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### Preliminary communication

## Synthesis and crystal structure of a pentanuclear heterometallic acetylide complex $\text{Cp}_2\text{Mo}_2\text{Ru}_3(\text{CO})_{10}(\text{C}\equiv\text{CPh})_2$

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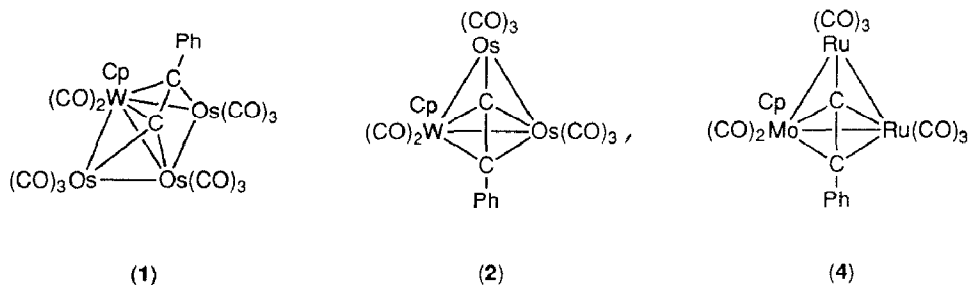
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### Abstract

The pentanuclear heterometallic acetylide complex  $\text{Cp}_2\text{Mo}_2\text{Ru}_3(\text{CO})_{10}(\text{C}\equiv\text{CPh})_2$  (**3**) was prepared by the reaction of the metal acetylide  $\text{CpMo}(\text{CO})_3\text{C}\equiv\text{CPh}$  with  $\text{Ru}_3(\text{CO})_{12}$ . 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  $\mu_4\text{-}\eta^2$  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,  $\beta$  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  $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CR}$  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  $\text{L}_n\text{MC}\equiv\text{CR}$  in attempts to prepare heterometallic clusters containing a multisite cluster-bound acetylide fragment [4].

We have performed the reaction between  $\text{CpW}(\text{CO})_3\text{C}\equiv\text{CPh}$  and the triosmium derivative  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  [5]. Two heterometallic acetylide complexes,  $\text{CpW}\text{Os}_3(\text{CO})_{11}(\text{C}\equiv\text{CPh})$  (**1**) and  $\text{CpW}\text{Os}_2(\text{CO})_8(\text{C}\equiv\text{CPh})$  (**2**), have been isolated and characterized by X-ray crystal structure determination (Scheme 1). However, the analogous reaction with  $\text{Ru}_3(\text{CO})_{12}$  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

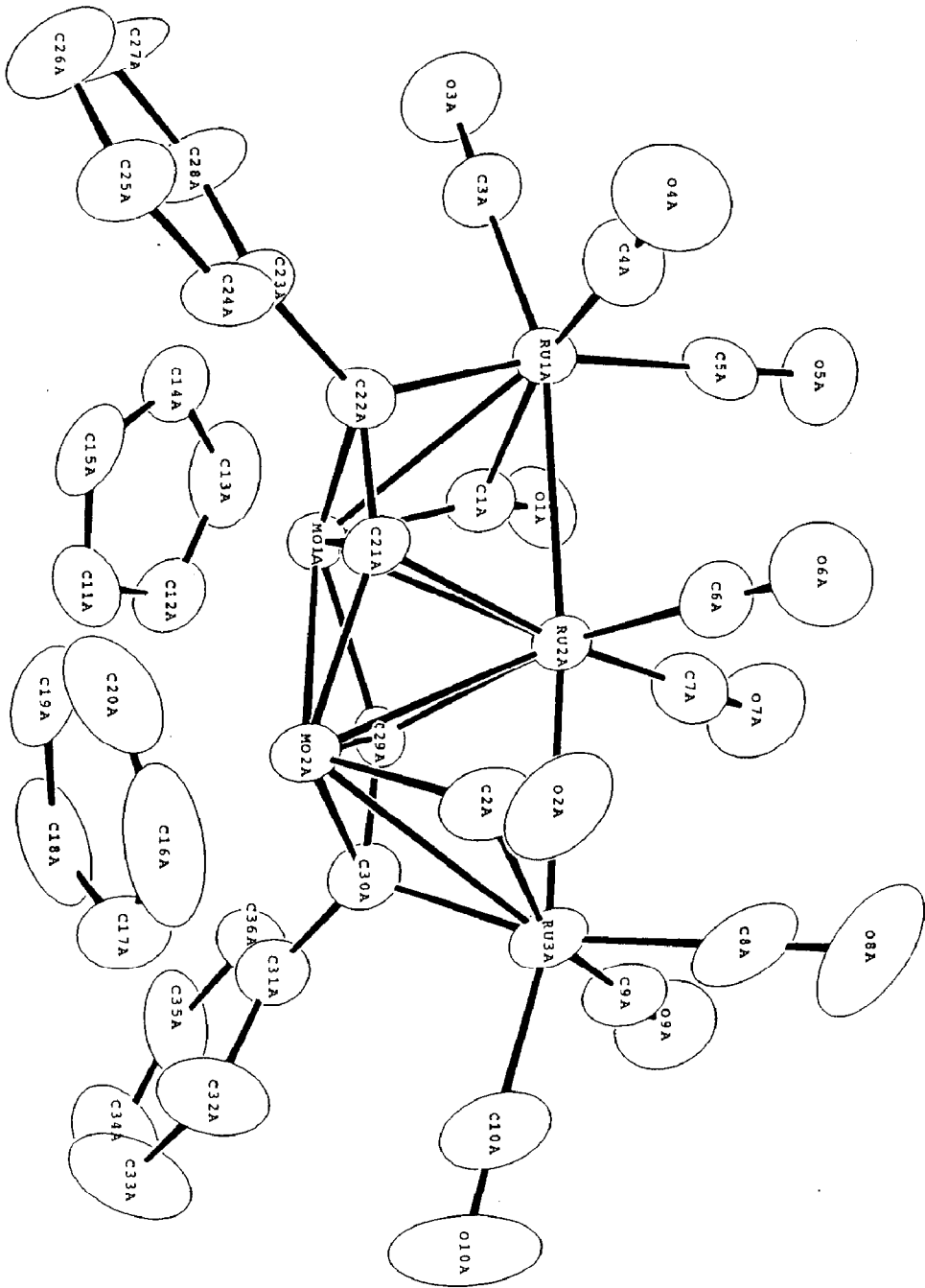
derivative  $\text{Cp}_2\text{Mo}_2\text{Ru}_3(\text{CO})_{10}(\text{C}\equiv\text{CPh})_2$  (**3**), generated by condensation of  $\text{CpMo}(\text{CO})_3\text{C}\equiv\text{CPh}$  with  $\text{Ru}_3(\text{CO})_{12}$ . Notable structural features of the new complex **3** include an uncommon symmetrical pentametallic double butterfly skeleton [7] and a novel  $\mu_4\text{-}\eta^2$  bonding mode for the acetylide ligand [5].

Treatment of a mixture of  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{CpMo}(\text{CO})_3\text{C}\equiv\text{CPh}$  in a molar ratio 2:3 in refluxing toluene under nitrogen for 40 min, followed by thin-layer chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$ :hexane = 2:3), gave the expected trinuclear acetylide derivative  $\text{CpMoRu}_2(\text{CO})_8(\text{C}\equiv\text{CPh})$  (**4**, 42%), unreacted  $\text{Ru}_3(\text{CO})_{12}$  (7%), and small proportions of dark-brown complex **3** (5%). The complex **3** was identified primarily from its spectroscopic data: FAB MS ( $^{102}\text{Ru}$ ,  $^{98}\text{Mo}$ ):  $m/z$  1114 ( $M^+$ ); IR( $\text{CCl}_4$ ):  $\nu(\text{CO})$ , 2073 (vs), 2054 (s), 2014 (m, br), 1986 (w), 1973 (w), 1940 (vw)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 294 K):  $\delta$  7.56 (d, 4H,  $J(\text{H-H}) = 7.1$  Hz), 7.42 (t, 4H,  $J(\text{H-H}) = 7.3$  Hz), 7.30 (t, 2H,  $J(\text{H-H}) = 7.3$  Hz), 5.23 (s, 10H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 294 K):  $\delta$  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  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and the parent ion in the mass spectrum suggest the presence of two identical acetylide ligands and two identical  $\text{CpMo}$  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  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  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  $\text{CH}_2\text{Cl}_2$  molecule. There is no interaction between the cluster complexes nor between the

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

Fig. 1. Molecular structure of  $\text{Cp}_2\text{Mo}_2\text{Ru}_3(\text{CO})_{10}(\text{C}\equiv\text{CPh})_2$  (**3**) showing the atomic numbering scheme. Important dimensions include: bond lengths ( $\text{\AA}$ ): 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 ( $^\circ$ ): 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).



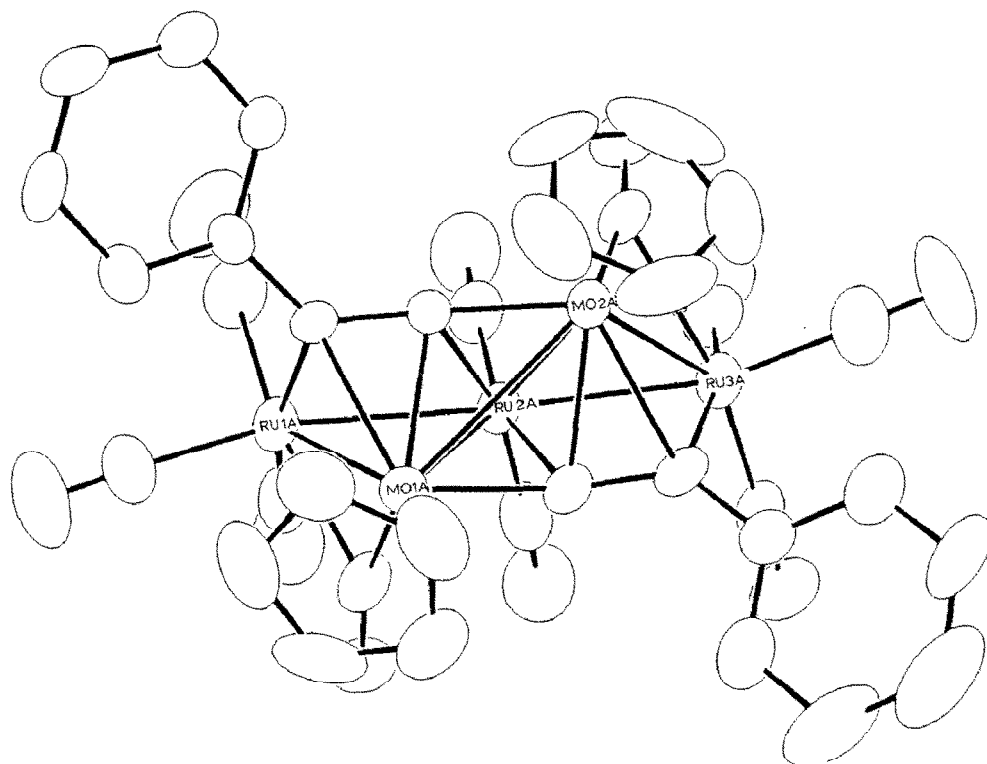


Fig. 2. An ORTEP view of **3** showing the  $C_2$  rotational symmetry of this molecule.

cluster and the solvent molecules. The  $\text{Mo}_2\text{Ru}_3$  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  $\text{Mo}_2\text{Ru}_2$  butterfly skeleton related by a  $180^\circ$  rotation, and are coordinated in multisite fashion with each  $\alpha$ -carbon bound to the three center metal atoms Mo(1A), Mo(2A) and Ru(2A), and with the  $\beta$ -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  $135.59(4)^\circ$ , respectively. The  $\mu_4\text{-}\eta^2$  bonding mode of the acetylide ligand is of interest. The related  $\mu_4\text{-}\eta^2$  bonding interaction has been reported in the

spiked triangular  $\text{Ni}_2\text{Fe}_2$  and  $\text{FeRuCo}_2$  complexes, [10] the square pyramidal  $\text{Ru}_5$  complex [11] and the wing-tip bridged butterfly  $\text{NiRu}_4$  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  $\text{Fe}_4$  and  $\text{Ru}_4$  nitrile complexes which possess similar  $\mu_4\text{-}\eta^2$  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  $\text{CpMoRu}_3(\text{CO})_{11}(\text{C}\equiv\text{CPh})$  with a structure similar to **1**, followed by further condensation with  $\text{CpMo}(\text{CO})_3\text{C}\equiv\text{CPh}$  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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