

Synthesis and First Separation of Chiral Trimetal Carbonyl Clusters containing an RuCoMo(μ_3 -S) Core

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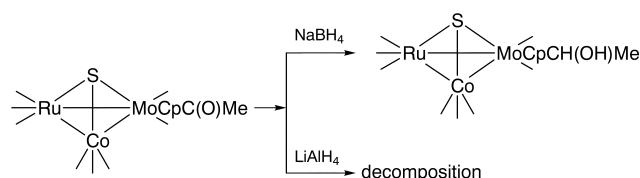
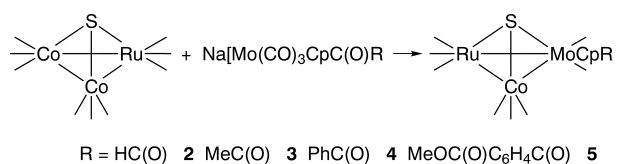
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Clusters RuCoMo(μ_3 -S)(CO)₈C₅H₄R [R = HC(O) **2**, MeC(O) **3**, PhC(O) **4**, MeOC(O)C₆H₄C(O) **5**] were obtained by the reaction of (μ_3 -S)RuCo₂(CO)₉ **1** and [M(CO)₃RC(O)Cp]⁻, clusters **3** and **5** have been solved by single crystal X-ray diffraction and cluster **3** was resolved on amylopectin tris(phenylcarbamate) (ATP) chiral stationary phases (CSPs).

Transition-metal cluster compounds are currently under intensive scrutiny because of their potential catalytic applications, both as models for understanding catalytic metal surfaces¹ and as catalysts in their own right.³ Our interest in the reactivity of chiral clusters prompted us to prepare tetrahedral skeleton complexes containing RuCoMoS cores and to find a good method of resolution of enantiomers by liquid chromatography on CSPs.

Refluxing a solution of NaMo(CO)₃(C₅H₄)R [R = HC(O), MeC(O), PhC(O), MeOC(O)C₆H₄C(O)] with cluster **1** in THF gave clusters **2–5** in moderate yield (Scheme 1). Reduction of cluster **3** by NaBH₄ in methanol at room temperature gave cluster **6**. The IR spectra of all clusters exhibited a large number of absorption bands between 1856 and 2087 cm⁻¹, which were assigned to terminal carbonyl vibrations. The spectra of the cluster **6** revealed OH absorption peaks at 3383 cm⁻¹. These results are consistent with the reduction of the C=O groups (1686 cm⁻¹) in cluster **3** by the action of NaBH₄.

The structures of clusters **3** and **5** were determined by X-ray structure analysis and crystal data are collected in Table 1. The structure of cluster **3** unexpectedly reveals the presence of two isomeric molecules **A** and **B** in the unit cell (Fig. 1). Each unit displays a RuCoMoS tetrahedral geometry. The acute angles in the tetrahedral core of cluster **3** about the basal atoms range from 50.12 to 64.09°, and those about the sulfur atom average 73.46°, which deviate considerably from perfect tetrahedral geometry. This results because the metal–metal bonded RuCoMo triangle restricts



Scheme 1

the angles around the sulfur atom. The distances from the sulfur atom to the metal are not equal [Ru–S 2.330(3) Å, Mo–S 2.37692 Å, Co–S 2.205(3) Å]. The Ru–S bond length is roughly equal to that in a known complex HRu₃(CO)₉[(μ_2 -S)Mo(CO)₃(NCMe)₂] (Ru–S 2.334 Å) but is shorter than that found typically.¹¹ Cluster **5** contains a tetrahedral skeleton formed by Ru, Co, Mo and S, the slightly distanced triangular Ru–Co–Mo moiety being capped by a sulfide ligand as in cluster **3** (Fig. 2). The distance of the Mo atom to the Cp ring center is 1.992 Å. Treating μ_3 -S as a four-electron donor and the cyclopentadienyl group as a five-electron donor, cluster **5** contains a total of 48 valence electrons and is electronically saturated.

Table 1 Summary of crystal and intensity data for complexes **3** and **5**

Complex	3	5
Formula	C ₁₅ H ₇ O ₉ SRuCoMo	C ₂₂ H ₁₁ O ₁₁ SCoRuMo
<i>M_w</i>	619.22	739.11
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	<i>P1</i>
<i>a</i> /Å	26.229(7)	8.174(3)
<i>b</i> /Å	18.200(6)	19.454(4)
<i>c</i> /Å	15.929(4)	8.042(3)
α /°		92.78(2)
β /°		108.74(3)
γ /°		88.73(1)
<i>Z</i>	8	2
<i>V</i> /Å ³	7604(6)	1209.5(7)
<i>D_c</i> /g cm ⁻³	2.163	2.030
λ /Å	0.71069	0.71069
<i>T</i> /°C	20	20
μ (mK α) cm ⁻¹	24.51	19.51
<i>F</i> (000)	4768.00	720.00
No observations [<i>I</i> > 3.00 σ (<i>I</i>)]	3343	2674
Total no. reflections	4883	3861
Residuals: <i>R</i> , <i>R_w</i>	0.033, 0.045	0.056, 0.074

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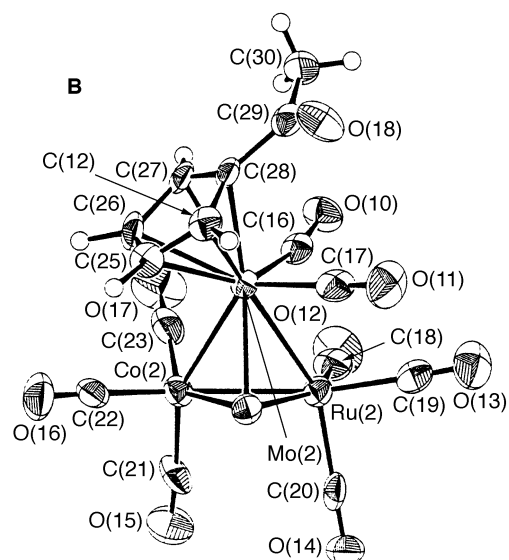
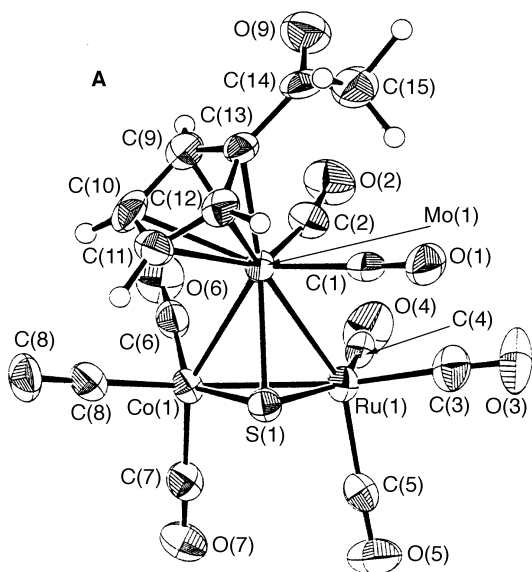


Fig. 1 Crystal structure of cluster **3**

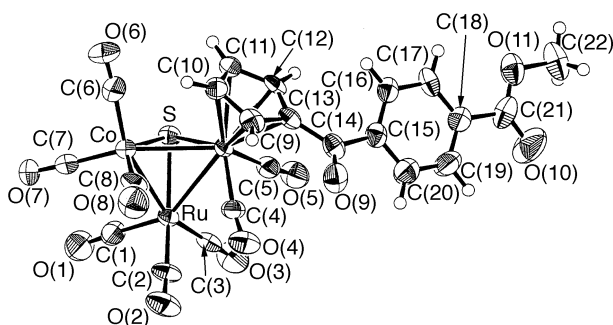


Fig. 2 Crystal structure of cluster **5**

In our attempts to separate the enantiomers of **3** we found that a general separation procedure did not apply. However, an enantiomer separation *via* chromatography over an optically active adsorbent was successful. The chiral ability of the CSP depends on the thickness of the

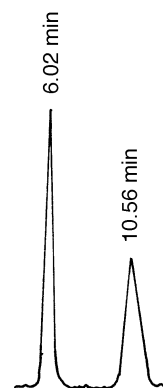


Fig. 3 The chromatograms of resolution of the cluster **3** on a 15% ATP-coated column Mobile phase: hexane-propan-2-ol = 95:5 (v/v); Flow rate: 0.5 ml min⁻¹; 0.02 AUF

coating. Usually, the greater the amount of chiral agent, the better the chiral discrimination. For coated cellulose CSP, Okamoto *et al.*¹² chose a coating of *ca.* 20–25 mass%. However, we found that this level resulted in low optical resolution on the 25 mass % ATP-coated phase; a coating of 15 mass % appeared to be optimal. This indicates that it is important to reduce non-chiral interactions with Si–OH or –NH₂ groups by a well distributed and ordered coating and overloading may destroy this characteristic. Fig. 3 shows the chromatogram of **3** on a 15 mass % coated phase.

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Techniques used: IR, ¹H NMR, MS, HPLC

Table 2: Atomic coordinates and B_{iso}/B_{eq} for cluster **3**

Table 3: Atomic coordinates and B_{iso}/B_{eq} for cluster **5**

Table 4: Selected intramolecular distances (Å) and bond angles (°) for cluster **3**

Table 5: Selected intramolecular distances (Å) and bond angles (°) for cluster **5**

Table 6: The effects of propan-2-ol concentration on the resolution

References: 18

Appendix: Crystallographic data for cluster **3** and **5**

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