Synthesis and resolution of a tetrahedral cluster containing the SeRuCoMo core

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A new cluster derivative (μ_3-Se)RuCoMo(CO)$_8$CpCOOCH$_3$ **3** was obtained by the reaction of SeRuCo$_2$(CO)$_9$ **1** with the functionally-substituted sodium cyclopendiene [Mo(CO)$_8$CpCOOCH$_3$]Na **2** in THF at 60°C and its structure has been determined by single-crystal X-ray diffraction.

Keywords: tetrahedral cluster, SeRuCoMo core

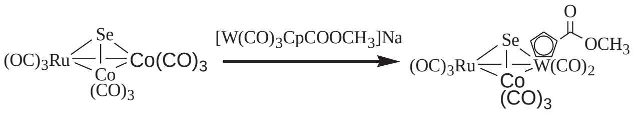
Mixed-transition-metal clusters have high potential to serve as efficient catalysts for a variety of homogeneous catalytic reactions as well as providing unique reagents for organic syntheses.[1] However, no unequivocal proof exists that metal clusters themselves serve as the true catalysts. In many 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 catalyse an asymmetric reaction with the subsequent isolation of chiral products.[2]

It has been reported that the metal exchange which Richter and Vahrenkamp pioneered,[3] proves to be the most efficient and versatile way to prepare tetrahedral mixed metal clusters. In addition, tetrahedral clusters containing an aldehyde-, ketone- or ester- substituted[4] cyclopentadienyl ligand can give some information about enantiomers when they react with the reagents. In order to gain more understanding about the chirality of tetrahedral mixed-metal clusters, here we report the synthesis of a new mixed-metal tetrahedral clusters [(μ_3-Se) RuCoMo(CO)$_8$(CpCOOCH$_3$)]**3** racemate by the reaction of [SeRuCo$_2$(CO)$_9$] **1** with the substituted sodium cyclopendiene [Mo(CO)$_8$CpCOOCH$_3$]Na **2** in THF at 60°C followed by resolution of two enantiomers by HPLC.

The cluster **1** reacted readily with **2** to give **3** (Scheme 1). The new cluster **3** is sensitive to air, and soluble in common organic solvents (such as dichloromethane). This behaviour is similar to those of other clusters of this type.[5]

The IR spectrum of **3** shows a large number of strong terminal carbonyl and bridged carbonyl absorption bands located at 2081–1879cm^{-1}. The absorption band at 1721 cm^{-1} arrives from the ester carbonyl. The ^{1}H NMR spectrum of cluster **3** is consistent with the expected structure. The singlet at about δ 3.77 ppm is caused by the proton of the methoxy on the Cp ring coordinated to the Mo atom. This noteworthy downfield shift of the methoxy hydrogen is characteristic of a hydrogen atom bound to carbons interacting either σ- or π-with metals.[1a,6] The ^{1}H NMR spectrum of **3** exhibits a triplet in the range δ 5.88–5.42ppm assigned to the protons of the substituted Cp ring.

The structure of compound **3** has been established by X-ray diffraction analysis. Its molecular structure is shown in Fig. 1. The metal skeleton of **3** has a tetrahedral structure, in which the three metal atoms occupy the three different vertex positions consisting of a distorted tetrahedral framework (μ_3-Se)RuCoMo. In the molecule, there are two carbonyl and one Cp ligand substituted by C (O)OCH$_3$ attached on Mo atom, three Co ligands on the Ru atom and the other three on the Co atom. The range of acute angles in the tetrahedral core of cluster **3** about the basal atoms is from 51.94° to 72.10°, and those about the Se atom average 70.14°, which deviate considerably from perfect tetrahedral geometry. This is due to the metal–metal bonded RuCoMo triangle, which restricts the angles around the Se atom. The bond lengths within the cluster core are very close to the corresponding analogues.[5] The bond distance of C (13)–C(14) is 1.469(10) Å, and the torsion angle of C(11)–C(12)–C(13)–C(14) is 180°, so the π system of C(14)=O(9) is conjugated together with π system of Cp and they are located in one plane.



1

3

Scheme 1

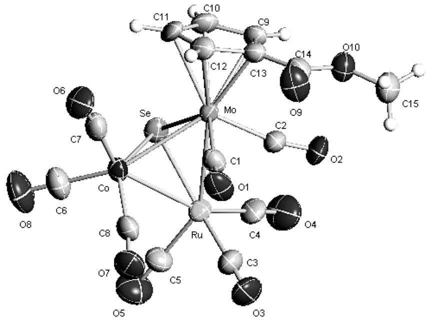


Fig. 1 Crystal structure of the cluster **3**.
Selected bond distances (Å) and angles (°): Mo–Se 2.4961(8); Mo–Co 2.7758(10); Mo–Ru 2.8960(7); Ru–Se 2.4242(9); Ru–Co 2.6584(10); Co–Se 2.3223(10); Se-Mo–Co 51.94(2); Se–Mo–Ru 52.80(2); Co–Mo–Ru 55.85(2); Se–Ru–Co 54.14(3); Se–Ru–Mo 55.10(2); Co–Ru–Mo 59.78(2); Se–Co–Ru 57.78(3); Se–Co–Mo 57.81(3); Ru–Co–Mo 64.36(2); Co–Se–Ru 68.08(3); Co–Se–Mo 70.24(3); Ru–Se–Mo 72.10(2).

It should be noted that the carbonyl of C(2)–O(2) attached to Mo atom is possibly semi-bridging, according to the bond angle Mo–C(2)–O(2) 166.4° and the other similar bond angles approaching 180°. The coexistence of both terminal and semi-bridging carbonyls are in good agreement with the IR spectrum showing several strong absorption bands from 2081cm^{-1} to 1879cm^{-1}of cluster **3**.

The cluster **3** was not separated in the presence of the chiral shift reagent such as [Eu(tfc)$_3$], possibly because the functional group COOCH$_3$ is far away from the tetrahedral chiral framework. The ^{1}H NMR signals of the protons in COOCH$_3$ of the two diastereoisomers have no distinct difference, when they are formed by the reaction of the cluster **3** and the chiral reagent. However, all the chemical shifts including that of protons in Cp were downshifted by about 0.1–0.5ppm compared with absence of the chiral reagent. HPLC was used to separate cluster **3.** At present, a chiral column suitable for cluster separation is not available, and no one knows what kinds of columns are more effective.[7] We were also

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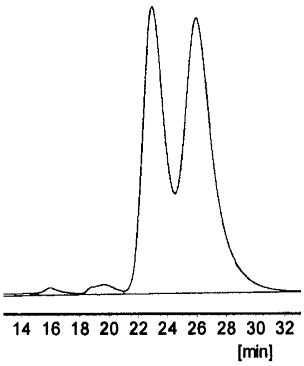

Fig. 2

unsuccessful, using self-made columns. It was found that when an S atom takes the place of the Se atom in **3**, the racemic clusters containing an S atom could be separated better than those containing the Se atom. The reason for this is unclear.

Experimental

All preparative work was carried out under an atmosphere of pure nitrogen by using standard Schlenk or vacuum-line techniques. Column chromatography was carried out by using silica gel columns of 160–200 mesh. Thin-layer chromatography (TLC) was performed on commercial Merck plates coated with a 0.20 mm layer of silica gel. $RuCo_2(CO)_9(\mu_3\text{-}Se)$,[8] $Na[C_5H_4CO_2Me]$, were prepared according to literature modified methods. Infrared spectra were recorded on a Nicolet FTIR 10DX spectrophotometer. ^1H NMR spectra were measured on a Brucker AM-400 MHz spectrometer; Elemental analyses (C, H) were performed on a Carlo-Erba 1106 type analyzer.

Synthesis of compound **3**: $[Mo(CO)_6]$ (264 mg, 1.0 mmol) was added to a solution of $Na(C_5H_4CO_2CH_3)$ (150 mg, 1.0 mmol) in THF (25 ml). The mixture was refluxed for 16h and cooled to room temperature. Then 550 mg (1.0 mmol) of cluster $[(\mu_3\text{-}Se)RuCo_2(CO)_9]$ was added and the mixture was stirred at 60°C for another 2h. The solvent was removed *in vacuo*, the residue was extracted by a small amount of CH_2Cl_2 and the extract was subjected to a 2.5 × 40 cm silica gel column chromatography. Elution with CH_2Cl_2/petroleum ether (2:1) afforded the major red band. Condensing the solvent and crystallisation at –20°C gave dark red crystals 239 mg (35%). Anal. Calcd. For $C_{15}H_7O_{10}CoMoRuSe$: C, 26.4; H, 1.0%. Found: C, 26.4; H, 1.1%. IR (KBr disk): 2081vs, 2041vs, 2004vs, 1973vs, 1879s, 1721s cm^{-1}. ^1H NMR ($CDCl_3$, δ): 5.88–5.42 (t, 4H, C_5H_4), 3.77 (s, 3H, CH_3).

Resolution of compound **3** *by HPLC*: Resolution was performed by LC-6A (shimadzu, Japan) chromatograph, with SPD-6AV violet-visible inspector, wavelength λ =254nm, room temperature, flow phase hexane/isopropanol (98/2), flow rate 0.5ml/min. Chromatograph column was of length 25cm, i.d = 4.6mm, cellulose-*tris* (3.5-dimethyl-phenylcarbamate) upon absorbed over silica gel (chiralcel OD) as chiral stationary phase. The best result is showed in Fig.2.

Crystal structure determination of cluster 3: A dark purple block crystal of cluster **3** with dimensions of 0.407mm × 0.232mm × 0.047mm was mounted in a thin capillary. All of the diffraction data were collected on a Bruker CCD APEX diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ=0.71073Å) at 293(2) K by the φ–ω scan mode (2.53 < θ < 28.33°). A total of 6001 reflections were collected with 4360 unique reflections ($R_{(int)}$ = 0.1135). The intensity data were corrected by *Sadabs* absorption. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added according to the geometrical method. The final cycle of full-matrix least-squares refinement was based on 4360 unique reflections and 263 variable parameters and converged with unweighted and weighted agreement factors. The final R = 0.0609, wR = 0.1469, ($w = 1/[(\sigma^2 F_o^2) + (0.0792P)^2]$, where $P = (F_o^2+2F_c^2)/3$, S = 1.060, (Δ/σ_{max} = 0.001) for 4360 observed reflections [I>2$\sigma(I)$]. The minimum and maximum final electron densities were –1.415 and 1.979 eÅ^{-3}. All the calculations were performed using the SHELXL-97[9] crystallographic program package. Crystallographic data: $C_{15}H_7\ O_{10}SeRuCoMo$, Mr = 682.11, triclinic, space group $P\text{-}1$, a = 7.6650(7), b = 8.3448(8), c = 16.3255(17) Å. V = 978.84(16) Å^3, Z = 2, D_c = 2.314 g/cm^3.

Received 21 November 2003; accepted 3 December 2003
Paper 03/2221

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