

## Asymmetric Inducing Synthesis of Optically Active Tetrahedral Cluster Containing SMCoW Core

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The chiral clusters  $(\mu_3\text{-S})\text{MCoW}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3]$  [ $\text{M}=\text{Ru}$  (**2**),  $\text{Fe}$  (**3**)] were synthesized by asymmetric induction of *N*-benzylcinchonium chloride as phase-transfer catalyst (PTC). The most suitable amount of PTC is 70 mol%. Cluster **3** was determined by single crystal X-ray diffraction analysis. The best *ee* of the chiral cluster is over 20%.

**Keywords**      asymmetric synthesis, optically active cluster, SMCoW core

### Introduction

Transition-metal cluster complexes have been receiving considerable attention due to their synergetic catalysis among different metals.<sup>1</sup> In last decade, we reported the syntheses of a large number of racemic tetrahedral chiral clusters and investigated their catalysis in asymmetric reactions.<sup>2</sup> Among these, we demonstrated the chiral structures of tetrahedral cluster  $(\mu_3\text{-S})\text{RuCoMo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{R}]$  ( $\text{R}=\text{CH}_3$ ,  $\text{OC}_2\text{H}_5$ ,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ,  $\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$ ) by X-ray single crystal diffraction methods.<sup>3</sup> Further investigation showed that the cluster  $(\mu_3\text{-S})\text{RuCoMo}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3]$  is an active catalyst precursor in the reduction of ethyl acetoacetate to ethyl 3-hydroxybutyrate, and found that the cluster holds intactness during the catalytic process by IR spectrum.<sup>4</sup> It was proved that this coordination process reliably took place on the nuclear framework of cluster, rather than on the mononuclear metal complex which may come from decomposition of cluster. This is an essential premise for asymmetric catalysis. However, the product has no *ee* value because the cluster is racemate. Up to now, it is not easy to obtain optically active enantiomer of clusters due to their special structure and properties. Here we report the results on synthesis of clusters  $(\mu_3\text{-S})\text{RuCoW}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3]$  and  $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3]$  by induction of *N*-benzylcinchonium chloride as phase-transfer catalyst.

### Experimental

All solvents were dried by standard methods and distilled under nitrogen prior to use.

*N*-Benzylcinchonium chloride,  $\text{SRuCo}_2(\text{CO})_9$  or  $\text{SFeCo}_2(\text{CO})_9$  and  $\text{Na}[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{CH}_3]$  were prepared according to literature, respectively.<sup>5-7</sup>

IR spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer, and <sup>1</sup>H NMR on a Bruker AM-400 MHz spectrometer. Elemental analyses (C/H) were performed on a Carlo Erba 1106 type analyzer. *Ee* determination was performed with an LC-6A (shimadzu, Japan) chromatograph, equipped with an SPD-6AV violet-visible inspector, wavelength  $\lambda=254$  nm, at room temperature; flow phase: hexane/isopropanol (97/3), flow rate 0.5 mL/min. Chromatograph column was homemade, with length of 15 cm, i.d.=4.6 mm, using cellulose-tris(3,5-dimethylphenylcarbamate) absorbed on silica gel as chiral stationary phase. Optical rotation was determined on a J-20 (Japan) circular dichroism spectrometer. Crystal structure was determined by an automated R3m/E CAD-4 diffractometer with graphite monochromated Mo K $\alpha$  radiation.

The synthesis of  $(\mu_3\text{-S})\text{RuCoW}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3]$  (**2**) was carried out under highly pure nitrogen using standard Schlenk and vacuum line techniques.  $\text{W}(\text{CO})_6$  (352 mg, 1.0 mmol) and  $[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3]\text{-Na}$  (130 mg, 1.0 mmol) were dissolved in DMF and the mixture was refluxed for 3 h. After having removed DMF, added 30 mL of THF, and stirred for 0.5 h at room temperature, *N*-benzylcinchonium chloride (0.1 mmol) was added, and 0.5 h later,  $(\mu_3\text{-S})\text{RuCo}_2(\text{CO})_9$  (503 mg, 1.0 mmol) was added. The mixture was heated at reflux with strong stirring for 2 h. The solvent was removed *in vacuo*, and the residue was separated on a 2.5 cm  $\times$  35 cm silica gel column, using dichloromethane/petroleum ether (*V/V*=2 : 1) as eluent. After

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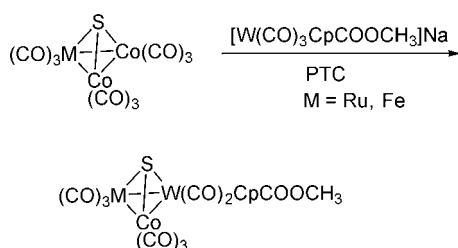
the solvent was removed, the product of complex **2** was recrystallized in hexane-dichloromethane at  $-18\text{ }^{\circ}\text{C}$  to afford black crystals 293 mg. Yield 38.0%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 5.58 (s, 1H, Cp), 5.68 (s, 1H, Cp), 6.05 (s, 2H, Cp), 3.97 (s, 3H,  $\text{OCH}_3$ ); IR (KBr)  $\nu$ : 2082 (vs), 2029 (vs), 2000 (vs), 1963 (s), 1945 (s), 1880 (s) ( $\text{C}\equiv\text{O}$ ), 1721 ( $\text{C}=\text{O}$ ), 1463 (w), 1427 (w)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{15}\text{H}_7\text{O}_{10}\text{RuCoWS}$ : C 24.90, H 0.97; found C 24.92, H 0.96.

The synthetic procedure for cluster  $(\mu_3\text{-S})\text{FeCoW}(\text{CO})_8[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3]$  (**3**) was the same as that for cluster **2** mentioned above, affording black crystals 254 mg. Yield 37.5%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 5.56 (s, 1H, Cp), 5.75 (s, 1H, Cp), 6.13 (s, 2H, Cp), 4.03 (s, 3H,  $\text{OCH}_3$ ). IR (KBr)  $\nu$ : 2078 (vs), 2029 (vs), 2001 (vs), 1940 (s), 1861 (m) ( $\text{C}\equiv\text{O}$ ), 1717 (s) ( $\text{C}=\text{O}$ ), 1462 (w, Cp), 1428 (w, Cp)  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{15}\text{H}_7\text{O}_{10}\text{FeCoWS}$ : C 26.56, H 1.03; found C 26.54, H 1.01.

## Results and discussion

The synthetic route of the title compounds is shown as follows (Scheme 1):

Scheme 1



The IR spectra of the both title compounds exhibit a large number of absorption bands between 2082 and 1861  $\text{cm}^{-1}$ , which are assigned to terminal carbonyl vibrations. The absorption bands at 1717 and 1721  $\text{cm}^{-1}$  are characteristic of the carbonyl group of the functional substituent. For  $^1\text{H NMR}$  assignment, chemical shifts of the substituted cyclopentadienyl in clusters appear at  $\delta$  5.56–6.13. The singlets at  $\delta$  3.97 and 4.03 are assigned to  $\text{OCH}_3$ .

Cluster **3** was determined by single crystal X-ray diffraction analysis, and its some parameters are given in Table 1. The molecular structure is shown in Figure 1.

The racemic clusters are obtained usually by exchange of metal fragments. The prochiral precursor  $\text{S-RuCo}_2(\text{CO})_9$  contains a symmetry plane (Figure 2), and the metal framework becomes a chiral unit if one of the two enantiotopic  $\text{Co}(\text{CO})_3$  fragments is replaced by a  $\text{W}(\text{CO})_2[\eta^5\text{-C}_5\text{H}_4\text{C}(\text{O})\text{OCH}_3]$  fragment. Under achiral conditions, metal exchange at both sides is equally probable, and the enantiomers are formed in a 1 : 1 ratio. In asymmetric environment arising from the optically active induction of *N*-benzylcinchonium chloride, however, the two cobalt sites are no longer equivalent, and two enantiomers will be formed in an unequal ratio

Table 1 Crystal and refinement data for cluster **3**

Empirical formula	$\text{C}_{15}\text{H}_7\text{O}_{10}\text{FeCoWS}$
Formula weight	677.90
$F(000)$	2560
Temperature	293(2) K
Crystal system	Monoclinic
Space group	$C2/c$
$a$	3.1356(15) nm
$b$	0.7790(4) nm
$c$	1.6108(7) nm
$\alpha$	$90^\circ$
$\beta$	$90.00(14)^\circ$
$\gamma$	$90^\circ$
Volume	$3.934(3) \text{ nm}^3$
$Z$	8
Calculated density	$2.289 \text{ g/cm}^3$
Absorption coefficient	$7.551 \text{ mm}^{-1}$
Goodness-of-fit on $F^2$	1.013
$2\theta$ range	$2.53^\circ\text{--}28.45^\circ$
Data restraints parameters	4578/0/264
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.0432, wR_2=0.1086$
$R$ indices (all data)	$R_1=0.0494, wR_2=0.1112$
Reflections collected unique	11339, 4578 [ $R(\text{int})=0.1526$ ]

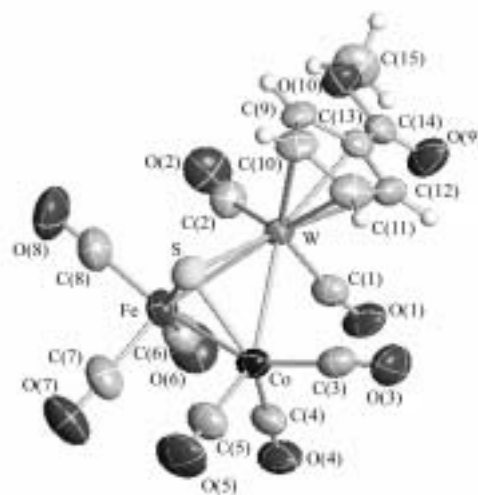


Figure 1 The molecular structure of cluster **3**.

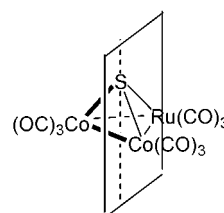


Figure 2 Structure of prochiral precursor  $\text{SRuCo}_2(\text{CO})_9$ .

during the metal exchange reaction, the corresponding products are optically active. Moreover, the amount of *N*-benzylcinchonium chloride can affect specific rotation of the product. The results of cluster **1** as reactant are shown in Table 2. Specific rotation is not in line with the PTC, and when the PTC is 0.7 mmol, its value is the biggest. Of course, the concentration of the clusters affects the results on measurement because the clusters are red-dark. At present, determination of *ee* value is not easy, mainly because there is no commercial chiral column all over the world. We try to measure *ee* value by NMR before this, but the clusters did not show chiral difference except that all the shifts move downfield about 0.2 ppm using Eu(tfc)<sub>3</sub> as shift reagent. In Table 3, cluster **1** was separated at basic line, but the *ee* value was very low, only 2.12%; clusters **2** and **3** were not separated at basic line, but clusters **2** showed distinct *ee* value from Figure 3. The best *ee* value of the optically active cluster obtained was over 20% when the middle-cut method was used. The *ee* value of cluster **2** is

higher than that of cluster **3**, but the specific rotation on the contrary, which is corresponding with that the specific rotation of the cluster containing Fe atom is higher than that of containing Ru atom.<sup>8</sup>

Our previous study indicated that the solvent affected specific rotation of cluster product. Ether was found to be the most suitable solvent.<sup>8</sup>

According to the results mentioned above, it may be hoped that synthetic condition could affect enantiomer excess value. *Ee* value could be raised with the synthetic conditions improved. Alternatively, measuring *ee* value could be more exact with the better and suitable chiral column applied.

## Conclusions

Asymmetric synthesis using *N*-benzylcinchonium chloride as phase-transfer catalyst demonstrated a practicable way to get optically active tetrahedral transition-metal clusters, and the best *ee* value is over 20%.

**Table 2** Effects of *N*-benzylcinchonium chloride on the optically active product

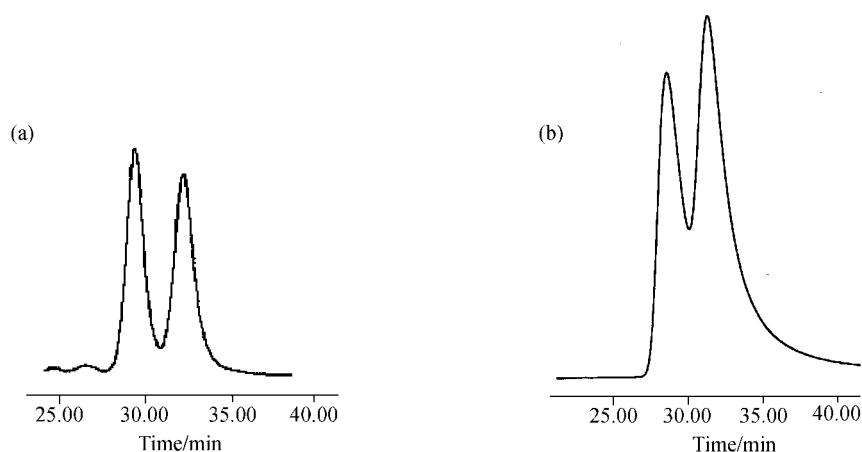
Cluster <b>1</b>	Benzylcinchonium chloride/mmol	Specific rotation <sup>a</sup>	Concentration <i>c</i> (g/100 mL)
SRuCoMo(CO) <sub>8</sub> CpCOCH <sub>3</sub>	0.5	+9.56	0.46
SRuCoMo(CO) <sub>8</sub> CpCOCH <sub>3</sub>	0.7	+30.77	0.60
SRuCoMo(CO) <sub>8</sub> CpCOCH <sub>3</sub>	0.9	+25.63	0.48
SRuCoMo(CO) <sub>8</sub> CpCOCH <sub>3</sub>	1.1	+15.25	0.40

<sup>a</sup> Solvent: CH<sub>2</sub>Cl<sub>2</sub>.

**Table 3** The cluster *ee* value of asymmetric inducing synthesis

Sample	PTC/mmol	Concentration (g/100 mL)	Specific rotation	Molar rotation <sup>a</sup>	Yield/%	<i>ee</i> <sup>b</sup> /%
SRuCoMo(CO) <sub>8</sub> CpCOCH <sub>3</sub> ( <b>1</b> )	0.1	0.40	+18.8°	+116.6°	32.54	2.12
SRuCoW(CO) <sub>8</sub> CpCOOCH <sub>3</sub> ( <b>2</b> )	0.7	0.70	+11.9°	+75.8°	38.0	26.6
SFeCoW(CO) <sub>8</sub> CpCOOCH <sub>3</sub> ( <b>3</b> )	0.7	0.52	+21.0°	+142.0°	37.5	20.4

<sup>a</sup> Solvent: CH<sub>2</sub>Cl<sub>2</sub>,  $[\alpha]_D^{22}$ . <sup>b</sup> Determined by chiral HPLC with cellulose-tris(3,5-dimethylphenylcarbamate) absorbed on silica gel as chiral stationary phase; flow phase: for cluster **1**, hexane/isopropanol (99/1); for clusters **2** and **3**, hexane/isopropanol (97/3). *Ee* values are calculated through middle-cutting method. Their chromatograms are shown in Figure 3. The former (a) refers to cluster **1**, and the latter (b) is cluster **2**'s.



**Figure 3** Chromatogram of clusters **1** and **2**.

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