

The cluster $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ as a ligand to Mo(II) and W(II)

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Abstract

The complexes $[\text{M}_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]$ {M = W (**1**) or Mo (**2**)}, $[\text{M}(\text{SR})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]$ {R = Ph; M = W (**3**) or Mo (**4**): R = C₆H₂Me₃-2,4,6; M = W (**5**) or Mo (**6**)}, $[\text{M}(\text{SR})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]$ {R = SPh; M = W (**7**) or Mo (**8**): R = C₆H₂Me₃-2,4,6; M = W (**9**) or Mo (**10**)}, $[\text{M}(\text{CO})_3(\text{PPh}_3)(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]\text{I}$ {M = W (**11**) or Mo (**12**)}, $[\text{M}(\text{CO})_3(\text{PPh}_3)(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]\text{I}_2$ {M = W (**13**) or Mo (**14**)}, $[\text{M}(\text{CO})_3(\text{P-P})(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]\text{I}_2$ {P-P = diphenylphosphinoethane (dippe); M = W (**15**) or Mo (**16**): P-P = diphenylphosphinopropane (dppp); M = W (**17**) or Mo (**18**)} and $[\text{W}(\text{CO})(\eta^2\text{-RC}_2\text{R})_2(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]\text{I}$ {R = Me (**19**) or Ph (**20**)} have been prepared. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum(II); Tungsten(II); Iron–sulfur cluster; Carbonyl; Mössbauer

1. Introduction

Prompted by the sulfur-ligand environment of molybdenum in nitrogenase [1], we have been exploring the chemistry of sulfur-donor ligands at this metal [2,3], in particular, the preparation and structural properties of thioether complexes of seven-coordinated Mo(II) and W(II) [4,5]. It has been observed by Coucouvanis, in the complexes $[\text{Fe}_6\text{S}_6\text{Cl}_6\{\text{M}(\text{CO})_3\}_2]^{n-}$ (M = Mo or W; $n = 3$ or 4) [6] and by Jordanov in the complexes $[\text{Mo}(\text{CO})_4(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]$ and $[\text{MoBr}(\text{CO})_2(\text{NCMe})(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]$ [7] that Fe–S clusters can act as ligands to lower valent molybdenum and in so doing behave as ‘metallo–thioethers’. In the above complexes the molybdenum or tungsten are six-coordinate and in oxidation state zero or very unusually one. We were interested therefore to use metallo–thioethers to extend our studies of seven-coordination at Mo(II) or W(II)

centres with sulfur coligands and accordingly we present here a series of complexes of the $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ ligand obtained from the versatile starting compounds $[\text{M}_2(\text{CO})_3(\text{MeCN})_2]$ [8]. Included in this series are the first examples of isolated compounds in which an alkyne is coordinated to a tungsten atom in an iron–sulfur cluster environment, obtained from the six-coordinated complexes $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ [9].

2. Results and discussion

The reactions of the complexes $[\text{M}_2(\text{CO})_3(\text{NCMe})_2]$ [10] (M = W or Mo), with the iron–sulfur cluster $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ [11] in dichloromethane gave the new seven-coordinate complexes $[\text{M}_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6-S,S')]$ {M = W (**1**) or Mo (**2**)} where the W or Mo is bound to the cluster through the two capping sulfur atoms of the cluster Fig. 1. The molybdenum complex is formed more rapidly than its tungsten analogue. Cluster complexes **1** and **2** react with one or two equivalents of the sodium salts of thiophenol or 2,4,6-trimethylthiophenol (Htmt) to generate, by substitution of iodide, the thio-

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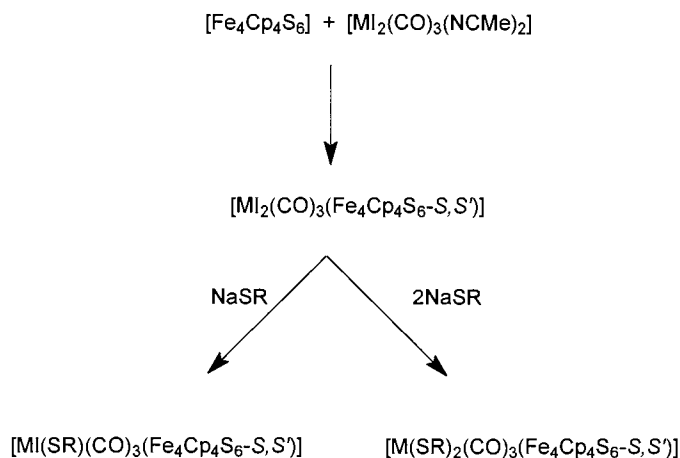
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late-ligated complexes $[\text{M}(\text{SR})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ $\{\text{R} = \text{SPh}; \text{M} = \text{W}$ (**3**) or Mo (**4**). $\text{R} = \text{tmt}; \text{M} = \text{W}$ (**5**) or Mo (**6**) $\}$ and $[\text{M}(\text{SR})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ $\{\text{R} = \text{SPh}; \text{M} = \text{W}$ (**7**) or Mo (**8**); $\text{R} = \text{tmt}; \text{M} = \text{W}$ (**9**) or Mo (**10**) $\}$ Scheme 1.

Triphenylphosphine-substituted complexes were prepared by first reacting one or two equivalents of the phosphine with $[\text{M}_2(\text{CO})_3(\text{NCMe})_2]$, followed by addition of $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ to give the salts $[\text{M}(\text{CO})_3(\text{PPh}_3)(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]\text{I}$ $\{\text{M} = \text{W}$ (**11**) or Mo (**12**) $\}$ or $[\text{M}(\text{CO})_3(\text{PPh}_3)_2(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]\text{I}_2$ $\{\text{M} = \text{W}$ (**13**) or Mo (**14**) $\}$. Similarly, bidentate phosphines can be employed to give $[\text{M}(\text{CO})_3(\text{P-P})(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]\text{I}_2$ $\{\text{P-P} = \text{diphenylphosphinoethane (dppe)}; \text{M} = \text{W}$ (**15**) or Mo (**16**); $\text{P-P} = \text{diphenylphosphinopropane (dppp)}; \text{M} = \text{W}$ (**17**) or Mo (**18**) $\}$. The alkyne-ligated cluster complexes $[\text{W}(\text{CO})(\eta^2\text{-RC}_2\text{R})_2(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]\text{I}$ $\{\text{R} = \text{Me}$ (**19**) or Ph (**20**) $\}$ were prepared by direct reaction of the complexes $[\text{W}(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ $\{\text{R} = \text{Me}$ or $\text{Ph}\}$ [9] with $[\text{Fe}_4\text{Cp}_4\text{S}_6]$.

All materials were isolated in reasonable yields and are sensitive to air, in solution and in the solid state. Compounds **1** and **2** are sparingly soluble, and the thiolate-ligated compounds **3–10** are more soluble in dichloromethane and chloroform but are relatively insoluble in other common organic solvents. The phosphine-ligated compounds **11–18** are sparingly soluble in dichloromethane, but more soluble in acetonitrile. Compounds **19** and **20** dissolve in dichloromethane and acetonitrile and are relatively insoluble in diethyl ether and hexanes. These diamagnetic complexes have been characterised by elemental analysis (Table 1) and IR, $^1\text{H-NMR}$ and, in some cases, Mössbauer spectroscopies. Repeated attempts to grow crystals suitable for X-ray structure determination have failed.

The IR spectra of all complexes **1–20** in the solid state show bands due to Cp at 3040–3090 (C–H stretch), 1420 (C–C asymmetric stretch) and 840 cm^{-1}



Scheme 1.

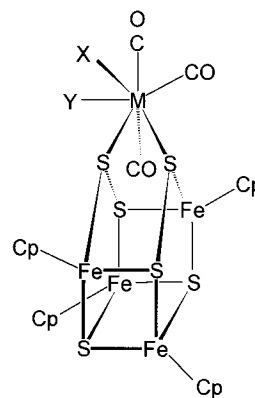


Fig. 1. The proposed geometry about M (M = W or Mo) in compounds **1–10** (X, Y = I, SR).

(C–H perpendicular bending). This latter band is most characteristic of the $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ structure and oxidation state [7,12] and indicates that this structure has been maintained in the complexes. The S–S stretching bands of $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ at 498 and 507 cm^{-1} have disappeared and the Fe–($\mu_3\text{-S}$) stretching band moves slightly from 442 cm^{-1} Table 1. This is fully consistent with the tungsten or molybdenum atoms binding to the Fe_4S_6 moiety through the two capping sulfur atoms. Similar spectral properties have been observed for $[\text{Mo}(\text{CO})_4(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ and $[\text{MoBr}(\text{CO})_2(\text{NCMe})(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ [7]. There is no evidence for the formation of $[\text{Fe}_4\text{Cp}_4\text{S}_5]^+$ or $[\text{Fe}_4\text{Cp}_4\text{S}_4]$, which are obtained when $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ reacts with high oxidation state molybdenum complexes [13]. In each of the complexes **1–18** there are three strong absorptions Table 1, which are assigned to the (CO) stretching vibrations and are consistent with retention of three carbonyl groups. The absorbance due to MeCN observed for the starting material is absent. The higher $\nu(\text{CO})$ value, at, for example 2010 cm^{-1} for **1** is in the normal range attributed to the capping carbonyl position in seven-coordinated capped octahedral complexes of the type $[\text{MX}_2(\text{CO})_3\text{L}_2]$ (X = Br or I; $\text{L}_2 = \text{bidentate sulfur-donor ligand}$) [4,14] and suggests a similar geometry about the M atom in **1–10** Fig. 1. The IR spectra of dichloromethane solutions of **1** and **2** also show three (CO) absorptions, which implies the presence of only one isomer in solution. The alkyne-ligated complexes **19** and **20** show one strong carbonyl band and a weak (C=C) band at 1650 (**19**) and 1635 (**20**) cm^{-1} indicating retention of the carbonyl and alkyne ligands on coordination to $[\text{Fe}_4\text{Cp}_4\text{S}_6]$. The IR spectral properties of **19** and **20**, and in particular the relatively high $\nu(\text{CO})$ value, are very similar to those of the crystallographically characterised complex $[\text{W}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ [15]. This molecule adopts a distorted octahedral geometry with the 2-butynyl ligands (each occupying a single coordination site) mutually *cis* and parallel to one another, the carbonyl group *trans* to the iodide, with the remaining

Table 1
Elemental analyses and solid state IR and Mössbauer parameters^a

Complex	Elemental analyses (%)				IR (cm ⁻¹) ^b			Mössbauer (mm s ⁻¹) ^c		
	C	H	S	v(CO)	v(μ_3 -S)	i.s.	q.s.	h.w.h.m		
1 [W] ₂ (CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	22.6, (23.0)	1.7, (1.7)	16.0, (16.1)	1873, 1934, 2010	448	0.40, 0.40	1.34, 0.95	0.13, 0.23		
2 [Mo] ₂ (CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	23.9, (24.9)	1.8, (1.8)	16.9, (17.3)	1886, 1945, 2014	447	0.40, 0.41	1.40, 0.93	0.21, 0.27		
3 [W](SPH)(CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	29.7, (29.5)	2.4, (2.1)	18.3, (19.0)	1919, 1988, 2056	448	0.41, 0.41	1.34, 0.98	0.20, 0.18		
4 [Mo](SPH)(CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	31.2, (31.9)	1.9, (2.3)	21.1, (20.6)	1821, 1858, 1988	450	0.41, 0.41	1.43, 0.97	0.25, 0.21		
5 [W](tmt)(CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	31.3, (31.5)	2.7, (2.6)	16.8, (18.4)	1880, 1936, 2000	451	0.41, 0.41	1.34, 0.98	0.20, 0.18		
6 [Mo](tmt)(CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	33.8, (33.9)	2.6, (2.8)	18.7, (19.8)	1829, 1858, 1989	449	0.40, 0.41	1.44, 0.97	0.25, 0.21		
7 [W](SPH) ₂ (CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	36.0, (36.2)	3.1, (2.6)	23.0, (22.1)	1830, 1850, 1981	450	0.41, 0.41	1.39, 0.98	0.19, 0.18		
8 [Mo](SPH) ₂ (CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	39.1, (39.1)	2.7, (2.8)	25.9, (23.9)	1832, 1869, 1995	448	0.41, 0.41	1.35, 0.98	0.22, 0.17		
9 [W](tmt) ₂ (CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	40.6, (39.5)	3.8, (3.9)	17.6, (20.6)	1833, 1849, 1985	452	0.40, 0.42	1.38, 1.05	0.17, 0.18		
10 [Mo](tmt) ₂ (CO) ₃ (Fe ₄ Cp ₄ S ₆ -S,S')]	42.5, (42.5)	3.8, (3.7)	22.2, (22.1)	1830, 1861, 1992	450	0.41, 0.41	1.35, 0.98	0.22, 0.17		
11 [W](CO) ₃ (PPh ₃)(Fe ₄ Cp ₄ S ₆ -S,S')]	33.1, (33.7)	2.5, (2.4)	n.m.	1925, 1953, 2001	450	0.39, 0.40	1.40, 0.88	0.26, 0.28		
12 [Mo](CO) ₃ (PPh ₃)(Fe ₄ Cp ₄ S ₆ -S,S')]	35.6, (35.9)	2.5, (2.6)	n.m.	1931, 1955, 2001	450	n.m.	n.m.	n.m.		
13 [W](CO) ₃ (PPh ₃) ₂ (Fe ₄ Cp ₄ S ₆ -S,S')]	40.9, (41.1)	2.8, (2.9)	n.m.	1881, 1909, 1932	453	0.40, 0.40	1.33, 0.88	0.19, 0.20		
14 [Mo](CO) ₃ (PPh ₃) ₂ (Fe ₄ Cp ₄ S ₆ -S,S')]	43.0, (43.4)	2.9, (3.1)	n.m.	1895, 1940, 1990	450	n.m.	n.m.	n.m.		
15 [W](CO) ₃ (dippe- <i>P,P'</i>)(Fe ₄ Cp ₄ S ₆ -S,S')]	36.1, (36.9)	2.9, (2.8)	11.6, (12.1)	1909, 1963, 2034	449	n.m.	n.m.	n.m.		
16 [Mo](CO) ₃ (dippe- <i>P,P'</i>)(Fe ₄ Cp ₄ S ₆ -S,S')]	39.1, (39.0)	3.0, (2.9)	12.6, (12.8)	1919, 1976, 2041	448	n.m.	n.m.	n.m.		
17 [W](CO) ₃ (dppp- <i>P,P'</i>)(Fe ₄ Cp ₄ S ₆ -S,S')]	36.9, (37.8)	2.7, (2.9)	10.8, (11.9)	1919, 1969, 2039	447	n.m.	n.m.	n.m.		
18 [Mo](CO) ₃ (dppp- <i>P,P'</i>)(Fe ₄ Cp ₄ S ₆ -S,S')]	39.3, (39.9)	2.5, (3.0)	13.3, (12.5)	1908, 1964, 2042	448	n.m.	n.m.	n.m.		
19 [W](CO)(<i>η</i> ² -MeC ₂ Me) ₂ (Fe ₄ Cp ₄ S ₆ -S,S')]	27.0, (28.5)	2.4, (2.5)	14.3, (14.7)	2040	455	n.m.	n.m.	n.m.		
20 [W](CO)(<i>η</i> ² -PhC ₂ Ph) ₂ (Fe ₄ Cp ₄ S ₆ -S,S')]	38.8, (39.4)	2.1, (2.6)	12.1, (12.4)	2070	455	n.m.	n.m.	n.m.		

^a n.m. = not measured.

^b KBr discs.

^c At 77 K: i.s., isomer shift; q.s., quadrupole splitting; h.w.h.m., half-width at half-maxima. Errors in i.s. and h.w.h.m. $\pm \leq 0.01$ mm s⁻¹ and in q.s. $\pm \leq 0.03$ mm s⁻¹.

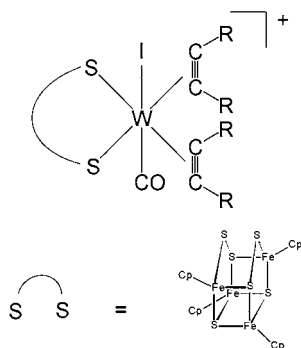


Fig. 2. The structure predicted for $[\text{W}(\text{CO})(\eta^2\text{-RC}_2\text{R})_2(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}$, R = Me (**19**), Ph (**20**).

two coordination sites occupied by the nitrogen atoms of the bipyridine ligand. By analogy similar structures can be envisaged for **19** and **20**, where bipyridine is replaced by $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ Fig. 2.

The Mössbauer parameters for compounds **1–11** and **13** in the solid state at 77 K are shown in Table 1. The spectrum for each complex was best fitted by two overlapping, nested, quadrupole split doublets of equal intensity with no constraints. The isomer shifts are similar for each doublet and also for each compound and are comparable to those of $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ (i.s. = 0.43 mm s⁻¹; q.s. = 1.11 mm s⁻¹) recorded at the same temperature. The quadrupole split doublet with the larger splitting is tentatively assigned to the two iron atoms nearest to the heterometal which sense a different environment from that of the two more remote iron atoms. The related complexes, $[\text{Mo}(\text{CO})_4(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$ (i.s. = 0.43 mm s⁻¹; q.s. = 1.07 mm s⁻¹) and $[\text{MoBr}(\text{CO})_2(\text{NCMe})(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$ (i.s. = 0.44 mm s⁻¹; q.s. = 1.11 mm s⁻¹), at 4 K, have been reported to give only one doublet [7]. Our results are fully consistent with the formulations proposed for the new compounds and it is apparent that coordination of the tungsten or molybdenum complexes to $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ changes little the electronic distribution within the cluster.

In deuteriochloroform solution, clusters **3–20** all exhibit a pair of ¹H-NMR resonances at ca. 1.2 and 1.6 ppm assignable to the Cp ligands coordinated to the cluster iron atoms. These resonances are shifted upfield by ca. 3 ppm relative to the resonances of the Cp ligands in $[\text{Fe}_4\text{Cp}_4\text{S}_6]$. The origin of this shift is unclear. However, if a solution is left for a period of time and the spectrum rerecorded, the Cp resonances of $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ reappear as the complex dissociates on decomposition. Although the resonances of the pairs of Cp ligands in **3–20** are of equal intensity they often exhibit different line-shapes. The ¹H-NMR parameters for the ligands coordinated to tungsten or molybdenum in complexes **3–20** are listed in Table 2.

Conductivity measurements further support the formulation of the complexes: compounds **1–10** are non-conductors in CH₂Cl₂; the phosphine-substituted complexes **13–18** conduct as diiodide salts in CH₃CN (2:1 electrolytes, λ_M = 179–175 S cm² mol⁻¹); and the complexes **11**, **12**, **19** and **20** conduct as monoiodide salts in CH₃CN (1:1 electrolytes, λ_M = 139–142 S cm² mol⁻¹).

Table 2

¹H-NMR parameters (ppm) in CDCl₃ solution^a

Complex	Aromatic H	Me	CH ₂
3 $[\text{W}(\text{SPh})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$	7.5 (o), 7.2 (m,p)	–	–
4 $[\text{MoI}(\text{SPh})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$	7.5 (o), 7.2 (m,p)	–	–
5 $[\text{W}(\text{tmt})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$	6.9 (m)	–	–
6 $[\text{MoI}(\text{tmt})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$	6.8 (m)	–	–
7 $[\text{W}(\text{SPh})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$	7.5 (o), 7.2 (m,p)	2.3 (p), 2.2 (o)	–
8 $[\text{Mo}(\text{SPh})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$	7.5 (o), 7.3 (m,p)	2.4 (p), 2.3 (o)	–
9 $[\text{W}(\text{tmt})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$	6.8 (m)	2.3 (p), 2.2 (o)	–
10 $[\text{Mo}(\text{tmt})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]$	6.8 (m)	2.3 (p), 2.2 (o)	–
11 $[\text{W}(\text{CO})_3(\text{PPh}_3)(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}$	7.8 (o), 7.4 (m,p)	–	–
12 $[\text{MoI}(\text{CO})_3(\text{PPh}_3)(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}$	7.8 (o), 7.4 (m,p)	–	–
13 $[\text{W}(\text{CO})_3(\text{PPh}_3)_2(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}_2$	7.8 (o), 7.4 (m,p)	–	–
14 $[\text{Mo}(\text{CO})_3(\text{PPh}_3)_2(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}_2$	7.8 (o), 7.4 (m,p)	–	–
15 $[\text{W}(\text{CO})_3(\text{dppe-}P,P')(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}_2$	7.6 ^b	–	2.7
16 $[\text{Mo}(\text{CO})_3(\text{dppe-}P,P')(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}_2$	7.5 ^b	–	2.8
17 $[\text{W}(\text{CO})_3(\text{dppp-}P,P')(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}_2$	7.6 ^b	–	2.9, 2.1
18 $[\text{Mo}(\text{CO})_3(\text{dppp-}P,P')(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}_2$	7.5 ^b	–	2.9, 2.1
19 $[\text{W}(\text{CO})(\eta^2\text{-MeC}_2\text{Me})_2(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}$	–	3.0 ^c	–
20 $[\text{W}(\text{CO})(\eta^2\text{-PhC}_2\text{Ph})_2(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S}')]\text{I}$	7.5 ^b	–	–

^a In all complexes Cp resonances are observed at 1.2 and 1.6 ppm.

^b Multiple multiplets.

^c Broad.

3. Conclusions

We have extended the range of seven-coordinated complexes of Mo(II) and W(II) to include an iron–sulfur cluster ‘metallo–thioether’ as a ligand. The system thus obtained is quite robust and versatile. It allows the preparation of a range of derivatives, either by metathesis of halide at the M(II) centre by thiolate with retention of the Fe–S ligand and seven coordination at M, or by the displacement of halide from M with *tertiary* phosphine or alkynes, giving six-coordinated M–Fe–S complexes.

4. Experimental

All manipulations were performed under dinitrogen using standard syringe and Schlenk techniques. Solvents were dried before use by distillation under dinitrogen from phosphorus pentoxide (CH_2Cl_2) or sodium wire (diethyl ether and THF). The compounds $[\text{M}_2(\text{CO})_3(\text{NCMe})_2]$ and $[\text{M}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{-R})_2]$, where M = W or Mo and R = Me or Ph, were prepared by published procedures [9,10], as was the cluster $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ [11]. Sodium salts of HSPh and Htmt (2,4,6-trimethylbenzenethiol) were prepared by the reaction of the thiol with sodium in THF. All other materials were obtained commercially and used without further purification.

Proton NMR spectra were recorded on a Bruker AC/250 or a Jeol GSX270 spectrometer and referenced to TMS. IR spectra were recorded as KBr disks on a Perkin-Elmer 1600 series FTIR spectrometer. Mössbauer parameters were measured, in the solid state at 77 K in a zero magnetic field, on an ES-Technology MS105 spectrometer with a 925 MBq ^{57}Co source in a rhodium matrix at ambient temperature, and were referenced to a 25 μm iron foil at 298 K. Elemental analyses (C, H, S) were determined on a Carlo Erba Elemental Analyser MOD1108 (using helium as carrier gas) at the University of Wales, Bangor. A Portlands Electronics conductivity bridge was used to measure conductivities.

4.1. Preparation of $[\text{W}(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **1** and $[\text{Mo}(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **2**

To a stirred solution of $[\text{W}(\text{CO})_3(\text{NCMe})_2]$ (0.30 g, 0.50 mmol) in degassed CH_2Cl_2 (45 cm^3) was added $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ (0.34 g, 0.50 mmol). After 2 h the volume was reduced by half and the solution filtered to give a black solid which was recrystallised from a minimum of CH_2Cl_2 and dried in vacuo (0.39 g, 65%).

4.2. Preparation of $[\text{W}(\text{SPh})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **3**

To a stirred solution of $[\text{W}(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **1**

(0.20 g, 0.17 mmol) in degassed CH_2Cl_2 (45 cm^3) was added NaSPh (0.02 g, 0.17 mmol), the mixture was stirred for 2 h. After filtration solvent was removed in vacuo. The resultant black solid was recrystallised from a minimum of CH_2Cl_2 at 273 K, collected by filtration and dried in vacuo (0.09 g, 48%).

4.3. Preparation of $[\text{MoI}(\text{SPh})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **4**, $[\text{W}(\text{tmt})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **5** and $[\text{MoI}(\text{tmt})(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **6**

The compounds were prepared by similar procedures to (**1**) in a 45–51% yield.

4.4. Preparation of $[\text{W}(\text{SPh})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **7**

Reaction of $[\text{W}(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **1** (0.20 g, 0.17 mmol) in degassed CH_2Cl_2 (45 cm^3) with two equivalents of NaSPh (0.04 g, 0.34 mmol) for 3 h gave, after a similar work up to that described above, a black solid (0.12 g, 61%).

4.5. Preparation of $[\text{Mo}(\text{SPh})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **8**, $[\text{W}(\text{tmt})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **9** and $[\text{Mo}(\text{tmt})_2(\text{CO})_3(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **10**

The compounds were prepared by similar procedures to (**7**) in a 50–58% yield.

4.6. Preparation of $[\text{W}(\text{CO})_3(\text{PPh}_3)(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **11**

To a rapidly stirred solution of $[\text{W}(\text{CO})_3(\text{NCMe})_2]$ **1** (0.30 g, 0.50 mmol) in degassed CH_2Cl_2 (45 cm^3) was added PPh_3 (0.15 g, 0.50 mmol), after 5 min $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ (0.39 g, 0.58 mmol) was added and stirring continued for a further 1 h. After filtration, the solvent was removed in vacuo to give the black product (0.55 g, 75%).

4.7. Preparation of $[\text{MoI}(\text{CO})_3(\text{PPh}_3)(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **12**

This complex was prepared by a similar procedure to **11** (86%).

4.8. Preparation of $[\text{W}(\text{CO})_3(\text{PPh}_3)_2(\text{Fe}_4\text{Cp}_4\text{S}_6\text{-S,S'})]$ **13**

To a rapidly stirred solution of $[\text{W}(\text{CO})_3(\text{NCMe})_2]$ **1** (0.30 g, 0.50 mmol) in degassed CH_2Cl_2 (45 cm^3) was added two equivalents of PPh_3 (0.34 g, 1.00 mmol), after 20 min $[\text{Fe}_4\text{Cp}_4\text{S}_6]$ (0.34 g, 0.50 mmol) was added and stirring continued for a further 1 h. After filtration, the solvent was removed in vacuo to give the black product (0.64 g, 82%).

4.9. Preparation of $[Mo(CO)_3(PPh_3)(Fe_4Cp_4S_6-S,S')]I_2$ **14**

This compound was prepared by a similar procedure to **13** (76%).

4.10. Preparation of

$[M(CO)_3(dppe-P,P')(Fe_4Cp_4S_6-S,S')]I_2$ {*M* = *W* **15**;
Mo **16**} and $[M(CO)_3(dppp-P,P')(Fe_4Cp_4S_6-S,S')]I_2$
{*M* = *W* **17**; *Mo* **18**}

To a stirred solution of $[Wl_2(CO)_3(NCMe)_2]$ (**1**) (0.30 g, 0.50 mmol) in degassed CH_2Cl_2 (45 cm³) was added either dppe (0.20 g, 0.50 mmol) or dppp (0.21 g, 0.50 mmol), after 5 min $[Fe_4Cp_4S_6]$ (0.34 g, 0.50 mmol) was added and stirring continued for a further 2 h. After filtration through Celite, the solvent was removed in vacuo. The resultant black solids were recrystallised from a minimum of CH_2Cl_2/Et_2O and dried in vacuo to give **15** (0.52 g, 65%) and **17** (0.54 g, 67%), respectively.

Similarly, to a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (**2**) (0.30 g, 0.58 mmol) in degassed CH_2Cl_2 (45 cm³) was added dppe (0.23 g, 0.58 mmol) or dppp (0.21 g, 0.58 mmol), after 5 min $[Fe_4Cp_4S_6]$ (0.39 g, 0.58 mmol) was added. The mixture was stirred for 1 h, the solution filtered through Celite and solvent removed in vacuo. After recrystallisation from a minimum volume of CH_2Cl_2/Et_2O the black products were dried in vacuo (**16**, 0.49 g, 56%; **18**, 0.69 g, 78%).

4.11. Preparation of

$[Wl(CO)(\eta^2-MeC_2Me)_2(Fe_4Cp_4S_6-S,S')]I$ (**19**)

The compounds $[Wl_2(CO)(NCMe)(\eta^2-MeC_2Me)_2]$ (0.30 g, 0.35 mmol) and $[Fe_4Cp_4S_6]$ (0.24 g, 0.35 mmol) were stirred together in CH_2Cl_2 (45 cm³) for 20 h. After filtration through Celite, the solvent was removed. Recrystallisation from a minimum volume of CH_2Cl_2/Et_2O gave a black solid (0.22 g, 50%).

4.12. Preparation of

$[Wl(CO)(\eta^2-PhC_2Ph)_2(Fe_4Cp_4S_6-S,S')]I$ (**20**)

The compounds $[Wl_2(CO)(NCMe)(\eta^2-PhC_2Ph)_2]$

(0.30 g, 0.49 mmol) and $[Fe_4Cp_4S_6]$ (0.32 g, 0.49 mmol) were stirred together in CH_2Cl_2 (45 cm³) for 24 h. After filtration through Celite, the solvent was removed. Recrystallisation from a minimum volume of CH_2Cl_2/Et_2O gave a black solid (0.48 g, 67%).

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References

- [1] D.J. Evans, R.A. Henderson, B.E. Smith, in: J. Reedijk, E. Bouwman (Eds.), *Bioinorganic Catalysis*, Ch. 7, 2nd edn., Marcel Dekker, New York, 1988, pp. 153–207.
- [2] P.B. Hitchcock, D.L. Hughes, M.J. Maguire, K. Marjani, R.L. Richards, *J. Chem. Soc. Dalton Trans.* (1997) 4747.
- [3] P.K. Baker, A.I. Clark, S.J. Coles, et al., *J. Chem. Soc. Dalton Trans.* (1998) 1281.
- [4] P.K. Baker, S.D. Harris, M.C. Durrant, D.L. Hughes, R.L. Richards, *J. Chem. Soc. Dalton Trans.* (1994) 1401.
- [5] P.K. Baker, M.C. Durrant, S.D. Harris, D.L. Hughes, R.L. Richards, *J. Chem. Soc. Dalton Trans.* (1997) 509.
- [6] (a) D. Coucouvanis, M.G. Kanatzidis, *J. Am. Chem. Soc.* 107 (1985) 5005. (b) M.G. Kanatzidis, D. Coucouvanis, *J. Am. Chem. Soc.* 108 (1986) 337.
- [7] J. Jordanov, H.M.J. Hendriks, N. Dupré, A. Viari, P. Vigny, G. Diakun, *Inorg. Chem.* 27 (1988) 2997.
- [8] P.K. Baker, *Chem. Soc. Rev.* 27 (1998) 125.
- [9] E.M. Armstrong, P.K. Baker, M.G.B. Drew, *Organometallics* 7 (1988) 319.
- [10] P.K. Baker, S.G. Fraser, E.M. Keys, *J. Organomet. Chem.* 309 (1986) 319.
- [11] G.J. Kubas, P.J. Vergamini, *Inorg. Chem.* 20 (1981) 2667.
- [12] (a) J.A. Kramer, D.N. Hendrickson, *Inorg. Chem.* 19 (1980) 3330. (b) T.Y. Dong, D.N. Hendrickson, C.G. Pierpont, M.F. Moore, *J. Am. Chem. Soc.* 108 (1986) 963.
- [13] (a) N. Dupré, H.M. Hendriks, J. Jordanov, *J. Chem. Soc. Dalton Trans.* (1984) 1463. (b) N. Dupré, H.M. Hendriks, J. Jordanov, J. Gaillard, P. Auric, *Organometallics* 3 (1984) 800.
- [14] P.K. Baker, A.I. Clark, M.G.B. Drew, M.C. Durrant, R.L. Richards, *Polyhedron* 17 (1998) 1407.
- [15] P.K. Baker, E.M. Armstrong, M.G.B. Drew, *Inorg. Chem.* 27 (1988) 2287.