Syntheses of $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)_2$ and $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ from Pentametallic Molybdenum-Iridium Cluster Precursors

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Abstract: Reaction of $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ with $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$ afforded the four-valence-electron-deficient butterfly cluster $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)_2$; its stability has been rationalized with the aid of density functional theory calculations, which suggest that significant additional intracluster bonding alleviates the formal electron deficiency. Reaction of $MoIr_4(CO)_{10}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ with $[N(PPh_3)_2][Ir(CO)_4]$ afforded the capped octahedral cluster $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ which possesses three semi-face-capping CO ligands. These outcomes demonstrate that heterometallic clusters may serve as a potential source of new homometallic clusters following appropriate M-M' cleavage.
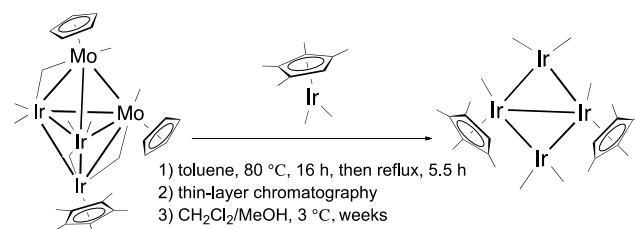
Introduction

Iridium carbonyl cluster chemistry has been of long-standing interest.[1] Iridium clusters with core nuclearities from three to fourteen are extant, the most thoroughly-studied being tetranuclear clusters formally derived from $Ir_4(CO)_{12}$ and hexanuclear clusters related to $Ir_6(CO)_{16}$. Synthetic routes to iridium clusters have (not surprisingly) employed iridium-containing precursors. For example, mono- or diiridium complexes have been used to synthesize triiridium clusters,[1(b)] while reductive carbonylation of iridium-containing salts affords $Ir_4(CO)_{12}$,[2] a tetrahedral cluster which is itself a fertile source of other clusters.[1(b,c)]

A thus-far-unexploited synthetic approach to iridium clusters is to use heterometallic complexes with metal-iridium bonds that are sufficiently weak that their cleavage may afford suitably reactive fragments for the assembly of new homometallic clusters; this is the reverse of the most widely applied protocol for the construction of heterometallic clusters, namely, introduction of a heterometal to a pre-formed homometallic cluster. Heterometal removal is not likely to have significant predictive utility, and the construction and then cleavage of heterometallic bonds is overall not an efficient synthetic protocol, but such an approach may enhance diversity and afford species inaccessible by conventional methods. We report herein reactions of molybdenum-iridium clusters with iridium-containing reagents that

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have afforded the new homometallic clusters $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)_2$ (**1**) and $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ (**2**), structural studies of **1** and **2**, and theoretical studies of **1** rationalizing its unusual electron deficiency.

Results and Discussion

Reacting $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ with $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$ afforded small amounts of an unknown product.[3] After several weeks, crystals of **1** were obtained (Scheme 1), an X-ray study of which afforded the structure depicted in Figure 1, presumably from decomposition of the initial product. The different polyalkylcyclopentadienyl ligands of the precursors serve to distinguish the iridium atoms, and thereby identify $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$ as the origin of two iridium vertices of **1**.[4]

1) toluene, 80 °C, 16 h, then reflux, 5.5 h
2) thin-layer chromatography
3) CH_2Cl_2/MeOH, 3 °C, weeks

Scheme 1. Synthesis of $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)$ (**1**).

The Ir-Ir distances of the butterfly core of **1** are short, but within the previously reported range; in contrast, the Ir2…Ir2A vector is clearly non-bonding [4.1370(4) Å]. Ir2/Ir2A possess distorted square planar geometries [maximum deviation from the refined least squares plane through Ir1, C21, C22, Ir1A, Ir2: 0.0096(0.0030) Å]. Cluster **1** possesses $4 \times 9(Ir) + 2 \times 5(\eta^5\text{-}C_5Me_4H) + 6 \times 2(CO) = 58$ cluster valence electrons (CVE), four fewer than the 62 CVE required by the EAN rule.[5] This electron deficiency, the *syn* disposed tetramethylcyclopentadienyl ligands at the sterically more constrained iridium atoms, and the existence of the electron-precise tetrahedral cluster $Rh_2Ir_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)(CO)_4(\eta^5\text{-}C_5Me_5)$[6] (the metal content of which is related to **1** by conceptual replacement of two Ir atoms by Rh atoms), and which contains an extra four CVE arising from an additional CO ligand and M-M bond, prompted a detailed theoretical study of **1** to rationalize its stability.

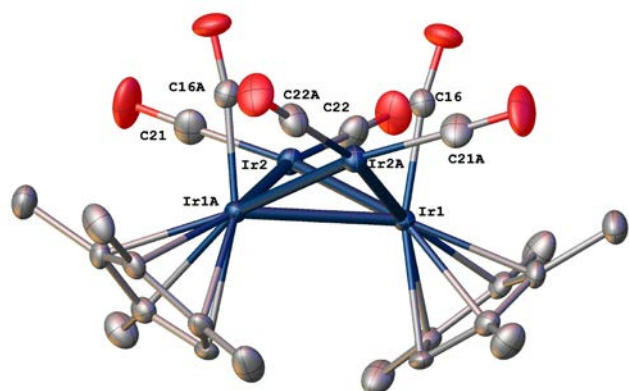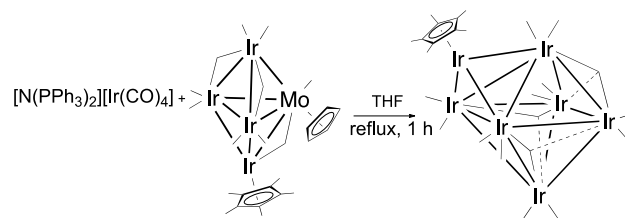**Figure 1.** Molecular structure of $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)_2$ (**1**), with thermal ellipsoids set at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ir1-Ir2 2.6374(3), Ir1-Ir1A 2.7512(4), Ir1-Ir2A 2.6343(3), Ir1-C16 1.868(7), Ir2-C21 1.838(8), Ir2-C22 1.849(7). Symmetry operation used to generate equivalent atoms A: -x, +y, ½-z.

Cluster **1** is four-electrons deficient, and so two CO ligands were added to afford a theoretical species with an electron precise composition for comparison. Adding one CO ligand to each wingtip iridium atom afforded the lowest energy 62 CVE geometry-optimized structure, $Ir_4(CO)_8(\eta^5\text{-}C_5Me_4H)_2$ (**3**) [Figure S1; bond distances and dihedral angles: Tables S1 (**1**) and S2 (**3**)]. Gibbs free energies for the theoretical CO dissociation reaction **3** → **1** + 2CO (Scheme S1) are ca. 0 kcal/mol (Table S3), consistent with the observed stability of **1**. The aforementioned $Rh_2Ir_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)(CO)_4(\eta^5\text{-}C_5Me_5)_2$ (**4**), an electron precise tetrahedral cluster, was similarly evaluated to explore whether or not an analogue of **1** may be accessible in the Rh_2Ir_2 system (experimental structure: Figure S3; bond distances and dihedral angles: Table S4). Cleavage of the Ir-Ir bond and removal of one CO ligand from **4** and geometry optimization afforded $Rh_2Ir_2(\mu\text{-}CO)_2(CO)_4(\eta^5\text{-}C_5Me_5)_2$ (**5**) as the lowest energy form (structure: Figure S4; bond distances and dihedral angles: Table S5). Gibbs free energies for the theoretical CO dissociation and bond cleavage reaction **4** → **5** + CO (Scheme S2) are strongly positive for all methods employed (Table S6), consistent with the observed stability of **4**.

The foregoing calculations suggest that, at room temperature, the isolated butterfly cluster **1** is stable, but the potential analogue $Rh_2Ir_2(\mu\text{-}CO)_2(CO)_4(\eta^5\text{-}C_5Me_5)_2$ (**5**) is not, consistent with the thus-far-existing chemistry. Bond critical points (BCPs: Table S7) were then examined to shed light on the nature of the bonding. $Ir_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2$ (**6**), with a formal Ir=Ir linkage (Figure S5), and $Ir_4(CO)_{12}$ (**7**), comprised solely of single bonds (Figure S6), were selected to benchmark BCPs in the iridium system. For **6**, the BCP of the Ir=Ir bond is 0.0773 e/bohr^3, while the BCP of the Ir-Ir bond in **7** is 0.0600 e/bohr^3. For **1**, the BCP of the Ir1-Ir1A bond is 0.0625 e/bohr^3, and the BCPs of Ir1-Ir2/Ir1A-Ir2A and Ir1-Ir2A/Ir1A-Ir2 are 0.0686 and 0.0694 e/bohr^3, respectively; thus, the latter bond interactions are significantly greater than those of Ir1-Ir1A, possibly between single and double in nature. Electron counting assigns 19 valence electrons to Ir1/Ir1A and 15 electrons to Ir2/Ir2A, so the MOs were examined to explore the possibility of strong donor(Ir1/Ir1A)-acceptor(Ir2/Ir2A) interactions (Figure S8); the results are consistent with s and p interactions at all Ir-Ir

bonds and delocalized Ir_4 interactions alleviating the electron deficiency.

We then explored an alternative iridium-containing reagent. Reacting $[N(PPh_3)_2][Ir(CO)_4]$ with $MoIr_4(CO)_{10}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ in refluxing tetrahydrofuran afforded $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ (**2**) (Scheme 2);[7] the 19% yield is noteworthy, given the bond cleavage/formation required.

Scheme 2. Synthesis of $Ir_7(\mu\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ (**2**). Dashed lines indicate the weak bonding interactions of the semi-face-capping CO ligands.
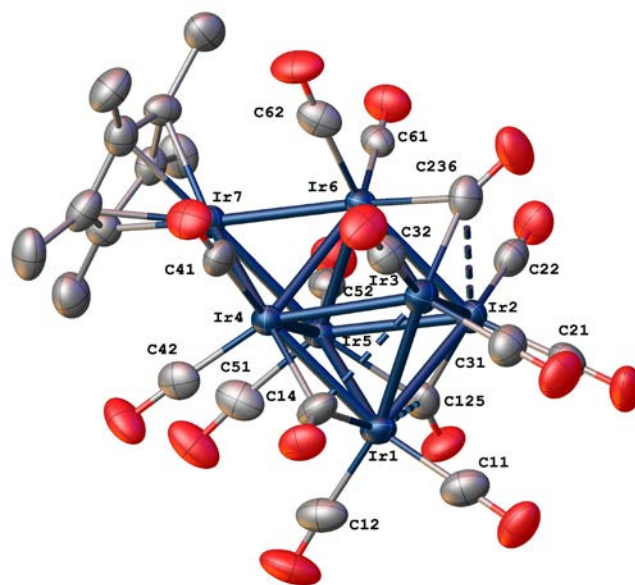

Figure 2. Molecular structure of $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ (**2**), with thermal ellipsoids set at the 30% probability level. Hydrogen atoms and the lattice chloroform molecule have been omitted for clarity. Dashed lines indicate the weak bonding interactions of the semi-face-capping CO ligands. Selected bond lengths (Å): Ir1-Ir2 2.7913(9), Ir1-Ir3 2.7807(10), Ir1-Ir4 2.7287(9), Ir1-Ir5 2.8200(9), Ir2-Ir3 2.7937(9), Ir2-Ir5 2.7458(9), Ir2-Ir6 2.7955(9), Ir3-Ir4 2.8026(9), Ir3-Ir6 2.7326(9), Ir4-Ir5 2.7776(8), Ir4-Ir6 2.7954(8), Ir4-Ir7 2.7359(8), Ir5-Ir6 2.7801(8), Ir5-Ir7 2.7729(9), Ir6-Ir7 2.7247(9), Ir1-C11 1.88(2), Ir1-C12 1.88(2), Ir1-C14 2.10(2), Ir1…C125 2.601(19), Ir2-C21 1.87(2), Ir2-C22 1.88(2), Ir2-C125 2.06(2), Ir2…C236 2.687(19), Ir3-C31 1.89(2), Ir3-C32 1.87(2), Ir3-C236 2.06(2), Ir3…C14 2.665(19), Ir4-C41 1.871(19), Ir4-C42 1.87(2), Ir4-C14 2.134(18), Ir5-C51 1.88(2), Ir5-C52 1.891(19), Ir5-C125 2.14(2), Ir6-C61 1.848(17), Ir6-C62 1.92(2), Ir6-C236 2.094(18).

The metal core of **2** possesses a capped octahedral geometry, with Ir-Ir distances within precedent lengths. The capping iridium is ligated by a pentamethylcyclopentadienyl ligand, the cluster coordination being completed by twelve terminal and three bridging carbonyl ligands. Cluster **2** possesses 7 x 9(Ir) + 5(η^5-C_5Me_5) + 15 x 2(CO) = 98 CVE, electron precise by polyhedral skeletal electron pair theory for a capped octahedral cluster.[8] An

unusual feature of the structure of **2** is the presence of three semi-face-capping carbonyl ligands, i.e. three CO groups unsymmetrically bound to a trimetallic face of a cluster.

Conclusions

In summary, two reactions of molybdenum-iridium clusters with iridium-containing reagents have afforded clusters thus far unobserved in the corresponding homometallic chemistry. While this methodology lacks predictive merit or broad applicability, and the products of the reactions are obtained in variable yield, the clusters obtained have unusual features. $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ (**2**) possesses three semi-face-capping CO ligands and is synthesized in high yield. $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)$ (**1**) is a "rule breaker", being formally very electron deficient; theoretical studies suggest that it is presumably stabilized by significant intra-cluster multiple Ir-Ir bonding.

Experimental Section

General Considerations. Reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran and toluene used in reactions were AR grade and were distilled under nitrogen over sodium benzophenone ketyl; all other solvents were used as received. Petroleum ether refers to a fraction of boiling range 60-80 °C. Cluster products were purified by preparative thin-layer chromatography (TLC) on 20 × 20 cm glass plates coated with Merck GF$_{254}$ silica gel (0.5 mm). Analytical TLC was conducted on aluminum sheets coated with 0.25 mm Merck GF$_{254}$ silica gel. Literature procedures were used to synthesize $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$, $MoIr_4(CO)_{10}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$, $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$[9] and $[N(PPh_3)_2][Ir(CO)_4]$.[10]

Instrumentation. Infrared spectra were recorded on PerkinElmer System 2000 or Spectrum One FT-IR spectrometers using a CaF$_2$ cell. Spectral features are reported in cm^{-1}. IR spectra were recorded in AR grade cyclohexane or CH$_2$Cl$_2$ solvents. The ^1H NMR spectrum was recorded on a Varian Gemini-300 spectrometer at 300 MHz in CDCl$_3$ (Cambridge Isotope Laboratories) and referenced to residual non-deuterated solvent (δ 7.26). Unit- and high-resolution ESI mass spectra were recorded on a Micromass-Waters LC-ZMD single quadrupole liquid chromatograph-MS instrument. The mass spectrum of **2** is reported in the form: m/z (assignment, relative intensity).

Synthesis of $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)_2$ (1). $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ (7.0 mg, 5.4 μmol) and $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$ (6.4 mg, 17 μmol) were dissolved in toluene (ca. 5 mL) and stirred at 80 °C for 16 h. At this point, no new species were observed in the solution by TLC; consequently, the reaction mixture was stirred at reflux for a further 5.5 h. The solvent was removed by rotary evaporation, and the crude solid was dissolved in minimal CH$_2$Cl$_2$ and applied to a preparative silica TLC plate with CH$_2$Cl$_2$ as eluent, affording four bands. The first (R$_f$ = 0.89, orange), second (R$_f$ = 0.58, light brown) and third (R$_f$ = 0.21, brown) bands appeared only in trace amounts and consequently were not extracted. The contents of the fourth and main band (R$_f$ = 0.17, dark brown) were extracted with CH$_2$Cl$_2$ and reduced in volume, producing a dark brown solid (1.9 mg). IR (CH$_2$Cl$_2$): ν(CO) 2021 (m), 2004 (s), 1991 (w), 1962 (w), 1948 (m), 1924 (w). HR-MS (ESI): found 1588.9114 (presumed [M]$^+$). Crystallization by liquid diffusion of methanol into a CH$_2$Cl$_2$ solution afforded, after a number of weeks at ca. 3 °C, several small crystals of $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)_2$ (1) suitable for a

single-crystal X-ray diffraction study. IR (*n*-hexane): ν(CO) 2028 (s), 1953 (w), 1895 (m) cm^{-1}. Insufficient material precluded microanalysis.

Synthesis of $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ (2). $[N(PPh_3)_2][Ir(CO)_4]$ (12.1 mg, 14.3 μmol) was added to a solution of $MoIr_4(CO)_{10}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (8.2 mg, 6.1 μmol) in tetrahydrofuran (7 mL) and the resultant mixture was heated at reflux for 1 h, the extent of reaction being monitored by IR spectroscopy. The solution was taken to dryness in vacuo, and the crude residue dissolved in the minimum amount of CH$_2$Cl$_2$ and applied to preparative silica TLC plates. Elution with CH$_2$Cl$_2$/petroleum ether (3:2) afforded approximately 10 bands. The contents of the major band (R$_f$ = 0.6, brown) were extracted with CH$_2$Cl$_2$ and reduced in volume to afford a brown solid, identified as $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ (2) (1.7 mg, 0.89 μmol, 19% assuming product formed from $MoIr_4(CO)_{10}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ + 3[N(PPh_3)_2][Ir(CO)_4]$). IR (CH$_2Cl_2$): ν(CO) 2086 (w), 2067 (m), 2045 (vs), 2009 (w), 1827 (w) cm^{-1}. ^1H NMR (CDCl$_3$): δ 1.85 (s, 15H, C$_5$Me$_5$). MS (ESI): calc., C$_{24}$H$_{15}$Ir$_7$O$_{14}$, 1902 ([M]$^+$); found, 1925 ([M + Na]$^+$, 90), 1902 ([M]$^+$, 90), 1874 ([M − CO]$^+$, 50), 1846 ([M − 2CO]$^+$, 100), 1818 ([M − 3CO]$^+$, 30). Insufficient material precluded microanalysis.

X-ray Crystallographic Studies. *General Considerations.* Crystals suitable for the X-ray structural analyses were grown by liquid diffusion of methanol into a CH$_2$Cl$_2$ solution (**1**) or ethanol into a chloroform solution (**2**). Intensity data were collected using an Enraf-Nonius KAPPA CCD at 200 K with MoK$_\alpha$ radiation (λ = 0.7170 Å). Suitable crystals were immersed in viscous hydrocarbon oil and mounted on glass fibers that were mounted on the diffractometer. Using psi and omega scans, N_t (total) reflections were measured, which were reduced to N_0 unique reflections, with F_0 > $2\sigma(F_0)$ being considered "observed". Data were initially processed and corrected for absorption using the programs DENZO[11] and maXus.[12] 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 program CRYSTALS.[13] Olex2[14] was used to generate the figures.

Crystal Data for 1. C$_{24}$H$_{26}$Ir$_4$O$_6$, M = 1179.35, red prism, 0.18 × 0.09 × 0.05 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 18.6767(5), b = 8.2105(3), c = 17.7929(4) Å, β = 104.0221(16)°, V = 2647.15(14) Å^3, Z = 4, D_c = 2.959 g/cm^3, F_{000} = 2104, μ = 20.08 mm^{-1}, $2\theta_{max}$ = 57.4°, 30589 reflections collected, 3419 unique. Final GoF = 1.009, $R1$ = 0.0297, $wR2$ = 0.0616, R indices based on 2795 reflections with $I > 2$ ⬚(refinement on F^2), 154 parameters, 0 restraints.

Crystal Data for 2. C$_{25}$H$_{15}$Ir$_7$O$_{15}$.CHCl$_3$, M = 2020.30, brown plate, 0.13 × 0.13 × 0.02 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 15.6050(2), b = 9.5705(2), c = 25.2703(4) Å, β = 105.2951(11)°, V = 3640.38(11) Å^3, Z = 4, D_c = 3.686 g/cm^3, F_{000} = 3528, μ = 25.770 mm^{-1}, $2\theta_{max}$ = 50.1°, 49035 reflections collected, 6430 unique. Final GoF = 1.018, $R1$ = 0.0451, $wR2$ = 0.1112, R indices based on 5338 reflections with $I > 2$ ⬚(refinement on F^2), 460 parameters, 0 restraints.

In both **1** and **2**, the largest peaks in the final difference electron map are located near the iridium atoms. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 1038018 (**1**) and 1038017 (**2**). Copies of this information may be obtained, free of charge, from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccd.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Computational Studies. Computational studies were carried out using the Amsterdam Density Functional (ADF) program, version 2013.[15] Calculations were executed on the raijin supercomputer housed at the ANU Supercomputer Facility and operated under the National Computer Infrastructure Scheme. The calculations employed all-electron basis sets

of triple-ζ quality with a single polarization function (TZP), spin-unrestricted on each atom. Relativistic effects were accounted for using the zero-order relativistic approximation (ZORA).[16] Geometry-optimized calculations were carried out with gradient-corrected exchange–correlation functionals (generalized gradient approximation: GGA), suggested by BP[17] or PBE[18], in a self-consistent fashion. BP or PBE optimizations were repeated with the inclusion of solvent effects through the conductor-like screening model (COSMO) method using parameters appropriate to solvation by dichloromethane.[19] Gibbs free energy data were obtained through frequency calculations.[20] Electron densities at the bond critical points were calculated by using the Bader quantum theory of atoms in molecules (QTAIM) model.[21]

Acknowledgements

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[3] a) The high-resolution mass spectral signal at 1588.911 (see Experimental Section) is most likely consistent with $[Mo_2Ir_4(CO)_9(C_5H_5)_2(C_5Me_4H)_2 + H]^+$ (1588.903), which would necessitate a core expansion to form $M_2Ir_4(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4H)$, followed by a vertex replacement of $Ir(\eta^5\text{-}C_5Me_5)$ by $Ir(\eta^5\text{-}C_5Me_4H)$; a precedent exists for the latter in the group 6-iridium cluster system,[3(b)] but further speculation is not warranted. (b) A. J. Usher, N. T. Lucas, G. T. Dalton, M. D. Randles, L. Viau, M. G. Humphrey, S. Petrie, R. Stranger, A. C. Willis, A. D. Rae, *Inorg. Chem.* **2006**, *45*, 10859-10872.

[4] $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$ is probably not the sole source of **1**; cyclopentadienyl ligands are generally strongly bound to iridium, rendering the monometallic reagent an unlikely source of the remaining two vertices, and attempts to synthesize **1** from thermolysis of $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$ were unsuccessful. Note that $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ was recovered unchanged after being heated for 2 days in refluxing toluene.

[5] At the level of the individual iridium atoms, this localized bonding perspective assigns 19 electrons to each of Ir1 and Ir1A, but only 15 electrons to each of Ir2 and Ir2A.

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[7] Similar reactions of $[N(PPh_3)_2][Ir(CO)_4]$ with $Mo_2Ir_3(CO)_9(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$, $MoIr_3(\mu\text{-}CO)_3(CO)_8(\eta^5\text{-}C_5H_5)$ or $Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)_2$ in a range of solvents (dichloromethane, tetrahydrofuran, toluene) failed to afford any identifiable cluster products.

[8] Two heptairidium clusters with capped octahedral cluster cores have been previously reported: a) $Ir_7(\mu_3\text{-}\eta^2\text{-}C_8H_{10})(\mu\text{-}\eta^2\text{-}C_8H_{11})(\mu\text{-}CO)(CO)_{11}(\eta^4\text{-}1,5\text{-}C_8H_{12})$: C. G. Pierpont, *Inorg. Chem.* **1979**, *18*, 2972-2977; b) $Ir_7(\mu_3\text{-}\kappa^2\text{-}P,C\text{-}PPhC_6H_4)(\mu\text{-}CO)(\mu\text{-}PPh_2)(CO)_{13}$: M. H. de Araujo, M. D. Vargas, D. Braga, F. Grepioni, *Polyhedron* **1998**, *17*, 2865-2875.

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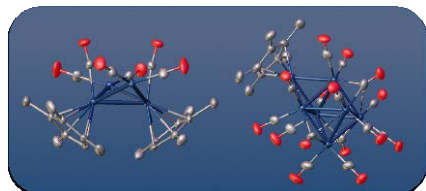
Reactions of molybdenum-iridium clusters with iridium-containing reagents afforded new homometallic clusters. $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ possesses three semi-face-capping CO ligands, while $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)$ is formally very electron deficient; theoretical studies suggest stabilization by significant intra-cluster multiple Ir-Ir bonding.

Key Topic: Cluster Synthesis

Junhong Fu, Michael D. Randles, Alan L. Criddle, Graeme J. Moxey, Torsten Schwich, Robert Stranger, Marie P. Cifuentes and Mark G. Humphrey*

Syntheses of $Ir_4(CO)_6(\eta^5\text{-}C_5Me_4H)_2$ and $Ir_7(\mu_3\text{-}CO)_3(CO)_{12}(\eta^5\text{-}C_5Me_5)$ from Pentametallic Molybdenum-Iridium Cluster Precursors