Synthesis and reactions of chiral clusters containing an SRuCoMo core

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In order to resolve tetrahedron-type chiral clusters, three chiral clusters containing a functionally substituted cyclopentadienyl ligand were prepared, and the reactions of functional substituents were investigated. The ester group was hard to hydrolyze while hydrazide can easily condense with the ketonic carbonyl on the cyclopentadienyl ring to form a cluster hydrazone. Two optically active auxiliaries have been attached to the chiral framework; however, the diastereoisomers cannot be separated by silica gel chromatography. Their presence was established by ^{13}C NMR spectra.

Hetero-metal cluster complexes have been attracting intense attention since the mid-70s, due to the diversity of their reactions and structures, as well as their potential ability for catalysis. Such clusters have been suggested as active catalysts in a variety of homogeneous catalyzed reactions; 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. Unambiguous evidence would be the use of a rigid chiral cluster to catalyze an asymmetric reaction with the subsequent isolation of chiral products.[1]

Hetero-metal clusters with chiral frameworks can be prepared directly in multi-step addition and substitution reactions by systematic incorporation of organometallic units[2,3] or by a metal exchange reaction using $MeAsMCp(CO)_3$, $M_2Cp_2(CO)_6$, $HMCp(CO)_3$, $ClM(CO)_3$ and $NaMCp(CO)_3$ as metal exchange reagents.[1e,4] Among these methods, the metal exchange procedure, which Beurich and Vahrenkamp pioneered,[5] has proven to be the most efficient and versatile for the preparation of tetrahedral hetero-metal clusters in which each of the four vertices is chemically different.

The major problem remaining is that of enantiomeric separation. Until now, tens of metal clusters with tetrahedron-type chiral frameworks have been reported, only a few of which can be separated into pure enantiomers.[1e,6] To obtain pure enantiomers, the most direct way should be by chromatography over an optically active adsorbent, but this method was found to be time-consuming, inefficient and only applicable to some special types of clusters.[2d,7] More successful were the enantiomer separations *via* the formation of diastereoisomers. But it was found that in some cases, after separation of the diastereoisomers, the auxiliary optically active group could not be removed without destruction of the cluster or loss of the optical activity.[7,8] The successful introduction of organic groups into metal clusters[9] provides us with a new route to separate racemic clusters. It is possible to resolve chiral clusters by separating racemic organic compounds. In this paper, reactions of organic moieties on the SRuCoMo cluster were investigated, and two kinds of optically active compounds have been introduced into racemic clusters, but the diastereoisomers cannot be separated through silica gel chromatography. From ^{13}C NMR spectra, the presence of diastereoisomers can be established.

Experimental

Material and methods

$RuCo_2(CO)_9(\mu_3\text{-}S)$,[8] $[\eta^5\text{-}C_5H_4C(O)CH_3]RuCoMo(CO)_8(\mu_3\text{-}S)$ (**1**),[9d] $Na(C_5H_4CO_2C_2H_5)$,[9h] $Na[C_5H_4C(O)CH_2CH_2CO_2CH_3]$,[10] (−)-5-(α-phenyl)semioxamazide[11] and L-(+)-menthydrazide[12] were prepared according to the literature methods. All other compounds were purchased from Aldrich and Fluka and used as received. Solvents were dried and purified by conventional methods before use. Hexane and tetrahydrofuran (THF) were freshly distilled from sodium–lead alloy under nitrogen, and dichloromethane (CH_2Cl_2) was dried with CaH_2. All reactions were carried out under an atmosphere of pure nitrogen by using standard Schlenk techniques. Chromatographic separations were carried out using silica gel columns (160–200 mesh) of varying lengths. 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 or as pressed KBr discs on a Nicolet FT-IR 10DX spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 MHz spectrometer in $CDCl_3$. Chemical shifts are given on the δ scale relative to $SiMe_4$ (0.0 ppm). Elemental analyses were performed on an 1106-type analyzer.

Syntheses

$(\eta^5\text{-}C_5H_4CO_2C_2H_5)RuCoMo(CO)_8(\mu_3\text{-}S)$ (2). $Na(C_5H_4CO_2C_2H_5)$ (160 mg, 1 mmol) and $Mo(CO)_6$ (264 mg, 1 mmol) were dissolved in 25 ml of THF and the mixture refluxed for 12 h. After cooling to room temperature, $RuCo_2(CO)_9(\mu_3\text{-}S)$ (503 mg, 1 mmol) was added, then the mixture was heated at 60 °C for another 2 h with stirring. After removal of THF *in vacuo*, the residual oil was separated on a 2.5 cm × 30 cm silica gel column. Elution with CH_2Cl_2–hexane (1 : 1) afforded

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Table 1 Crystallographic data and structure refinement for clusters **2** and **3**

	2	**3**
Formula	$C_{16}H_9O_9RuMoCoS$	$C_{18}H_{11}O_{11}RuMoCoS$
Formula weight	649.24	691.27
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$
Z	4	4
T/K	296	294(2)
a/Å	10.075(1)	7.670(3)
b/Å	9.034(2)	22.001(10)
c/Å	22.973(7)	13.392(6)
β/°	92.70(1)	92.230(9)
U/Å^3	2088.7(8)	2258.3(17)
μ/mm^{-1}	2.207	2.082
Reflections collected	4470	14867
Independent reflections	4378	5166
Reflections used [$I > 2\sigma(I)$]	3686	3455
R_{int}	0.016	0.0789
R/R_w [for data $I > 2\sigma(I)$]	0.030/0.042	0.0594/0.1462

the product band. Condensation of the solvent and crystallization from CH_2Cl_2–hexane at −20 °C gave black–red crystals (265 mg, yield 41%). Anal. found: C 29.65, H 1.38; calc. for $C_{16}H_9O_{10}SCoMoRu$: C 29.60, H 1.40%. IR (KBr): 2082vs, 2040vs, 2003vs, 1971vs, 1879s, 1721s (CO_2Et) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.98–5.47 (q, 4H, C_5H_4), 4.34–4.29 (q, 2H, CH_2), 1.33 (t, 3H, CH_3).

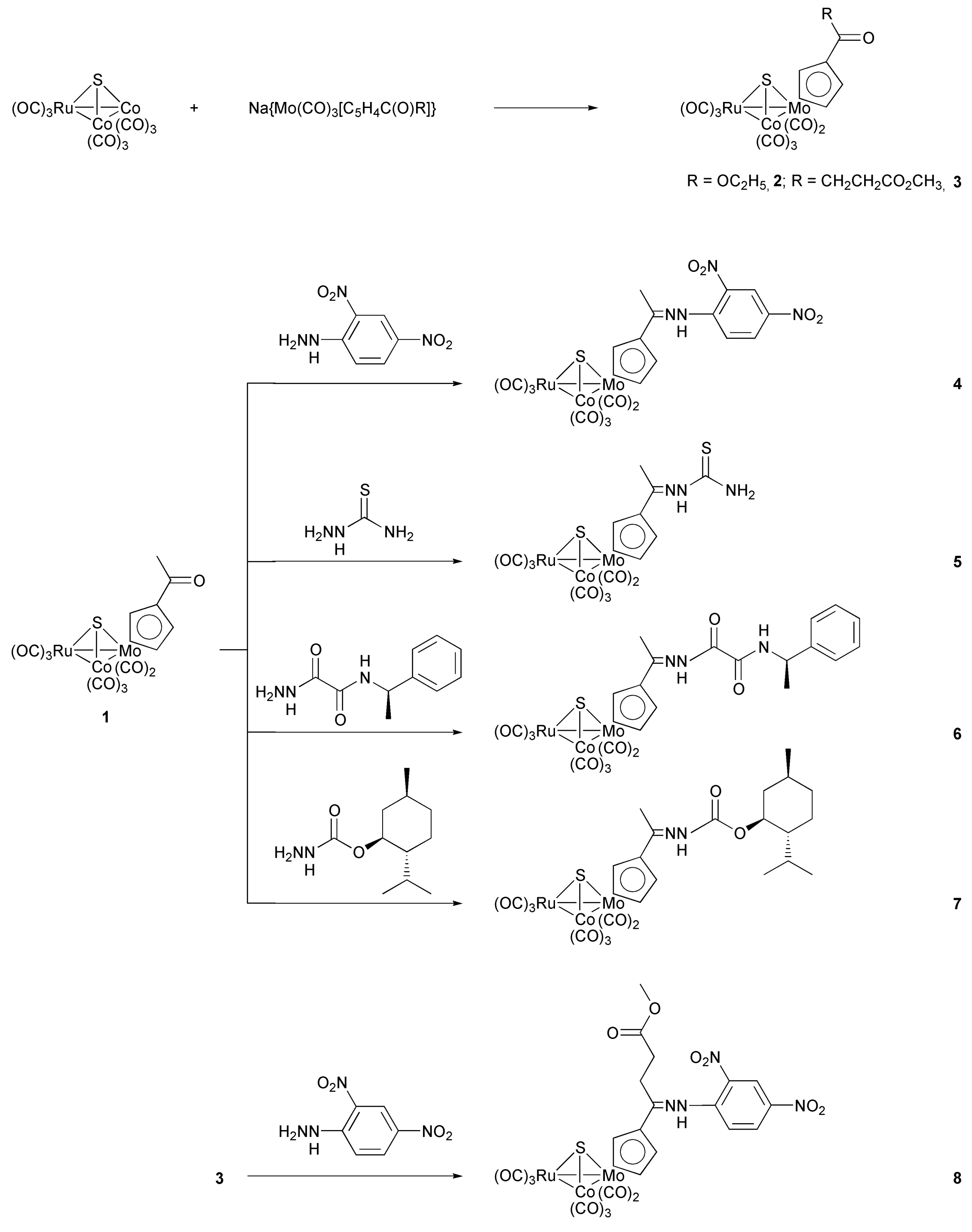
[η^5-$C_5H_4C(O)CH_2CH_2CO_2CH_3$]$RuCoMo(CO)_8(\mu_3$-S) (3). The preparation procedure compound **3** was similar to that cluster **2** except that Na[$C_5H_4C(O)CH_2CH_2CO_2CH_3$] was used instead of Na($C_5H_4CO_2C_2H_5$). CH_2Cl_2–hexane (3 : 1) eluted the main black band. Removal of the solvent and crystallization from CH_2Cl_2–hexane at −20 °C gave black–red crystals (185 mg, yield 27%). Anal. found: C 31.30, H 1.58; calc. for $C_{18}H_{11}O_{11}SCoMoRu$: C 31.27, H 1.60%. IR (KBr): 2081vs, 2043vs, 2006vs, 1987vs, 1966s, 1919m, 1846s, 1738s (CO_2Me), 1692s (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.92–5.48 (q, 4H, C_5H_4), 3.69 (s, 3H, CH_3), 3.02 (s, 2H, CH_2), 2.73 (s, 2H, CH_2).

[η^5-$C_5H_4C(NR)CH_3$]$RuCoMo(CO)_8(\mu_3$-S) [R = NH-C_6H_3-2,4-$(NO_2)_2$] (4). 2,4-Dinitrophenylhydrazine solution (1.0 ml), prepared by dissolving 2,4-dinitrophenylhydrazine (500 mg) in 98% H_2SO_4 (2.5 ml), H_2O (5 ml) and ethanol (17.5 ml), was added to an ethanol solution (25 ml) in which cluster **1** (50 mg, 0.081 mmol) was dissolved. The mixture was reacted at room temperature for 4 h. The precipitate was filtered out and washed with ethanol. The washed precipitate was extracted with the minimum quantity of CH_2Cl_2 and subjected to silica gel column chromatography. Elution with CH_2Cl_2–hexane (1 : 1) gave the product band. The solvent was pumped off and the residue was crystallized from CH_2Cl_2–hexane at −20 °C to yield a brown solid (32 mg, yield 49%). Anal. found: C 31.53, H 1.41; calc. for $C_{21}H_{11}O_{12}N_4SCoMoRu$: C 31.55, H 1.39%. IR (KBr): 3304w, 3119w, 2079s, 2045s, 2027vs, 2005vs, 1974s, 1834m, 1616s (C=N) and 1592s (NO_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.21 (s, 1H, N–H), 9.08 (d, 1H, H^3 of benzene ring, J = 2.28), 8.31–8.28 (q, 1H, H^5 of benzene ring, J = 2.2, 7.2, 2.2), 7.88–7.85 (d, 1H, H^6 of benzene ring, J = 9.52 Hz), 5.89–5.43 (m, 4H, C_5H_4) and 2.19 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 231.61, 224.98, 193.62 (carbonyls bound to metals), 145.16, 144.25, 138.82, 130.20, 123.33, 116.62 (C=N and C_6H_3), 106.09, 92.76, 91.88, 90.23, 88.31 (C_5H_4), 14.06 (CH_3).

[η^5-$C_5H_4C(NR)CH_3$]$RuCoMo(CO)_8(\mu_3$-S) [R = NH-C(S)NH_2] (5). The preparation procedure for **5** was similar to that described above for **4**. Cluster **1** (100 mg, 0.16 mmol) was dissolved in anhydrous ethanol (10 ml), to which was slowly added a thiosemicarbazide solution (1.5 ml), prepared by dissolving thiosemicarbazide (200 mg) in 98% H_2SO_4 (2 ml), 95% ethanol (10 ml) and H_2O (3 ml), with stirring. The reaction was complete after stirring at room temperature for 5 h. The ethanol was removed and the residue was separated on a silica gel column. Elution with CH_2Cl_2–hexane (1 : 1) gave the unreacted material (38 mg). CH_2Cl_2–ether (50 : 1) afforded the main brown band; removal of the solvent and crystallization from CH_2Cl_2–hexane at −20 °C gave a brown solid (54 mg, yield 48%). Anal. found: C 27.77, H 1.48; calc. for $C_{16}H_{10}O_8N_3S_2CoMoRu$: C 27.76, H 1.46%. IR (KBr): 3421w, 3379w, 2081s, 2039vs, 2002vs, 1869s, 1595m (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.12 (s, 1H, N–H), 5.80–5.33 (m, 6H, C_5H_4, NH_2) and 2.23 (s, 3H, CH_3).

[η^5-$C_5H_4C(NR)CH_3$]$RuCoMo(CO)_8(\mu_3$-S) [R = NH-C(O)C(O)NHCH(CH_3)(C_6H_5)] (6). Cluster **1** (280 mg, 0.45 mmol) and (−)-5-(α-phenyl)semioxamazide (100 mg, 0.45 mmol) were dissolved in a solution of ethanol (25 ml) and benzene (10 ml). After several drops of 98% H_2SO_4 were added, the mixture was stirred at room temperature for 12 h until TLC monitoring showed the reaction was completed. The reaction mixture was condensed and the residue separated on a 2.5 × 40 cm 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. Removal of the solvent and crystallization from CH_2Cl_2– hexane at −20 °C yielded a brown solid (236 mg, yield 29%). Anal. found: C 37.10, H 2.21; calc. for $C_{25}H_{18}O_{10}N_3SCoMoRu$: C 37.14, H 2.24%. IR (KBr): 3310w, 2081vs, 2039vs, 2004vs, 1869w, 1715w (C=O), 1670m (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.08 (s, 1H, N–H), 7.73–7.71 (d, 1H, N–H, J = 7.48), 7.26 (s, 5H, C_6H_5), 5.86–5.35 (q, 4H, C_5H_4), 5.01 (s, 1H, CH), 2.05 (s, 3H, CH_3) and 1.52–1.50 (d, 3H, CH_3, J = 6.84 Hz). ^{13}C NMR ($CDCl_3$): δ 231.48, 224.37, 193.45 (carbonyls bound to metals), 158.59, 155.20 (2 C=O), 149.05 (C=N), 141.66, 128.82, 127.83, 126.12 (C_6H_5), 106.10, 92.81, 91.81, 90.47, 88.54 (C_5H_4), 49.76 (CH), 21.55 (CH_3) and 13.88 (CH_3).

[η^5-$C_5H_4C(NR)CH_3$]$MoRuCo(CO)_8(\mu_3$-S) (R = $NHCO_2$-menthyl) (7). Cluster **1** (170 mg, 0.275 mmol) and L-(+)-menthydrazide (60 mg, 0.28 mmol) were dissolved in ethanol (30 ml). After addition of several drops of 98% H_2SO_4, the mixture was stirred at room temperature for 12 h. Then the mixture was condensed and the residue separated on silica gel column. 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 yielded a brown solid (102 mg, yield 45%).



Scheme 1

Anal. found: C 38.31, H 3.37; calc. for $C_{26}H_{27}O_{10}N_2S$-CoMoRu: C 38.29, H 3.34%. IR (KBr): 3390w, 2079vs, 2037vs, 2000vs, 1890s, 1732m, 1700m (CO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.96 (s, 1H, N–H), 5.80–5.33 (q, 4H, C_5H_4), 4.61 (s, 1H, H^1 of menthol unit), 1.96–0.73 (m, 21H, protons of menthol and CH_3 groups). ^{13}C NMR ($CDCl_3$): δ 231.68, 224.41, 193.85 (carbonyls bound to metals), 153.05 (ester carbonyl), 140.60 (C=N), 108.95, 91.93/91.83, 90.94/90.61, 89.63/89.38, 88.22/87.57 (C_5H_4), 76.68, 47.13, 40.97, 34.08, 31.28, 26.22, 23.49, 21.91, 20.58, 16.42 (10 carbons of menthol unit) and 13.44 (CH_3).

[η^5-$C_5H_4C(NR)CH_2CH_2CO_2CH_3$]MoRuCo(CO)$_8$($\mu_3$-S) [R = NHC_6H_3-2,4-$(NO_2)_2$] (8). The preparation of cluster **8** was similar to that of cluster **4**. CH_2Cl_2 eluted the main dark red band. Condensation of the solvent and crystallization from CH_2Cl_2–hexane at −20 °C gave a brown solid (73 mg, yield 46%). Anal. found: C 33.07, H 1.75; calc. for $C_{24}H_{15}O_{14}$-N_4SCoMoRu: C 33.08, H 1.73%. IR (KBr): 2079s, 2033s, 1998vs, 1725m (CO_2CH_3), 1615s (C=N), 1590m (NO_2) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.42 (s, 1H, N–H), 9.08 (s, 1H, H^3 of benzene ring), 8.30–8.29 (d, 1H, H^5 of benzene ring, $J = 7.24$), 7.84–7.82 (d, 1H, H^6 of benzene ring, $J = 8.04$ Hz), 5.84–5.43 (m, 4H, C_5H_4), 3.67 (s, 3H, CH_3), 2.84 (s, 2H, CH_2) and 2.79 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 231.66, 224.46, 193.65 (carbonyls bound to transition metals), 172.11 (ester carbonyl), 145.25, 144.28, 138.87, 130.55, 130.24, 123.31, 116.63 (C=N and C_6H_3), 106.11, 92.75, 91.85, 90.30, 88.27 (C_5H_4), 52.56 (CH_3), 30.05, 23.16 (2C, $2CH_2$).

X-Ray structure determination

Crystals used for the X-ray structure determination were obtained from hexane–CH_2Cl_2 at −20 °C. The crystals were mounted on a glass fiber. Preliminary examination and data collection were performed with Mo-Kα radiation (λ = 0.710 73 Å) on an Enraf (Nonius CAD4 diffractometer (for **2**) or a CCD area detector (for **3**) equipped with a graphite monochromator. Crystal data, data collection parameters and the results of the analyses are collected in Table 1. The structures of the two clusters were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Full-matrix least-squares refinements for the two clusters were used.

CCDC reference numbers 159433 and 159434. See http://www.rsc.org/suppdata/nj/b1/b102368n/ for crystallographic data in CIF or other electronic format.

Results and discussion

Functionally substituted cyclopentadienyl tricarbonyl group 6 metal anions, prepared by refluxing a solution of the corresponding substituted cyclopentadienyl sodium salt and $M(CO)_6$, have proved to be important in the synthesis of organometallic and metal cluster complexes containing the structural unit $[\eta^5\text{-}RC_5H_4(CO)_2]M$.[13] Their isolobal displacement reactions with prochiral clusters, such as $RuCo_2(CO)_9(\mu_3\text{-}S)$ and $RuCo_2(CO)_9(\mu_3\text{-}Se)$, in refluxing THF could allow the organic group to attach to the chiral clusters. These procedures have been studied systematically, however, the reactions of organic groups on chiral frameworks have been less widely investigated.[9f,13b,14,15] In this paper, two novel chiral clusters containing the SRuCoMo core have been prepared and the reactivity of organic substituents bound to the cyclopentadienyl ring have been investigated, as shown in Scheme 1.

In principle, the reactions of functional groups are strongly influenced by the cluster framework and may even lead to cluster decomposition. $(\eta^5\text{-}C_5H_4CO_2C_2H_5)RuCoMo(CO)_8(\mu_3\text{-}S)$ (**2**) was first treated with aqueous potassium hydroxide in ethanol, followed by acidification, with the aim of obtaining the cluster carboxylic acid. However, the cluster molecule was found to be destroyed, as indicated by the color change from brown–red to black which was observed immediately upon addition of potassium hydroxide. Song *et al.* also reported a similar discovery.[13b] Treatment of $[\eta^5\text{-}C_5H_4C(O)CH_3]RuCoMo(CO)_8(\mu_3\text{-}S)$ (**1**) with hydrazides to form cluster hydrazones was more successful. Four kinds of hydrazone clusters have been prepared, catalyzed by 98% H_2SO_4. But the extension reactions of $[\eta^5\text{-}C_5H_4C(O)CH_2CH_2CO_2CH_3]RuCoMo(CO)_8(\mu_3\text{-}S)$ (**3**) with the four hydrazides were not as successful. Except for $[\eta^5\text{-}C_5H_4C(NR)CH_2CH_2CO_2CH_3]RuCoMo(CO)_8(\mu_3\text{-}S)$ [R = $NHC_6H_3\text{-}2,4\text{-}(NO_2)_2$] (**8**), the other three expected cluster hydrazones were not obtained from the reactions. This might be due to the blocking effect of $CH_2CH_2CO_2CH_3$, a group too large to allow the reaction to proceed. In any case, the successful preparations of the cluster hydrazone derivatives $[\eta^5\text{-}C_5H_4C(NR)CH_3]RuCoMo(CO)_8(\mu_3\text{-}S)$ [R = $NHC(O)C(O)NHCH(CH_3)(C_6H_5)$ (**6**), R = $NHCO_2$-menthyl (**7**)] were particularly pleasing. Two kinds of optically active groups have been attached to the racemic clusters but unfortunately the pair of diastereoisomers cannot be separated. Several attempts were made, none of which were successful. The reason might be that the optically active center is too far away from the tetrahedral framework.

All spectroscopic data obtained are in accord with the expected compositions of **2**–**8**. Their IR spectra are somewhat complicated due to the number of carbonyl ligands and the organic groups on the cyclopentadienyl ligands. The absorptions of terminal carbonyls bound to transition metals correspond closely to those reported for the analog **1**[9d] and appear in the range of 2082–1919 cm^{-1}. The absorption bands at 1898–1885 cm^{-1} suggest that a bridging carbonyl exists in the cluster molecules. Other characteristic absorptions for organic units can be easily assigned.

The ^1H NMR spectra of all clusters show the presence of hydrogen atoms in their corresponding organic groups. The multiplets in the range δ 5.99–5.41 are assigned to the four protons of the cyclopentadienyl ring.[9d] The ^{13}C NMR spectra gave the exact carbon assignment. In cluster **6**, the diastereotopic splitting for the five cyclopentadienyl carbons was observed in the range of 108.95–87.57. Based on the HMBC spectrum of cluster **6**, the singlet at δ 108.95 is due to C(1), the resonances at δ 91.93/91.83 and 90.94/90.61 can be assigned to C(3) and C(4), and the other two upfield signals are resonances for C(2) and C(5). We are sure that it is the chiral framework that makes the five carbons different from each other in the ^{13}C NMR spectrum as compared to those in cluster **1**.[16] However, we are uncertain as to why the C(1) peak appears downfield while the four other carbon resonances appear upfield when the organic group is attached, in comparison to the resonances due to the corresponding carbons in cluster **1**; it is also unclear whether the carbon signal whose splitting is the most distinct among the five carbons is due to C(2) or C(5). From the molecular structures of **2** and **3**, we know only that either C(2) or C(5) is near to the S atom while the other is near to the Co atom, and these two carbons are closer than C(3) and C(4) to the chiral framework. In order to confirm the structure of compound **6**, its HMBC spectrum was recorded and is shown in Fig. 1. Strong couplings of ^{13}C signals between δ 106.10 and 88.54 with the bonding proton signals in the region δ 5.86–5.35 are the C–H correlations in the cyclopentadienyl ring. Intense couplings of the carbon signals at δ 141.66, 128.82, 127.83 and 126.12 with the ^1H resonance at δ 7.26 show that a benzene ring is present in the molecule. The peak at δ 5.01 coupling with ^{13}C signals at δ 21.55, 126.12, 141.66 and 158.59 should be due to the methenyl proton, and the ^1H signal at δ 7.73–7.71 should be the methylbenzylamine proton resonance, as indicated by the coupling with the three ^{13}C signals (δ 21.55, 49.76 and 158.59). All of other carbon–

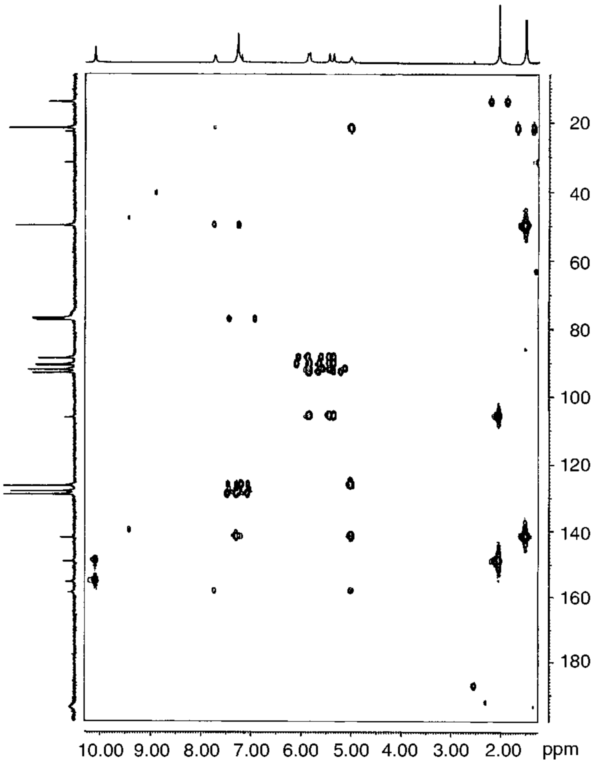


Fig. 1 The HMBC spectrum for cluster **6**.

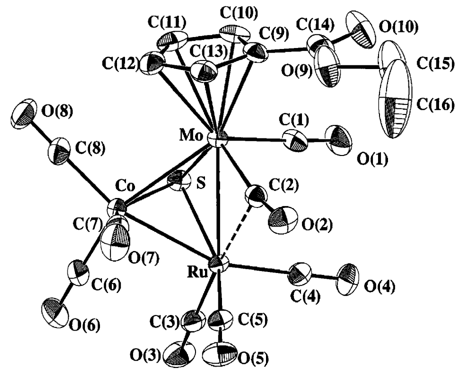


Fig. 2 An ORTEP view of the crystal structure of cluster **2**.

proton correlations can be identified from the HMBC analysis.

It was possible to obtain crystals of clusters **2** and **3** which were suitable for an X-ray crystal structure analysis, shown in Fig. 2 and 3. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. As seen in Fig. 2, the structure of cluster **2** contains a tetrahedral framework comprised of S, Ru, Co and Mo atoms. Eight carbonyls and one five-electron cyclopentadienyl ligand are coordinated to the three transition metals. On the cyclopentadienyl, a $CO_2C_2H_5$ unit is attached. The bond lengths and angles involving the cluster core are very close to those in the corresponding analog.[9d,f,h] The bond length C(9)–C(14) is 1.476 Å and the torsion angle C(13)–C(9)–C(14)–O(9) is 2.0(6)°, so that all the C atoms in the cyclopentadienyl ligand, together with C(14), O(10) and O(9) in the $CO_2C_2H_5$ group, are located in a plane, such that the π system of the $CO_2C_2H_5$ substituent is fully conjugated with the cyclopentadienyl π system.

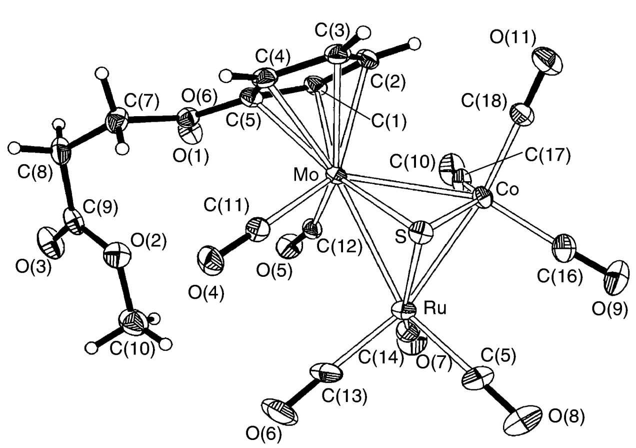


Fig. 3 An ORTEP view of the crystal structure of cluster **3**.

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

Ru–S	2.324(1)	Ru–C(3)	1.896(4)
Ru–Co	2.6061(7)	Ru–C(4)	1.897(4)
Ru–Mo	2.8631(7)	Ru–C(5)	1.914(4)
Mo–S	2.380(1)	Co–C(7)	1.771(5)
Mo–Co	2.7440(6)	Co–C(6)	1.784(5)
Co–S	2.199(1)	Co–C(8)	1.806(4)
Mo–C(2)	1.978(4)	Mo–C(10)	2.293(4)
Mo–C(1)	1.994(4)	Mo–C(13)	2.331(4)
Mo–C(9)	2.280(4)	Mo–C(11)	2.346(4)
Mo–C(12)	2.380(4)	C(9)–C(14)	1.476(6)
Ru–C(2)	2.746(4)		
S–Ru–Co	52.59(3)	Ru–Co–Mo	64.65(2)
S–Ru–Mo	53.39(3)	Co–S–Ru	70.30(3)
Co–Ru–Mo	60.01(2)	Co–S–Mo	73.52(4)
S–Mo–Co	50.21(3)	Ru–S–Mo	74.97(3)
S–Mo–Ru	51.64(3)	S–Co–Ru	57.11(3)
Co–Mo–Ru	55.34(2)	S–Co–Mo	56.27(3)
O(2)–C(2)–Mo	166.9(3)		

Table 3 Selected bond distances (Å) and angles (°) for cluster **3**

Ru–S	2.3234(12)	Ru–C(13)	1.887(4)
Ru–Co	2.6203(10)	Ru–C(15)	1.906(4)
Ru–Mo	2.8773(11)	Ru–C(14)	1.926(4)
Mo–S	2.3973(11)	Co–C(17)	1.770(4)
Mo–Co	2.7471(10)	Co–C(16)	1.790(4)
Co–S	2.2037(12)	Co–C(18)	1.815(4)
Mo–C(12)	1.964(4)	Mo–C(4)	2.313(3)
Mo–C(11)	2.006(4)	Mo–C(3)	2.367(4)
Mo–C(5)	2.296(3)	Mo–C(2)	2.382(3)
Mo–C(1)	2.311(3)	C(5)–C(6)	1.467(5)
Ru–C(12)	2.702		
S–Ru–Co	52.53(3)	S–Co–Ru	56.80(4)
S–Ru–Mo	53.62(2)	S–Co–Mo	56.65(3)
Co–Ru–Mo	59.741(15)	Ru–Co–Mo	64.78(2)
S–Mo–Co	50.16(3)	Co–S–Ru	70.68(3)
S–Mo–Ru	51.29(3)	Co–S–Mo	73.18(3)
Co–Mo–Ru	55.48(3)	Ru–S–Mo	75.09(4)
O(5)–C(12)–Mo	164.3(3)		

Cluster **3** shown in Fig. 3 exhibits the same SRuCoMo tetrahedral geometry as in cluster **2**. The tetrahedral core in **3** also contains a slightly distorted triangular RuCoMo base capped by a sulfido ligand with S–Ru = 2.3234(12), S–Co = 2.2037(12) and S–Mo = 2.3973(11) Å. It should be pointed out that the carbonyl C(2)–O(2) in cluster **2** and carbonyl C(12)–O(5) in **3** are slightly nonlinear, and the asymmetry parameter α (0.39 for cluster **2** and 0.38 for cluster **3**) is well within the range for semi-bridging carbonyls.[17] The IR and ^{13}C NMR spectral data also support the presence of semi-bridging carbonyls. Clusters **2** and **3** contain a total of 48 electrons and are thus electronically saturated.

Conclusions

We have prepared chiral clusters containing a SRuCoMo core and functionally substituted cyclopentadienyl ligands; their reactions with organic compounds were investigated with the intention of resolving chiral clusters. Although two kinds of optically active auxiliaries have been attached to the racemic cluster, the mixture of diastereoisomers cannot be separated by silica gel chromatography. In spite of this failure, this appears be a promising direction to explore for the separation of racemic clusters.

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