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Chalcogen–acetylide interaction and unusual reactivity of coordinated acetylide with water: synthesis and characterisation of $[(\eta^5\text{-}C_5R_5)Fe_3(CO)_6(\mu_3\text{-}E)(\mu_3\text{-}ECCH_2R^I)]$ (R = H, Me; R^I = Ph, Fc; E = S, Se) and $[(\eta^5\text{-}C_5R_5)MoFe_2(CO)_6(\mu_3\text{-}S)\text{-}(\mu\text{-}SCCH_2Ph)]$ (R = H, Me)

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Abstract

Photolysis of a benzene solution containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se), $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(C{\equiv}CR^I)]$ (R = H, Me; R^I = Ph, Fc), H_2O and Et_3N results in formation of new metal clusters $[(\eta^5\text{-}C_5R_5)Fe_3(CO)_6(\mu_3\text{-}E)(\mu_3\text{-}ECCH_2R^I)]$ (R = H, R^I = Ph, E = S **1** or Se **2**; R = Me, R^I = Ph, E = S **3** or Se **4**; R = H, R^I = Fc, E = S **5**; R = Me, R^I = Fc, E = S **6** or Se **7**). Reaction of $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$with $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(C{\equiv}CPh)]$ (R = H, Me), under same conditions, produces mixed-metal clusters $[(\eta^5\text{-}C_5R_5)MoFe_2(CO)_6(\mu_3\text{-}S)(\mu\text{-}SCCH_2Ph)]$ (R = H **8**; R = Me **9**). Compounds **1**–**9** have been characterised by IR and ^1H and ^{13}C-NMR spectroscopy. Structures of **1**, **5** and **9** have been established crystallographically. A common feature in all these products is the formation of new C-chalcogen bond to give rise to a $(ECCH_2R^I)$ ligand.

Keywords: Acetylides; Mixed-metal; Chalcogen; Crystal structure

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1. Introduction

Chalcogen atoms have been found to be important bridging ligands in metal carbonyl cluster chemistry [1–3]. An important aspect of chalcogen ligands is their ability to adopt different bonding modes, thus providing flexibility in a cluster framework for the metal atoms to participate in various types of reactions with organic and inorganic moieties. The stabilising role of chalcogens has led to the preparation of numerous types of chalcogen-bridged mixed-metal clusters containing acetylide ligands [4–9]. Bonding of acetylides to the cluster framework has been shown to be quite sensitive to the nature of chalcogen present, as well as reaction conditions used. Thus, by careful selection of the conditions, different types of acetylide couplings are observed and under certain aerobic conditions, some oxo- and acetylide-containing clusters can be prepared [10,11]. In all such clusters, the chalcogen atom serves as stabilising caps over certain faces of the cluster framework, but does not itself interact directly with the acetylide groups. For instance, reactions of $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S or Se) with $[(\eta^5\text{-}C_5R_5)M(CO)_3(C{\equiv}CPh)]$ (M = Mo or W; R = H or Me) yield a number of different $Fe_3M_2E_2$ or $Fe_4M_2E_2$ clusters in which the two multi-coordinated acetylide groups undergo head-to-head, head-to-tail or tail-to-tail coupling reactions without any new C-chalcogen bond formation being observed [12–14]. In this paper we describe the isolation of two types of acetylide-containing clusters in which an acetylide group directly interacts with a chalcogen atom. Protonation at a carbon atom of the coordinated acetylide group gives rise to an unusual ligand system, not previously seen in chalcogen- and acetylide-bridged clusters.

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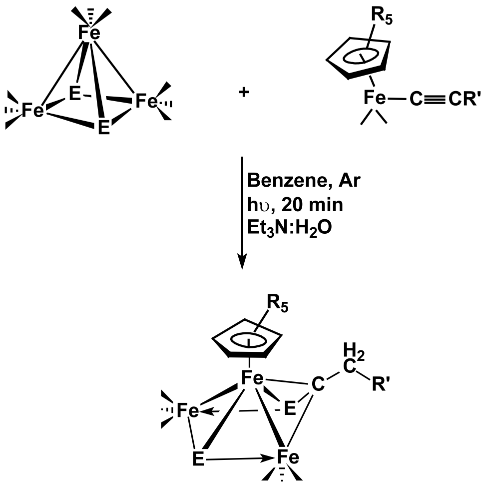
2. Results and discussion

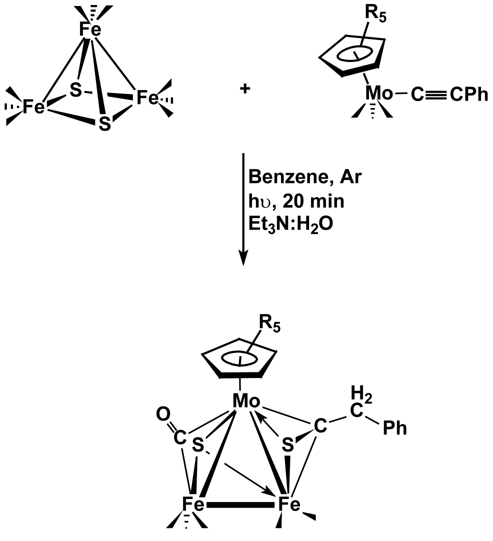
2.1. Synthesis and characterisation

When a benzene solution containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se), $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(C{\equiv}CR^I)]$ (R = H, Me; R^I = Ph), $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Fe$, hereafter denoted by Fc), H_2O and Et_3N was photolysed with continuous bubbling of argon, the new clusters, $[(\eta^5\text{-}C_5R_5)Fe_3(CO)_6(\mu_3\text{-}E)(\mu_3\text{-}ECCH_2R^I)]$ (R = H, R^I = Ph, E = S **1** or Se **2**; R = Me, R^I = Ph, E = S **3** or Se **4**; R = H, R^I = Fc, E = S **5**; R = Me, R^I = Fc, E = S **6** or Se **7**) were obtained as major products after chromatographic work-up (Scheme 1). Under the same conditions of photolysis, if $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(C{\equiv}CPh)]$ (R = H, Me) is used for reaction with $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$, we observe formation of $[(\eta^5\text{-}C_5R_5)MoFe_2(CO)_6(\mu_3\text{-}S)(\mu\text{-}SCCH_2Ph)]$ (R = H **8**; R = Me **9**) (Scheme 2). This reaction also produced several other compounds, which were observed during chromatographic work-up, but could not be characterised due to their low yields. The new clusters are stable in air in the solid state but slowly decompose in solution over a period of days. Reaction with the tellurium bridged starting compound $[Fe_3(CO)_9(\mu_3\text{-}Te)_2]$ led to substantial decomposition and only trace amounts of the starting materials were isolated after 0.5 h of photolysis. Compounds **1**–**9** are formed only in the presence of $Et_3N{-}H_2O$, where H_2O acts as a source of protons and Et_3N works as a phase transfer catalyst. Use of H_2O without Et_3N in the reaction medium did not yield any of compounds **1**–**9**.



Cpd	R	R^I	E
1	H	Ph	S
2	H	Ph	Se
3	Me	Ph	S
4	Me	Ph	Se
5	H	Fc	S
6	Me	Fc	S
7	Me	Fc	Se

Scheme 1.



8 R = H
9 R = Me

Scheme 2.

Deuterated studies confirm that the origin of the protons is H_2O. Compounds **1**–**9** were characterised by IR and ^1H- and ^{13}C-NMR spectroscopy (Table 1). Further, the structures of **1**, **5** and **9** were confirmed crystallographically. Infrared spectra of compounds **1**–**7** display an identical carbonyl stretching pattern, confirming the presence of only terminally bonded carbonyl groups. The ^1H-NMR spectra of these compounds show a single peak for $(\eta^5\text{-}C_5R_5)$ group and a multiplet for phenyl or ferrocenyl groups. Two sets of doublets are observed in each of these compounds which indicate the presence of non-equivalent protons on CH_2 group. The ^{13}C-NMR spectra of **1**–**7** also indicate presence of $(\eta^5\text{-}C_5R_5)$, CH_2 and phenyl or ferrocenyl groups.

Dark purple crystals of **1** and **5** were grown from hexane-dichloromethane solvent mixtures at −5 °C and X-ray diffraction studies were undertaken. The molecular structures of **1** and **5** are depicted in Fig. 1 and Fig. 2 respectively. The basic geometry of these structures can be described as consisting of a $(\eta^5\text{-}C_5H_5)Fe$ group connected to the corners of a non-planar five-membered ring composed of two Fe, two E and one C atoms. The ring Fe atoms bear three terminal carbonyls each, and a CH_2R^I (R^I = Ph in **1** and Fc in **5**) group is attached to the carbon atom. Assuming that each chalcogen atom formally donates 4-electrons, the 18-electron count around each metal atom is satisfied. The average Fe–Fe bond distance of 2.627 Å in **1** is slightly longer than in **5** (2.598 Å) as well as in $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ (2.594 Å) [15]. One of the Fe–C bonds, Fe(1)–C(6), 2.016(4) Å in **1** and 2.020(3) Å in **5** is longer than the other one, Fe(2)–C(6), 1.934(3) Å in **1** and 1.935(3) Å in **5**, as well as the $Fe{-}C_{acetylide}$ bond in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C{\equiv}CPh)]$ (1.920(6) Å) [16]. In both compounds there is a lengthening of the acetylide C–C

Table 1
Spectroscopic data for compounds **1**–**9**

Compound	IR, [ν(CO), cm^{-1}, hexane]	^{1}H NMR, (δ, $CDCl_3$)	^{13}C NMR, (δ, $CDCl_3$)
1	2064 (s), 2037 (vs), 2026 (m), 2002 (s), 1991 (m), 1967 (m)	4.73 (s, C_5H_5), 4.65, 4.70 (d, CH_2), 5.53, 5.58 (d, CH_2), 7.3–7.5 (m, C_6H_5)	64.3 (s, CH_2), 82.8 (s, C_5H_5), 126.7–128.6 (m, C_6H_5), 142.6 (s, CCH_2Ph), 205.4 (CO)
2	2060 (s), 2036 (vs), 2013 (w), 2001 (m), 1987 (w), 1960 (m)	4.73 (s, C_5H_5), 5.00, 5.04 (d, CH_2), 5.76, 5.81 (d, CH_2), 7.3–7.5 (m, C_6H_5)	67.2 (s, CH_2), 82.0 (s, C_5H_5), 127.5–128.5 (m, C_6H_5), 143.1 (s, CCH_2Ph), 207.2 (CO)
3	2057 (s), 2030 (vs), 1994 (m), 1981 (s), 1957 (m)	1.74 (s, C_5Me_5), 4.55, 4.59 (d, CH_2), 5.49, 5.53 (d, CH_2), 7.3–7.5 (m, C_6H_5)	11.8 (s, C_5Me_5), 60.1 (s, CH_2), 95.4 (s, C_5Me_5), 126.5–129.5 (m, C_6H_5), 142.8 (s, CCH_2Ph), 207.2 (CO)
4	2053 (s), 2026 (vs), 2013 (m), 1989 (w), 1976 (s), 1955 (m)	1.68 (s, C_5Me_5), 5.16, 5.20 (d, CH_2), 5.83, 5.88 (d, CH_2), 7.3–7.5 (m, C_6H_5)	12.3 (s, C_5Me_5), 64.0 (s, CH_2), 94.5 (s, C_5Me_5), 126.6–129.7 (m, C_6H_5), 143.4 (s, CCH_2Ph), 209.4 (CO)
5	2064 (s), 2036 (vs), 2001 (s), 1991 (w), 1966 (s), 1895 (m)	4.69 (s, C_5H_5), 4.36, 4.40 (d, CH_2), 5.23, 5.28 (d, CH_2),4.13 (s, 2H, Fc), 4.24 (d, 2H, Fc), 4.20 (s, 5H, Fc)	59.1 (s, CH_2), 67.6–68.8 (m, Fc-sub), 68.1 (s, Fc-unsub), 79.0 (s, C_5H_5), 142.4 (s, CCH_2Fc), 206.1 (CO)
6	2057 (s), 2029 (vs), 1994 (s), 1980 (w), 1956 (s), 1895 (m)	1.72 (s, C_5Me_5), 4.27, 4.30 (d, CH_2), 5.17, 5.22 (d, CH_2),4.13 (s, 2H, Fc), 4.22 (d, 2H, Fc), 4.20 (s, 5H, Fc)	11.9 (s, C_5Me_5) 54.9 (s, CH_2), 68.1–70.0 (m, Fc-sub), 68.8 (s, Fc-unsub), 95.3 (s, C_5Me_5), 142.6 (s, CCH_2Fc), 207.6 (CO)
7	2052 (s), 2025 (vs), 2012 (w) 1987 (s), 1975 (s), 1954 (s), 1895 (m)	1.66 (s, C_5Me_5), 4.83, 4.88 (d, CH_2), 5.53, 5.58 (d, CH_2), 4.15 (s, 2H, Fc), 4.27 (d, 2H, Fc), 4.23 (s, 5H, Fc)	11.6 (s, C_5Me_5) 57.6 (s, CH_2), 67.7–70.0 (m, Fc-sub), 68.5 (s, Fc-unsub), 94.3 (s, C_5Me_5), 143.3 (s, CCH_2Fc), 209.5 (CO)
8	2056 (s), 2033 (w), 2001 (vs) 1970 (s), 1953 (m), 1893 (w), 1841 (s)	5.41 (s, C_5H_5), 4.24, 4.28 (d, CH_2), 4.34, 4.38 (d, CH_2), 7.26–7.38 (m, C_6H_5)	42.1 (s, CH_2), 97.2 (s, C_5H_5), 127.0–129.0 (m, C_6H_5), 142.6 (s, CCH_2Ph), 208.9 (CO)
9	2048 (s), 1992 (vs) 1969 (s), 1945 (s), 1893 (w), 1853 (s)	1.62 (s, C_5Me_5), 4.24, 4.26 (d, CH_2), 4.32, 4.36 (d, CH_2), 7.20–7.30 (m, C_6H_5)	11.1 (s, C_5Me_5), 43.3 (s, CH_2), 109.1 (s, C_5Me_5), 126.9–129.5 (m, C_6H_5), 141.9 (s, CCH_2Ph), 210.0 (CO)

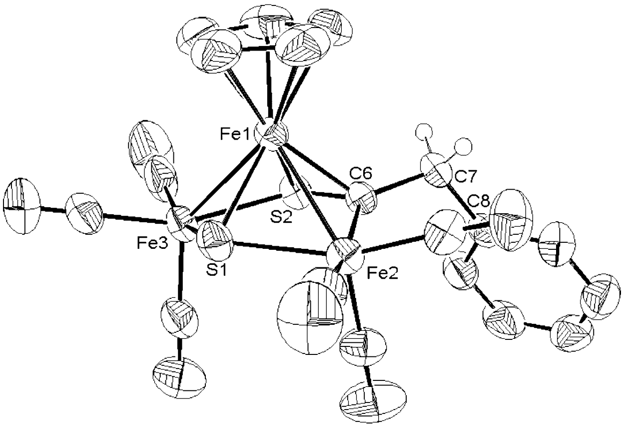


Fig. 1. ORTEP diagram of **1** with 50% probability ellipsoids.

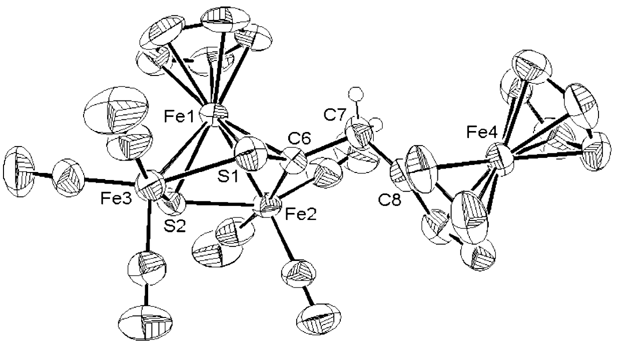


Fig. 2. ORTEP diagram of **5** with 50% probability ellipsoids.

bond distance, 1.533(5) Å and 1.544(4) Å in **1** and **5** respectively (1.201(9) Å in [(η^5-C_5H_5)Fe(CO)$_2$(C≡CPh)]), consistent with a single bond distance. The average Fe–S bond lengths of 2.211 Å and 2.207 Å in **1** and **5** respectively are comparable with the average bond length of 2.238 Å observed in [$Fe_3(CO)_9(\mu_3\text{-}S)_2$] [15].

The infrared spectra of **8** and **9** show the presence of both terminal and bridging carbonyl groups and the stretching pattern indicates that these two compounds are isostructural with each other. The ^{1}H-NMR spectra of **8** and **9** are similar to those of **1**–**7**, showing a single peak each for (η^5-C_5R_5) group, a multiplet for phenyl group and two sets of doublets for non-equivalent protons on CH_2 group. The ^{13}C-NMR spectra of these compounds confirm the presence of (η^5-C_5R_5), CH_2 and phenyl groups.

Crystals of **9** were grown from hexane-dichloromethane solvent mixtures at −5 °C and X-ray diffraction study was undertaken. An ORTEP plot of molecular structure of **9** is shown in Fig. 3. It consists of a Fe_2Mo triangle in which one of the Fe–Mo edges is bridged by a CO group and the other by a $SCCH_2Ph$ unit. The Fe_2Mo face is bridged by a μ_3-S ligand. One iron atom contains three terminal carbonyls while the other bears two carbonyl groups. The molybdenum atom bears a (η^5-C_5Me_5) group. The Fe–Fe bond distance of 2.5931(8) Å in **9** is shorter than the Fe–Fe bond distance of 2.660(3) Å in [$Fe_2Ru(CO)_9(\mu_3\text{-}S)_2$] [17]. The carbonyl-bridged edge of the Fe_2Mo triangle, Fe(1)–Mo

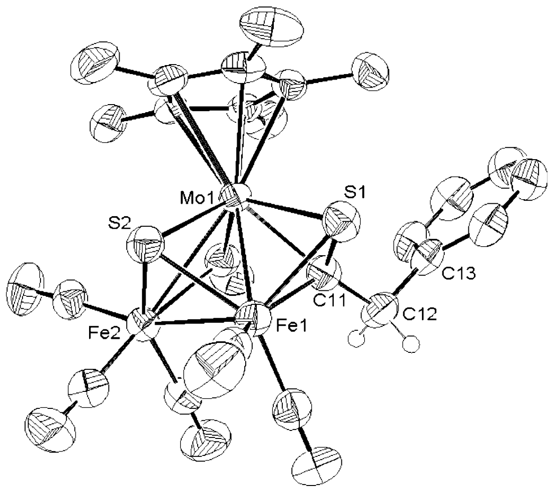


Fig. 3. ORTEP diagram of **9** with 50% probability ellipsoids.

(2.6308(8) Å) is shorter than the ($SCCH_2Ph$) bridged edge, Fe(2)–Mo (2.8211(6) Å). The short Fe–Mo bond length is in fact considerably shorter than the Fe–Mo bond lengths reported for some related chalcogen-bridged Fe–Mo clusters as: $Cp_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_8$, 2.816 Å av. [18]; *trans*-$Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Se)(CO)_8$, 2.813 Å av. [19]; $Fe_2Mo(\mu_3\text{-}Se)_2(CO)_{10}$, 2.809 Å av. [20]. The acetylide C–C bond distance, 1.510(5) Å, is consistent with a single bond distance.

2.2. Mechanistic aspects

A common feature in the formation of **1**–**9** is the formal replacement of the $Fe(CO)_3$ group of $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ by $(\eta^5\text{-}C_5R_5)Fe(CCH_2R^I)$ (**1**–**7**) or $(\eta^5\text{-}C_5R_5)Mo(CCH_2Ph)$ (**8** and **9**) groups. In both types of clusters, a new carbon–chalcogen bond is formed. Although the exact mechanistic details are unknown at present, Scheme 3 outlines possible steps involved in the formation of **1**–**7**. The absence of a Fe–Fe bond in **1**–**7** or presence in **8** and **9** differentiates the two cluster types. Therefore, the formation of **1**–**7** may be regarded as involving formal replacement of a apical $Fe(CO)_3$ group of the starting cluster $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ by a $[(\eta^5\text{-}C_5R_5)Fe(C{\equiv}CR^I)]$ unit (**10** and **11** in Scheme 3), while formation of **8** and **9** can be thought of to occur by a formal replacement of a basal iron carbonyl group by a $[(\eta^5\text{-}C_5R_5)Mo(C{\equiv}CPh)]$ unit. A similar contrast is seen in formation of $[CpCoFe_2(CO)_6(\mu_3\text{-}E)_2]$ and $[Fe_2Ru(CO)_9(\mu_3\text{-}E)_2]$. In the former case, an apical $Fe(CO)_3$ group of $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ is replaced by a CpCo group while in the latter case, a basal $Fe(CO)_3$ group is formally substituted by a $Ru(CO)_3$ group [17,21]. Attack of a proton at the β-carbon atom on the σ-bonded acetylide group forms the intermediate vinylidene **12**. A nucleophilic attack by one of the chalcogens at the α-carbon atom of the acetylide group gives a vinyl system **13** [22]. Since the vinyl group is still susceptible towards electrophiles another proton adds at the β-carbon of the acetylide unit to form the thiolato carbene **14**. Insertion of the α-carbon into a Fe–E bond yields the observed products, **1**–**7**.

3. Conclusion

Under photolytic conditions and in presence of an $H_2O{:}NEt_3$ mixture, an apical or a basal $Fe(CO)_3$ group of $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ is formally replaced by a iron- or molybdenum-acetylide moiety. In both types of reactions, new chalcogen–acetylide interactions and the formation of a $(ECCH_2R^I)$ bound to either three (**1**–**7**) or two (**8** and **9**) metal atoms are observed. The unusual μ_2, $\eta^2{:}\eta^2$-bonded $SCCH_2R^I$ ligand in **8** and **9** can be thought of formally as being the anion of the thiocarbene $HSCCH_2R$.

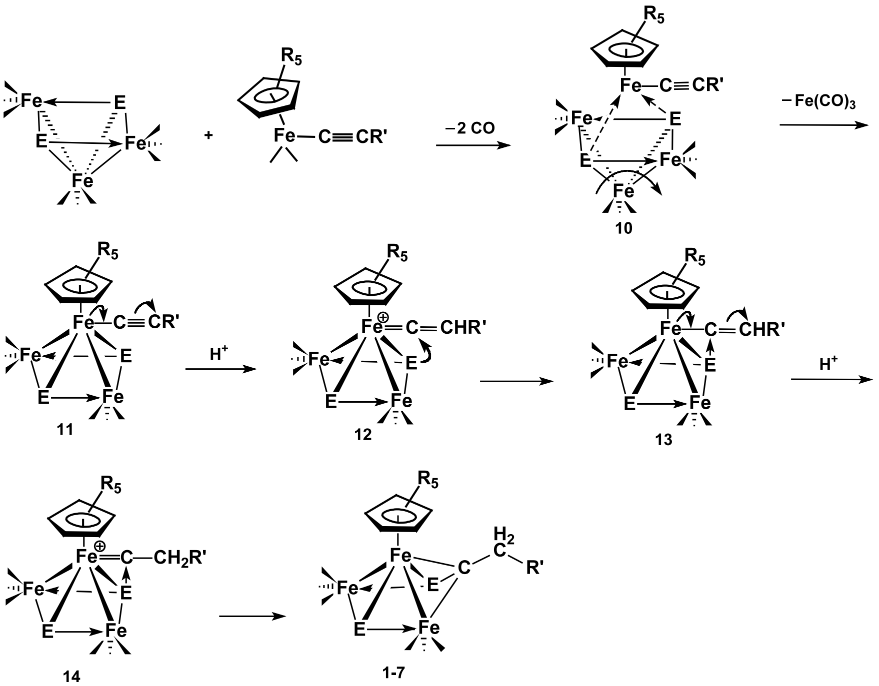
4. Experimental

4.1. General procedures

Reactions and manipulations were performed using standard Schlenk techniques under an atmosphere of pre-purified argon. Solvents were purified, dried and distilled under an argon or nitrogen atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as dichloromethane solutions in 0.1 mm path length cells and NMR spectra on a Varian VXRO-300S spectrometer in $CDCl_3$. Elemental analyses were performed on a Carlo-Erba automatic analyser. The compounds $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se) [23], $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(C{\equiv}CPh)]$ (R = H, Me) [24], and $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(C{\equiv}CFc)]$ (R = H, Me) [25] were prepared by established procedures. Details of quantities of starting materials used and yields of products obtained are given in Table 2.

4.2. Reaction of $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se) with $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(C{\equiv}CR^I)]$ (R = H, Me; R^I = Ph, Fc) or $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(C{\equiv}CPh)]$ (R = H, Me)

In a typical preparation, a benzene solution (120 ml) containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se), $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(C{\equiv}CR^I)]$ (R = H, Me; R^I = Ph, Fc) or $[(\eta^5\text{-}C_5R_5)Mo(CO)_3(C{\equiv}CPh)]$ (R = H, Me), H_2O (2 ml), and Et_3N (3 ml) was irradiated with a 125 W high-pressure Hg lamp for 20 min at 0 °C under bubbling of argon. After the solution had been concentrated in vacuo to a small volume, it was filtered and dried over Na_2SO_4. After filtration and removal of solvent, the residue was subjected to chromatographic work-up on silica-gel TLC plates. Elution with CH_2Cl_2/*n*-hexane (10/90 v/v) mixture yielded, a major purple band $[(\eta^5\text{-}$



Scheme 3.

$C_5R_5)Fe_3(CO)_6(\mu_3-E)_2(CCH_2R^I)]$ (R = H, R^I = Ph, E = S **1** or Se **2**; R = Me, R^I = Ph, E = S **3** or Se **4**; R = H, R^I = Fc, E = S **5**; R = Me, R^I = Fc, E = S **6** or Se **7**) or a brown band $[(\eta^5-C_5R_5)MoFe_2(CO)_6(\mu_3-S)(\mu-SCCH_2-Ph)]$ (R = H **8**; R = Me **9**) with trace amounts of starting materials. Some other bands were observable but these were of insufficient amounts to facilitate their isolation and identification.

*4.3. Crystal structure determination of **1**, **5** and **9***

Suitable X-ray quality crystals of **1**, **5** and **9** were grown by slow evaporation of CH_2Cl_2-*n*-hexane solvent mixture at −5°C and X-ray diffraction study was undertaken. Relevant crystallographic data and details of measurements are given in Table 3. Selected bond lengths (Å) and angles (°) are listed in Table 4 for **1**,

Table 2
Experimental conditions used for the preparation of **1**–**9**

$[(\eta^5-C_5R_5)Fe(CO)_2(C_2R^I)]$ [mg, (mmol)]	$[Fe_3(CO)_9(\mu_3-E)_2]$ [mg, (mmol)]	Product obtained	Yield: mg (%)	Anal. calc. (found)	m.p. per °C [a]
$[(\eta^5-C_5H_5)Fe(CO)_2(C_2Ph)]$ [60, (0.2169)]	$[Fe_3(CO)_9(\mu_3-S)_2]$ [70, (0.1446)]	**1**	36 (44)	C, 40.2 (40.58) H, 2.12 (2.26)	124–126
$[(\eta^5-C_5H_5)Fe(CO)_2(C_2Ph)]$ [50, (0.1817)]	$[Fe_3(CO)_9(\mu_3-Se)_2]$ [70, (0.1211)]	**2**	22 (28)	C, 34.5 (34.29) H, 1.82 (1.76)	120–122
$[(\eta^5-C_5Me_5)Fe(CO)_2(C_2Ph)]$ [65, (0.1860)]	$[Fe_3(CO)_9(\mu_3-S)_2]$ [60, (0.1240)]	**3**	30 (39)	C, 45.2 (45.67) H, 3.5 (3.63)	131–133
$[(\eta^5-C_5Me_5)Fe(CO)_2(C_2Ph)]$ [59, (0.1687)]	$[Fe_3(CO)_9(\mu_3-Se)_2]$ [65, (0.1125)]	**4**	29 (36)	C, 39.4 (39.08) H, 3.0 (2.84)	127–129
$[(\eta^5-C_5H_5)Fe(CO)_2(C_2Fc)]$ [60, (0.2169)]	$[Fe_3(CO)_9(\mu_3-S)_2]$ [70, (0.1446)]	**5**	37 (38)	C, 40.87 (40.76) H, 2.38 (2.26)	118–120
$[(\eta^5-C_5Me_5)Fe(CO)_2(C_2Fc)]$ [65, (0.1860)]	$Fe_3(CO)_9(\mu_3-S)_2]$ [60, (0.1240)]	**6**	31 (34)	C, 45.08 (44.91) H, 3.51 (3.38)	112–114
$[(\eta^5-C_5Me_5)Fe(CO)_2(C_2Fc)]$ [59, (0.1687)]	$Fe_3(CO)_9(\mu_3-Se)_2]$ [65, (0.1125)]	**7**	24 (26)	C, 40.08 (39.93) H, 3.12 (2.96)	96–98
$[(\eta^5-C_5H_5)Mo(CO)_3(C_2Ph)]$ [75, (0.2169)]	$Fe_3(CO)_9(\mu_3-S)_2]$ [70, (0.1446)]	**8**	28 (32)	C, 37.53 (37.68) H, 1.99 (2.12)	143–145
$[(\eta^5-C_5Me_5)Mo(CO)_3(C_2Ph)]$ [90, (0.2169)]	$Fe_3(CO)_9(\mu_3-S)_2]$ [70, (0.1446)]	**9**	28 (29)	C, 42.5 (42.32) H, 3.27 (3.15)	139–141

[a] With decomposition.

Table 3
Crystal data and structure refinement parameters for **1**, **5** and **9**

	1	**5**	**9**
Empirical formula	$C_{19}H_{12}Fe_3O_6S_2$	$C_{23}H_{16}Fe_4O_6S_2$	$C_{24}H_{22}MoFe_2O_6S_2$
Formula weight	567.96	675.88	678.18
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.70930	0.70930	0.70930
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P(\bar{1})$	Monoclinic, $P2_1/n$
Unit cell dimensions			
a (Å)	9.4660(9)	7.8030(8)	9.9280(9)
b (Å)	18.510(2)	12.2850(6)	14.6480(8)
c (Å)	13.1120(16)	13.3220(8)	17.6990(16)
α (°)		85.908(5)	
β (°)	110.961(8)	84.348(6)	93.045(8)
γ (°)		80.862(6)	
Volume (Å^3)	2145(4)	1252.69(16)	2570.2(4)
Z, calculated density (mg m^{-3})	4, 1.758	2, 1.792	4, 1.753
Absorption coefficient (mm^{-1})	2.229	2.474	1.794
$F(0\ 0\ 0)$	1136	676	1360
Crystal size	0.4 × 0.2 × 0.2	0.35 × 0.15 × 0.10	0.2 × 0.2 × 0.2
θ range for data collection (°)	1.99–24.92	1.54–24.92	1.80–24.92
Index ranges	$0 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 21$, $-15 \leqslant l \leqslant 14$	$0 \leqslant h \leqslant 9$, $-14 \leqslant k \leqslant 14$, $-15 \leqslant l \leqslant 15$	$0 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 17$, $-21 \leqslant l \leqslant 20$
Reflection collected/unique	3321/3321 [$R_{int} = 0.0000$]	3989/3989 [$R_{int} = 0.0000$]	3894/3894 [$R_{int} = 0.0000$]
Completeness to $\theta = 24.92$	85.2%	90.5%	82.6%
Absorption correction	Psi-scan	Psi-scan	Psi-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3321/0/319	3989/0/380	3894/0/404
Goodness-of-fit on F^2	1.113	1.077	1.079
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0422$, $wR_2 = 0.1094$	$R_1 = 0.0299$, $wR_2 = 0.0679$	$R_1 = 0.0281$, $wR_2 = 0.0555$
R indices (all data)	$R_1 = 0.0467$, $wR_2 = 0.1145$	$R_1 = 0.0384$, $wR_2 = 0.0731$	$R_1 = 0.04$, $wR_2 = 0.062$
Largest difference peak and hole (e Å^{-3})	1.212 and −0.644	0.477 and −0.344	0.278 and −0.302

Table 4
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths			
Fe(1)–C(6)	2.016(4)	Fe(2)–S(1)	2.2129(12)
Fe(1)–S(1)	2.1866(11)	Fe(3)–S(2)	2.2003(11)
Fe(1)–S(2)	2.2246(11)	Fe(3)–S(1)	2.2306(11)
Fe(1)–Fe(2)	2.6245(8)	S(2)–C(6)	1.761(3)
Fe(1)–Fe(3)	2.6290(8)	C(6)–C(7)	1.533(5)
Fe(2)–C(6)	1.934(3)	C(7)–C(8)	1.507(5)
Bond angles			
C(6)–Fe(1)–S(1)	88.96(10)	S(2)–Fe(1)–Fe(2)	84.49(3)
C(6)–Fe(1)–S(2)	48.78(10)	C(6)–Fe(1)–Fe(3)	89.53(10)
S(1)–Fe(1)–S(2)	90.82(4)	S(1)–Fe(1)–Fe(3)	54.25(3)
C(6)–Fe(1)–Fe(2)	47.05(10)	S(2)–Fe(1)–Fe(3)	53.12(3)
S(1)–Fe(1)–Fe(2)	53.84(3)	C(6)–S(2)–Fe(3)	112.33(12)
C(7)–C(6)–S(2)	108.2(2)	C(7)–C(6)–Fe(1)	127.4(2)

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

Bond lengths			
Fe(1)–C(6)	2.020(3)	Fe(3)–S(1)	2.1935(10)
Fe(1)–S(2)	2.1844(9)	Fe(3)–S(2)	2.2241(9)
Fe(1)–S(1)	2.2271(10)	S(1)–C(6)	1.752(3)
Fe(1)–Fe(2)	2.5910(6)	C(6)–C(7)	1.544(4)
Fe(1)–Fe(3)	2.6037(7)	C(7)–C(8)	1.494(5)
Fe(2)–C(6)	1.935(3)	Fe(2)–S(2)	2.2044(9)
Bond angles			
C(6)–Fe(1)–Fe(2)	47.66(9)	C(6)–S(1)–Fe(3)	112.66(11)
C(6)–Fe(1)–S(2)	88.41(9)	C(6)–S(1)–Fe(1)	59.60(10)
C(6)–Fe(1)–S(1)	48.43(9)	Fe(3)–S(1)–Fe(1)	72.17(3)
S(2)–Fe(1)–S(1)	90.18(4)	Fe(1)–S(2)–Fe(2)	72.36(3)
S(1)–Fe(1)–Fe(2)	85.41(3)	Fe(1)–S(2)–Fe(3)	72.39(3)
C(6)–Fe(1)–Fe(3)	89.90(9)	Fe(2)–C(6)–Fe(1)	81.83(12)
Fe(2)–Fe(1)–Fe(3)	93.21(2)		

Table 5 for **5** and Table 6 for **9**. X-ray crystallographic data were collected from single crystal samples of **1** (0.4 × 0.2 × 0.2 mm^3), **5** (0.35 × 0.15 × 0.1 mm^3) and **9** (0.2 × 0.2 × 0.2 mm^3) mounted on a Nonius MACH3 diffractometer. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares against F^2 using SHELXL-97 software [26]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Table 6
Selected bond lengths (Å) and bond angles (°) for **9**

Bond lengths			
Mo–C(11)	2.087(4)	Fe(1)–S(2)	2.2289(11)
Mo–S(2)	2.3093(10)	Fe(1)–S(1)	2.2404(11)
Mo–S(1)	2.4293(10)	S(1)–C(11)	1.720(4)
Mo–Fe(1)	2.6308(6)	C(11)–C(12)	1.510(5)
Mo–Fe(2)	2.8211(6)	Fe(2)–Fe(1)	2.5931(8)
Fe(2)–S(2)	2.2022(11)	Fe(1)–C(11)	2.061(4)
Bond angles			
C(11)–Mo–S(2)	103.29(10)	S(1)–Mo(1)–Fe(2)	108.67(3)
C(11)–Mo–S(1)	43.96(10)	Fe(1)–Mo(1)–Fe(2)	56.671(18)
Fe(1)–C(11)–Mo(1)	78.72(13)	Fe(2)–Fe(1)–Mo(1)	65.369(19)
C(11)–Mo(1)–Fe(1)	50.20(10)	C(11)–Fe(1)–Fe(2)	92.07(10)
S(2)–Mo(1)–Fe(1)	53.16(3)	Fe(1)–Fe(2)–Mo(1)	57.960(17)
S(1)–Mo(1)–Fe(1)	52.37(3)	S(2)–Fe(1)–Fe(2)	53.71(3)
C(11)–Mo(1)–Fe(2)	85.34(10)	C(11)–Fe(1)–Mo(1)	51.08(10)

Data Centre, CCDC Nos. 196216–196218 for compounds **1**, **5** and **9**, 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 http://www.ccdc.cam.ac.uk).

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