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Mixed-metal cluster chemistry. 35. Syntheses and structural studies of $Mo_3Ir_3(\mu_3\text{-}O)(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)_3$, $Mo_4Ir_4(\mu\text{-}CO)_4(CO)_9(\eta^5\text{-}C_5H_5)_4$ and $Mo_3Ir_5(\mu\text{-}CO)_3(Cl)(CO)_6(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5HMe_4)$☆

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Dedicated to Professor Mike Mingos, an inspirational chemist.

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ABSTRACT

The reaction of $Ir(CO)_2(\eta^5\text{-}C_5HMe_4)$ with $Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2$ affords a complex mixture from which three structurally-characterized products were obtained following thin-layer chromatography. $Mo_3Ir_3(\mu_3\text{-}O)(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)_3$ (**1**) is Effective Atomic Number (EAN) Rule EAN-precise and possesses an edge-bridged trigonal bipyramidal core with the face-capping oxo ligand located in a Mo_2Ir_2 butterfly cleft in the structure. $Mo_4Ir_4(\mu\text{-}CO)_4(CO)_9(\eta^5\text{-}C_5H_5)_4$ (**2**) possesses four electrons less than the Polyhedral Skeletal Electron Pair Theory (PSEPT)-expected count for a capped pentagonal bipyramidal cluster with the apical atoms within bonding distance. $Mo_3Ir_5(\mu\text{-}CO)_3(Cl)(CO)_6(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5HMe_4)$ (**3**) possesses a tetracapped tetrahedral core and has six electrons less than the PSEPT-predicted electron count. The core geometries exhibited by clusters **2** and **3** have previously only been observed for clusters including significant group 10 and group 11 metal content.

Introduction

Transition metal clusters occupy the regime between monometallic complexes and nanocrystalline materials. The challenge of rationalizing the stability of such species has spurred the development of theory, one key example of which is the polyhedral skeletal electron-pair theory (PSEPT, also known as the Wade-Mingos rules) [1,2]. The field of transition metal carbonyl clusters increased explosively following the advent of routine single-crystal X-ray diffraction studies that were needed to conclusively establish the identity of these clusters [3], to the extent that the field can now be considered mature. Notwithstanding the now-well-established nature of this area, it is still the case that mixed-metal clusters incorporating disparate metals remain comparatively underexploited, despite the practical advantages that locating two differing metals in the one cluster may afford, such as enhancing the prospects of controlling chemistry via metal- or bond-selectivity for substrates, labelling vertices to establish ligand fluxionality pathways, and controlling the spatial disposition and connectivity of heterobimetallic species in subsequent catalytic processes [4].

We have reported comprehensive studies of the syntheses and chemistry of tetranuclear mixed molybdenum/tungsten–iridium carbonyl clusters [5] and have recently extended these studies to embrace pentanuclear examples [6]. On modifying the reaction conditions employed for the syntheses of one of the pentanuclear clusters, we observed the unexpected formation of several higher-nuclearity species, the syntheses and structural characterization of which are reported herein.

Experimental

General experimental conditions and starting materials

The reaction was performed under an atmosphere of nitrogen using standard Schlenk techniques. The product clusters proved indefinitely stable in air as solids and for at least short periods of time in solution, and thus no special precautions were taken to exclude air in their work-up. The toluene reaction solvent was AR

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grade and was distilled under nitrogen over sodium benzophenone ketyl. Literature procedures were used to synthesize $Ir(CO)_2(\eta^5\text{-}C_5HMe_4)$ [6] and $Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2$ [7]. All other solvents and other reagents were obtained commercially and were used as received. Petrol refers to a fraction of boiling range 60–80 °C. The cluster products were purified by preparative thin-layer chromatography (TLC) on a 20 × 20 cm glass plate coated with Merck GF_{254} silica gel (0.5 mm). IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using a CaF_2 solution cell and AR grade *n*-hexane solvent.

*Synthesis of $Mo_3Ir_3(\mu_3\text{-}O)(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)_3$ (**1**), $Mo_4Ir_4(\mu\text{-}CO)_4(CO)_9(\eta^5\text{-}C_5H_5)_4$ (**2**) and $Mo_3Ir_5(\mu\text{-}CO)_3(Cl)(CO)_6(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5HMe_4)$ (**3**)*

$Ir(CO)_2(\eta^5\text{-}C_5HMe_4)$ (16.0 mg, 43.2 μmol) was added to a red solution of $Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2$ (46.0 mg, 46.4 μmol) in toluene (30 mL), and the resultant solution was heated at reflux for 90 min, the extent of reaction being monitored by IR spectroscopy. The solution reaction mixture was taken to dryness in vacuo, and the crude residue was dissolved in a minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (9:1) afforded 6 bands. The contents of the first ($R_f = 0.93$, yellow), second ($R_f = 0.75$, orange) and fourth ($R_f = 0.50$, red) bands were in trace amounts and the products contained therein could not be identified. The contents of the third band ($R_f = 0.68$, dark yellow) were extracted with CH_2Cl_2 and reduced in volume, producing a dark yellow solid (ca. 0.5 mg), identified as $Mo_3Ir_3(\mu_3\text{-}O)(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)_3$ (**1**) by a single-crystal X-ray crystallography study [IR: ν(CO) 2025 w, 2002 s, 1969 s, 1935 sh, 1886 w, 1721 w cm^{-1}]. The contents of the fifth band ($R_f = 0.43$, brown) were extracted with CH_2Cl_2 and reduced in volume to afford a black solid identified as $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)$ (23.8 mg, 18.6 μmol, 31%) by IR spectral comparison to an authentic sample [6]. The contents of the sixth band ($R_f = 0.31$, brown) were extracted with CH_2Cl_2 and reduced in volume, producing a brown solid. Crystallization from *n*-hexane afforded co-crystallized $Mo_4Ir_4(\mu\text{-}CO)_4(CO)_9(\eta^5\text{-}C_5H_5)_4$ (2) and $Mo_3Ir_5(\mu\text{-}CO)_3(Cl)(CO)_6(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5HMe_4)$ (3) (ca. 0.5 mg) [IR: ν(CO) 2025 m, 1997 s, 1969 m, 1944 sh, 1886 w, 1837 w, 1706 w cm^{-1}].

*X-ray structural studies of $Mo_3Ir_3(\mu_3\text{-}O)(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)_3$ (**1**) and $Mo_4Ir_4(\mu\text{-}CO)_4(CO)_9(\eta^5\text{-}C_5H_5)_4$ (**2**),$Mo_3Ir_5(\mu\text{-}CO)_3(Cl)(CO)_6(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5HMe_4)$ (**3**)*

Crystals of **1** and **2**,**3** suitable for the X-ray structural analyses were grown from *n*-hexane solutions. Intensity data were collected using an Enraf-Nonius KAPPA CCD diffractometer at 200 K with MoK_α radiation (λ = 0.7170 Å). Suitable crystals were immersed in viscous hydrocarbon oil and mounted on a glass fibre that was mounted on the diffractometer. Using psi and omega scans N_t (total) reflections were measured, which were reduced to N_o unique reflections, with $F_o > 2\sigma(F_o)$ being considered "observed". Data were initially processed and corrected for absorption using the programs DENZO [8] and SORTAV [9]. The structures were solved using direct methods, and observed reflections were used in least squares refinement on F^2, with anisotropic thermal parameters refined for non-hydrogen atoms. Hydrogen atoms were constrained in calculated positions and refined with a riding model. Structure solutions and refinements were performed using the programs SHELXS-97 and SHELXL-2013 [10] through the graphical interface Olex2 [11], which was also used to generate the figures. Crystal data for **1**: $C_{26}H_{15}Ir_3Mo_3O_{12}$, $M = 1383.80$, brown block, 0.09 × 0.09 × 0.07 mm^3, triclinic, space group *P*-1 (No. 2), $a = 10.690(2)$, $b = 11.239(2)$, $c = 11.950(2)$ Å, $\alpha = 98.22(3)$, $\beta = 91.51(3)$, $\gamma = 91.60(3)°$, $V = 1419.8(5)$ Å^3, $Z = 2$, $D_c = 3.237$ g/cm^3, $F_{000} = 1248$, $\mu = 15.35$ mm^{-1}, $2\theta_{max} = 56.6°$, 30,544 reflections collected, 7033 unique. Final *GoF* = 1.01, *R1* = 0.040, *wR2* = 0.097, *R* indices based on 5591 reflections with $I > 2\sigma(I)$ (refinement on F^2), 397 parameters, 3 restraints. Crystal data for **2**, **3**: $C_{33}H_{20}Ir_4Mo_4O_{13}.C_{33}H_{28}ClIr_5Mo_3O_9$, $M = 3629.87$, brown plate, 0.08 × 0.07 × 0.01 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 20.459(4)$, $b = 17.297(4)$, $c = 22.038(4)$ Å, $\beta = 100.56(3)°$, $V = 7667(3)$ Å^3, $Z = 4$, $D_c = 3.145$ g/cm^3, $F_{000} = 6496$, $\mu = 16.75$ mm^{-1}, $2\theta_{max} = 52.8°$, 120,726 reflections collected, 15,673 unique. Final *GoF* = 0.96, *R1* = 0.055, *wR2* = 0.131, *R* indices based on 10,419 reflections with $I > 2\sigma(I)$ (refinement on F^2), 950 parameters, 285 restraints. *Variata.* In **1**, anisotropic displacement parameter restraints were applied to carbonyl ligand C121–O121. In **2**,**3**, disordered lattice solvent could not be successfully modelled, and was therefore removed from the refinement using PLATON SQUEEZE [12]. Anisotropic displacement parameter restraints and constraints were applied to cyclopentadienyl ligands C1–C5, C6–C10, C11–C15, C21–C25, and carbonyl ligands C4A–O4A, C34A–O34A.

Results and discussion

*Synthesis of $Mo_3Ir_3(\mu_3\text{-}O)(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)_3$ (**1**) and $Mo_4Ir_4(\mu\text{-}CO)_4(CO)_9(\eta^5\text{-}C_5H_5)_4$ (**2**),$Mo_3Ir_5(\mu\text{-}CO)_3(Cl)(CO)_6(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5HMe_4)$ (**3**)*

The reaction between $Ir(CO)_2(\eta^5\text{-}C_5HMe_4)$ (43.2 μmol) and $Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2$ (46.4 μmol) in refluxing toluene (30 mL) for 90 min afforded a complex mixture of products that were separated by thin-layer chromatography (Scheme 1). The major product [$Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5HMe_4)$, 31%] has been previously obtained in a significantly higher yield (68%) from the reaction between the same reagents, but under different conditions, varying the molar ratio, quantity of solvent, and reaction duration [$Ir(CO)_2(\eta^5\text{-}C_5HMe_4)$ (28.9 μmol) and $Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2$ (19.3 μmol) in refluxing toluene (7 mL) for 1 h] [6]; thus, the reaction outcomes are highly sensitive to the specific reaction conditions. In the present case, several minor bands in essentially trace amounts were separable. Attempts to crystallize the contents afforded suitable single crystals for X-ray diffraction studies from two of the bands (the third and sixth, as described in the Experimental Section).

*X-ray structural study of $Mo_3Ir_3(\mu_3\text{-}O)(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)_3$ (**1**)*

The structural study of the crystal obtained from the contents of the third band from the TLC plate revealed its identity to be $Mo_3Ir_3(\mu_3\text{-}O)(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)_3$ (**1**). An ORTEP diagram of **1** is shown in Fig. 1, while selected bond lengths are collected in the figure caption.

Cluster **1** possesses an edge-bridged trigonal bipyramidal core with the three iridium atoms defining one face of the trigonal bipyramid and a molybdenum atom bridging an apical Ir – equatorial Ir vector. The molybdenum atoms are each ligated by a η^5-cyclopentadienyl ligand, and the cluster contains eleven carbonyl ligands (three edge-bridging, eight terminally-ligated). A μ_3-oxo ligand, assumed to derive from cleavage of a CO ligand, completes the coordination sphere (note that we cannot discount the possibility that it derives from oxidation on work-up); its assignment as O rather than C is consistent with its refinement behaviour (more plausible thermal parameters) and chemical precedent (see below: a face-capping residue is far more likely to be an oxo than a carbido ligand, particularly in situations such as this where a higher metal loading is possible). The Ir–Ir [2.7410(9)–2.7546(8) Å], Mo–Ir [2.6817(11)–2.8947(11) Å], and Mo–Mo [3.1062(13) Å] bond distances lie within the range of literature precedents. The three bridging CO ligands all bridge Mo–Ir vectors and are all formally

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