Iridium-Bismuth Carbonyl Cluster Complexes[†]

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[†]Dedicated to the memory of Professor Jack Lewis, the Lord Lewis of Newnham, a pioneer in the chemistry of polynuclear metal carbonyl cluster complexes.

Introduction

Interest in transition metal - bismuth compounds stems from ability of these materials to serve as catalysts for the selective oxidation and ammoxidation of hydrocarbons [1]. In recent studies we have synthesized new ReBi carbonyl cluster compounds that have been found to be precursors to effective catalysts for the ammoxidation of 3-picoline to nicotinonitrile eq. (1) [2].

There are very few examples of iridium-bismuth carbonyl cluster complexes [3-5]. We have previously shown that the compound $\text{Ir}_3(\text{CO})_9(\mu_3\text{-Bi})$, **1** [3] can be converted into the higher

nuclearity complex $\text{Ir}_5(\text{CO})_{10}(\mu_3\text{-Bi})_2(\mu_4\text{-Bi})$ by reaction with BiPh_3 , eq. (2) [4], and have shown that **1** and $\text{Ir}_5(\text{CO})_{10}(\mu_3\text{-Bi})_2(\mu_4\text{-Bi})$ are precursors to effective catalysts for the direct oxidation of 3-picoline to nicotinic acid, also known as Niacin, by using the oxidant acetylperoxyborate, eq. (3) [4].

We have also prepared a number of iridium-bismuth complexes containing germanium and tin ligands from complex **1** by reactions with HGePh_3 and HSnPh_3 , eq. (4) [5].

In the continuation of our studies of the chemistry of iridium-bismuth carbonyl cluster complexes, we have now investigated the self-condensation of **1** and its reactions with PPh_3 and with $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$. The results of these studies are reported herein.

Experimental Section

General Data. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. Room temperature ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. $^{31}\text{P}\{^1\text{H}\}$ NMR were recorded on a Bruker Avance/DRX 400 NMR spectrometer operating at 162.0 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe using either electron impact ionization (EI) or electrospray ionization (ES) using a Micromass Q-TOF instrument. $\text{Ir}_4(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$ and PPh_3 were obtained from STREM and Sigma-Aldrich, respectively and were used without further purification. $[\text{PPN}]\text{Ir}(\text{CO})_4$ [6] and $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ [7] were prepared according to the previously reported procedures. $\text{Ir}_3(\text{CO})_9(\mu_3\text{-Bi})$, **1** [3] was prepared by a modified procedure reported previously [4]. All product separations were performed by TLC in air on Analtech 0.25mm silica gel 60 Å F254 and 0.25mm aluminum oxide 60 Å F254 glass plates.

Synthesis of $\text{Ir}_6(\text{CO})_{13}(\mu_3\text{-Bi})(\mu_4\text{-Bi})$, **2**.

A 13.2 mg (0.013 mmol) portion of **1** were dissolved in 15 mL of hexane. The reaction was heated to reflux for 18 h. The solvent was then removed *in vacuo*, and the product was isolated by TLC with a 4/1 hexane/methylene chloride solvent ratio as the eluent. This gave 10.3 mg (0.0050 mmol) of dark green $\text{Ir}_6(\text{CO})_{13}(\mu_3\text{-Bi})(\mu_4\text{-Bi})$, **2** (84% yield). Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2095(w), 2067(w), 2042 (vs), 2021 (w), 2007 (w), 1992 (w). ES (negative)/MS

for **2**: $m/z = 2015$ ($M + Br^-$). The isotope distribution pattern is consistent with the presence of six iridium atoms and two bismuth atoms.

Synthesis of $Ir_3(CO)_8(PPh_3)(\mu_3-Bi)$, **3**.

24.00 mg (0.023 mmol) of **1** was dissolved in 10 mL of CH_2Cl_2 . 6.00 mg (0.023 mmol) of PPh_3 was added and the reaction mixture was heated to reflux for 15.5 h. The solvent was then removed *in vacuo*, and the product was isolated by TLC with a 6/1 hexane/methylene chloride solvent ratio as the eluent. This gave 16.50 mg of the product yellow $Ir_3(CO)_8(PPh_3)(\mu_3-Bi)$, **3** (56 % yield). Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2073(m), 2041 (vs), 2018 (s), 2007 (m); ^{31}P { 1H } NMR ($CDCl_3$) $\delta = -8.54$ ppm (s, 1 PPh_3) Mass Spec. ES (positive) /MS for **3**: $m/z = 1272$ (M^+). The isotope distribution pattern is consistent with the presence of three iridium atoms and one bismuth atom.

Synthesis of $Ir_3(CO)_7(PPh_3)_2(\mu_3-Bi)$, **4**.

A 13.0 mg (0.050 mmol) portion of PPh_3 was added to 25.0 mg (0.024 mmol) of **1** that was dissolved in 15 mL of methylene chloride. The reaction was heated to reflux for 3.5 h. The solvent was then removed *in vacuo*, and the product was isolated by TLC with a 6/1 hexane/methylene chloride solvent ratio as the eluent. This gave 30.0 mg (0.02 mmol) of orange $Ir_3(CO)_7(PPh_3)_2(\mu_3-Bi)$, (**4**, 83% yield). Spectral data for **4**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2046(m), 2014(s), 1984 (s), 1952 (vw); ^{31}P { 1H } NMR ($CDCl_3$) $\delta = -11.13$ ppm (s, 2 PPh_3). ES (positive)/MS for **4**: $m/z = 1506$ (M^+). The isotope distribution pattern is consistent with the presence of three iridium atoms and one bismuth atom.

Synthesis of $Ir_3(CO)_6(PPh_3)_3(\mu_3-Bi)$, **5**.

A 17.0 mg (0.065 mmol) portion of PPh_3 was added to 33.0 mg (0.022 mmol) of **1** that was dissolved in 15 mL of methylene chloride. The reaction was heated to reflux for 3 h. The solvent was then removed *in vacuo*, and the product was isolated by TLC with a 6/1 hexane/methylene chloride solvent ratio as the eluent. This gave 27.8 mg (0.016 mmol) of dark orange $\text{Ir}_3(\text{CO})_6(\text{PPh}_3)_3(\mu_3\text{-Bi})$, **5** (73% yield). Spectral data for **5**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2006(m), 1973(vs), 1951 (s); ^{31}P { ^1H } NMR (CDCl_3) $\delta = -4.96$ ppm (s, 3 PPh_3) ES (positive) /MS for **5**: $m/z = 1740$ (M^+). The isotope distribution pattern is consistent with the presence of three iridium atoms and one bismuth atom.

Synthesis of $\text{Ir}_6(\text{CO})_{12}(\text{PPh}_3)(\mu_3\text{-Bi})(\mu_4\text{-Bi})_3$, **6**.

A 12.0 mg (0.046 mmol) portion of PPh_3 were added to 10.0 mg (0.005 mmol) of **2** that had been previously dissolved in 10 mL of benzene. The reaction was heated to reflux for 0.5 h. The solvent was then removed *in vacuo*, and the product was isolated by TLC with a 4/1 hexane/methylene chloride solvent ratio as the eluent. This gave 8.00 mg (0.0040 mmol) of brown $\text{Ir}_6(\text{CO})_{12}(\text{PPh}_3)(\mu_3\text{-Bi})(\mu_4\text{-Bi})_3$, **6** (69 % yield). Spectral data for **6**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2062 (w), 2027(s), 2008 (m), 1983 (w). ^{31}P { ^1H } NMR (CD_2Cl_2) $\delta = -27.35$ ppm (s, 1 PPh_3) ES (negative) /MS for **6**: $m/z = 2205$ ($\text{M} + \text{Cl}^-$). The isotope distribution pattern is consistent with the presence of six iridium atoms and two bismuth atoms.

Synthesis of $\text{Ir}_3(\text{CO})_6(\text{PPh}_3)(\mu\text{-C}_6\text{H}_4\text{PPh}_2)(\mu\text{-H})(\mu_3\text{-Bi})$, **7**.

A 17.0 mg (0.011 mmol) portion of **4** was dissolved in 15 mL of benzene. The reaction mixture was heated to reflux for 5.5 h. The solvent was then removed *in vacuo*, and the product was isolated by TLC with a 6/1 hexane/methylene chloride solvent ratio as the eluent. This gave 14.6 mg (0.010 mmol) of orange $\text{Ir}_3(\text{CO})_6(\text{PPh}_3)(\mu\text{-C}_6\text{H}_4\text{PPh}_2)(\mu\text{-H})(\mu_3\text{-Bi})$, **7** (87 % yield). Spectral

data for **7**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2039 (m), 2016(vs), 1988 (s), 1948 (w). ^1H NMR (CD_2Cl_2): δ = -19.78 (d, 1 H, $J_{\text{P-H}}$ = 9Hz), 7.54-7.10 ppm (m, 25 H, phenyls on PPh_3 and PPh_2), 5.90 (t d, 1 H, H_{52} , $^3J_{\text{P-H}}$ = 9Hz, $^3J_{\text{H-H}}$ = 7Hz), 6.69 (d of t, 1 H, H_{53} , $^3J_{\text{H-H}}$ = 7Hz), 6.93 (dt, 1 H, H_{54} , $^3J_{\text{H-H}}$ = 7Hz), 7.70 (d of d, 1 H, H_{55} , $^3J_{\text{H-H}}$ = 6.4 Hz). ^{31}P $\{^1\text{H}\}$ NMR (CD_2Cl_2) δ = -11.23 ppm (d, 1 PPh_3 , $J_{\text{P-P}}$ = 62Hz), -47.53 ppm (d, 1 PPh_2 , $J_{\text{P-P}}$ = 62Hz). EI /MS for **7**: m/z = 1478. The isotope distribution pattern is consistent with the presence of three iridium atoms and one bismuth atom.

Pyrolysis of **3**.

A 33.0 mg (0.026 mmol) portion of **3** was dissolved in 20 mL of benzene. The reaction mixture was heated to reflux for 6 h. The solvent was then removed *in vacuo*, and the products were isolated by TLC with a 6/1 hexane/methylene chloride solvent ratio as the eluent. This yielded three bands in order of elution: band 1 (orange) 6.0 mg of **7** (16 % yield); band 2 (brown) 1.0 mg, $\text{Ir}_5(\text{CO})_9(\mu\text{-PPh}_2)_2(\mu\text{-C}_6\text{H}_4)(\mu_4\text{-Bi})$, **8** (3.4% yield) and band 3 (green) 12.0 mg of **6** (43% yield). Spectral data for **8**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2053 (w), 2029(s), 1997 (m). EI /MS for **8**: m/z = 1868. The isotope distribution pattern is consistent with the presence of five iridium atoms and one bismuth atom.

Synthesis of $\text{Ir}_3\text{Ru}_4(\text{CO})_{18}(\mu_3\text{-Bi})$, **9**.

A 11.6 mg (0.011 mmol) amount of **1** was dissolved in 15 mL of CH_2Cl_2 and the reaction flask was placed in a dry ice/acetone bath and a 30.0 mg (0.045 mmol) amount of $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ was added. The reaction mixture was allowed to warm to 25 °C and was then allowed to stir for 18 h. The solvent was then removed *in vacuo*, and the products were isolated by TLC by using a 4/1 hexane/methylene chloride solvent mixture as the eluent. Band 4 yielded 5.8 mg (0.003 mmol) of brown $\text{Ir}_3\text{Ru}_4(\text{CO})_{18}(\mu_3\text{-Bi})$, **9** (30% yield). Spectral data for **9**: IR ν_{CO}

(cm^{-1} in CH_2Cl_2) 2097 (w), 2069 (s), 2045 (vs), 2031 (m), 2027 (m), 1996 (vw). EI/MS for **9**: $m/z = 1695$. The isotope distribution pattern is consistent with the presence of three iridium atoms and one bismuth atom and four ruthenium atoms.

Crystallographic Analyses: Green crystals of **2** and orange crystals of **3** and **4** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution of the compound in hexane at room temperature. Yellow crystals of **5** suitable for x-ray diffraction analyses were obtained by slow evaporation of solvent from a solution of the compound in benzene at room temperature. Brown crystals of **6** and black crystals of **9** suitable for x-ray diffraction were obtained by slow evaporation of solvent from a solution of the pure compound in methylene chloride and a hexane mixture at room temperature. Orange crystals of **7** and brown crystals of **8** suitable for x-ray diffraction analyses were obtained from solutions in methylene chloride/benzene solvent mixtures by slow evaporation of the solvent at room temperature. All data crystals were glued onto the end of a thin glass fibers. X-ray intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using 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]. Correction for Lorentz and polarization effects was also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied 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 by 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 final cycles of least-squares

refinements. Crystal data, data collection parameters, and results of the analyses are listed in Tables 1 –3.

Compounds **2**, **3**, **6**, **7**, and **8** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was indicated by the systematic absences in the data for all of these crystals except for compound **8** for which the alternative setting $P2_1/c$ was used. All analyses were confirmed by the successful solution and refinement of each structure. Compound **4** crystallized in the triclinic crystal system. The space group $P-1$ was chosen and confirmed by the successful solution and refinement of the structure. One molecule of hexane (disordered) from the crystallization solvent was co-crystallized with compound **4**. Compound **5** crystallized in the orthorhombic crystal system. The space group Pbc_a was identified on the basis on the systematic absences in the data and confirmed by the successful solution and refinement of the structure. One molecule of benzene co-crystallized with the asymmetric crystal unit of compound **5** from the crystallization solvent. It was disordered and was refined as a rigid group. The hydrido ligand in **7** was located in a difference Fourier map as a bridge across the Ir(1) – Ir(2) bond, and was refined with a isotropic thermal parameter. Compound **9** crystallized in the orthorhombic crystal system. The space group $Pnma$ was indicated on the basis of the systematic absences in the data and confirmed by the successful solution and refinement of the structure.

Results and Discussion

The new compound $\text{Ir}_6(\text{CO})_{13}(\mu_3\text{-Bi})(\mu_4\text{-Bi})$, **2** was obtained in 84% yield by the thermal decarbonylation and self-condensation of **1** by heating a solution in hexane solvent to reflux for 18 h. Compound **2** was characterized by IR and mass spectral analysis and by a single crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **2** as it is found in the

solid state is shown in Figure 1. The cluster of compound **2** can be described as a capped square-pyramidal cluster of six iridium atoms which contains one quadruply bridging bismuth ligand Bi(1) across the base of the square pyramid and triply bridging bismuth ligand Bi(2) across the Ir(2), Ir(5), Ir(6) triangular face. The Ir – Ir bond distances in the square pyramid range from 2.7286(7) Å to 2.7996(7) Å and are similar in length to the Ir – Ir distances observed in the square pyramid of the pentairidium cluster in the compound $\text{Ir}_5(\text{CO})_{10}(\mu_3\text{-Bi})_2(\mu_4\text{-Bi})$, **10**, 2.7796(9) Å - 2.8255(9) Å [4]. Two of the Ir – Ir distances to the capping $\text{Ir}(\text{CO})_3$ group in **2** are relatively short, $\text{Ir}(1) - \text{Ir}(3) = 2.6533(7)\text{Å}$, $\text{Ir}(1) - \text{Ir}(4) = 2.6632(7) \text{Å}$ while the distance to the apical atom of the square pyramid Ir(2) is much longer, $\text{Ir}(1) - \text{Ir}(2) = 2.7317(7)\text{Å}$. The longer $\text{Ir}(1) - \text{Ir}(2)$ distance could be a steric effect because Ir(2) has eight atoms bonded to it while atoms Ir(2) and Ir(3) have only seven atoms bonded to them. The Ir – Bi distances to the quadruply bridging bismuth ligand Bi(1), 2.7800(7) Å – 2.8153(7) Å are similar in length to those observed in **10**, 2.8004(7) Å – 2.8185(7) Å. The Ir – Bi distances to the triply bridging Bi atom Bi(2) are significantly different; two are short, $\text{Ir}(5) - \text{Bi}(2) = 2.7031(7)\text{Å}$, $\text{Ir}(6) - \text{Bi}(2) = 2.7066(8) \text{Å}$ and one $\text{Ir}(2) - \text{Bi}(2) = 2.7803(7) \text{Å}$ is long. As described above for the bonding to Ir(1), this could also be explained by a steric effect. Assuming that each Bi ligand serves as a three electron donor, then cluster of **2** contains a total of 86 cluster valence electrons and its structure obeys the predictions of the Wade-Mingos Skeletal Electron Pair Theory [10].

Three PPh_3 derivatives of **1**, $\text{Ir}_3(\text{CO})_{9-n}(\text{PPh}_3)_n(\mu_3\text{-Bi})$, (**3** – **5**, $n = 1-3$) were obtained by the reactions of **1** with PPh_3 in the stoichiometrically appropriate quantities. Each of these new compounds was characterized by IR, ^1H NMR, ^{31}P NMR, mass spec and single crystal X-ray diffraction analyses. ORTEP diagrams of these three new compounds are shown in Figures 2 – 4, respectively. Each compound contains a triangular cluster of three iridium atoms with three Ir –

Ir bonds with a triply bridging bismuth atom. The Ir – Ir distances in each product: **2**, 2.7668(6) Å – 2.7916(6) Å; **3**, 2.7725(4) Å – 2.7930(4) Å and **4**, 2.7907(6) Å – 2.8029(6) Å, are slightly longer than those in **1**, 2.759(2) Å. The increased Ir – Ir bond lengths may be due in part to steric effects produced by the bulky PPh₃ ligands. All PPh₃ ligands occupy “equatorial” coordination sites in the Ir₃ plane, *cis* to the bridging Bi ligand. These sites should have lower steric effects than the “axial” sites. The Ir – Bi distances are not significantly different from those in **1**.

When compound **2** was treated with PPh₃ in benzene solution at reflux, the new compound Ir₆(CO)₁₂(PPh₃)(μ₃-Bi)(μ₄-Bi), **6** was formed in 69 % yield. Compound **6** was formed by the replacement of one of the CO ligands in **2** with a PPh₃ ligand. The location of the substitution was established by a single crystal X-ray diffraction analysis of **6**, see Figure 5. The cluster of **6** contains a capped square-pyramidal cluster of six Ir atoms with a quadruply bridging bismuth ligand and a triply bridging bismuth ligand arranged similar to that of **2**. The PPh₃ ligand is located on the Ir capping group *trans* to the Ir(1) – Ir(2) bond. As in **2**, the Ir – Ir bond distance to the apical Ir atom, Ir(1) – Ir(2) = 2.7550(8) Å, is significantly longer than the other two Ir – Ir bonds to the capping atom Ir(1), Ir(1) – Ir(3) = 2.6644(7) Å and Ir(1) – Ir(4) = 2.6854(7) Å. The Ir(1) – Ir(2) bond in **6** is also slightly longer than that in **2**, 2.7317(7) Å. This could be due to a slight *trans*-structural effect caused by the PPh₃ ligand. The other Ir – Ir and Ir – Bi bonds in **6** are similar to those in **2**.

Efforts were made to try to obtain self-condensation products from **3** and **4** by thermal treatments. Pyrolysis of **3** in benzene solution at reflux for 6 h (80 °C) yielded **6** (43% yield), a new compound Ir₃(CO)₆(PPh₃)(μ-C₆H₄PPh₂)(μ-H)(μ₃-Bi), **7** (16% yield) and a trace of a Ir₅Bi complex **8** (3.4% yield). Compound **7** was obtained in a much better yield (87%) by the pyrolysis of **4** in benzene solvent at reflux.

An ORTEP diagram of the molecular structure of **7** is shown in Figure 6. Compound **7** contains a bismuth-bridged Ir₃ triangular cluster similar to those of **1** and **3** – **5**. There is a PPh₃ ligand on atom Ir(1) and an *o*-metallated PPh₃ ligand bridging the Ir(2) – Ir(3) bond. The Ir(2) – Ir(3) bond distance, Ir(2) – Ir(3) = 2.7278(6) Å, is slightly shorter than the Ir – Ir bonds in **1** and **3** – **5**, perhaps due to the presence of the bridging C₆H₄PPh₂ ligand. The Ir(1) – Ir(3) bond is normal, 2.7775(6) Å. The Ir(1) – Ir(2) bond is significantly longer, 2.9255(6) Å, which is almost certainly a consequence of the presence of a hydrido ligand that bridges this bond [11], $\delta = -19.78$ (d, $J_{\text{P-H}} = 9\text{Hz}$). The cluster of **7** contains 48 valence electrons which is consistent with the observation of a closed cluster having three Ir – Ir bonds.

An ORTEP diagram of the molecular structure of Ir₅(CO)₉(μ-PPh₂)₂(μ-C₆H₄)(μ₄-Bi), **8** is shown in Figure 7. Compound **8** contains a square pyramidal cluster of five iridium atoms with a quadruply bridging bismuth atom across the base of the square pyramid. Compound **8** contains nine carbonyl ligands, two bridging phosphido (PPh₂) ligands and one edge bridging μ-η²-benzyne (C₆H₄) ligand; the latter was almost certainly derived from a phenyl ring cleaved from a PPh₃ ligand which then also yielded one of the bridging PPh₂ ligands. The eight Ir – Ir bond distances in cluster range from 2.7309(7) Å to 2.8510(8) Å. The shortest distance, Ir(2) – Ir(3) = 2.7309(7) Å, is bridged by one of the phosphido ligands. The Ir – Bi distances 2.8294(8) Å – 2.8817(7) Å are similar to the Ir – Bi distances to the quadruply bridging Bi ligands found in **2** and **6**. μ-η²-C₆H₄ ligands are rare. Previous examples include the compounds: Os₅(CO)₁₈(μ-η²-C₆H₄)(μ₄-Bi)(μ-H) [12] and Os₆(CO)₂₀(μ-η²-C₆H₄)(μ₄-Bi)(μ-H) [13]. The Ir – C σ-bonding distances to the benzyne ligand in **8** are Ir(1) – C(53) = 2.077(14) Å and Ir(3) – C(58) = 2.091(14) Å. Assuming the phosphido ligands serve as 3-electron donors and the benzyne ligand is a 2-electron donor, then the metal atoms of the cluster of **8** contains a total of 74 valence

electrons which is consistent with the observation of a square pyramidal cluster of five metal atoms [10].

Years ago, Lewis and Johnson reported the synthesis and structures of a number of bismuth-ruthenium carbonyl cluster complexes by reactions of the ruthenium carbonyl cluster complexes with $\text{Bi}(\text{NO}_3)_3$ and NaBiO_3 [14 - 15]. To complete the current study, it was decided to try to synthesize the first bismuth-containing iridium-ruthenium complexes by condensation of **1** with $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$. The reaction of **1** with $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ at 25 °C for 18 h yielded the new iridium-ruthenium compound $\text{Ir}_3\text{Ru}_4(\text{CO})_{18}(\mu_3\text{-Bi})$, **9** (30% yield). Compound **9** was characterized by IR, mass spec and single crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **9** is shown in Figure 8. Compound **9** contains a total of seven metal atoms, three of iridium and four of ruthenium. The molecule contains reflection symmetry in the solid state. The cluster can be described as a $\text{Ru}(\text{CO})_3$ capped Ir_3Ru_3 octahedron. The $\text{Ru}(\text{CO})_3$ group caps an Ir_3 triangle. There is a triply bridging bismuth ligand on one of the IrRu_2 triangles. Compound **9** contains eighteen CO ligands distributed as shown in Figure 8. The cluster of **9** contains a total of 98 electrons which is consistent with the observed structure of a monocapped octahedral arrangement for the seven metal atoms [10].

Summary and Conclusions

A summary of the results of this work are presented in Schemes 1 and 2. Compound **1** readily loses CO upon heating and condenses to form the hexairidium product **2**. Years ago, Adams et al. showed that bridging sulfido ligands could facilitate condensation and self-condensation reactions of osmium and ruthenium carbonyl cluster complexes to produce higher nuclearity complexes [16 – 19]. The lone pair of electrons on the sulfido ligands clearly played a key role in

the formation of new bonds between the condensing species [17-19]. The bridging bismuth ligand in **1** formally contains a lone pair of electrons and these electrons may also serve to facilitate the self-condensation of **1** to form the hexairidium complex **2** even though no intermediates were isolated that would confirm that such interactions did in fact occur in the course of the formation of **2**. Because of its facile elimination of CO, it was easy to prepare the PPh₃ derivatives **3** - **5** of **1** by reactions between **1** and PPh₃. Compound **3** eliminated CO and PPh₃ to yield **6**, the PPh₃ derivative of **2** by a condensation reaction, but **6** could be obtained in an even better yield by treatment of **2** with PPh₃. Pyrolysis of **3** also yielded a pentairidium complex **8** having a square pyramidal cluster of metal atoms in a very low yield by a combination of cluster and ligand degradation and reassembly. Compound **8** has an interesting structure and ligands. Unfortunately, we have not yet been able to synthesize compound **8** in a systematic way. Pyrolysis of **4** did not yield any higher nuclearity metal compounds, but did yield the complex **7**, an o-metallated PPh₃ derivative of **4** in a high yield. Complex **7** was also obtained in a low yield from the pyrolysis of **3**. The condensation of **1** with Ru₃(CO)₁₀(NCMe)₂ yielded the bimetallic compound **9**, see Scheme 2, the first example of an iridium-ruthenium carbonyl complex containing bismuth ligands.

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Supplementary Material. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1407730-1407737 for compounds **2** - **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [Fax. (int code) +44(1223)336-033, or Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

References

1. (a) R. K. Grasselli, *Catal. Today* 238 (2014) 10–27. (b) R. K. Grasselli, *Topics in Catal.* 21 (2002) 79-88. (c) R. K. Grasselli, *Handbook of Heterogeneous Catalysis*, Ertl, G., Knozinger, H., Weitkamp, J., VCH Publishers, Weinheim, vol. 5, 1997, pp 2302-2326. (d) R. K. Grasselli, *Catal. Today*, 99 (2005) 23-31. (e) W. A. Goddard III, K. Chenoweth, S. Pudar, A. C. T. van Duin, M.-J. Cheng, *Top Catal.* 50 (2008) 2-18. (f) Y. H. Jang, W. A. Goddard III, *J. Phys. Chem. B* 106 (2002) 5997-6013. (g) T. A. Hanna, *Coord. Chem. Rev.* 248 (2004) 429-440.
2. (a) R. Raja, R. D. Adams, D. A. Blom, W. C. Pearl, Jr., E. Gianotti, J. M. Thomas, *Langmuir* 25 (2009) 7200-7204. (b) E. Gianotti, V. N. Shetti, M. Manzoli, J. A. L. Blaine, W. C. Pearl, Jr., R. D. Adams, S. Coluccia, R. Raja, *Chem Eur. J.* 16 (2010) 8202-8209.
3. W. Kruppa, D. Blaeser, R. Boese, G. Schmid, *Organische Chem.*, 37B (1982) 209-213.
4. R. D. Adams, M. Chen, G. Elpitiya, M. E. Potter, R. Raja, R., *ACS Catal.*, 3 (2013) 3106-3110.
5. R. D. Adams, M. Chen, G. Elpitiya, Q. Zhang, *Organometallics* 31 (2012) 7264-7271.
6. L. Garlaschelli, R. Della Pergola, S. Martinengo, *Inorg. Synth.*, 28 (1990) 211-215.
7. G. A. Foulds, B. F. G. Johnson, J. Lewis, *J. Organomet. Chem.*, 296 (1985) 147-153.
8. SAINT+, version 6.2a, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.
9. G. M. Sheldrick, SHELXTL, version 6.1, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.
10. D. M. P Mingos, *Acc. Chem. Res.* 17 (1984) 311-319.
11. (a) R. Bau, M. H. Drabnis, *Inorg. Chim. Acta* 259 (1997) 27-50. (b) R. G. Teller, R. Bau, *Struc. Bonding* 41 (1981) 1-82.

12. R.D. Adams, W.C. Pearl, Jr., *Inorg. Chem.* 49 (2010) 7170 - 7175.
13. R. D. Adams, Y. Kan, Q. Zhang, *J. Organomet. Chem.*, 751 (2014) 475 - 481.
14. B. F. G. Johnson, J.Lewis, P. R. Raithby and A. J. Whitton, *J. Chem. Soc., Chem. Commun.* (1988) 401 - 402.
15. C. M. Hay, B. F. G. Johnson, J.Lewis, P. R. Raithby and A. J. Whitton, *J. Chem. Soc., Dalton Trans.* (1988) 2091 - 2097.
16. R. D. Adams in *The Chemistry of Metal Cluster Complexes*, D. F. Shriver, H. D. Kaesz and R. D. Adams, Ed., VCH Publishers, New York, 1990, Ch. 3.
17. R. D. Adams, Z. Dawoodi, D. F. Foust, B. Segmueller, *J. Am. Chem. Soc.* 105(1983)831-838.
18. R. D. Adams, J. E. Babin, T. A. Wolfe, *Polyhedron* 8(1989)1123 - 1134.
19. R. D. Adams, G. Chen, J. T. Tanner, J. Yin, *Organometallics* 9 (1990) 1240 - 1245.

Table 1. Crystallographic Data for Compounds 2 - 4.

Compound	2	3	4
Empirical formula	Ir ₆ Bi ₂ O ₁₃ C ₁₃	Ir ₃ BiPO ₈ C ₂₆ H ₁₅	Ir ₃ BiP ₂ O ₇ C ₄₉ H ₄₄
Formula weight	1935.29	1271.93	1592.42
Crystal system	Monoclinic	Monoclinic	Triclinic
Lattice parameters			
<i>a</i> (Å)	9.9809 (5)	12.1768(5)	12.3518(11)
<i>b</i> (Å)	20.9530 (11)	16.4651(7)	15.2697(14)
<i>c</i> (Å)	11.7111 (6)	15.3158(7)	15.6403(14)
α (deg)	90	90	65.838(2)
β (deg)	92.295 (10)	105.836(1)	75.427(2)
γ (deg)	90	90	66.874(2)
<i>V</i> (Å ³)	2447.2 (2)	2954.2 (2)	2460.6 (4)
Space group	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n	<i>P</i> -1
Z value	4	4	2
ρ_{calc} (g / cm ³)	5.253	2.860	2.149
μ (Mo K α) (mm ⁻¹)	46.874	19.509	11.764
Temperature (K)	294(2)	294(2)	294(2)
2 Θ_{max} (°)	50.04	50.06	50.06
No. Obs. (<i>I</i> > 2 σ (<i>I</i>))	4316	5218	8702
No. Parameters	307	352	505
Goodness of fit (GOF)	1.039	1.045	1.057
Max. shift in cycle	0.001	0.001	0.001
Residuals*: R1; wR2	0.0326; 0.0928	0.0434; 0.0515	0.0308; 0.0837
Absorption Corr.	Multi-scan	Multi-scan	Multi-scan
Max/min	1.000/0.264	1.000/0.838	1.000/0.696
Largest peak in Final Diff.	1.456	0.884	2.788
Map (e ⁻ / Å ³)			

*R1 = $\sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{\text{hkl}} |F_{\text{obs}}|$; wR2 = $[\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}$; $w = 1/\sigma^2(F_{\text{obs}})$; GOF = $[\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$.

Table2. Crystallographic Data for Compounds 5 - 7.

Compound	5	6	7
Empirical formula	Ir ₃ BiP ₃ O ₆ C ₆₆ H ₅₁	Ir ₆ Bi ₂ PO ₁₂ C ₃₀ H ₁₅	Ir ₃ BiP ₂ O ₆ C ₄₂ H ₃₀
Formula weight	1818.56	2169.55	1478.18
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Lattice parameters			
<i>a</i> (Å)	23.6355(13)	9.7831 (7)	13.7951 (5)
<i>b</i> (Å)	18.0823(10)	15.1472 (11)	16.6035 (6)
<i>c</i> (Å)	29.6151(17)	25.0740 (18)	19.0814 (7)
α (deg)	90	90	90
β (deg)	90	94.881(2)	109.376 (10)
γ (deg)	90	90	90
<i>V</i> (Å ³)	12657.0 (12)	3702.2 (5)	4123.0 (3)
Space group	<i>Pbca</i> <i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	
Z value	84	4	
ρ_{calc} (g / cm ³)	1.9093.892	2.381	
μ (Mo K α) (mm ⁻¹)	9.18531.047	14.030	
Temperature (K)	294(2)	294(2)	294(2)
2 Θ_{max} (°)	50.0650.06	50.06	
No. Obs. (<i>I</i> > 2 σ (<i>I</i>))	111836543	7290	
No. Parameters	670460	490	
Goodness of fit (GOF)	1.0961.005	1.017	
Max. shift in cycle	0.0040.006	0.001	
Residuals*: R1; wR2	0.0508; 0.1108	0.0368; 0.0745	0.0394; 0.0914
Absorption Corr.	Multi-scan	Multi-scan	Multi-scan
Max/min	1.000/0.402	1.000/0.303	1.000/0.513
Largest peak in Final Diff.	1.320	1.739	2.633
Map	(e ⁻		/
Å ³)			*R1 =
$\sum_{\text{hkl}} (F_{\text{obs}} - F_{\text{calc}}) / \sum_{\text{hkl}} F_{\text{obs}} $; wR2 = $[\sum_{\text{hkl}} w(F_{\text{obs}} - F_{\text{calc}})^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}$; $w = 1/\sigma^2(F_{\text{obs}})$;			
GOF = $[\sum_{\text{hkl}} w(F_{\text{obs}} - F_{\text{calc}})^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$.			

Table 3. Crystallographic Data for Compounds 8 and 9.

Compound	8	9
Empirical formula	Ir ₅ Bi ₁ P ₂ O ₉ C ₃₉ H ₂₄	Ir ₃ Bi ₁ Ru ₄ O ₁₈ C ₁₈
Formula weight	1868.50	1694.0
Crystal system	Monoclinic	Orthorhombic
Lattice parameters		
<i>a</i> (Å)	14.4576 (6)	11.9089(5)
<i>b</i> (Å)	16.9071(7)	15.2262(7)
<i>c</i> (Å)	17.5453 (7)	15.8791(7)
α (deg)	90	90
β (deg)	100.245(1)	90
γ (deg)	90	90
<i>V</i> (Å ³)	4220.3(3)	2879.3(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>
Z value	4	4
ρ_{calc} (g / cm ³)	2.941	3.908
μ (Mo K α) (mm ⁻¹)	19.987	22.012
Temperature (K)	294(2)	294(2)
2 Θ_{max} (°)	50.06	50.04
No. Obs. (<i>I</i> > 2 σ (<i>I</i>))	7454	2639
No. Parameters	505	211
Goodness of fit (GOF)	1.025	1.215
Max. shift in cycle	0.001	0.001
Residuals*: R1; wR2	0.0435; 0.0924	0.0525 ;0.1191
Absorption Correction,	Multi-scan	Multi-scan
Max/min	1.000 / 0.511	1.000/0.452
Largest peak in Final Diff Map (e ⁻ / Å ³)	4.066	1.681

*R1 = $\sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{\text{hkl}} |F_{\text{obs}}|$; wR2 = $[\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}$; $w = 1/\sigma^2(F_{\text{obs}})$; GOF = $[\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$.

Figure 1. An ORTEP diagram of the molecular structure of $\text{Ir}_6(\text{CO})_{13}(\mu_3\text{-Bi})(\mu_4\text{-Bi})_2$ showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follow: Ir(1) – Ir(3) = 2.6533(7), Ir(1) – Ir(4) = 2.6632(7), Ir(1) – Ir(2) = 2.7317(7), Ir(2) – Ir(3) = 2.7286(7), Ir(2) – Ir(4) = 2.7345(7), Ir(2) – Bi(2) = 2.7803(7), Ir(2) – Ir(6) = 2.7883(7), Ir(2) – Ir(5) = 2.7996(7), Ir(3) – Ir(4) = 2.7362(7), Ir(3) – Ir(5) = 2.7644(7), Ir(3) – Bi(1) = 2.8116(7), Ir(4) – Bi(1) = 2.7800(7), Ir(4) – Ir(6) = 2.7979(7), Ir(5) – Bi(2) = 2.7031(7), Ir(5) – Ir(6) = 2.8064(7), Ir(5) – Bi(1) = 2.8153(7), Ir(6) – Bi(2) = 2.7066(8), Ir(6) – Bi(1) = 2.7997(7).

Figure 2. An ORTEP diagram of the molecular structure of $\text{Ir}_3(\text{CO})_8(\text{PPh}_3)(\mu_3\text{-Bi})$, **3** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (°) are as follow: $\text{Ir}(1) - \text{Ir}(2) = 2.7722(7)$, $\text{Ir}(1) - \text{Ir}(3) = 2.7916(6)$, $\text{Ir}(2) - \text{Ir}(3) = 2.7668(6)$, $\text{Ir}(1) - \text{Bi}(1) = 2.7304(6)$, $\text{Ir}(2) - \text{Bi}(1) = 2.7421(7)$, $\text{Ir}(3) - \text{P}(1) = 2.320(3)$, $\text{Ir}(3) - \text{Bi}(1) = 2.7203(6)$, $\text{Bi}(1) - \text{Ir}(1) - \text{Ir}(2) = 59.773(17)$, $\text{Ir}(2) - \text{Ir}(1) - \text{Ir}(3) = 59.641(17)$, $\text{Bi}(1) - \text{Ir}(2) - \text{Ir}(3) = 59.179(17)$, $\text{Bi}(1) - \text{Ir}(2) - \text{Ir}(1) = 59.356(17)$, $\text{Ir}(3) - \text{Ir}(2) - \text{Ir}(1) = 60.528(17)$, $\text{Ir}(2) - \text{Ir}(3) - \text{Ir}(1) = 59.831(17)$, $\text{Ir}(3) - \text{Bi}(1) - \text{Ir}(1) = 61.614(16)$, $\text{Ir}(3) - \text{Bi}(1) - \text{Ir}(2) = 60.863(17)$, $\text{Ir}(1) - \text{Bi}(1) - \text{Ir}(2) = 60.870(18)$.

Figure 3. An ORTEP diagram of the molecular structure of $\text{Ir}_3(\text{CO})_7(\text{PPh}_3)_2(\mu_3\text{-Bi})$, **4** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (°) are as follows: $\text{Bi}(1)\text{-Ir}(1) = 2.7295(5)$, $\text{Bi}(1)\text{-Ir}(2) = 2.7312(5)$, $\text{Bi}(1)\text{-Ir}(3) = 2.7211(5)$, $\text{Ir}(1)\text{-Ir}(2) = 2.7725(4)$, $\text{Ir}(1)\text{-Ir}(3) = 2.7930(4)$, $\text{Ir}(2)\text{-Ir}(3) = 2.7896(4)$, $\text{Ir}(1)\text{-P}(1) = 2.3249(18)$, $\text{Ir}(2)\text{-P}(2) = 2.3270(18)$; $\text{Ir}(3)\text{-Bi}(1)\text{-Ir}(1) = 61.650(11)$, $\text{Ir}(3)\text{-Bi}(1)\text{-Ir}(2) = 61.546(11)$, $\text{Ir}(1)\text{-Bi}(1)\text{-Ir}(2) = 61.026(11)$, $\text{Ir}(2)\text{-Ir}(1)\text{-Ir}(3) = 60.161(10)$, $\text{Ir}(1)\text{-Ir}(2)\text{-Ir}(3) = 60.283(10)$, $\text{Ir}(2)\text{-Ir}(3)\text{-Ir}(1) = 59.556(11)$.

Figure 4. An ORTEP diagram of the molecular structure of $\text{Ir}_3(\text{CO})_6(\text{PPh}_3)_3(\mu_3\text{-Bi})$, **5** showing 30% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (°) are as follows: $\text{Ir}(1) - \text{P}(1) = 2.325(3)$, $\text{Ir}(1) - \text{Bi}(1) = 2.7204(6)$, $\text{Ir}(1) - \text{Ir}(2) = 2.7907(6)$, $\text{Ir}(1) - \text{Ir}(3) = 2.8029(6)$, $\text{Ir}(2) - \text{P}(2) = 2.315(3)$, $\text{Ir}(2) - \text{Bi}(1) = 2.7306(6)$, $\text{Ir}(2) - \text{Ir}(3) = 2.7973(6)$, $\text{Ir}(3) - \text{P}(3) = 2.321(3)$, $\text{Ir}(3) - \text{Bi}(1) = 2.7224(6)$, $\text{Ir}(2) - \text{Ir}(1) - \text{Ir}(3) = 60.012(15)$, $\text{Ir}(1) - \text{Ir}(2) - \text{Ir}(3) = 60.211(15)$, $\text{Ir}(2) - \text{Ir}(3) - \text{Ir}(1) = 59.777(15)$, $\text{Ir}(1) - \text{Bi}(1) - \text{Ir}(3) = 61.990(16)$, $\text{Ir}(1) - \text{Bi}(1) - \text{Ir}(2) = 61.587(16)$, $\text{Ir}(3) - \text{Bi}(1) - \text{Ir}(2) = 61.725(16)$.

Figure 5. An ORTEP diagram of the molecular structure of $\text{Ir}_6(\text{CO})_{12}(\text{PPh}_3)(\mu_3\text{-Bi})(\mu_4\text{-Bi})_6$ showing 30% thermal ellipsoid probability. Selected interatomic bond distances ($\text{\AA}$) are as follow: $\text{Bi}(1) - \text{Ir}(3) = 2.7903(7)$, $\text{Bi}(1) - \text{Ir}(6) = 2.7941(8)$, $\text{Bi}(1) - \text{Ir}(4) = 2.8181(7)$, $\text{Bi}(1) - \text{Ir}(5) = 2.8217(7)$, $\text{Bi}(2) - \text{Ir}(6) = 2.6997(8)$, $\text{Bi}(2) - \text{Ir}(5) = 2.7100(8)$, $\text{Bi}(2) - \text{Ir}(2) = 2.7768(8)$, $\text{Ir}(1) - \text{Ir}(2) = 2.7550(8)$, $\text{Ir}(1) - \text{Ir}(4) = 2.6854(7)$, $\text{Ir}(3) - \text{Ir}(4) = 2.7293(7)$, $\text{Ir}(2) - \text{Ir}(4) = 2.7406(7)$, $\text{Ir}(4) - \text{Ir}(6) = 2.7965(8)$, $\text{Ir}(2) - \text{Ir}(6) = 2.7917(7)$, $\text{Ir}(5) - \text{Ir}(6) = 2.8052(7)$, $\text{Ir}(3) - \text{Ir}(5) = 2.7791(8)$, $\text{Ir}(2) - \text{Ir}(5) = 2.7913(7)$, $\text{Ir}(1) - \text{Ir}(3) = 2.6644(7)$, $\text{Ir}(2) - \text{Ir}(3) = 2.7631(7)$, $\text{Ir}(1) - \text{P}(1) = 2.342(4)$.

Figure 6. An ORTEP diagram of the molecular structure of $\text{Ir}_3(\text{CO})_6(\text{PPh}_3)(\mu_2\text{-C}_6\text{H}_4\text{PPh}_2)(\mu\text{-H})(\mu_3\text{-Bi})$, **7** showing 20% thermal ellipsoid probability. Selected interatomic bond distances ($\text{\AA}$) and angles ($^\circ$) are as follows: $\text{Bi}(1) - \text{Ir}(2) = 2.7127(6)$, $\text{Bi}(1) - \text{Ir}(3) = 2.7295(6)$, $\text{Bi}(1) - \text{Ir}(1) = 2.7898(6)$, $\text{Ir}(1) - \text{P}(1) = 2.336(3)$, $\text{Ir}(1) - \text{Ir}(3) = 2.7775(6)$, $\text{Ir}(1) - \text{Ir}(2) = 2.9255(6)$, $\text{Ir}(1) - \text{H}(1) = 1.82(13)$, $\text{Ir}(2) - \text{Ir}(3) = 2.7278(6)$, $\text{Ir}(2) - \text{H}(1) = 1.53(12)$, $\text{Ir}(3) - \text{P}(2) = 2.288(3)$, $\text{Ir}(2) - \text{Bi}(1) - \text{Ir}(3) = 60.163(15)$, $\text{Ir}(2) - \text{Bi}(1) - \text{Ir}(1) = 64.219(15)$, $\text{Ir}(3) - \text{Bi}(1) - \text{Ir}(1) = 60.417(15)$.

Figure 7. An ORTEP diagram of the molecular structure of $\text{Ir}_5(\text{CO})_9(\mu\text{-PPh}_2)_2(\mu\text{-}\eta^2\text{-C}_6\text{H}_4)(\mu_4\text{-Bi})$, **8** showing 15% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (°) are as follows: $\text{Bi}(1) - \text{Ir}(1) = 2.8294(8)$, $\text{Bi}(1) - \text{Ir}(4) = 2.8342(7)$, $\text{Bi}(1) - \text{Ir}(2) = 2.8411(7)$, $\text{Bi}(1) - \text{Ir}(5) = 2.8817(7)$, $\text{Ir}(1) - \text{Ir}(5) = 2.7637(8)$, $\text{Ir}(1) - \text{Ir}(3) = 2.7642(7)$, $\text{Ir}(1) - \text{Ir}(2) = 2.8510(8)$, $\text{Ir}(2) - \text{Ir}(3) = 2.7309(7)$, $\text{Ir}(2) - \text{Ir}(4) = 2.8124(7)$, $\text{Ir}(3) - \text{Ir}(5) = 2.7694(8)$, $\text{Ir}(3) - \text{Ir}(4) = 2.8178(8)$, $\text{Ir}(4) - \text{Ir}(5) = 2.7853(7)$, $\text{Ir}(2) - \text{P}(1) = 2.331(4)$, $\text{Ir}(3) - \text{P}(1) = 2.238(4)$, $\text{Ir}(4) - \text{P}(2) = 2.285(3)$, $\text{Ir}(5) - \text{P}(2) = 2.272(3)$, $\text{Ir}(1) - \text{C}(53) = 2.077(14)$, $\text{Ir}(3) - \text{C}(58) = 2.091(14)$.

Figure 8. An ORTEP diagram of the molecular structure of $\text{Ir}_3\text{Ru}_4(\text{CO})_{18}(\mu_3\text{-Bi})$, **9** showing 40% thermal ellipsoid probability. Selected interatomic bond distances ($\text{\AA}$) and angles ($^\circ$) are as follows: $\text{Bi}(1)\text{-Ir}(1) = 2.7319(14)$, $\text{Bi}(1)\text{-Ru}(1)^i = 2.7514(17)$, $\text{Bi}(1)\text{-Ru}(1) = 2.7514(17)$, $\text{Ir}(1)\text{-Ir}(2)^i = 2.7308(10)$, $\text{Ir}(1)\text{-Ir}(2) = 2.7308(10)$, $\text{Ir}(1)\text{-Ru}(3) = 2.757(2)$, $\text{Ir}(1)\text{-Ru}(1) = 2.8684(15)$, $\text{Ir}(1)\text{-Ru}(1)^i = 2.8684(15)$, $\text{Ir}(2)\text{-Ru}(3) = 2.6718(17)$, $\text{Ir}(2)\text{-Ir}(2)^i = 2.7428(13)$, $\text{Ir}(2)\text{-Ru}(1) = 2.7866(14)$, $\text{Ir}(2)\text{-Ru}(2) = 2.8304(17)$, $\text{Ru}(1)\text{-Ru}(1)^i = 2.857(3)$, $\text{Ru}(1)\text{-Ru}(2) = 2.873(2)$, $\text{Ru}(2)\text{-Ir}(2) = 2.8304(17)$, $\text{Ru}(2)\text{-Ru}(1)^i = 2.873(2)$, $\text{Ru}(3)\text{-Ir}(2)^i = 2.6718(17)$, $\text{Ir}(1)\text{-Bi}(1)\text{-Ru}(1)^i = 63.08(4)$, $\text{Ir}(1)\text{-Bi}(1)\text{-Ru}(1) = 63.08(4)$, $\text{Ru}(1)^i\text{-Bi}(1)\text{-Ru}(1) = 62.54(6)$.

Scheme 1

Scheme 1. A summary of the reactions and products described in this report.

Scheme 2

Scheme 2. A schematic representation of the synthesis and structure of compound **9**.

Graphical Abstract