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Synthesis of Cluster Derivatives Containing the MRuCoSe (M = Mo or W) Core†

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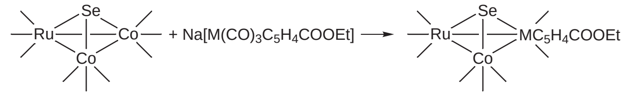
The new clusters [MRuCo(CO)$_8$(μ_3-Se){η^5-C$_5$H$_4$C(O)OEt}](M = Mo **2** or W **3**) are isolated from the reaction of [RuCo$_2$(CO)$_9$(μ_3-Se)] **1** and [M(CO)$_3${η^5-C$_5$H$_4$C(O)OEt]$^-$(M = Mo or W), and the structure of cluster **2** has been established by single crystal X-ray diffraction methods.

Asymmetric catalysis induced by a cluster which contains a chiral metal framework would be the strongest evidence for catalysis by an intact cluster. Considerable efforts have been directed to the synthesis of chiral tetrahedral clusters containing four different atoms at the vertices of the tetrahedron.[1–6] Recently we have described the synthesis and structure of chiral clusters containing the core MoRuCoSe.[6] Here we report a further two novel chiral cluster derivatives MRuCo(CO)$_8$(μ_3-Se){η^5-C$_5$H$_4$C(O)Et}] (M = Mo **2** or W **3**), which have been obtained from the reaction of Na[M(CO)$_3${η^5-C$_5$H$_4$C(O)OEt}](M = Mo or W) with cluster [RuCo$_2$(CO)$_9$(μ_3-Se)] **1** in refluxing THF (Scheme 1). Both clusters **2** and **3** are air-stable red crystals and are soluble in polar solvents such as THF, toluene and chloroform. Satisfactory C, H analyses were obtained for the two compounds.



1

2 M = Mo
3 M = W

Scheme 1 Synthesis of compounds **2** and **3**

The similar spectral characteristics of compounds **2** and **3** suggest the same configuration for these clusters. In the IR spectra there were several intense absorption bands in the range 1879–2081 cm^{-1}, characteristic of CO ligands bound to transition metals, and also the corresponding ethoxycarbonyl absorption bands at 1720.6 (for Mo) and 1726.4 (for W) cm^{-1}, which were similar to that of EtOC=O in the known clusters [FeCoM(CO)$_8$(μ_3-S)-{η^5-C$_5$H$_4$C(O)Et}](M = Mo or W).[2,3] The ^{1}H NMR resonances of the substituted cyclopentadienyls appeared downfield (δ 5.86–5.42) relative to that of unsubstituted cyclopentadienyls owing to their electron-withdrawing effect.

The structural features of these two chiral clusters have been established by X-ray diffraction analysis of a suitable crystal of **2**. The structure contains a tetrahedral skeleton composed of Ru, Co, Mo and Se (Fig. 1) with the slightly distorted RuCoMo triangle capped by a selenium ligand. The acute angles in the tetrahedral core of cluster **2** about the basal atoms range from 51.81 to 64.39°, and those about the Se atom average 69.48°, reflecting the relative sizes of the atoms(Mo > Ru > Co ≫ Se). Similarly, the distances from the Se atom to the metals are not equal [Ru-Se 2.4373(9), Co–Se 2.316(1), Mo–Se 2.5024(9) Å]. The distance from the Mo atom to the Cp ring center is 2.169 Å. All the atoms in the cyclopentadienyl ligand together with C(14), O(10) and O(9) in the EtO$_2$C group are located in a plane, the torsion angle of C(13)–C(9)–C(14)–O(9) being 0(1)°, and the bond length of C(9)–C(14) (1.49 Å) being shorter than a normal C–C bond (1.54 Å). Thus the π system of the EtO$_2$ substituent is fully conjugated with the cyclopentadienyl π system. Finally it should be noted that the carbonyl C(2)–O(2) bound to Mo atom is semibridging; the asymmetric parameter α (= 0.41) being well within the range for semibridging carbonyls.[7]

Experimental

All reactions were performed under an atmosphere of pure nitrogen by using standard Schlenk and vacuum-line techniques. Column chromatography was carried out by using silica gel of 160–200 mesh. Compounds [Mo(CO)$_6$] and [W(CO)$_6$] were purchased from Fluka and Aldrich Chem. Co. IR spectra were recorded on a Nicolet FT-IR

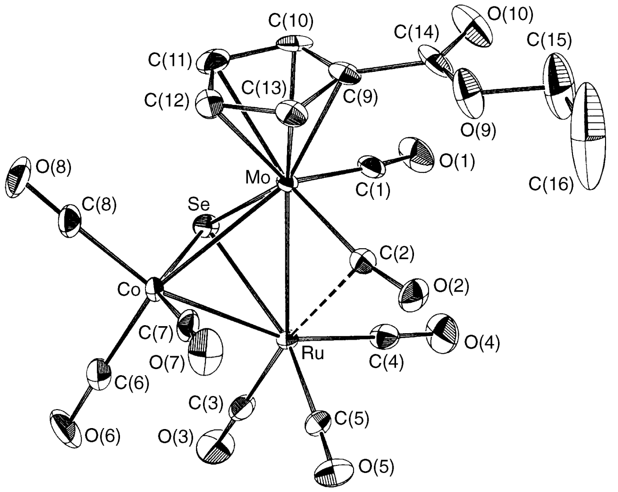


Fig. 1 Crystal structure of cluster **2**. Selected bond distances (Å) and angles (°): Ru–Se 2.4373(9), Ru–Co 2.629(1), Ru–Mo 2.8788(9), Mo–Se 2.5024(9), Mo–Co 2.770(1), Se–Co 2.316(1), Ru–C(2) 2.766(7), Mo–C(2) 1.964(7), Mo–Cp 2.169, C(9)–C(14) 1.49(1); Se–Ru–Co 54.24(3), Se–Ru–Mo 55.41(2), Co–Ru–Mo 60.19(3), Se–Mo–Co 51.81(3), Se–Mo–Ru 53.31(2), Co–Mo–Ru 55.43(3), Co–Se–Ru 67.10(3), Co–Se–Mo 70.06(3), Ru–Se–Mo 71.28(3), Se–Co–Ru 58.66(3), Se–Co–Mo 58.13(3), Ru–Co–Mo 64.39(3), C(2)–Mo–Ru 66.6(2)

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10 DX spectrometer; ^{1}H NMR spectra on a Bruker AM-400 MHz spectrometer; analyses (C, H) were performed on an 1106-type analyzer.

Preparation of $Na[M(CO)_3\{\eta^5\text{-}C_5H_4C(O)OEt\}](M = Mo\ or\ W)$.—The compound $Na(C_5H_5)$ (88 mg, 1.0 mmol) and diethyl carbonate (118 mg, 1.0 mmol) were dissolved in THF (30 cm^{-3}). After the mixture was refluxed for 24 h, $[M(CO)_6]$ (1.0 mmol) was added and refluxed for 12 h (for Mo) or 32 h (for W). The solvent was removed under reduced pressure and then the residue was washed with pentane; it can be directly used in the following reaction.

Preparation of $[RuCoMo(CO)_8(\mu_3\text{-}Se\{\eta^5\text{-}C_5H_4C(O)OEt\}]$ **2**.—The cluster $[RuCo_2(CO)_9(\mu_3\text{-Se})]$ **1** (550 mg, 1.0 mmol) and $Na[Mo(CO)_3\{\eta^5\text{-}C_5H_4C(O)OEt\}]$ (340 mg, 1.0 mmol) were dissolved in THF (30 cm^3). After the mixture was refluxed for 2 h, the THF was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (5 cm^3) and then the extracts were subjected to column chromatography. The main product **2** was obtained in 223 mg (32%) yield (Calc. for $C_{16}H_9O_{10}CoMoRuSe$: C, 27.61; H, 1.30. Found: C, 27.53; H, 1.28%). IR (KBr disk): 2081.3vs, 2040.8vs, 2004.2vs, 1973.3vs, 1878.8s (C≡O), 1720.6s (C=O). $\delta_H(CDCl_3)$: 5.88–5.42 (t, 4H C_5H_4), 4.35–4.29 (q, 2H CH_2), 133 (t 3H CH_3).

Preparation of $[RuCoW(CO)_8(\mu_3\text{-}Se)\{\eta^5\text{-}C(O)OEt\}]$ **3**.—The synthetic method for cluster **3** was the same as that for **2**. Yield: 213 mg (27%) (Calc. for $C_{16}H_9O_{10}CoRuSeW$: C, 24.51; H, 1.16. Found: C, 24.67; H, 1.09%). IR(KBr disk): 2077.5vs, 2037.0vs, 2013.8vs, 1992.6vs, 1967.5vs, 1917.4s (C≡O), 1726.4s (C=O). δ_H $(CDCl_3)$: 5.86–5.49 (t, 4H, C_5H_4), 4.33 (s, 2H, CH_2), 1.34 (s, 3H, CH_3).

Crystal Data for **2**.—A crystal of compound **2** ($C_{19}H_9O_{10}CoMoRuSe$, $M_r = 696.14$) was grown from a $C_6H_{14}-CH_2Cl_2$ solution. The space group was $P2_1/n$(no. 14). The cell parameters were determined on a Rigaku AFC 5R diffractometer with graphite-monochromated Mo-Kα radiation: $\alpha = 10.168(2)$; $b = 9.018(2)$, $c = 23.121(3)$ Å, $\beta = 92.50(1)^\circ$, $Z = 4$, $V = 2118.1(6)$ Å^3, $D_c = 2.183$ g cm^{-3}, $\mu = 37.83$ cm^{-1}, $2\theta_{max} = 51.9^\circ$ and $F(000) = 1328$. 4515 unique reflections were collected at 23 °C. Refinement converged to $R = 0.047$, $R_w = 0.057$ based on 3359 observed reflections. Minimum and maximum final electron densities were −1.71 and 1.24 e Å^{-3}. The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/26. See http://www.rsc.org/suppdata/jc/1999/550/ for crystallographic files in .cif format.

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7 The asymmetric parameter is defined as $\alpha = (d_2 - d_1)/d_1$ where d_2 is the long M···C distance and d_1 is the short M–C distance. If $0.1 \le \alpha \le 0.6$, a semibridging carbonyl is designated according to Curtis' suggestion. M. D. Curtis, K. R. Han and W. M. Butler, *Inorg. Chem.*, 1980, **19**, 2096.