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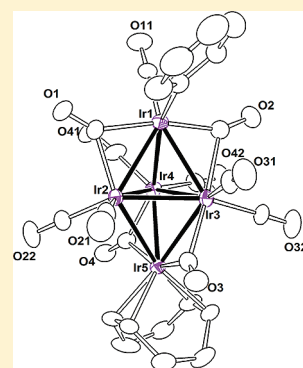
Synthesis of Higher Nuclearity Iridium Clusters: Reaction of $[\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$

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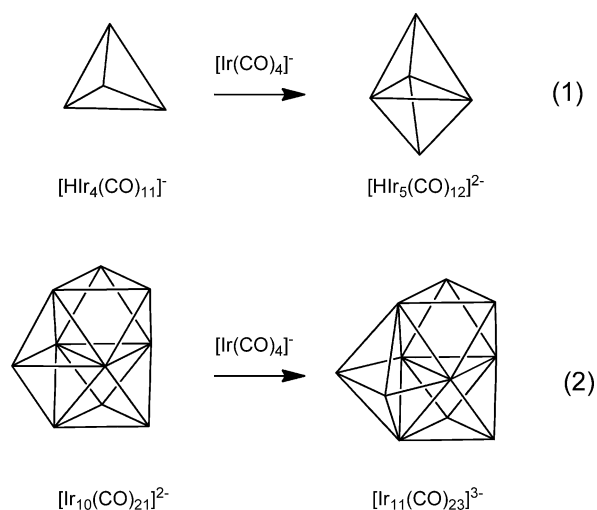
Supporting Information

ABSTRACT: The reaction of the σ -phenyl tetrairidium carbonyl anion $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ with $[\text{Ir}(\text{COD})\text{Cl}]$ (COD = 1,5-cyclooctadiene) yielded the two known tetrairidium compounds $\text{Ir}_4(\text{CO})_{10}(\text{COD})$ and $\text{Ir}_4(\text{CO})_7(\text{COD})(\mu_4\text{-C}_8\text{H}_{10})$ (**1**) and the three new higher nuclearity complexes $\text{Ir}_5(\text{CO})_{11}(\text{Ph})(\text{COD})$ (**2**), $\text{Ir}_5(\text{CO})_9(\text{Ph})(\text{COD})_2$ (**3**), and $\text{Ir}_9(\text{CO})_{15}(\text{Ph})(\mu_3\text{-C}_8\text{H}_{10})(\text{COD})$ (**4**), containing σ -coordinated phenyl ligands. Compounds **2** and **3** contain trigonal-bipyramidal Ir_5 clusters. Compound **4** contains nine iridium atoms in the form of a tricapped octahedron. Compound **4** was shown to be formed by the condensation of **1** and **2**. Compound **3** reacts with COD to yield the compound $\text{Ir}_5(\text{CO})_7(\text{COD})_2(\mu_4\text{-}\eta^2\text{-}\eta^1\text{-C}_8\text{H}_{11})$ (**5**) in a cluster-opening process that cleaves two hydrogen atoms from one of the COD C–C double bonds, eliminates the σ -phenyl ligand, and transfers one of the hydrogen atoms the other C–C double bond to form a metalated $\mu_4\text{-}\eta^2\text{-}\eta^1\text{-C}_8\text{H}_{11}$ cyclooctyne ligand.



INTRODUCTION

The synthesis of higher nuclearity metal carbonyl cluster compounds by “redox” condensation processes has been successfully used for many years.¹ Following Chini’s successful synthesis of a range of large metal carbonyl cluster complexes of rhodium,^{1a} della Pergola and his colleagues in Milan prepared some interesting higher nuclearity cluster complexes of iridium by using a similar methodology: e.g., eqs 1 and 2 (CO ligands are not shown in the structures).^{2,3}



Recently, Mondloch et al. have reported the formation of supported iridium nanoparticles by H_2 reduction of $[\text{Ir}(\text{COD})\text{Cl}]$ (COD = 1,5-cyclooctadiene) on $\gamma\text{-Al}_2\text{O}_3$ during the catalytic hydrogenations of cyclohexene.⁴ Gates has shown that iridium

carbonyl cluster complexes are precursors to nanocatalysts that exhibit good activity for the hydrogenation of aromatics.⁵

We have recently prepared the anionic σ -phenyl tetrairidium complex $[\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ by phenyl for Br transmetalation reactions between $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$ and SnPh_3OH or SnPh_4 (see Scheme 1).⁶ We also found that $[\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ reacts with $\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$ to form the uncharged pentairidium complex $\text{Ir}_5(\text{CO})_{12}(\text{Ph})(\text{PPh}_3)$ (Scheme 1).⁶

We have now investigated the reaction of $[\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$ and have obtained three new higher nuclearity COD iridium complexes containing σ -phenyl ligands: $\text{Ir}_5(\text{CO})_{11}(\text{Ph})(\text{COD})$ (**2**), $\text{Ir}_5(\text{CO})_9(\text{Ph})(\text{COD})_2$ (**3**), and $\text{Ir}_9(\text{CO})_{15}(\text{Ph})(\mu_3\text{-C}_8\text{H}_{10})(\text{COD})$ (**4**). The results of these studies are reported herein.

EXPERIMENTAL SECTION

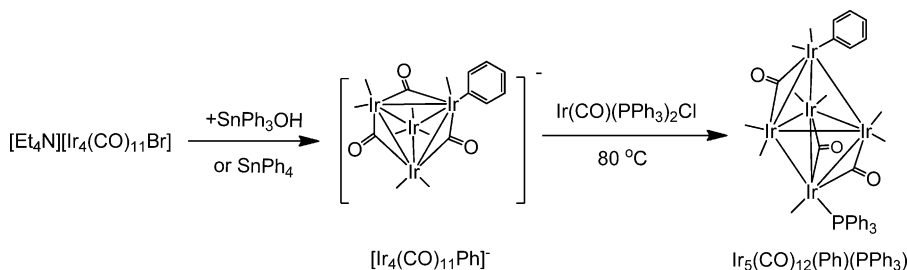
General Data. Reagent grade solvents were dried by standard procedures and were freshly distilled under nitrogen prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements were performed by using electrospray ionization (ESI) positive ion or negative ion on a VG 70S instrument. $[\text{Ir}(\text{COD})\text{Cl}]_2$ (COD = 1,5-cyclooctadiene) was obtained from STREM and was used without further purification. $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ was prepared according to our published procedure.⁶ Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Reaction of $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$ in Benzene at Reflux. An 8.0 mg portion (0.012 mmol) of $[\text{Ir}(\text{COD})\text{Cl}]_2$ was added to 14.0 mg (0.011 mmol) of $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ that had been dissolved in 25 mL of benzene. The reaction solution was heated

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Scheme 1



to reflux (80°C) for 2 h. The solvent was then removed in vacuo, and the products were isolated by TLC by eluting with a 3/1 hexane/methylene chloride solvent mixture. This yielded the following, in order of elution: 0.30 mg of yellow $\text{Ir}_4(\text{CO})_{10}(\text{COD})$,⁷ (2.4% yield), 1.45 mg of yellow $\text{Ir}_4(\text{CO})_7(\text{COD})(\mu_4\text{-C}_8\text{H}_{10})$ ⁷ (**1**; 11.3% yield), 1.24 mg of orange $\text{Ir}_5(\text{CO})_{11}(\text{Ph})(\text{COD})$ (**2**; 9.8% yield), 0.84 mg of brown $\text{Ir}_9(\text{CO})_{15}(\text{Ph})(\mu_3\text{-C}_8\text{H}_{10})(\text{COD})$ (**4**; 7.1% yield), 1.16 mg of orange $\text{Ir}_5(\text{CO})_9(\text{Ph})(\text{COD})_2$ (**3**; 8.8% yield), and other minor products. Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2080 (w), 2055 (vs), 2044 (vs), 2027 (s), 2006 (m), 1844 (m), 1804 (m); ^1H NMR (CDCl_3 , in ppm) δ 6.71–6.84 (m, 5H, σ -Ph) 5.23–5.57 (m, 4H, CH), 1.97–2.53 (m, 8H, CH_2); MS ES (negative ion) for **2** m/z 1451 ($\text{M} - \text{H} - \text{H}_2$)[−]. The isotope distribution pattern is consistent with the presence of five iridium atoms. Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2068 (m), 2035 (vs), 2016 (s), 1997 (m), 1844 (w), 1825 (w), 1785 (w); ^1H NMR (CDCl_3 , in ppm) δ 6.84–6.93 (m, 5H, Ph), 5.21–5.37 (m, 8H, COD), 1.95–2.11 (m, 16H, CH_2); MS ES (negative ion) for **3** m/z 1503 ($\text{M} - \text{H} - \text{H}_2$)[−]. The isotope distribution pattern is consistent with the presence of five iridium atoms. Spectral data for **4**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2074 (m), 2043 (s), 2031 (vs), 2025 (vs), 1995 (w), 1968 (w), 1813 (w); ^1H NMR (CDCl_3 , in ppm) δ 6.84–6.91 (m, 5H, Ph), 5.23–5.51 (m, 6H, CH), 2.25–2.37 (m, 16H, CH_2); MS ES (positive ion) for **4** m/z 2442 (M^+), 2481 ($\text{M} + \text{K}$)⁺. The isotope distribution pattern is consistent with the presence of nine iridium atoms.

Synthesis of $\text{Ir}_5(\text{CO})_7(\mu_4\text{-}\eta^2\text{-}\eta^1\text{-C}_8\text{H}_{11})(\text{COD})_2$ (5**).** A 6.7 mg portion (0.004 mmol) of compound **3** and 7 μL of 1,5-COD dissolved in 10 mL of heptane were heated to reflux for 2 h. A 3.34 mg amount (51% yield) of **5** was isolated from this reaction mixture by TLC by eluting with a 3/1 hexane/methylene chloride solvent mixture. Spectral data for **5**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2030 (m), 1997 (vs), 1942 (m), 1844 (m). ^1H NMR (CDCl_3 , in ppm) δ 5.23–5.40 (m, 9H, CH-cod), 1.55–1.93 (m, 26H, CH_2 -cod); MS ES (positive ion) for **5** m/z 1480 (M^+), 1481 ($\text{M} + \text{H}$)⁺. The isotope distribution pattern is consistent with the presence of five iridium atoms.

Improved Yield of **3.** A 4.4 mg portion (0.007 mmol) of $[\text{Ir}(\text{COD})\text{Cl}]_2$ was added to 9.0 mg (0.007 mmol) of **1** that was dissolved in 15 mL of benzene. A 7 μL amount of 1,5-COD was added to the above mixture, and the reaction solution was heated to reflux for 2 h. The solvent was then removed in vacuo, and the product was isolated by TLC by elution with a 3/1 hexane/methylene chloride solvent mixture. This yielded the following, in order of elution: 0.30 mg of yellow $\text{Ir}_4(\text{CO})_{10}(\text{C}_8\text{H}_{12})$, (3.7% yield), 0.94 mg of compound **1** (11.4% yield), 0.44 mg of compound **2** (5.4% yield), 0.41 mg of red $\text{Ir}_5(\text{CO})_7(\mu_4\text{-}\eta^2\text{-}\eta^1\text{-C}_8\text{H}_{11})(\text{C}_8\text{H}_{12})_2$ (**5**; 4.0% yield), 2.52 mg of orange compound **3** (30% yield).

Improved Yield of **4 from the Reaction of **1** with **2** at 98°C .** An 8.1 mg portion (0.007 mmol) of compound **1** and 6.2 mg (0.004 mmol) of compound **2** were dissolved in 15 mL of heptane. The reaction solution was heated to reflux for 1 h. The solvent was then removed in vacuo, and the product was isolated by TLC by elution with a 3/1 hexane/methylene chloride solvent mixture to yield 1.71 mg of $\text{Ir}_9(\text{CO})_{15}(\text{Ph})(\mu_3\text{-C}_8\text{H}_{10})(\text{COD})$ (**4**; 16% yield).

Synthesis of $\text{Ir}_4(\text{CO})_{10}(\text{COD})$ and $\text{Ir}_4(\text{CO})_8(\text{COD})_2$ from $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}(\text{Ph})]$. A 10.1 mg portion (0.008 mmol) of $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}(\text{Ph})]$ was dissolved in 10 mL of benzene stirred with 14 μL of COD at room temperature. A 7.0 μL amount of HBF_4 was added

to the above mixture, which was then stirred for 30 min. The solvent was then removed in vacuo, and the products were isolated by TLC by eluting with a 3/1 hexane/methylene chloride solvent mixture to yield 5.3 mg of $\text{Ir}_4(\text{CO})_{10}(\text{COD})$ (58% yield) and 2.0 mg of $\text{Ir}_4(\text{CO})_8(\text{COD})_2$, (21% yield).

Crystallographic Analyses. Black single crystals of **1–3** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from solutions in hexane/methylene chloride solvent mixtures by cooling to -25°C . Black single crystals of **4** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a benzene/methylene chloride solvent mixture at room temperature. Black single crystals of **5** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a benzene/octane solvent mixture at room temperature. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer and Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.⁸ Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied in each analysis by using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least squares on F^2 , using the SHELXTL software package.⁹ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the analyses are given in Table S1 (Supporting Information). Compounds **1–5** all crystallized in the monoclinic crystal system. The space group $P2_1/n$ was uniquely identified by the systematic absences in the intensity data for compounds **1**, **2**, and **4** and subsequently confirmed by the successful solutions and refinements of the structures. There is one symmetry-independent molecule in the asymmetric unit in the crystal structures of **1**, **2**, and **4**. For compound **4** one and a half molecules of benzene from the crystallization solvent were cocrystallized with the complex in the asymmetric crystal unit. The solvent molecules were refined with isotropic thermal parameters. For compounds **3** and **5** the space group $P2_1/c$ was identified uniquely on the basis of the systematic absences in the intensity data. There is one symmetry-independent molecule in the asymmetric crystal unit in the structures of **3** and **5**. For compound **3** one molecule of methylene chloride from the crystallization solvent was cocrystallized with the complex in the asymmetric crystal unit. For compound **5**, after location of all non-hydrogen atoms, a very large (ca. 8 e/\AA^3) residual electron density peak remained, approximately at the midpoint of the C64–C65 bond. This peak was interpreted to arise from an fractionally occupied iridium atom of a disordered $\text{Ir}(\text{COD})(\text{CO})_2$ group. Refining this peak as a fractionally occupied iridium atom yielded an occupancy value near 10%. At the same time, refining the occupancy of iridium atom Ir2 yielded an occupancy value of ca. 90% (FVAR = 0.896240), accompanied by a sharp decrease in R values and a flattening of the difference map, with the major peak now being 1.97 e/\AA^3 , located near Ir5. The sum of the occupancies of Ir2 and Ir2B was very close to unity upon free refinement, which strongly supports the $\text{Ir}(\text{COD})(\text{CO})_2$ disorder model. For the final refinement cycles, the total occupancy of the disordered Ir atoms (Ir2 and Ir2B)

was constrained to unity. The cod and carbonyl groups bonded to the minor-disorder component (Ir2B) could not be modeled, since they are populated in the crystal only to the extent of ca. 10%.

RESULTS AND DISCUSSION

The reaction of the σ -phenyl tetrairidium carbonyl anion $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}\text{Ph}]$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$ has yielded the two tetrairidium compounds $\text{Ir}_4(\text{CO})_{10}(\text{COD})^7$ (2.4% yield) and $\text{Ir}_4(\text{CO})_7(\text{COD})(\mu_4\text{-C}_8\text{H}_{10})^7$ (**1**; 11.3% yield) and the three new higher nuclearity complexes $\text{Ir}_5(\text{CO})_{11}(\text{Ph})(\text{COD})$ (**2**; 9.8% yield), $\text{Ir}_5(\text{CO})_9(\text{Ph})(\text{COD})_2$ (**3**; 8.8% yield), and $\text{Ir}_9(\text{CO})_{15}(\text{Ph})(\mu_3\text{-C}_8\text{H}_{10})(\text{COD})$ (**4**; 7.1% yield), which contain σ -phenyl ligands. $\text{Ir}_4(\text{CO})_{10}(\text{COD})$ was obtained previously from the reaction of $\text{Ir}_4(\text{CO})_{12}$ with COD in refluxing thf in the presence of Me_3NO .⁷ We have found that $\text{Ir}_4(\text{CO})_{10}(\text{COD})$ can be obtained in good yield (58%) along with some $\text{Ir}_4(\text{CO})_8(\text{COD})_2^7$ (23% yield) from the reaction of $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}\text{Ph}]$ with COD in the presence of HBF_4 . We suspect that some free COD (derived from the $[\text{Ir}(\text{COD})\text{Cl}]_2$) and adventitious H^+ in our reaction of $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}\text{Ph}]$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$ led to the formation of the small quantities of $\text{Ir}_4(\text{CO})_{10}(\text{COD})$ in this reaction. Compound **1** was obtained previously from the reaction of $\text{Ir}_4(\text{CO})_{12}$ with COD by heating in chlorobenzene to reflux and by heating $\text{Ir}_4(\text{CO})_8(\text{COD})_2$ in cyclohexane to reflux.⁷

Compound **1** has not yet been characterized crystallographically, and thus, a single-crystal X-ray diffraction analysis of the molecular structure of **1** was performed as a part of this work. An ORTEP diagram of the molecular structure of compound **1** as found in the solid state is shown in Figure 1. The

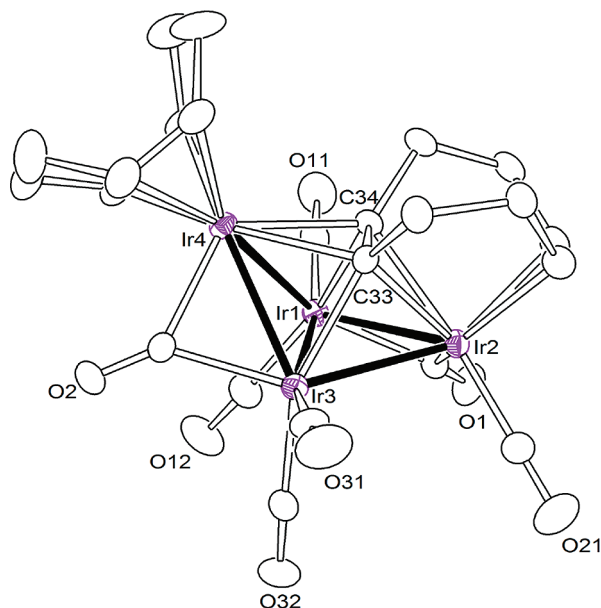


Figure 1. ORTEP diagram of the molecular structure of $\text{Ir}_4(\text{CO})_7(\text{COD})(\mu_4\text{-C}_8\text{H}_{10})$ (**1**) showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) are as follows: $\text{Ir}(1)\text{--Ir}(3) = 2.7818(3)$, $\text{Ir}(1)\text{--Ir}(4) = 2.7294(3)$, $\text{Ir}(1)\text{--Ir}(2) = 2.6909(3)$, $\text{Ir}(2)\text{--Ir}(3) = 2.6965(3)$, $\text{Ir}(3)\text{--Ir}(4) = 2.6911(4)$, $\text{Ir}(1)\text{--C}(34) = 2.128(6)$, $\text{Ir}(2)\text{--C}(33) = 2.205(6)$, $\text{Ir}(2)\text{--C}(34) = 2.264(6)$, $\text{Ir}(3)\text{--C}(33) = 2.147(6)$, $\text{Ir}(4)\text{--C}(33) = 2.312(6)$, $\text{Ir}(4)\text{--C}(34) = 2.267(6)$, $\text{C}(33)\text{--C}(34) = 1.443(8)$.

structure consists of a butterfly tetrahedral cluster of four iridium atoms with seven carbonyl ligands. Two of the seven CO ligands are bridging ligands across oppositely positioned

hinge-wingtip Ir–Ir edges of the cluster. There is a bidentate COD ligand coordinated to the wingtip metal atom Ir(4) and a C_8H_{10} cycloocta-1-en-5-yne ligand that bridges all four metal atoms. The yne functional group lies in the fold of the butterfly cluster and exhibits a typically long C–C bond length: $\text{C}(33)\text{--C}(34) = 1.443(8)$ Å. Although they are not common, cycloocta-1-en-5-yne ligands have been formed previously in high-temperature reactions of metal cluster complexes with COD, including the synthesis of a similar tetranuclear Ir_4 derivative of **1**, $\text{Ir}_4(\text{CO})_5(\text{COD})_2(\mu_4\text{-C}_8\text{H}_{10})$.⁷

An ORTEP diagram of the molecular of **2** is shown in Figure 2. Compound **2** contains five iridium atoms in the form of a trigonal

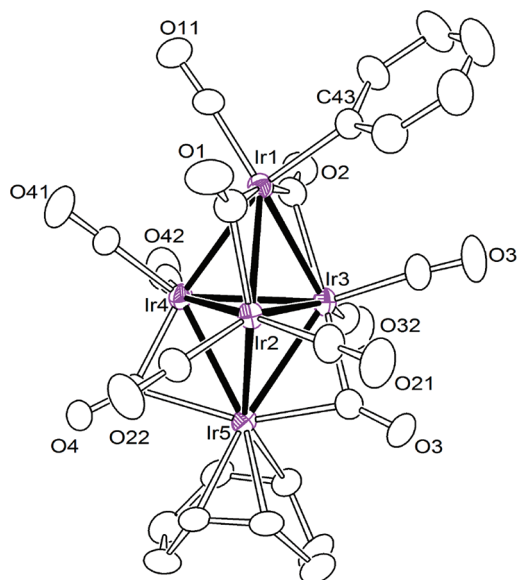


Figure 2. ORTEP diagram of the molecular structure of $\text{Ir}_5(\text{CO})_{11}(\text{Ph})(\text{COD})$, **2** showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) are as follows: $\text{Ir}1\text{--Ir}2 = 2.7150(5)$, $\text{Ir}1\text{--Ir}3 = 2.7408(5)$, $\text{Ir}1\text{--Ir}4 = 2.8009(5)$, $\text{Ir}2\text{--Ir}4 = 2.6965(5)$, $\text{Ir}2\text{--Ir}3 = 2.7490(5)$, $\text{Ir}2\text{--Ir}5 = 2.7985(5)$, $\text{Ir}3\text{--Ir}4 = 2.7803(5)$, $\text{Ir}3\text{--Ir}5 = 2.7874(5)$, $\text{Ir}4\text{--Ir}5 = 2.7054(5)$, $\text{Ir}1\text{--C}43 = 2.082(10)$.

bipyramid. There is a COD ligand on the apical atom Ir(5) and a σ -phenyl ligand that is terminally coordinated to the other apical atom iridium atom Ir(1). The Ir–C bond distance to the σ -phenyl ligand, $\text{Ir}1\text{--C}43 = 2.082(10)$ Å, is slightly shorter than the Ir–C distance to the σ -phenyl ligand in $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}(\text{Ph})]$, 2.125(13) Å,⁶ but is similar to those in the complexes: $\text{Ir}_5(\text{CO})_{12}(\text{Ph})(\text{PPh}_3)$ (**6**; 2.096(12) Å),⁶ $\text{Ir}_3(\text{CO})_9(\text{Ph})(\mu_3\text{-PPh})(\mu\text{-dppm})$ (2.084(16) Å),¹⁰ $\text{Ir}_4(\text{CO})_8(\sigma\text{-Ph})[\mu_4\text{-}\eta^3\text{-PhPC(H)CPh}](\mu\text{-PPh}_2)$ (2.09(1) Å),¹¹ and $\text{Ir}_8(\text{CO})_{16}(\sigma\text{-Ph})(\mu\text{-PPh}_2)(\mu_4\text{-PPh})$ (2.06(4) Å).¹² Compound **6** contains a trigonal-bipyramidal Ir_5 cluster similar to **2** and also has a σ -phenyl ligand on one of the apical Ir atoms of the trigonal bipyramid. The principal difference between **2** and **6** is the presence of a COD ligand on the other apical iridium atom in **2** in the place of the PPh_3 ligand and one CO ligand in **6**. The Ir–Ir bond distances in **2** are very similar to those in **6**. The cluster of **2** contains a total of 72 valence electrons: i.e., all 5 iridium atoms have 18-electron configurations.

Compound **3** can be viewed as a COD derivative of **2**, and it was obtained in a better yield (30%) when COD was added to the reaction mixture of $[\text{Et}_4\text{N}][\text{Ir}_4(\text{CO})_{11}\text{Ph}]$ and $[\text{Ir}(\text{COD})\text{Cl}]_2$. An ORTEP diagram of the molecular structure of **3** is shown

in Figure 3. Like **2** and **6**, the metal cluster of **3** also has the shape of a trigonal bipyramid, but its σ -phenyl ligand is

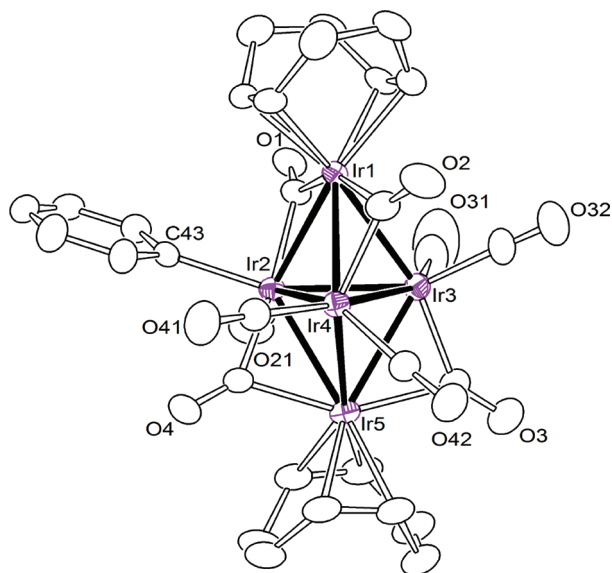


Figure 3. ORTEP diagram of the molecular structure of $\text{Ir}_5(\text{CO})_9(\text{Ph})(\text{COD})_2$ (**3**) showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) are as follows: Ir1–Ir4 = 2.7206(5), Ir1–Ir2 = 2.7631(5), Ir1–Ir3 = 2.7952(5), Ir2–Ir3 = 2.7794(5), Ir2–Ir4 = 2.7796(5), Ir3–Ir4 = 2.6968(5), Ir2–Ir5 = 2.7741(5), Ir3–Ir5 = 2.7567(5), Ir4–Ir5 = 2.7972(5), Ir2–C43 = 2.120(9).

coordinated to one of the equatorial Ir atoms instead of one of the apical Ir atoms. The Ir–C bond Ir2–C43 = 2.120(9) Å is longer than that in **2** and **6**, probably due to the increased sterics of the equatorial metal site. There are two COD ligands in **3**, and both are coordinated to the apical Ir atoms, one COD to each Ir. The Ir–Ir bond distances in **3** are very similar to those in **2** and **6**. The cluster of **3** contains a total of 72 valence electrons; thus, all 5 iridium atoms have an 18-electron configuration. Interestingly, the parent ions observed in negative ion electrospray mass spectra of **2** and **3** show the loss of two hydrogen atoms. Loss of H_2 has been observed previously in the mass spectra of iridium carbonyl cluster complexes containing COD ligands.⁷ The H_2 elimination may be related to the conversion of the COD olefinic functions into “yne” functions, as shown by the formation of the cycloocta-1-en-5-yne ligands in **1** and **4** and also by the conversion of **3** to **5** described below.

Compound **4** is perhaps the most interesting product from this study, and it turns out that it is really derived from a secondary condensation reaction between compounds **1** and **2** (16% yield) that is accompanied by the loss of three CO ligands and one COD ligand. Compound **4** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 4. Compound **4** contains nine iridium atoms. The cluster is best described as a tricapped octahedron. Although there are many examples of multicapped octahedra among the families of higher nuclearity metal carbonyl cluster complexes,¹³ they are very rare in the iridium group. In fact, this is the first structural characterization of a pure iridium multicapped Ir_6 octahedron, although there are examples of heteronuclear capped Ir_6 octahedra, e.g. $[\text{Ir}_6\text{Ru}_3(\text{CO})_{23}]^{2-}$ and $[\text{Ir}_6(\text{CO})_{23}(\text{HgCl})_2]^{2-}$,^{14,15} and the osmium anion $[\text{HOs}_9(\text{CO})_{24}]^-$ was found to contain a tricapped

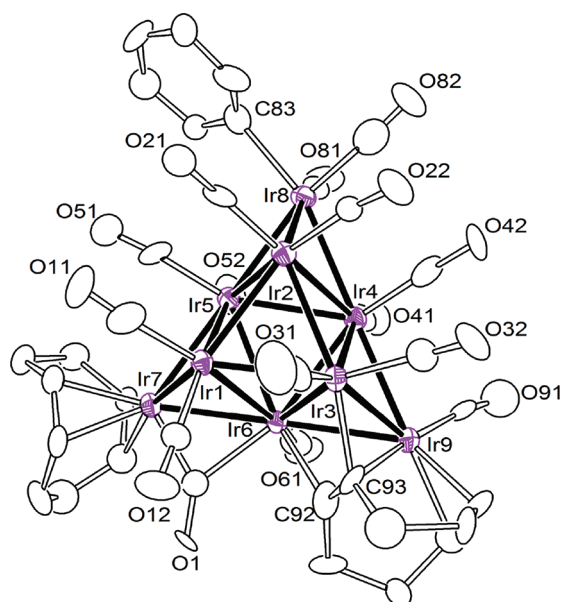


Figure 4. ORTEP diagram of the molecular structure of $\text{Ir}_9(\text{CO})_{15}(\text{Ph})(\text{COD})(\mu_3\text{-C}_8\text{H}_{10})$ (**4**), showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) are as follows: Ir(1)–Ir(7) = 2.685(2), Ir(1)–Ir(3) = 2.740(2), Ir(1)–Ir(5) = 2.740(2), Ir(1)–Ir(2) = 2.755(2), Ir(1)–Ir(5) = 2.740(2), Ir(1)–Ir(6) = 2.760(2), Ir(2)–Ir(8) = 2.656(2), Ir(2)–Ir(5) = 2.745(2), Ir(2)–Ir(3) = 2.757(2), Ir(2)–Ir(4) = 2.782(2), Ir(3)–Ir(4) = 2.730(2), Ir(3)–Ir(9) = 2.732(2), Ir(3)–Ir(6) = 2.816(2), Ir(4)–Ir(5) = 2.729(2), Ir(4)–Ir(6) = 2.730(2), Ir(4)–Ir(8) = 2.820(2), Ir(4)–Ir(9) = 2.820(2), Ir(5)–Ir(8) = 2.669(2), Ir(5)–Ir(7) = 2.806(2), Ir(5)–Ir(6) = 2.832(2), Ir(6)–Ir(7) = 2.717(2), Ir(6)–Ir(9) = 2.806(2), Ir(9)–C(92) = 2.17(5), Ir(9)–C(93) = 2.16(4), Ir(6)–C(92) = 2.13(5), Ir(8)–C(83) = 2.17(5), Ir(3)–C(93) = 2.10(4), C(92)–C(93) = 1.33(7).

octahedral Os_9 cluster at its core.¹⁶ The capping atom Ir(8) in **4** contains a σ -phenyl ligand carried in from **2**, and the triangular group Ir(3), Ir(6), and Ir(9) contains a cycloocta-1-en-5-yne ligand carried in from **1**. Unlike the case for **1**, the cycloocta-1-en-5-yne ligand in **4** is only a triply bridging ligand, and as a result the C–C bond of the yne function has decreased in length: C(92)–C(93) = 1.33(7) Å. Capping atom Ir(7) contains a COD ligand, but there is no way to determine if that ligand was derived from the COD ligand in **1** or **2**. The Ir–C bond distance to the σ -phenyl ligand is Ir(8)–C(83) = 2.17(5) Å. Compound **4** contains a total of 122 cluster valence electrons, which is in accord with the predictions of the condensed polyhedra principles of the polyhedral skeletal electron pair theory.¹⁷

When compound **3** was allowed to react with COD at 98 °C for 2 h, the new compound **5** was obtained in 51% yield. The structure of **5** was established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 5. Compound **5** contains five iridium atoms, and the structure of the metal cluster can be described as a Ir-capped (Ir(1)) butterfly tetrahedron (Ir(2)–Ir(5)). Atoms Ir(1) and Ir(5) contain COD ligands, and there is a quadruply bridging $\eta^2\text{-}\eta^1\text{-C}_8\text{H}_{11}$ (1-iridacycloocta-4-yne) ligand coordinated to the butterfly portion of the cluster, with the C–C triple bond lying in the fold of the butterfly. The C–C triple bond was formed by the abstraction of the two hydrogen atoms from one of the C–C double bonds of a COD

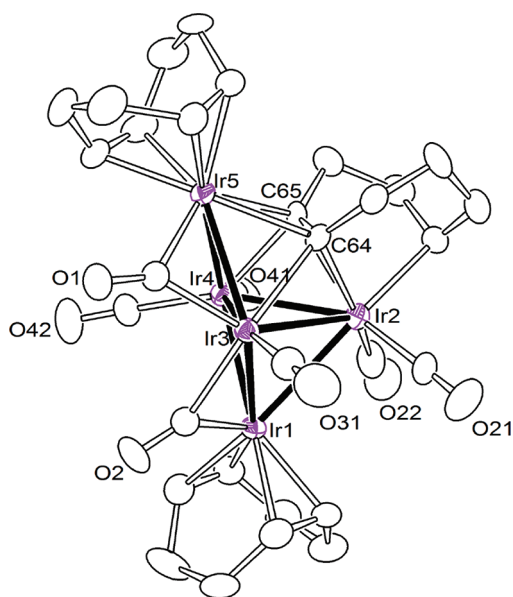


Figure 5. ORTEP diagram of the molecular structure of $\text{Ir}_5(\text{CO})_7(\text{COD})_2(\mu_4\text{-}\eta^2\text{:}\eta^1\text{-C}_8\text{H}_{11})$ (**5**), showing 30% probability thermal ellipsoids. Selected interatomic bond distances (Å) are as follows: $\text{Ir}(1)\text{--Ir}(4) = 2.6825(6)$, $\text{Ir}(1)\text{--Ir}(3) = 2.7008(6)$, $\text{Ir}(1)\text{--Ir}(2) = 2.8947(7)$, $\text{Ir}(2)\text{--Ir}(3) = 2.7721(7)$, $\text{Ir}(2)\text{--Ir}(4) = 2.7022(7)$, $\text{Ir}(3)\text{--Ir}(4) = 2.6804(6)$, $\text{Ir}(3)\text{--Ir}(5) = 2.7027(6)$, $\text{Ir}(4)\text{--Ir}(5) = 2.7299(6)$, $\text{Ir}(2)\text{--C}(60) = 2.173(13)$, $\text{Ir}(5)\text{--C}(65) = 2.182(12)$, $\text{Ir}(4)\text{--C}(65) = 2.183(13)$, $\text{Ir}(2)\text{--C}(64) = 2.132(15)$, $\text{Ir}(3)\text{--C}(64) = 2.190(14)$, $\text{Ir}(5)\text{--C}(64) = 2.271(12)$, $\text{C}(64)\text{--C}(65) = 1.48(3)$.

ligand. One of these hydrogen atoms was apparently transferred to one of the carbon atoms of the other C–C double bond of that COD ligand. The remaining carbon atom of that double bond is σ -bonded to the cluster at atom Ir(2): $\text{Ir}(2)\text{--C}(60) = 2.173(13)$ Å. The second of the abstracted hydrogen atoms was probably combined with the phenyl ligand and eliminated as benzene. The C–C triple-bond distance is long, $\text{C}(64)\text{--C}(65) = 1.48(3)$ Å, due to its coordination to the four metal atoms.

Compound **5** contains a total of 72 cluster valence electrons and is thus formally unsaturated by the amount of 2 electrons.¹⁷ Curiously, the $\text{Ir}(1)\text{--Ir}(2)$ distance, 2.8947(7) Å, is much longer than all of the other Ir–Ir bonds in this molecule. If this bond was ignored, then atom Ir(1) would formally have a 16-electron configuration and the “unsaturation” would be located formally on Ir(1). A similarly long Ir–Ir bond was found for the $\text{Ir}(\text{CO})_2$ capping group in the anion $[\text{Ir}_{12}(\text{CO})_{24}]^{2-}$.¹⁶

SUMMARY AND CONCLUSIONS

The anion $[\text{Ir}_4(\text{CO})_{11}\text{Ph}]^-$ has been shown to undergo condensation reactions with $[\text{Ir}(\text{COD})\text{Cl}]_2$ to yield higher nuclearity iridium carbonyl cluster complexes that contain σ -phenyl ligands. A summary of the reactions described in this report is shown in Scheme 2. The two new pentairidium carbonyl cluster complexes **2** and **3** have been obtained and structurally characterized. The compounds $\text{Ir}_4(\text{CO})_{10}(\text{COD})$ and **1** are side products whose yields are greatly increased by the addition of H^+ , which is believed to facilitate the removal of the phenyl ligand, presumably as benzene. The unusual nine-metal cluster complex **4** that was also obtained was shown to be a secondary product formed by the reaction of **1** with **2**. The reaction of **3** with COD yielded the open pentanuclear iridium cluster complex **5**, which contains a metalated quadruply bridging cyclooctyne ligand. Investigations of reactions of **1** with other metal halide complexes are in progress.

ASSOCIATED CONTENT

Supporting Information

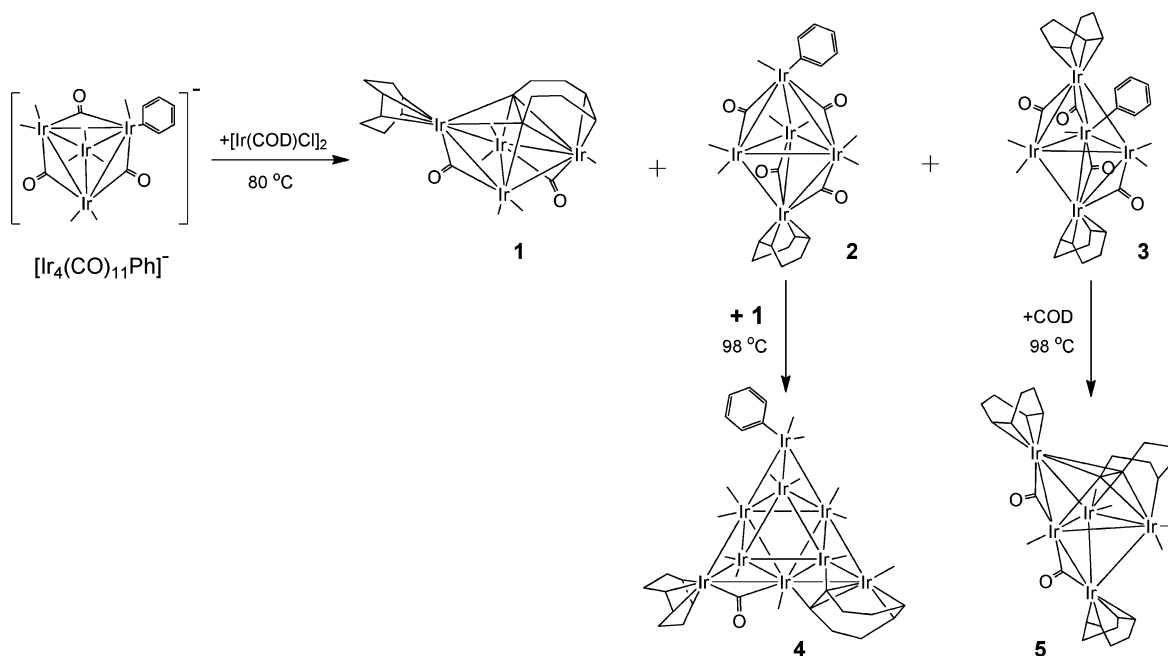
CIF files for the structural analyses, tables giving crystallographic data for compounds **1**–**5**, and figures giving mass spectra of compounds **2**–**5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Scheme 2



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