Preliminary communication

Synthesis and crystal structure of a pentanuclear heterometallic acetylide complex $Cp_2Mo_2Ru_3(CO)_{10}(C\equiv CPh)_2$

Der-Kweng Hwang, Yun Chi [*]

Department of Chemistry, National Tsing Hua University, Hsinchu 30043 (Taiwan)

Shie-Ming Peng and Gene-Hsiang Lee

*Department of Chemistry, National Taiwan University, Taipei 10764 (Taiwan)*

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Abstract

The pentanuclear heterometallic acetylide complex $Cp_2Mo_2Ru_3(CO)_{10}(C\equiv CPh)_2$ (3) was prepared by the reaction of the metal acetylide $CpMo(CO)_3C\equiv CPh$ with $Ru_3(CO)_{12}$. This complex was characterized by spectroscopic methods and by X-ray single-crystal structure determination. Notable structural features of the new complex 3 include an unusual symmetric pentametallic double butterfly skeleton and a novel μ_4-η^2 bonding mode for the acetylide ligand. Crystal data for 3: space group $P2_1/c$; a 24.119(10), b 20.739(4), c 15.358(3) Å, β 101.68(4)°, $Z = 8$; final $R = 0.038$, $R_w = 0.034$ and GOF = 1.57.

Heterometallic transition metal chemistry has experienced rapid growth for many years [1]. One of the key factors is due to the belief that cooperative effects between different metal atoms may promote unique patterns of substrate activation. In seeking to develop a systematic method to synthesize mixed-metal complexes by using the concept of isolobal analogy [2], Stone and coworkers have used alkylidyne derivatives $Cp(CO)_2W\equiv CR$ to prepare many mixed-metal clusters containing a bridging alkylidyne fragment [3]. Recently, a few research groups have started to use transition metal acetylide complexes $L_nMC\equiv CR$ in attempts to prepare heterometallic clusters containing a multisite cluster-bound acetylide fragment [4].

We have performed the reaction between $CpW(CO)_3C\equiv CPh$ and the triosmium derivative $Os_3(CO)_{10}(NCMe)_2$ [5]. Two heterometallic acetylide complexes, $CpWOs_3(CO)_{11}(C\equiv CPh)$ (1) and $CpWOs_2(CO)_8(C\equiv CPh)$ (2), have been isolated and characterized by X-ray crystal structure determination (Scheme 1). However, the analogous reaction with $Ru_3(CO)_{12}$ failed to produce the analogous tetranuclear derivative, but provided only the trinuclear complex [6]. In this paper, we report the preparation and crystal structure of an analogous pentanuclear heterometallic
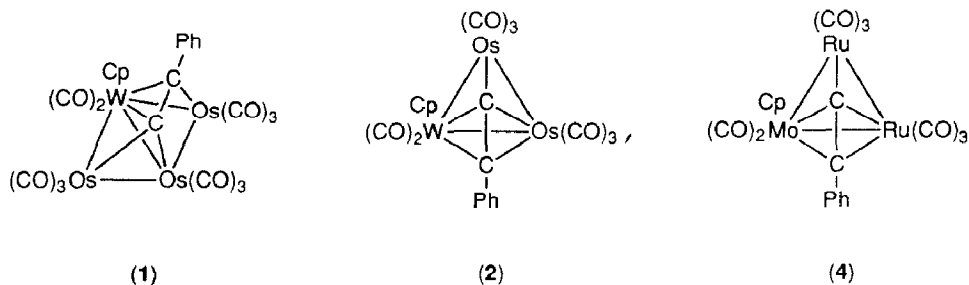
Scheme 1

derivative $Cp_2Mo_2Ru_3(CO)_{10}(C\equiv CPh)_2$ (**3**), generated by condensation of CpMo $(CO)_3C\equiv CPh$ with $Ru_3(CO)_{12}$. Notable structural features of the new complex **3** include an uncommon symmetrical pentametallic double butterfly skeleton [7] and a novel μ_4-η^2 bonding mode for the acetylide ligand [5].

Treatment of a mixture of $Ru_3(CO)_{12}$ and $CpMo(CO)_3C\equiv CPh$ in a molar ratio 2 : 3 in refluxing toluene under nitrogen for 40 min, followed by thin-layer chromatography on silica gel (CH_2Cl_2 : hexane = 2 : 3), gave the expected trinuclear acetylide derivative $CpMoRu_2(CO)_8(C\equiv CPh)$ (**4**, 42%), unreacted $Ru_3(CO)_{12}$ (7%), and small proportions of dark-brown complex **3** (5%). The complex **3** was identified primarily from its spectroscopic data: FAB MS (^{102}Ru, ^{98}Mo): m/z 1114 (M^+); IR(CCl_4): $\nu(CO)$, 2073 (vs), 2054 (s), 2014 (m, br), 1986 (w), 1973 (w), 1940 (vw) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 294 K): δ 7.56 (d, 4H, $J(H-H)$ = 7.1 Hz), 7.42 (t, 4H, $J(H-H)$ = 7.3 Hz), 7.30 (t, 2H, $J(H-H)$ = 7.3 Hz), 5.23 (s, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, 294 K): δ 238.1 (Mo–CO, 2C), 198.9 (Ru–CO, 2C), 196.9 (Ru–CO, 2C), 195.8 (Ru–CO, 2C), 193.3 (Ru–CO, 2C). The ^1H and ^{13}C NMR spectra and the parent ion in the mass spectrum suggest the presence of two identical acetylide ligands and two identical CpMo units. Cluster complexes possessing such high molecular symmetry are rather uncommon.

Precise structural details have been provided by X-ray analysis. Crystals suitable for single-crystal X-ray diffraction study were obtained from a solution in CH_2Cl_2/CH_3OH at room temperature. According to the X-ray structure determination, the asymmetric unit contains two crystallographically distinct, but structurally similar molecules [8*]. An ORTEP diagram of one of these molecules is shown in Fig. 1, together with selected bond distances and angles. The molecule crystallizes in the monoclinic space group $P2_1/c$ with the presence of one independent CH_2Cl_2 molecule. There is no interaction between the cluster complexes nor between the

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* Reference number with asterisk indicates a note in the list of references.

Fig. 1. Molecular structure of $Cp_2Mo_2Ru_3(CO)_{10}(C\equiv CPh)_2$ (**3**) showing the atomic numbering scheme. Important dimensions include: bond lengths (Å): Mo(1A)–Mo(2A) 3.063(2), Mo(1A)–Ru(1A) 2.830(2), Mo(1A)–Ru(2A) 2.729(1), Mo(2A)–Ru(2A) 2.755(2), Mo(2A)–Ru(3A) 2.822(2), Ru(1A)–Ru(2A) 2.778(2), Ru(2A)–Ru(3A) 2.770(2), Mo(1A)–C(21A), 2.22(1), Mo(2A)–C(21A) 1.99(1), Ru(2A)–C(21A) 2.146(9), Mo(1A)–C(22A) 2.303(9), Ru(1A)–C(22A) 2.11(1), C(21A)–C(22A), 1.37(1), Mo(1A)–C(29A), 2.02(1), Mo(2A)–C(29A) 2.25(1), Ru(2A)–C(29A) 2.14(1), Mo(2A)–C(30A) 2.28(1). Ru(3A)–C(30A) 2.12(1), C(29A)–C(30A) 1.36(1), Mo(1A)–C(1A) 2.00(1), Ru(1A)–C(1A) 2.33(1), Mo(2A)–C(2A) 2.01(1), Ru(3A)–C(2A) 2.36(1); bond angles (°): Mo(1A)–C(1A)–O(1A) 152.9(9). Ru(1A)–C(1A)–O(1A) 125.4(8), Mo(2A)–C(2A)–O(2A) 152.9(9), Ru(3A)–C(2A)–O(2A) 126.6(8).
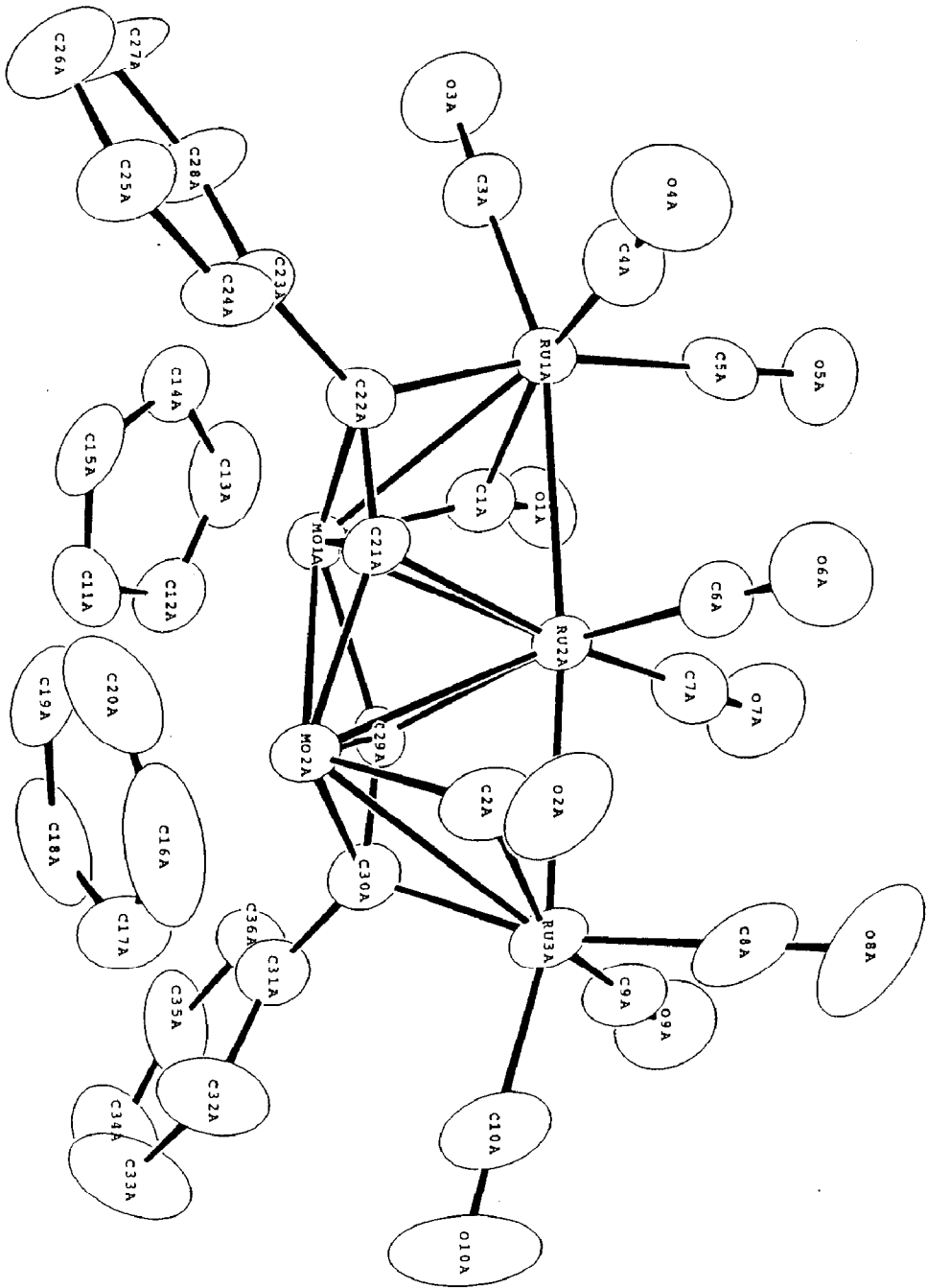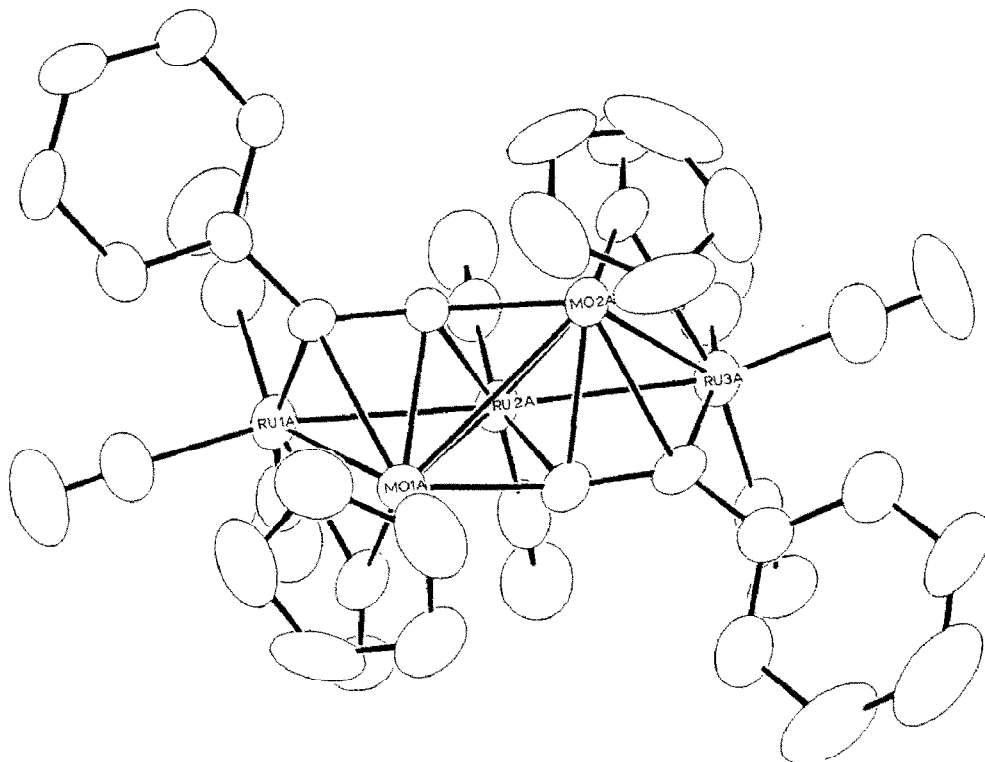
Fig. 2. An ORTEP view of 3 showing the C_2 rotational symmetry of this molecule.

cluster and the solvent molecules. The Mo_2Ru_3 cluster core adopts a novel double butterfly geometry [7], as expected for the pentametallic complexes characterized by the presence of 76 outer valence electrons [9]. Atoms Ru(2A), Mo(1A) and Mo(2A) constitute the metal triangle located in the center, of which the ruthenium atom Ru(2A) associates with two terminal CO ligands and each molybdenum atom associates with one bridging CO ligand and one Cp ligand. There are two further ruthenium atoms, Ru(1A) and Ru(3A), each of which is located on one of the two Ru–Mo edges of the central triangle and is coordinated by three terminal CO ligands. Furthermore, the arrangement of the transition metal atoms and their surrounding ligands of this molecule suggests that there is a C_2 rotational axis which passes the Ru(2A) atom and the middle of the Mo(1A)–Mo(2A) vector. A side-view of this molecule, which emphasizes the C_2 symmetry, is depicted in Fig. 2.

Due to the existence of C_2 symmetry, the acetylide ligands, C(21A)–C(22A) and C(29A)–C(30A), occupy opposite faces of the Mo_2Ru_2 butterfly skeleton related by a 180° rotation, and are coordinated in multisite fashion with each α-carbon bound to the three center metal atoms Mo(1A), Mo(2A) and Ru(2A), and with the β-carbon atom bridged to the Mo–Ru bond at the edge. The dihedral angles between the planes Mo(1A)–Mo(2A)–Ru(2A) and Mo(1A)–Ru(1A)–Ru(2A) and between the planes Mo(1A)–Mo(2A)–Ru(2A) and Mo(2A)–Ru(2A)–Ru(3A) are 132.72(4) and 135.59(4)°, respectively. The μ_4-η^2 bonding mode of the acetylide ligand is of interest. The related μ_4-η^2 bonding interaction has been reported in the

spiked triangular Ni_2Fe_2 and $FeRuCo_2$ complexes, [10] the square pyramidal Ru_5 complex [11] and the wing-tip bridged butterfly $NiRu_4$ complex [12]. However, the pentametallic derivative **3** and the tetranuclear complex **1** represent rare examples, in which the acetylide lies on the face of the tetrametallic butterfly skeleton and adopts a $1\sigma + 2\pi$ bonding interaction [13] supplying a total of five electrons to the cluster orbitals. Tetranuclear Fe_4 and Ru_4 nitrile complexes which possess similar μ_4-η^2 bonding interactions have been documented [14].

The mechanism for the formation of **3** is unknown at present. However, it is reasonable to propose that the mechanism involves the generation of a tetrametallic intermediate $CpMoRu_3(CO)_{11}(C{\equiv}CPh)$ with a structure similar to **1**, followed by further condensation with $CpMo(CO)_3C{\equiv}CPh$ to give the isolated product. Unfortunately, no such species was observed during the reaction, suggesting that the proposed intermediate may be unstable under the conditions studied.

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8 Selected crystal data for **3**: $C_{36}H_{20}Mo_2O_{10}Ru_3 \cdot \frac{1}{2}CH_2Cl_2$, $M = 1150.1$, monoclinic, space group $P\,2_1/c$, a 24.119(10), b 20.739(4), c 15.358(3) Å, β 101.68(4)°, V 7523(4) Å^3, $Z = 8$, D_c 2.03 g/cm^3, $F(000) = 4422.9$, Mo-K_α radiation with λ 0.70930 Å, Ψ scan absorption correction was made and 9816 unique reflections were measured of which 6262 were considered observed with $I > 2\sigma(I)$. The structure was solved by a direct method and refined by full matrix least-squares refinement. Final $R = 0.038$, $R_w = 0.034$ and GOF $= 1.57$. Tables of bond distances and angles, a table of positional parameters and anisotropic thermal parameters, and listings of the observed and calculated structural factors are available from the authors.

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