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## 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.

## Keywords:

Iridium  
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Condensation

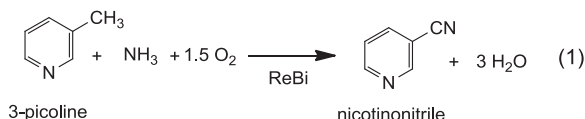
## ABSTRACT

The compound  $\text{Ir}_3(\text{CO})_9(\mu_3\text{-Bi})$ , **1** loses CO when heated and condenses to form the hexairidium compound  $\text{Ir}_6(\text{CO})_{13}(\mu_3\text{-Bi})(\mu_4\text{-Bi})$ , **2**. Compounds **1** and **2** react with  $\text{PPh}_3$  to form the  $\text{PPh}_3$  derivatives  $\text{Ir}_3(\text{CO})_9\text{-n}(\text{PPh}_3)_n(\mu_3\text{-Bi})$ , **3** – **5**,  $n = 1\text{--}3$  and  $\text{Ir}_6(\text{CO})_{12}(\text{PPh}_3)(\mu_3\text{-Bi})(\mu_4\text{-Bi})$ , **6**, respectively. Compound **4** loses CO and converts to the *o*-metallated product  $\text{Ir}_3(\text{CO})_6(\text{PPh}_3)(\mu\text{-C}_6\text{H}_4\text{PPh}_2)(\mu\text{-H})(\mu_3\text{-Bi})$ , **7**. Compound **1** reacts with  $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$  to yield the bimetallic cluster complex  $\text{Ir}_3\text{Ru}_4(\text{CO})_{18}(\mu_3\text{-Bi})$ , **9**. The structures of all new products were established by single-crystal X-ray diffraction analyses. The hexairidium products **2** and **6** contain square pyramidal  $\text{Ir}_5$  clusters with a quadruply bridging bismuth ligand across the square base and a triply bridging bismuth ligand on one of the  $\text{Ir}_3$  triangles. The sixth Ir grouping is a capping group on one of the remaining  $\text{Ir}_3$  triangles. Compound **9** contains an octahedral  $\text{Ir}_3\text{Ru}_3$  cluster with a  $\text{Ru}(\text{CO})_3$  group capping an  $\text{Ir}_3$  triangle and a triply bridging bismuth ligand on one of the  $\text{IrRu}_2$  triangles.

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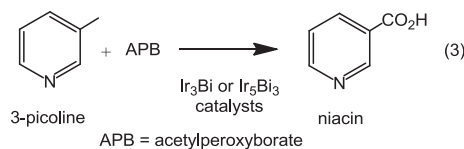
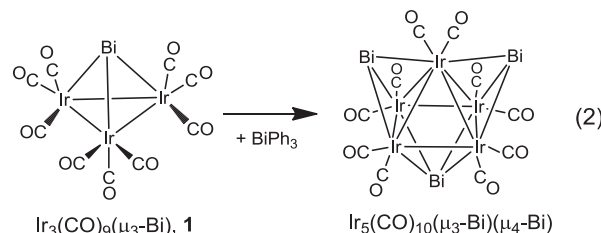
## 1. Introduction

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  $\text{BiPh}_3$ , 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].

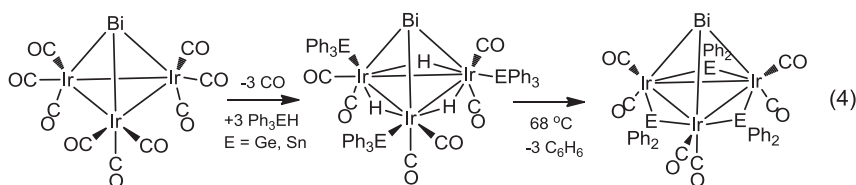


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We have also prepared a number of iridium-bismuth complexes containing germanium and tin ligands from complex **1** by reactions

with HGePh<sub>3</sub> and HSnPh<sub>3</sub>, 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<sub>3</sub> and with Ru<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>. The results of these studies are reported herein.

## 2. Experimental section

### 2.1. 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 <sup>1</sup>H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. <sup>31</sup>P{<sup>1</sup>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. Ir<sub>4</sub>(CO)<sub>12</sub>, Ru<sub>3</sub>(CO)<sub>12</sub> and PPh<sub>3</sub> were obtained from STREM and Sigma–Aldrich, respectively and were used without further purification. [PPN]Ir(CO)<sub>4</sub> [6] and Ru<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub> [7] were prepared according to the previously reported procedures. Ir<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-Bi), **1** [3] was prepared by a modified procedure reported previously [4]. All product separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F254 and 0.25 mm aluminum oxide 60 Å F254 glass plates.

#### 2.1.1. Synthesis of Ir<sub>6</sub>(CO)<sub>13</sub>(μ<sub>3</sub>-Bi)(μ<sub>4</sub>-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 Ir<sub>6</sub>(CO)<sub>13</sub>(μ<sub>3</sub>-Bi)(μ<sub>4</sub>-Bi), **2** (84% yield). Spectral data for **2**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) 2095(w), 2067(w), 2042 (vs), 2021 (w), 2007 (w), 1992 (w). ES (negative)/MS for **2**: *m/z* = 2015 (M + Br<sup>-</sup>). The isotope distribution pattern is consistent with the presence of six iridium atoms and two bismuth atoms.

#### 2.1.2. Synthesis of Ir<sub>3</sub>(CO)<sub>8</sub>(PPh<sub>3</sub>)(μ<sub>3</sub>-Bi), **3**

24.00 mg (0.023 mmol) of **1** was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. 6.00 mg (0.023 mmol) of PPh<sub>3</sub> 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<sub>3</sub>(CO)<sub>8</sub>(PPh<sub>3</sub>)(μ<sub>3</sub>-Bi), **3** (56% yield). Spectral data for **3**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) 2073(m), 2041 (vs), 2018 (s), 2007 (m); <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ = -8.54 ppm (s, 1 PPh<sub>3</sub>) Mass Spec. ES (positive)/MS for **3**: *m/z* = 1272 (M<sup>+</sup>). The isotope distribution pattern is consistent with the presence of three iridium atoms and one bismuth atom.

#### 2.1.3. Synthesis of Ir<sub>3</sub>(CO)<sub>7</sub>(PPh<sub>3</sub>)<sub>2</sub>(μ<sub>3</sub>-Bi), **4**

A 13.0 mg (0.050 mmol) portion of PPh<sub>3</sub> 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<sub>3</sub>(CO)<sub>7</sub>(PPh<sub>3</sub>)<sub>2</sub>(μ<sub>3</sub>-Bi), **4**, (83% yield). Spectral data for **4**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) 2046(m), 2014(s), 1984 (s), 1952 (vw); <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ = -11.13 ppm (s, 2 PPh<sub>3</sub>). ES (positive)/MS for **4**: *m/z* = 1506 (M<sup>+</sup>). The isotope distribution pattern is consistent with the presence of three iridium atoms and one bismuth atom.

#### 2.1.4. Synthesis of Ir<sub>3</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>3</sub>(μ<sub>3</sub>-Bi), **5**

A 17.0 mg (0.065 mmol) portion of PPh<sub>3</sub> 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 Ir<sub>3</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>3</sub>(μ<sub>3</sub>-Bi), **5** (73% yield). Spectral data for **5**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) 2006(m), 1973(vs), 1951 (s); <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ = -4.96 ppm (s, 3 PPh<sub>3</sub>) ES (positive)/MS for **5**: *m/z* = 1740 (M<sup>+</sup>). The isotope distribution pattern is consistent with the presence of three iridium atoms and one bismuth atom.

#### 2.1.5. Synthesis of Ir<sub>6</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)(μ<sub>3</sub>-Bi)(μ<sub>4</sub>-Bi)<sub>3</sub>, **6**

A 12.0 mg (0.046 mmol) portion of PPh<sub>3</sub> 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 Ir<sub>6</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)(μ<sub>3</sub>-Bi)(μ<sub>4</sub>-Bi)<sub>3</sub>, **6** (69% yield). Spectral data for **6**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) 2062 (w), 2027(s), 2008 (m), 1983 (w). <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ = -27.35 ppm (s, 1 PPh<sub>3</sub>) ES (negative)/MS for **6**: *m/z* = 2205 (M + Cl<sup>-</sup>). The isotope distribution pattern is consistent with the presence of six iridium atoms and two bismuth atoms.

#### 2.1.6. Synthesis of Ir<sub>3</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)(μ-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(μ-H)(μ<sub>3</sub>-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 Ir<sub>3</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)(μ-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(μ-H)(μ<sub>3</sub>-Bi), **7** (87% yield). Spectral data for **7**: IR ν<sub>CO</sub> (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) 2039 (m), 2016(vs), 1988 (s), 1948 (w). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = -19.78 (d, 1H, J<sub>P-H</sub> = 9 Hz), 7.54–7.10 ppm (m, 25H, phenyls on PPh<sub>3</sub> and PPh<sub>2</sub>), 5.90 (t d, 1H, H<sub>52</sub>, <sup>3</sup>J<sub>P-H</sub> = 9 Hz, <sup>3</sup>J<sub>H-H</sub> = 7 Hz), 6.69 (d of t, 1H, H<sub>53</sub>, <sup>3</sup>J<sub>H-H</sub> = 7 Hz), 6.93 (dt, 1H, H<sub>54</sub>, <sup>3</sup>J<sub>H-H</sub> = 7 Hz), 7.70 (d of d, 1H, H<sub>55</sub>, <sup>3</sup>J<sub>H-H</sub> = 6.4 Hz). <sup>31</sup>P {<sup>1</sup>H} NMR

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