The preparation of the mixed thiolato–isocyanide complexes cis- and trans-(η^5-C$_5$H$_5$)W(CO)$_2$(SR)(CNR′): the structure of trans-(η^5-C$_5$H$_5$)W(CO)$_2$(S-4-C$_6$H$_4$Me)(CNCMe$_3$)

Alan Shaver *, Rosemary C. Hynes, Darlene Trojansek

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada

Abstract

Treatment of the thiolato complexes CpW(CO)$_2$(PPh$_3$)(SR), as a mixture of *cis* and *trans* isomers, with isocyanides gave *cis*- and *trans*-CpW(CO)$_2$(SR)(CNR′), where R = CHMe$_2$ or 4-C$_6$H$_4$Me, and R′ = CMe$_3$ or 2,6-C$_6$H$_3$Me$_2$. The *cis* isomer of the thiolato complex was preferentially consumed before the *trans* isomer. The structure of *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$Me)(CN-CMe$_3$) was determined by X-ray crystallography: P2$_1$/a: a = 12.242(4), b = 17.592(5), c = 18.728(8) Å, β = 92.01(3)°; V = 4030.8(2) Å^3; Z = 2.

1. Introduction

Complexes of the type *cis*- and *trans*-CpW(CO)$_2$-(PPh$_3$)(SR), where R = alkyl or aryl, lose PPh$_3$ in solution to form the unsaturated 16-electron intermediate "CpW(CO)$_2$SR" [1]. Heating a solution of a mixture of *cis*-and *trans*-CpW(CO)$_2$(PPh$_3$)SCHMe$_2$ led to sequential loss of first PPh$_3$ and then one CO ligand to give the dimers [CpW(CO)$_2$SCHMe$_2$]$_2$ and [CpW-(CO)SCHMe$_2$]$_2$ respectively [2]. The starting thiolato complexes easily add CO to give the tricarbonyls CpW(CO)$_3$SR. Treatment with CS$_2$ leads to insertion into the W–S bond to give the thioxanthates CpW(CO)$_2$S$_2$CSR. The mechanism of the latter reaction probably involves dissociation of PPh$_3$, followed by coordination of CS$_2$ and then insertion [1].

Isocyanides are very versatile ligands [3,4] and they undergo insertion reactions with metal–carbon σ bonds [5]. The factors which affect such reactions include the steric congestion in the coordination sphere of the metal upon coordination of the isocyanide [6], the nucleophilicity of the migrating atoms or group [7] and the electrophilicity of the coordinated isocyanide [8]. It

became of interest to test the reactivity of the thiolato tungsten complexes above with isocyanides to see whether coordination and/or insertion would occur. There are a few examples of insertion by isocyanides into metal–heteroatom bonds namely M–N [9] and M–O [10]. Examples of complexes containing a three-membered M–C–S moiety, which might possibly form via insertion of an isocyanide into a metal thiolate, have been prepared via addition of the HS$^-$ anion to a coordinated isocyanide [11]. Finally insertion of iso-cyanides into activated carbon–sulfur bonds (C–S) in organic systems have been reported [12]. Therefore a complex of the type CpW(CO)$_2$(SR)(CNR′) has many attributes that might lead to insertion of the isocyanide into the metal–sulfur bond.

2. Results and discussion

Treatment of solutions of mixtures of *cis*- and *trans*-CpW(CO)$_2$(PPh$_3$)SR, as obtained from methods previously described [1], with isocyanides gave the products of substitution of the PPh$_3$ ligand, namely CpW(CO)$_2$-(SR)CNR′, where R = CHMe$_2$ or 4-C$_6$H$_4$Me and R′ = CMe$_3$ or 2,6-C$_6$H$_3$Me$_2$. The crude yields, as obtained from alumina columns, were high (greater than 83%)

* Corresponding author.

and the compounds were quite pure by NMR. The isolated yields were considerably reduced owing to high solubility in the recrystallizing solvents.

The compounds were formed as a mixture of *cis* and *trans* isomers as revealed by their NMR spectra which showed complete sets of peaks for each isomer. The ratios of isomers (see Section 3) were determined by integration of the NMR spectra and were invariant at all stages of the work-up. The peaks due to the isomers containing the SCHMe$_2$ ligand were assigned on the basis of the pattern of the Me resonances. These appear as a doublet of doublets in the *cis* isomer consistent with their diastereotopic environment while they appear as simple doublets in the *trans* isomers. It was not possible, on the basis of the room temperature ^{1}H NMR spectra, to assign the peaks to the isomers of the two other complexes which contained the S-4-C$_6$H$_4$Me ligand. No evidence was detected for separation of the isomers during the work-up which included chromatography on alumina. Crystallization of all four products gave only one type of crystal for each when examined under the microscope. No further effort was made to separate the isomers. Earlier attempts to separate the isomers of the starting complexes CpW-(CO)$_2$(PPh$_3$)SR were unsuccessful because they equilibrate in solution [1]. The solution IR spectra of the complexes in the v(CO) and v(CN) regions were consistent with their formulation and are given in Section 3.

The reactions were monitored by ^{1}H NMR spectroscopy which demonstrated that the *cis* isomer of the starting complexes was consumed first before the *trans* isomer reacted. The peaks due to the *cis* and *trans* isomers of the products appeared and grew in intensity at the same rate. This observation is consistent with a dissociative mechanism whereby the greater congestion in the *cis* isomers leads to steric acceleration of their rates of reaction. No evidence for possible insertion reactions was detected. A solution of CpW(CO)$_2$(S-4-C$_6$H$_4$Me)CNCMe$_3$ in CDCl$_3$ was treated with a slight excess of ligand and its NMR spectrum revealed strong peaks due to the coordinated and free ligands, consistent with very slow ligand exchange on the NMR time scale.

Recrystallization of CpW(CO)$_2$(S-4-C$_6$H$_4$Me)CNC-Me$_3$ from hexanes gave red crystals, one of which was chosen at random and its structure determined. It proved to be the *trans* isomer. There were two very similar independent molecules in the unit cell; only one (molecule A) is depicted in Fig. 1. Crystal data and atomic coordinates are given in Tables 1 and 2 respectively. The structure is of the classic piano-stool type with the bulky CNCMe$_3$ and S-4-C$_6$H$_4$Me groups at extreme range; the latter bent downwards away from the Cp ring. The W–S bond length of 2.501(3) Å is very similar to that observed for CpW(CO)$_3$SS-4-C$_6$H$_4$Me
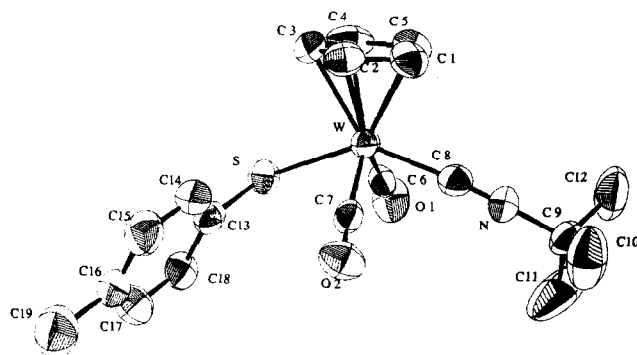

Fig. 1. ORTEP view of *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$Me)(CNCMe$_3$) (molecule A). Selected bond lengths (Å) and angles (°) are as follows: W–Cp(average), 2.332 (12); W–S, 2.501 (3); W–C(6), 1.990 (13); W–C(7), 1.976 (11); W–C(8), 2.079 (12); S–W–C(8), 138.4 (3); W–S–C(13), 114.6(4); W–C(8)–N, 176.1 (10); C(8)–N–C(9), 176.1 (12).

(2.506(2) Å) [13] but much longer than that in CpW(η^2-C$_4$(CF$_3$)$_4$CNMe$_3$)(SCHMe$_2$)CNCMe$_3$ (2.374(3) Å) [14]. The thiolato and isocyanide ligands are adjacent in this complex owing to the bulky fulvalene ligand. The W–CNCMe$_3$ bond length in our complex is 2.079(12) Å and in the fulvalene complex it is 2.017(9) Å.

A sample of the red crystals of *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$Me)CNCMe$_3$ was dissolved in CDCl$_3$ at −60°C. The solution was immediately inserted into the probe of the NMR instrument at room temperature and its spectrum taken. This initial spectrum showed only one set of peaks presumably due to the *trans* isomer (Cp, 5.60 ppm). After 2 min, the peaks due to the *cis* isomer began to appear and, after a further 8 min, equilibrium had been reached. The inability to separate the isomers of any of the isocyanide complexes is consistent with the rapid attainment of equi-

Table 1
X-ray crystallographic data for *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$Me)(CN-CMe$_3$)

Chemical formula	C$_{19}$H$_{21}$NO$_2$SW
Formula weight	511.28
Space group	$P2_1/a$
a	12.242 (4) Å
b	17.592 (5) Å
c	18.728 (8) Å
β	92.01 (3)°
V	4030.8 (24) Å
Z	2
T	22°C
λ	0.70930 Å^3
ρ_{calc}	1.685 g cm^{-3}
μ(Mo Kα)	59.6 cm^{-1}
Transmission factors	0.14–0.29
R^1	0.037
R_w^2	0.026

$^1 R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$.
$^2 R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

Table 2

Positional parameters and isotropic thermal parameters for *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$CH$_3$)(CNC(CH$_3$)$_3$) where B_{eq} is the mean of the principal axes on the thermal ellipsoid

	x	y	z	B_{eq} (Å^2)
W	0.03325(4)	0.80443(3)	0.45683(3)	3.62(3)
S	−0.1191(3)	0.88656(17)	0.49786(20)	4.41(18)
O(1)	−0.1391(7)	0.8065(5)	0.3293(4)	7.0(6)
O(2)	−0.0512(7)	0.6928(5)	0.5719(4)	5.8(5)
N	0.0604(9)	0.6391(5)	0.3868(6)	5.4(6)
C(1)	0.2205(9)	0.7968(7)	0.4674(7)	5.2(8)
C(2)	0.1918(10)	0.8363(6)	0.5258(7)	4.8(7)
C(3)	0.1433(10)	0.9065(7)	0.4998(7)	5.7(8)
C(4)	0.1420(10)	0.9067(7)	0.4268(8)	6.2(9)
C(5)	0.1952(10)	0.8389(7)	0.4064(8)	5.9(9)
C(6)	−0.0780(9)	0.8043(6)	0.3768(6)	4.5(7)
C(7)	−0.0249(10)	0.7355(6)	0.5296(6)	3.9(6)
C(8)	0.0531(9)	0.6986(7)	0.4097(6)	4.1(6)
C(9)	0.0617(11)	0.5635(6)	0.3569(7)	4.8(8)
C(10)	0.1049(15)	0.5094(8)	0.4106(8)	9.6(12)
C(11)	−0.0475(15)	0.5439(9)	0.3345(13)	14.8(16)
C(12)	0.1339(15)	0.5660(7)	0.2968(8)	9.5(11)
C(13)	−0.1592(10)	0.8684(6)	0.5874(7)	4.1(7)
C(14)	−0.0836(10)	0.8589(7)	0.6442(8)	5.3(8)
C(15)	−0.1209(11)	0.8486(7)	0.7127(7)	5.8(8)
C(16)	−0.2281(11)	0.8451(6)	0.7254(7)	5.1(7)
C(17)	−0.3010(10)	0.8538(7)	0.6701(8)	6.0(8)
C(18)	−0.2674(9)	0.8648(6)	0.6003(7)	4.5(7)
C(19)	−0.2641(14)	0.8310(7)	0.8015(8)	7.9(10)
W'	1.06084(4)	0.69323(3)	1.06880(3)	3.53(3)
S'	0.9040(3)	0.60800(18)	1.03443(19)	4.47(18)
O(1')	0.9625(7)	0.7960(5)	0.9467(4)	5.6(5)
O(2')	0.9028(7)	0.7003(5)	1.1968(5)	6.9(6)
N'	1.0908(9)	0.8619(5)	1.1314(6)	5.8(7)
C(1')	1.1666(10)	0.5896(6)	1.0281(7)	4.7(7)
C(2')	1.1726(11)	0.5923(6)	1.1041(7)	5.0(8)
C(3')	1.2247(10)	0.6600(7)	1.1230(7)	5.1(7)
C(4')	1.2469(9)	0.7004(7)	1.0599(7)	4.9(7)
C(5')	1.2112(9)	0.6548(6)	1.0013(7)	4.5(7)
C(6')	0.9956(10)	0.7573(7)	0.9964(7)	4.7(7)
C(7')	0.9574(9)	0.6974(7)	1.1481(7)	4.8(7)
C(8')	1.0844(9)	0.8001(7)	1.1097(7)	4.6(7)
C(9')	1.0919(11)	0.9383(6)	1.1611(7)	5.6(8)
C(10')	0.9977(14)	0.9450(8)	1.2074(10)	10.0(12)
C(11')	1.1951(13)	0.9467(7)	1.2024(9)	8.4(10)
C(12')	1.0760(18)	0.9941(8)	1.1002(9)	12.2(15)
C(13')	0.8568(9)	0.6201(6)	0.9433(6)	3.7(6)
C(14')	0.7494(9)	0.6204(6)	0.9274(7)	4.3(7)
C(15')	0.7057(10)	0.6254(7)	0.8600(7)	5.5(8)
C(16')	0.7727(11)	0.6288(7)	0.8028(7)	5.6(7)
C(17')	0.8857(11)	0.6258(7)	0.8164(7)	5.6(8)
C(18')	0.9278(10)	0.6209(7)	0.8857(8)	5.2(8)
C(19')	0.7320(12)	0.6351(7)	0.7255(8)	7.3(9)

librium of the isomers of *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$-Me)CNCMe$_3$.

3. Experimental section

All reactions were performed in 100 ml three-necked flasks equipped with a nitrogen inlet. Standard inert-atmosphere techniques were used in all manipulations [1,2]. Flasks charged with solids were evacuated twice and filled with nitrogen. Solvents were transferred by syringe. Filtrations were performed under nitrogen, and filtrates were reduced to dryness under vacuum (oil pump). The packing and elution of chromatography columns were performed under nitrogen with solvents which were deoxygenated. Activated alumina (80–200 mesh) was purchased from Anachemia. Recrystallizations were done under nitrogen in three-necked flasks using distilled solvents and were stored at −16°C overnight or longer. The mother liquors were removed via a cannula and the crystals washed with cold hexanes and dried overnight under vacuum. Hexanes were refluxed over sodium metal and benzophenone, and dichloromethane was refluxed over P$_2$O$_5$ under nitrogen. The compounds 2,6-dimethylphenylisocyanide (CN-2,6-C$_6$H$_3$Me$_2$) (Fluka, AG) and *tert*-butylisocyanide (CNCMe$_3$) (Aldrich) were used as purchased. The tungsten thiolates *cis*- and *trans*-CpW (CO)$_2$(PPh$_3$)SR, where R = CHMe$_2$ and 4-C$_6$H$_4$Me were prepared according to published procedures [1].

All IR spectra were recorded on a BOMEM Michelson model 100 Fourier transform IR spectrophotometer at 4 cm^{-1} resolution (deuterium triglyane sulfate (DTGS) detector). Solution spectra were recorded by using NaCl cells of 0.1 mm path length. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian XL-200 spectrometer and all chemical shifts are in δ (ppm) units ($\pm$0.002 ppm) relative to tetramethylsilane (TMS) at 0 ppm. Elemental analyses were carried out by Spang Microanalytical Laboratories, Eagle Harbour, MI. Melting points were determined in grease-sealed capillary tubes under nitrogen using a Thomas Hoover capillary melting-point (m.p.) apparatus and are uncorrected.

3.1. η^5-Cyclopentadienyl(dicarbonyl)(2-propylthiolato)-(2,6-dimethylphenylisocyanide)tungsten(II), CpW(CO)$_2$-(SCHMe$_2$)(CN-2,6-C$_6$H$_4$Me$_2$)

A three-necked flask was charged with *cis*- and *trans*-CpW(CO)$_2$(PPh$_3$)(SCHMe$_2$) (0.33 g, 0.51 mmol) and CH$_2$Cl$_2$ (40 ml). A solution of CN-2,6-C$_6$H$_3$Me$_2$ (0.08 g, 0.61 mmol) in CH$_2$Cl$_2$ (10 ml) was transferred by cannula to a dropping funnel and added dropwise to the above solution over a period of 30 min. The solution was stirred for 16 h, after which it was reduced to dryness by vacuum pump. The residue was dissolved in a minimum amount of CH$_2$Cl$_2$ and chromatographed on alumina (2.5 × 20 cm). Eluting with hexanes to remove PPh$_3$ followed by 1 : 1 CH$_2$Cl$_2$: hexanes gave an orange band which contained the product (crude yield, 85%). A brown residue remained at the top of the column. The orange band was reduced to dryness by rotary evaporation and crystallized from hexanes

(−16°C) to give a red solid (0.044 g; 17%; m.p. 90–92°C).

^{1}H NMR (CDCl$_3$): *cis* 7.10 (m, 3H, C$_6$H$_3$Me$_2$); 5.62 (s, 5H, Cp); 2.76 (septet, 1H, C*H*Me$_2$, *J*(H–H) = 6.6 Hz); 2.45 (s, 6H, C$_6$H$_3$*Me$_2$*); 1.20, 1.33 (dd, 6H, CH*Me$_2$*); *trans* 7.13 (m, 3H, C$_6$H$_3$*Me$_2$*); 5.48 (s, 5H, Cp); 2.74 (septet, H, C*H*Me$_2$, *J*(H–H) = 6.6 Hz); 2.40 (s, 6H, C$_6$H$_3$*Me$_2$*); 1.28 (d, 6H C*H*Me$_2$); *cis*:*trans*, 1:1.5. IR (cyclohexane): v(CO) 1904 (s), 1952 (sh, s); v(CN) 2092 (s) cm^{-1}. Anal. Found: C, 44.73; H, 4.01; N, 2.81; S, 6.20. C$_{19}$H$_{21}$N$_1$O$_2$S$_1$W$_1$ calc.: C, 44.63; H, 4.14; N, 2.74; S, 6.27%.

3.2. η^5-Cyclopentadienyl(dicarbonyl)(2-propylthiolato)-(tert-butylisocyanide)tungsten(II), CpW(CO)$_2$-(SCHMe$_2$)(CNCMe$_3$)

As above, *cis*- and *trans*-CpW(CO)$_2$(PPh$_3$)(SCHMe$_2$) (0.35 g, 0.56 mmol) in CH$_2$Cl$_2$ (30 ml) was treated with CNCMe$_3$ (0.75 ml, 0.65 mmol) added dropwise via a gas-tight syringe and the solution was stirred for 23 h. The yellow residue obtained from the chromatography column (crude yield, 92%) was crystallized from hexanes to give an orange solid (0.061 g; 32%) and then recrystallized from hexanes to give a light-yellow crystalline solid (0.041 g; 16%; m.p. 68–70%).

^{1}H NMR (CDCl$_3$): *cis* 5.52 (s, 5H, Cp); 2.69 (septet, 1H, C*H*Me$_2$, *J*(H–H) = 6.8 Hz); 1.20, 1.27 (dd, 6H, CH*Me$_2$*); 1.51 (s, 9H, CNC*Me$_3$*); *trans* 5.32 (s, 5H, Cp); 2.69 (septet, H, C*H*Me$_2$, *J*(H–H) = 6.8 Hz); 1.24 (d, 6H, CH*Me$_2$*); 1.57 (s, 9H, CNC*Me$_3$*); *cis*:*trans*, 1:1.4. IR (cyclohexane): v(CO) 1898 (sh, s), 1952 (sh, s); v(CN) 2119 (s) cm^{-1}. Anal. Found: C, 38.77; H, 4.58; N, 2.96; S, 6.86. C$_{15}$H$_{21}$N$_1$O$_2$S$_1$W$_1$ calc.: C, 38.98; H, 4.57; N, 3.02; S, 6.92.

3.3. η^5-Cyclopentadienyl(dicarbonyl)(4-methylphenyl-thiolato)(2,6-dimethylphenylisocyanide)tungsten(II), CpW(CO)$_2$(S-4-C$_6$H$_4$Me)(CN-2,6-C$_6$H$_3$Me$_2$)

As above, *cis* and *trans*-CpW(CO)$_2$(PPh$_3$)(S-4-C$_6$-H$_4$Me) (0.23 g, 0.33 mmol) in CH$_2$Cl$_2$ (25 ml) was treated with CN-2,6-C$_6$H$_3$Me$_2$ (0.06 g, 0.40 mmol) in CH$_2$Cl$_2$ (10 ml), added dropwise, and the solution was stirred for 23 h. During this time, the color changed from orange to bright red. The orange residue from the chromatography (crude yield, 83%) was crystallized from hexanes to give red crystals (0.055 g; 30%: m.p. 96–98°C).

^{1}H NMR (CDCl$_3$): isomer A 7.13, 7.33 (m, 3H, CNC$_6$H$_3$Me$_2$); 6.87 (m, 4H, SC$_6$H$_4$Me); 5.66 (s, 5H, Cp); 2.21 (s, 3H, SC$_6$H$_4$*Me*); 2.34 (s, 6H, CNC$_6$H$_3$*Me$_2$*); isomer B 7.09, 7.30 (m, 3H, CNC$_6$*H$_3$*Me$_2$); 6.97 (m, 4H, SC$_6$*H$_4$*Me); 5.53 (s, 5H, Cp); 2.28 (s, 3H, SC$_6$H$_4$*Me*); 2.66 (s, 6H, CNC$_6$H$_3$*Me$_2$*); ratio of iso-

mers, 1:1.1. IR (cyclohexane): v(CO) 1912 (s), 1960 (sh, s); v(CN) 2092 (s) cm^{-1}. Anal. Found: C, 49.20; H, 3.79; N, 2.43; S, 5.73. C$_{23}$H$_{21}$N$_1$O$_2$S$_1$W$_1$ calcd.: C, 49.39; H, 3.78; N, 2.50; S, 5.73%.

3.4. η^5-Cyclopentadienyl(dicarbonyl)(4-methylphenyl-thiolato)(tert-butylisocyanide)tungsten(II), CpW(CO)$_2$-(S-4-C$_6$H$_4$Me)(CNCMe$_3$)

As above, *cis*- and *trans*-CpW(CO)$_2$(PPh$_3$)(S-4-C$_6$-H$_4$Me) (0.21 g, 0.31 mmol) in CH$_2$Cl$_2$ (30 ml) was treated with CNCMe$_3$ (0.50 ml, 0.44 mmol) for 17 h. During this time, the color changed from orange to red. The orange residue obtained from the chromatography (crude yield, 89%) was crystallized from hexanes to give orange–red crystals as thin plates (0.095 g; 60%, m.p. 89–92°C).

^{1}H NMR (CDCl$_3$): *trans* 6.94 (AB quartet, 4H, SC$_6$H$_4$Me, *J*(H–H) = 4.9 Hz); 5.60 (s, 5H, Cp); 2.27 (s, 3H, SC$_6$H$_4$*Me*); 1.32 (s, 9H, CNC*Me$_3$*); *cis* 7.27 (AB quartet, 4H, SC$_6$H$_4$Me), *J*(H–H) = 7.9 Hz); 5.38 (s, 5H, Cp); 2.25 (s, 3H, SC$_6$H$_4$*Me*); 1.57 (s, 9H, CNC*Me$_3$*); ratio of isomers, 1:1.2. IR (cyclohexane): v(CO) 1904 (sh, s), 1961 (s); v(CN) 2135 (sh, s) cm^{-1}. Anal. Found: C, 44.59; H, 4.29; N, 2.67; S, 6.10. C$_{19}$H$_{21}$N$_1$O$_2$S$_1$W$_1$ calc.: C, 44.63; H, 4.14; N 2.74; S, 6.27%.

3.5. X-ray structure determination

Table 1 contains the crystal parameters for *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$Me)(CNCMe$_3$). Single crystals suitable for crystallographic studies were obtained by recrystallization from hexanes. A red crystal was glued with epoxy in a thin-walled glass capillary. Cell dimensions were obtained from 25 reflections with 2θ in the range 30.00–35.00°. A total of 5552 reflections were collected using the ω–2θ scan technique, where $2\theta <$ 50° on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation ($-13 \leqslant h \leqslant 13$; $0 \leqslant k \leqslant 18$; $0 \leqslant l \leqslant 20$); of these, 5256 were unique (merging $R = 2.6\%$) and 3012 having $I > 2.5\sigma$ were used in the final cycle of full-matrix least-squares refinement. The intensities of three representative reflections remained constant throughout data collection. An absorption correction was made from four ψ scans. The structure was solved by direct methods followed by a difference Fourier technique. An extinction correction was made. Anisotropic thermal parameters were used for all non-hydrogen atoms. All hydrogen atoms were added in calculated positions. All computing was performed using the NRCVAX system of programs [15].

4. Supplementary material available

An ORTEP drawing of molecule A' of *trans*-CpW-(CO)$_2$(S-4-C$_6$H$_4$Me)(CNCMe$_3$), a full-length table of

crystallographic data, a table of anisotropic temperature parameters, a table of bond lengths and angles, a table of hydrogen atom coordinates, and a table of observed and calculated structure factors are available upon request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Any request should be accompanied by the full literature citation for this communication.

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