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# Mixed-metal cluster chemistry. 37. Syntheses, structural, spectroscopic, electrochemical, and optical power limiting studies of tetranuclear molybdenum–iridium clusters<sup>☆</sup>

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Dedicated to Professor Jack Lewis, a cluster chemist par excellence.

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## ABSTRACT

Tetrahedral  $\text{Mo}_2\text{Ir}_2(\mu_3\text{-CO})(\mu\text{-CO})_5(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2$  (**1**) reacted with  $\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3$ ,  $\text{P}(\text{C}_6\text{H}_2\text{Me}_2\text{-3,5-OMe-4})_3$ , and  $\text{AsPh}_3$  to afford the substitution products  $\text{Mo}_2\text{Ir}_2(\mu\text{-CO})_3(\text{CO})_6(\text{L})(\eta^5\text{-C}_5\text{H}_5)_2$  [ $\text{L} = \text{P}(\text{C}_6\text{H}_4\text{Me-4})_3$  (**3**),  $\text{P}(\text{C}_6\text{H}_2\text{Me}_2\text{-3,5-OMe-4})_3$  (**4**),  $\text{AsPh}_3$  (**5**)] in fair to good yields, while reaction of **1** with  $\text{HC}\equiv\text{CSiPr}^t_3$  proceeded by insertion into the Mo–Mo bond to give the pseudo-octahedral  $\text{Mo}_2\text{Ir}_2(\mu_4\text{-}\eta^2\text{-HC}_2\text{SiPr}^t_3)(\mu\text{-CO})_4(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2$  (**6**) in fair yield. While  $\text{MoIr}_3(\mu\text{-CO})_3(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)$  reacted with  $\text{HC}\equiv\text{CSiMe}_3$  to give a complex mixture of thus-far-uncharacterized products, its phosphine substitution product  $\text{MoIr}_3(\mu\text{-CO})_3(\text{CO})_5(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$  reacted with the same alkyne via insertion into a Mo–Ir bond to afford the pseudo-octahedral  $\text{MoIr}_3(\mu_4\text{-}\eta^2\text{-HC}_2\text{SiMe}_3)(\mu\text{-CO})_3(\text{CO})_4(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$  (**8**) in good yield. Clusters **4**, **5** (two isomers), **6** and **8** have been characterized by single-crystal X-ray diffraction studies. Cyclic voltammetric studies of  $\text{Mo}_2\text{Ir}_2(\mu\text{-CO})_3(\text{CO})_6(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)_2$  (**2**), **3–6** and **8** confirmed the tuning of redox potentials upon phosphines/arsine introduction and alkyne modification. IR spectroelectrochemical studies of **2**, **6**, and **8** suggest decreasing proclivity for bridging carbonyl ligands following oxidation. Variable temperature  $^{31}\text{P}$  NMR studies of **3** and **4** revealed interconverting isomers in solution, the structures of which are assigned as analogues of the X-ray diffraction-confirmed isomers of **5**. Studies of **2–5** using ns pulses and the open-aperture Z-scan technique revealed that all are optical limiters at wavelengths in the visible region.

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## 1. Introduction

Pioneering studies carried out by the Lewis group and others in the 1960s and 1970s established metal carbonyl cluster chemistry as a vibrant research field, unveiling a diverse array of structures, bonding modes, and reactivity patterns with these aesthetically appealing species [1,2]. The majority of the early reports focused on homonuclear clusters, because these are frequently accessible by simple thermolyses of low-nuclearity or mononuclear precursors. The somewhat later growth of mixed-metal cluster chemistry followed the development of rational routes to heteronuclear clusters

[3–5], the resultant complexes possessing several interesting features (e.g. polar M–M' linkages that potentially facilitate organic substrate activation, differing metal centres that can “select” for specific reagents, and the possibility of such species either functioning as homogeneous heterobimetallic catalysts or precursors to heterogeneous heterobimetallic catalysts with precise control of the metal disposition) [6].

We have previously reported studies of the phosphine and alkyne chemistry of the tetrahedral molybdenum–iridium carbonyl clusters  $\text{MoIr}_3(\mu\text{-CO})_3(\text{CO})_7(\eta^5\text{-C}_5\text{H}_5)$  and  $\text{Mo}_2\text{Ir}_2(\mu_3\text{-CO})(\mu\text{-CO})_5(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2$  and related clusters possessing varying degrees of cyclopentadienyl alkylation [7–16]. In continuing studies of this system, we report, inter alia, alkyne chemistry at a phosphine-substituted cluster that proceeds via a differing pathway to its non-phosphine-substituted analogue, electrochemical studies of phosphine- and alkyne-functionalized derivatives confirming that cluster electron richness can be tuned systematically, spectroelectrochemical studies

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revealing that oxidation disfavours bridging carbonyls in this system, and Z-scan studies of systematically-substituted examples that explore the impact of phosphine ligation on optical limiting merit.

## 2. Experimental

### 2.1. General experimental conditions and starting materials

Reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, although no special precautions were taken to exclude air in the work-ups. Reactions were monitored regularly by IR spectroscopy to ensure consumption of the starting cluster. Dichloromethane used in reactions was AR grade and distilled over CaH<sub>2</sub> under nitrogen. All other solvents and other reagents were obtained commercially and were used as received. Petrol refers to a fraction of boiling range 60–80 °C. Cluster products were purified by preparative thin-layer chromatography (TLC) on 20 × 20 cm glass plates coated with Merck GF<sub>254</sub> silica gel (0.5 mm). Analytical TLC was conducted on aluminum sheets coated with 0.25 mm Merck GF<sub>254</sub> silica gel. Literature procedures were used to synthesize Mo<sub>2</sub>Ir<sub>2</sub>(μ<sub>3</sub>-CO)(μ-CO)<sub>5</sub>(CO)<sub>4</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**1**) [7], MoIr<sub>3</sub>(μ-CO)<sub>3</sub>(CO)<sub>8</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) [17], Mo<sub>2</sub>Ir<sub>2</sub>(μ-CO)<sub>3</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**2**), and MoIr<sub>3</sub>(μ-CO)<sub>3</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) (**7**) [8]. P(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>, P(C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>-3,5-OMe-4)<sub>3</sub>, AsPh<sub>3</sub>, HC≡CSiMe<sub>3</sub>, and HC≡CSiPr<sub>3</sub> were obtained commercially and were used as received.

### 2.2. Instrumentation

Infrared spectra were recorded on PerkinElmer System 2000 and PerkinElmer Spectrum One FT-IR spectrometers using a CaF<sub>2</sub> solution cell and AR grade CH<sub>2</sub>Cl<sub>2</sub> solvent; spectral features are reported in cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded on a Bruker Ascend-400 spectrometer at 400 MHz in CDCl<sub>3</sub> (Cambridge Isotope Laboratories) and referenced to non-deuterated solvent (δ 7.26). Variable-temperature <sup>31</sup>P NMR spectra were recorded on a Bruker Ascend-400 spectrometer at 162 MHz, Varian Inova-500 spectrometer at 202 MHz, or a Bruker Avance spectrometer at 324 MHz in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> or toluene-*d*<sub>8</sub>. Unit resolution and high-resolution ESI mass spectra were recorded on a Micromass-Waters LC-ZMD single quadrupole liquid chromatograph-MS instrument, and are reported in the form: *m/z* (assignment, relative intensity). Microanalyses were carried out at the School of Human Sciences, Science Centre, London Metropolitan University, UK. Cyclic voltammograms were recorded at room temperature using an EA161 potentiostat and e-corder from eDAQ Pty Ltd, with 1 mm diameter platinum disk working, platinum wire auxiliary, and Ag/AgCl reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.56 V (*i*<sub>pc</sub>/*i*<sub>pa</sub> = 1; Δ*E*<sub>p</sub> = 0.09 V). Scan rates were typically 100 mV s<sup>-1</sup>. Solutions contained 0.1 M (NBu<sub>4</sub>)PF<sub>6</sub> and ca. 10<sup>-3</sup> M complex in dried, distilled dichloromethane, and were deoxygenated and maintained under a nitrogen atmosphere. IR spectroelectrochemical data were recorded on a PerkinElmer Frontier FT-IR spectrometer. Solutions were made up using 0.3 M (NBu<sub>4</sub>)PF<sub>6</sub> in dried and distilled dichloromethane. Solution spectra of the oxidized species were obtained at 298 K by electrogeneration with an applied potential of 700 mV in an optically transparent thin-layer electrochemical (OTTLE) cell.

### 2.3. Synthesis of Mo<sub>2</sub>Ir<sub>2</sub>(μ-CO)<sub>3</sub>(CO)<sub>6</sub>{P(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**3**)

P(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub> (2.9 mg, 9.5 μmol) was added to an orange solution of Mo<sub>2</sub>Ir<sub>2</sub>(μ<sub>3</sub>-CO)(μ-CO)<sub>5</sub>(CO)<sub>4</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**1**, 9.2 mg, 9.3 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the resultant mixture was stirred for 23 h. The solution was taken to dryness in vacuo, and the crude residue dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and applied to

a preparative silica TLC plate. Elution with CH<sub>2</sub>Cl<sub>2</sub>/petrol (9:1) afforded 1 band (R<sub>f</sub> = 0.8, dark orange). Extraction with CH<sub>2</sub>Cl<sub>2</sub> and reduction of the solvent volume afforded a brown solid identified as Mo<sub>2</sub>Ir<sub>2</sub>(μ-CO)<sub>3</sub>(CO)<sub>6</sub>{P(C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**3**) (6.5 mg, 5.1 μmol, 56%). IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2037 s, 1991 vs, 1953 vw, 1915 s, 1857 m, 1823 m, 1746 m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.15–7.22 (m, 12H, C<sub>6</sub>H<sub>4</sub>), 4.67 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 2.39 (s, 9H, Me). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 273 K): δ 14.5, 2.9. MS (ESI): calculated, C<sub>40</sub>H<sub>32</sub>Ir<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub>P, 1268.9151 ([M + H]<sup>+</sup>); found, 1268.9164 ([M + H]<sup>+</sup>, 5). Analysis calculated for C<sub>40</sub>H<sub>31</sub>Ir<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub>P: C 38.04, H 2.57%; found, C 38.14, H 2.51%.

### 2.4. Synthesis of Mo<sub>2</sub>Ir<sub>2</sub>(μ-CO)<sub>3</sub>(CO)<sub>6</sub>{P(C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>-3,5-OMe-4)<sub>3</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**4**)

P(C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>-3,5-OMe-4)<sub>3</sub> (4.2 mg, 9.6 μmol) was added to an orange solution of Mo<sub>2</sub>Ir<sub>2</sub>(μ<sub>3</sub>-CO)(μ-CO)<sub>5</sub>(CO)<sub>4</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**1**, 9.3 mg, 9.4 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the resultant mixture was stirred for 24 h. The solution was taken to dryness in vacuo, and the crude residue dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and applied to a preparative silica TLC plate. Elution with CH<sub>2</sub>Cl<sub>2</sub>/petrol (9:1) afforded 2 bands. The contents of the first band (R<sub>f</sub> = 0.8, orange) were identified as unreacted **1** (1.3 mg, 1.3 μmol, 14%). The contents of the second band (R<sub>f</sub> = 0.6, dark orange) were identified as Mo<sub>2</sub>Ir<sub>2</sub>(μ-CO)<sub>3</sub>(CO)<sub>6</sub>{P(C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>-3,5-OMe-4)<sub>3</sub>}(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**4**) (6.8 mg, 4.9 μmol, 52%). IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2038 s, 1992 vs, 1954 vw, 1915 s, 1854 m, 1820 m, 1745 m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.98–7.08 (m, 6H, C<sub>6</sub>H<sub>2</sub>), 4.74 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 3.73 (s, 9H, OMe), 2.23 (s, 18H, Me). <sup>31</sup>P NMR (toluene-*d*<sub>8</sub>, 273 K): δ 13.5, -0.7. MS (ESI): calculated, C<sub>46</sub>H<sub>44</sub>Ir<sub>2</sub>Mo<sub>2</sub>O<sub>12</sub>P, 1400.9937 ([M + H]<sup>+</sup>); found, 1400.9908 ([M + H]<sup>+</sup>, 5). Analysis calculated for C<sub>46</sub>H<sub>43</sub>Ir<sub>2</sub>Mo<sub>2</sub>O<sub>12</sub>P: C 39.60, H 3.10%; found, C 39.48, H 2.99%.

### 2.5. Synthesis of Mo<sub>2</sub>Ir<sub>2</sub>(μ-CO)<sub>3</sub>(AsPh<sub>3</sub>)(CO)<sub>6</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**5**)

AsPh<sub>3</sub> (2.6 mg, 8.5 μmol) was added to an orange solution of Mo<sub>2</sub>Ir<sub>2</sub>(μ<sub>3</sub>-CO)(μ-CO)<sub>5</sub>(CO)<sub>4</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**1**, 7.9 mg, 8.0 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and the resultant mixture was stirred for 16 h. The solution was taken to dryness in vacuo, and the crude residue dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and applied to a preparative silica TLC plate. Elution with CH<sub>2</sub>Cl<sub>2</sub> afforded 1 band (R<sub>f</sub> = 0.9, dark orange). Extraction with CH<sub>2</sub>Cl<sub>2</sub> and reduction of the solvent volume afforded a brown solid identified as Mo<sub>2</sub>Ir<sub>2</sub>(μ-CO)<sub>3</sub>(AsPh<sub>3</sub>)(CO)<sub>6</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**5**) (3.8 mg, 3.0 μmol, 38%). Two isomers, **5a** and **5b**, crystallized simultaneously and could not be separated. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2037 s, 1990 vs, 1951 vw, 1918 m, 1861 m, 1826 m, 1747 m cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 7.38–7.45 (m, 15H, Ph), 4.81 (s, 10H, C<sub>5</sub>H<sub>5</sub>). MS (ESI): calculated, C<sub>37</sub>H<sub>25</sub>Ir<sub>2</sub>Mo<sub>2</sub>NaO<sub>9</sub>, 1288.7932 ([M + Na]<sup>+</sup>); found, 1288.7936 ([M + Na]<sup>+</sup>, 6). Insufficient material precluded microanalysis.

### 2.6. Synthesis of Mo<sub>2</sub>Ir<sub>2</sub>(μ<sub>4</sub>-η<sup>2</sup>-HC<sub>2</sub>SiPr<sub>3</sub>)(μ-CO)<sub>4</sub>(CO)<sub>4</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**6**)

HC≡CSiPr<sub>3</sub> (0.01 mL, 89 μmol) was added to an orange solution of Mo<sub>2</sub>Ir<sub>2</sub>(μ<sub>3</sub>-CO)(μ-CO)<sub>5</sub>(CO)<sub>4</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**1**, 16.0 mg, 16.1 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and the resultant mixture was refluxed for 23 h. The solution was taken to dryness in vacuo, and the crude residue dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and applied to a preparative silica TLC plate. Elution with CH<sub>2</sub>Cl<sub>2</sub>/petrol (1:1) afforded 7 bands. The contents of the sixth band (R<sub>f</sub> = 0.2, blue green) were identified as Mo<sub>2</sub>Ir<sub>2</sub>(μ<sub>4</sub>-η<sup>2</sup>-HC<sub>2</sub>SiPr<sub>3</sub>)(μ-CO)<sub>4</sub>(CO)<sub>4</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> (**6**) (4.5 mg, 4.0 μmol, 25%). IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2072 s, 2036 vs, 2013 w, 1991 sh, 1812 br, 1765 br cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 9.78 (s, 1H, HC<sub>2</sub>), 5.36 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 1.25 (m, 21H, SiPr<sub>3</sub>). MS (ESI): calculated, C<sub>29</sub>H<sub>33</sub>Ir<sub>2</sub>Mo<sub>2</sub>O<sub>8</sub>Si, 1118.9312 ([M + H]<sup>+</sup>); found, 1118.9330 ([M + H]<sup>+</sup>, 1). Insufficient material precluded microanalysis.

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