Pergamon

PII: S0277–5387(97)00077–6

Polyhedron Vol. 16, No. 17, pp. 3067–3069, 1997

0277–5387/97 $17.00+0.00

COMMUNICATION

Synthesis and characterization of the novel type of heterometal clusters $[(\mu_3\text{-S})RuCoM(CO)_8CpC(O)]_2C_6H_4$ (M = Mo, W) and crystal structure of $[(\mu_3\text{-S})RuCoW(CO)_8CpC(O)]_2C_6H_4$

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(Received 13 November 1996; accepted 13 February 1997)

Abstract—The reaction of $(\mu_3\text{-S})RuCo_2(CO)_9$ (**1**) with $[NaM(CO)_3CpC(O)]_2C_6H_4$ [(M = Mo (**2**), M = W (**3**)] in refluxing THF gave two new carbonyl clusters, $[(\mu_3\text{-S})RuCoM(CO)_8CpC(O)]_2C_6H_4$ [M = Mo (**4**), M = W (**5**)]. The structure of cluster **5** was established by X-ray diffraction analysis. © 1997 Elsevier Science Ltd

Keywords: sulfur; ruthenium; cobalt; molybdenum; tungsten; carbonyl cluster.

In recent years transition-metal cluster complexes have been receiving considerable attention because of their unusual structures and reactions [1–3]. Among these, however, there are very few cluster complexes containing the tetrahedral skeleton SRuCoM (M = Mo, W). To the best of our knowledge, no compound containing two tetrahedral skeletons formed mixed-metal clusters connected by $CpC(O)C_6H_4C(O)Cp$ has been reported. We describe here the synthesis and characterization of this novel type of cluster complex.

In the presence of ethanethiol $Co_2(CO)_8$ reacted with $Ru_3(CO)_{12}$ under 200 atm and 160°C in hexane giving the cluster $SRuCo_2(CO)_9$ (80%) [4]. The novel metal fragment exchange reagents of $[NaM(CO)_3CpC(O)]_2C_6H_4$ [M = Mo (**2**), M = W (**3**)] were formed in refluxing THF by $M(CO)_6$ (M = Mo, W) reacted with $[NaCpC(O)]_2C_6H_4$ which was prepared from NaCp and dimethyl terephthalate in refluxing THF. The addition of an equimolar amount of $(\mu_3\text{-S})RuCo_2(CO)_9$ to the THF solution of complexes **2** or **3** produced the title complexes **4** and **5** in moderate yields, which could also be prepared at ambient temperature, but in low yield (10–20%, Scheme 1) [5]. The clusters **4** and **5** are air-stable red solids. They are soluble in polar solvents like THF, toluene and chloroform, etc.

The structural features of this new series of mixed-metal clusters have been established by the X-ray diffraction analysis of a suitable crystal of $[(\mu_3\text{-S})RuCoMo(CO)_8CpC(O)]_2C_6H_4$. The structure of cluster **5** contains two independent, centrosymmetric molecules, each of which contains two tetrahedral skeletons connected through the $CpC(O)C_6H_4(O)Cp$ bridge (Fig. 1). The tetrahedral skeleton is composed of S, Ru, Co and W atoms. The slightly distorted triangular RuCoW is capped by a μ_3-bond sulfide ligand. The Ru and Co atoms were coordinated by three two-electron carbonyl ligands. The W atom was coordinated by two carbonyl ligands and one five-electron carbonylcyclopentadienyl ligand. The capping sulfide atom bonds to the Ru, Co and W atoms with bond lengths 2.320(4), 2.197(4) and 2.376(4) Å,

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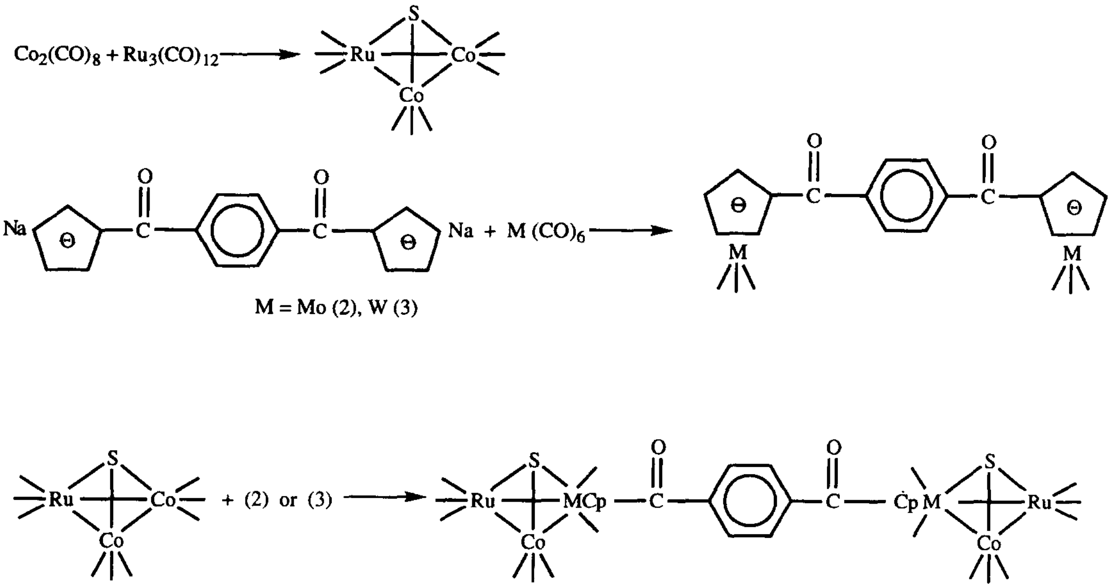

Scheme 1.

respectively. The bond length of Ru—S is roughly equal to that in the known complex $HRu_3(CO)_9[\mu_3\text{-}S)Mo(CO)_3(N(CH_3)_2]$ (Ru—S = 2.334 Å), but shorter than that of the typical Ru—S bond length [6]. The W atom-Cp ring centroid distance is 1.970 Å. Since the π-system of the bridge —CO—C_6H_4—CO— would be quite well conjugated with that of the Cp ring and thus the bond length of C(5)—C(6) (1.46 Å) and C(6)—C(7) (1.47) becomes much shorter than a normal C—C single bond (1.54 Å), but longer than a C=C double bond (1.34 Å). Cluster **5** contains a total of 48 × 2 electrons and is electronically saturated.

The similar spectral characterization of compounds **4** and **5** suggests the same configuration for these clusters. No double cluster complexes containing tetrahedral subcluster cores SRuCoM (M = Mo, W) have been reported, although a few such single cluster complexes have appeared in the literature, but without crystal structures [4]. The IR spectra of clusters **4** and **5** all showed intense terminal carbonyl absorption bands in the range 1899–2085 cm^{-1} and all of them also showed corresponding carbonyl absorption bands for the acetyl at 1650 and 1661 cm^{-1}, which were much lower than that of the RC=O in known clusters $(\mu_3\text{-}CPh)FeCoM(CO)_8[CpC(O)R]$ [7]. This is because of the conjugative effect of the aromatic ring in these complexes. The ^{1}H NMR assignment of substituted cyclopentadienyls appeared downfield relative to that of unsubstituted cyclopentadienyls [8], which was due to the shielding effect of the π-system —$C(O)C_6H_4C(O)$—. It should be mentioned that the molecular structure of **5** is that of an achiral molecule

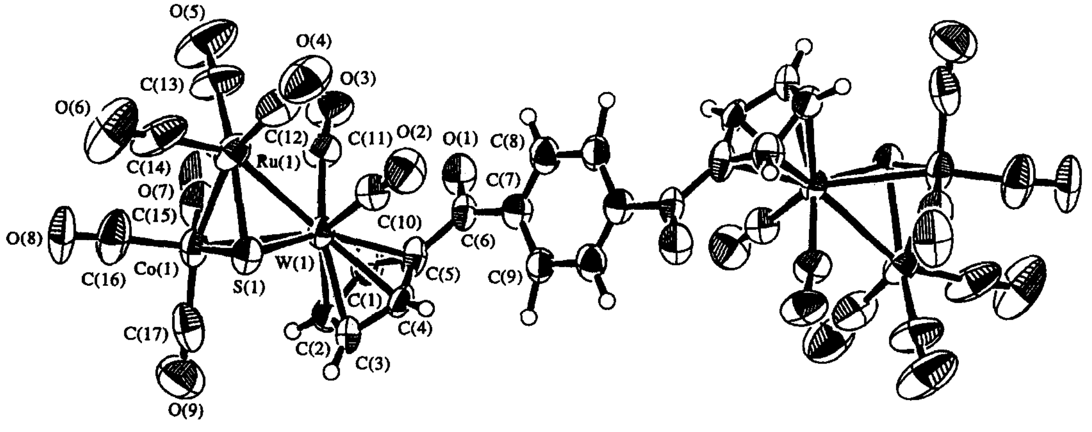

Fig. 1.

containing a symmetric center. However, the ^{1}H NMR spectra of the cyclopentadienyl protons of **4** and **5** show an A_2BB' pattern instead of an A_2B_2 pattern, which is because of the presence of the chiral tetrahedral subcluster SRuCoM in these clusters [9].

Acknowledgement—We are grateful to the Laboratory of Organometallic Chemistry at Shanghai Institute of Organic Chemistry, Chinese Academy of Science for the financial support of our work.

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5. All steps were performed under nitrogen in dried, N_2-saturated solvent. Characterization data for $[SRuCoMo(CO)_8(C_5H_4)C(O)]_2C_6H_4$ (**4**): yield 49%. IR (KBr): 2085vs, 2009vs, 1907m, 1650m, (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ5.32–6.03 (m, 8H, 2Cp), δ7.94 (s, 4H, Ph). ^{13}C NMR ($CDCl_3$, 300 MHz): δ215.2 and 208.15 (t-CO), δ193.40 and 188.34 (C=O), δ140.87 and 128.40 (Ph), δ94.41, 93.61, 91.73, 86.66 (Cp). MS (FAB, Ru^{102}): 1230 ($M^+ - 2CO$), 1174 ($M^+ - 4CO$). For $[SRuCoW(CO)_8C_5H_4C(O)]_2C_6H_4$ (**5**): Yield: 327 mg (42%). IR (KBr disk): 2083vs, 2040vs, 2002vs, 1899m, 1661m (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ5.35–6.01 (m, 8H, 2Cp), δ7.92 (s, 4H, Ph). Satisfactory C/H analyses were obtained for all compounds. Rigaku AFC7R diffractometer [Mo-K_α radiation is 0.71069 Å graphite monochromator, ω–2θ scan technique], solution with Patterson Methods (DIRDIF92PATTY), refinement with Full-Matrix least-squares. Crystal data for: $C_{34}H_{12}O_{18}S_2Ru_2W_2Co_2$ Mr = 1460.28, crystal system triclinic, space group $P1$, $a = 12.688(4)$, $b = 20.290(7)$, $c = 9.429(3)$ Å, $\alpha = 99.78(3)$, $\beta = 90.64(2)$, $\gamma = 78.28(3)^\circ$. $V = 2341(1)$ Å^3, $Z = 2$, $Dc = 2.071$ g cm^{-3}, $\mu = 63.73$ cm^{-1}, $2\theta_{max} = 45.0$. Crystal size $0.20 \times 0.20 \times 0.40$ mm. Of the 6460 reflections collected, 6123 were unique ($R_{int} = 0.031$). The intensities of three representative reflection were measured after every 200 reflections. Refinement converged at final $R = 0.042$, $Rw = 0.063$. The minimum and maximum final electron densities were -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 anistropically. Hydrogen atoms were included but not refined.
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