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Journal of Organometallic Chemistry 670 (2003) 144–150

Journal of Organometallic Chemistry

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Reactivity of metal acetylides with chalcogen-bridged metal carbonyl cluster in presence of free alkyne molecule: synthesis and characterisation of $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{(\mu_3\text{-}C(H){=}C(R)S\}\text{-}(CO)_6(\mu_3\text{-}CCPh)]$ (R = Ph, *n*-Bu and M = W, Mo) and $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{(\mu_3\text{-}C(Fc){=}C(H)S\}(CO)_7(\mu_3\text{-}CCPh)]$ (M = W, Mo)

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Received 3 October 2002; received in revised form 13 December 2002; accepted 14 December 2002

Abstract

Photolysis of benzene solution of $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ (**1**), $[(\eta^5\text{-}C_5Me_5)M(CO)_3(C\equiv CPh)]$ (**2a**: M = W, **2b**: M = Mo) and $HC\equiv CR$ (**3a**: R = Ph, **3b**: R = *n*-Bu, **3c**: R = $\{(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Fe\}$(Fc) yields two types of clusters: $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{(\mu_3\text{-}C(H){=}C(R)S\}(CO)_6(\mu_3\text{-}CCPh)]$ (**4**: M = W, R = Ph; **5**: M = Mo, R = Ph: **6**: M = W, R = *n* -Bu; **7**: M = Mo, R = *n*-Bu) and $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{(\mu_3\text{-}C(Fc){=}C(H)S\}(CO)_7(\mu_3\text{-}CCPh)]$ (**8**: M = W; **9**: M = Mo) featuring new C–S bond formation. The formation of **8** and **9** involve an unusual head to tail flip of the coordinated acetylide group. All compounds have been characterised by IR and ^{1}H- and ^{13}C-NMR spectroscopy. The structures of **5** and **8** have been established by X-ray crystallography.
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Keywords: Heterometallic clusters; Acetylides; Crystal structures

1. Introduction

Numerous types of mixed-metal clusters have been synthesised by the use of mononuclear acetylide complexes [1–6]. Apart from imparting stability to the heteronuclear frameworks, the bridging acetylide ligands undergo different types of coupling reactions resulting in clusters containing multisite-bound polycarbon units. As part of our studies on chalcogen-bridged clusters, we have examined the reactivity of mononuclear acetylide complexes with $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se, Te) and have isolated several types of acetylide and chalcogen bridged mixed-metal clusters [7–10]. These reactions have been found to be quite sensitive to the conditions used, but a common feature in all reactions studied so far has been the absence of any bond formation between the chalcogen atoms and the coordinated acetylide groups.

In this paper we report on our investigation of the reactions of $[(\eta^5\text{-}C_5Me_5)M(CO)_3(C\equiv CPh)]$ (M = Mo, W) with $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ in presence of acetylenes, $HC\equiv CR$ (R = Ph, *n*-Bu, Fc). Motivation for this study was to explore whether coupling of acetylide with acetylene takes place on the mixed-metal cluster fragments and since acetylenes are known to form bonds with S-bridges in several clusters [11–13], we anticipated the possibility of a S-containing multisite-bound polycarbon unit being formed. Also, we expected that the presence of a third type of bridging ligand (acetylene) on

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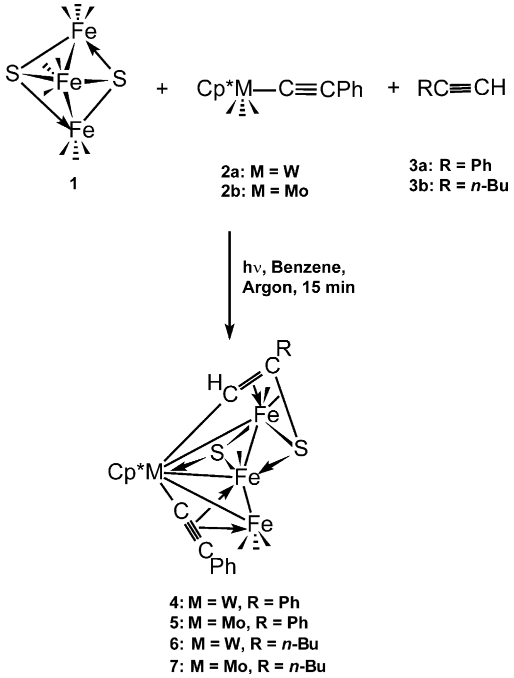
PII: S0022-328X(02)02180-0

the mixed-metal cluster may introduce a new type of acetylide bonding, hitherto unobserved.

2. Results and discussion

2.1. Synthesis and characterisation

Photolysis of a benzene solution containing a mixture of $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ (**1**), $[(\eta^5\text{-}C_5Me_5)M(CO)_3(C\equiv CPh)]$ (**2a**: M = W, **2b**: M = Mo) and HC ≡ CR (**3a**: R = Ph, **3b**: R = *n*-Bu, **3c**: R = $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Fe$, (hereafter denoted by Fc) yields two types of clusters, formation of each depending on the nature of acetylene used. When **3a** or **3b** are used, cluster type $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{(\mu_3\text{-}C(H){=}C(R)S\}(CO)_6(CCPh)]$ is formed as depicted by **4**–**7** in Scheme 1. Use of ferrocenylacetylene (**3c**) in the reaction medium results in formation of $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{(\mu_3\text{-}C(Fc){=}C(H)S\}(CO)_7(\mu_3\text{-}CCPh)]$ (**8**: M = W; **9**: M = Mo). The new clusters are stable in solid state, but decompose in solution over a period of days. They have been characterised by IR and ^1H- and ^{13}C-NMR spectroscopy (Table 2). An identical carbonyl stretching frequency pattern of **4**–**7** indicates that these are isostructural. ^1H- and ^{13}C-NMR spectra of these four compounds are consistent with the presence of $(\eta^5\text{-}C_5Me_5)$, (CCPh) and (HCCR) groups, in addition to the carbonyls. The infrared spectra of **8** and **9** also indicate only terminally bonded carbonyls and the stretching pattern indicates that these two compounds are isostructural with each other. ^1H- and ^{13}C-NMR spectra of **8** and **9** indicate the presence of $(\eta^5\text{-}C_5Me_5)$, (CCPh) and (HCCFc) groups in addition to the terminal carbonyl groups (Scheme 2). For establishing the structure of the new compounds, single crystals of **5** and **8** were grown and single crystal X-ray analyses were carried out.



Scheme 1.

An ORTEP plot of molecular structure of **5** is shown in Fig. 1. The structure can be described as consisting of a $MoFe_3$ butterfly core in which the hinge is composed of the Mo and a Fe atom. One $MoFe_2$ face is capped by μ_3-S ligand as well as an unusual {HC=C(Ph)S} ligand. The second butterfly face is capped by a $\eta^1{:}\eta^2{:}\eta^2$-CCPh group. The wing-tip Fe atoms bear two and three carbonyl groups each and the hinge Fe atom has one terminal carbonyl bonded to it. The Mo atom bears a $(\eta^5\text{-}C_5Me_5)$ group. The average Mo–Fe bond distance of 2.7949 Å is comparable with the average Mo–Fe bond distance of 2.8035 Å in $[Cp_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2]$ [14]. The C(14)–C(15) distance of 1.404 (4) Å is indicative of partial multiple bond. The acetylide bond distance C(6)–C(7) 1.338(4) Å indicates olefinic bond order. The C(15)–S(5) bond length of 1.763(3) Å is slightly shorter than the carbon–sulfur bond in $Os4(CO)12[(\mu_4\text{-}\eta^3\text{-}SC(Ph){=}CH]$ [11].

The molecular structure of **8** is shown in Fig. 2. It consists of a Fe_3 triangle, which is capped by a sulfido ligand. One of the iron atoms is bonded to a $(\eta^5\text{-}C_5Me_5)W$ group. The Fe–W bond is bridged by a ferrocenylacetylene group. A second sulfido ligand triply-bridges the terminal carbon atom of this acetylene with the tungsten and one of the iron atoms. A (CCPh) group forms an unusual quadruple bridge in which the β-carbon of the acetylide is now η^1-bonded to the tungsten atom. Seven terminal carbonyls distributed on the three iron atoms and on the tungsten atom complete the ligand environment of the cluster. The Fe–W bond distance of 2.7006(9) Å is considerably shorter than the W–Fe bond distances of 2.802(4) and 2.829(4) Å in $[Fe_2W(CO)_{10}Se_2]$ [15]. The C(19)–C(20) bond distance of 1.408(9) Å indicates that multiple bonding is present. The C(11)–C(12) bond distance of 1.388(9) Å also indicates the presence of multiple bond. The C(19)–S(1) bond length of 1.757(1) Å is similar with that of **5**.

The two types of structures, butterfly for **4**–**7** and spiked triangle for **8** and **9** conform to electron counts of 62 and 64, respectively.

3. Conclusion

Reactivity of $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ with a mixture of metal acetylide complex, $[(\eta^5\text{-}C_5Me_5)M(CO)_3(C\equiv CPh)]$ and acetylene RC ≡ CH has been studied. In all cases mixed-metal clusters bearing coordinated acetylide and coordinated acetylene are obtained. The nature of the free acetylene in the reaction mixture influences the type of product formed. Thus, for, R = Ph, or *n*-Bu in

Table 1
Experimental conditions used for the preparation of **4**–**9**

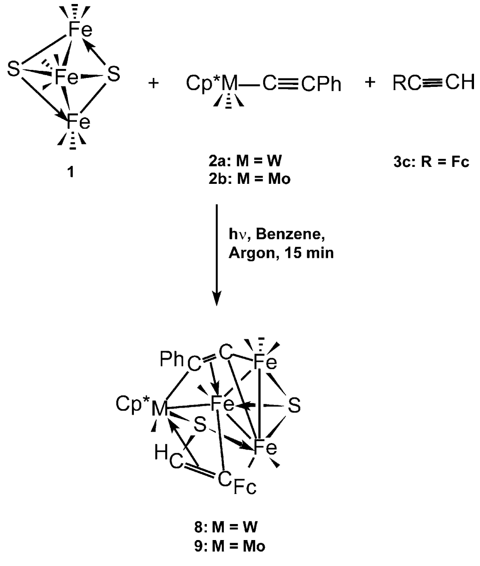
Compounds	$Fe_3S_2(CO)_9$ (mg mmol^{-1})	$Cp^*Mo(CO)_3C_2Ph$ (mg mmol^{-1})	$Cp^*W(CO)_3C_2Ph$ (mg mmol^{-1})	PhC_2H (ml mmol^{-1})	1-Hexyne (ml mmol^{-1})	FcC_2H (mg mmol^{-1})	Yield (mg, %)	Anal. Calc. (Found)		M.p. (°C) [a]
								C	H	
4	54 (0.11)		70 (0.13)	0.02 (0.15)			39 (40)	41.68 (41.42)	2.84 (2.61)	164–166
5	54.(0.1)	54 (0.13)		0.02 (0.15)			25 (27)	46.08 (46.16)	3.14 (2.90)	152–154
6	54 (0.11)		70 (0.13)		0.017 (0.15)		32 (31)	39.94 (40.16)	3.35 (3.40)	172–174
7	54.(0.11)	54 (0.13)			0.017 (0.15)		20 (23)	44.25 (44.41)	3.71 (3.40)	140–142
8	54 (0.11)		70 (0.13)			31 (0.15)	37 (32)	42.00 (42.18)	2.85 (3.12)	196–198
9	54 (0.11)	54 (0.13)				31 (0.15)	20 (23)	44.25 (44.41)	3.71 (3.40)	140–142

[a] With decomposition.

Table 2
Spectroscopic data for compounds **4**–**9**

Compounds	IR [ν(CO), cm^{-1}, hexane]	^{1}H-NMR (δ, $CDCl_3$)	^{13}C-NMR (δ, $CDCl_3$)
4	2033s, 2015s, 1967s, 1948w, 1939w	8.69 (s, 1H, CH), 7.17–7.70 (m, 10H, C_6H_5), 2.35 (s, 15H, $C_5(CH_3)_5$)	13 (CH_3), 25 (PhC2H), 110 ($C_5(CH_3)_5$), 127–130 (C_6H_5), 151 [PhC_2], 166 [PhC_2], 180 [PhC_2H], 206, 208, 212 (CO)
5	2046m, 2034s, 2016s, 2006m, 1992m, 1969s, 1951m, 1941m	8.84 (s, 1H,CH), 7.40–7.67 (m, 10H, 2 × C_6H_5), 2.18 (s, 15H, $C_5(CH_3)_5$)	13 (CH_3), 62 (PhC2H), 110 ($C_5(CH_3)_5$), 125–130 (C_6H_5), 151 (PhC_2), 181 (PhC_2), 190 (PhC_2H), 215 (CO)
6	2032s, 2012s, 1964s, 1948w, 1939w	8.19 (s, 1H, CH), 7.18–7.59 (m, 5H, C_6H_5), 2.91–3.08 (m, 2H, CH_2CH_2), 2.3 (s, 15H, $C_5(CH_3)_5$), 1.71–1.79 (t, 2H, CH_2C, $J = 7$ Hz), 1.41–1.49 (m, 2H, CH_2CH_3), 0.85–1.05 (t, 3H, CH_3, $J = 6$ Hz).	13 (CH_3 of $C_5(CH_3)_5$), 14 (CH_3 of C_6H_{10}), 22 (CH_2), 35 (CH_2), 47 (CH_2), 110 ($C_5(CH_3)_5$), 127–129 (C_6H_5), 156 (PhC_2), 166 (PhC_2H), 181 (PhC_2)206 (CO)
7	2044m, 2034s, 2015s, 2008m, 1990m, 1969s, 1951m, 1941m	8.95 (s, 1H, CH), 7.20–7.39 (m, 5H, C_6H_5), 2.90–3.05 (m, 2H, CH_2CH_2), 2.05 (s, 15H, $C_5(CH_3)_5$)), 1.65–1.71 (t, 2H, CH_2C, $J = 7$ Hz), 1.41–1.49 (m, 2H, CH_2CH_3), 0.85–1.05 (t, 3H, CH_3, $J = 6$ Hz)	13 (CH_3 of $C_5(CH_3)_5$), 14 (CH_3 of C_6H_{10}), 22 (CH_2), 35 (CH_2), 47 (CH_2), 69 ($C_2H(CH_2)_3CH_3$), 110 ($C_5(CH_3)_5$), 127–129 (C_6H_5), 152 (PhC_2H, 181 (PhC_2), 187 ($C_2H(CH_2)_3CH_3$), 212 (CO)
8	2050s, 2031s, 2014s, 2001m, 1990m, 1963m, 1946w	8.47 (s, 1H, CH), 7.30–7.69 (m, 5H, C_6H_5), 4.39–4.48 (m, 4H, C_5H_4), 3.99 (s, 5H, C_5H_5), 2.37 (s, 15H, ($C_5(CH_3)_5$)	13 (CH_3), 49 (FcC_2H), 68, 70, 71 (C_5H_5 of FcC_2H), 110 ($C_5(CH_3)_5$), 127–130 (C_6H_5), 159 (PhC_2), 162 (FcC_2H), 168 (PhC_2), 209 (CO)
9	2062s, 2044s, 2044s, 2024m, 2008m	8.44 (s, 1H, CH), 7.26–7.46 (m, 5H, C_6H_5), 4.21–4.26 (m, 4H, C_5H_5), 4.15 (s, 5H, C_5H_5), 2.17 (s, 15H, ($C_5(CH_3)_5$)	13 (CH_3), 56 (FcC_2H), 69, 70 and 71 (C_5H_5 of FcC_2H), 110 ($C_5(CH_3)_5$), 126–130 (C_6H_5), 162 (PhC_2), 168(FcC_2H), 176 (PhC_2), 209, 218(CO)

RC $\equiv$ CH clusters **4**–**7** are formed. In these a new C–S bond is formed yielding a {HCC(R)S} ligand which bridges a MFe_2 face of the cluster framework. When FcC $\equiv$ CH is used in the reaction mixture, new clusters **8** and **9** are formed. In these, a significant feature is the switching of the α and β carbons of the coordinated acetylide on going from the mononuclear to polynuclear mode of bonding. As a result, the phenyl-bearing carbon atom of the coordinated acetylides in **8** and **9** is now sigma bonded to the molybdenum or tungsten atom. Such a head to tail flip of an acetylide ligand is unprecedented. Nature of the sulfido–acetylene coupling may be an important factor in determining which cluster type is formed, with the bulky ferrocene ligand disfavouring the expected S–C (subs) coupling.



Scheme 2.

4. Experimental

4.1. General considerations

Reactions and manipulations were carried out using Schlenk line techniques under an atmosphere of prepurified argon. Solvents were purified, dried and distilled under an argon atmosphere prior to use. Infrared

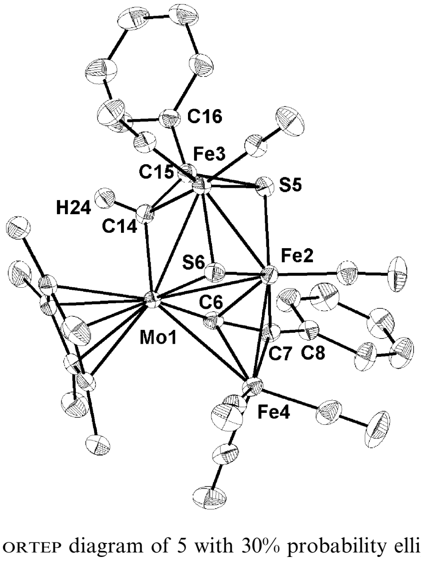


Fig. 1. ORTEP diagram of 5 with 30% probability ellipsoids.

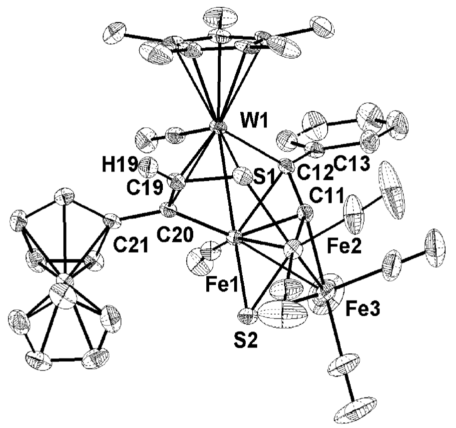


Fig. 2. ORTEP diagram of 8 with 30% probability ellipsoids.

spectra were recorded on a Nicolet Impact 400 FT spectrophotometer, as hexane solution of the sample in 0.1 mm path lengths NaCl cell; ^{1}H- and ^{13}C-NMR were recorded on a Varian VXR-300S spectrometer in $CDCl_3$. Elemental analyses were performed using a Carlo Erba automatic analyser. The compounds $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ [16], $[M(\eta^5\text{-}C_5(CH_3)_5)(CO)_3(C\equiv CPh)]$ (M = Mo, W) [17] and $FcC\equiv CH$ [18] were prepared by established procedures. Photochemical reactions were carried out in a water-cooled double-walled quartz vessel having a 125-W immersion type mercury lamp manufactured by Applied Photophysics Ltd. Conditions used for preparation of **4** –**9** and yield of products are summarised in Table 1.

Tungsten hexacarbonyl and molybdenum hexacarbonyl were purchased from Strem Chemical Co., phenylacetylene, cyclopentadiene and ferrocene were purchased from Aldrich Chemical Co., and these were used without further purification.

*4.2. Preparation of $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{(\mu_3\text{-}C(H)=C(R)S\}(CO)_6(\mu_3\text{-}CCPh)]$ (**4**: M = W, R = Ph; **5**: M = Mo, R = Ph: **6**: M = W, R = n-Bu; 7: M = Mo, R = n-Bu) and $[(\eta^5\text{-}C_5Me_5)MFe_3(\mu_3\text{-}S)\{(\mu_3\text{-}C(Fc)=C(H)S\}(CO)_7(\mu_3\text{-}CCPh)]$ (**8**: M = W; **9**: M = Mo)*

In a typical reaction a benzene solution (70 ml) containing $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ (54 mg, 0.11 mmol), $[(\eta^5\text{-}C_5(CH_3)_5)M(CO)_3(CCPh)]$.(M = W, Mo) (70 mg, 0.13 mmol, M = W and 54 mg, 0.13 mmol, M = Mo) and $RC\equiv CH$ (0.02 ml, 0.15 mmol, R = Ph, 0.017 ml, 0.15 mmol, R = *n*-Bu and 31 mg, 0.15 mmol, R = Fc) were subjected to photolysis for 15 min in a photochemical reaction vessel under a continuous flow of argon. The solvent was removed under vacuo. The residue was dissolved in minimum amount of dichloromethane. The dichloromethane solution was filtered through Celite to remove insoluble material and the solution was subjected to chromatographic work-up on silica-gel tlc plates. Elution with CH_2Cl_2/hexane (40:60 v/v) mixture yielded a dark brown compound (**4**–**9**) together with unreacted $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$. Traces of other products were observed during the chromatographic work-up, which eventually decompose and hence could not be isolated and characterised.

*4.3. Crystal structure determination of **5** and **8***

Crystals of compounds **5** and **8** suitable for X-ray diffraction analysis were grown from hexane-dichloromethane solvent mixtures by slow evaporation of the

Table 3
Crystal data and details of measurements of compounds **5** and **8**

Compounds	**5**	**8**
Empirical formula	$C_{32}H_{26}Fe_3MoO_6S_2$	$C_{37}H_{30}Fe_4O_7S_2W$
Formula weight	834.14	1057.98
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.70930	0.70930
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	13.2610 (17)	10.0500(9)
b (Å)	14.718(3)	11.7520(14)
c (Å)	17.666(2)	16.8150(12)
α (°)		83.407 (9)
β (°)	108.417 (9)	76.548 (8)
γ (°)		71.606(8)
V (Å^3)	3271.4(9)	1831.0(3)
Z	4	2
D_{calc} (mg m^{-3})	1.694	1.919
Absorption coefficient (mm^{-1})	1.848	4.839
Crystal size (mm^3)	0.3 × 0.3 × 0.275	0.35 × 0.25 × 0.2
θ Range for data collection (°)	1.69–24.92	1.24–24.93
Index ranges	$0\leq h\leq 15$, $0\leq k\leq 17$, $-20\leq l\leq 19$	$0\leq h\leq 11$, $-12\leq k\leq 13$, $-19\leq l\leq 19$
Reflections collected/unique	5061/5061 [R_{int} = 0.0000]	6121/6121 [R_{int} = 0.0000]
Completeness to 2θ = 24.92 (%)	84.5	95.5
Absorption correction	Ψ-scan	Ψ-scan
Max. and min. transmission	1.000 and 0.931	1.000 and 0.856
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5061/0/501	6121/0/464
Goodness-of-fit on F^2	1.101	1.219
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0291, wR_2 = 0.0676	R_1 = 0.0443, wR_2 = 0.1125
R indices (all data)	R_1 = 0.0363, wR_2 = 0.0720	R_1 = 0.0474, wR_2 = 0.1158
Largest difference peak and hole (e Å^{-3})	0.671 and −0.513	3.674 and −3.845

Table 4
Selected bond lengths (Å) and bond angles (°) for **5**

Bond lengths			
C(14)–C(15)	1.404(4)	Mo(1)–C(14)	2.091(3)
C(7)–C(6)	1.338(4)	Fe(3)–C(14)	2.102(3)
S(5)–C(15)	1.763(3)	Fe(3)–S(6)	2.2240(11)(3)
Fe(2)–C(6)	2.021(3)	Mo(1)–Fe(3)	2.8157(6)
Fe(4)–C(6)	2.067(3)	Mo(1)–Fe(2)	2.6352(6)
Fe(2)–C(7)	2.087(3)	Fe(2)–Fe(3)	2.5744(8)
Mo(1)–Fe(4)	2.9340(8)	Fe(2)–Fe(4)	2.4951(8)
Fe(3)–C(15)	2.156(3)	Fe(3)–C(14)	2.102(3)
Bond angles			
C(16)–C(15)–C(14)	123.5(3)	Fe(3)–S(6)–Mo(1)	76.35(3)
C(8)–C(7)–C(6)	141.2(3)	Mo(1)–S(6)–Fe(2)	70.85(3)
Fe(3)–Fe(2)–Fe(4)	132.66(2)	Fe(2)–S(5)–Fe(3)	70.46(3)
Fe(3)–Mo(1)–Fe(4)	107.70(2)	Fe(2)–Fe(4)–Mo(1)	57.393(18)
Fe(2)–Mo(1)–Fe(3)	56.250(18)	C(15)–S(5)–Fe(2)	106.47(11)
Mo(1)–C(6)–Fe(4)	93.88(13)		

solvents at 4 °C. Relevant crystallographic data and details of measurements are given in Table 3. Selected bond angles and bond lengths of **5** and **8** are given in Tables 4 and 5, respectively. Data were collected on a Nonius MACH3 four-circle diffractometer (graphite-monochromatized Mo–K_α radiation) for the cell determination and intensity data collection. The unit cell parameters were derived and refined by using randomly selected reflections in the θ range 6.40–14.01 (compound **5**) and 6.880–12.320 (compound **8**). The structures were solved by direct methods using the SHELXS-97 program [19] and refined by using SHELXL-97 software [20]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms were generated and refined using riding model for compound **5** and the hydrogen atoms were geometrically fixed and refined using a riding model for compound **8**. Absorption corrections were employed using Ψ-scans.

Table 5
Selected bond lengths (Å) and bond angles (°) for **8**

Bond lengths			
C(19)–C(20)	1.408(9)	Fe(2)–S(1)	2.2199(19)
C(11)–C(12)	1.388(9)	W(1)–S(1)	2.4785(16)
C(19)–S(1)	1.757(7)	W(1)–C(19)	2.217(6)
W(1)–Fe(1)	2.7006(9)	W(1)–C(20)	2.317(6)
Fe(1)–Fe(2)	2.5569(12)	Fe(1)–C(11)	1.874(6)
Fe(1)–Fe(3)	2.5905(13)	Fe(1)–C(20)	1.967(6)
Fe(2)–Fe(3)	2.5223(14)	Fe(1)–C(12)	2.134(6)
Fe(2)–S(2)	2.214(2)	Fe(3)–C(11)	1.977(7)
Fe(1)–S(2)	2.1270(18)		
Bond angles			
Fe(2)–Fe(1)–Fe(3)	58.68(4)	C(11)–C(12)–Fe(1)	59.9(3)
C(19)–S(1)–W(1)	60.3(2)	Fe(1)–C(12)–W(1)	78.4(2)
Fe(2)–Fe(1)–W(1)	90.37(3)	C(20)–C(19)–S(1)	118.4(5)
Fe(3)–Fe(2)–Fe(1)	61.33(4)	S(1)–C(19)–W(1)	76.2(2)
Fe(2)–Fe(3)–Fe(1)	60.00(3)	C(19)–C(20)–C(21)	117.3(5)
Fe(1)–C(11)–Fe(2)	84.3(3)	Fe(1)–C(20)–W(1)	77.7(2)
Fe(1)–C(11)–Fe(3)	84.5(3)	Fe(2)–C(11)–Fe(3)	80.3(2)
C(11)–C(12)–C(13)	118.5(5)		

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 194622 and 194623 for compounds **5** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

A.K.B is grateful to the Council of Scientific and Industrial Research, Government of India, for a research fellowship.

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