	1.51–25.00	1.08–27.50
R_1	0.0429	0.0393
wR_2	0.0651	0.0893
Goodness-of-fit on F^2	0.999	1.113

0.25 mm^3) and a crystal of $\mathbf{1}^{+2}\mathbf{Tf}_2$ (ca. 0.40 × 0.38 × 0.20 mm^3) were each mounted in a thin-walled glass capillary and aligned on the Nonius CAD-4 and Simens SMART-CCD diffractometer, respectively, with graphite-monochromated Mo–K$_\alpha$ radiation, The data were collected at 298 K for $\mathbf{2}^{+}\mathbf{I}_3$ and 150 K for $\mathbf{1}^{+2}\mathbf{Tf}_2$. All data were corrected for the effects of absorption. For $\mathbf{1}^{+2}\mathbf{Tf}_2$, half of the $CF_3SO_3^-$ anions are disordered. The structures were solved by the direct method and refined by full-matrix least-square on F^2. The program used was the SHELXTLE package [29]. The data collection and refinement parameters are presented in Table 4.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 140052 for compound $\mathbf{2}^{+}\mathbf{I}_3$ and CCDC no. 145272 for compound $\mathbf{1}^{+2}\mathbf{Tf}_2$. 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).

Acknowledgements

We are grateful for support of this work by the National Science Council of Taiwan.

References

[1] R. Davis, L.A.P. Kane-Maguire, Comprehensive Organometallic Chemistry, vol. 3, Pergamon, Oxford, 1982, p. 953.

[2] M.J. Morris, Comprehensive Organometallic Chemistry II, vol. 5, Pergamon, Oxford, 1995, p. 393.

[3] R.N. Perutz, J.C. Scaiano, J. Chem. Soc. Chem. Commun. (1984) 457.

[4] J. Chetwynd-Talbot, P. Grebenik, R.N. Perutz, Inorg. Chem. 21 (1982) 3647.

[5] P.A. Cox, P. Grebenik, R.N. Perutz, M.D. Robinson, R. Grinter, D.R. Stern, Inorg. Chem. 22 (1983) 3614.

[6] J.F. Hartwig, X. He, Angew. Chem. Int. Ed. Engl. 35 (1996) 315.

[7] W. Hübel, R. Merényi, J. Organomet. Chem. 2 (1964) 213.

[8] W.-Y. Yeh, L.-K. Liu, J. Am. Chem. Soc. 114 (1992) 2267.

[9] W.-Y. Yeh, C.-L. Ho, M.Y. Chiang, I.-T. Chen, Organometallics 16 (1997) 2698.

[10] W.-Y. Yeh, S.-M. Peng, G.-H. Lee, J. Organomet. Chem. 572 (1999) 125.

[11] J.M. O'Connor, K. Hiibner, R. Merwin, P.K. Gantzel, B.S. Fong, M. Adams, A.L. Rheingold, J. Am. Chem. Soc. 119 (1997) 3631.

[12] N.E. Schore, Chem. Rev. 88 (1988) 1081.

[13] D.B. Grotjahn, Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 741.

[14] M. Dub, Organometallic Compounds, vol. 1, Springer-Verlag, Berlin, 1966.

[15] J.L. Robbins, N. Edelstein, B. Spencer, J.C. Smart, J. Am. Chem. Soc. 104 (1982) 1882.

[16] M.P. Castellani, S.J. Geib, A.L. Rheingold, W.C. Trogler, Organometallics 6 (1987) 1703.

[17] M.J. Heeg, C. Janiak, J.J. Zuckerman, J. Am. Chem. Soc. 106 (1984) 4259.

[18] H. Schumann, A. Lentz, R. Weimann, J. Pickardt, Angew. Chem. Int. Ed. Engl. 33 (1994) 1731.

[19] L.D. Field, T.W. Hambley, P.A. Humphrey, C.M. Lindall, G.J. Gainsford, A.F. Masters, T.G. St. Pierre, J. Webb, Aust. J. Chem. 48 (1995) 851.

[20] M.J. Heeg, R.H. Herber, C. Janiak, J.J. Zucherman, H. Shumann, W.F. Manders, J. Organomet. Chem. 346 (1988) 321.

[21] A. Schott, H. Schott, G. Wilker, J. Brandt, H. Hoberg, E.C. Hoffmann, Justus Liebigs Ann. Chem. (1973) 508.

[22] G. Parkin, J.E. Bercaw, Polyhedron 7 (1988) 2053.

[23] A. Togni, R.L. Halterman, Metallocenes, Wiley–VCH, Weinheim, 1998.

[24] J. Powell, N.I. Dowling, Organometallics 2 (1983) 1742.

[25] M.J. Aroney, I.E. Buys, G.D. Dennis, L.D. Field, T.W. Hambley, P.A. Lay, A.F. Masters, Polyhedron 12 (1993) 2051.

[26] H.P. Fritz, K.E. Schwarzhans, J. Organomet. Chem. 1 (1964) 208.

[27] E.O. Fischer, K. Ulm, Chem. Ber. 95 (1962) 692.

[28] J.H. Ammeter, J. Magn. Reson. 30 (1978) 299.

[29] G.M. Sheldrick, SHELXTL, University of Göttingen, Germany, 1985.