

Synthesis and characterisation of cationic bis(cyclopentadienyl)-tungsten(IV) complexes†

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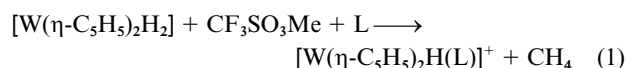
Cationic hydride complexes of bis(cyclopentadienyl)tungsten(IV) have been prepared and studied. The complex $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{thf})][\text{SO}_3\text{CF}_3]$ reacts with CS_2 in d^6 -acetone to form the chelated *O*-alkyl dithiocarbonate tungsten hydride insertion product $[W(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-S}_2\text{COCH}(\text{CD}_3)_2\text{-S,S'})][\text{SO}_3\text{CF}_3]$ as demonstrated by single crystal X-ray diffraction and NMR spectroscopy. The styrene complex $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-CH}_2\text{CHC}_6\text{H}_5)][\text{PF}_6]$ has been prepared as a mixture of *exo* and *endo* isomers. This isomeric mixture reacts thermally with NCMc to give $[W(\eta\text{-C}_5\text{H}_5)_2\text{-}(\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)(\text{NCMe})][\text{PF}_6]$ and photochemically with NCMc to give $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{NCMe})][\text{PF}_6]$. The molecular structures of the *exo* isomer and of the benzonitrile complex $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{NCPH})][\text{SO}_3\text{CF}_3]$ are reported.

Introduction

In several catalytic cycles the insertion of an unsaturated molecule into a transition metal–hydride bond is a fundamental step.^{1,2} Catalytically active transition metal–hydride complexes can be prepared and isolated, but in many reactions they are generated *in situ* and are highly transient in nature. The high degree of reactivity and selectivity afforded by these complexes, and the short existence of many, has generated a lot of interest in the synthesis and characterisation of stable transition metal–hydride complexes. For example, a series of ruthenium cations such as $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{H}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)]^+$ have been characterised and shown to be active catalysts for ring opening metathesis polymerisation of norbornene.³ The complex $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)\text{H}_3(\text{PCy}_3)]$ has been prepared and used as a catalyst precursor for the selective “head-to-tail” dimerisation of acrylic compounds,⁴ and the Group 6 transition metal complexes $[\text{MH}(\text{CO})_5]^-$ have been employed in the study of carbon dioxide activation.^{5,6}

The first bis(cyclopentadienyl) complex of tungsten, $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$, was prepared by Green *et al.* in 1961.⁷ Since this report, a large number of bent metallocene derivatives have been prepared and studied.^{8,9} Most of this research has relied on Green’s original method,⁷ or on his improved scaled up version,¹⁰ as the entry route. Alternative entry routes have been reported and include a metal–vapour synthesis¹¹ and a synthesis from $[\text{WCl}_4(\text{dme})]$.¹² Routes to bent metallocene complexes of tungsten containing substituted cyclopentadienyl ligands and η^5 -cyclic analogues have been described;^{13–15} the preparation of *ansa*-metallocenes has also been reported.^{16–18}

As part of a programme investigating small molecule activation, new methods for the preparation of cationic $[W(\eta\text{-C}_5\text{H}_5)_2]$ -based compounds have been sought.^{19,20} We recently reported a synthetic route to the cationic hydride complexes $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{L})]^+$ ($\text{L} = \text{NCR}$, CN^tBu or thf), eqn. (1).²⁰ These



complexes have been characterised by spectroscopic techniques, and in the case of $\text{L} = \text{thf}$, $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{thf})][\text{SO}_3\text{CF}_3]$ **1**, by

crystallography.²⁰ We now describe reactions of **1** together with the crystal structure of one of the products, the complex resulting from the insertion of CS_2 into d^6 -acetone, $[W(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-S}_2\text{COCH}(\text{CD}_3)_2\text{-S,S'})][\text{SO}_3\text{CF}_3]$ **2**. The crystal structure of the complex where $\text{L} = \text{NCPH}$, $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{NCPH})][\text{SO}_3\text{CF}_3]$ **3**, is presented, and also detailed are the synthesis, reactions and molecular structure of the complex $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-CH}_2\text{-CHC}_6\text{H}_5)][\text{PF}_6]$ **4**.

Results and discussion

The hydride complexes $[W(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{L})]^+$ undergo ligand dissociation forming the 16-electron transient $[W(\eta\text{-C}_5\text{H}_5)_2\text{-H}]^+$.^{19,20} In the case of **1** where donor ligand $\text{L} = \text{thf}$, the transient can be generated under moderate conditions at a rate suitable for synthetic purposes. Generation of this intermediate by heating d^6 -acetone solutions of **1** in the presence of additional ligands (CO_2 , CS_2 , styrene and methyl acrylate) was carried out. Monitoring by ^1H NMR spectroscopy showed that unco-ordinated thf was produced, however no isolable organometallic products were obtained except for the reaction with carbon disulfide. This reaction, unlike the others, gives a clean ^1H NMR spectrum with resonances at δ 5.81 and 3.76 (Table 1). With the aid of a single crystal X-ray diffraction structure of the product, Fig. 1, the resonances were respectively assigned to the cyclopentadienyl ligands and the methine hydrogen in $[W(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-S}_2\text{COCH}(\text{CD}_3)_2\text{-S,S'})][\text{SO}_3\text{CF}_3]$ **2**. Only one resonance is observed for the cyclopentadienyl ligands indicating that an equilibrium process, fast on the NMR time-scale, is occurring: this is most likely rotation about the C(11)–O(1) bond. The resonances for the deuterated methyl groups were indistinguishable from the resonance for the solvent, d^6 -acetone.

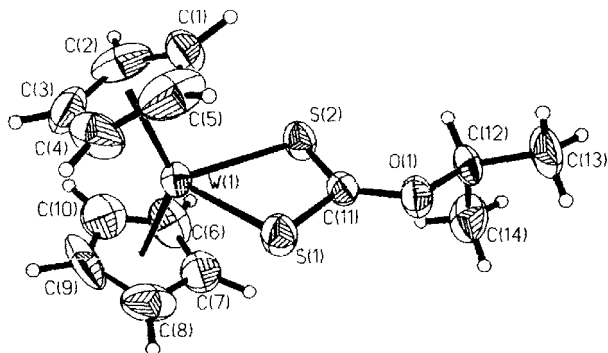
The single crystal structure of complex **2** is shown in Fig. 1; selected bond lengths and angles are given in Table 2. The structure shows a distorted tetrahedral geometry about the tungsten centre with two η^5 -cyclopentadienyl ligands co-ordinated and the remaining sites occupied by two sulfur atoms of a chelated *O*-alkyl dithiocarbonate ligand. The four-membered metallocyclic ring defined by W1, S1, S2 and C11 is essentially planar with the maximum deviation of any atom from the plane being 0.001 Å (O1 is only 0.019 Å above this plane). The tungsten–sulfur bond length of 2.470(4) Å is

† This paper is dedicated to the late Dr Andrew McCamley.

Table 1 Analytical and spectroscopic data

Complex	Analysis ^a (%)	IR ^b (cm ⁻¹)	¹ H NMR ^c	¹³ C NMR
2^d			5.81 [10H, s, η-C ₅ H ₅] 3.76 [1H, s, OCH(CD ₃) ₂]	
4^e	C 38.00 (38.30) H 3.3 (3.40)	1436 [ν(C=C)]	<i>endo</i> 7.21 [5H, m, C ₆ H ₅] 5.79 [5H, s, η-C ₅ H ₅] 5.31 [5H, s, η-C ₅ H ₅] 4.27 [1H, dd, <i>J</i> (HH) = 14.1, 10.4, CH ₂ CHC ₆ H ₅] 2.49 [1H, dd, <i>J</i> (HH) = 14.1, 5.5, CH ₂ CHC ₆ H ₅ - <i>cis</i>] 2.28 [1H, dd, <i>J</i> (HH) = 10.4, 5.5, CH ₂ CHC ₆ H ₅ - <i>trans</i>] −6.01 [1H, s, hydride, <i>J</i> (¹⁸³ WH) = 50.1] <i>exo</i> 7.21 [5H, m, C ₆ H ₅] 5.81 [5H, s, η-C ₅ H ₅] 5.15 [5H, s, η-C ₅ H ₅] 3.99 [1H, dd, <i>J</i> (HH) = 14.0, 10.4, CH ₂ CHC ₆ H ₅] 2.42 [1H, ddd, <i>J</i> (HH) = 14.0, 6.7, 1.2, CH ₂ CHC ₆ H ₅ - <i>cis</i>] 2.19 [1H, ddd, <i>J</i> (HH) = 10.4, 6.7, 1.2, CH ₂ CHC ₆ H ₅ - <i>trans</i>] −6.53 [1H, s, hydride, <i>J</i> (¹⁸³ WH) = 48.2]	145.76, 144.36 [C _q , C ₆ H ₅] 129.22, 129.05, 128.91, 127.47, 126.91 [CH, C ₆ H ₅] 92.15, 91.87, 91.74, 90.88 [η-C ₅ H ₅] 40.05, 35.29 [CH ₂ CHC ₆ H ₅] 15.29, 7.37 [CH ₂ CHC ₆ H ₅]
5	C 39.35 (39.70) H 3.65 (3.65) N 2.40 (2.30)	2343 [ν(CC) + δ(CH ₃)] 2268 [ν(CN)]	7.18 [5H, m, C ₆ H ₅] 5.49 [10H, s, η-C ₅ H ₅] 2.77 [3H, s, CH ₃ CN] 2.72 [2H, m, CH ₂ CH ₂ C ₆ H ₅] 1.11 [2H, m, CH ₂ CH ₂ C ₆ H ₅]	148.75 [C _q , C ₆ H ₅] 136.42 [CN] 128.91 [CH, C ₆ H ₅] 128.43 [CH, C ₆ H ₅] 125.75 [CH, C ₆ H ₅] 92.19 [η-C ₅ H ₅] 45.12 [CH ₂ CH ₂ C ₆ H ₅] 4.80 [CH ₃ CN] −3.73 [CH ₂ CH ₂ C ₆ H ₅]

^a Analytical data given as found (required). ^b Nujol mull. Complexes **4** and **5** also show strong bands at 828 and 557 cm⁻¹, assigned as ν(P–F) of PF₆⁻ counter ion. ^c In (CD₃)₂CO solution (295 K), data given as chemical shift (δ) (relative intensity, multiplicity, *J*/Hz, assignment). ^d Characterisation by ¹H NMR and X-ray diffraction data only. ^e Combined ¹³C NMR data for *endo* and *exo* isomers.

**Fig. 1** Molecular structure of the cation of complex **2**.

typical of that found in tungstenocene sulfur complexes as shown in Table 3. Both C–S bonds are essentially equal in length and shorter than the typical C–S single bond,^{21,22} which, along with the observed planarity, is consistent with delocalisation in the chelated *O*-alkyl dithiocarbonate ligand. The S1–W–S2 angle of 70.12(15)° is smaller than the related angle in many other reported d² tungstenocene complexes as a result of compression enforced by the ring size.^{23–25} This angle is similar in size to that found in the related four-membered ring complexes [(η-C₅H₅)₂W(μ-SC₆H₅)₂M(CO)₄] (M = Cr, Mo or W).²⁶

In [W(η-C₅H₅)₂H(L)][SO₃CF₃] where L = PhCN **3** the ‘L’ ligand is much more tightly bound than where L = thf **1**; at 44 °C *t*_{1/2} for L substitution is 315 and 6.7 hours respectively,²⁰ making **3** much less useful as a synthetic source of the 16-electron trans-ient [W(η-C₅H₅)₂H]⁺. Crystals of **3** suitable for X-ray diffraction were grown from benzonitrile–Et₂O and a molecular structure obtained as illustrated in Fig. 2. Selected bond lengths and angles are given in Table 2. A pseudo-tetrahedral tungsten centre with a ring centroid–tungsten–ring centroid angle of 143.7° is observed. The hydride ligand was not located in the difference map, however, positioning of the hydride ligand at the site observed in Fig. 2 would complete the pseudo-

Table 2 Selected bond lengths (Å) and angles (°) for the complexes **2**, **3** and *exo*-**4**

[W(η-C ₅ H ₅) ₂ (η ² -S ₂ COCH(CD ₃) ₂ -S,S')][SO ₃ CF ₃] 2			
W–Cp	1.98	Cp–W(1)–Cp	135.7
W(1)–S(1)	2.470(4)	S(1)–W(1)–S(2)	70.12(15)
W(1)–S(2)	2.470(4)	W(1)–S(1)–C(11)	88.2(6)
S(1)–C(11)	1.699(17)	W(1)–S(2)–C(11)	88.3(6)
S(2)–C(11)	1.696(17)	S(1)–C(11)–S(2)	113.4(9)
C(11)–O(1)	1.312(19)	S(1)–C(11)–O(1)	119.3(12)
O(1)–C(12)	1.477(19)	S(2)–C(11)–O(1)	127.3(13)
		C(11)–O(1)–C(12)	121.1(13)
[W(η-C ₅ H ₅) ₂ H(NCPh)][SO ₃ CF ₃] 3			
W–Cp	1.96	Cp–W–Cp	143.7
W–N	2.096(9)	W–N–C(11)	176.9(9)
N–C(11)	1.159(14)	N–C(11)–C(12)	174.4(13)
C(11)–C(12)	1.44(2)		
<i>exo</i> -[W(η-C ₅ H ₅) ₂ H(η ² -CH ₂ CHC ₆ H ₅)] [PF ₆] <i>exo</i> - 4			
W–Cp	1.98	Cp–W–Cp	139.7
W–C(11)	2.264(16)	C(11)–W–C(12)	36.2(6)
W–C(12)	2.323(15)	W–C(11)–C(12)	74.1(9)
C(11)–C(12)	1.43(3)	W–C(12)–C(11)	69.6(9)
C(12)–C(13)	1.47(2)	W–C(12)–C(13)	120.9(11)
		C(11)–C(12)–C(13)	123.3(15)

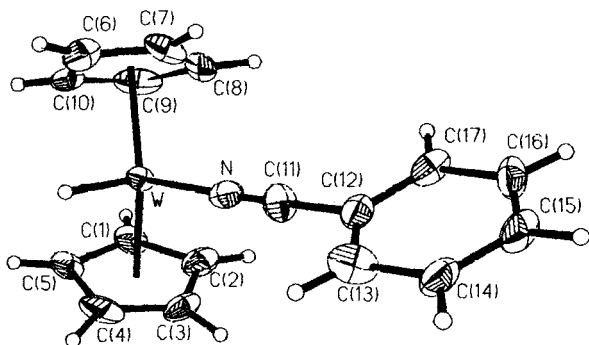
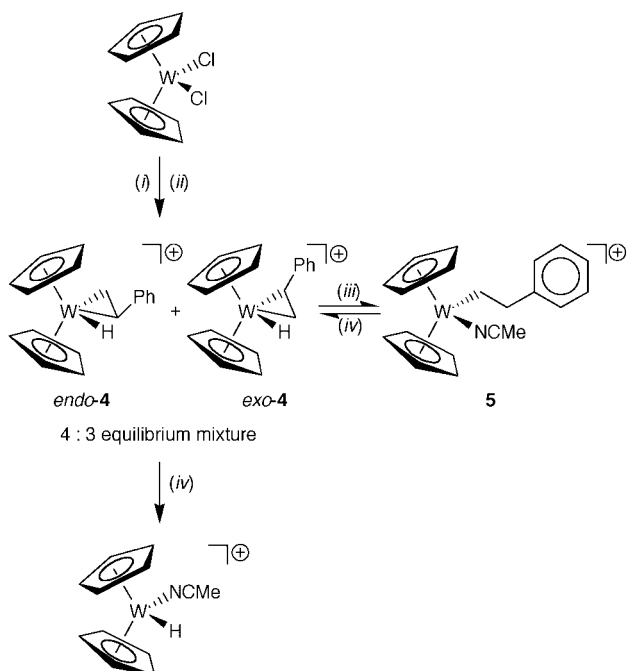
Cp = C₅H₅ ring centroid.

tetrahedral geometry around the tungsten centre, as observed in all complexes of this type. The W–N bond length (2.096(9) Å) is similar to that reported by us for related cationic tungsten–acetonitrile complexes.^{19,20}

The olefin complex [W(η-C₅H₅)₂H(η²-CH₂CHC₆H₅)] [PF₆] **4** was prepared as described for related complexes^{27,28} by treating the neutral dichloride [W(η-C₅H₅)₂Cl₂] with an excess of the Grignard reagent²⁹ [MgBr(CHCH₃C₆H₅)]. Compound **4** was isolated as a mixture of *endo* and *exo* isomers in the ratio 4 : 3, a typical ratio found for olefin hydride complexes of tungstenocene,²⁸ Scheme 1. We presume that the observed isomer ratio is an equilibrium position attained by a base catalysed proton-

Table 3 Tungsten–sulfur bond lengths in tungstenocene complexes

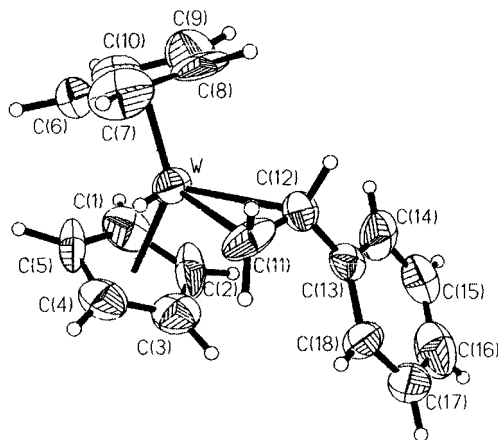
Complex	W–S/Å	Ref.
$[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\mu\text{-SC}_6\text{H}_5)_2\text{Cr}(\text{CO})_4]$	2.504(6)	26
$[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\mu\text{-SC}_6\text{H}_5)_2\text{Mo}(\text{CO})_4]$	2.487(7)	26
$[(\eta\text{-C}_5\text{H}_5)_2\text{W}(\mu\text{-SC}_6\text{H}_5)_2\text{W}(\text{CO})_4]$	2.49(1)	26
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{S}_2\text{C}_6\text{H}_4)]$	2.421(2)	43
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-S}_4)]$	2.42	44
$[\text{W}(\eta\text{-C}_5\text{H}_5)_2(2\text{-SN}_2\text{OC}_4\text{H}_9)][\text{PF}_6]$	2.495(7)	45
2	2.470(4)	This work

**Fig. 2** Molecular structure of the cation of complex **3**.**Scheme 1** Synthesis and reactions of complex **4**. (i) 20 °C, toluene, $[\text{MgBr}(\text{CHCH}_3\text{C}_6\text{H}_5)]$; (ii) 20 °C, water, NH_4PF_6 ; (iii) 20 °C, MeCN; (iv) $h\nu$, 20 °C, MeCN.

ation/deprotonation process of the hydride ligand during work-up.²⁸

The analytical and spectroscopic data for **4** are given in Table 1. The resonances for the *endo* and *exo* forms in the ^1H NMR spectrum of the isomeric mixture were assigned using integrals, and an observed coupling between the methylene protons of the lesser isomer ($J(\text{HH}) = 1.2$ Hz) by a through-space interaction. The methine resonance of the major isomer was somewhat broader, compared with that of the minor isomer, indicating an analogous, but unresolved, through-space interaction. The IR spectrum of **4** shows a reduction of 194 cm^{-1} for the $\nu(\text{C}=\text{C})$ band compared to that of free styrene.

Crystals of complex **4** suitable for X-ray diffraction study were difficult to obtain. After repeated attempts, a misshapen crystal was grown by slow diffusion of Et_2O into an acetone

**Fig. 3** Molecular structure of the cation of complex *exo*-**4**.

solution of **4** at 0 °C, and a molecular structure obtained as illustrated in Fig. 3. Selected bond lengths and angles are presented in Table 2. The structure shows a tungsten centre with the two cyclopentadienyl ligands co-ordinated in the conventional η^5 fashion. The hydride ligand was located in the difference map, at the site shown in Fig. 3, thus assigning the stereochemistry about the tungsten centre as *exo*. The olefinic carbon–carbon bond length (C11–C12) of $1.43(3)\text{ Å}$ is longer than that of a free olefin (e.g. ethene, $1.337(2)\text{ Å}$)³⁰ and is similar to that found in olefin complexes of electron rich, low valent metal centres.^{31–33} The observed long olefinic bond length in *exo*-**4**, along with the W–olefin carbon bond lengths ($2.264(16)$ and $2.323(15)\text{ Å}$) which are similar to those reported in related complexes,^{34,35} for a tungsten–carbon σ bond, mean that **4** has considerable metallocyclopropane character. This is consistent with the observed spectroscopic data for **4**. A search of the Cambridge Crystallographic Database revealed that no mononuclear tungsten–styrene compounds have previously been characterised by crystallography. In fact, only two η^2 -olefin complexes of the bis(cyclopentadienyl)tungsten unit have been structurally characterised: $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{CH}_3(\eta^2\text{-CH}_2\text{CH}_2)][\text{PF}_6]$ and the *ansa* complex $[\text{W}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{H}(\eta^2\text{-CH}_2\text{CH}_2)][\text{B}(\text{C}_6\text{F}_5)_4]$.^{36,37} The olefin ligand in these complexes is bound in a manner similar to that found in **4**.

The reaction of the isomeric mixture of complex **4** with MeCN under thermal conditions is similar to that reported for $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-CH}_2\text{CH}_2)][\text{PF}_6]$.¹⁹ The styrene in **4** inserts into the tungsten–hydride bond, followed by co-ordination of an NCMe molecule at the vacant site to yield only one product, $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)(\text{NCMe})][\text{PF}_6]$ **5**, and not a mixture of isomers (Scheme 1). The NMR spectra show the presence of two methylene groups, and the IR spectrum is similar to that for the acetonitrile complexes reported previously,^{19,20} thus confirming the structure of **5** as that resulting from primary insertion with a terminal nitrile co-ordinated.

The analogous reaction with d^3 -MeCN was carried out, thus allowing it to be followed by ^1H NMR. This showed that the reaction was slower than that with $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-CH}_2\text{-CH}_2)][\text{PF}_6]$.^{19,38} This may be reasonably ascribed to the electron withdrawing substituent on the olefin double bond of **4** which encourages back donation and makes the olefin bond more strongly to the tungsten in **4**. The insertion rates for the *exo* and *endo* isomers are different, the *endo* undergoing insertion *ca.* 3.5 times as fast. This fits with the trend observed in the $[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-CH}_2\text{CHCH}_3)][\text{PF}_6]$ system, in which insertion of the propene ligand into the tungsten–hydride bond has been studied using Spin Population Transfer experiments.²⁸ The insertion product **5** contains an alkyl with an electron withdrawing group which has the effect of stabilising the alkyl towards β -hydride elimination. Qualitative analysis of a series of d^6 -acetone ^1H NMR spectra of **5** taken over a period of

Table 4 Crystal data for complexes **2**, **3** and *exo-4*

	2	3	<i>exo-4</i>
Formula	C ₁₅ H ₁₇ F ₃ O ₄ S ₃ W	C ₁₈ H ₁₆ F ₃ NO ₃ SW	C ₁₈ H ₁₉ F ₆ PW
<i>M</i>	598.32	567.23	564.15
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	7.3175(2)	8.759(2)	6.5260(13)
<i>b</i> /Å	20.8936(7)	13.161(3)	17.464(4)
<i>c</i> /Å	14.3418(4)	15.623(3)	15.736(3)
β /°	92.71		94.67(3)
<i>U</i> /Å ³	2190.24(11)	1801.0(7)	1787.5(6)
<i>Z</i>	4	4	4
μ (Mo-K α)/mm ⁻¹	5.600	6.579	6.610
<i>T</i> /K	200(2)	150(2)	220(2)
Reflections collected	11216	8181	3998
Unique reflections	2714	2741	2220
<i>R</i>	0.0735	0.0493	0.0705
<i>wR</i> 2 (all data)	0.2375	0.1122	0.1589

several days shows that β -hydride elimination occurs, but at a slower rate than found in [W(η -C₅H₅)₂(CH₂CH₃)(NCMe)]-[PF₆],^{19,38} generating **4** and free MeCN. The *endo* isomer is formed first, and with time the ratio of *endo*:*exo* isomers approaches that found for the synthesis of **4**. Photolysis of **5** in d³-MeCN generates free styrene and the CD₃CN analogue [W(η -C₅H₅)₂H(NCCD₃)]-[PF₆], with complete conversion achieved within one hour (Scheme 1). The formation of [W(η -C₅H₅)₂H(NCCD₃)]-[PF₆] is consistent with the photochemical mechanism proposed earlier.¹⁹

In conclusion, we have described some tungstenocene-hydride complexes, including X-ray crystallographic studies, and presented examples of their reactivity. The unsaturated molecules CS₂ and styrene have been shown to insert into the W–H bond to give isolable organometallic complexes.

Experimental

All manipulations of air- and moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques under an atmosphere of argon, or in a dry-box under an atmosphere of nitrogen. All solvents were purified and dried by refluxing over a suitable drying agent, followed by distillation under a nitrogen atmosphere. Toluene was dried over molten sodium, diethyl ether over sodium–potassium alloy (NaK_{2,2}), tetrahydrofuran over molten potassium, ethanol over magnesium turnings, acetonitrile and chloroform over calcium hydride and acetone over anhydrous magnesium sulfate. Carbon disulfide, styrene, methyl acrylate and benzonitrile were distilled and degassed by three freeze–pump–thaw cycles. Other materials were purchased from commercial sources and used without further purification.

The compounds [W(η -C₅H₅)₂H(thf)]-[SO₃CF₃] **1**,²⁰ [W(η -C₅H₅)₂H(NCPh)]-[SO₃CF₃] **3**²⁰ and [W(η -C₅H₅)₂Cl₂]³⁹ were prepared according to literature methods.

Photochemical reactions were carried out using a water-cooled 150 W medium-pressure mercury lamp irradiating stirred solutions in ampoules or NMR tubes fitted with airtight Young's taps (Young's ampoule or Young's NMR tube). Nuclear magnetic resonance spectra were recorded using Bruker AS-250 and WH-400 spectrometers, referenced using the resonances of residual protons in the deuterated solvents, infrared spectra using a Perkin-Elmer 1720X FTIR spectrometer using NaCl plates. Microanalyses were obtained using a Leeman Labs CE440 analyser.

Preparations

[W(η -C₅H₅)₂(η^2 -S₂COCH(CD₃)₂-S,S')] [SO₃CF₃] **2**. A solution of [W(η -C₅H₅)₂H(thf)] [CF₃SO₃] **1** (ca. 50 mg) in d⁶-acetone (2 cm³) was made up in a Young's NMR tube. To this was

added either a drop of CS₂, styrene or methyl acrylate, or it was placed under an atmosphere of CO₂. The samples were heated to 50 °C and ¹H NMR spectra ran at intervals. When the ¹H NMR spectra indicated reaction was complete, all volatiles were removed under reduced pressure, and d⁶-acetone ¹H NMR spectra were taken of the residues. For the reaction with CS₂ the residue was recrystallised from acetone–diethyl ether to yield brown crystals of [W(η -C₅H₅)₂(η^2 -S₂COCH(CD₃)₂-S,S')] [SO₃-CF₃] **2**.

[MgBr(CHCH₃C₆H₅)]. To a diethyl ether (100 cm³) suspension of magnesium turnings (5.3 g, 218 mmol) at 0 °C was added dropwise 1-phenylethyl bromide (10 g, 54 mmol) in diethyl ether (50 cm³). The mixture was stirred for 2 hours at 0 °C and refluxed for 2 hours. The resultant solution was decanted and the magnesium turnings washed with diethyl ether (3 \times 15 cm³). The washings were combined to give a 0.27 M solution of [MgBr(CHCH₃C₆H₅)] in diethyl ether (standardised by reaction of an aliquot (5 cm³) with 1.72 M HCl (3 cm³), and titration of excess of acid with 0.1 M NaOH).

[W(η -C₅H₅)₂H(η^2 -CH₂CHC₆H₅)] [PF₆] **4**. To a stirred toluene (30 cm³) suspension of [W(η -C₅H₅)₂Cl₂] (0.3 g, 0.78 mmol) was slowly added [MgBr(CHCH₃C₆H₅)] (2.5 mmol) in diethyl ether. The mixture was stirred at room temperature for 12 hours giving an orange suspension. The solvent was removed *in vacuo* and to the resultant orange solid at –80 °C was added ethanol (30 cm³). The mixture was warmed to room temperature and the solvent removed under reduced pressure. The residue was extracted with water (3 \times 50 cm³) and the extracts filtered through Celite. Addition of NH₄PF₆ (0.15 g, 0.92 mmol) to this solution gave a cream precipitate which was collected by filtration, washed with water (3 \times 10 cm³) and diethyl ether (3 \times 10 cm³) and dried under vacuum. Recrystallisation from acetone–diethyl ether yielded ca. 0.13 g (30%) of a cream crystalline solid of **4** as a mixture of *exo* and *endo* isomers in the ratio 3:4.

[W(η -C₅H₅)₂(CH₂CH₂C₆H₅)(NCMe)] [PF₆] **5**. A pale solution of [W(η -C₅H₅)₂H(η^2 -CH₂CHC₆H₅)] [PF₆] **4** (0.1 g, 0.18 mmol) in MeCN (20 cm³) was stirred in the dark at room temperature for two weeks to give an orange solution. Removal of solvent under reduced pressure followed by recrystallisation from acetonitrile–diethyl ether yielded ca. 93 mg (85%) of orange crystals of **5**.

Photochemical reaction of [W(η -C₅H₅)₂(CH₂CH₂C₆H₅)(NCMe)] [PF₆] **5 with CD₃CN.** A CD₃CN (2 cm³) solution of [W(η -C₅H₅)₂(CH₂CH₂C₆H₅)(NCMe)] [PF₆] **5** (ca. 50 mg) in a Young's NMR tube was irradiated for 1 hour, during which time the solution became yellow. ¹H NMR spectroscopy showed

the yellow solution to contain $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{H})(\text{NCCD}_3)][\text{PF}_6]$ and unco-ordinated styrene only.

Crystal structure determinations

Crystallographic data for complexes **2**, **3** and *exo-4* are summarised in Table 4. Single crystals were glued to quartz fibres, coated in Nujol and cooled in the cold gas stream of the diffractometer. Data for **2** and **4** were collected on a Siemens 3 circle diffractometer equipped with a SMART CCD area detector. Data for **3** were collected on a Siemens R3 four circle diffractometer operating in the ω - 2θ mode; three standard reflections were monitored every 197. No decay was measured. Both instruments used graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using SHELXTL⁴⁰ version 5 software; refinements were carried out using SHELXTL 96,⁴¹ minimising on the weighted *R* factor *wR*². Anisotropic thermal parameters were used for all non-H atoms with hydrogen atoms placed at calculated positions and fixed, with isotropic thermal parameters ($U = 0.08 \text{ \AA}^2$), riding on the supporting atom. The trifluoromethanesulfonate anion of **2** was disordered; a similarity restraint was applied to the C–F bond lengths in order to obtain satisfactory refinement. The hydride in **3** was not located in the difference map and was positioned to complete the pseudotetrahedral geometry around the tungsten centre. A dummy atom representing the hydride ligand was placed in the requisite position, as shown in Fig. 2, for illustrative purposes, but was not included in any refinement. The hydride ligand in **4** was placed at a site of electron density located on the difference map, and the W–H bond length was fixed at 1.6 \AA .⁴²

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See <http://www.rsc.org/suppdata/doi/a9/a909732e/> for crystallographic files in .cif format.

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