Linked Cluster Complex: Crystal Structure of $[RuCo_2(CO)_9](\mu_3\text{-}\eta^2HC_2CH_2OC_6H_4OCH_2C_2H\eta^2\text{-}\mu_3)[RuCo_2(CO)_9]$

Xue-Nian Chen, Jie Zhang, Yuan-Qi Yin,* and Wen-Ling Wang†

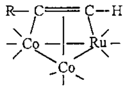
State Key Laboratory for Oxo Synthesis and Selected Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P.R. China

†*Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P.R. China*

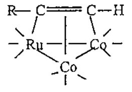
(Received March 15, 1999; CL-990172)

Two configurations of $RuCo_2(CO)_9(HC_2R)$ unit confirmed by the crystal structure of the linked cluster complex $[RuCo_2(CO)_9](\mu_3\text{–}\eta^2HC_2CH_2OC_6H_4OCH_2C_2H\eta^2\text{-}\mu_3)[RuCo_2(CO)_9]$ are reported.

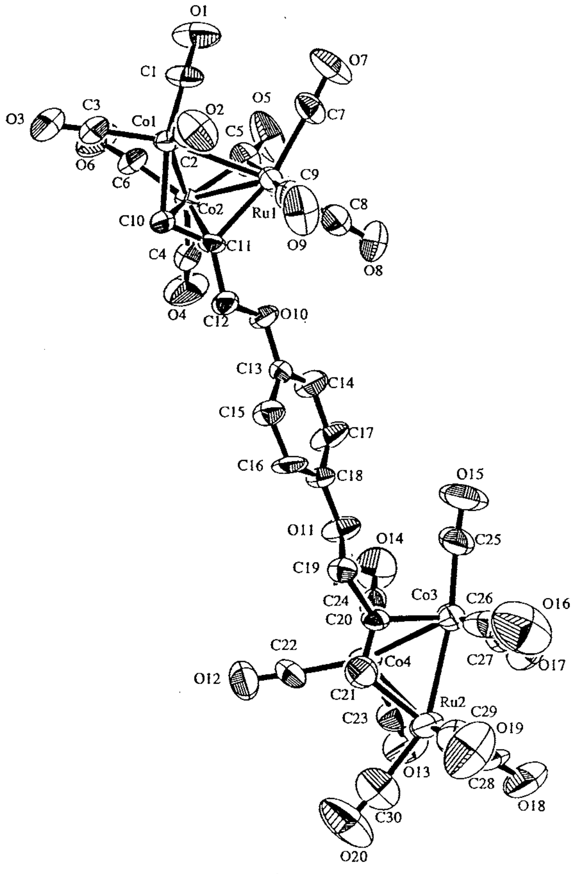
Although $RuCo_2(CO)_{11}$ is saturated according to the 18-electron rule, due to the combined lability of its Co- and Ru-CO ligands, it reacts like an unsaturated compounds and is suitable for all kind of capping reactions.[1] Cluster $RuCo_2(CO)_{11}$ reacts with terminal alkyne in mild condition to produce complexes and it is rationalized by their ^1H NMR spectra that these complexes could contain two isomers A and B,[2] but it is difficult to demonstrate that the two isomers occur in a crystal structure .[3]



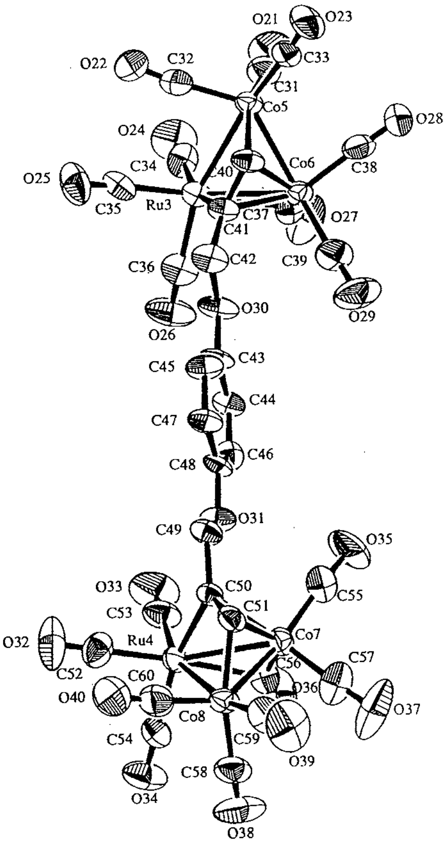
A



B



4a



4b

Figure 1. Molecular structure of complexes **4a** and **4b**.
Selected bond lengths (Å) and angles (°) of **4a**: C(10)-C(11) 1.35(2), C(20)-C(21) 1.33(2), Co(1)-Co(2) 2.480(2), Co(3)-Co(4) 2.448(3), Ru(1)-Co(1) 2.717(2), Ru(2)-Co(3) 2.698(2), Ru(1)-Co(2) 2.601(2), Ru(2)-Co(4) 2.573(2), Ru(1)-C(11) 2.12(1), Ru(2)-C(21) 2.08(2), Co(1)-C(10) 1.98(1), Co(3)-C(20) 1.98(1), Co(2)-C(10) 2.09(1), Co(4)-C(21) 2.07(1), Co(2)-C(11) 2.06(1), Co(4)-C(20) 2.05(1), Ru(1)-C(5)-O(5) 131(1), Co(2)-C(5)-O(5) 151(1), Co(4)-C(23)-O(13).
Selected bond lengths (Å) and angles (°) of **4b**: C(40)-C(41) 1.37(2), C(50)-C(51) 1.37(2), Co(5)-Co(6) 2.484(2), Co(7)-Co(8) 2.491(2), Ru(3)-Co(5) 2.719(2), Ru(4)-Co(8) 2.704(2), Ru(3)-Co(6) 2.597(2), Ru(4)-Co(7) 2.598(2), Ru(3)-C(41) 2.11(1), Ru(4)-C(50) 2.09(1), Co(5)-C(40) 1.95(1), Co(8)-C(51) 1.95(1), Co(6)-C(40) 2.05(1), Co(7)-C(51) 2.07(1), Co(6)-C(41) 2.08(1), Co(7)-C(50) 2.07(1), Ru(3)-C(37)-O(27) 131(1), Ru(4)-C(56)-O(36) 133(1), Co(6)-C(37)-O(27) 153(1), Co(7)-C(56)-O(36) 149(1).

To our knowledge numerous complexes consisted of $RuCo_2(CO)_{11}$ with μ_3–alkyne are synthesized by these capping reactions, but only the crystal structure of 3,3-dimethyl-1-butyne-$RuCo_2$ complex has been determined and only isomer A is observed in the crystalline state.[4] So far the two isomers have not been realized for one linking alkyne on the same complex, and it could previously only be postulated that two isomers occur in these complexes. We have now succeeded to confirm by crystal structure that the complex contained two configurations.

In order to prepare desired complexes, diyne ligands were used to react with $RuCo_2(CO)_{11}$ under mild conditions. The reaction is a cluster-capping reaction, which is not unusual for alkyne and occurs for many M_3 clusters in combination with μ_3–4e capping ligands.[5] The desired complexes $[RuCo_2(CO)_9](\mu_3\text{–}\eta^2HC_2RC_2H\eta^2\text{–}\mu_3)[RuCo_2(CO)_9]$ [R = $(CH_2)_5$ **1**, CH_2OCH_2 **2**, C_6H_4-1,2-$(COOCH_2)_2$ **3**, C_6H_4-1,4-$(OCH_2)_2$ **4**] were obtained by capping reactions and were characterized by C/H analyses, IR and ^1H NMR spectra.[6] Complex **4** was characterized by single crystal X-ray diffraction method.[7] And its molecular structure is shown in Figure 1.

Satisfactory analyses of C/H have been obtained for all complexes. The overall similarity of carbonyl absorption bands of IR spectra reveals the similarity of the $RuCo_2(CO)_9$ unit in all complexes. For the proton of terminal alkyne, the ^1H NMR spectra exhibit two broad signals of equal intensity around δ 9.45-7.70 resulting from the different chemical environment in complexes, it suggested that both possible arrangements (A and B) of the alkynic substituents H and R would be exhibit a rapid interconversion between two configurations in solution. In addition to the above signals, all complexes show the presence of protons in other corresponding organic groups.

As seen in Figure 1, two independent **4a** and **4b** molecules appear in one asymmetric unit. Four $RuCo_2(CO)_9(\mu_3\text{–}\eta^2HC_2)$ moieties are similar in both molecules. From the torsion angles of C(10)-C(11)-Ru(1)-Co(1) of -2.8(8), C(21)-C(20)-Co(3)-Ru(2) of -0.9(10), C(40)-C(41)-Ru(3)-Co(5) of 1.6(8) and C(51)-C(50)-Ru(4)-Co(8) of -2.1(7)°, we could know that the C≡C multiple bond lies over RuCo2 triangle and parallel to one Ru-Co bond but not to the Co-Co bond in the metal atom triangle. However, the orientation of acetylenic bond is exactly reversed in $Ru(2)Co(3)Co(4)(CO)_9(\mu_3\text{–}\eta^2HC_2)$ moiety and in other three $RuCo_2(CO)_9(\mu_3\text{–}\eta^2HC_2)$ moieties. One terminal carbon of the diyne ligand lies on Ru atom side in $Ru(2)Co(3)Co(4)(CO)_9(\mu_3\text{–}\eta^2HC_2)$ moiety but it lies on Co atom side in other three $RuCo_2(CO)_9(\mu_3\text{–}\eta^2HC_2)$ moieties. Thus the two configurations are observed in the crystalline state and the ratio of two configurations is 3 to 1. However, two broad signals of equal intensity in the ^1H NMR spectra indicated the presence of A and B in 1:1 ratio. Probably, these structure are rapidly interconverted in solution with almost the same thermodynamic stability, but they exist in a 3:1 ratio due to crystal packing.

According to 18-electron rule, a bridging carbonyl should occur between Ru atom and Co atom located at the apex of the metal triangle. The crystal structure appears a semi-bridging carbonyl. This is because the asymmetry parameters α (0.27) of C(5)-O(5), α (0.40) of C(23)-O(13), α (0.30) of C(37)-O(27) and α (0.24) of C(56)-O(36) are well with in the range (0.1-0.6) for semi-bridging carbonyls.[8] It should be noted if the H atom lies on Ru(2) atom side, the distance of Ru(2)-C(23) of 2.46 Å is longer than bond average distance 2.32 Å of other Ru-C (C atom represents of semi-bridging carbonyl group).

This work was supported by the NNSF of China, and the foundation of the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

References and Notes

1 E. Roland and H. Vahrenkamp, *Organometallics*, **2**, 1048 (1983).

2 E. Roland and H. Vahrenkamp, *J. Mol. Catal.*, **21**, 233 (1983).

3 W. Bernhardt and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, **23**, 141 (1984).

4 E. Roland, W. Bernhardt, and H. Vahrenkamp, *Chem. Ber.*, **118**, 2858 (1985).

5 A. J. Deeming, In "*Transition Metal Clusters*" ed by B. F. G. Johnson, Wiley, New York (1980), p. 391.

6 Selected data for new complexes [25 °C, IR (KBr, Disc), ^1H NMR ($CDCl_3$)]. Syntheses were carried out in benzene or hexane at room temperature, monitoring the reaction progress by TLC (typically 2-3 h) using 0.2 mmol ligand and 0.4 mmol $RuCo_2(CO)_{11}$. **1**: Found: C, 30.60; H, 1.21%. Calcd. for $C_{27}H_{12}O_{18}Co_4Ru_2$: C, 30.53; H, 1.14%. IR: 2094s, 2048vs, 2020vs, 2002vs, 1897m [υ (CO)] cm^{-1}. ^1H NMR: δ: 9.21 (s, 1H, CH), 7.70 (s, 1H, CH), 2.79 (s, 4H, $2CH_2$), 1.65 (m, 6H, $CH_2CH_2CH_2$). **2**: Found: C, 27.78; H, 0.65%. Calcd. for $C_{24}H_6O_{19}Co_4Ru_2$: C, 27.82; H, 0.58%. IR: 2101s, 2072sh, 2051vs, 2032vs, 2024vs, 2002vs, 1926s, 1902sh, 1882m [υ (CO)] cm^{-1}. ^1H NMR: δ: 9.38 (s, 1H, CH), 7.93 (s, 1H, CH), 4.30 (s, 4H, $2CH_2$). **3**: Found: C, 32.40; H, 0.82%. Calcd. for $C_{32}H_{10}O_{22}Co_4Ru_2$: C, 32.45; H, 0.85%. IR: 2104s, 2052vs, 2038vs, 2020sh, 1990sh, 1911s, 1900m [υ (CO)] cm^{-1}. 1730s, 1712s [υ (C=O)] cm^{-1}. ^1H NMR: δ: 9.42 (s, 1H, CH), 8.02 (s, 1H, CH), 7.68-7.57 (m, 4H, C_6H_4), 5.10 (s, 4H, $2CH_2$). **4**: Found: C, 31.98; H, 0.95%. Calcd. for $C_{30}H_{10}O_{20}Co_4Ru_2$: C, 31.93; H, 0.89%. IR: 2102s, 2052sh, 2042vs, 2022vs, 2002sh, 1916sh, 1892m, 1876sh [υ (CO)] cm^{-1}. ^1H NMR: δ: 9.45 (s, 1H, CH), 8.04 (s, 1H, CH), 6.85 (m, 4H, C_6H_4), 4.61 (s, 4H, $2CH_2$).

7 Crystal data for **4**: all measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation. $C_{30}H_{10}O_{20}Co_4Ru_2$, M = 1128.27, momoclinic, space group $P2_1/n$ (no. 14), a = 13.740(3), b = 34.228(8), c = 16.50(2) Å, β = 101.117(4)°, U = 7614(6) $Å^3$, Z = 8, μ (Mo-Kα) = 25.6 cm^{-1}. Of the 10563 total reflections which were collected, 6969 with $I > 3.00\ \sigma(I)$ were observed. Data were corrected for *Lorentz* and Polarization effects. The structure was solved by the direct method and yielded final R = 0.052; R_w = 0.072 for 1070 least-squares parameters.

8 M.D. Curtis, K. R. Han, and W. M. Butler, *Inorg. Chem.*, **19**, 2096 (1980).