

# Cyclopentadienyl tungsten complexes with thiocarboxylate and thiosulfonate ligands: Structures of $\text{CpW}(\text{CO})_3\text{SCOPh}$ and $\text{CpW}(\text{CO})_3\text{SSO}_2\text{-4-C}_6\text{H}_4\text{Cl}$

Mohammad El-khateeb<sup>a,\*</sup>, Helmar Görls<sup>b</sup>, Wolfgang Weigand<sup>b</sup>

<sup>a</sup> Chemistry Department, Jordan University of Science and Technology, Irbid 22110, Jordan

<sup>b</sup> Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, August-Bebel Strasse 2, Jena 07743, Germany

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## Abstract

Treatment of the hydrosulfido tungsten complex  $\text{CpW}(\text{CO})_3\text{SH}$  with acid chlorides ( $\text{RCOCl}$ ) or sulfonyl chlorides ( $\text{RSO}_2\text{Cl}$ ) affords  $\text{CpW}(\text{CO})_3\text{SCOR}$  (**1**) [ $\text{R} = \text{Me}$  (**a**),  $\text{CH}_2\text{Cl}$  (**b**),  $\text{Ph}$  (**c**),  $4\text{-C}_6\text{H}_4\text{NO}_2$  (**d**)] and  $\text{CpW}(\text{CO})_3\text{SSO}_2\text{R}$  (**2**) [ $\text{R} = \text{Me}$  (**a**),  $\text{Ph}$  (**b**),  $4\text{-C}_6\text{H}_4\text{Cl}$  (**c**),  $4\text{-C}_6\text{H}_4\text{NO}_2$  (**d**)], respectively. The novel complexes, **1** and **2**, were fully characterized by elemental analyses, IR and  $^1\text{H}$  NMR spectroscopy. The solid state structures of  $\text{CpW}(\text{CO})_3\text{SCOPh}$  (**1c**) and  $\text{CpW}(\text{CO})_3\text{SSO}_2\text{-4-C}_6\text{H}_4\text{Cl}$  (**2c**) were determined by an X-ray crystal structure analysis.

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**Keywords:** Organometallics; Tungsten; Sulfur; Thiocarboxylate; Thiosulfonate; Complexes; Structure

## 1. Introduction

Organotungsten complexes supported by sulfur-donor ligands have attracted continuous interest in recent years [1–4]. The thiolato complexes  $\text{CpW}(\text{CO})_2(\text{L})\text{SR}$  ( $\text{L} = \text{CO}$ ,  $\text{PPh}_3$ ) are accessible by several routes [5–10]. These include substitution reactions of the tungsten chlorides ( $\text{CpW}(\text{CO})_2(\text{L})\text{Cl}$ ) by thiolate anions [5,6], addition of the sulfur transfer reagent ( $\text{RSphth}$ ;  $\text{phth} = \text{phthalimido}$ ) to the corresponding tungsten anions ( $[\text{CpW}(\text{CO})_2(\text{L})]^-$ ) [7,8], and oxidative addition of organic disulfides to the tungsten dimer,  $[\text{CpW}(\text{CO})_3]_2$  [9,10]. Oxidation of some of these tungsten thiolates by 3-chloroperoxybenzoic acid gave the sulfinato complexes  $\text{CpW}(\text{CO})_2(\text{L})\text{SO}_2\text{R}$  [11]. Photolysis using UV-light or heating solutions of the tricarbonyl-tungsten thiolates produced the thiolato-bridged dimers  $(\mu\text{-SR})_2[\text{CpW}(\text{CO})_2]_2$  [12].

The preparation and characterization of the hydrosulfido complex  $\text{CpW}(\text{CO})_3\text{SH}$  are reported by several groups [13–16]. Its reactions with the sulfur transfer reagents ( $\text{RSphth}$ ,  $\text{RSSphth}$ ,  $\text{RS}(\text{O})\text{phth}$ ) have been reported by Shaver and Hartgerink [17]. Reactions with  $\text{RSphth}$  or  $\text{RSSphth}$  gave the polysulfido complexes,  $\text{CpW}(\text{CO})_3\text{S}_n\text{R}$  ( $n = 2, 3$ ), while the reaction with  $\text{RS}(\text{O})\text{phth}$  afforded the thiosulfinato complexes  $\text{CpW}(\text{CO})_3\text{SS}(\text{O})\text{R}$  [17].

In our laboratory, the reactions of hydrosulfido metal complexes with electrophiles have been investigated [18–20]. The reactions of the chelate hydrosulfido complexes  $\text{CpRu}(\text{dppa})\text{SH}$  ( $\text{dppa} = \text{dppm}$ ,  $\text{dppe}$ ) with various sulfonyl chlorides afforded the expected thiosulfonato species  $\text{CpRu}(\text{dppa})\text{SSO}_2\text{R}$  [18]. Recently, the reactions of  $\text{CpRu}(\text{L})(\text{L}')\text{SH}$  ( $\text{L} = \text{L}' = \text{PPh}_3$ ,  $1/2\text{dppe}$ ;  $\text{L} = \text{PPh}_3$ ,  $\text{L}' = \text{CO}$ ) complexes with chloroformates ( $\text{ROCOCl}$ ) or *O*-alkyloxalyl chlorides ( $\text{ROCOCOCl}$ ) were found to produce the appropriate thiocarbonato complexes  $\text{CpRu}(\text{L})(\text{L}')\text{SCO}_2\text{R}$  or thiooxalato complexes  $\text{CpRu}(\text{L})(\text{L}')\text{SCOCO}_2\text{R}$  ( $\text{R} = \text{alkyl}$ ,  $\text{aryl}$ ), respectively [19,20]. The reaction of these hydrosulfido ruthenium complexes with

\* Corresponding author. Tel.: +962 2 7201000; fax: +962 2 7095014.  
E-mail address: [kateeb@just.edu.jo](mailto:kateeb@just.edu.jo) (M. El-khateeb).

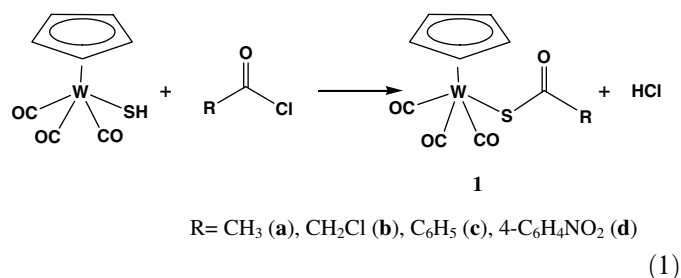
acid chlorides, which was reported by Schenk, produced the thiocarboxylato complexes  $\text{CpRu(L)(L')SCOR}$  [21]. The analogous reaction of the molybdenum hydrosulfido complex  $\text{CpMo(CO)}_3\text{SH}$  with acid chlorides was also reported to give the corresponding molybdenum-thiocarboxylato complexes  $\text{CpMo(CO)}_3\text{SCOR}$  [22].

As part of our study on the reactions of hydrosulfido metal complexes with electrophiles, we describe in this paper the synthesis and characterization of tungsten thiocarboxylato and thiosulfonato complexes. The reactions between  $\text{CpW(CO)}_3\text{SH}$  and acid chlorides or sulfonyl chlorides, which gave the expected thiocarboxylato complexes  $\text{CpW(CO)}_3\text{SCOR}$  or thiosulfonato complexes  $\text{CpW(CO)}_3\text{SSO}_2\text{R}$ , are discussed in this report.

## 2. Results and discussion

### 2.1. Synthesis and characterization

When the tungsten hydrosulfido complex  $\text{CpW(CO)}_3\text{SH}$  was reacted with slight excess of acid chlorides at low temperature, the thiocarboxylato complexes  $\text{CpW(CO)}_3\text{SCOR}$  (**1**) were obtained as shown in the following equation:

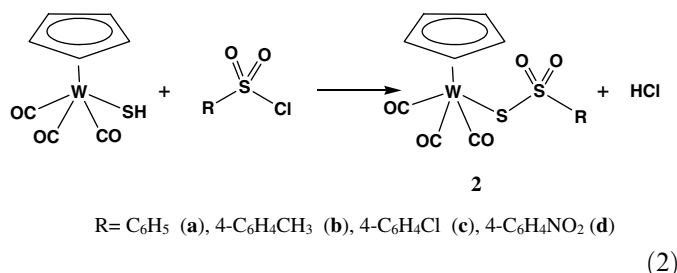


The resulting red thiocarboxylato complexes, **1**, are air stable as solids. In solution, they decompose to brown insoluble materials over few days. In some experiments small amounts of the chloride complex  $\text{CpW(CO)}_3\text{Cl}$  were also obtained as a side product. Complexes **1** have been fully characterized by IR,  $^1\text{H}$  NMR spectra, elemental analysis and by single-crystal X-ray structure determination of **1c**. The IR spectra of **1** display three absorption bands in the ranges of 2045–2032, 1962–1957 and 1944–1939  $\text{cm}^{-1}$  for the terminal carbonyl ligands. These CO stretching vibrations are comparable to those of the precursor,  $\text{CpW(CO)}_3\text{SH}$  (2028, 1961, 1949  $\text{cm}^{-1}$ ) [13] and to the selenocarboxylato analogs,  $\text{CpW(CO)}_3\text{SeCOR}$  (2038–2032, 1962–1955, 1942–1935  $\text{cm}^{-1}$ ) [23]. In the ketonic carbonyl region, a band attributed to the carbonyl group of the thiocarboxylato ligand was observed in the range of 1716–1621  $\text{cm}^{-1}$ . These values are at higher wave numbers with respect to the corresponding band of the selenocarboxylato analogs,  $\text{CpW(CO)}_3\text{SeCOR}$  (1663–1616  $\text{cm}^{-1}$ ) [23] and comparable to those of molybdenum thiocarboxylato complexes (1736–1644  $\text{cm}^{-1}$ ) [22].

All complexes **1** showed a sharp singlet in the range of 5.72–5.64 ppm in their  $^1\text{H}$  NMR spectra, which can be assigned to the resonance of the cyclopentadienyl ligand.

This range is similar to those reported for  $\text{CpW(CO)}_3\text{Q}$  {Q = SH (5.66 ppm), SR (5.71–5.34 ppm), SSR (5.66–5.54 ppm)} [13,17]. The peaks for the R-group of the thiocarboxylato ligands are shown in the expected ranges with the expected multiplicities.

The tungsten thiosulfonato derivatives  $\text{CpW(CO)}_3\text{S-SO}_2\text{R}$  (**2**) (R =  $\text{C}_6\text{H}_5$  (a),  $4\text{-C}_6\text{H}_4\text{CH}_3$  (b),  $4\text{-C}_6\text{H}_4\text{Cl}$  (c),  $4\text{-C}_6\text{H}_4\text{NO}_2$  (d)) were synthesized by the reaction of the hydrosulfido complex with sulfonyl chlorides as shown in the following equation:



Complexes **2** are stable as solids, but they are air sensitive in solution. They are soluble in most organic solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_2\text{O}$ , THF, and are slightly soluble in hydrocarbon solvents.

The IR spectra of the products, **2**, indicate the presence of three strong bands in the ranges 2065–2060  $\text{cm}^{-1}$ , 1970–1968 and 1951–1943  $\text{cm}^{-1}$  corresponding to the stretching band of the terminal carbonyl ligands bonded to the tungsten atom. These frequencies are higher than those for **1** suggesting that the thiosulfonato ligands are weaker  $\pi$ -donor than the thiocarboxylato ligands. A similar observation was found for the analogous selenocarboxylato versus selenosulfonato tungsten complexes [23]. The thiosulfonato group has intense bands in the ranges of 1281–1280 and 1133–1130  $\text{cm}^{-1}$  assigned to the asymmetric and the symmetric S–O stretching modes, respectively, as confirmed by other reported thiosulfonato metal complexes [18,24].

The Cp-ring protons for complexes **2** appear as a singlet in the range 5.94–5.91 ppm in their NMR spectra. This range is higher than that of **1**, due to stronger  $\pi$ -donor properties of the thiocarboxylato ligands compared to that of the thiosulfonato analogs. This range is also higher than that reported for  $\text{CpW(CO)}_3\text{SSOR}$  complexes (5.89–5.78 ppm). The peaks for the R-group of the thiosulfonato moiety are also present in the spectra of **2**.

### 2.2. Crystal structures of 1c and 2c

The molecular structures of **1c** and **2c** were established by single-crystal X-ray diffraction studies. The ORTEP views of these complexes, with the atom numbering schemes are shown in Figs. 1 and 2. Selected bond distances and bond angles for these complexes are listed in Table 1. These complexes show the expected W geometry as a piano stool with the Cp ring as the base and the carbonyls and the sulfur containing ligands as the legs. The

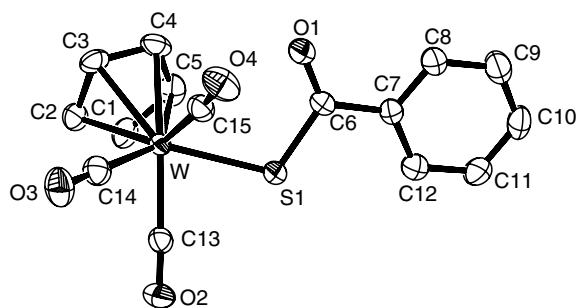
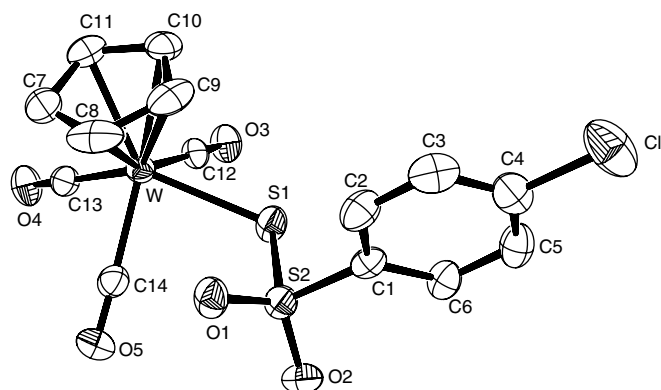
Fig. 1. ORTEP drawing of CpW(CO)<sub>3</sub>SCOPh (**1c**).Fig. 2. ORTEP drawing of CpW(CO)<sub>3</sub>SSO<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>Cl (**2c**).

Table 1  
Selected bond length (Å) and selected bond angles (°) for CpW(CO)<sub>3</sub>S-COC<sub>6</sub>H<sub>5</sub> (**1c**) and CpW(CO)<sub>3</sub>SSO<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>Cl (**2c**)

Compound <b>1c</b>		Compound <b>2c</b>	
W–C1	2.358(4)	W–C7	2.305(7)
W–C2	2.299(4)	W–C8	2.343(6)
W–C3	2.294(4)	W–C9	2.368(6)
W–C4	2.338(4)	W–C10	2.340(6)
W–C5	2.365(4)	W–C11	2.284(6)
W–C13	1.987(4)	W–C12	1.982(7)
W–C14	1.985(5)	W–C13	2.013(7)
W–C15	2.015(4)	W–C14	2.022(7)
W–S	2.505(1)	W–S1	2.4948(16)
C13–O2	1.153(5)	C12–O3	1.257(7)
C14–O3	1.149(5)	C13–O4	1.135(7)
C15–O4	1.127(5)	C14–O5	1.138(7)
C6–O1	1.215(5)	S2–O1	1.440(4)
S–C6	1.771(4)	S2–O2	1.438(4)
		S1–S2	2.055(2)
C14–W–C13	75.95(17)	C12–W–C13	75.7(2)
C14–W–C15	75.23(17)	C12–W–C14	108.3(3)
C13–W–C15	112.27(16)	C13–W–C14	77.1(3)
C14–W–S	131.07(13)	C12–W–S1	73.72(18)
C13–W–S	75.71(12)	C13–W–S1	133.76(18)
C15–W–S	79.79(14)	C14–W–S1	80.57(18)
C6–S–W	108.44(14)	S2–S1–W	112.09(8)
		O2–S2–O1	118.1(39)
O1–C6–S	123.6(3)	O2–S2–S1	109.5(2)
O2–C13–W	177.5(3)	O3–C12–W	178.3(5)
O3–C14–W	179.0(4)	O4–C13–W	177.0(6)
O4–C15–W	175.2(5)	O5–C14–W	177.1(6)

X-ray structure of **1c** (Fig. 1) shows that the thiocarboxylate ligand is bonded to the W atom in a monodentate fashion through the S atom with a W–S bond length of 2.358(4) Å. The W–C<sub>CO</sub> bond distances (average 1.996 Å) are similar to those reported for CpW(CO)<sub>3</sub>-containing complexes [13,25]. The C=O bond length of the thiocarboxylate ligand of 1.215(5) Å is comparable to those found in CpMo(CO)<sub>3</sub>SCOPh (1.214(5) Å) [22] and CpFe(CO)<sub>2</sub>-SCO-2-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> (1.209(5) Å) [26]. The thiosulfonate group of **2c** is also bonded to tungsten in a monodentate fashion through the S-atom as shown in Fig. 2. The W–S bond length of 2.4948(16) Å is longer than the corresponding length of **1**. The W–C<sub>CO</sub> distances (average 2.005 Å) are comparable to those of **1c**. The S–S bond length of 2.055(2) Å is in good agreement to those reported for thiosulfonate complexes {e.g. CpFe(CO)<sub>2</sub>SSO<sub>2</sub>CCl<sub>3</sub> (2.022(2) Å) [27], CpRu(dppe)SSO<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>Cl (2.032(2) Å) [18]}. The W–S–S angle of **2c** (112.09(8)°) and the W–S–C of **1c** (108.44(14)°) indicate an sp<sup>2</sup> hybridization around the sulfur atom in these molecules.

### 3. Experimental

#### 3.1. General

Synthetic work was carried out under a dinitrogen atmosphere using Schlenk techniques. Tetrahydrofuran, diethyl ether, hexane and dichloromethane were dried, distilled and stored under nitrogen. The reagent, CpW(CO)<sub>3</sub>SH was prepared as described previously [13,14]. Acid chlorides, sulfonyl chlorides, tungsten hexacarbonyl, and sulfur were obtained commercially and were used as received.

Infrared (IR) spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer in CH<sub>2</sub>Cl<sub>2</sub> solutions. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker spectrometer operating at 200 or 400 MHz with chemical shifts reported in ppm downfield from TMS, using the solvent residual peak as internal reference. Elemental analyses were performed by the Institute of Organic and Macromolecular Chemistry, FSU-Jena. Melting points were recorded on a polarization-microscope (Axiolab) connected to a heating unit (THMS-600) using the softwares Linkam LNP and CI 93.

#### 3.2. General procedure for the preparation of CpW(CO)<sub>3</sub>SCOR (**1**)

A diethyl ether solution of CpW(CO)<sub>3</sub>SH (0.28 g, 1.00 mmol) was cooled to –78 °C. A solution of the acid chloride (1.10 mmol) in 10 mL Et<sub>2</sub>O was added dropwise. The cooling bath was removed and the solution was stirred for 2 h at room temperature. The resulting mixture was filtered over celite, concentrated to 2 mL under reduced pressure and transferred to a silica gel column made up in hexane. Elution with hexane removes the excess acid chloride and with (1:1 v:v) ratio of diethyl ether:hexane gives an orange band. This band was collected and the volatiles

were removed under vacuum. The resulting orange solid was recrystallized from dichloromethane/hexane at 0 °C.

### 3.2.1. $CpW(CO)_3SCOMe$ (**1a**)

Yield: 65%. M.p.: 132–134 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2038 (s), 1957 (s), 1942 (s) (ν(C≡O)), 1649 (m), (ν(C=O)). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.49 (s, 3H, CH<sub>3</sub>); 5.66 (s, 5H, C<sub>5</sub>H<sub>5</sub>). Anal. Calc. for C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>SW: C, 29.43; H, 1.98; S, 7.68. Found: C, 29.30; H, 2.02; S, 7.88%.

### 3.2.2. $CpW(CO)_3SCOCH_2Cl$ (**1b**)

Yield: 68%. M.p.: 110–112 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2045 (s), 1962 (s), 1944 (ν(C≡O)), 1716 (m) (ν(C=O)). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.36 (s, 2H, CH<sub>2</sub>Cl); 5.69 (s, 5H, C<sub>5</sub>H<sub>5</sub>). Anal. Calc. for C<sub>10</sub>H<sub>7</sub>ClO<sub>4</sub>SW: C, 27.14; H, 1.59; S, 7.25. Found: C, 26.93; H, 1.42; S, 7.43%.

### 3.2.3. $CpW(CO)_3SCOPh$ (**1c**)

Yield: 72%. M.p.: 122–123 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2041 (s), 1962 (s), 1940 (s) (ν(C≡O)), 1621 (m) (ν(C=O)). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.72 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.40 (m, 3H, C<sub>6</sub>H<sub>5</sub>); 8.14 (dd, 2H, C<sub>6</sub>H<sub>5</sub>,  $J_o = 7.6$  Hz,  $J_m = 1.4$  Hz). Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>4</sub>SW: C, 38.32; H, 2.14; S, 6.82. Found: C, 38.22; H, 2.05; S, 7.69%.

### 3.2.4. $CpW(CO)_3SCO-4-C_6H_4NO_2$ (**1d**)

Yield: 85%. M.p.: 180(d) °C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2032 (s), 1960 (s), 1939 (s) (ν(C≡O)), 1621 (m) (ν(C=O)). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.64 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 8.22 (two d, 4H, C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>,  $J_o = 9.2$  Hz). Anal. Calc. for C<sub>15</sub>H<sub>9</sub>NO<sub>6</sub>SW: C, 34.97; H, 1.76; N, 2.72; S, 6.22. Found: C, 35.28; H, 1.97; N, 2.55; S, 6.62%.

## 3.3. General procedure for the preparation of $CpW(CO)_3SSO_2R$ (**2**)

A diethyl ether solution of CpW(CO)<sub>3</sub>SH (0.28 g, 1.00 mmol) was cooled to -78 °C. A solution of sulfonyl chloride (1.10 mmol) in 10 mL Et<sub>2</sub>O was added dropwise. The reaction time and workup is as shown in Section 3.2.

### 3.3.1. $CpW(CO)_3SSO_2Ph$ (**2a**)

Yield: 62%. M.p.: 103–105 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2060 (s), 1970 (s), 1951 (s) (ν(C≡O)), 1280 (m), 1133 (ν(S=O)). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.91 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.60 (m, 3H, C<sub>6</sub>H<sub>5</sub>); 8.02 (d, 2H, C<sub>6</sub>H<sub>5</sub>,  $J_o = 7.2$  Hz). Anal. Calc. for C<sub>14</sub>H<sub>10</sub>O<sub>5</sub>S<sub>2</sub>W: C, 33.22; H, 1.99; S, 12.67. Found: C, 33.11; H, 2.28; S, 12.05%.

### 3.3.2. $CpW(CO)_3SSO_2-4-C_6H_4CH_3$ (**2b**)

Yield: 75%. M.p.: 109–111 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2061 (s), 1968 (s), 1943 (ν(C≡O)), 1280 (m), 1130 (m) (ν(S=O)). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.40 (s, 3H, CH<sub>3</sub>); 5.92 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.26 (d, 2H, C<sub>6</sub>H<sub>4</sub>,  $J_o = 8.4$  Hz); 7.78 (d, 2H, C<sub>6</sub>H<sub>4</sub>,  $J_o = 8.4$  Hz). Anal. Calc. for C<sub>15</sub>H<sub>12</sub>O<sub>5</sub>S<sub>2</sub>W: C, 34.63; H, 2.33; S, 12.33. Found: C, 33.95; H, 2.21; S, 11.84%.

### 3.3.3. $CpW(CO)_3SSO_2-4-C_6H_4Cl$ (**2c**)

Yield: 78%. M.p.: 117–118 °C. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2064 (s), 1969 (s), 1948 (s) (ν(C≡O)), 1281 (m), 1132 (ν(S=O)). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.92 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.40 (d, 2H, C<sub>6</sub>H<sub>4</sub>,  $J_o = 8.6$  Hz); 7.80 (d, 2H, C<sub>6</sub>H<sub>4</sub>,  $J_o = 8.6$  Hz). Anal. Calc. for C<sub>14</sub>H<sub>9</sub>ClO<sub>5</sub>S<sub>2</sub>W: C, 31.10; H, 1.68; S, 11.86. Found: C, 30.84; H, 1.78; S, 11.50%.

### 3.3.4. $CpW(CO)_3SSO_2-4-C_6H_4NO_2$ (**2d**)

Yield: 80%. M.p.: 152 °C (decomp.). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2065 (s), 1968 (s), 1944 (s) (ν(C≡O)), 1280 (m), 1133 (m) (ν(S=O)). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.94 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.46 (d, 2H, C<sub>6</sub>H<sub>4</sub>,  $J_o = 8.0$  Hz); 7.80 (d, 2H, C<sub>6</sub>H<sub>4</sub>,  $J_o = 8.0$  Hz). Anal. Calc. for C<sub>14</sub>H<sub>9</sub>NO<sub>7</sub>S<sub>2</sub>W: C, 30.51; H, 1.65; S, 11.63. Found: C, 30.02; H, 1.67; S, 10.88%.

## 3.4. X-ray structure analysis

X-ray data of red crystals of CpW(CO)<sub>3</sub>SCOPh (**1c**) and CpW(CO)<sub>3</sub>SSO<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>Cl (**2c**) were collected by a Nonius Kappa CCD diffractometer with a graphite monochromator λ(Mo Kα) = 0.71073 Å. Selected crystal data for these complexes are presented in Table 2. The structures were solved by direct methods using SHELXS-97 [28] and refined by full-matrix least-square procedures on |F<sup>2</sup>|, using SHELXTL-97 [29]. All non-hydrogen atoms are refined anisotropically and the hydrogen atom positions have been refined using the atom corresponded riding model. The structure

Table 2  
Selected crystal data and refinement parameters for CpW(CO)<sub>3</sub>SCOC<sub>6</sub>H<sub>5</sub> (**1c**) and CpW(CO)<sub>3</sub>SSO<sub>2</sub>-4-C<sub>6</sub>H<sub>4</sub>Cl (**2c**)

Compound	<b>1c</b>	<b>2c</b>
Empirical formula	C <sub>15</sub> H <sub>10</sub> O <sub>4</sub> SW	C <sub>14</sub> H <sub>9</sub> ClO <sub>5</sub> S <sub>2</sub> W
Formula weight (g/mol)	470.14	540.63
Crystal size (mm)	0.05 × 0.05 × 0.04	0.06 × 0.06 × 0.04
Crystal system	Monoclinic	Orthorhombic
Space group	P2 <sub>1</sub> /n	Pbca
Volume (Å <sup>3</sup> )	1453.96(10)	3250.7(2)
Z	4	8
Unit cell dimensions		
a (Å)	8.0953(3)	10.3159(5)
b (Å)	10.7904(5)	12.7234(6)
c (Å)	17.0655(5)	24.7668(9)
α (°)	90	90
β (°)	102.746(2)	90
γ (°)	90	90
Index range	-9 ≤ h ≤ 10, -12 ≤ k ≤ 13, -22 ≤ l ≤ 19	-12 ≤ h ≤ 13, -16 ≤ k ≤ 14, -31 ≤ l ≤ 32
Radiation type	Mo Kα	Mo Kα
D <sub>calc</sub> (Mg/m <sup>3</sup> )	2.148	2.209
μ (mm <sup>-1</sup> )	8.099	7.548
θ Range (°)	2.25–27.43	2.67–27.47
λ (Å)	0.71073	0.71073
R [F <sup>2</sup> > 2σ(F <sup>2</sup> )]	0.0253	0.0383
ωR(F <sup>2</sup> ) <sup>a</sup>	0.0623	0.0648

<sup>a</sup> ω = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.1007P)<sup>2</sup>] where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3.

was determined by the refinement of the Flack  $x$  parameter. The asymmetric unit comprises two independent molecules.

#### 4. Supplementary material

CCDC 615800 and 615801 contain the supplementary crystallographic data for **1c** and **2c**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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