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Synthesis, characterization and reactions of cluster complexes containing SeRuCoM (M = Mo or W) core and a functionally substituted cyclopentadienyl ligand

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Abstract

Reactions of monoanions $\{M(CO)_3[\eta^5\text{-}C_5H_4C(O)CH_2CH_2CO_2Me]\}^-$ with $RuCo_2(CO)_9(\mu_3\text{-}Se)$ in THF at 60°C gave two new cluster derivatives $(\mu_3\text{-}Se)CoMRu(CO)_8[\eta^5\text{-}C_5H_4C(O)CH_2CH_2CO_2Me]$ (M = Mo **1**, M = W **2**). Similarly, reactions of dianions $^-\{M(CO)_3[(\eta^5\text{-}C_5H_4)C(O)CH_2CH_2C(O)(\eta^5\text{-}C_5H_4)](CO)_3M\}^-$ with two molecules of $RuCo_2(CO)_9(\mu_3\text{-}Se)$ gave 1,4-succinoyl(biscyclopentadienyl)-bridged double cluster complexes $(\mu_3\text{-}Se)CoMRu(CO)_8[(\eta^5\text{-}C_5H_4)C(O)CH_2CH_2C(O)(\eta^5\text{-}C_5H_4)]CoMRu(CO)_8(\mu_3\text{-}Se)$ (M = Mo **3**, M = W **4**). Treatment of cluster $(\mu_3\text{-}Se)CoMoRu(CO)_8[(\eta^5\text{-}C_5H_4)C(O)Me]$ with ammine derivatives 2,4-dinitrophenylhydrazine, $NH_2NHC(S)NH_2$, (−)-5-(α-phenyl)semioxamazide and L-(+)-menthydrazide, respectively, at room temperature produced four new hydrazone cluster derivatives $(\mu_3\text{-}Se)CoMoRu(CO)_8[\eta^5\text{-}C_5H_4C(NR)Me]$ ($R = NHC_6H_3\text{-}2,4\text{-}(NO_2)_2$ **5**, $R = NHC(S)NH_2$ **6**, $R = NHC(O)C(O)NHCH(Me)(C_6H_5)$ **7**, $R = NHCO_2$-menthyl **8**). However, cluster **1** can only react with 2,4-dinitrophenylhydrazine to give the formation of cluster $(\mu_3\text{-}Se)CoMoRu(CO)_8[\eta^5\text{-}C_5H_4C(NR)CH_2CH_2CO_2Me]$ ($R = NHC_6H_3\text{-}2,4\text{-}(NO_2)_2$ **9**) under similar condition. Although, two kinds of optically active groups have been introduced into cluster $(\mu_3\text{-}Se)CoMoRu(CO)_8[(\eta^5\text{-}C_5H_4)C(O)Me]$, the mixture of diastereoisomers could not be separated by silica gel chromatography. The ^{13}C-NMR spectra showed the presence of a pair of diastereoisomers.

Keywords: Transition metal; Cluster complex; Chiral; Crystal structure; Enantiomeric separation; Diastereoisomers

1. Introduction

Transition metal clusters have been suggested as active catalysts in a variety of homogeneous catalyzed reactions ranging from the oxidation of cyclohexane to adipic acid to the reduction of CO/H_2 to ethylene glycol. However, no unequivocal proof exists that metal clusters themselves serve as the true catalysts. In many cases it is known that fragments of the original clusters are the actual catalytic species. The unambiguous evidence would be the use of a rigid chiral cluster to catalyze an asymmetric reaction with the subsequent isolation of chiral products [1].

In recent years, the syntheses of chiral clusters have been studied extensively and various types of chiral clusters are accessible [2]. The metal exchange procedure, which Richter and Vahrenkamp pioneered [3], proves to be the most efficient and versatile to prepare tetrahedral mixed metal clusters in which each of the four vertices is chemically different.

However, enantiomer separation remains as another major problem [1b]. The cluster as a single pure enantiomer could be obtained by introducing an optically active phosphine into a chiral cluster [4]. But it was found that the cluster diastereoisomer can racemize by an opening–inversion–closing sequence under CO when the auxiliary phosphine is removed [5]. In order to avoid the racemization of the optically active cluster

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resulting from the action of CO on the cluster core, we have described the synthesis and structure of tetrahedral clusters containing aldehyde, ketone or ester in cyclopentadienyl ligand in recent years [6]. The reactivity of functional group in cylcopentadienyl ring could give us some information for the enanitomeric resolution, it is considerably practicable to separate racemic clusters by separating racemic organic compounds. As a continuation of our previous work, four new chiral cluster derivatives containing CoRuSeM (M = Mo or W) core have been prepared and the investigations of clusters' reactions with organic compounds were explored. Two kinds of optically active hydrazides have been introduced into the racemic cluster. Unfortunately, the mixture of diastereoisomers cannot be separated into single pure diastereoisomers. The diastereotopic splitting in the ^{13}C-NMR spectra showed the presence of a pair of diastereoisomers.

2. Experimental

2.1. General details

All reactions were carried out under an atmosphere of pure nitrogen by using standard Schlenk techniques. Hexane and tetrahydrofuran (THF) were dried by sodium, CH_2Cl_2 was distilled from CaH_2, and *N*,*N*-dimethyl formamide (DMF) was dried by molecular sieve. Chromatographic separations were carried out using silica gel columns (160–200 mesh) of varying length. Thin-layer chromatography (TLC) was performed on commercial Merck plates coated with a 0.20 mm layer of silica gel.

Infrared spectra were recorded in NaCl cells on a Nicolet FTIR 10DX spectrophotometer. Spectra of compounds in the solid state were recorded as pressed KBr discs. ^{1}H- and ^{13}C-NMR spectra were recorded on a Brucker AM-400 MHz spectrometer in $CDCl_3$ solvent. Chemical shifts are given on the δ scale relative to $SiMe_4$ (0.0 ppm). Elemental analyses were performed on an 1106-type analyzer.

$Mo(CO)_6$, $W(CO)_6$, $RuCo_2(CO)_9(\mu_3\text{-Se})$ [7], $[\eta^5\text{-}C_5H_4C(O)Me]RuCoMo(CO)_8(\mu_3\text{-Se})$ [6e], $Na[C_5H_4C(O)CH_2CH_2CO_2Me]$ [8], $[Na(C_5H_4C(O)CH_2)]_2$ [9], (−)-5-(α-phenyl)semioxamazide (m.p. 167–169°C, $[\alpha]_D^{25} = -107.6°$, $CHCl_3$, *c* 0.1, *l* 1) [10] and L-(+)-menthydrazide (m.p. 94–95°C, $[\Phi]_D^{25} = +173.3°$, EtOH, *c* 1, *l* 1) [11] were prepared according to literature methods or slight modifications thereof. $NH_2NHC(S)NH_2$ and 2,4-dinitrophenylhydrazine were commercial samples.

2.2. Synthesis of compound **1**

$Mo(CO)_6$ (264 mg, 1.0 mmol) and $Na[C_5H_4C(O)CH_2CH_2CO_2Me]$ (202 mg, 1.0 mmol) were dissolved in THF (25 cm^3). The mixture was refluxed for 16 h and cooled to room temperature (r.t.). Then $RuCo_2(CO)(\mu_3\text{-Se})$ (550 mg, 1.0 mmol) was added, the mixture was heated at 60°C for 2 h with stirring. After THF was removed, the residue was extracted by a small amount of CH_2Cl_2 and transferred to the top of a 2.5 × 25 cm^2 silica gel chromatography column. Elution with CH_2Cl_2–hexane (3:1) afforded the major red band. Removing the solvent and crystallization from CH_2Cl_2–hexane at −20°C gave dark red crystals (348 mg, 47%). Anal. Found: C, 29.23; H, 1.54. Calc. for $C_{18}H_{11}O_{11}CoMoRuSe$: C, 29.29; H, 1.50%. IR (cm^{-1}): ν(CO) 2076vs, 2039vs, 2020vs, 1997vs, 1975s, 1871s and ν(C=O) 1734s, 1684m. ^{1}H-NMR: δ 5.99–5.52 (t, 4H, C_5H_4), 3.69 (s, 3H, CH_3), 2.99(s, 2H, CH2), 2.72 (s, 2H, CH_2).

2.3. Synthesis of compound **2**

$W(CO)_6$ (352 mg, 1.0 mmol) was added to a solution of $Na[C_5H_4C(O)CH_2CH_2CO_2Me]$ (202 mg, 1.0 mmol) in DMF (25 cm^3). The mixture was refluxed for 14 h and cooled to r.t. After the solvent was removed under reduced pressure, cluster $RuCo_2(CO)_9(\mu_3\text{-Se})$ (550 mg, 1.0 mmol) and THF (25 cm^3) were added, then the mixture was stirred at 60°C for 2 h. The solvent was removed in vacuo, the residue was dissolved in a minimum quantity of CH_2Cl_2 and the extract was subjected to a silica gel chromatography column. Elution with CH_2Cl_2–hexane (3:1) afforded the main red band. Condensing the solvent and crystallization at −20°C yielded dark red crystals (349 mg, 42%). Crystals suitable for single-crystal X-ray analysis were grown from CH_2Cl_2–hexane at −20°C. Anal. Found: C, 26.26; H, 1.43. Calc. for $C_{18}H_{11}O_{11}CoRuSeW$: C, 26.17; H, 1.34%. IR (cm^{-1}): ν(CO) 2082vs, 2039vs, 2012vs, 1967s, 1896w, 1826m and ν(C=O) 1730s, 1678m. ^{1}H-NMR: δ 5.91–5.53 (q, 4H, C_5H_4), 3.69 (s, 3H, CH_3), 2.99 (s, 2H, CH_2), 2.75 (s, 2H, CH_2).

2.4. Preparation of linked cluster **3**

$Mo(CO)_6$ (264 mg, 1.0 mmol) and $[NaC_5H_4C(O)CH_2]_2$ (129 mg, 0.5 mmol) were dissolved in THF (25 cm^3). The subsequent procedure was similar to that for the preparation of cluster **1**. 245 mg (37%) of red crystals was obtained. Anal. Found: C, 27.13; H, 0.11. Calc. for $C_{30}H_{12}O_{18}Co_2Mo_2Ru_2Se_2$: C, 27.09; H, 0.09%. IR (cm^{-1}): ν(CO) 2081vs, 2038vs, 2002vs, 1886s and ν(C=O) 1684m. ^{1}H-NMR: δ 5.86–5.41 (q, 8H, C_5H_4), 3.07–2.99 (m, 4H, $2CH_2$).

2.5. Preparation of linked cluster **4**

$W(CO)_6$ (352 mg, 1.0 mmol) and $[NaC_5H_4C(O)CH_2]_2$ (129 mg, 0.5 mmol) were dissolved in DMF (25 cm^3). The subsequent procedure was the same as that for the preparation of cluster **2**, CH_2Cl_2–hexane (3:1) afforded the major dark red band. Crystallization from CH_2Cl_2–hexane at −20°C yielded black red crystals (272 mg, 36%) which were separated by filtration at r.t. Anal. Found: C, 23.92; H, 0.07. Calc. for $C_{30}H_{12}O_{18}Co_2Ru_2Se_2W_2$: C, 23.93; H, 0.08%. IR (cm^{-1}): ν(CO) 2079vs, 2035vs, 1996vs, 1886s and ν(C=O) 1684m. ^{1}H-NMR: δ 5.85–5.48 (q, 8H, C_5H_4), 3.09–2.99 (m, 4H, $2CH_2$).

2.6. Synthesis of compound **5**

1.0 ml of 2,4-dinitrophenylhydrazine solution, prepared by dissolving 2,4-dinitrophenylhydrazine (500 mg) in 98% H_2SO_4 (2.5 cm^3), H_2O (5 cm^3) and EtOH (17.5 cm^3), was added to EtOH solution (25 cm^3) in which cluster [η^5-$C_5H_4C(O)Me$]RuCoMo$(CO)_8(\mu_3$-Se) (50 mg, 0.075 mmol) was dissolved. The mixture was reacted at r.t. for 4 h. The precipitate was filtered out and washed with EtOH. The washed precipitate was extracted with minimum quantity of CH_2Cl_2 and subjected to a silica gel column. Elution with CH_2Cl_2–hexane (1:1) gave the product band. The solution was pumped off and the residue was crystallized from CH_2Cl_2–hexane at −20°C to yield brown solids (32 mg, 50%). Anal. Found: C, 29.77; H, 1.35; N, 6.68. Calc. for $C_{21}H_{11}O_{12}N_4$SeCoRuMo: C, 29.81; H, 1.31; N, 6.62%. IR (cm^{-1}): ν(N−H) 3304w; ν(CO) 2077s, 2041s, 2024vs, 2003vs, 1826m; ν(C=N) 1616s and $\nu(NO_2)$ 1592s. ^{1}H-NMR: δ 11.21 (s, 1H, N–H), 9.08 (s, 1H, H^3 of benzene ring), 8.31–8.28 (q, 1H, H^5 of benzene ring), 7.87–7.84 (d, 1H, H^6 of benzene ring), 5.83–5.41 (m, 4H, C_5H_4), 2.21 (s, 3H, CH_3).

2.7. Synthesis of compound **6**

The preparation procedure for **6** was similar to that described above. Cluster [η^5-$C_5H_4C(O)Me$]RuCoMo$(CO)_8(\mu_3$-Se) (100 mg, 0.15 mmol) was dissolved in anhydrous EtOH (10 cm^3), to which was slowly added a thiosemicarbazide solution (1.5 cm^3), prepared by dissolving thiosemicarbazide (200 mg) in 98% H_2SO_4 (2 cm^3), 95% EtOH (10 cm^3) and H_2O (2 cm^3), with stirring. The reaction had finished after stirring at r.t. for 5 h. Then EtOH was removed and the residue was separated on a silica gel column. Elution with CH_2Cl_2–hexane (1:1) gave the unreacted material (43 mg). CH_2Cl_2–ether (50:1) afforded the main brown band, removing the solvent and crystallization from CH_2Cl_2–hexane at −20°C to give brown solids (50 mg, 45%). Anal. Found: C, 25.97; H, 1.39; N, 5.72; S, 4.34. Calc. for $C_{16}H_{10}O_8N_3$SSeCoMoRu: C, 26.00; H, 1.36; N, 5.68; S, 4.34%. IR (cm^{-1}): ν(CO) 2097s, 2035vs, 2008vs, 1950vs, 1889s and ν(C=N) 1586m. ^{1}H-NMR: δ 7.04 (s, 1H, N–H), 5.65–5.33 (m, 6H, C_5H_4, NH_2), 2.33 (s, 3H, CH_3).

2.8. Synthesis of compound **7**

[η^5-$C_5H_4C(O)Me$]RuCoMo$(CO)_8(\mu_3$-Se) (300 mg, 0.45 mmol) and (−)-5-(α-phenyl)semioxamazide (100 mg, 0.45 mmol) were dissolved in a solution of ethanol (25 cm^3) and benzene (10 cm^3). After several drops of 98% H_2SO_4 were added, the mixture was stirred at r.t. for 12 h and TLC monitoring showed the reaction had completed. The solvent was condensed and the residue was separated on a 2.5 × 40 cm^2 silica gel chromatography column. Elution with CH_2Cl_2–hexane afforded the unreacted cluster **1** (100 mg). CH_2Cl_2–ether–benzene (1:1:1) gave the product band. Removing the solvent and crystallization from CH_2Cl_2–hexane at −20°C yielded brown solids (104 mg, 27%). Anal. Found: C, 35.14; H, 2.11; N, 4.53. Calc. for $C_{25}H_{18}O_{10}N_3$SeCoRuMo: C, 35.11; H, 2.12; N, 4.91%. IR (cm^{-1}): ν(CO) 2078vs, 2035vs, 2000vs, 1887w and ν(C=O) 1709 m, 1670 m. ^{1}H-NMR: δ 10.17 (s, 1H, N–H), 7.81 (s, 1H, N–H), 7.35 (s, 5H, C_6H_5), 5.92–5.41 (q, 4H, C_5H_4), 5.09–5.07 (d, 1H, CH, $J=6.12$ Hz), 2.15 (s, 3H, CH_3), 1.60–1.59 (d, 3H, CH_3, $J=5.44$ Hz). ^{13}C-NMR: δ 231.60, 224.10, 193.29 (C≡O), 158.41, 155.15 (2C, C=O), 149.02 (C=N), 141.68, 128.77, 127.76, 126.08 (6C, C_6H_5), 104.30, 91.40, 91.33, 88.24, 87.58/87.49 (5C, C_5H_4), 49.72 (1C, CH), 21.51 (1C, CH_3) and 13.80 (1C, CH_3).

2.9. Synthesis of compound **8**

[η^5-$C_5H_4C(O)Me$]RuCoMo$(CO)_8(\mu_3$-Se) (200 mg, 0.3 mmol) and L-(+)-menthydrazide (60 mg, 0.28 mmol) were dissolved in EtOH (30 cm^3). After several drops of 98% H_2SO_4 was added, the mixture was stirred at r.t. for 12 h. Then the mixture was condensed and the residue was separated on a silica gel column. After CH_2Cl_2–hexane eluted the unreacted cluster **1**, hexane–CH_2Cl_2–ether (2:2:1) gave the product band. Removal of the solvent and crystallization from CH_2Cl_2–hexane at −20°C to yield brown solids (112 mg, 43%). Anal. Found: C, 36.25; H, 3.20; N, 3,24. Calc. for $C_{26}H_{27}O_{10}N_2$SeCoRuMo: C, 36.21; H, 3.16; N, 3.25%. IR (cm^{-1}): ν(CO) 2078vs, 2036vs, 1999vs, 1888m and ν(C=O) 1734m. ^{1}H-NMR: δ 7.80 (s, 1H, N–H), 5.80–5.30 (m, 4H, C_5H_4), 4.64 (s, 1H, H^1 of menthol unit), 2.02–0.73 (m, 18H, protons of menthol unit). ^{13}C-NMR: δ 231.88, 224.44, 193.61 (C≡O), 153.14 (ester carbonyl), 140.60 (C=N), 107.17/107.05, 90.67/90.56, 90.45/90.28, 87.58/87.44, 87.39/86.83 (C_5H_4), 76.49, 47.29, 41.09, 34.19, 31.37, 26.33, 23.58, 21.98, 20.68, 16.50 (10 carbons of menthol unit), 13.30 (CH_3).

2.10. Synthesis of compound **9**

The preparation of cluster **9** was similar to that of cluster **5**. CH_2Cl_2 eluted the main dark red band.

Table 1
Crystal and refinement data for the clusters **2**

Empirical formula	$C_{18}H_{11}O_{11}CoRuSeW$
Formula weight	826.08
Crystal system	Monoclinic
Space group	$P2_1/c$
$F(000)$	1544
Unit cell dimensions	
a (Å)	7.7251(15)
b (Å)	21.880(4)
c (Å)	13.416(3)
α (°)	90
β (°)	91.93(3)
γ (°)	90
V (Å^3)	2266.4(8)
Z	4
D_{calc} (g cm^{-3})	2.421
Absorption coefficient (cm^{-1})	81.07
Radiation (Mo–K$_\alpha$) (Å)	0.71073
Temperature (°C)	20
$2\theta_{max}$	51.98
Number of observations [$I > 2\sigma(I)$]	3506
Number of variables	298
R[a], R_w[b]	0.0816, 0.2206
Goodness-of-fit on F^2	1.013
Largest difference peak and hole (e Å^{-3})	4.435, −3.914

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

Condensation of the solvent and crystallization from CH_2Cl_2–hexane at −20°C gave brown solids (yield 52%). Anal. Found: C, 31.35; H, 1.69; N, 6.13. Calc. for $C_{24}H_{15}O_{14}N_4SeCoRuMo$: C, 31.39; H, 1.65; N; 6.10%. IR (cm^{-1}): ν(CO) 2079s, 2035s, 1994vs; ν(C=O) 1731m; ν(C=N) 1615s and ν(NO_2) 1590m. ^{1}H-NMR: δ 11.62 (s, 1H, N–H), 9.08 (s, 1H, H^3 of benzene ring), 8.29–8.28 (d, 1H, H^5 of benzene ring, $J = 7.26$ Hz), 7.84–7.82 (d, 1H, H^6 of benzene ring, $J = 8.04$ Hz), 5.85–5.40 (q, 4H, C_5H_4), 3.66 (s, 3H, CH_3), 2.85 (s, 2H, CH_2), 2.79 (s, 2H, CH_2).

2.11. X-ray crystallography of cluster 2

Crystals used for X-ray determination were obtained from CH_2Cl_2–hexane at −20°C. The crystals were mounted on a glass fiber. Preliminary examination and data collection were performed with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. An empirical absorption was applied for the two clusters.

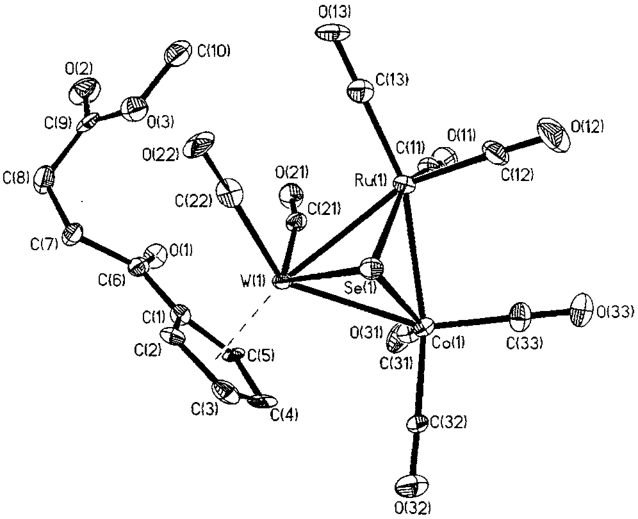


Fig. 1. Molecular structure of cluster **2**.

All the structures were solved by direct method and expanded using Fourier technique. The non-hydrogen atoms were refined by the full-matrix least-squares method anisotropically, hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN program system. Crystal data and experimental details for **2** are collected in Table 1. Selected bond lengths and angles are listed in Table 2. The molecular structure of **2** is presented in Fig. 1.

3. Results and discussion

Functionally substituted cyclopentadienyl tricarbonyl Group 6 metal anions $[M(CO)_3(\eta^5\text{-}C_5H_4R)]^-$ (R = C(O)Me, CO_2Et, $C(O)C_6H_4CO_2Me$, etc.) have proved to be important in the synthesis of organometallic and metal cluster complexes containing the structural unit $[M(CO)_2(\eta^5\text{-}C_5H_4R)]$ [12]. Their metal exchange reactions with a prochiral cluster, such as $RuCo_2(CO)_9(\mu_3\text{-}Se)$ and $FeCo_2(CO)_9(\mu_3\text{-}S)$, could give rise to the formation of chiral clusters which contain organic func-

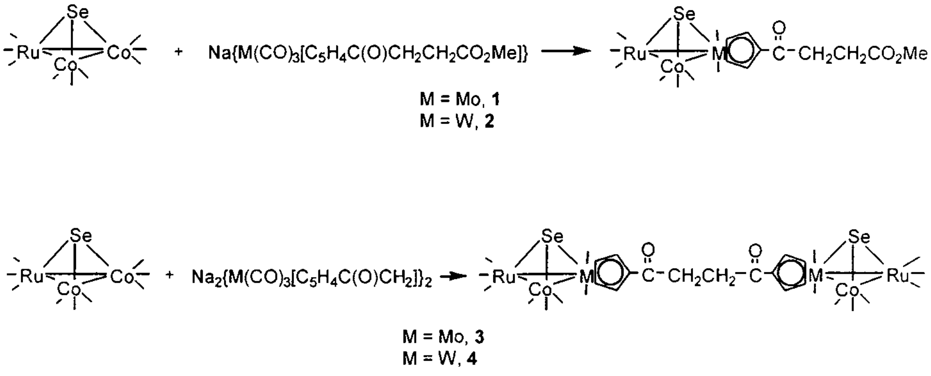
Table 2
Selected bond lengths (Å) and angles (°) for cluster **2**

Ru–Se	2.452(2)	W–Se	2.5173(16)	C(1)–C(6)	1.48(2)
Ru–Co	2.644(3)	W–Co	2.759(2)	W–C(21)	1.943(16)
Ru–W	2.8911(14)	Co–Se	2.326(3)	Ru–C(21)	2.733
Se–Ru–Co	54.17(6)	Se–W–Ru	53.39(5)	Co–Se–W	69.31(7)
Se–Ru–W	55.48(4)	Co–W–Ru	55.74(5)	Ru–Se–W	71.13(5)
Co–Ru–W	59.59(5)	Se–Co–W	58.61(6)	O(21)–C(21)–W	164.8(14)
Se–W–Co	52.08(6)	Ru–Co–W	64.67(5)		
C(21)–W–Ru	65.5(5)	Co–Se–Ru	67.11(8)		

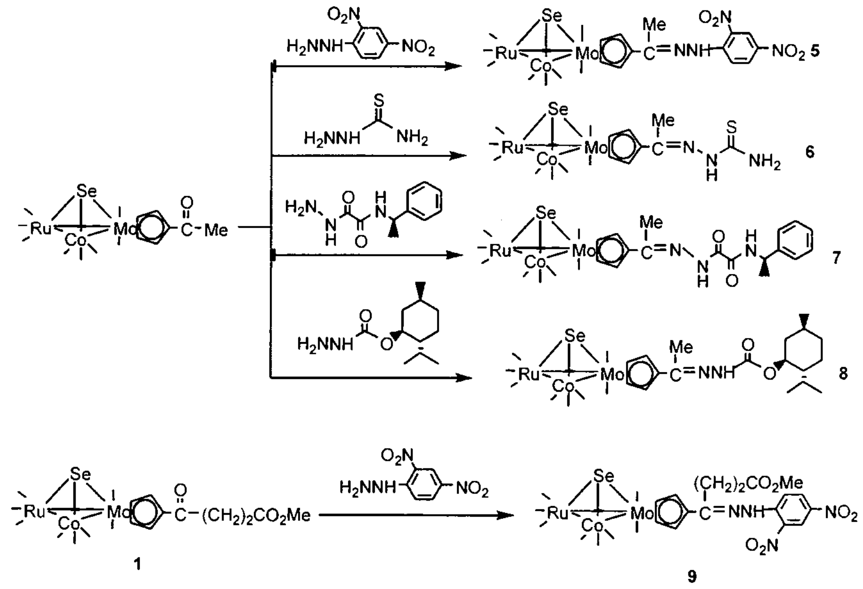
tional groups. In this paper, four novel chiral clusters have been prepared by this procedure, which are shown in Scheme 1.

Although, the preparations of functional groups of a cyclopentadienyl ring in cluster systems have been studied extensively, the investigations of their reactions are less reported [6f,12b,13]. In principle, the cluster core in a cluster complex may influence the reactivity of the functional group on the cyclopentadienyl ring and also could be destroyed under the reaction conditions used. Some reactions, which can proceed in mononuclear transition metal complexes are not successful in cluster system. According to the methods described by Rausch [14], treatment of cluster [η^5-$C_5H_4CO_2Et$]RuCoMo(CO)$_8$(μ_3-Se) [6g] in ethanol with aqueous potassium hydroxide, followed by acidification, did not give the expected carboxylic acid, and the cluster core was found to be destroyed. Song [12b] also reported similar phenomenon. The formation of a Schiff base should be a very common reaction for ketones by condensing with amine catalyzed by acid. Dey reported that acetylferrocene could react with phenylamine catalyzed by glacial acetic acid to produce the ferrocenyl Schiff base [15]. However, treatment of [η^5-$C_5H_4C(O)Me$]RuCoMo(CO)$_8$(μ_3-Se) with phenylamine under the same condition did not give the expected cluster Schiff base. Except the unreacted material, nothing could be separated, even with 98% H_2SO_4 as catalyst. Another common reaction for ketone is condensation with hydrazine to form the hydrazone compound. Song reported that 2,4-dinitrophenylhydrazide could react with the acetyl in cluster complexes to yield the expected hydrazone cluster derivatives [13]. Under the same condition, treatment of clusters [η^5-$C_5H_4C(O)Me$]RuCoMo(CO)$_8$(μ_3-Se) and **1**, respectively, with 2,4-dinitrophenylhydrazide afforded the expected clusters **5** and **9**, however the extension reactions of [η^5-$C_5H_4C(O)$Me]RuCoMo(CO)$_8$(μ_3-Se) with phenylhydrazine and hydrazine hydrate failed. The reason should be that the two nitro groups make the terminal nitrogen atom more nucleophilic, easy to attack the carbonyl in ketone. In contrast to the reactions with hydrazine, condensations of cluster ketone with hydrazides to form hydrazones are much more successful. Four kinds of hydrazides were treated with cluster [η^5-$C_5H_4C(O)Me$]RuCoMo(CO)$_8$(μ_3-Se). Except carbohydrazide, other three hydrazides can be condensed with it to form the expected hydrazone cluster complexes **6**–**8** shown in Scheme 2. Our initial attempt to synthesize compound **6** was catalyzed by glacial acetic acid, and found it takes a whole day to finish the reaction; when catalyzed by 98% H_2SO_4, 3–5 h is enough. However, when attempting to prepare the diastereoisomers of clusters **7** and **8**, the reaction cannot be finished in several days in the presence of acetic acid; after several drops of 98% H_2SO_4 was added, it became fast. In summary, 98% H_2SO_4 is more suitable as catalyst in the preparation of these cluster hydrazones. On the other hand, when methyl in acetyl group is changed to $CH_2CH_2CO_2Me$, its reactions with hydrazides described above are not the same. None of the four hydrazides is found to be condensed with **1** to form the hydrazone cluster complex. Besides the nucleophilicity of the terminal nitrogen of hydrazides, the block effect of $CH_2CH_2CO_2Me$ should be another reason to prevent the condensation. The block of $CH_2CH_2CO_2Me$ is larger than that of methyl group, which might prevent hydrazide attack of the carbon in carbonyl bound to cyclopentadienyl ring. Whatever, the successful preparations of cluster complexes **7** and **8** are most favorable to us. Two kinds of optically active groups have been introduced into the racemic cluster successfully, but the mixture of diastereoisomers cannot be separated into a pure single diastereoisomer by silica gel chromatography. Several attempts have been made, none of which were successful. The explanation might be that the chiral carbon is too far away from the tetrahedral framework.

Cluster complexes **1**–**9** are solids colored from brown to dark red. They are fully characterized by elemental analysis and IR, ^{1}H- and ^{13}C-NMR spectroscopies. In their IR spectra all showed terminal carbonyl absorption bands in the range of 2097–1950 cm^{-1} and bridg-



Scheme 1.



Scheme 2.

Table 3
Selected ^{13}C-NMR data for compounds **7** and **8**

Compound	$\delta_{CO\text{–}metals}$			$\delta_{C(1)}$	$\delta_{C(3)}$ and $\delta_{C(4)}$		$\delta_{C(2)}$ and $\delta_{C(5)}$	
7	231.60	224.10	193.29	104.30	91.40	91.33	88.24	87.58/87.49
8	231.88	224.44	193.61	107.17/107.05	90.67/90.56	90.45/90.28	87.58/87.44	87.39/86.83

ing or semi-bridging carbonyl bands between 1900 and 1800 cm^{-1}. The IR spectra of **1**–**4** showed corresponding carbonyl absorption bands of ester at around 1720 cm^{-1} and ketone at 1860 cm^{-1}, and those of **5**, **6** and **9** showed middle absorption band around 1614 cm^{-1} for C=N stretching. The middle absorption bands around 1590 cm^{-1} in spectra of **5** and **9** are characteristic for the nitro units bound to benzene ring. The absorption bands at 1709 and 1670 cm^{-1} in the IR spectrum of **7** are for the two ketonic carbonyls, while the absorption band at 1734 cm^{-1} in the IR spectrum of **8** arises from the ester carbonyl.

The ^{1}H-NMR spectra of all clusters show the presence of protons in their corresponding organic group. The chemical shifts of four protons in substituted cyclopentadienyl rings appeared as a multiplet in the range of δ 5.99–5.41. And because of the introduction of optically active center, the ^{1}H-NMR spectrum of cluster **8** showed the diastereotopic splitting of proton in cyclopentadienyl ring. For clusters **1**, **2** and **9**, the methyl chemical shift is observed at δ 3.69 and the two methylenes appeared between δ 2.99 and 2.72 as two singlets, while in the ^{1}H-NMR spectra of **3** and **4** the two methylenes appeared as multiplet at δ 3.00. For the hydrazone cluster complexes **5**–**9**, the singlet between δ 11.62 and 7.04 at the downfield side was assigned to the proton in the N–NH unit. The spectra of **5** and **9** showed 2,4-nitrophenyl group resonances in the range of δ 9.08–7.82. In the ^{1}H-NMR spectrum of cluster **7**, the singlet at δ 7.35 was assigned to the five protons in the benzene ring, the doublet at δ 5.09 is for the methenyl proton attached to benzene, and the doublet at δ 1.60 together with the singlet at δ 2.15 are the resonances of two methyl protons. While in the ^{1}H-NMR spectrum of **8**, the signals in the range of δ 4.64–0.73 are for the protons in menthol unit and methyl protons, which are in accord with literature [16].

The ^{13}C-NMR spectra of compounds **7** and **8** confirm their structures. There are three resonances at downfield between δ 232 and 190 assigned to the carbonyls bound to transition metals seen in Table 3. Based on the comparison of ^{13}C-NMR data for the related organometallic complexes [17], we tentatively assign resonances at δ 232 and 225 to the two carbonyls attached to Mo atom, and it is suggested that one of them is semi-bridging. And the singlet at δ 194 is the chemical shifts of terminal carbonyls bound to Ru and Co atoms, which appeared slightly downfield with respect to literatures [17a–c,e]. In the ^{13}C-NMR spectrum of cluster **7**, the resonances at δ 158.41 and 155.15 can be assigned to the two carbonyls between the two nitrogens, and the singlet at δ 149.02 is due to the carbon in C=N bond. The benzene chemical shift is exhibited in the range of δ 141.69–126.08 as four singlets. And the singlet at δ 49.72 is the chemical shift of methenyl, while two methyl resonances are observed at δ 21.51 and 13.80. In the ^{13}C-NMR spectrum of compound **8**, the singlet at δ 153.14 is the resonance for ester carbonyl, and the signal appearing at δ 140.60 can be assigned to the carbon in the C=N unit. The methyl resonance is observed at δ 13.30. All the chemical shifts of carbons in the menthol unit are in good agreement with literature [16].

It is worthy to note that because of the introduction of an optically active group, the ^{13}C-NMR spectra of **7** and **8** showed diastereotopic splitting of the cyclopentadienyl five-membered ring carbons, which are shown in Table 3. McGlinchey found the further splitting of cylcopentadienyl carbons by introducing a menthol unit into clusters capped by carbon atom in 1989 [16]. In this paper we, respectively, introduced two kinds of optically active groups into chiral cluster capped by Se atom, and found the distinct carbon splitting because of the same reason. The cyclopentadienyl carbon resonances of **7** and **8** are different from those of cluster $[\eta^5\text{-}C_5H_4C(O)Me]RuCoMo(CO)_8(\mu_3\text{-}Se)$. And the diastereotopic splitting of **8** is much more distinctive than that of **7**, which might be because of the distance between the optically active center and chiral framework in **7** is longer than that in **8**, the influence decreases with the distance. The resonance in the range of δ 108–104 is assigned to C(1). Based on our previous report [6c], the doublet in **7** and the quartet in **8** between δ 91.40 and 90.28 should be resonances of C(3) and C(4), and the triplet in the range of δ 88.24–86.83 can be assigned to C(2) and C(5). We are sure it is the chiral framework that makes the five carbons different from each other in the ^{13}C-NMR spectra such as those in cluster $[\eta^5\text{-}C_5H_4C(O)Me]RuCoMo(CO)_8(\mu_3\text{-}Se)$, but do not understand why the carbon C(1) chemical shift appeared downfield and other four carbon resonances appeared upfield when an optically active group is attached, in contrast to those of cluster $[\eta^5\text{-}C_5H_4C(O)\text{-}Me]RuCoMo(CO)_8(\mu_3\text{-}Se)$, and the carbon, whose splitting is the most distinct among the five carbons, is one of C(2) and C(5). From the molecular structures of **2**, we only know that one carbon of C(2) and C(5) is near to Se atom and the other is near to Co atom.

As seen in Fig. 1, the molecule of cluster **2** contains a tetrahedral skeleton composed of Ru, Co, W and Se. The Ru and Co atoms each are coordinated to three carbonyls, and W atom is coordinated to two carbonyl ligands and one five-electron cyclopentadienyl ligand one of whose protons was substituted by $C(O)CH_2CH_2\text{-}CO_2CH_3$ group. The bond lengths and angles involving the cluster core are very closer to the corresponding analog [6f,g]. The bond length of C(1)–C(6) is 1.48(2) Å, and the torsion angle of C(3)–C(2)–C(1)–C(6) is 176.6°. So C(6)=O(1) and the cyclopentadienyl ring are located in one plane, and the π system of C(6)=O(1) is conjugated with the cyclopentadienyl π system. However, the distance of C(7)–C(8) is 1.55(2) Å, and the torsion angle of C(6)–C(7)–C(8)–C(9) is −63(2)°, so the CH_2COOCH_3 substituent is not in a plane with the cyclopentadienyl. And it should be noted that the carbonyl of C(21)–O(21) bound to W atom is semi-bridging, due to its asymmetric parameter $\alpha = (d_2 - d_1)/d_1 = 0.41$ $[d_2 = \text{Ru}(1)\cdots\text{C}(21) = 2.733$ Å, $d_1 = \text{W}(1)\text{–C}(21) = 1.943(16)$ Å] falls in the range of α value defined for semi-bridging carbonyls by Curtis [18]. Since the bond angle of O(21)–C(21)–W(1) is 164.8(14)° and the angle of C(21)–W(1)–Ru(1) is 65.5(5)°, the semi-bridging C(21)–O(21) is bridged across on the Ru(1)–W(1) bond.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 153199 for compound **2**. 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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References

[1] (a) C.U. Pittman, G.M. Richmond, M. Absi-Halabi, H. Beurich, F. Richter, H. Vahrenkamp, Angew. Chem. Int. Ed. Engl. 21 (1982) 786. (b) R. Whyman, Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis, Kluwer, Dordrecht, 1988, pp. 75–95. (c) R.D. Adams, F.A. Cotton, Catalysis by Di- and Polynuclear Metal Cluster Complexes, Wiley/VCH, Weinheim/New York, 1998, p. 27.

[2] (a) H. Vahrenkamp, J. Organomet. Chem. 370 (1989) 65. (b) F.G.A. Stone, Angew. Chem. Int. Ed. Engl. 23 (1984) 89. (c) J. Zhang, Y.-H. Zhang, Y.-Q. Yin, J. Mol. Catal. (China) 13 (1999) 70.

[3] F. Richter, H. Vahrenkamp, Chem. Ber. 115 (1982) 3224.

[4] F. Richter, H. Vahrenkamp, Chem. Ber. 115 (1982) 3243.

[5] R.P. Planalp, H. Vahrenkamp, Organometallics 6 (1987) 492.

[6] (a) H.-P. Wu, Zh.-Y. Zhao, Sh.-M. Liu, Er.-R. Ding, Y.-Q. Yin, Polyhedron 15 (1996) 4117. (b) H.-P. Wu, Y.-Q. Yin, X.-Y. Huang, K.-B. Yu, J. Organomet. Chem. 498 (1995) 119. (c) H.-P. Wu, Y.-Q. Yin, Q.-C. Yang, Polyhedron 15 (1996) 43. (d) Er.-R. Ding, Sh.-L. Wu, Ch.-G. Xia, Y.-Q. Yin, J. Sun, J. Organomet. Chem. 568 (1999) 157. (e) Er.-R. Ding, Sh.-M. Liu, Y.-Q. Yin, J. Sun, Polyhedron 17 (1997) 3273. (f) Er.-R. Ding, Y.-Q. Yin, J. Sun, J. Organomet. Chem. 559 (1998) 157. (g) Y.-H. Zhang, Sh.-L. Wu, Q.-Sh. Li, Y.-Q. Yin, X.-Y. Huang, J. Chem. Res. (S) (1999) 550.

[7] E. Roland, W. Bernhardt, H. Vahrenkamp, Chem. Ber. 119 (1986) 2566.

[8] W.P. Hart, S. Dong, M.D. Rausch, J. Organomet. Chem. 282 (1985) 111.

[9] T.E. Bitterwolf, J. Organomet. Chem. 386 (1990) 9.

[10] R.B. Woodward, T.P. Kohman, G.C. Harris, J. Am. Chem. Soc. 63 (1941) 120.

[11] N.J. Leonard, J.H. Boyer, J. Org. Chem. 15 (1950) 42.

[12] (a) D.W. Macomber, W.P. Hart, M.D. Rausch, Advances in Organometallic Chemistry, Academic Press, New York, vol. 21, 1982, p. 1. (b) L.Ch. Song, J.Y. Shen, Q.M. Hu, X.Y. Huang, Organometallics 14 (1995) 98. (c) R. Hoffmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 711.

[13] (a) L.-C. Song, Y.-B. Dong, Q.-M. Hu, Y.-K. Li, J. Sun, Polyhedron 17 (1998) 1579. (b) L.-C. Song, Q.-M. Hu, J.-S. Yang, J.-Y. Shen, J. Chem. Res. (S). (1998) 344.

[14] (a) D.W. Macomber, M.D. Rausch, J. Organomet. Chem. 258 (1983) 331. (b) W.P. Hart, D. Shihua, M.D. Rausch, J. Organomet. Chem. 282 (1985) 111.

[15] K. Dey, K.K. Nandi, Indian J. Chem. 33 (1994) 908.

[16] D.T. Clark, K.A. Sutin, M.J. McGlinchey, Organometallics 8 (1989) 155.

[17] (a) C.J. Adams, M.I. Bruce, B.W. Skelton, A.H. White, J. Organomet. Chem. 506 (1996) 191. (b) L.T. Byrne, J.P. Hos, G.A. Koutsantonis, B.W. Skelton, A.H. White, J. Organomet. Chem. 598 (2000) 28. (c) P. Mathur, A.K. Dash, M.M. Hossain, C.V.V. Satyanarayana, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, J. Organomet. Chem. 532 (1997) 189. (d) L.-R. Lue, S.-C. Lo, C.-C. Lin, F.-E. Hong, Polyhedron 14 (1995) 419. (e) S.M. Draper, M. Delamesiere, E. Champeil, B. Twamley, J.J. Byrne, C. Long, J. Organomet. Chem. 589 (1999) 157.

[18] An asymmetric parameter is defined as $\alpha = (d_2 - d_1)/d_1$ where d_2 is the long M···C distance and d_1 is the short M–C distance. If $0.1 \leq \alpha \leq 0.6$, a semi-bridging carbonyl is designated according to Curtis' suggestion. M.D. Curtis, K.R. Han, W.M. Butler, Inorg. Chem. 19 (1980) 2096.