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Synthesis of Clusters containing the MRuCoS (M = M or W) Cores†

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The new clusters [{MRuCo(CO)$_8$(μ_3-S)}$_2${η^5-C$_5$H$_4$C(O)C$_6$H$_4$C(O)C$_5$H$_4$-η^5}] (M = Mo **2** or W **3**) have been isolated from the reaction of [RuCo$_2$(CO)$_9$(μ_3-S)] **1** and [{M(CO)$_3$}{η^5-C$_5$H$_4$C(O)C$_6$H$_4$C(O)C$_5$H$_4$-η^5}]$^{2-}$ (M = Mo or W), and the structure of cluster **3** has been established by single-crystal X-ray diffraction methods.

Clusters with unique structural features and unusual reactivities have been obtained by using chalcogen atoms as bridging ligands.[1] Chalcogen ligands display a wide variety of bonding modes when these are incorporated in transition-metal carbonyl cluster frameworks. The compound [RuCo$_2$(CO)$_9$(μ_3-S)] is a useful procluster, which was first reported in 1984 by Roland and Vahrenkamp.[2] Here the new novel double tetrahedral clusters [{MRuCo(CO)$_8$(μ_3-S)}$_2${η^5-C$_5$H$_4$C(O)C$_6$H$_4$C(O)C$_5$H$_4$-η^5}] (M = Mo **2** or W **3**) have been obtained from the reaction of Na$_2$[{M(CO)$_3$}$_2${η^5-C$_5$H$_4$C(O)C$_6$H$_4$C(O)C$_9$H$_4$-η^5}] (M = Mo or W) with the cluster **1** in refluxing THF (Scheme 1). The clusters **2** and **3** are air-stable red solids. They are soluble in polar solvents like THF, toluene and chloroform. Satisfactory C,H analyses were obtained for all compounds.

The similar spectral characterization of compounds **2** and **3** suggests the same configuration for these clusters. The infrared spectra of cluster **2** and **3** showed intense terminal carbonyl absorption bands in the range 1899–2085 cm^{-1}, and also the corresponding carbonyl bands for the acyl at 1650 and 1661 cm^{-1}, which were much lower than that of RC=O in known clusters [FeCoM(CO)$_8$(μ_3-S)-{C$_5$H$_4$C(O)R}].[3] This is because of the conjugative effect of the aromatic ring in these complexes. The ^{1}H NMR resonances of the substituted cyclopentadienyls appeared downfield relative to that of unsubstituted cyclopentadienyls,[4] due to the shielding effect of the π system of the C(O)C$_6$H$_4$C(O) group. It should be mentioned that the moleculer structure of **2** and **3** is achiral containing a symmetric center. However, the cyclopentadienyl protons of **2** and **3** show an A$_2$BB′ instead of an A$_2$B$_2$ pattern, because of the presence of a chiral tetrahedral subcluster SRuCoM.[5]

The structural features of this new series of mixed-metal clusters have been established by X-ray diffraction analysis of a suitable crystal of **3**. The structure contains two independent centrosymmetric molecules in a unit cell, each of which has two tetrahedral skeletons (SRuCoW) connected through a C$_5$H$_4$C(O)C$_6$H$_4$C(O)C$_5$H$_4$ bridge (Fig. 1). The slightly distorted triangular RuCoW is capped by a μ_3-sulfide ligand. The Ru and Co atoms are co-ordinated by three two-electron carbonyl ligands, the W atom by two carbonyl ligands and one five-electron carbonylcyclopentadienyl ligand. The capping sulfide atom bonds to Ru, Co, and W with bond lengths of 2.325(4), 2.191(4) and 2.376(4) Å, respectively. The W atom–C$_5$H$_4$ ring centroid distance is 1.790 Å. Since the π system of the COC$_6$H$_4$CO bridge would be quite well conjugated with that of the C$_5$H$_4$ ring, the bond lengths C(5)—C(6) (1.46 Å) and C(6)—C(7) (1.47 Å) become much shorter than a normal C—C single bond (1.54 Å), but longer than a C=C double bond (1.34 Å). Cluster **3** contains a total of 48 × 2 electrons and is electronically saturated.

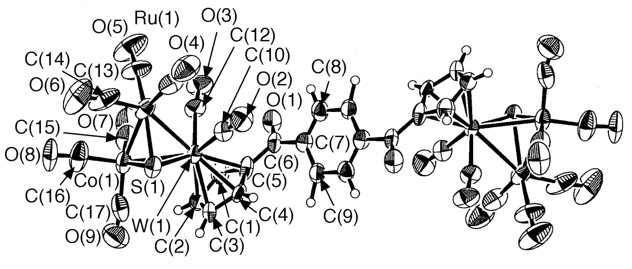
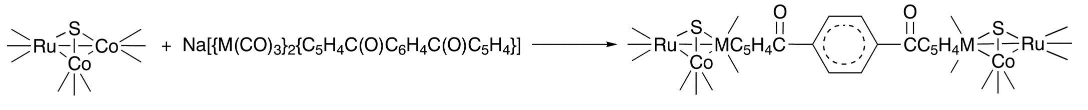


Fig. 1 Crystal structure of the cluster **3**. Selected bond distances (Å) and angles (°): W(1)—Ru(1) 2.873(1), W(1)—Co(1) 2.750(1), W(1)—S(1) 2.376(4), Ru(1)—Co(1) 2.633(3), Ru(1)—S(1) 2.325(4), Co(1)—S(1) 2.191(4), C(5)—C(6) 1.46(2) and W(1)—Cp 1.790; Ru(1)—W(1)—Co(1) 55.80(6), Ru(1)—W(1)—S(1) 51.52(10), Ru(1)—S(1)—Co(1) 71.3(1), Co(1)—W(1)—S(1) 50.0(1), Ru(1)—Co(1)—S(1) 56.1(1), Ru(1)—Co(1)—W(1) 64.47(6), Ru(1)—S(1)—W(1) 75.4(1), W(1)—S(1)—Co(1) 73.9(1), W(1)—Ru(1)—Co(1) 59.73(5), W(1)—Ru(1)—S(1) 53.13(9) and Co(1)—Ru(1)—S(1) 52.0(1)

Experimental

All reactions were performed under an atmosphere of pure nitrogen by using standard Schlenk or vacuum-line techniques. Column chromatography was carried out by using silica gel of 300–400 mesh. The compounds [Mo(CO)$_6$] and [W(CO)$_6$] were purchased from Fluka and Aldrich Chem. Co. Infrared spectra were recorded on a Nicolet FT-IR 10 DX spectrophotometer; ^{1}H NMR spectra on a Bruker AM-300 MHz spectrometer; analyses (C, H) were performed on a 1106-type analyzer.



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

Preparation of Na$_2$[{M(CO)$_3$}$_2${η^5-C$_5$H$_4$C(O)C$_6$H$_4$C(O)C$_5$H$_4$-η^5}] [M = Mo or W].—The compound Na(C$_5$H$_5$) (88 mg, 1.0 mmol) and dimethyl terephthalate (194 mg, 0.5 mmol) were dissolved in THF (50 cm^3). After the mixture was refluxed for 8 h, [M(CO)$_6$]

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]: there is therefore no corresponding material in *J. Chem. Research (M)*.

(1.0 mmol) was added and refluxed for 12 (for Mo) or 24 h (for W). The solvent was removed under reduced pressure and then the residue was washed with pentane; it can be used directly in the following reactions.

Preparation of $[\{MoRuCo(CO)_8(\mu_3\text{-}S)\}_2\{\eta^5\text{-}C_5H_4C(O)C_6H_4C(O)\text{-}C_5H_4\text{-}\eta^5\}]$ **2**.—The cluster $[RuCo_2(CO)_9(\mu_3\text{-}S)]$ **1** (503 mg, 1.0 mmol) and $Na_2[\{Mo(CO)_3\}_2\{\eta^5\text{-}C_5H_4C(O)C_6H_4C(O)C_5H_4\text{-}\eta^5\}]$ (305 mg, 0.5 mmol) were dissolved in THF (50 cm^3). After the mixture was refluxed, 3 h, the red-brown solution was evaporated to dryness. 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 315 mg (49%) yield. IR(KBr disc): 2085vs, 2042vs, 2009vs, 1907m and 1650m cm^{-1} (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz); δ 5.32–6.03 (m, 8 H, $2C_5H_4$) and 7.94 (s, 4H, C_6H_4). ^{13}C NMR($CDCl_3$, 300 MHz): δ 215.2 and 208.15 (terminal CO), 193.40 and 188.34 (C═O), 140.87 and 128.40 (C_6H_4), 94.41, 93.61, 91.73, 87.71 and 86.66 (C_5H_4).

Preparation of $[\{WRuCo(CO)_8(\mu_3\text{-}S)\}_2\{\eta^5\text{-}C_5H_4C(O)C_6H_4C(O)\text{-}C_5H_4\text{-}\eta^5\}]$ **3**.—The synthetic method for cluster **3** was the same as that for **2**. Yield: 327 mg (42%). IR(KBr disc): 2083vs, 2040vs, 2002vs, 1899m and 1661m cm^{-1} (C═O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.35–6.01 (m, 8 H, $2C_5H_4$) and 7.92 (s, 4 H, C_6H_4).

Crystal data of **3**.—A crystal of compound **3** ($C_{34}H_{12}Co_2O_{18}\text{-}Ru_2S_2W_2$, $M_r = 1460.28$) was grown from a CH_2Cl_2 solution. The space group was $P\bar{1}$. The cell parameters were determined on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation: as a = 12.688(4); b = 20.290(7); c = 9.429(3) Å, α = 99.78(3); β = 90.64(2); γ = 78.28(3)°, Z = 2; V = 2341(1) Å^3; $D_c = 2.071$ g cm^{-3}, μ = 63.73 cm^{-1}, $2\theta_{max} = 45.0°$, and $F(000)$ = 1364.00. Crystal size 0.20 × 0.20 × 0.40 mm. Of the 6460 reflections collected, 6123 were unique ($R_{int} = 0.031$). The intensities of three representative reflections were measured every 200. Refinement converged at final R = 0.042, $R_w = 0.063$. Minimum and maximum final electron densities –0.79 and 1.28 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.

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