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Syntheses and structural characterization of transition metal tetrahedral clusters (η^5-RC_5H_4)$(CO)_8MoRu_2H(\mu_3$-S) and [(η^5-RC_5H_4)$(CO)_4MoRu(\mu_3$-S)$]_2$ generated by isolobal reactions

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Abstract

Interestingly, the single-tetrahedral MoNiFeS clusters (η^5-C_5H_5)(η^5-RC_5H_4)$(CO)_5$MoNiFe(μ_3-S) (R = Me, MeCO, MeO_2C) react with $Ru_3(CO)_{12}$ in refluxing toluene to give both single-tetrahedral $MoRu_2S$ clusters (η^5-RC_5H_4)$(CO)_8MoRu_2H(\mu_3$-S) (**1a**, R = Me; **1b**, R = MeCO; **1c**, R = MeO_2C) and double-tetrahedral $Mo_2Ru_2S_2$ co-edged clusters [(η^5-RC_5H_4)$(CO)_4$MoRu(μ_3-S)$]_2$ (**2a**, R = Me; **2b**, R = MeCO; **2c**, R = MeO_2C) in combined 58–94% yields. Products **1a**–**c** and **2a**–**c** have been characterized by elemental analysis, and IR and ^{1}H-NMR spectroscopy, as well as single-crystal X-ray diffraction analyzes for **1a**–**c** and **2b**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: MoNiFeS clusters; $MoRu_2S$ clusters; $Mo_2Ru_2S_2$ clusters; Synthesis; X-ray structures

1. Introduction

During recent years transition metal clusters have been receiving considerable attention, mainly because of their potential applications such as in catalysis, as well as the novelty and diversity of their reactions and structures [1–3]. Among the reactions studied so far, the isolobal reactions based on the principle of 'isolobal analogy' [4] are of great interest and have been utilized in the rational synthesis of a wide variety of such cluster complexes [5–13]. Recently, we have reported a novel type of isolobal reactions of the single-tetrahedral MoNiFeS clusters (η^5-C_5H_5)(η^5-RC_5H_4)$(CO)_5$MoNiFe(μ_3-S) with $Fe_2(CO)_9$ [13d]. Now, as a continuation of this project, we wish to report the reactions of the tetrahedral MoNiFeS clusters (η^5-C_5H_5)(η^5-RC_5H_4)$(CO)_5$MoNiFe(μ_3-S) (R = Me, MeCO, MeO_2C) with metal carbonyl $Ru_3(CO)_{12}$. Interestingly, these reactions afforded single-tetrahedral $MoRu_2S$ clusters (η^5-RC_5H_4)$(CO)_8MoRu_2H(\mu_3$-S) and double-tetrahedral $Mo_2Ru_2S_2$ co-edged clusters [(η^5-RC_5H_4)$(CO)_4$MoRu(μ_3-S)$]_2$ (R = Me, MeCO, MeO_2C), whose structures have been characterized by elemental analysis, spectroscopy and crystal X-ray diffraction techniques.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of (η^5-RC_5H_4)$(CO)_8MoRu_2H(\mu_3$-S) (1a–c) and [(η^5-RC_5H_4)$(CO)_4$MoRu(μ_3-S)$]_2$ (2a–c)

It was found that the thermal reactions of single-tetrahedral MoNiFeS clusters (η^5-C_5H_5)(η^5-RC_5H_4)$(CO)_5$MoNiFe(μ_3-S) (R = Me, MeCO, MeO_2C) with $Ru_3(CO)_{12}$ in toluene at reflux afforded single-tetrahedral $MoRu_2S$ clusters (η^5-RC_5H_4)$(CO)_8MoRu_2H(\mu_3$-S) (**1a**–**c**) and double-tetrahedral $Mo_2Ru_2S_2$ co-edged clusters [(η^5-RC_5H_4)$(CO)_4$MoRu(μ_3-S)$]_2$ (**2a**–**c**) in a total of 58–94% yields, as shown in Scheme 1.

It is noteworthy that the formation of products **1a**–**c** and **2a**–**c** is unexpected, but it is understandable in

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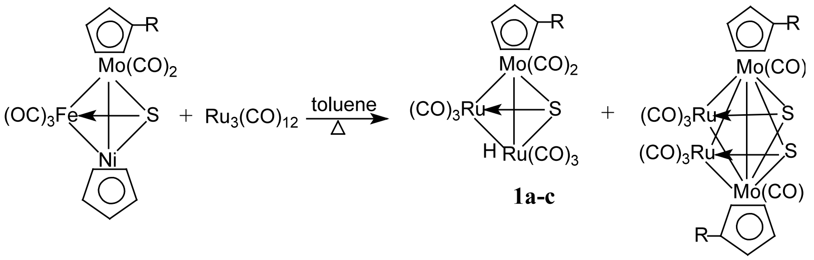

2a-c

Clusters	1a	1b	1c	2a	2b	2c
R	Me	MeCO	MeO_2C	Me	MeCO	MeO_2C

Scheme 1.

terms of the principle of ‘isolobal analogy’ [4]. As we know, the structural units $Fe(CO)_3$ (d^8ML_3) and CpNi (d^9ML_3) in starting clusters (η^5-C_5H_5)(η^5-RC_5H_4)$(CO)_5$MoNiFe(μ_3-S) are actually isolobal with fragments $Ru(CO)_3$ (d^8ML_3) (formed in situ from $Ru_3(CO)_{12}$) and $HRu(CO)_3$ (d^7ML_4) (derived most likely from interaction of $Ru_3(CO)_{12}$ with H-containing ligands such as η^5-RC_5H_4 or solvent toluene), respectively. So, products **1a**–**c** might be regarded as produced from isolobal displacement of $Fe(CO)_3$ and CpNi in the starting clusters by $Ru(CO)_3$ and $HRu(CO)_3$. As to products **2a**–**c**, they could be regarded as produced through isolobal addition of the two identical isolobal fragments (η^5-RC_5H_4)$(CO)_4$MoRuS, which were generated from isolobal displacement of $Fe(CO)_3$ in starting clusters (η^5-C_5H_5)(η^5-RC_5H_4)$(CO)_5$MoNiFe(μ_3-S) by $Ru(CO)_3$ and subsequent loss of fragment CpNi and one CO ligand attached to the Mo atom. Products **1a**–**c** and **2a**–**b** have been characterized by elemental and spectroscopic analyzes. For example, while IR spectra of **1a**–**c** showed six absorption bands in the range 2098–1752 cm^{-1} for their hydrido and carbonyl ligands attached to metal atoms, those of **2a**–**c** displayed five absorption bands in the region 2100–1744 cm^{-1} for their carbonyl ligands attached to metal atoms. The ^{1}H-NMR spectra of **1a**–**c** showed one singlet at ca. −19 ppm for their hydrido ligands. Although the hydrido ligand in **1a**, **1b** or **1c** should be assigned as a terminal ligand attached to one of the two Ru atoms in terms of the 18-electron rule, it would be best described as a bridged ligand along the Ru–Ru bond or a ligand capped over the triangular Ru_2Mo face. This is because that clusters **1a**–**c** are actually isostructural with clusters (η^5-RC_5H_4)$(CO)_8MFe_2H$(μ_3-E) (M = Mo, W; E = S, Se) in which the hydrido ligands have been previously reasonably assigned as bridging or facial ligands mainly based on the fact of W–H coupling in the above W-containing clusters [14]. In addition, the ^{1}H-NMR spectra of **1a**–**c** and **2a**–**c** exhibited respective signals corresponding to their substituted Cp groups. It is worthwhile to note that the four hydrogen atoms for each Cp ring in **1a**–**c** and **2a**–**c** displayed two singlets in the range 5.04–6.07 ppm; for **1a** and **2a** the upfield singlet should be assigned to H^2 and H^5 and the downfield singlet to H^3 and H^4, whereas for **1b**, **c** and **2b**, **c** the upfield singlet should be attributed to H^3 and H^4 and the downfield singlet to H^2 and H^5. Such assignment is obviously based on the different electronic effects of the substituents Me and MeCO–MeO_2C in **1a**–**c** and **2a**–**c** [14].

2.2. Crystal structures of **1a**–**c** and **2b**

In order to further confirm the structures of **1a**–**c** and **2a**–**c**, single-crystal X-ray diffraction analyzes of **1a**–**c** and **2b** were undertaken. The molecular structures of **1a**–**c** and **2b** are presented in Figs. 1–4, whereas their selected bond lengths and angles are listed in Tables 1–4, respectively. As can be seen in Figs. 1–3, **1a**–**c** are actually isostructural; they consist of a distorted tetrahedral $MoRu_2$(μ_3-S) cluster core, which carries six carbonyl ligands coordinated to the two Ru atoms, and two carbonyl ligands and one substituted cyclopentadienyl ligand coordinated to the Mo atom. It is worthy of note that the six carbonyls bonded to the two Ru

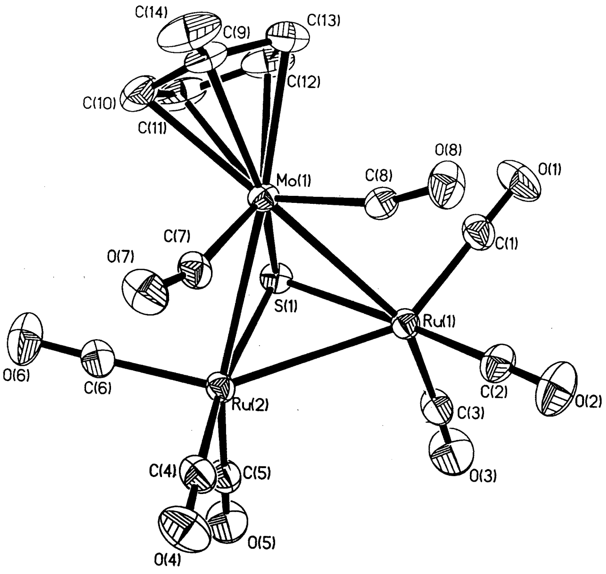

Fig. 1. ORTEP plot of **1a** with the atom labeling scheme.

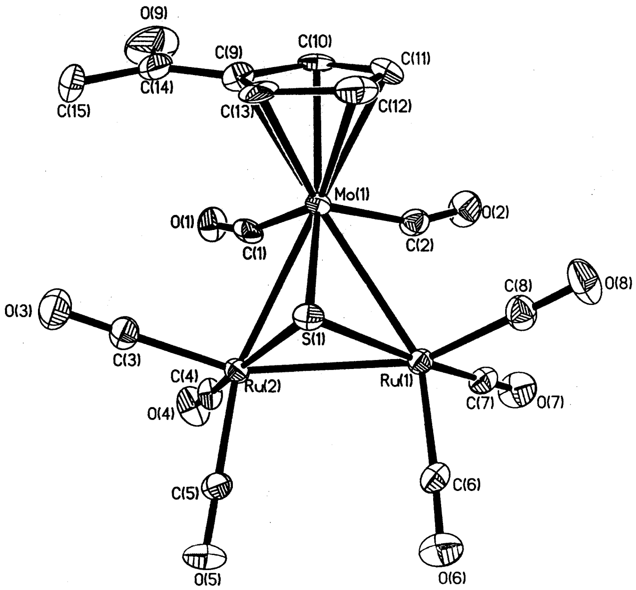

Fig. 2. ORTEP plot of **1b** with the atom labeling scheme.

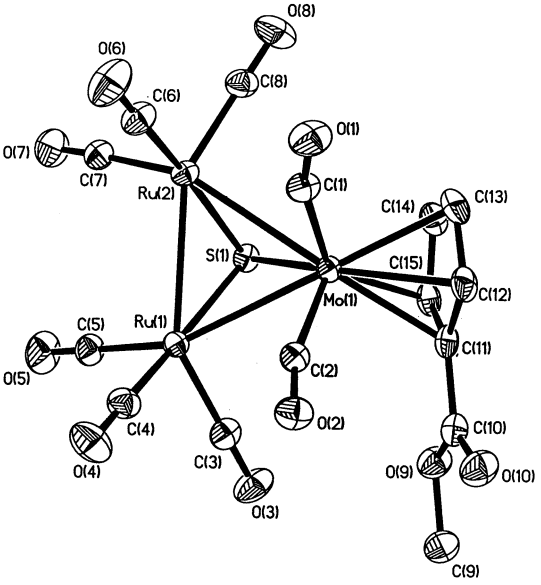

Fig. 3. ORTEP plot of **1c** with the atom labeling scheme.

atoms are terminal, whereas the two carbonyls attached to the Mo atom are semi-bridging [15], which coincides very well with their IR frequencies in the region 2128–1779 cm^{-1}. Tables 1–3 show that the cooresponding geometric parameters of **1a**–**c** are very close to each other. In fact, these parameters, for instance, the bond lengths involved in the cluster cores of **1a**–**c**, namely Ru–Ru, Ru–Mo, Ru–S and Mo–S are also found to be comparable with corresponding those reported in literature [16,17]. In addition, the π-systems of the substituents acetyl group in **1b** and methoxycarbonyl group in **1c** are well conjugated with those of the Cp rings. This can be confirmed by the facts that the dihedral angle between the Cp ring and the plane C(14)–O(9)–C(15) in **1b** or the plane O(9)–C(10)–O(10) in **1c** is quite small (6.7 and 6.2°, respectively), as well as the bond lengths of C(9)–C(14) in **1b** (1.470(14) Å) and C(10)–C(11) in **1c** (1.476(7) Å) are much shorter than a normal C–C single bond (1.54 Å).

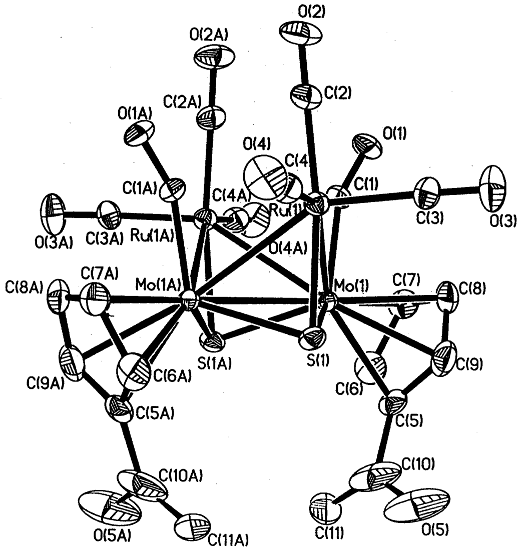

Fig. 4. ORTEP plot of **2b** with the atom labeling scheme.

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

Bond lengths			
Ru(1)–C(1)	1.915(6)	Ru(2)–S(1)	2.3566(14)
Ru(1)–S(1)	2.3526(14)	Ru(2)–Mo(1)	2.8996(7)
Ru(1)–Ru(2)	2.8929(7)	Mo(1)–C(7)	1.964(6)
Ru(1)–Mo(1)	2.9109(8)	Mo(1)–C(9)	2.342(5)
Ru(2)–C(4)	1.932(6)	Mo(1)–S(1)	2.3931(13)
Bond angles			
S(1)–Ru(1)–Ru(2)	52.16(3)	S(1)–Ru(2)–Mo(1)	52.95(3)
S(1)–Ru(1)–Mo(1)	52.80(3)	Ru(1)–Ru(2)–Mo(1)	60.334(18)
Ru(2)–Ru(1)–Mo(1)	59.946(15)	S(1)–Mo(1)–Ru(2)	51.81(3)
S(1)–Ru(2)–Ru(1)	52.04(3)	S(1)–Mo(1)–Ru(1)	51.54(3)
Ru(1)–S(1)–Mo(1)	75.66(4)	Ru(1)–S(1)–Ru(2)	75.80(4)

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

Bond lengths			
Ru(1)–C(6)	1.920(8)	Ru(2)–S(1)	2.337(2)
Ru(1)–S(1)	2.346(2)	Ru(2)–Mo(1)	2.8969(15)
Ru(1)–Ru(2)	2.8679(13)	Mo(1)–C(1)	1.968(9)
Ru(1)–Mo(1)	2.9016(17)	Mo(1)–C(9)	2.316(8)
Ru(2)–C(3)	1.889(9)	Mo(1)–S(1)	2.386(2)
Bond angles			
S(1)–Ru(1)–Ru(2)	52.10(5)	S(1)–Ru(2)–Mo(1)	52.94(5)
S(1)–Ru(1)–Mo(1)	52.81(5)	Ru(1)–Ru(2)–Mo(1)	60.44(4)
Ru(2)–Ru(1)–Mo(1)	60.28(3)	S(1)–Mo(1)–Ru(2)	51.41(5)
S(1)–Ru(2)–Ru(1)	52.37(5)	S(1)–Mo(1)–Ru(1)	51.55(5)
Ru(1)–S(1)–Mo(1)	75.64(7)	Ru(1)–S(1)–Ru(2)	75.53(7)

Table 3
Selected bond lengths (Å) and angles (°) for **1c**

Bond lengths			
Ru(1)–C(3)	1.905(5)	Ru(2)–S(1)	2.3469(11)
Ru(1)–S(1)	2.3468(12)	Ru(2)–Mo(1)	2.9055(6)
Ru(1)–Ru(2)	2.8849(5)	Mo(1)–C(1)	1.954(5)
Ru(1)–Mo(1)	2.9026(5)	Mo(1)–C(11)	2.338(4)
Ru(2)–C(6)	1.932(5)	Mo(1)–S(1)	2.3904(11)
Bond angles			
S(1)–Ru(2)–Ru(1)	52.07(3)	S(1)–Ru(1)–Mo(1)	52.90(3)
S(1)–Ru(2)–Mo(1)	52.85(3)	Ru(2)–Ru(1)–Mo(1)	60.268(14)
Ru(1)–Ru(2)–Mo(1)	60.167(12)	S(1)–Mo(1)–Ru(2)	51.50(3)
S(1)–Ru(1)–Ru(2)	52.08(3)	S(1)–Mo(1)–Ru(1)	51.54(3)
Ru(1)–S(1)–Mo(1)	75.57(3)	Ru(1)–S(1)–Ru(2)	75.85(4)

Table 4
Selected bond lengths (Å) and angles (°) for **2b**

Bond lengths			
Mo(1)–C(1)	1.964(7)	Ru(1)–S(1)	2.325(2)
Mo(1)–S(1)	2.360(2)	Ru(1)–Mo(1)#	2.9046(10)
Mo(1)–Mo(1)#	2.8703(13)	S(1)–Mo(1)#	2.365(2)
Ru(1)–Mo(1)	2.8976(11)	Mo(1)–S(1)#	2.365(2)
Ru(1)–C(2)	1.913(8)	Mo(1)–Ru(1)#	2.9046(10)
Bond angles			
S(1)–Mo(1)–Mo(1)#	52.67(5)	S(1)–Ru(1)–Mo(1)#	52.36(5)
S(1)–Mo(1)–Ru(1)	51.24(5)	Ru(1)–S(1)–Mo(1)	76.41(5)
S(1)–Mo(1)–Ru(1)#	110.92(5)	Ru(1)–S(1)–Mo(1)#	76.53(5)
S(1)–Ru(1)–Mo(1)	52.35(5)	Mo(1)–S(1)–Mo(1)#	74.81(6)
Mo(1)–Ru(1)–Mo(1)#	59.30(2)	Ru(1)–Mo(1)–Ru(1)#	83.98(3)

Fig. 4 shows that **2b** consists of a Mo–Mo co-edged double-tetrahedral $Mo_2Ru_2S_2$ cluster core, which contains six carbonyls attached to the two Ru atoms, and two carbonyls along with two acetyl-substituted cyclopentadienyls coordinated to the two Mo atoms. While the six carbonyls attached to the two Ru atoms are terminal, the two carbonyls bound to the two Mo atoms are semi-bridging [15], which is consistent with its IR frequencies in the range 2090–1744cm^{-1}. Compound **2b** has a two-fold axis through the centers of Mo(1)–Mo(1A) and S(1)–S(1A) vectors. The two substituted cyclopentadienyl groups and two carbonyls bonded to Mo atoms are all *cis* with respect to the Mo(1)–Mo(1A) bond. The dihedral angle between the planes Ru(1)–Mo(1)–Mo(1A) and Ru(1A)–Mo(1)–Mo(1A) is 100.7°. In addition, the π-systems of the acetyl groups in **2b** are well conjugated with those of its two Cp rings, since the dihedral angle between the Cp ring and the plane C(10)–O(5)–C(11) or C(10A)–O(5A)–C(11A) is quite small (11.7°) and the bond length of C(5)–C(10) or C(5A)–C(10A)(1.460(17) Å) is much shorter than a normal C–C single bond (1.54 Å). In fact, **2b** is isostructural with **2c** which can also be prepared by another method [18]. However, our new method for preparation of **2c** reported in this article not only gives a higher yield of **2c**, but also produces another type of cluster **1c** in quite high yield.

3. Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. Toluene was distilled from Na–benzophenone ketyl under nitrogen and deoxygenated by bubbling N_2 for about 15 min prior to use. $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}RC_5H_4)(CO)_5MoNiFe(\mu_3\text{-}S)$ (R = Me [19], MeCO [20], MeO_2C [13d]) were prepared according to the literature methods. $Ru_3(CO)_{12}$ was purchased from Strem Chemicals Inc. and used as received. Preparative TLC was carried out on glass plates (26 × 20 cm) coated with silica gel (10–40 μm). IR spectra were recorded on a Nicolet Magna 560 FT-IR or a Bruker Vector 22 infrared spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AC-P 200 spectrometer. C/H analyzes were performed on an Elementar Vario EL analyzer. M.p. were determined on a Yanaco MP-500 apparatus and were uncorrected.

3.1. Preparation of $(\eta^5\text{-}MeC_5H_4)(CO)_8MoRu_2H(\mu_3\text{-}S)$ (*1a*) and $[(\eta^5\text{-}MeC_5H_4)(CO)_4MoRu(\mu_3\text{-}S)]_2$ (*2a*)

A 100 ml three-necked flask equipped with a magnetic stir bar, a rubber septum, and a reflux condenser topped with a nitrogen inlet tube was charged with 0.527 g (1.0 mmol) of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}MeC_5H_4)(CO)_5MoNiFe(\mu_3\text{-}S)$, 0.480 g (0.75 mmol) of $Ru_3(CO)_{12}$ and 25 ml of $C_6H_5CH_3$. The mixture was stirred at reflux for 30 h. Solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2. The extracts were subjected to TLC using CH_2Cl_2–petroleum ether (v/v = 1:2) as eluent. From the first orange band was obtained 0.267 g (42%) of **1a** as an orange solid. m.p. 166–167 °C. Anal. Found: C, 26.19; H, 1.35. Calc. for $C_{14}H_8MoO_8Ru_2S$: C, 26.48; H, 1.26%. IR (KBr disk): $\nu_{C\equiv O}$ 2098s, 2078s, 2018vs, 1993vs, 1819s, 1779m cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.12 (s, 3H, CH_3), 5.22 (s, 2H, H^2, H^5), 5.27 (s, 2H, H^3, H^4), −19.03 (s, 1H, RuH). From the second brown band was obtained 0.217 g (52%) of **2a** as a brown solid. m.p. 177 °C (dec.). Anal. Found: C, 28.75; H, 1.80. Calc. for $C_{20}H_{14}Mo_2O_8Ru_2S_2$: C, 28.58; H, 1.67%. IR (KBr disk): $\nu_{C\equiv O}$ 2074s, 2042vs, 1997s, 1973vs, 1752s cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.16 (s, 6H, $2CH_3$), 5.04 (s, 4H, $2H^2$, $2H^5$), 5.16 (s, 4H, $2H^3$, $2H^4$).

3.2. Preparation of *(η^5-MeCOC$_5$H$_4$)(CO)$_8$MoRu$_2$H(μ_3-S)* (**1b**) *and [(η^5-MeCOC$_5$H$_4$)(CO)$_4$MoRu(μ_3-S)]$_2$* (**2b**)

To the flask described above were charged 0.555 g (1.0 mmol) of (η^5-C$_5$H$_5$)(η^5-MeCOC$_5$H$_4$)(CO)$_5$MoNiFe(μ_3-S), 0.480 g (0.75 mmol) of $Ru_3(CO)_{12}$ and 25 ml of $C_6H_5CH_3$. The mixture was stirred at reflux for 30 h. Solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2. The extracts were subjected to TLC using CH_2Cl_2–petroleum ether (v/v = 5:1)as eluent. From the first orange band was obtained 0.311 g (47%) of **1b** as an orange solid. m.p. 164–165 °C. Anal. Found: C, 27.08; H, 1.16. Calc. for $C_{15}H_8MoO_9Ru_2S$: C, 27.20; H, 1.21%. IR (KBr disk): $\nu_{C\equiv O}$ 2128s, 2098s, 2030s, 2010vs, 1827s, 1787m; $\nu_{C=O}$ 1684s cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 2.31 (s, 3H, CH$_3$), 5.42 (s, 2H, H^3, H^4), 5.97 (s, 2H, H^2, H^5), −18.99 (s, 1H, RuH). From the second brown band was obtained 0.065 g (15%) of **2b** as a brown solid. m.p. 174 °C (dec.). Anal. Found: C, 29.33; H, 1.57. Calc. for $C_{22}H_{14}Mo_2O_{10}Ru_2S_2$: C, 29.45; H, 1.56%. IR (KBr disk): $\nu_{C\equiv O}$ 2090s, 2050vs, 2018s, 1981vs, 1744s; $\nu_{C=O}$ 1684s cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 2.35 (s, 6H, 2CH$_3$), 5.09 (s, 4H, 2H^3, 2H^4), 6.07 (s, 4H, 2H^2, 2H^5).

3.3. Preparation of *(η^5-MeO$_2$CC$_5$H$_4$)(CO)$_8$MoRu$_2$H(μ_3-S)* (**1c**) *and [(η^5-MeO$_2$C C$_5$H$_4$)(CO)$_4$MoRu(μ_3-S)]$_2$* (**2c**)

To the flask described above were charged 0.571 g (1 mmol) of (η^5-C$_5$H$_5$)(η^5-MeO$_2$CC$_5$H$_4$)(CO)$_5$MoNiFe(μ_3-S), 0.480 g (0.75 mmol) of $Ru_3(CO)_{12}$ and 25 ml of $C_6H_5CH_3$. The mixture was stirred at reflux for 30 h. Solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2. The extracts were subjected to TLC using CH_2Cl_2–petroleum ether (v/v = 5:1) as eluent. From the first orange band was obtained 0.236 g (35%) of **1c** as an orange solid. m.p. 145–146 °C. Anal. Found: C, 26.22; H, 1.14. Calc. for $C_{15}H_8MoO_{10}Ru_2S$: C, 26.56; H, 1.18%. IR (KBr disk): $\nu_{C\equiv O}$ 2100s, 2084s, 2030vs, 2010vs, 1836s, 1795m; $\nu_{C=O}$ 1724s cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 3.74 (s, 3H, CH$_3$), 5.38 (s, 2H, H^3, H^4), 5.99 (s, 2H, H^2, H^5), −19.06 (s, 1H, RuH). From the second brown band was obtained 0.106 g (23%) of **2c** as a brown solid. m.p. 170 °C (dec.). Anal. Found: C, 28.93; H, 1.64. Calc. for $C_{22}H_{14}Mo_2O_{12}Ru_2S_2$: C, 28.50; H, 1.52%. IR (KBr disk): $\nu_{C\equiv O}$ 2073vs, 2054vs, 2000vs, 1981vs, 1772s; $\nu_{C=O}$ 1717s cm^{-1}. ^{1}H-NMR (200 MHz, CDCl$_3$): δ 3.87 (s, 6H, 2CH$_3$), 5.11 (s, 4H, 2H^3, 2H^4), 5.97 (s, 4H, 2H^2, 2H^5).

Table 5
Crystal data and structural refinements details for **1a**–**c** and **2b**

	1a	**1b**	**1c**	**2b**
Empirical formula	$C_{14}H_8MoO_8Ru_2S$	$C_{15}H_8MoO_9Ru_2S$	$C_{15}H_8MoO_{10}Ru_2S$	$C_{22}H_{14}Mo_2O_{10}Ru_2S_2$
Formula weight	634.34	662.35	678.35	896.47
Temperature (K)	293(2)	293(2)	293(2)	298(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	$P2_12_12$
a (Å)	16.979(3)	6.260(3)	6.4283(6)	10.453(3)
b (Å)	6.6014(11)	9.151(5)	9.2114(9)	10.724(3)
c (Å)	33.319(6)	17.603(9)	17.6564(18)	11.885(4)
α (°)	90	93.183(8)	95.505(2)	90
β (°)	94.409(3)	92.996(8)	91.106(2)	90
γ (°)	90	109.853(8)	108.167(2)	90
V (Å^3)	3723.5(11)	944.4(8)	987.46(17)	1332.3(7)
Z	8	2	2	2
D_{calc} (g cm^{-3})	2.263	2.329	2.281	2.235
μ(Mo–K$_\alpha$) (mm^{-1})	2.414	2.389	2.292	2.241
F(000)	2416	632	648	860
Scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$ (°)	50.06	50.04	52.82	50.04
Data/restraints/parameters	3235/0235	3061/0/253	3968/0/266	2359/0/172
R	0.0333	0.0380	0.0366	0.0308
Rw	0.0599	0.0791	0.0994	0.0787
Goodness-of-fit	1.083	1.019	1.006	1.103
Largest difference peak and hole (e Å^{-3})	0.591 and −0.692	0.917 and −0.706	0.869 and −1.149	0.701 and −0.953

3.4. X-ray structure determinations of *1a–c* and *2b*

Suitable crystals of **1a**–**c** and **2b** for X-ray diffraction analyzes were obtained by slow evaporation of their CH_2Cl_2–C_6H_{14} solutions at about −5 °C. Each crystal was mounted on a glass fiber and placed on a Bruker Smart 1000 automated diffractometer equipped with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct method and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were located by using the geometric method. All calculations were performed on a Bruker Smart computer using the SHELXTL-97 program system. Details of the crystal data, data collections, and structure refinements were summarized in Table 5.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 181567–181570 for compounds **1a**, **1b**, **1c** and **2b**, 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).

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