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Synthesis, reaction and enantiomeric resolution of chiral clusters containing SRuNiM (M = Mo, W) core

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Abstract

The treatment of $[(\eta^5\text{-}C_5H_4R)CoRuM(CO)_8(\mu_3\text{-}S)]$ with $NiCp_2$ in THF at refluxing temperature gives six novel clusters containing functionally substituted cyclopentadienyl ligand $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COR)NiRuM(CO)_5(\mu_3\text{-}S)]$ (**1**, M = Mo, R = CH_3; **2**, M = W, R = CH_3; **3**, M = Mo, R = OC_2H_5; **4**, M = W, R = OC_2H_5; **5**, M = Mo, R = $COC_6H_4COOCH_3$; **6** M = W, R = $COC_6H_4COOCH_3$). The reactions of clusters (**1**–**6**) with 2,4-dinitrophenylhydrazine were investigated. The ester group was difficult to hydrolyze (clusters **3**–**6**). Hydrazide can easily condense with the ketonic carbonyl (cluster **1** and **2**) on the cyclopentadienyl ring to form complexes $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4C(NR)CH_3)NiRuM(CO)_5(\mu_3\text{-}S)]$ (**7**, M = Mo, R = NH-C_6H_3-2,4-$(NO_2)_2$; **8**, M = W, R = NH–C_6H_3-2,4-$(NO_2)_2$). The structures of **1**, **2** and **7** have been established by the single crystal X-ray diffraction method and the enantiomers of chiral complexes **1**, **3** and **5** were successfully separated by liquid chromatography.

Keywords: Cluster; Chiral; Tetrahedron; Crystal structure; Enantiomeric resolution

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1. Introduction

The chemistry of transition metal clusters has been attracting intense attention since the mid-1970s [1–3]. Recently, the hetero-metal clusters with a tetrahedral skeleton comprised by four different atoms have attracted interest by their chiral properties [4]. Hetero-metal clusters with chiral frameworks can be prepared directly in multi-step addition and substitution reactions by systematic incorporation of organometallic units [2,4] 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 [5,6]. The metal exchange procedure has proven to be the most efficient and versatile method for their preparation, and therefore, continues to attract much attention [7].

Additional impetus for research on these clusters has been provided by the recent investigations of the catalytic properties of clusters in general framework or of transition metal fragments in particular [8]. Unambiguous evidence for cluster catalysis would be the use of a rigid chiral cluster to produce catalysis with asymmetric induction [8,9]. One major problem is that of enantiomeric resolution of the cluster complexes. Until now, many chiral clusters have been reported, but only a few of which have been separated into pure enantiomers [8b,9]. Our research group has begun investigations on the synthesis, enantiomeric resolution and catalysis of the chiral tetrahedral clusters since early 1990s [10]. As a continuation of this project, in this paper we described our study of reactions of clusters containing the SRuCoM core with $NiCp_2$ and the enantiomeric separation of the cluster containing the SRuNiM core. Eight novel clusters were prepared and the crystal structures of **1**, **2** and **7** were determined. The

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enantiomers of chiral clusters **1**, **3** and **5** were successfully separated by liquid chromatography.

2. Experimental

2.1. General details

All reactions were carried out under pure nitrogen using standard Schlenk techniques. All solvents were dried and deoxygenated according to standard procedures before use. Chromatographic separations and purifications were performed on 160–200 mesh silica gel. Infrared spectra were recorded as pressed KBr disks on a Nicolet FTIR 10 DX spectrometer. ^{1}H-NMR spectra were recorded on a Bruker AM-400 MHz spectrometer in $CDCl_3$-deuterated solvent at ambient temperature. Chemical shifts are given in δ relative to $SiMe_4$ (0.0 ppm). Elemental analyses were performed on an 1106-type analyzer. Compounds $NiCp_2$ [18], [η^5-$C_5H_4C(O)R$]RuCoM(CO)$_8$(μ_3-S) (M = Mo, W; R = CH_3, OC_2H_5, $COC_6H_4COOCH_3$) [19] were prepared according to literature methods.

The HPLC system consisted of a M6000 pump (Water, Milford, USA), a model SPD-1 UV variable wavelength detector (Shimadzu, Japan). The CSP **(**chiral stationary phase**)** was packed into a 150 × 4.6 mm I.D. stainless-steel column by the conventional high-pressure slurry-packing procedure.

2.2. Preparation of **1**–**6**

The complex [η^5-$C_5H_4C(O)CH_3$]RuCoMo(CO)$_8$(μ_3-S) (450 mg, 0.73 mmol) and $NiCp_2$ (200 mg, 1.06mmol) were dissolved in THF (25 ml). After the mixture was refluxed for 30 h, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (5 ml). Then the extracts were subjected to column chromatography separation by using 1:2 CH_2Cl_2–petroleum ether as eluent. Several small bands and a major one were separated. From the main black band was obtained 110 mg (25%) of [η^5-C_5H_5][η^5-$C_5H_4C(O)CH_3$]RuNiMo(CO)$_5$(μ_3-S) (**1**) as a black solid. IR (νCO) 2072vs, 2010s, 1987vs, 1931s, 1871s cm^{-1}; (C=O) 1667s cm^{-1}. ^{1}H-NMR δ, 6.01–5.54 (m, 4H, C_5H_4), 5.35 (s, 5H, C_5H_5), 2.37 (s, 3H, CH_3). Anal. Calc. for $C_{17}H_{12}O_6MoNiRuS$: C, 34.03; H, 2.02. Found: C, 34.05; H, 2.02%.

The following compounds **2**–**6** were similarly prepared.

*2.2.1. [η^5-C_5H_5][η^5-$C_5H_4C(O)CH_3$]RuNiW(CO)$_5$(μ_3-S) (**2**)*

A purple solid (60 mg, 25%); IR (νCO) 2069vs, 2008s, 1987vs, 1929s, 1870s cm^{-1}; (C=O) 1663s cm^{-1}. ^{1}H-NMR δ 5.99–5.61 (m, 4H, C_5H_4), 5.42 (s, 5H, C_5H_5), 2.37 (s, 3H, CH_3). Anal. Calc. for $C_{17}H_{12}O_6WNiRuS$: C, 29.68; H, 1.76. Found: C, 29.70; H, 1.75%.

*2.2.2. [η^5-C_5H_5][η^5-$C_5H_4C(O)OC_2H_5$]RuNiMo(CO)$_5$(μ_3-S) (**3**)*

A black solid (120 mg, 46%); IR (νCO) 2057vs, 1981vs, 1934m, 1853m cm^{-1}; (C=O) 1717s cm^{-1}. ^{1}H-NMR δ 6.05–5.53 (q, 4H, C_5H_4), 5.37 (s, 5H, C_5H_5), 4.33–4.27 (q, 2H, CH_2), 1.36–1.26 (t, 3H, CH_3). Anal. Calc. for $C_{18}H_{14}O_7MoNiRuS$: C,34.31; H, 2.24. Found: C, 34.29; H, 2.27%.

2.2.3. [η^5-C_5H_5][η^5-$C_5H_4C(O)OC_2H_5$]RuNiW(CO)$_5$(μ_3-S) (4)

A purple solid (70 mg, 35%); IR (νCO) 2054vs, 1979vs, 1936m, 1872m cm^{-1}; (C=O) 1720s cm^{-1}. ^{1}H-NMR δ 6.05–5.62 (q, 4H, C_5H_4), 5.44 (s, 5H, C_5H_5), 4.33–4.32 (q, 2H, CH_2), 1.35–1.27 (t, 3H, CH_3). Anal. Calc. for $C_{18}H_{14}O_7WNiRuS$: C, 30.11; H, 1.97. Found: C, 30.12; H, 1.93%.

*2.2.4. [η^5-C_5H_5][η^5-$C_5H_4C(O)C_6H_4C(O)OCH_3$]RuNiMo(CO)$_5$($\mu_3$-S) (**5**)*

A black solid (100 mg, 30%); IR (νCO) 2059vs, 2037vs, 1960m, 1917m, 1858m cm^{-1}; (C=O) 1721m cm^{-1}. ^{1}H-NMR δ 8.16–7.84 (q, 4H,C_6H_4), 6.12–5.62 (q, 4H, C_5H_4), 5.32 (s, 5H, C_5H_5), 3.97(s, 3H, CH_3). Anal. Calc. for $C_{24}H_{16}O_8MoNiRuS$: C, 40.03; H, 2.24. Found: C, 40.00; H, 2.26%.

*2.2.5. [η^5-C_5H_5][η^5-$C_5H_4C(O)C_6H_4C(O)OCH_3$]RuNiW(CO)$_5$($\mu_3$-S) (**6**)*

A black solid (50 mg, 19%); IR (νCO) 2046vs, 1978vs, 1960vs, 1917m, 1838m cm^{-1}; (C=O) 1721m cm^{-1}. ^{1}H-NMR δ 8.16–7.83 (q, 4H,C_6H_4), 6.06–5.69 (q, 4H, C_5H_4), 5.38 (s, 5H, C_5H_5), 3.96(s, 3H, CH_3). Anal. Calc. for $C_{24}H_{16}O_8WNiRuS$: C, 35.67; H, 1.98. Found: C, 35.63; H, 2.01%.

2.3. Preparation of 7–**8**

A 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) in ethanol (17.5 ml), was added to an ethanol solution (15 ml) in which cluster **1** (30 mg, 0.050 mmol). After the mixture was stirred at room temperature (r.t.) for 1 h, the solvent was removed under reduce pressure and the residue was extracted with CH_2Cl_2 (5 ml). Then the extracts were subjected to silica gel column chromatography separation by using 1:1 CH_2Cl_2–petroleum ether as eluent. Several small bands with a major brown one were separated. From the main brown band was obtained 35 mg, (89.7%) of [η^5-C_5H_5][η^5-$C_5H_4C(NR)CH_3$]RuNiMo(CO)$_5$(μ_3-S) [R = NH–C_6H_3-2,4-$(NO_2)_2$] (**7**) as a brown solid. IR 3110w (N–H), 2051vs, 1972vs, 1928m, 1858m, 1613s (C=N), and 1592s (NO_2) cm^{-1}. ^1H-NMR δ 11.26 (s, 1H, N–H), 9.17 (s, 1H, H^3 of benzene ring), 8.39–8.37 (d, 1H, H^5 of benzene ring, $J = 9.36$ Hz), 7.99–7.96 (d, 1H, H^6 of benzene ring, $J = 9.48$), 6.09–5.57 (q, 4H, C_5H_4), 5.35 (s, 5H, C_5H_5), 2.23 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{16}O_9N_4MoNiRuS$: C, 35.41; H, 2.07; N, 7.18. Found: C, 35.40; H, 2.08; N, 7.16%.

The compound **8** was prepared similarly.

2.3.1. *[η^5-C_5H_5][η^5-$C_5H_4C(NR)CH_3$]RuNiW(CO)$_5$-(μ_3-S) [R = NH–C_6H_3-2-4-(NO_2)$_2$, **8**]*

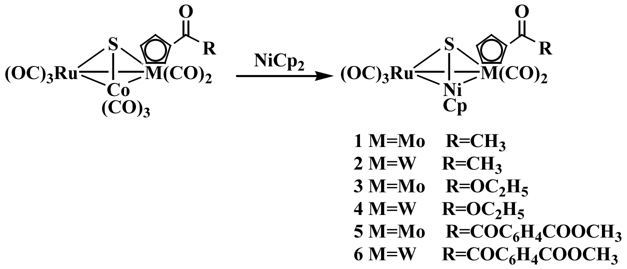
A brown solid (30 mg, 68%); IR 3111w (N–H), 2053vs, 1978vs, 1930m, 1861m, 1616s (C=N), and 1592s (NO_2) cm^{-1}. ^1H-NMR δ 11.20 (s, 1H, N–H), 9.09 (s, 1H, H^3 of benzene ring), 8.32–8.29 (d, 1H, H^5 of benzene ring, $J = 9.88$ Hz), 7.90–7.87 (d, 1H, H^6 of benzene ring, $J = 9.08$), 6.01–5.53 (q, 4H, C_5H_4), 5.34 (s, 5H, C_5H_5), 2.16 (s, 3H, CH_3). Anal. Calc. for $C_{23}H_{16}O_9N_4WNiRuS$: C, 31.82; H, 1.86; N, 6.45. Found: C, 31.79; H, 1.88; N, 6.46%.

2.4. *Separation of enantiomers complexes **1**, **3** and **5***

The enantiomeric resolution of complexes **1**, **3** and **5** was performed at an OD column at r.t. The mobile phase used in the study was composed of mixture of hexane–alcohol (95:5). The flow rate was maintained at 0.33 ml min^{-1}, with UV detection was at 254 nm. The chromatograms obtained from compounds **1**, **3**, **5** are shown in Fig. 4.

2.5. *Crystal structure determination of **1**, **2** and **7***

Crystals of **1** and **2** used for the X-ray structure determination were obtained from hexane–CH_2Cl_2 (1:1) solution at −20 °C. Crystals of **7** were grown from a hexane–acetone(2:1) solution at −20 °C. The crystals were mounted on a glass fiber. Preliminary examination and data collection were performed with Mo–K_α ($\lambda = 0.71073$ Å) radiation on a CCD area detector equipped with graphite monochromator. Data were collected by the ω/φ scan technique. Absorption corrections were applied using SADABS. The structures were solved by direct method using the SHELXS-97 program and refined by the full-matrix least-squares on F^2 using SHELXS-97 program [20]. The non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated by geometrical methods.



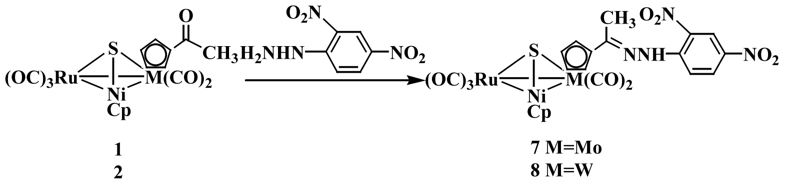
Scheme 1.

3. Result and discussion

3.1. *Preparation of **1**–**8***

The reactions described in this work are summarized in Scheme 1. It was found that the tetrahedral SRuCoM (M = Mo, W) clusters containing functionally substituted cyclopentadienyl ligands [η^5-$C_5H_4C(O)R$]RuCoM$(CO)_8(\mu_3$-S) reacted with $NiCp_2$ in THF at refluxing temperature to give the corresponding functionally substituted cyclopentadienyl SRuNiM complexes [η^5-C_5H_5][η^5-$C_5H_4C(O)R$]RuNiM $(CO)_5(\mu_3$-S) (**1**–**6**). Complexes **1**–**6** were derived by displacement of a d^9 ML_3 $Co(CO)_3$ vertex by an isolobal NiCp moiety generated in situ by thermal decomposition of nickelocene [11,12]. Although η^5-$C_5H_4M(CO)_2$(d^5 ML_5) is also isolobal with η^5-C_5H_5Ni(d^9 ML_3), no products derived from isolobal displacement of the former by η^5-C_5H_5Ni were found under these conditions. This suggests that the isolobal fragment $Co(CO)_3$ is a much better leaving group than η^5-$C_5H_4M(CO)_2$ in these reaction conditions. All metal exchange reactions require a long time at high temperature (refluxing THF) with moderate to low yields.

The reactivity of organic substituents bound to the cyclopentadienyl ring toward 2,4-dinitrophenylhydrazine in ethanol at room temperature catalyzed by 98% H_2SO_4 were investigated, as shown in Scheme 2. The reaction of clusters **1** and **2** produce the novel chiral clusters **7** and **8** in high yields, Hydrazones of **5** and **6** were not obtained from these reactions. This might be due to the steric effect of the $C_6H_4COCH_3$.



Scheme 2.

3.2. Characterization of **1–8**

Cluster complexes **1**–**8** are solids colored from brown to black. All spectroscopic data obtained are in accord with the indicated compositions of **1**–**8**. Their IR spectra are somewhat complicated due to the number of carbonyl ligands and the organic groups on the cyclopentadienyl ligands. Clusters **1**–**8** show a large number of strong terminal carbonyl absorption bands located at the range of 2072–1917 cm^{-1} in their IR spectra. The absorption bands from 1853 to 1872 cm^{-1} suggest the presence of bridging carbonyl ligand. In IR spectra of **1**–**6** also showed carbonyl absorption bands of the ester at around 1720 cm^{-1} and ketone at 1663 cm^{-1}, and those of **7**, **8** showed an absorption band around 1613 cm^{-1} for C=N stretching. The absorption bands around 1592 cm^{-1} in spectral **7** and **8** are characteristic for the nitro units bound to benzene ring. Other characteristic absorptions for organic units can be easily assigned.

The ^{1}H-NMR spectra of all clusters show the presence of the hydrogen atoms in their corresponding organic group. For the substituted cyclopentadienyl ligands, the ^{1}H-NMR spectra of all clusters exhibit four asymmetric singlets in the range δ 6.09–5.53 instead of two groups of triplets (A_2B_2 type), comprising two upfield singlets assignable to the two protons at the 3,4-positions of the substituted cyclopentadienyl rings and two downfield singlets assignable to the 2,5-protons, resulting from the different deshielding effects of electron-withdrawing groups $COCH_3$, $COOC_2H_5$ and $COC_6H_4COCH_3$ on these nuclei [13,14]. However, the protons of the unsubstituted cyclopentadienyl ligands appear as a singlet in the range of δ 5.44–5.34 ppm. In addition, for **1** and **2**, the ^{1}H-NMR spectra display one singlet at about δ 2.37 ppm for the methyl group. The ^{1}H-NMR spectra of **3**, **4** show a triplet at the range of δ 1.36–1.26 ppm and a quartet in the range of δ 4.33–4.27, respectively, assigned to the protons CH_3 and CH_2. The ^{1}H-NMR spectra of **5**, **6** show a singlet around δ 3.97 assigned to the protons CH_3 and a quartet in the range of δ 8.16–7.83 assigned to the protons C_6H_4. For the hydrazone cluster complexes **7** and **8**, the proton signals of the N–NH unit appear as the singlet around δ 11.20 at the downfield side, and the signals of the 2,4-nitrophenyl groups in **7** and **8** appear in the range of δ 9.17–7.87, which is in accord with literature [7b,15].

3.3. Structures of **1**, **2** and **7**

The crystal structures of **1**, **2**and **7** were determined by single-crystal X-ray diffraction methods. Crystallographic data are collected in Table 1 and selected bond lengths and angles are listed in Tables 2–4. Figs. 1–3 show the molecular structure of complexes **1**, **2** and **7**, respectively.

As can be seen from Figs. 1 and 2, the structure of the clusters of **1** and **2** contain a slightly distorted tetra-

Table 1
Summary of the crystallographic data for compounds **1**, **2** and **7**

Clusters	**1**	**2**	**7**
Empirical formula	$C_{17}H_{12}MoNiO_6RuS$	$C_{17}H_{12}WNiO_6RuS$	$C_{23}H_{16}MoN_4NiO_9RuS$
Formula weight (F_w)	600.05	687.96	780.18
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*
a (Å)	7.9606(8)	7.9267(4)	13.207(4)
b (Å)	8.5604(9)	8.5850(5)	16.036(5)
c (Å)	14.7793(16)	14.7024(8)	25.513(8)
α (°)	93.908(2)	93.7200(10)	90
β (°)	105.057(2)	104.9610(10)	90
γ (°)	101.463(2)	101.5470(10)	90
V (Å^3)	945.51(17)	939.82(9)	5403(3)
Z	2	2	8
D_{calc} (g cm^{-3})	2.108	2.431	1.918
Radiation	Mo–K_α	Mo–K_α	Mo–K_α
Temperature (K)	293	293	293
F(000)	584	648	3072
μ (mm^{-1})	2.568	8.031	1.834
Scan type	ω/φ	ω/φ	ω/φ
$2\theta_{max}$ (°)	56.48	56.50	50.06
Number of observations	4192 ($I > 2.00\sigma(I)$)	4173 ($I > 2.00\sigma(I)$)	3918 ($I > 2.00\sigma(I)$)
Number of variables	292	246	365
R	0.0380	0.0514	0.0512
R_w	0.0674	0.1313	0.1132
Goodness-of-fit indicator	0.818	1.071	0.985
Largest peak in final difference map (e Å^{-3})	0.874	4.615	0.928

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

Bond distances			
Mo–S	2.3819(13)	Mo–C(9)	1.975(6)
Mo–Ni	2.6479(7)	Mo–C(10)	1.961(6)
Mo–Ru	2.8498(6)	C(15)–C(16)	1.465(7)
Ru–S	2.3138(13)	Ni–C(av. Cp)	2.088
Ni–S	2.1337(14)	Mo–C(av. Cp)	2.3282
Ni–Ru	2.5699(8)	Ru–C(av. Cp)	1.913
Bond angles			
S–Mo–Ni	49.86(3)	S–Ni–Ru	58.05(4)
S–Mo–Ru	51.55(3)	S–Ni–Mo	58.58(4)
Ni–Mo–Ru	55.592(18)	Ru–Ni–Mo	66.19(2)
S–Ru–Mo	53.73(3)	Ni–S–Ru	70.46(4)
Ni–Ru–Mo	58.218(19)	Ni–S–Mo	71.56(4)
S–Ru–Ni	51.49(4)	Ru–S–Mo	74.72(4)
C(10)–Mo–Ru	66.37(15)	C(9)–Mo–Ru	77.48(16)

Table 3
Selected bond distance (Å) and angles (°) for cluster **2**

Bond distances			
Ru–S	2.312(2)	N(1)–C(16)	1.312(8)
Ru–Ni	2.5715(14)	N(1)–N(2)	1.372(7)
Ru–Mo	2.8299(11)	N–C(18)	1.308(8)
Mo–S	2.3167(19)	Ru–C(av)	1.878
Mo–Ni	2.7261(14)	Mo–C(av. Cp)	2.3482
Ni–S	2.147(2)	Ni–C(av. Cp)	2.087
Ni–C(4)	2.497(9)	Mo–C(4)	2.031(9)
Bond angles			
S–Ru–Mo	52.39(5)	S–Mo–Ni	49.59(6)
Ni–Ru–Mo	60.40(3)	S–Mo–Ru	52.23(6)
S–Ru–Ni	51.84(6)	Ni–Mo–Ru	55.10(3)
Ni–S–Ru	70.33(6)	Ru–Ni–Mo	64.50(3)
Ni–S–Mo	75.17(7)	S–Ni–Ru	57.83(6)
Ru–S–Mo	75.38(6)	S–Ni–Mo	55.24(6)

Table 4
Selected bond distance (Å) and angles (°) for cluster **7**

Bond distancess			
W–S	2.3768(16)	W–C(1)	1.965(9)
W–Ni	2.6380(9)	W–C(2)	2.004(8)
W–Ru	2.8414(6)	Ni–C(av. Cp)	2.093
Ru–S	2.3224(17)	W–C(av. Cp)	2.3258
Ru–Ni	2.5673(10)	Ru–C(av. C)	1.903
Ni–S	2.1419(18)	C(11)–C(12)	1.474(11)
Bond angles			
S–W–Ni	50.24(4)	S–Ni–Ru	58.26(5)
S–W–Ru	51.93(4)	S–Ni–W	58.54(5)
Ni–W–Ru	55.73(2)	Ru–Ni–W	66.15(2)
S–Ru–W	53.68(4)	Ni–S–Ru	70.08(5)
Ni–Ru–W	58.12(2)	Ni–S–W	71.22(5)
S–Ru–Ni	51.66(5)	Ru–S–W	74.40(5)
C(1)–W–Ru	67.3(2)	C(2)–W–Ru	77.6(2)

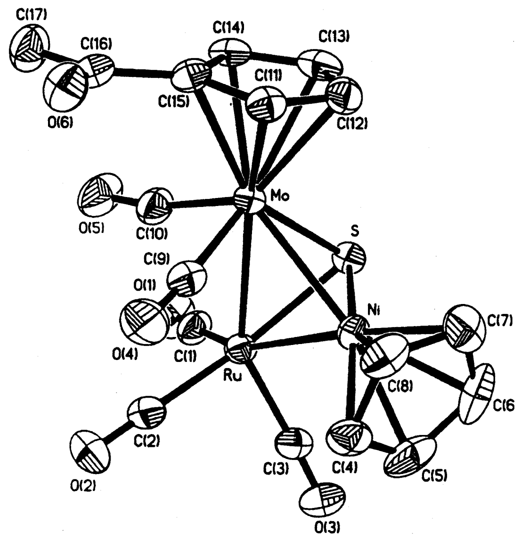


Fig. 1. An ORTEP view of the crystal structure of cluster **1** (thermal ellipsoids are drawn at 30% probability).

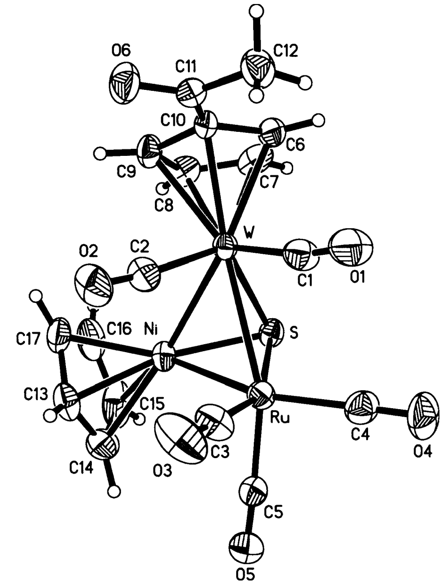


Fig. 2. An ORTEP view of the crystal structure of cluster **2** (thermal ellipsoids are drawn at 30% probability).

hedral core MNiRuS (M = Mo, W), which contains two carbonyl ligands on M (Mo, W) atom, three carbonyls on Ru atom, one cyclopentadienyl ligand attached to the Ni atom, and one substituted cyclopentadienyl ligand coordinated to the M (Mo, W) atom. The bond length and angles involving the two cluster cores are slightly different because of the effects of the two different atoms Mo and W. In the two clusters the distance from M (Mo, W) atom to centroid of cyclopentadienyl ring denoted as M–Cp_{cent} is longer than the Ni–Cp_{cent}. In cluster **1** all the C atoms in the substituted cyclopentadienyl ligand together with C(16), C(17) and O(6) in the $COCH_3$ group and in cluster **2** all the C

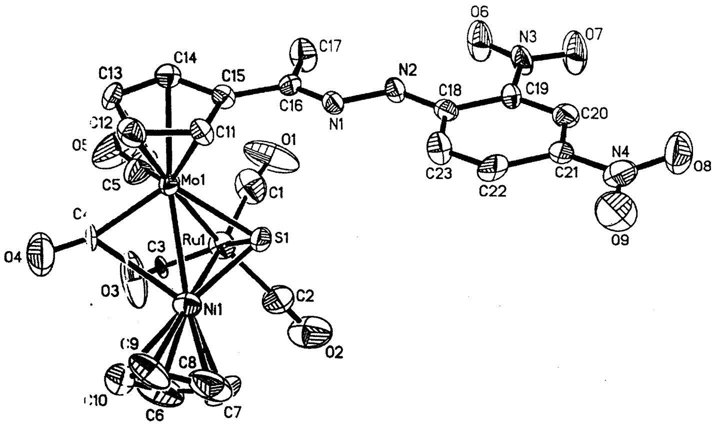


Fig. 3. An ORTEP view of the crystal structure of cluster **7** (thermal ellipsoids are drawn at 30% probability).

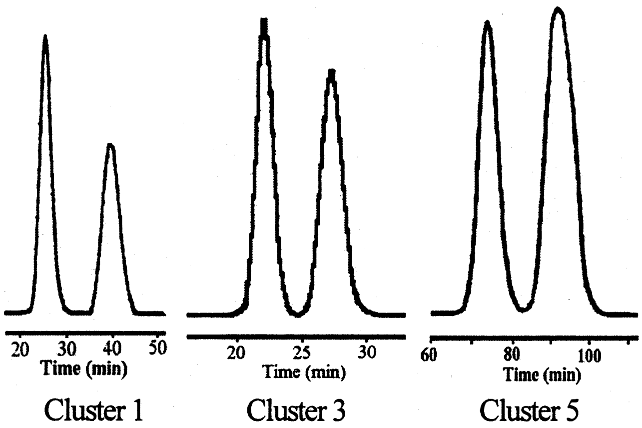


Fig. 4. The chromatograms of resolution of cluster **1**, **3** and **5**.

atoms in the substituted cyclopentadienyl ligand together with C(11), C(12) and O(6) in the $COCH_3$ group, are located in one plane. So the π-system of the substituted group $COCH_3$ is fully conjugated with the cyclopentadienyl π-system. This result is in contrast to that reported by Song et al. [16]. The tetrahedral core SRuNiM of cluster **1** and **2** deviate considerably from perfect tetrahedral geometry. This is because RuNiM triangle restricts the angles around the sulfur atom.

Cluster **7** shown in Fig. 3 exhibits the same SRuMoNi tetrahedral geometry as in cluster **1**. Again, the Ru atom is coordinated by three terminal carbonyl ligands, and the Mo atom is coordinated by two carbonyls and one substituted cyclopentadienyl ligand. In the molecule of **7**, a $NNHC_6H_3$-2,4-$(NO_2)_2$ group is connected with the substituted cyclopentadienyl ring through a C=N double bond. The acute angles about the sulfur atom average 73.63° (Ni–S–Ru 70.33°, Ni–S–Mo 75.17°, Ru–S–Mo 75.38°), which is larger than that in cluster **1** (72.25°).

It is important to note that while the three carbonyls attached to the Ru atom are terminal in the two molecular structures, there are semi-bridging carbonyls (one carbonyl bound to Mo atom C10 in compound **1**, one carbonyl bound to W atom C1 in compound **2** and one carbonyl bound to Mo atom C4 in compound **7**) in the fragment $M(CO)_2(C_5H_4COCH_3)$. The asymmetry parameter α (0.395 for cluster **1**, 0.405 for cluster **2** and 0.229 for cluster **7**) is well within the range for semi-bridging carbonyls [17]. The coexistence of both terminal carbonyls and semi-bridging carbonyls is consistent with the IR spectra of **1**, **2** and **7** showing several absorption bands from 1853 to 1872 cm^{-1}. Complexes **1**, **2** and **7** contain a total of 48 electrons and are electronically precise.

3.4. *Resolution of cluster **1**, **3** and **5***

To obtain pure enantiomers, the most direct way should be by chromatography over an optically active adsorbent. The chromatograms obtained from the clusters **1**, **3** and **5** are shown in Fig. 4. The optimized mobile phase compositions and analytical results for chiral complexes (**1**, **3** and **5**) are summarized in Table 5. The results show that the enantiomeric resolution via

Table 5
Optimum enantioseparation of chiral clusters **1**, **3** and **5**

Cluster	Eluent (V/V = 95/5)	T (°C)	k_1	k_2	α
1	Hexane–2-propanol	25	9.64	12.7	1.32
3	Hexane–1-butanol	25	3.56	4.63	1.30
5	Hexane–2-propanol	25	14.4	18.1	1.26

chromatography over an optically active adsorbent was successful, and the pure enantiomers can be obtained.

4. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 173148 for compound **1**, No. 173149 for compound **2** and No. 181134 for compound **7**. 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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