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Synthesis, characterization and reaction of the cluster complexes containing tetrahedral core MRuCoSe. The single crystal X-ray structures of the clusters $RuCoMo(CO)_8(\mu_3\text{-}Se)C_5H_4C(O)R$ [$R = CH_3$, $C_6H_4C(O)OCH_3$]

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Abstract

Several chiral cluster derivatives $RuCoMo(\mu_3\text{-}Se)(CO)_8C_5H_4C(O)R$ [$R = H$ **2**, CH_3 **3**, C_6H_5 **4**, $C_6H_4C(O)OCH_3$ **5**] were synthesized by the thermal reaction of the precursor $(\mu_3\text{-}Se)RuCo_2(CO)_9$ **1** with the functionally substituted cyclopentadienyl tricarbonyl metal complex anions $[Mo(CO)_3(\eta^5\text{-}C_5H_4)C(O)R]^-$ without using benzophenone ketyl as initiator. Similarly, the reaction of the novel type of dianions $^-Mo(CO)_3[(\eta^5\text{-}C_5H_4)C(O)C_6H_4C(O)(\eta^5\text{-}C_5H_4)](CO)_3Mo^-$ with two molecules of cluster **1** gave a terephthaloyl(biscyclopentadienyl) bridged cluster complex $(\mu_3\text{-}Se)RuCoMo(CO)_8(\eta^5\text{-}C_5H_4)C(O)C_6H_4C(O)(\eta^5\text{-}C_5H_4)RuCoMo(CO)_8(\mu_3\text{-}Se)$ **6**. The cluster **3** reacted with $NaBH_4$ in MeOH to give the secondary alcohol cluster $RuCoMo(\mu_3\text{-}Se)(CO)_8C_5H_4CH(OH)CH_3$ **7**. Cluster **3** reacted with $Na_2Fe(CO)_4$ in THF under reflux followed by acidic treatment with 40% H_3PO_4 to yield the new cluster $HRuFeMo(\mu_3\text{-}Se)(CO)_8C_5H_4C(O)CH_3$ **8**. Cluster **3** and **5** have been solved by single-crystal X-ray diffraction. Crystal data for cluster **3**: orthorhombic, space group *Pbca*, $a = 26.387(3)$ Å, $b = 18.273(2)$ Å, $c = 15.963(2)$ Å, $V = 7696(2)$ Å^3, $Z = 16$ and $R = 0.023$, $wR = 0.027$. Crystal data for cluster **5**: triclinic, space group $P\bar{1}$, $a = 8.200(2)$ Å, $b = 19.631(7)$ Å, $c = 7.997(2)$ Å, $\alpha = 92.50(2)°$, $\beta = 108.66(2)°$, $\gamma = 88.97(2)°$, $V = 1218.5(6)$ Å^3, $Z = 2$ and $R = 0.054$, $wR = 0.077$.

Keywords: Transition metal; Cluster complex; Chiral; Crystal structure

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1. Introduction

Intense interest in transition-metal clusters continues because they represent possible conceptual bridges between homogeneous and heterogeneous catalysts moreover also because they represent synthetic challenges. The use of elements of Group 16 of the Periodic Table as single atom ligands for cluster growth and stabilization of the metal core are now well established [1]. In recent years, the increased use of tellurium for this purpose has indicted that differences exist in the behavior of Te-bridged clusters from that containing bridging S atom [2]. There is an increasing interest in the use of Se-bridged clusters. Many reactions of $SeFe_2(CO)_6$ and $Se_2Fe_3(CO)_9$ have been reported [3]; however, there was very little work concerning the selenium–ruthenium mixed-metal clusters. We have not found the X-ray structure of the clusters containing tetrahedral core RuCoMSe before our work, although the synthetic method of $SeRuCoMoC_5H_5(CO)_9$ has been reported by Vahrenkamp [4]. In this paper, the synthesis, characterization and reactions of this novel type of cluster complexes were reported.

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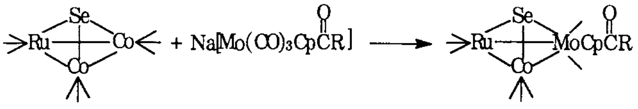
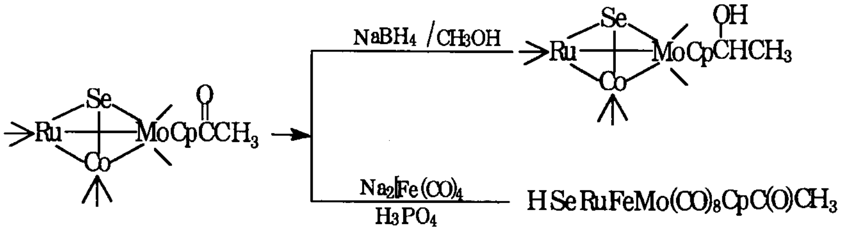
2. Results and discussion

2.1. The chemistry starting from the monoanions $[Mo(CO)_3(\eta^5\text{-}C_5H_4)C(O)R]^-$ *[R=H,* CH_3*,* C_6H_5*,* $C_6H_4C(O)OCH_3$*] (**I**). Preparation of **2–5***



R = H **2**, CH_3 **3**, C_6H_5 **4**, $C_6H_5C(O)OCH_3$ **5**

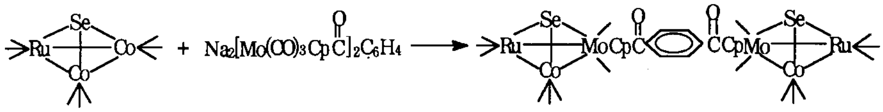
Functionally substituted cyclopentadienyl tricarbonyl group 16 metal anions $[Mo(CO)_3(\eta^5\text{-}C_5H_4)C(O)R]^-$ were proved to be important in the synthesis of organometallic and metal cluster complexes containing the structure unit $Mo(CO)_3(\eta^5\text{-}C_5H_4)R]^-$ [5]. Now we have found an additional use of the monoanions in the synthesis of tetrahedral RuCoMoSe core cluster complexes. The reaction of cluster **1** with $[Mo(CO)_3(\eta^5\text{-}C_5H_4)C(O)R]^-$ in refluxing THF afforded a moderate yield of clusters $RuCoMo(\mu_3\text{-}Se)(CO)_8C_5H_4C(O)R$ [R = H **2**, CH_3 **3**, C_6H_5 **4**, $C_6H_4C(O)OCH_3$ **5**] as shown in Scheme 1. These air-stable clusters are black in solid and red-purple in solution. Data of C/H analysis, IR, ^{1}H-NMR, ^{13}C-NMR and MS of them were consistent with the expected structure presented in Fig. 1. The results showed that one of the $Co(CO)_3$ unit in cluster **1** could be exchange by isoelectronic $Mo(CO)_2C_5H_4C(O)R$ unit and gave the new chiral skeleton clusters **2**–**5**.



Cluster **3** could be reduced by $NaBH_4$ in methanol at room temperature to the secondary alcohol cluster $RuCoMo(\mu_3\text{-}Se)(CO)_8C_5H_4CH(OH)CH_3$ **7** in high yield, and we attempted to reduce cluster **3** with $LiAlH_4/AlCl_3$ in CH_2Cl_2 but failed, While it was decomposed by this stronger reduction agent. The reaction of **3** with $Na_2[Fe(CO)_4]$ in refluxing THF, followed by acid treatment of the reaction mixture by deoxygenated 40% H_3PO_4, gave a new air-sensitive cluster $HRuFeMo(\mu_3\text{-}Se)(CO)_8C_5H_4C(O)CH_3$ **8** in low yield, which was confirmed by C/H analysis, IR and ^{1}H-NMR spectra. The results show that the metal fragment $Co(CO)_3$ in **3** could be exchanged by $HFe(CO)_3$ through thermal reaction. The H atom in cluster **8** may be bonded to the RuFeCo triangular metal base as a face bridging position as described previously [6] (See Scheme 1).

*2.2. Characterization of **2–5** and **7–8***

All the clusters showed a large number of stronger terminal carbonyl absorption bands located at 2097–1849 cm^{-1} in IR spectra. The IR spectra of **2**–**5** and **7** also showed corresponding C=O absorption at 1653–1688 cm^{-1}, and the absorption of hydroxyl group of **7** appeared at around 3379 cm^{-1}. For the ^{1}H-NMR assignment of the clusters, proton chemical shifts of the substituted cyclopentadienyl groups appeared downfield than the unsubstituted cyclopentadienyl [7], since formyl, acetyl and ester carbonyls are well known electron-withdrawing groups. It is interesting that the ^{1}H-NMR spectra of cyclopentadienyl in the clusters showed four singlets at 5.22–6.05 ppm, all the protons in cyclopentadienyl are non-equivalent, we believe that was caused by the chirality of the tetrahedral cluster core RuMMoSe (M = Co, Fe). The same reason there are five Cp Carbon signals quoted for the ^{13}C-NMR spectra of clusters **2**, **3**, and **5**. The proton bonded to metal atoms in **8** appears at − 16.67 ppm. The FAB MS spectra of clusters **2**, **3**, **5** do not contain molecular ion peaks but show peaks of species produced by substantial release of carbonyls from the clusters.



Cluster 6

Scheme 1.

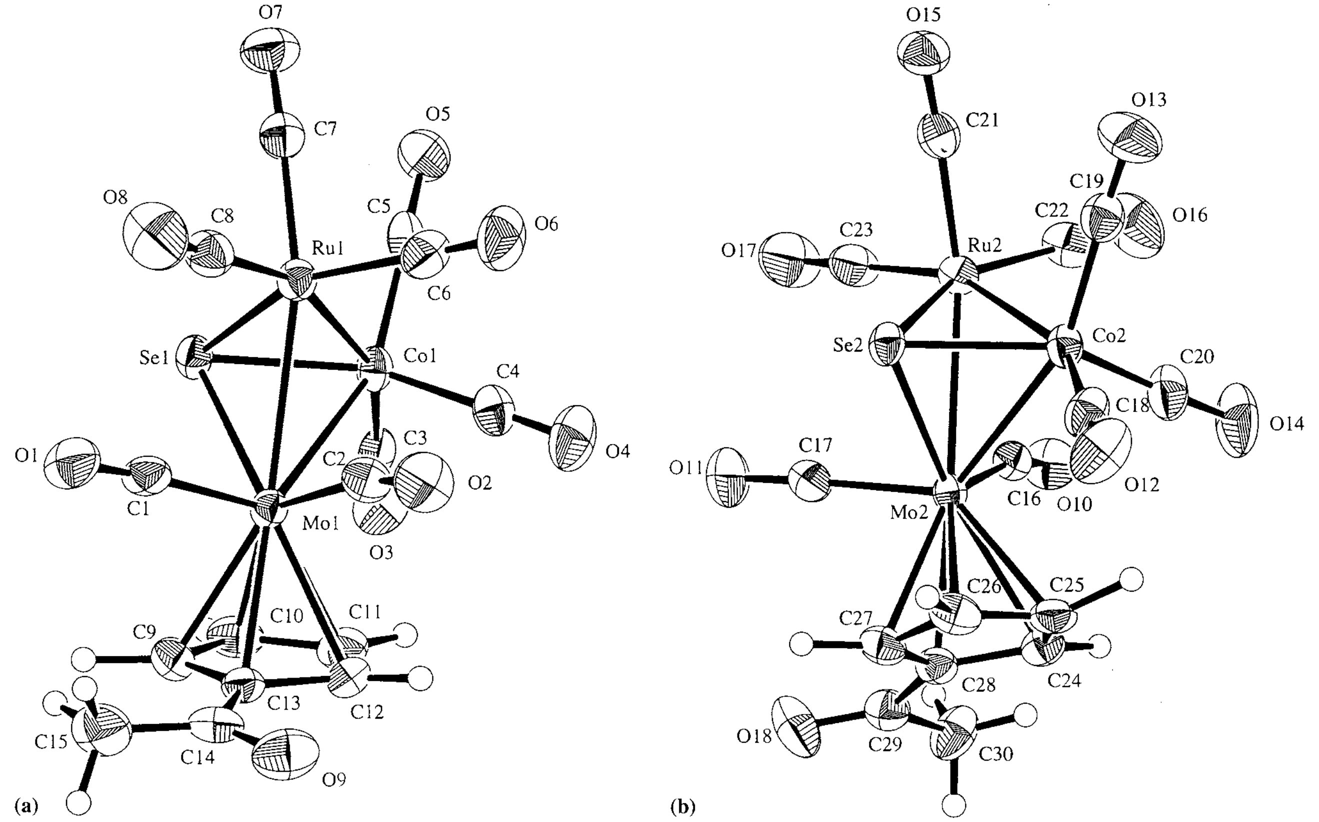


Fig. 1. Perspective view of the molecular unit of **3**.

*2.3. The chemistry generated from the bridging dianions – Mo(CO)$_3$[(η^5-C$_5$H$_4$)C(O)C$_6$H$_4$C(O)(η^5-C$_5$H$_4$)](CO)$_3$Mo – (**II**). Preparation of the cluster **6***

The novel metal exchange reagent of **II** was formed in refluxing THF by the reaction of two equivalents of $Mo(CO)_6$ with $[NaC_5H_4C(O)]_2C_6H_4$ obtained the reaction of NaC_5H_4 and dimethy terephthalate in THF. Reaction of two molecules **1** with **II** in reluxing THF gave a new two-tetrahedral core cluster (μ_3-Se)$(CO)_8(\eta^5 - C_5H_4)C(O)C_6H_4C(O)(\eta^5 - C_5H_4)$RuCoMo $(CO)_8(\mu_3$-Se) **6**. The formula was confirmed by the elemental analysis and FAB MS. Cluster **6** is believed to be isostructural to the cluster [RuCoW(μ_3-S) $(CO)_8(\eta^5$-$C_5H_4)C(O)]_2C_6H_4$ based on the similar spectra of ^{1}H-NMR and IR absorption patterns, the crystal structure of which was determined by X-ray diffraction [8]. Cluster **6** is made of two identical tetrahedral skeletons subclusters RuCoMoSe, which connected with the bridge of η^5-$C_5H_4C(O)C_6H_4C(O)C_5H_4$-$\eta^5$ ligand through Mo atoms (Scheme 1). No cluster complexes containing two RuCoMSe subcluster cores were reported, although a few such single cluster complexes have appeared in literature [4].

*2.4. Structure of **3** and **5***

Cluster **3** and **5** were determined by X-ray structure analysis. Crystal data were collected in Table 1. Tables 2 and 3 give the atomic coordinates, selected bond length and angles are listed in Tables 4 and 5. Unexpectedly, the structure of **3** contains two isomeric molecules (A and B) in a unit cell, (Fig. 1), the tetrahedral core of each molecule in **3** is composed of four elements that are Ru, Co, Mo and Se. The acute angles in tetrahedral geometry of **3** about the basal atoms range from 53.07 to 64.62°, and those about the selenium atom average 69.98°, which deviates a bit from a perfect tetrahedral geometry. The electron count for the **3** is conventional. The chiral cluster **3** is structurally related to known clusters $SFeCoMo(CO)_8C_5H_4C(O)R$ [R = H, CH_3, C_2H_3O, $C_6H_4CO_2CH_3$] [9,10]. It is isostructural and isoelectronic with them.

The cluster **5** shown in Fig. 2 exhibits a same RuCoMoSe tetrahedron geometry as in cluster **3**. The tetrahedral core in **5** also contains a slightly distorted triangular RuCoMo capped by a selenium ligand with Se–Ru = 2.455(2), Se–Co = 2.296(2) and Se–Mo = 2.538(2) Å. Six of the CO ligands bond terminally to the Ru and Co atoms, while for the Mo atom the remaining CO ligands are slightly nonlinear. Cluster **5** contains total of 48 electrons and it is electronically saturated.

3. Experimental details

All reactions were carried out under an atmosphere of pure nitrogen by using standard Schlenk techniques. All solvents were thoroughly dried and distilled immediately before use. IR spectra were recorded on a Nicokel FT-IR 10D spectrophotometer, ^{1}H-NMR spectra were recorded on a Brucker AM-300 MHz spectrometer, elemental analyses and FAB MS were performed on an 1106-type analyzer and Finnigan MAT 8430 respectively. $Mo(CO)_6$ was bought from

Table 1
Crystal and refinement data for the clusters **3** and **5**

Cluster	**3**	**5**
Formula	$C_{30}H_{14}O_{18}Ru_2Co_2Mo_2Se_2$	$C_{22}H_{11}O_{11}RuCoMoSe$
M_r	1332.24	786.23
System	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
$F(000)$	5056.00	756.00
a (Å)	26.387(3)	8.200(2)
b (Å)	18.273(2)	19.631(7)
c (Å)	15.963(2)	7.997(2)
α (°)		92.50(2)
β (°)		108.66(2)
γ (°)		88.97(2)
V (Å^3)	7696(2)	1218.5(6)
Z	16	2
D_{calc} (g cm^{-3})	2.299	2.143
μ(Mo–K$_\alpha$) cm^{-1}	42.05	33.44
Crystal dimensions	0.20 × 0.20 × 0.30 mm	0.20 × 0.20 × 0.30 mm
Temperature (°C)	20.0	20.0
Scan type	$\omega-2\theta$	$\omega-2\theta$
Absorption correction	Lorentz-polarization	Lorentz-polarization
$2\theta_{max}$ (°)	50.0	45.5
No. of reflections measured	6138	3454
No. observations [$I > 3.00(s)$]	4599	2644
No. variables	506	335
Reflections/parameter ratio	9.09	7.89
R[a]	0.023	0.054
wR[b]	0.027	0.077
Goodness-of-fit indicator	1.41	2.76
Max peak in final diff. map (e Å^{-3})	0.42	2.82
Min peak in final diff. map (e Å^{-3})	−0.41	−1.24

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.
[b] $wR = [\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2]^{1/2}$.

Table 2
Non-hydrogen atomic coordinates and isotropic thermal parameters for **3**

Atom	x	y	z	B_{eq}
Ru(1)	0.99099(1)	0.19796(2)	0.12405(3)	2.795(9)
Ru(2)	0.77413(1)	0.02714(2)	0.20465(3)	2.796(9)
Mo(1)	0.99563(2)	0.08674(2)	0.25385(3)	2.489(9)
Mo(2)	0.77187(1)	−0.12334(2)	0.26076(3)	2.312(9)
Se(1)	0.95560(2)	0.07490(3)	0.11253(3)	2.72(1)
Se(2)	0.84773(2)	−0.05437(3)	0.20858(3)	2.84(1)
Co(1)	1.04304(2)	0.07631(3)	0.09840(4)	2.67(1)
Co(2)	0.79361(2)	−0.07988(4)	0.09819(4)	2.84(1)
O(1)	0.8932(1)	0.1620(2)	0.3002(2)	5.1(1)
O(2)	1.0565(2)	0.2229(2)	0.3160(3)	5.4(1)
O(3)	1.0654(1)	−0.0808(2)	0.0999(2)	4.6(1)
O(4)	1.1357(1)	0.1285(2)	0.1767(3)	5.4(1)
O(5)	1.0557(1)	0.1164(2)	−0.0781(2)	4.59(10)
O(6)	1.0777(1)	0.3070(2)	0.1427(3)	6.0(1)
O(7)	0.9663(1)	0.2388(2)	−0.0563(2)	4.9(1)
O(8)	0.9119(2)	0.3035(2)	0.1883(3)	6.7(1)
O(9)	1.0092(2)	0.1134(2)	0.5055(3)	5.6(1)
O(10)	0.6646(1)	−0.0544(2)	0.2742(2)	4.38(10)
O(11)	0.8034(2)	−0.0540(2)	0.4334(2)	5.7(1)
O(12)	0.8453(2)	−0.2095(2)	0.0312(3)	5.9(1)
O(13)	0.8189(2)	0.0249(2)	−0.0338(3)	6.4(1)
O(14)	0.6872(1)	−0.1114(3)	0.0652(3)	6.6(1)
O(15)	0.8348(1)	0.1503(2)	0.1266(2)	4.42(10)
O(16)	0.6723(1)	0.0779(3)	0.1364(3)	6.4(1)
O(17)	0.7661(2)	0.1081(2)	0.3698(3)	6.3(1)
O(18)	0.7431(1)	−0.2092(2)	0.4859(2)	5.3(1)
C(1)	0.9313(2)	0.1376(3)	0.2815(3)	3.3(1)
C(2)	1.0334(2)	0.1767(3)	0.2850(3)	3.7(1)
C(3)	1.0561(2)	−0.0201(3)	0.0987(3)	3.1(1)
C(4)	1.0982(2)	0.1100(3)	0.1472(3)	3.5(1)
C(5)	1.0512(2)	0.1010(3)	−0.0096(4)	3.3(1)
C(6)	1.0456(2)	0.2667(3)	0.1366(4)	4.0(1)
C(7)	0.9765(2)	0.2240(3)	0.0109(4)	3.4(1)
C(8)	0.9416(2)	0.2632(3)	0.1645(4)	3.9(1)
C(9)	0.9633(2)	−0.0050(3)	0.3359(3)	3.3(1)
C(10)	0.9955(2)	−0.0394(3)	0.2781(3)	3.8(1)
C(11)	1.0456(2)	−0.0157(3)	0.2926(3)	3.9(1)
C(12)	1.0449(2)	0.0345(3)	0.3596(3)	3.7(1)
C(13)	0.9932(2)	0.0412(3)	0.3880(3)	2.8(1)
C(14)	0.9775(2)	0.0833(3)	0.4632(3)	4.0(1)
C(15)	0.9236(2)	0.0845(3)	0.4855(4)	5.4(2)
C(16)	0.7062(2)	−0.0712(3)	0.2649(3)	2.9(1)
C(17)	0.7911(2)	−0.0773(3)	0.3704(3)	3.5(1)
C(18)	0.8251(2)	−0.1606(3)	0.0578(3)	3.9(1)
C(19)	0.8093(2)	−0.0146(3)	0.0190(3)	3.8(1)
C(20)	0.7283(2)	−0.0990(3)	0.0804(3)	4.2(1)
C(21)	0.8116(2)	0.1044(3)	0.1540(3)	3.4(1)
C(22)	0.7095(2)	0.0587(3)	0.1626(4)	4.0(1)
C(23)	0.7690(2)	0.0777(3)	0.3074(4)	4.0(1)
C(24)	0.7215(2)	−0.2277(2)	0.2587(3)	3.1(1)
C(25)	0.7605(2)	−0.2413(3)	0.2012(3)	3.5(1)
C(26)	0.8075(2)	−0.2402(3)	0.2432(3)	3.6(1)
C(27)	0.7976(2)	−0.2275(3)	0.3289(3)	3.3(1)
C(28)	0.7435(2)	−0.2190(2)	0.3397(3)	2.9(1)
C(29)	0.7184(2)	−0.2117(3)	0.4225(3)	3.4(1)
C(30)	0.6625(2)	−0.2086(3)	0.4235(4)	4.4(1)

$$B_{eq} = 8/3\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$$

Aldrich, $Co_2(CO)_8$ [11], $Ru_3(CO)_{12}$ [12], (μ_3-Se)$RuCo_2(CO)_9$ [13], $RC(O)C_5H_4Na$ [R = H, CH_3, C_6H_5, $C_6H_4C(O)OCH_3$] [14] were prepared according to the literature.

3.0.1. Preparation of **2**, **3**, **4** and **5**

$Mo(CO)_6$ (264 mg, 1.0 mmol) was added to a solution of sodium formylcyclopentadienide (116 mg, 1.0 mmol) in THF (20 ml). The mixture was refluxed for 16 h and cooled to room temperature. Then 550 mg (1.0 mmol) of cluster **1** was added and the mixture was stirred at 60°C for 2 h. The solvent was removed under vacuum, the residue was extracted by minimum amount of CH_2Cl_2 and the products were chromatographed on a 2.5 × 20 cm silica gel column using CH_2Cl_2/hexane as eluent. The main product of **2** (340 mg, 52%) was obtained as black solid (m.p. 84–85°C). Anal. Calcd for $C_{14}H_5O_9RuCoMoSe$: C, 25.75; H, 0.77. Found: C, 25.89; H, 0.81. IR(KBr disk) 2086vs, 2037vs, 2024vs, 1997vs, 1968vs, 1947vs, 1910vs, 1866s, 1653vs cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 5.55, 5.66, 5.84, 5.90 (s, 4H, C_5H_4); δ 9.70 (s, 1H, CHO). ^{13}C-NMR ($CDCl_3$) δ 89.22, 89.05, 93.46, 94.97, 97.33, (C_5H_4); δ 184.92; ($C=O$), δ 210 (t-CO).

Table 3
Non-hydrogen atomic coordinates and isotropic thermal parameters for **5**

Atom	*x*	*y*	*z*	B_{eq}
Ru	0.3269(1)	0.83175(5)	0.0957(1)	3.06(2)
Mo	0.0376(1)	0.78602(5)	−0.2038(1)	2.61(2)
Se	0.0305(1)	0.87347(7)	0.0371(2)	3.41(3)
Co	0.1629(2)	0.91826(8)	−0.1464(2)	3.46(4)
O(1)	0.506(1)	0.9412(6)	0.365(1)	7.3(3)
O(2)	0.658(1)	0.7878(6)	0.034(1)	6.4(3)
O(3)	0.364(1)	0.7299(6)	0.378(1)	6.1(3)
O(4)	0.358(1)	0.7075(5)	−0.236(1)	4.8(2)
O(5)	0.014(1)	0.6834(5)	0.078(1)	5.2(3)
O(6)	−0.131(1)	0.9912(5)	−0.384(1)	5.9(3)
O(7)	0.347(1)	1.0374(5)	0.050(2)	6.3(3)
O(8)	0.371(1)	0.8724(6)	−0.366(1)	6.8(3)
O(9)	0.033(1)	0.6148(5)	−0.455(1)	5.2(3)
O(10)	−0.380(2)	0.3828(7)	−0.095(2)	9.2(5)
O(11)	−0.617(1)	0.4457(5)	−0.191(1)	5.0(3)
C(1)	0.437(2)	0.9006(7)	0.264(2)	4.2(3)
C(2)	0.534(2)	0.8044(8)	0.055(2)	4.4(3)
C(3)	0.350(1)	0.7674(7)	0.267(1)	3.5(3)
C(4)	0.252(1)	0.7393(6)	−0.210(1)	3.0(3)
C(5)	0.032(1)	0.7220(7)	−0.020(2)	3.4(3)
C(6)	−0.017(2)	0.9621(7)	−0.292(2)	4.6(3)
C(7)	0.276(2)	0.9899(7)	−0.024(2)	4.5(3)
C(8)	0.2906(9)	0.8785(5)	−0.253(1)	1.0(2)
C(9)	−0.058(2)	0.7556(7)	−0.504(1)	3.5(3)
C(10)	−0.131(2)	0.8196(7)	−0.487(2)	4.0(3)
C(11)	−0.238(1)	0.8170(6)	−0.386(2)	3.7(3)
C(12)	−0.236(1)	0.7483(6)	−0.334(1)	3.4(3)
C(13)	−0.126(1)	0.7091(6)	−0.409(1)	3.1(3)
C(14)	−0.085(2)	0.6357(6)	−0.404(1)	3.4(3)
C(15)	−0.187(2)	0.5850(6)	−0.341(1)	3.1(3)
C(16)	−0.360(2)	0.5940(6)	−0.358(1)	3.6(3)
C(17)	−0.450(2)	0.5458(6)	−0.307(1)	3.4(3)
C(18)	−0.364(2)	0.4881(6)	−0.226(1)	3.8(3)
C(19)	−0.192(2)	0.4789(7)	−0.214(2)	5.4(4)
C(20)	−0.105(2)	0.5278(7)	−0.270(2)	5.0(4)
C(21)	−0.452(2)	0.4324(7)	−0.166(2)	4.91(4)
C(22)	−0.704(2)	0.3905(9)	−0.146(2)	6.4(5)

$$B_{eq} = 8/3\pi^2[u_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$$

Procedures for the preparation of **3**, **4** and **5** were similar to that for the preparation of **2**.

3. (364 mg, 54%) m.p. 109–110°C. Anal. Calcd for $C_{15}O_9H_7RuCoMo$: C, 27.05; H, 1.05. Found: C, 27.11; H, 1.08. IR (KBr disk) 2079vs, 2048vs, 2038vs, 2014vs, 1991vs, 1893vs, 1854m, 1686m. ^{1}H-NMR ($CDCl_3$) δ 2.40 (s, 3H, CH_3); δ 5.46, 5.56, 5.67, 5.88 (s, 4H, C_5H_4). ^{13}C-NMR ($CDCl_3$) δ 27.31 (CH_3), δ 89.49, 89.98, 92.89, 95.02, 97.85 (C_5H_4); 198.82 ($C=O$), 215 (t-CO). MS (FAB Ru^{103}) 639 (M − CO), 611 (M − 2CO), 583 (M − 3CO), 499 (M − 6CO).

4. (320 mg, 44%) Anal. Calc. For $C_{20}H_9O_9RuCoMoSe$: C, 32.99; H, 1.24. Found: C, 33.04, H, 1.26. IR (KBr disk) 2081vs, 2046vs, 2004vs, 1979vs, 1887s, 1656m. ^{1}H-NMR ($CDCl_3$) δ 5.54, 5.69, 5.86, 6.05 (s, 4H, C_5H_4); δ 7.47–7.82 (m, 5H, C_6H_5).

5. (370 mg, 47%) Anal. Calc. For $C_{22}H_{11}O_{11}RuCoMoSe$: C, 33.61; H, 1.40. Found: C, 33.66; H, 1.44. IR (KBr disk) 2080vs, 2039vs, 1998vs, 1919m, 1726m, 1657m. ^{1}H-NMR ($CDCl_3$) δ 3.96 (s, 3H, CH_3), δ 5.30, 5.47, 5.71, 5.98 (s, 4H, C_5H_4), δ 7.83–8.08 (m, 4H, C_6H_4). ^{13}C-NMR ($CDCl_3$) δ 52.56 (CH_3); 90.58, 91.78, 93.07, 94.14, 97.88 (C_5H_4); 128.36, 130.00, 133.90, 141.30 (C_6H_4); 166.10, 189.41 ($C=O$); 229.6 (t-CO). MS (FAB Ru^{103}) 758 (M − CO), 730 (M − 2CO), 674 (M − 4CO), 646 (M − 5CO).

3.0.2. Preparation of **6**

The mixture of $Mo(CO)_6$ (264 mg, 1.0 mmol) and $[NaC_5H_4C(O)]_2C_6H_4$ (153 mg, 0.5 mmol) were dissolved in 20 ml THF. The procedure was similar to that for the preparation of cluster **2**, and 210 mg (30%) of **6** as a black solid of was obtained. Anal. Calcd. For $C_{34}H_{12}O_{18}Ru_2Co_2Mo_2Se$: C, 29.63; H, 0.87. Found: C, 29.72; H, 0.91. IR (KBr disk) 2082vs, 2039vs, 1999vs, 1873m, 1659m. cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 5.29, 5.46, 5.75, 5.96 (s, 8H, $2C_5H_4$), δ 7.88 (s, 4H, C_6H_4).

3.0.3. Reduction of **3**

7.6 mg (0.2 mmol) of $NaBH_4$ was added to a solution of **3** (65 mg, 0.1 mmol) in 8 ml MeOH. The

Table 4
Selected bond lengths (Å) and angles (°) for **3**

Molecule A					
Ru(1)–Mo(1)	2.9048(6)	Ru(1)–Se(1)	2.4417(6)	Ru(1)–Co(1)	2.6448(7)
Ru(1)–C(6)	1.922(6)	Ru(1)–C(7)	1.906(6)	Ru(1)–C(8)	1.880(6)
Mo(1)–Se(1)	2.5002(6)	Mo(1)–Co(1)	2.7854(8)	Mo(1)–C(1)	1.984(5)
Mo(1)–C(2)	1.986(6)	Se(1)–Co(1)	2.3184(8)	Co(1)–C(3)	1.795(6)
Co(1)–C(4)	1.762(5)	Co(1)–C(5)	1.795(6)	C(13)–C(14)	1.485(7)
C(14)–C(15)	1.467(8)	Mo(1)–Cp(1)	−1.988	C–O(tco, av)	1.140
Mo(1)–Ru(1)–Se(1)	54.94(2)	Mo(1)–Ru(1)–Co(1)	60.03(2)	Mo(1)–Ru(1)–C(6)	110.6(2)
Mo(1)–Ru(1)–C(7)	149.2(2)	Mo(1)–Ru(1)–C(8)	103.1(2)	Se(1)–Ru(1)–Co(1)	54.05(2)
Se(1)–Ru(1)–C(6)	153.7(2)	Se(1)–Ru(1)–C(7)	94.7(2)	Se(1)–Ru(1)–C(8)	110.1(2)
Co(1)–Ru(1)–C(6)	100.2(2)	Co(1)–Ru(1)–C(7)	99.7(2)	Co(1)–Ru(1)–C(8)	161.0(2)
Ru(1)–Mo(1)–Se(1)	53.07(2)	Ru(1)–Mo(1)–Co(1)	55.35(2)	Ru(1)–Mo(1)–C(1)	78.2(1)
Ru(1)–Mo(1)–C(2)	67.7(2)	Se(1)–Mo(1)–Co(1)	51.69(2)	Se(1)–Mo(1)–C(1)	83.1(1)
Se(1)–Mo(1)–C(2)	120.7(2)	Co(1)–Mo(1)–C(1)	127.9(1)	Co(1)–Mo(1)–C(2)	93.1(1)
Ru(1)–Se(1)–Mo(1)	71.99(2)	Ru(1)–Se(1)–Co(1)	67.45(2)	Mo(1)–Se(1)–Co(1)	70.51(2)
Ru(1)–Co(1)–Mo(1)	64.62(2)	Ru(1)–Co(1)–Se(1)	58.50(2)	Ru(1)–Co(1)–C(3)	157.5(2)
Ru(1)–Co(1)–C(4)	93.9(2)	Ru(1)–Co(1)–C(5)	90.0(2)	Mo(1)–Co(1)–Se(1)	57.80(2)
Mo(1)–Co(1)–C(3)	98.7(2)	Mo(1)–Co(1)–C(4)	87.3(2)	Mo(1)–Co(1)–C(5)	153.2(2)
Se(1)–Co(1)–C(3)	100.4(1)	Se(1)–Co(1)–C(4)	141.5(2)	Se(1)–Co(1)–C(5)	102.5(1)
Molecule B					
Ru(2)–Mo(2)	2.8924(6)	Ru(2)–Se(2)	2.4483(6)	Ru(2)–Co(2)	2.4612(8)
Ru(2)–C(21)	1.905(6)	Ru(2)–C(22)	1.921(6)	Ru(2)–C(23)	1.887(6)
Mo(2)–Se(2)	2.5078(6)	Mo(2)–Co(2)	2.7739(8)	Mo(2)–C(16)	1.977(5)
Mo(2)–C(17)	2.007(6)	Se(2)–Co(2)	2.3156(8)	Co(2)–C(18)	1.812(6)
Co(2)–C(19)	1.786(6)	Co(2)–C(20)	1.781(5)	C(28)–C(29)	1.485(7)
C(29)–C(30)	1.478(7)	Mo(2)–Cp(2)	1.985	C–O(tco, av)	1.135
Mo(2)–Ru(2)–Se(2)	55.26(2)	Mo(2)–Ru(2)–Co(2)	59.96(2)	Mo(2)–Ru(2)–C(21)	147.9(1)
Mo(2)–Ru(2)–C(22)	112.1(2)	Mo(2)–Ru(2)–C(23)	101.3(2)	Se(2)–Ru(2)–Co(2)	53.97(2)
Se(2)–Ru(2)–C(21)	92.9(1)	Se(2)–Ru(2)–C(22)	153.6(2)	Se(2)–Ru(2)–C(23)	109.4(2)
Co(2)–Ru(2)–C(21)	100.1(2)	Co(2)–Ru(2)–C(22)	99.8(2)	Co(2)–Ru(2)–C(23)	159.3(2)
Ru(2)–Mo(2)–Se(2)	53.34(2)	Ru(2)–Mo(2)–Co(2)	55.52(2)	Ru(2)–Mo(2)–C(16)	64.6(1)
Ru(2)–Mo(2)–C(17)	82.3(1)	Se(2)–Mo(2)–Co(2)	51.71(2)	Se(2)–Mo(2)–C(16)	117.9(1)
Se(2)–Mo(2)–C(17)	83.0(1)	Co(2)–Mo(2)–C(16)	94.3(1)	Co(2)–Mo(2)–C(17)	130.1(1)
Ru(2)–Se(2)–Mo(2)	71.40(2)	Ru(2)–Se(2)–Co(2)	67.28(2)	Mo(2)–Se(2)–Co(2)	70.08(2)
Ru(2)–Co(2)–Mo(2)	64.52(2)	Ru(2)–Co(2)–Se(2)	58.76(2)	Ru(2)–Co(2)–C(18)	157.1(2)
Ru(2)–Co(2)–C(19)	90.4(2)	Ru(2)–Co(2)–C(20)	93.4(2)	Mo(2)–Co(2)–Se(2)	58.21(2)
Mo(2)–Co(2)–C(18)	101.2(2)	Mo(2)–Co(2)–C(19)	154.3(2)	Mo(2)–Co(2)–C(20)	83.9(2)
Se(2)–Co(2)–C(18)	98.8(2)	Se(2)–Co(2)–C(19)	105.1(2)	Se(2)–Co(2)–C(20)	139.2(2)

mixture was stirred at room temperature for 9 h, then separated on silica gel column. 50 mg (85%) of cluster **7** as a brown-red solid was obtained. Anal Calcd. for $C_{15}H_9O_9RuCoMo$: C, 30.58; H, 1.53. Found: C, 30.36; H, 1.69. IR (KBr disk) 3379m, 2082vs, 2076vs, 1991vs, 1773vs, 1893vs. ^1H-NMR ($CDCl_3$) δ 1.46 (s, br, 3H, CH_3); δ 2.13 (s, H, OH); δ 4.59 (s, br, 1H, CH); δ 5.22, 5.33, 5.44, 5.54 (s, 4H, C_5H_4).

*3.0.4. Preparation of **8***

A mixture of $Na_2[Fe(CO)_4]$ (31.25 mg, 0.15 mmol) and cluster **3** (66.5 mg, 0.1 mmol) was dissolved in 20 ml THF. The mixture was refluxed for 6 h and cooled to room temperature, the solvent was removed in vacuo, and the resulting residue was acidified with 12 ml deoxygenated 40% H_3PO_4 in 10 min. The mixture was extracted with CH_2Cl_2. The organic layer was concentrated in vacuo, and was chromatographed on a 2.5×20 cm silica gel column using CH_2Cl_2/hexane as eluent. The main product **8** (black solid, 17 mg, 25%) and a trace of $Fe_3(CO)_{12}$ were obtained. Anal Calcd for $C_{15}H_8O_9RuFeMoSe$: C, 27.13; H, 1.20. Found: C, 27.09; H, 1.36. IR (KBr disk) 2079vs, 2067vs, 2021vs, 1998vs, 1983vs, 1849vs, 1685s. ^1H-NMR ($CDCl_3$) δ 2.35 (s, 3H, CH_3); δ 5.24, 5.47, 5.71, 5.94 (q, 4H, C_5H_4); δ 16.58 (s, 1H, H − M).

*3.0.5. X-ray structure characterization of **2** and **5***

Crystals of **2** suitable for diffraction analysis were grown from hexane/CH_2Cl_2 (1:1) solution and those of **5** suitable for diffraction analysis were grown from CH_2Cl_2 solution at − 18°C. The crystals were mounted on a glass fiber. An empirical absorption of **3** correction based on azimuthal scans of several

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

Ru–Mo	2.902(1)	Ru–Se	2.455(2)	Ru–Co	2.642(2)
Ru–C(1)	1.89(1)	Ru–C(2)	1.89(1)	Ru–C(3)	1.87(1)
Mo–Se	2.538(2)	Mo–Co	2.774(2)	Mo–C(4)	1.98(1)
Mo–C(5)	1.99(1)	Mo–Cp	1.981	Se–Co	2.296(2)
Co–C(6)	1.79(1)	Co–C(7)	1.77(1)	Co–C(8)	1.706(7)
O(9)–C(14)	1.22(1)	C(13)–C(14)	1.47(2)	C(14)–C(15)	1.51(2)
C(18)–C(21)	1.50(2)	C–O(tco, av)	1.159		
Mo–Ru–Se	55.80(4)	Mo–Ru–Co	59.83(4)	Mo–Ru–C(1)	149.9(4)
Mo–Ru–C(2)	108.9(4)	Mo–Ru–C(3)	105.5(4)	Se–Ru–Co	53.39(5)
Se–Ru–C(1)	97.4(4)	Se–Ru–C(2)	159.8(4)	Se–Ru–C(3)	103.4(4)
Co–Ru–C(1)	94.3(4)	Co–Ru–C(2)	108.8(4)	Co–Ru–C(3)	156.4(4)
Ru–Mo–Se	53.16(4)	Ru–Mo–Co	55.42(2)	Ru–Mo–C(4)	69.6(3)
Ru–Mo–C(5)	77.7(3)	Se–Mo–Co	50.98(5)	Se–Mo–C(4)	122.8(3)
Se–Mo–C(5)	81.7(3)	Co–Mo–C(4)	97.9(4)	Co–Mo–C(5)	126.5(3)
Ru–Se–Mo	71.05(4)	Ru–Se–Co	67.46(5)	Mo–Se–Co	69.84(5)
Ru–Co–Mo	64.75(5)	Ru–Co–Se	59.15(5)	Ru–Co–C(6)	157.6(4)
Ru–Co–C(7)	93.5(4)	Ru–Co–C(8)	80.3(3)	Mo–Co–Se	59.18(5)
Mo–Co–C(6)	99.8(4)	Mo–Co–C(7)	157.0(5)	Mo–Co–C(8)	77.0(3)
Se–Co–C(6)	99.4(4)	Se–Co–C(7)	104.2(5)	Se–Co–C(8)	129.1(3)

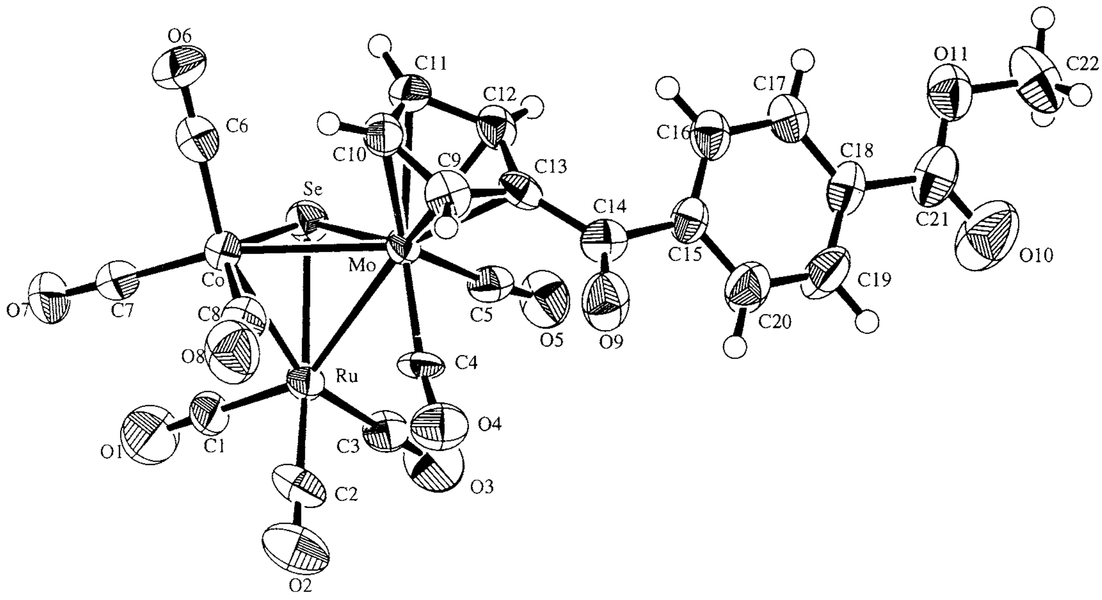


Fig. 2. Molecular structure of **5**.

reflection was applied and the program DIFABS [15] was applied to an empirical absorption of **5**. The data of **3** and **5** were corrected for Lorentz and polarization effects. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo–K_α radiation. A summary of selected crystallographic data for **2** and **5** is given in Table 1. All the data were collected at 20 ± 1°C using the $\omega - 2\theta$ scan techniques. All the structures were solved by direct methods [16] and expanded using Fourier technique [17]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Full-matrix least-squares refinements minimized the function $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = [\sigma^2(F_o)]^{-1} = 4F_o^2[\sigma^2(F_o^2)]^{-2}$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2][Lp]^{-2}$. Neutral atom scattering factors were taken from Cromer and Waber [18]. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

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