Pergamon

PII: S0277-5387(96)00538-4

Polyhedron Vol. 16, No. 13, pp. 2249–2255, 1997
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0277-5387/97 $17.00+0.00

Reaction of metal–metal triply-bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ with $(\mu\text{-R'S})_2\text{Fe}_2(\text{CO})_6$. Synthesis and structural characterization of $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mo}_2\text{Fe}(\mu_3\text{-S})(\text{CO})_7$, $(\eta^5\text{-RC}_5\text{H}_4)_4\text{Mo}_4(\mu_3\text{-S})_2(\mu\text{-CO})_4$ and $[\eta^5\text{-RC}_5\text{H}_4\text{Mo}(\text{CO})(\mu\text{-SPh})]_2$

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(Received 27 September 1996; accepted 30 October 1996)

Abstract—The dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2(\text{R} = \text{MeO}_2\text{C}, \text{EtO}_2\text{C})$ reacted with $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ in boiling xylene to give trinuclear clusters $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mo}_2\text{Fe}(\mu_3\text{-S})(\text{CO})_7$(**1a**, R = MeO_2C; **1b**, R = EtO_2C) and tetranuclear clusters $(\eta^5\text{-RC}_5\text{H}_4)_4\text{Mo}_4(\mu_3\text{-S})_2(\text{CO})_4$ (**2a**, R = MeO_2C; **2b**, R = EtO_2C), whereas they reacted with $(\mu\text{-PhS})_2\text{Fe}_2(\text{CO})_6$ in boiling xylene to give **1a–b**, **2a–b** and dinuclear complexes $[\eta^5\text{-RC}_5\text{H}_4\text{Mo}(\text{CO})(\mu\text{-SPh})]_2$ (**3a**, R = MeO_2C; **3b**, R = EtO_2C). However, reactions of $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$ (R = EtO_2C) with $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ and $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$(R = H) with $(\mu\text{-PhS})_2\text{Fe}_2(\text{CO})_6$ in benzene under UV irradiation gave only the trinuclear clusters **1b** and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}(\mu_3\text{-S})(\text{CO})_7$(**1c**), respectively. All new clusters **1b**, **2a–b** and **3a–b** were fully characterized by elemental analysis and spectroscopic methods, as well as for **2a** and **1c** by X-ray diffraction analysis. © 1997 Elsevier Science Ltd

Keywords: Mo≡Mo triple bond; $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$; reactions; Mo_2FeS clusters; Mo_4S_2 clusters; crystal structure.

The Group 6 metal–metal triply-bonded dimers $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{M}]_2(\eta^5\text{-RC}_5\text{H}_4$ = parent or substituted cyclopentadienyl; M = Cr, Mo, W) have been shown to react with organic, inorganic and organometallic substrates to yield a number of novel Group 6 metal-containing organometallics, particularly organometallic clusters [1–2]. It is however, worth pointing out that although reactions of the above dimers with Fe/S complexes $\mu\text{-S}_2\text{Fe}_2(\text{CO})_6$ are well documented [3–7], the corresponding reactions with Fe/S complexes $(\mu\text{-R'S})_2\text{Fe}_2(\text{CO})_6$ have not been described yet in the literature, except that part of our related results were briefly communicated very recently [8]. In this article we present the full results concerning reactions between $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2$(R = H, MeO_2C, EtO_2C) and $(\mu\text{-R'S})_2\text{Fe}_2(\text{CO})_6$ (R′ = Et, Ph).

RESULTS AND DISCUSSION

Thermolysis of $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2(\text{R} = \text{MeO}_2\text{C}, \text{EtO}_2\text{C})$ *with* $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ *or* $(\mu\text{-PhS})_2\text{Fe}_2(\text{CO})_6$*; synthesis of* **1a–b**, **2a–b** *and* **3a–b**; *crystal structure of* **2a**

The reactions of equimolar $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2(\text{R} = \text{MeO}_2\text{C}, \text{EtO}_2\text{C})$ with $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ in xylene were carried out under reflux for 7 h, after removal of the solvent with subsequent separation by TLC to give trinuclear clusters $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mo}_2\text{Fe}$ $(\mu_3\text{-S})(\text{CO})_7$ (**1a**, R = MeO_2C; **1b**, R = EtO_2C) and tetranuclear clusters $(\eta^5\text{-RC}_5\text{H}_4)_4\text{Mo}_4(\mu_3\text{-S})_2(\text{CO})_4$ (**2a**, R = MeO_2C; **2b**, R = EtO_2C; Scheme 1). However, when reactions of $[\eta^5\text{-RC}_5\text{H}_4(\text{CO})_2\text{Mo}]_2(\text{R} = \text{MeO}_2\text{C}, \text{EtO}_2\text{C})$ with $(\mu\text{-PhS})_2\text{Fe}_2(\text{CO})_6$ were similarly carried out, followed by the same work-up as that in reactions with

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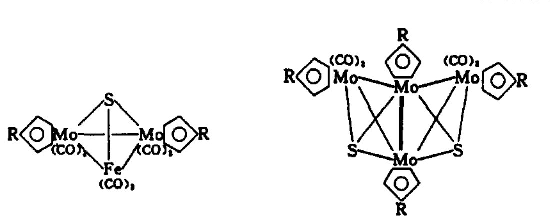


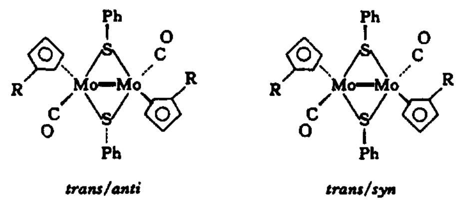
1a, R=MeO$_2$C
1b, R=EtO$_2$C
1c, R=H

2a, R=MeO$_2$C
2b, R=EtO$_2$C

Scheme 1.

(μEtS)$_2$Fe$_2$(CO)$_6$, the isomeric dinuclear complexes **3a–b** (Scheme 2) were produced, along with trinuclear and tetranuclear clusters **1a–b** and **2a–b** (Scheme 1). Apparently, the S—C(Ph) bonds of (μ-PhS)$_2$Fe$_2$(CO)$_6$ are more stable toward such thermal reactions than the S—C(Et) bonds of (μ-EtS)$_2$Fe$_2$(CO)$_6$, since the thiolato-containing complexes **3a–b** were obtained only from the reactions with (μ-PhS)$_2$Fe$_2$(CO)$_6$.

While cluster **1a** was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample [9], new clusters **1b, 2a–b** and **3a–b** were characterized by elemental analysis, IR, ^{1}H NMR and MS spectroscopies. All the characterization data are in good agreement with the corresponding structures shown in Schemes 1 and 2. It is noteworthy that each of the dinuclear complexes **3a** and **3b**, based on the arrangement of η^5-RC$_5$H$_4$/CO ligands and the mutual orientation of the phenyl groups on sulfur atoms, consists of two isomers, i.e. *trans/anti* and *trans/syn* isomers. This could be demonstrated by their ^{1}H NMR spectra. In the ^{1}H NMR spectrum of **3a** there exist three singlets from 3.45 to 3.65 ppm, one singlet at 3.55 ppm being assigned to the methyl groups in the *trans/anti* isomer and the other two singlets at 3.45 and 3.65 ppm with an equal intensity being assigned to the two methyl groups of *trans/syn* isomer. This is because the two methyl groups in the *trans/anti* isomer are in the same chemical environment, whereas those in the *trans/syn* isomer are not. In addition, according to the integrated values for corresponding methyl groups the ratio of *trans/anti* : *trans/syn* for **3a** was calculated as 1 : 4. The IR spectra of **3a–b** all showed three terminal carbonyl absorption bands between 1844 and 1934 cm^{-1} and one ester carbonyl absorption band at 1713 and 1704 cm^{-1}, respectively. Additionally, the MS data of **3a–b** are also in good agreement with their composition shown in Scheme 2.



3a, R=MeO$_2$C
3b, R=EtO$_2$C

Scheme 2.

In order to further confirm the structures of tetranuclear clusters **2a–b**, an X-ray diffraction analysis for **2a** was undertaken. The molecular structure is shown in Fig. 1. Table 1 lists its selected bond lengths and angles. Figure 2 depicts its Mo$_4$S$_2$ cluster skeleton, which clearly shows that the four molybdenum atoms are arranged as a butterfly shape and each wing consisting of Mo$_3$ is capped with a sulfido ligand.

For cluster **2a**, the dihedral angle of Mo(1)Mo(2)Mo(3) and Mo(2)Mo(3)Mo(4) is 132.99°. Four carbonyls are unsymmetrically bridged to the metal–metal single bonds of Mo(1)—Mo(2), Mo(1)—Mo(3), Mo(2)—Mo(4) and Mo(3)—Mo(4), respectively. The four Mo—Mo single bonds have almost the same length and average 2.913 Å, which is very close to the length of Mo—Mo single bonds in related clusters [10–11]. However, the Mo(2)—Mo(3) double bond [2.794(2) Å] is much shorter than those of the above Mo—Mo single bonds and its length is comparable with the Mo—Mo double bonds in some organometallic compounds [12–14]. It should be noted that there are four asymmetric units in an unit cell and each asymmetric unit includes one molecule of **2a** and one molecule of water which might originate from the solvent used for growing single crystals. In one asymmetric unit the oxygen atom O(5) of water is near to O(2) of the carbonyl C(2)O(2) [2.92(2) Å] and near to O(17) of the ester's group [2.83(2) Å] in another asymmetric unit. Thus, there are likely some hydrogen-bonding interactions of O(5)—H···O(2) and O(5)—H···O(17) in the molecular crystals.

Photolysis of [η^5-RC$_5$H$_4$(CO)$_2$Mo]$_2$ (R = H, EtO$_2$C) *with* (μ-EtS)$_2$Fe$_2$(CO)$_6$ *or* (μ-PhS)$_2$Fe$_2$(CO)$_6$; *synthesis of* **1b–c** *and crystal structure of* **1c**

A benzene solution of equimolar [η^5-RC$_5$H$_4$(CO)$_2$Mo]$_2$ (R = H, EtO$_2$C) and (μ-R′S)$_2$Fe$_2$(CO)$_6$ (R′ = Et, Ph) was irradiated for 12 h using a 400W high-pressure mercury lamp, after a similar work-up as that for the corresponding thermal reactions above, to give trinuclear clusters **1b** and (η^5-C$_5$H$_5$)$_2$Mo$_2$Fe(μ_3-S)(CO)$_7$ (**1c**), as shown in Scheme 1, respectively. Obviously, since no dinuclear complex [η^5-C$_5$H$_5$Mo(CO)(μ-SPh)]$_2$ was obtained from [η^5-C$_5$H$_5$(CO)$_2$Mo]$_2$ and (μ-PhS)$_2$Fe$_2$(CO)$_6$, the photolytic conditions should be much more severe than those of thermal reactions carried out above, under which conditions the C—S (Ph) bonds of (μ-PhS)$_2$Fe$_2$(CO)$_6$ had been completely cleaved during the photolysis reaction. Cluster **1c** was previously reported by others and has been identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample [15]. However, in order to unambiguously confirm its structure an X-ray crystallographic study has been undertaken. The crystals of **1c** are isomorphous with its tungsten analog [5]. In

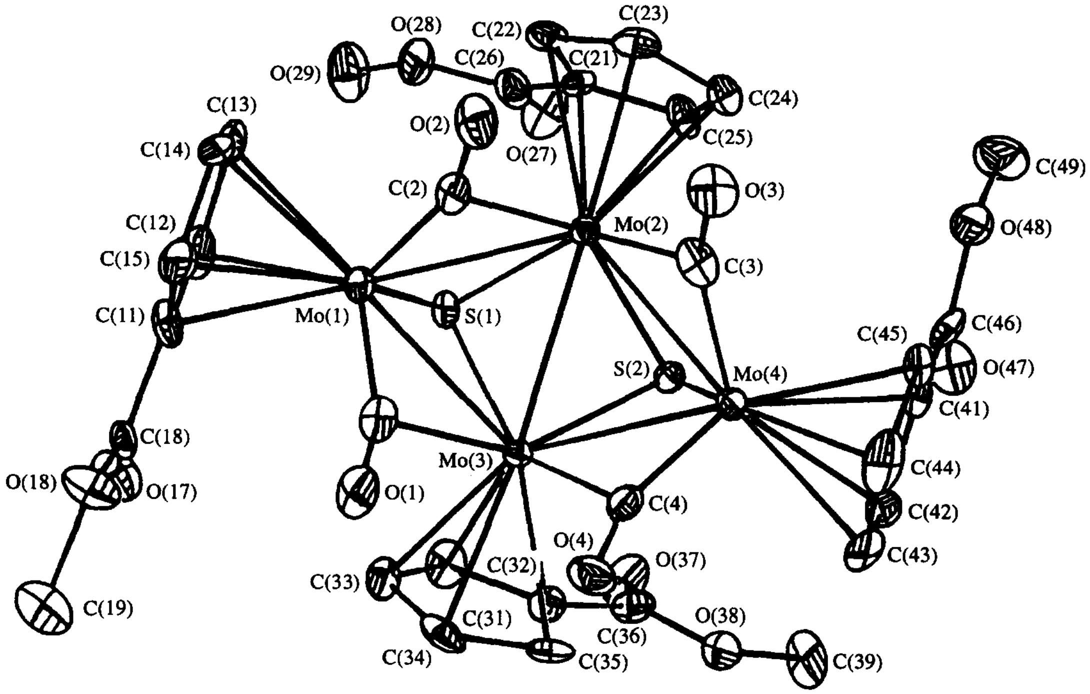


Fig. 1. An ORTEP plot of **2a**.

Table 1. Selected bond lengths (Å) and angles (°) for **2a**

Mo(1)—Mo(2)	2.924(2)	Mo(4)—S(2)	2.367(4)
Mo(1)—Mo(3)	2.928(2)	Mo(1)—C(2)	1.94(2)
Mo(2)—Mo(3)	2.794(2)	Mo(1)—C(1)	1.94(2)
Mo(2)—Mo(4)	2.906(2)	Mo(4)—C(4)	1.95(2)
Mo(3)—Mo(4)	2.894(2)	Mo(4)—C(3)	1.99(2)
Mo(1)—S(1)	2.362(4)	Mo(3)—C(4)	2.53(1)
Mo(2)—S(2)	2.352(4)	Mo(3)—C(1)	2.62(1)
Mo(2)—S(1)	2.364(4)	Mo(2)—C(3)	2.58(1)
Mo(3)—S(1)	2.352(4)	Mo(2)—C(2)	2.54(2)
Mo(3)—S(2)	2.361(4)		
C(2)—Mo(1)—Mo(2)	58.8(4)	S(1)—Mo(3)—S(2)	78.1(1)
C(2)—Mo(1)—Mo(3)	97.9(4)	Mo(2)—Mo(3)—Mo(4)	61.42(5)
C(1)—Mo(1)—Mo(2)	100.8(4)	Mo(2)—Mo(3)—Mo(1)	61.40(5)
C(1)—Mo(1)—Mo(3)	61.1(4)	Mo(4)—Mo(3)—Mo(1)	107.26(6)
Mo(2)—Mo(1)—Mo(3)	57.04(4)	C(4)—Mo(4)—Mo(3)	59.2(4)
S(2)—Mo(2)—S(1)	78.1(1)	C(4)—Mo(4)—Mo(2)	101.3(4)
Mo(3)—Mo(2)—Mo(4)	60.99(5)	C(3)—Mo(4)—Mo(3)	101.2(4)
Mo(3)—Mo(2)—Mo(1)	61.56(5)	C(3)—Mo(4)—Mo(2)	60.2(4)
Mo(4)—Mo(2)—Mo(1)	107.06(6)	Mo(3)—Mo(4)—Mo(2)	57.59(4)
O(1)—C(1)—Mo(1)	158(1)	Mo(2)—C(3)—Mo(4)	77.8(7)
O(2)—C(2)—Mo(1)	156(1)	Mo(2)—C(1)—Mo(1)	80.4(7)
O(3)—C(3)—Mo(4)	156(1)	O(4)—C(4)—Mo(4)	157(1)
Mo(3)—C(4)—O(4)	123(1)	Mo(3)—C(1)—O(1)	122(1)
Mo(2)—C(2)—O(2)	122(1)	Mo(2)—C(3)—O(3)	125(1)
Mo(3)—C(4)—Mo(4)	79.3(8)	Mo(3)—C(1)—Mo(1)	78.4(7)

the unit cell of **1c** there are two independent molecules A and B, whose structures are shown in Fig. 3. Since the geometrical parameters of A and B are very similar, only the selected bond lengths and angles of A are given in Table 2. Although molecule A is ordered, molecule B is disordered with the positions of Mo(3), Mo(4) and Fe(2). The positional disorder was modeled by replacing each disordered atom with two atom scattering sites and subsequent refining their site occupancies with the constraint that the site occupancy

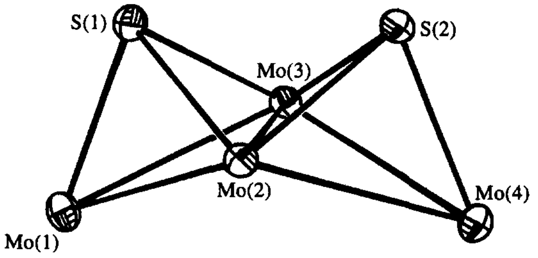


Fig. 2. The cluster skeleton of **2a**.

factors sum to 1.0. The final refined site occupancy factors for Mo(3)/Mo(4)/Fe(2) and Mo(3)′/Mo(4)′/Fe(2)′ were all equal to 0.50. The Mo—Mo [3.049(1) Å] and Mo—Fe (av. 2.810 Å) bond distances are within the normal range [10], which indicates that this trinuclear cluster does not show metal–metal bond contractions, although its metal–metal bonds are bridged by a sulfido ligand. The angles C(1)—Mo(1)—Fe(1), C(3)—Mo(2)—Mo(1) and C(4)—Mo(2)—Fe(1) in molecule A are 64.9(3), 64.7(3) and 71.8(4)°, thus the three carbonyls C(1)O(1), C(3)O(3) and C(4)O(4) are tipped over their respective metal–metal bond to interact with another metal atom of the metal–metal bond.

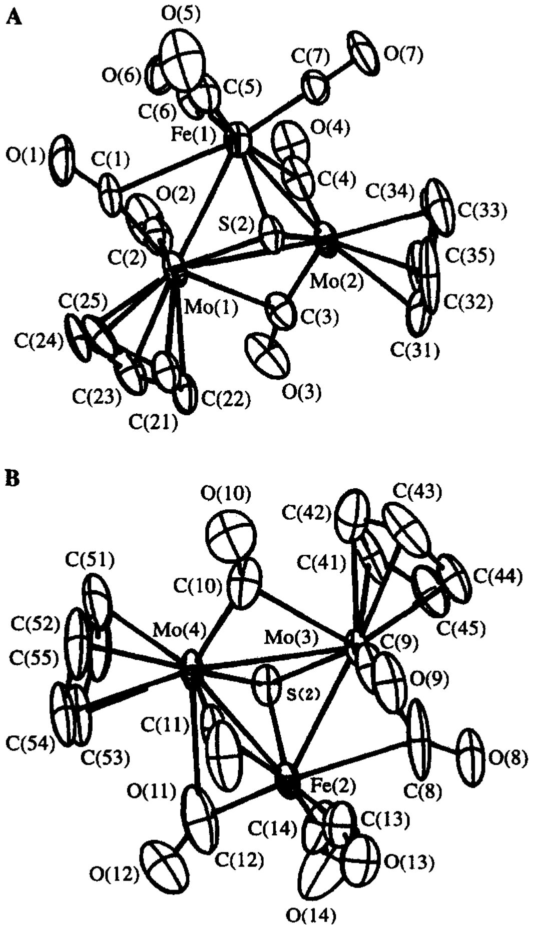


Fig. 3. ORTEP plots of **1c** (A and B).

EXPERIMENTAL

All reactions were carried out under highly purified tank nitrogen. TLC was performed on 26 × 19 cm glass plates coated with silica gel G (10–40 μm). Xylene and benzene were distilled from Na/benzophenone ketyl. $[\eta^5\text{-}RC_5H_4(CO)_2Mo]_2$(R = H, MeO_2C, EtO_2C) [16–17] and $(\mu\text{-}R'S)_2Fe_2(CO)_6$ (R′ = Et, Ph) [18] were prepared according to published methods. The UV irradiation was carried out in a Fuji HB-400 photolysis apparatus with a 400W high pressure mercury lamp. ^1H NMR and IR spectra were recorded on a JEOL FX 90Q or a BRUKER AC-P 200 NMR spectrometer and a NICOLET FX-5DX spectrophotometer, respectively. Mass spectra and elemental analyses were obtained with an HP 5988A or M-80 LC/GC spectrometer and a Perkin–Elmer model 240C analyser, respectively. Melting points were determined on a YANACO MP-500 apparatus and were uncorrected.

Thermal reaction of $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2$ *with* $(\mu\text{-}EtS)_2Fe_2(CO)_6$

A 100 cm^3 two-necked flask fitted with a magnetic stir-bar, a serum cap and a reflux condenser topped with a nitrogen inlet tube, was charged with $[\eta^5\text{-}MeO_2CC_5H_4(CO)_2Mo]_2$ (1.414 g, 2.570 mmol), $(\mu\text{-}EtS)_2Fe_2(CO)_6$ (1.033 g, 2.570 mmol) and xylene (30 cm^3). The mixture was refluxed for 7 h. The solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2. The extracts were subjected to TLC separation using 6 : 1 benzene : ether as eluent to give two bands: (i) the brown band, from which **1a** [9] (0.078 g, 4%) was obtained; (ii) the green band, from which **2a** (0.118 g, 9%) was obtained. **2a**: m.p. 185–186°C. Found: C, 36.6; H, 2.8. Calc. for $C_{32}H_{28}Mo_4O_{12}S_2$: C, 36.5; H, 2.7%. IR (KBr, discs): $\nu_{(C\equiv O)}$, 1819s, 1860s; $\nu_{(C=O)}$, 1712s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 3.72 (s, 6H, $2CH_3$), 3.80 (s, 6H, $2CH_3$), 5.04 [t, 4H, 2(H^3, H^4)], 5.44 [t, 4H, 2(H^3, H^4)], 6.14 [s, 8H, 4(H^2, H^5)]. MS (FD): m/z (^{98}Mo) 1060 (M$^+$, 4%).

Thermal reaction of $[\eta^5\text{-}EtO_2CC_5H_4(CO)_2Mo]_2$ *with* $(\mu\text{-}EtS)_2Fe_2(CO)_6$

A flask described above was charged with $[\eta^5\text{-}EtO_2CC_5H_4(CO)_2Mo]_2$ (1.000 g, 1.729 mmol), $(\mu\text{-}EtS)_2Fe_2(CO)_6$ (0.695 g, 1.729 mmol) and xylene (30 cm^3). The mixture was refluxed for 7 h. Similar work-up was followed to give two bands: (i) the brown band, from which **1b** (0.056 g, 4%) was obtained; (ii) the green band, from which **2b** (0.067 g, 7%) was obtained. **1b**: m.p. 97–98°C. Found: C, 36.7; H, 2.3. Calc. for $C_{23}H_{18}FeMo_2O_{11}S$: C, 36.8; H, 2.4%. IR

Table 2. Selected bond lengths (Å) and angles (°) for molecule A of **1c**

Mo(1)—Mo(2)	3.049(1)	Mo(2)—Fe(1)	2.800(2)
Mo(1)—Fe(1)	2.819(2)	Mo(1)—S(1)	2.364(3)
Mo(2)—S(1)	2.375(3)	Fe(1)—S(1)	2.198(3)
Mo(1)—C(1)	2.00(1)	Mo(1)—C(2)	2.00(1)
Mo(2)—C(3)	1.95(1)	Mo(2)—C(4)	1.99(1)
Fe(1)—C(5)	1.79(1)	Fe(1)—C(6)	1.77(1)
Fe(1)—C(7)	1.78(1)		
Fe(1)—Mo(1)—Mo(2)	56.84(5)	Fe(1)—Mo(2)—Mo(1)	57.44(5)
Mo(2)—Fe(1)—Mo(1)	65.72(5)	Fe(1)—S(1)—Mo(1)	76.3(1)
Fe(1)—S(1)—Mo(2)	75.4(1)	Mo(1)—S(1)—Mo(2)	80.1(1)
C(1)—Mo(1)—Fe(1)	64.9(3)	C(2)—Mo(1)—Fe(1)	84.2(3)
C(3)—Mo(2)—Mo(1)	64.7(3)	C(4)—Mo(2)—Fe(1)	71.8(4)

(KBr, disc): $\nu_{(C\equiv O)}$, 2049s, 2000s, 1975s, 1909s, 1827s; $\nu_{(C=O)}$, 1713s cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.36 (t, $J = 7.2$ Hz, 6H, $2CH_3$), 4.32 (q, $J = 7.2$ Hz, 4H, $2CH_2$), 5.22, 5.42 [br.s, br.s, 4H, 2(H^3, H^4)], 5.90 [br.s, 4H, 2(H^2, H^5)]. MS (EI): *m/z* (^{98}Mo, ^{56}Fe) 586 (M^+ −6CO, 0.4%), 580 (M^+-CO-2EtO_2C, 0.5), 440 [$(C_5H_4)_2Mo_2FeS(CO)^+$, 0.2], 412 [$(C_5H_4)_2Mo_2FeS^+$, 0.3], 348 ($C_5H_4Mo_2FeS^+$, 0.3), 228 (Mo_2S^+, 0.2), 137 ($EtO_2CC_5H_4^+$, 0.4), 98 (Mo^+, 0.4), 92 [$C_5H_4(CO)^+$, 2.9], 56 (Fe^+, 16.4). **2b**: m.p. 67–68°C. Found: C, 38.7; H, 3.1, Calc. for $C_{36}H_{36}Mo_4O_{12}S_2$: C, 39.0; H, 3.3%. IR (KBr, disc): $\nu_{(C\equiv O)}$, 1852s, 1811s; $\nu_{(C=O)}$, 1704s cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.25 (t, 6H, $2CH_3$), 1.32 (t, 6H, $2CH_3$), 4.20 (m, 8H, $4CH_2$), 5.04 [t, 4H, 2(H^3, H^4)], 5.43 [t, 4H, 2(H^3, H^4)], 6.12 [m, 8H, 4(H^2, H^5)].

Thermal reaction of [η^5-$MeO_2CC_5H_4(CO)_2Mo]_2$ *with* (μ-PhS)$_2$Fe$_2$(CO)$_6$

A flask described above was charged with [η^5-$MeO_2CC_5H_4(CO)_2Mo]_2$ (1.000 g, 1.818 mmol), (μ-PhS)$_2$Fe$_2$(CO)$_6$ (0.906 g, 1.818 mmol) and xylene (30 cm^3). The mixture was refluxed for 3 h. Similar work-up was followed to give three bands: (i) the dark-brown band, from which **3a** (0.070 g, 5%) was obtained; (ii) the brown band, from which **1a** [9] (0.029 g, 2%) was obtained; (iii) the green band, from which **2a** (0.042 g, 4%) was obtained. **3a**: m.p. 150°C (dec.). Found: C, 47.1; H, 3.3. Calc. for $C_{28}H_{24}Mo_2O_6S_2$: C, 47.2; H, 3.4%. IR (KBr, disc): $\nu_{(C\equiv O)}$, 1926s, 1885m, 1860s; $\nu_{(C=O)}$, 1713s cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.45 (s, 3H, CH_3), 3.55 (s, 6H, $2CH_3$), 3.65 (s, 3H, CH_3), 5.37 [t, 4H, 2(H^3, H^4)], 5.65 [t, 4H, 2(H^2, H^5)], 5.85 [t, 4H, 2(H^3, H^4)], 5.90 [t, 4H, 2(H^2, H^5)], 6.95–7.50 (m, 20H, $4C_6H_5$). MS(EI): *m/z* (^{98}Mo) 660 (M^+-2CO, 9.2%), 551 (M^+-2CO-PhS, 5.2), 465 [$(C_5H_4)_2Mo_2S(SPh)^+$, 3.8], 414 [$Mo_2(PhS)_2^+$, 6.6], 337 [$Mo_2S(SPh)^+$, 10.1], 324 [$(C_5H_4)_2Mo_2^+$, 5.9], 228 (Mo_2S^+, 3.9), 196 (Mo_2^+, 3.2), 186 (Ph_2S^+, 6.0), 154 (Ph_2^+, 13.4), 92 [$C_5H_4(CO)^+$, 100], 77 (Ph^+, 47.6).

Thermal reaction of [η^5-$EtO_2CC_5H_4(CO)_2Mo]_2$ *with* (μ-PhS)$_2$Fe$_2$(CO)$_6$

A flask as described above was charged with [η^5-$EtO_2CC_5H_4(CO)_2Mo]_2$ (1.000 g, 1.729 mmol), (μ-PhS)$_2$Fe$_2$(CO)$_6$ (0.861 g, 1.729 mmol) and xylene (30 cm^3). The mixture was refluxed for 3 h. Similar work-up was followed to give three bands: (i) the greenish-yellow to dark-brown band, from which **3b** (0.085 g, 7%) was obtained; (ii) the brown band, from which **1b** (0.030 g, 2%) was obtained; (iii) the green band, from which **2b** (0.020 g, 2%) was obtained. **3b**: m.p. 165–166°C. Found: C, 48.5; H, 3.8. Calc. for $C_{30}H_{28}Mo_2O_6S_2$: C, 48.6; H, 3.8%. IR (KBr, disc): $\nu_{(C\equiv O)}$, 1934s, 1885m, 1844vs; $\nu_{(C=O)}$, 1704s cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.80–1.32 (m, 12H, $4CH_3$), 3.76–4.32 (m, 8H, $4CH_2$), 5.40 [t, 4H, 2(H^3, H^4)], 5.68 [t, 4H, 2(H^3, H^4)], 5.84–6.04 [m, 8H, 4(H^2, H^5)], 7.12–7.40 (m, 20H, $4C_6H_5$). MS(EI): *m/z* (^{98}Mo) 388 [$(C_5H_4)_2Mo_2S_2^+$, 0.4%), 337 ($Mo_2S(SPh)^+$, 1.1), 324 ($C_5H_4Mo_2S_2^+$, 0.4], 228 (Mo_2S^+, 0.3), 154 (Ph_2^+, 1.2), 109 (PhS^+, 1.1), 92 [$C_5H_4(CO)^+$, 6.1], 77 (Ph^+, 6.3).

Photolytic reaction of [η^5-$EtO_2CC_5H_4(CO)_2Mo]_2$ *with* (μ-EtS)$_2$Fe$_2$(CO)$_6$

A reaction vessel equipped with a quartz immersion well and a 400W high pressure mercury lamp, was charged with [η^5-$EtO_2CC_5H_4(CO)_2Mo]_2$ (0.500 g, 0.865 mmol), (μ-EtS)$_2$Fe$_2$(CO)$_6$ (0.348 g, 0.865 mmol) and benzene (220 cm^3). The mixture was irradiated for 12 h. Solvent was removed *in vacuo* and the residue was subjected to TLC separation using 2 : 1 petroleum ether: CH_2Cl_2 as eluent to give a brown band, from which **1b** (0.027 g, 4%) was obtained.

Photolytic reaction of [η^5-$C_5H_5(CO)_2Mo]_2$ *with* (μ-PhS)$_2$Fe$_2$(CO)$_6$

The same photolysis vessel was charged with [η^5-$C_5H_5(CO)_2Mo]_2$ (1.000 g, 2.304 mmol), (μ-PhS)$_2$

Table 3. Summary of crystallographic data for compounds **1c** and **2a**·H_2O

	1c	**2a**·H_2O
Empirical formula	$C_{17}H_{10}FeMo_2O_7S$	$C_{32}H_{28}Mo_4O_{12}S_2 \cdot H_2O$
Formula weight	606.05	1070.46
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
a (Å)	16.280(8)	14.746(8)
b (Å)	12.682(2)	12.544(3)
c (Å)	20.289(3)	18.399(8)
β (°)	113.38(3)	91.72(4)
V (Å^3)	3845(4)	3402(4)
Z	8	4
D_{calc} (g cm^{-3})	2.09	2.09
F(000)	2352	2104
Absorption coefficient, μ (mm^{-1})	2.14	1.59
Radiation (Å)	Mo-K_α ($\lambda = 0.71069$)	Mo-K_α ($\lambda = 0.71069$)
Temperature (°C)	23	23
$(2\theta)_{max}$ (°)	50	49.9
Observed reflections $I > 3.00\ \sigma\ I$	4040	3865
No. of variables	532	460
R	0.053	0.068
Rw	0.062	0.076
GOF	1.16	1.48
$(\Delta/\sigma)_{max}$	0.03	0.07
$\Delta\rho_{max}$ (e Å^{-3})	1.16	1.39
$\Delta\rho_{min}$ (e Å^{-3})	−0.74	−1.16

$Fe_2(CO)_6$, (1.148 g, 2.305 mmol) and benzene (220 cm^3). The mixture was irradiated for 12 h. Similar work-up was followed to give a brown band from which **1c** [15] (0.120 g, 9%) was obtained.

Structure determination of 1c

The single crystals of **1c** were grown in its CH_2Cl_2/hexane solution at *ca* 4°C, from which a single crystal with dimension 0.20 × 0.18 × 0.07 mm was selected for X-ray diffraction analysis. Diffraction data were collected on an Enraf–Nonius CAD4 diffractometer using the $\omega/2\theta$ scan mode. Crystallographic data for **1c** are summarized in Table 3. The structure was solved by the direct method (MITHRIL) using TEXSAN package.

Structure determination of 2a·H_2O

The crystals of **2a**·H_2O were grown by slow evaporation of its CH_2Cl_2/hexane solution, from which a single crystal with dimension 0.25 × 0.15 × 0.10 mm was selected for X-ray diffraction analysis. Diffraction data were collected on an Enraf–Nonius CAD4 diffractometer with Mo-K_α radiation by the $\omega/2\theta$ scan mode. Crystallographic data for **2a**·H_2O are summarized in Table 3. The structure was solved by the direct method (MITHRIL) using the TEXSAN package.

Acknowledgments—We are grateful to the National Natural Science Foundation of China, the Special Foundation of State Education Committee of China and the Laboratory of Organometallic Chemistry at Shanghai Institute of Organic Chemistry for financial support of this work.

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