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# Reactivity studies of monoacetylide species towards chalcogen-bridged mixed-metal clusters: Synthesis and characterisation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{RuM}_2(\text{CO})_6(\mu_3\text{-E})_2\{\mu_4\text{-CC(Ph)C(Ph)C}\}]$ ( $\text{M} = \text{Mo}, \text{W}; \text{E} = \text{S}, \text{Se}$ ) and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{Ru}_2\text{M}_2(\text{CO})_9(\mu_3\text{-E})_2\{\mu\text{-CCPh}\}_2]$ ( $\text{M} = \text{W}, \text{E} = \text{S}, \text{Se}$ )

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## Abstract

Thermolysis of a toluene solution containing  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$  ( $\text{E} = \text{S}$  or  $\text{Se}$ ) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) results in coupling of monoacetylide ligands and formation of new mixed-metal clusters  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{RuM}_2(\text{CO})_6(\mu_3\text{-E})_2\{\mu_4\text{-CC(Ph)C(Ph)C}\}]$  ( $\text{M} = \text{Mo}, \text{E} = \text{S}$  **1** or  $\text{Se}$  **2**;  $\text{M} = \text{W}, \text{E} = \text{S}$  **3** or  $\text{Se}$  **4**) and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{Ru}_2\text{M}_2(\text{CO})_9(\mu_3\text{-E})_2\{\mu\text{-CCPh}\}_2]$  ( $\text{M} = \text{W}, \text{E} = \text{S}$  **5** or  $\text{Se}$  **6**). Compounds **1–6** have been characterised by IR and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. Structures of **1** and **5** have been established crystallographically. Compound **1** features a tail-to-tail type of coupling of two acetylide groups on a  $\text{Fe}_2\text{RuMoS}_2$  core and compound **5** is a hexanuclear  $\text{Fe-Ru-W}$  mixed-metal cluster with two uncoupled acetylide groups.

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**Keywords:** Cluster; Mixed-metal; Monoacetylide; Chalcogen; Crystal structures

## 1. Introduction

Chemistry of metal acetylide complexes continues to attract attention, particularly with regard to preparation of mixed-metal cluster compounds bearing multi-site bound polycarbon units [1–6]. In our previous studies, we have examined the reactions of  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) with  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]$  ( $\text{E} = \text{S}$  or  $\text{Se}$ ). The molybdenum acetylide complex reacts to form four types of clusters: ones which feature head-to-tail coupling of two acetylides, secondly, those which feature tail-to-tail coupling of two acetylides, thirdly, those which contain a head-to-head coupled acetylide unit, and lastly, the ones

which contain two acetylide groups which are directly bridged by a  $\text{Fe}(\text{CO})_2$  or a CO group. Further, the tungsten acetylide complex reacts to form clusters in which the acetylide units remain uncoupled [7–9]. Although the mechanistic details of the different products formed from the reaction of the mononuclear acetylide complexes with  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]$  are not established, their formation can be envisaged to arise from a common intermediate, in which the triply bridging chalcogen bonds initially to a  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{C}\equiv\text{CPh})]$  unit. Subsequent formation of isomeric  $\text{M}_2\text{Fe}_3$  clusters and migration of the chalcogens to one or both  $\text{Mo}_2\text{Fe}$  faces brings the alkynyl moieties in sites which can facilitate different modes of coupling or no coupling.

We have now looked at the reactivity of the molybdenum and tungsten acetylide complexes with the mixed-metal clusters,  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$  ( $\text{E} = \text{S}$  or

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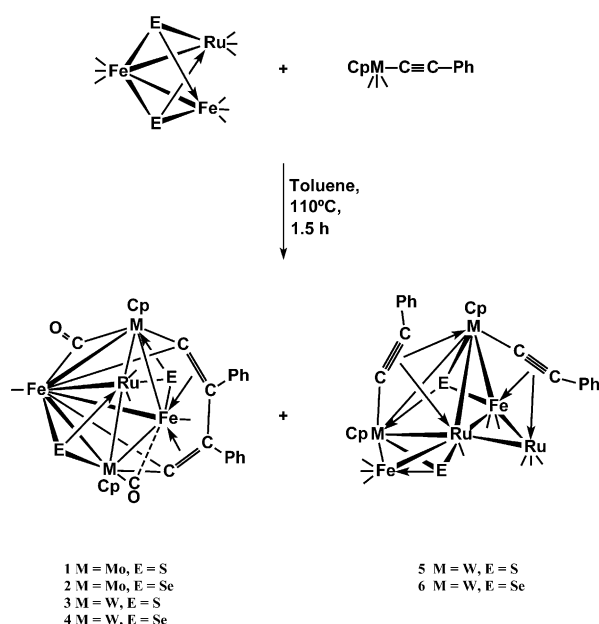
E-mail address: mathur@chem.iitb.ac.in (P. Mathur).

Se). Motivation for this study was to see: (i) whether we obtain products dissimilar to those obtained on using  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]$ ; (ii) whether the heterometal atom in the starting compound preferentially bonds to the acetylide moieties; and (iii) the nature of chalcogen migrations over the different types of hetero-atom faces of the new clusters formed.

## 2. Results and discussion

### 2.1. Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})]$ ( $M = \text{Mo}$ or $\text{W}$ ) and $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$ ( $E = \text{S}$ or $\text{Se}$ )

When a toluene solution containing  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})]$  ( $M = \text{Mo}$  or  $\text{W}$ ) and  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$  ( $E = \text{S}$  or  $\text{Se}$ ) was subjected to reflux, under argon atmosphere, the new mixed-metal clusters,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{RuM}_2(\text{CO})_6(\mu_3\text{-E})_2\{\mu_4\text{-CC(Ph)C(Ph)C}\}]$  ( $M = \text{Mo}$ ,  $E = \text{S}$  **1** or  $\text{Se}$  **2**;  $M = \text{W}$ ,  $E = \text{S}$  **3** or  $\text{Se}$  **4**) and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{Ru}_2\text{M}_2(\text{CO})_9(\mu_3\text{-E})_2\{\mu\text{-CCPh}\}]$  ( $M = \text{W}$ ,  $E = \text{S}$  **5** or  $\text{Se}$  **6**) were isolated from the reaction mixture after chromatographic work-up (Scheme 1). Trace amounts of the previously reported acetylide-coupled dimers,  $[\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}_2(\mu\text{-1, 2-PhC}\equiv\text{CC}\equiv\text{CPh})]$  (**7**) [10] and  $[\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}_2(\mu\text{-1, 2-PhC}\equiv\text{C}(\text{CO})\text{C}\equiv\text{CPh})]$  (**8**) [8] accompanied the formation of **1** and **2**. Even after prolonged reflux of toluene solution containing  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-Te})_2]$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{C}\equiv\text{CPh})]$ , no new Te-bridged clusters were obtained; only **7** and **8** were isolated from this reaction. The new clusters **1–6** are stable in air in the solid state but decompose in solution over a period of hours. The infrared spectra of **1–4** show identical  $\nu(\text{CO})$



Scheme 1.

pattern with bands corresponding to the presence of both terminal and bridging carbonyl groups. Their  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra indicate the presence of phenyl groups and two types of  $\eta^5\text{-C}_5\text{H}_5$  in each compound.

The molecular structure of **1**, shown in Fig. 1, consists of a  $\text{Fe}_2\text{RuMo}_2$  metal core which is enveloped by terminal and bridging carbonyl ligands, and a  $\mu_4\text{-}\{\text{CC(Ph)C(Ph)C}\}$  unit. The five metal atoms are arranged in the form of an open trigonal bipyramidal polyhedron wherein the two Fe and one Ru atoms occupy the equatorial plane while the two Mo centres are at axial positions. The metal–metal bond lengths in **1** (Ru–Fe 2.684(4) and Fe–Fe 2.558(7) Å) are comparable to the corresponding bond lengths reported for  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-S})_2]$  (Ru–Fe 2.717(3) and Fe–Fe 2.660(3) Å) [11]. One of the iron atoms, Fe(1), forms short bonds to the molybdenum atoms (2.625 Å av.). The longer Fe(2)–Mo bond lengths (2.811 Å av.) are comparable with the Fe–Mo bond lengths reported for some related chalcogen-bridged Fe–Mo clusters as:  $\text{Cp}_2\text{Mo}_2\text{Fe}_2(\mu_3\text{-S})_2(\text{CO})_8$ , 2.816 Å av. [12]; *trans*- $\text{Cp}_2\text{Mo}_2\text{Fe}_2(\mu_3\text{-S})(\mu_3\text{-Se})(\text{CO})_8$ , 2.813 Å av. [13];  $\text{Fe}_2\text{-Mo}(\mu_3\text{-Se})_2(\text{CO})_{10}$ , 2.809 Å av. [14]. Bonds between Ru and the two Mo atoms are unequal (2.916(4) and 2.952(4) Å), but comparable to the Ru–Mo bond lengths observed in other related compounds:  $\text{Cp}_2\text{Mo}_2\text{Ru}(\mu_3\text{-Se})(\text{CO})_7$ , 2.9073 Å av. [15];  $\text{Cp}_2\text{Mo}_2\text{Ru}(\mu_3\text{-S})(\text{CO})_7$ , 2.9059 Å av. [16]. Each molybdenum atom is bonded to a  $\text{C}_5\text{H}_5$  ligand in  $\eta^5$  fashion. Overall, there are six carbonyl groups in three different bonding modes. Ruthenium bears two terminal carbonyl atoms, while both Fe(1) and Fe(2) atoms bear only one terminal CO group each. One CO group symmetrically bridges the Fe(1)–Mo(2) bond, Mo(2)–C(6)–O(6) 143.0(2)°, and another, bonded to Mo(1) shows a semi-bridging character towards Fe(2), Mo(1)–C(3)–O(3) 158.5(3)°. Although both sulfur atoms in the molecule act as triply bridging four electron donors, they show some differences in the co-ordination geometry around them. For instance, the M–S–M bond

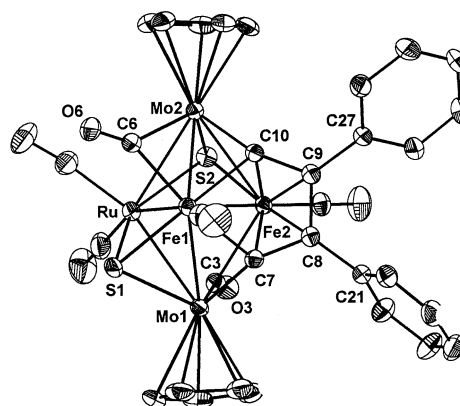


Fig. 1. ORTEP diagram of **1** with 30% probability ellipsoids.

angles around S(2) are wider (73.93(11), 77.80(16), 84.21(19)°) than those observed around the S(1) atom (71.27(15), 71.59(13), 76.90(15)°). The coupled acetylide unit {CC(Ph)C(Ph)C} is attached to both the Mo atoms and the two iron atoms, but not to the unique heterometal atom, ruthenium. Within the C<sub>4</sub> unit, the internal bond length (C(8)–C(9) 1.450(5) Å) is longer than the outer C–C bond lengths (C(7)–C(8) 1.415(5) and C(9)–C(10) 1.414(4) Å). In the only other example where tail-to-tail coupling of acetylides has occurred, the C–C bond lengths in the C<sub>4</sub> unit were much closer (1.428(5), 1.439(5), 1.421(6) Å) [8,9].

The infrared spectra of **5** and **6** show identical  $\nu(\text{CO})$  pattern, for terminal carbonyl groups. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra for **5** and **6** indicate the presence of two types of  $\eta^5\text{-C}_5\text{H}_5$  in each compound and a multiplet confirms the presence of phenyl group.

The molecular structure of **5**, shown in Fig. 2, can be described as a FeRuW<sub>2</sub>S distorted square pyramid core, in which the WRu edge is bridged by a Fe(CO)<sub>3</sub>S unit and the RuFe edge is bridged by a Ru(CO)<sub>3</sub> unit. One acetylide caps the W<sub>2</sub>Ru face in a  $\eta^1;\eta^2;\eta^2$  fashion, and another caps the FeRuW face in a similar bonding mode. The W–W bond distance of 3.017(3) Å in **5** is longer than the W–W bond distance of 2.825(5) Å observed in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Fe}_2(\text{CO})_4(\mu_3\text{-E})_2\{\mu\text{-CC(Ph)COC(Ph)C}\}]$  [8]. The average W–Fe bond distance of 2.732 Å in **5** is similar to the average W–Fe bond distance of 2.748 Å observed in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2\text{Fe}_3(\text{CO})_7(\mu_3\text{-E})_2(\mu_3\text{-}\eta^2\text{-CCPh})(\mu_3\text{-}\eta^1\text{-CCH}_2\text{Ph})]$  [7] but shorter than the 2.815 Å in  $[\text{Fe}_2\text{W}(\text{CO})_{10}(\mu_3\text{-Se})_2]$  [14]. In compound **5**, the average C–C bond distance of 1.356 Å is shorter than the average bond distance of 1.426 Å in **1**.

## 2.2. Mechanistic consideration

Although the exact mechanism of formation of these products is not established, we suggest a probable mechanistic pathway, starting from a common intermediate, which leads to different products. The initial

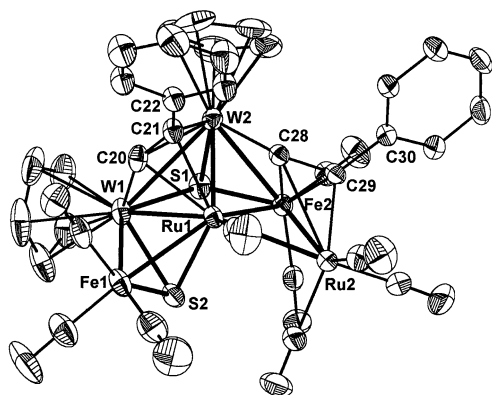
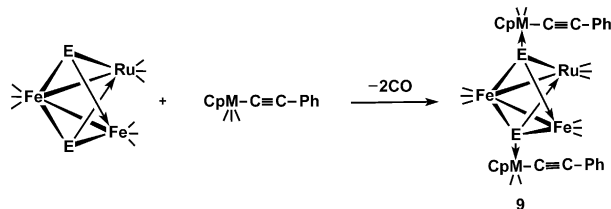


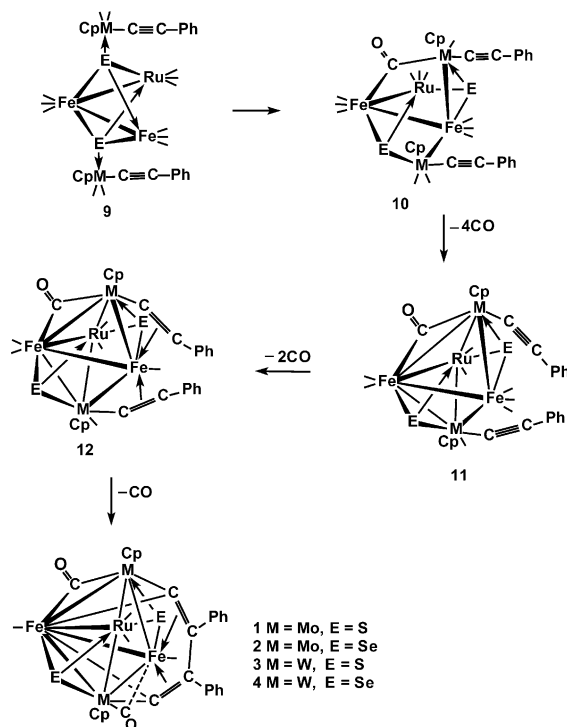
Fig. 2. ORTEP diagram of **5** with 30% probability ellipsoids.



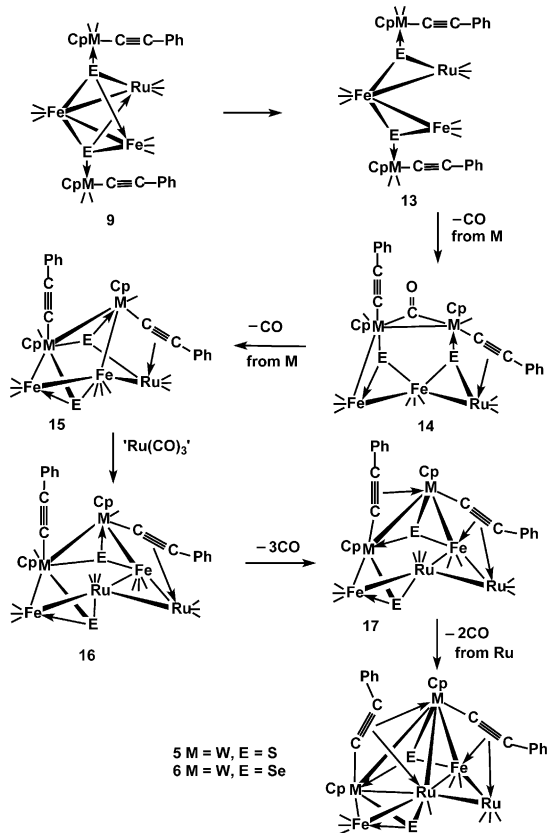
Pathway 1.

formation of intermediate cluster **9**, as shown in Pathway 1, is one in which the capping S (or Se) groups of  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$  each coordinates to  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{C}\equiv\text{CPh})]$  unit, analogous to previously known reactions of  $[\text{Os}_3(\text{CO})_9\text{S}_2]$  and  $\text{W}(\text{CO})_6$  which yields  $[\text{Os}_3(\text{CO})_9(\mu_3\text{-S})\{\mu_3\text{-S}\}\text{W}(\text{CO})_5\}]$  [17]. Here the process can diversify from **9** in one of two ways, as depicted in Pathways 2 and 3: (a) cleavage of each chalcogen bond to a  $\text{Fe}(\text{CO})_3$  unit to give **10**; or (b) cleavage of each chalcogen bond to a terminal metal unit to produce **13**.

In the first case, as depicted in Pathway 2, elimination of four carbonyls and formation of four Fe–M bonds and two Ru–M bonds produces **11**. As a consequence of loss of two more carbonyls from the terminal iron atom in **11**, **12** are formed, in which the terminal iron unit is bonded to each of acetylide unit in  $\eta^2$  fashion. Finally, the loss of CO ligand from the central iron accompanied by coupling of two acetylide units in a tail-to-tail fashion yields the observed products **1–4**.



Pathway 2.



Pathway 3.

In the second case, as depicted in Pathway 3, loss of two carbonyls from **13** gives rise to **14** and **15**, successively, where the two acetylide metal atoms join together and also form bonds with iron atoms. At this stage, insertion of a 'Ru(CO)<sub>3</sub>' unit between two iron atoms takes place to form **16**, which contains the Fe<sub>2</sub>Ru<sub>2</sub>E spiro unit. Formation of **17** is a consequence of loss of three carbonyls from **16**. Finally, one Ru atom loses two carbonyls and forms bonds with the two CpM units to complete the FeRuM<sub>2</sub>E distorted square pyramid core. One of the acetylide groups forms a cap over a RuM<sub>2</sub> face to give **5** (or **6**).

### 3. Conclusion

Reactivity of monoacetylide complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})]$  (M = Mo or W) with chalcogen bridged mixed-metal clusters,  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$  (E = S or Se) has been studied. Presence of a heterometal atom in the starting cluster core does not prevent cluster formation, nor tail-to-tail acetylide coupling of the type seen earlier in the reaction of the homometallic clusters,  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]$  with mononuclear acetylide complexes [8]. The molybdenum and tungsten acetylides show different reactivity towards  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$ .

Formation of **5** and **6** is seen only in the reaction of the tungsten acetylide compound.

## 4. Experimental

### 4.1. General procedures

Reactions and manipulations were performed using standard Schlenk techniques under an atmosphere of pre-purified Ar. Solvents were purified, dried and distilled under an Ar or nitrogen atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as CH<sub>2</sub>Cl<sub>2</sub> solutions in 0.1 mm path length cells, NMR spectra on a Varian VXRO-300S spectrometer in CDCl<sub>3</sub>. Elemental analyses were performed on a Carlo-Erba automatic analyser. The compounds  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$  (E = S, Se or Te) [18] and  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})]$  (M = Mo or W) [19] were prepared by established procedures.

4.2. Preparation of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{RuM}_2(\text{CO})_6(\mu_3\text{-E})_2\{\mu_4\text{-CC}(\text{Ph})\text{C}(\text{Ph})\text{C}\}]$  (M = Mo, E = S **1** or Se **2**; M = W, E = S **3** or Se **4**) and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{Ru}_2\text{M}_2(\text{CO})_9(\mu_3\text{-E})_2\{\mu\text{-CCPh}\}_2]$  (M = W, E = S **5** or Se **6**)

In a typical preparation, a C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> solution (50 ml) containing  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}\equiv\text{CPh})]$  (M = Mo, 80 mg, 0.23 mmol; M = W, 100 mg, 0.23 mmol), and one equivalent of  $[\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3\text{-E})_2]$  (E = S or Se) was subjected to reflux for 1.5 h. The solution was cooled to room temperature, filtered through Celite to remove insoluble material and the solvent was removed in vacuo. The residue was subjected to chromatographic work-up on silica-gel TLC plates. Elution with CH<sub>2</sub>Cl<sub>2</sub>–C<sub>6</sub>H<sub>14</sub> (40:60 v/v) yielded the following two bands, in order of elution: greenish brown  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{RuM}_2(\text{CO})_6(\mu_3\text{-E})_2\{\mu_4\text{-CC}(\text{Ph})\text{C}(\text{Ph})\text{C}\}]$  (M = Mo, E = S **1** or Se **2**; M = W, E = S **3** or Se **4**); and brown  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{Ru}_2\text{M}_2(\text{CO})_9(\mu_3\text{-E})_2\{\mu\text{-CCPh}\}_2]$  (M = W, E = S **5** or Se **6**).

Compound **1**: Yield: 68 mg (35%). IR ( $\nu(\text{CO})$ , cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>): 2005(s), 1963(vs), 1863(w), 1763(m). <sup>1</sup>H-NMR ( $\delta$ , CDCl<sub>3</sub>): 5.56 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.59 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 7.10–7.40 (m, 10H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C-NMR ( $\delta$ , CDCl<sub>3</sub>): 95.4 (s, C<sub>5</sub>H<sub>5</sub>), 97.0 (s, C<sub>5</sub>H<sub>5</sub>), 105.0 (s, C<sub>4</sub>Ph<sub>2</sub>), 107.3 (s, C<sub>4</sub>Ph<sub>2</sub>), 128.3–131.2 (C<sub>6</sub>H<sub>5</sub>), 207.6, 209.6, 211.5, 214.2 (CO). M.p. (°C): 198–200 (dec.). Anal. Calc. for C<sub>32</sub>H<sub>20</sub>Fe<sub>2</sub>Mo<sub>2</sub>O<sub>6</sub>RuS<sub>2</sub>: C, 39.65; H, 2.07. Found: C, 39.09; H, 2.02%.

Compound **2**: Yield: 49 mg (23%). IR ( $\nu(\text{CO})$ , cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>): 2003(s), 1957(vs), 1859(w), 1753(m). <sup>1</sup>H-NMR ( $\delta$ , CDCl<sub>3</sub>): 5.50 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.52 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 7.10–7.40 (m, 10H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C-NMR ( $\delta$ , CDCl<sub>3</sub>): 95.0 (s, C<sub>5</sub>H<sub>5</sub>), 96.9 (s, C<sub>5</sub>H<sub>5</sub>), 108.2 (s, C<sub>4</sub>Ph<sub>2</sub>), 110.1 (s, C<sub>4</sub>Ph<sub>2</sub>), 128.1–131.5 (C<sub>6</sub>H<sub>5</sub>), 208.2, 210.0, 216.4, 217.0

(CO). M.p. (°C): 200–202 (dec.). Anal. Calc. for  $C_{32}H_{20}Fe_2Mo_2O_6RuSe_2$ : C, 39.15; H, 1.89. Found: C, 36.22; H, 1.87%.

Compound 3: Yield: 62 mg (36%). IR ( $\nu(CO)$ ,  $cm^{-1}$ ,  $CH_2Cl_2$ ): 2054(m), 2003(s), 1956(vs), 1733(m), 1763(m).  $^1H$ -NMR ( $\delta$ ,  $CDCl_3$ ): 5.72 (s, 5H,  $C_5H_5$ ), 5.79 (s, 5H,  $C_5H_5$ ), 7.28–7.31 (m, 10H,  $C_6H_5$ ).  $^{13}C$ -NMR ( $\delta$ ,  $CDCl_3$ ): 93.6 (s,  $C_5H_5$ ), 96.0 (s,  $C_5H_5$ ), 108.2 (s,  $C_4Ph_2$ ), 109.6 (s,  $C_4Ph_2$ ), 128.2–130.2 ( $C_6H_5$ ), 208.1, 215.6, 217.6, 217.9 (CO). M.p. (°C): 196–198 (dec.). Anal. Calc. for  $C_{32}H_{20}Fe_2O_6RuS_2W_2$ : C, 34.79; H, 1.82. Found: C, 34.29; H, 1.79%.

Compound 4: Yield: 39 mg (29%). IR ( $\nu(CO)$ ,  $cm^{-1}$ ,  $CH_2Cl_2$ ): 2056(m), 2001(s), 1950(vs), 1735(m), 1763(m).  $^1H$ -NMR ( $\delta$ ,  $CDCl_3$ ): 5.63 (s, 5H,  $C_5H_5$ ), 5.71 (s, 5H,  $C_5H_5$ ), 7.29–7.32 (m, 10H,  $C_6H_5$ ).  $^{13}C$ -NMR ( $\delta$ ,  $CDCl_3$ ): 92.3 (s,  $C_5H_5$ ), 94.6 (s,  $C_5H_5$ ), 104.5 (s,  $C_4Ph_2$ ), 106.1 (s,  $C_4Ph_2$ ), 128.2–130.3 ( $C_6H_5$ ), 210.1, 212.4, 213.8, 218.3 (CO). M.p. (°C): 192–194 (dec.). Anal. Calc. for  $C_{32}H_{20}Fe_2O_6RuSe_2W_2$ : C, 32.05; H, 1.68. Found: C, 31.82; H, 1.64%.

Compound 5: Yield: 67 mg (26%). IR ( $\nu(CO)$ ,  $cm^{-1}$ ,  $CH_2Cl_2$ ): 2010(vs), 1986(s), 1966(m), 1943(m, br).  $^1H$ -NMR ( $\delta$ ,  $CDCl_3$ ): 5.39 (s, 5H,  $C_5H_5$ ), 5.84 (s, 5H,  $C_5H_5$ ), 7.27–7.31 (m, 10H,  $C_6H_5$ ).  $^{13}C$ -NMR ( $\delta$ ,  $CDCl_3$ ): 91.5 (s,  $C_5H_5$ ), 93.7 (s,  $C_5H_5$ ), 29.7 (CCPh), 53.4 (CCPh), 127–131.4 ( $C_6H_5$ ), 213.9, 218.7 (CO). M.p. (°C): 205–207 (dec.). Anal. Calc. for  $C_{35}H_{20}Fe_2O_9Ru_2S_2W_2$ : C, 31.6; H, 1.52. Found: C, 31.39; H, 1.49%.

Compound 6: Yield: 43 mg (22%). IR ( $\nu(CO)$ ,  $cm^{-1}$ ,  $CH_2Cl_2$ ): 2008(vs), 1985(s), 1962(m), 1944(m, br).  $^1H$ -NMR ( $\delta$ ,  $CDCl_3$ ): 5.29 (s, 5H,  $C_5H_5$ ), 5.75 (s, 5H,  $C_5H_5$ ), 7.27–7.31 (m, 10H,  $C_6H_5$ ).  $^{13}C$ -NMR ( $\delta$ ,  $CDCl_3$ ): 91.0 (s,  $C_5H_5$ ), 93.3 (s,  $C_5H_5$ ), 29.2 (CCPh), 52.6 (CCPh), 126–130.1 ( $C_6H_5$ ), 218.1, 218.6 (CO). M.p. (°C): 201–203 (dec.). Anal. Calc. for  $C_{35}H_{20}Fe_2O_9Ru_2Se_2W_2$ : C, 29.5; H, 1.42. Found: C, 30.06; H, 1.45%.

### 4.3. Crystal structure determination of 1

Suitable X-ray quality crystals of **1** were grown by slow evaporation of  $CH_2Cl_2$ – $C_6H_{14}$  solvent mixture and an X-ray diffraction study was undertaken. Relevant crystallographic data and details of measurements are given in Table 1. Selected bond lengths (Å) and angles (°) are listed in Table 2. Intensity data were collected using a  $0.45 \times 0.34 \times 0.22$  mm crystal on a Nonius MACH3 diffractometer (graphite monochromatized Mo– $K_\alpha$  radiation) in the  $2\theta$  range 2–50°. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares against  $F^2$  using SHELXL-97 software [20]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Crystals belong to monoclinic, space group  $P2_1/c$ ,  $a = 8.29(3)$ ,  $b = 18.73(4)$ ,  $c =$

Table 1  
Crystal data and structure refinement parameters for **1** and **5**

	$C_{32}H_{20}Fe_2Mo_2O_6RuS_2$	$C_{35}H_{20}Fe_2O_9Ru_2S_2W_2$
Empirical formula	$C_{32}H_{20}Fe_2Mo_2O_6RuS_2$	$C_{35}H_{20}Fe_2O_9Ru_2S_2W_2$
Molecular formula	969.25	1330.17
Description	Deep brown block	Deep brown needle
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.70930	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
$a$ (Å)	8.29(3)	11.5112(5)
$b$ (Å)	18.73(4)	17.5767(8)
$c$ (Å)	20.52(4)	19.3612(9)
$\beta$ (°)	99.45(01)	100.5750(10)
$V$ (Å <sup>3</sup> )	3143(15)	3850.8(3)
$Z$	4	4
$D_{calc}$ (mg m <sup>-3</sup> )	2.049	2.294
Absorption coefficient (mm <sup>-1</sup> )	2.324	7.607
$F(000)$	1888	2488
Crystal size (mm)	$0.45 \times 0.34 \times 0.22$	$0.2 \times 0.007 \times 0.005$
$\theta$ Range of data collection (°)	1.48–24.93	1.58–28.30
Index ranges	$-9 \leq h \leq 9, 0 \leq k \leq 22, 0 \leq l \leq 24$	$-15 \leq h \leq 15, -23 \leq k \leq 23, -25 \leq l \leq 25$
Reflections collected/unique	5520/5520 [ $R_{int} = 0.0000$ ]	44 180/9189 [ $R_{int} = 0.0530$ ]
Completeness to $2\theta = 24.93$	96.8%	
$2\theta = 28.30$		96.0%
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	5520/0/406	9189/0/470
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0236,$ $wR_2 = 0.0617$	$R_1 = 0.0317,$ $wR_2 = 0.0578$
$R$ indices (all data)	$R_1 = 0.0285,$ $wR_2 = 0.0629$	$R_1 = 0.0611,$ $wR_2 = 0.0622$
Goodness-of-fit on $F^2$	1.063	0.826
Largest difference peak and hole (e Å <sup>-3</sup> )	0.403 and $-0.914$	1.472 and $-0.546$

Table 2  
Selected bond lengths (Å) and angles (°) of compound **1**

Bond lengths			
C(10)–C(9)	1.414(2)	C(9)–C(27)	1.487(4)
C(9)–C(8)	1.450(3)	C(8)–C(21)	1.488(4)
C(8)–C(7)	1.415(2)	Fe(1)–Fe(2)	2.588(7)
Mo(1)–C(7)	1.975(3)	Fe(1)–Ru	2.684(4)
Mo(2)–C(10)	1.927(3)		
Bond angles			
Mo(2)–C(10)–C(9)	151.11(2)	C(8)–C(7)–Mo(1)	149.03(1)
C(10)–C(9)–C(8)	109.95(1)	C(7)–C(8)–C(21)	122.80(3)
C(9)–C(8)–C(7)	111.76(1)	C(10)–C(9)–C(27)	123.30(3)
Mo(1)–Ru–Mo(2)	101.79(1)	Mo(1)–Fe(2)–Mo(2)	108.21(1)

Table 3  
Selected bond lengths (Å) and angles (°) of compound **5**

Bond lengths			
W(1)–C(20)	1.950(6)	C(28)–C(29)	1.382(7)
C(20)–C(21)	1.330(7)	C(29)–Ru(2)	2.067(5)
C(21)–W(2)	2.187(5)	C(21)–C(22)	1.459(7)
W(2)–C(28)	1.970(5)	C(29)–C(30)	1.485(6)
Bond angles			
W(1)–C(20)–C(21)	153.70(4)	C(28)–C(29)–Ru(2)	102.80(3)
C(20)–C(21)–W(2)	75.10(3)	C(20)–C(21)–C(22)	142.40(5)
C(21)–W(2)–C(28)	82.02(1)	C(28)–C(29)–C(30)	124.80(5)
W(2)–C(28)–C(29)	151.40(4)	W(1)–Ru(1)–Fe(2)	87.60(2)
W(1)–W(2)–Fe(2)	82.522(2)	W(1)–S(1)–Fe(2)	108.31(6)

20.52(4) Å,  $\beta = 99.45(1)^\circ$ ,  $V = 3143(15) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 2.049 \text{ mg m}^{-3}$ ,  $\mu = 2.324 \text{ mm}^{-1}$ ,  $T = 293(2) \text{ K}$ . Final  $R$ : [ $I > 2\sigma(I)$ ],  $R_1 = 0.0236$ ,  $wR_2 = 0.0617$ ; all data,  $R_1 = 0.0285$ ,  $wR_2 = 0.0629$ .

#### 4.4. Crystal structure determination of **5**

Suitable X-ray quality crystals of **5** were grown by slow evaporation of  $\text{CH}_2\text{Cl}_2$ – $\text{C}_6\text{H}_{14}$  solvent mixture. Deep brown needle of approximate size  $0.2 \times 0.07 \times 0.005 \text{ mm}$ , was used for data collection on Bruker SMART APEX CCD diffractometer using Mo– $\text{K}\alpha$  radiation with fine focus tube with 50 kV and 40 mA. Crystal to detector distance 6.05 cm,  $512 \times 512$  pixels/frame, hemisphere data acquisition. Total scans = 3, total frames = 1271, oscillation/frame  $-0.3^\circ$ , exposure/frame = 30.0 s/frame, maximum detector swing angle =  $-30.0^\circ$ , beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration,  $2\theta$  range =  $3.16$ – $56.6^\circ$ , completeness to  $2\theta$  of  $56.6^\circ$  is 96.0%. SADABS correction applied.  $\text{C}_{35}\text{H}_{20}\text{Fe}_2\text{O}_9\text{Ru}_2\text{S}_2\text{W}_2$ ,  $M = 1330.2$ . Crystals belong to monoclinic, space group  $P2_1/n$ ,  $a = 11.5112(5)$ ,  $b = 17.5767(8)$ ,  $c = 19.3612(9) \text{ \AA}$ ,  $\beta = 100.575(1)^\circ$ ,  $V = 3850.8(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 2.294 \text{ mg m}^{-3}$ ,  $\mu(\text{Mo}–\text{K}\alpha) = 7.607 \text{ mm}^{-1}$ ,  $T = 293(2) \text{ K}$ , 44 180 reflections measured, 9189 unique [ $I > 2\sigma(I)$ ],  $R$  value 0.0318,  $wR_2 = 0.0576$  (all data  $R = 0.0612$ ,  $wR_2 = 0.0620$ ). All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (SHELXTL) [20] was used for structure solution and full-matrix least-squares refinement on  $F^2$ . Hydrogen atoms were included in the refinement as per the riding model. Data collection and refinement parameters are listed in Table 1. Selected bond lengths (Å) and angles (°) are listed in Table 3.

#### 5. Supplementary material

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

Data Centre, CCDC nos. 154266 and 182160 for compounds **1** and **5**. 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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