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# High nuclearity iridium clusters derived from the transformation of $[Ir_4(CO)_{11}(PPh_2CI)]$ on silica gel and the thermolysis of $[HIr_4(CO)_{10}(\mu-PPh_2)]$ ; synthesis and characterization of $[Ir_6(\mu-CO)$ $(CO)_{12}(\mu-PPh_2)_2]$ , $[Ir_7(\mu-CO)(CO)_{13}(\mu-PPh_2)$ $(\mu_3-PPhC_6H_4)]$ and $[Ir_8(\mu-CO)_2$ $(CO)_{14}(\eta^1-Ph)(\mu-PPh_2)(\mu_4-PPh)]^{\dagger}$

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**Abstract**—The monosubstituted compound  $[Ir_4(CO)_{11}(PPh_2Cl)]$  reacts on silica gel to give  $[HIr_4(CO)_{10}(\mu-PPh_2)]$  and the novel compounds  $[Ir_4(CO)_{11}(PPh_2OH)]$  and  $[Ir_6(\mu-CO)(CO)_{12}(\mu-PPh_2)_2]$  whose relative yields (up to 75, 10 and 40%, respectively) depend on cluster loading and the polarity of the eluent. The molecular structure of the hexanuclear compound was established by an X-ray analysis and consists of an octahedron of iridium atoms with two diphenylphosphido groups symmetrically bridging two non consecutive edges. Thermolysis of  $[HIr_4(CO)_{10}(\mu-PPh_2)]$  in THF results in the formation of the same hexanuclear compound (up to 40%), together with  $[Ir_7(\mu-CO)(CO)_{13}(\mu-PPh_2)(\mu_3-PPhC_6H_4)]$  (10%) and  $[Ir_8(\mu-CO)_2(CO)_{14}(\eta^1-Ph)(\mu-PPh_2)(\mu_4-PPh)]$  (40%), depending on the reaction conditions; their molecular structures were determined by X-ray analyses. The heptanuclear compound exhibits a capped octahedral metal frame with a diphenyl-phosphido and a phenyl orthometallated phosphido ligands bridging two opposite equatorial edges of the octahedron; the octanuclear cluster exhibits a fused octahedron-square based pyramid metal atom arrangement with the phosphinedene ligand bonded to the square face of the pyramid and the phosphido group to one of the edges of the octahedron. Possible mechanisms for the formation of these high nuclearity clusters are discussed. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: high nuclearity clusters; iridium; synthesis; thermolysis.

Surface mediated cluster synthesis has emerged in recent years as an extremely efficient and selective alternative to the established synthetic routes [1] involving vacuum pyrolysis, thermolysis and reduction of preformed carbonyls [2]. The selectivity of surface mediated syntheses is controlled by the choice of the inorganic oxide that plays the role of the solvent in conventional syntheses. A number of high nuclearity iridium clusters, which were previously obtained from the reduction of  $[Ir_4(CO)_{12}]$ , e.g.  $[Ir_6(CO)_{15}]^{2-}$  [3,4],  $[Ir_8(CO_{22}]^{2-}$  [5], have been produced by reductive carbonylation of  $[Ir_4(CO)_{12}]$  adsorbed on MgO surfaces [6,7]. Similarly, neutral carbonyl Ir, Rh, Os and Ru clusters have been synthesized from the reductive carbonylation of supported halide precursors on SiO<sub>2</sub> [1].

Transformations of cluster compounds on silica gel

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or alumina during purification have been described [8] and are certainly much more common than suggested by literature reports. To our knowledge, however, not a single case involving cluster build-up has been reported so far. This report describes our studies involving the synthesis and transformation of  $[Ir_4(CO)_{11}(PPh_2CI)]$  on silica gel plates to give the novel compound  $[Ir_6(\mu$ -CO)(CO)\_{12}( $\mu$ -PPh\_2)\_2], and an alternative route to this compound and to  $[Ir_7(\mu$ -CO)(CO)\_{13}( $\mu$ -PPh\_2)( $\mu_3$ -PPhC\_6H\_4)] (10%) and  $[Ir_8(\mu$ -CO)\_2(CO)\_{14}( $\eta^1$ -Ph)( $\mu$ -PPh\_2)-( $\mu_4$ -PPh)] (up to 40%), via thermolysis of  $[HIr_4(CO)_{10}(\mu$ -PPh\_2)].

### **RESULTS AND DISCUSSION**

Synthesis and characterisation of  $[\mathrm{Ir}_4(\mathrm{CO})_{11}(\mathrm{PPh}_2\mathrm{Cl})],$  3a

The cluster compound  $[Ir_4(CO)_{12}]$ , 1, reacts with equivalent amounts of Bu4NBr and PPNCl in refluxing THF to yield Bu<sub>4</sub>N[Ir<sub>4</sub>(CO)<sub>11</sub>Br], 2a, and PPN[Ir<sub>4</sub>  $(CO)_{11}Cl$ ], **2b**, respectively, in quantitative yields [9]. The reactions of 2a and 2b with 1 equivalent of PPh<sub>2</sub>Cl in CH<sub>2</sub>Cl<sub>2</sub> or acetone at room temperature lead to an immediate colour change from orange to yellow, and formation of [Ir<sub>4</sub>(CO)<sub>11</sub>(PPh<sub>2</sub>Cl)], **3a**, as evidenced by IR and <sup>31</sup>P NMR spectroscopies. If these reaction mixtures are left stirring, however, precipitation of 1 starts to occur, after 10 min. These reactions were monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy in CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>, for 4 h under atmospheres of Ar and CO. The spectra of the mixtures under Ar, just after the addition of PPh<sub>2</sub>Cl to 2a and 2b, showed only a very strong peak at  $\delta$  35.2 (s) attributed to **3a** and a weak broad peak at  $\delta$  -33.3, attributed to  $[Ir_4(CO)_{10}(PPh_2Cl)_2]$ , 4. A decrease in the concentration of 3a, concomitant with an increase in that of 4, was noted during the first hour, but no substantial change was evidenced during the next 3 h. Furthermore, no additional peaks were observed in the spectra of the supernatants of either reaction mixtures. Under an atmosphere of CO, the process occurred more rapidly, and the  $^{31}P\{^1H\}$  NMR spectra of the supernatants of both reaction mixtures showed only the presence of 4, after 30 min. Further precipitation of 1 and darkening of the solutions were observed after longer periods of time, in the absence of CO, due to the decomposition of 4 into unidentified species.

In order to investigate whether the presence of PPNCl or  $Bu_4NBr$  was necessary for the formation of **1** and **4**, pure samples of **3a** were left stirring in  $CH_2Cl_2/CDCl_3$  under Ar and under CO for 4 h, during which time precipitation of **1** was not noted and the  ${}^{31}P{}^{1}H$  NMR spectrum of **3b** stayed unchanged. It is well known that PPNCl catalyses CO substitution by nucleophiles in ruthenium carbonyl clusters [10]. In our case, however, the halide seems to be catalysing

the substitution, not only of a CO, but also of a  $PPh_2Cl$  ligand, according to the following equations:

$$\begin{split} [Ir_4(CO)_{11}(PPh_2Cl)], & 3a + X^- \rightarrow \\ & ``[Ir_4(CO)_{10}(PPh_2Cl)X]^{-}`' + CO \\ [Ir_4(CO)_{11}(PPh_2Cl)], & 3a + X^- \rightarrow \\ & ``[Ir_4(CO)_{11}X]^{-}`' + PPh_2Cl \\ ``[Ir_4(CO)_{10}(PPh_2Cl)X]^{-}`' + PPh_2Cl \rightarrow \\ & [Ir_4(CO)_{10}(PPh_2Cl)_2], & 4 + X^- \\ & ``[Ir_4(CO)_{11}X]^{-}`' + CO \rightarrow [Ir_4(CO)_{12}], & 1 + X^- \end{split}$$

 $X = Br^{-} \text{ or } Cl^{-}$ 

The process is driven by the precipitation of **1** and occurs, most probably, as a result of the high lability of the PPh<sub>2</sub>Cl ligand. By comparison, reaction of the analogous compound  $[Ir_4(CO)_{11}(PPh_2Me)]$  with PPNCl occurs only under much harsher conditions (THF, reflux, 3 h), to yield PPN[Ir\_4(CO)\_{10} (PPh\_2Me)Cl], and is readily reversed in the presence of CO, without formation of **1** [11]. In fact, labilization of ligands other than CO in the presence of halides has not yet been observed in tetranuclear iridium systems.

#### Study of the behaviour of **3a** on TLC plates

Purification of 3a by TLC was only possible if performed under specific conditions, such as very low cluster loading, quick elution of the compound and extraction from the plates, as soon as it separates out from the base line. Under the chromatographic conditions normally employed for the purification of the PR<sub>3</sub>, PR<sub>2</sub>H and PRH<sub>2</sub> derivatives of 1 [12a] (~20 mg of the compound per plate,  $CH_2Cl_2$ : hexane 1:4 as eluent), the mixture reacted on the silica gel to give three products, which separated out, and whose yields (based on 1) were extremely sensitive to cluster loading and to the polarity of the eluent. Low cluster loading (10 mg/plate) and solvent polarity (CH<sub>2</sub>Cl<sub>2</sub>/hexane 1.5:8.5) yielded the novel yellow compound  $[Ir_4(CO)_{11}(PPh_2OH)]$ , **3b** (10%) and the known orange species  $[HIr_4(CO)_{10}(\mu-PPh_2)]$  [12b], 5 in high yields (75%). This compound was previously obtained from  $[Ir_4(CO)_{10}(PPh_2H)]$ , 3c, upon deprotonation and protonation of the resulting anion  $[Ir_4(CO)_{10}(\mu$ -PPh<sub>2</sub>)]<sup>-</sup>, in 85% yield, based on 1. High cluster loading (40 mg/plate) and solvent polarity  $(CH_2Cl_2/hexane 3:7)$ , however, resulted in the darkening of the reaction mixture on the plates and separation of 5 (10%), 3b (10%) and of the dark brown species  $[Ir_6(\mu-CO)(CO)_{12}(\mu-PPh_2)_2]$ , 6 (40%), see Scheme 1.

Interestingly, compounds **3b**, **5** and **6** were formed in small amounts, when an excess silica gel for TLC was added to solutions of **3a** in  $CH_2Cl_2/CDCl_3$ , both



in the presence and in the absence of PPNCl or  $Bu_4NBr$ , and the mixtures were left stirring under Ar or in air for 1 h, as shown by <sup>31</sup>P NMR spectroscopy.

Quantitative formation of **3b** was shown to occur, by <sup>31</sup>P NMR spectroscopy, upon addition of degassed water to a solution of **3a** in CH<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub>. Furthermore, this compound is stable on TLC plates, and therefore, it must result from the reaction of **3a** with the silica gel surface water. This process is related to the previously reported hydrolysis of the aminophosphinidene ligand of [Ru<sub>4</sub>(CO)<sub>12</sub>( $\mu_3$ -P(NPr<sup>i</sup><sub>2</sub>)<sub>2</sub>)] absorbed onto silica that yields [Pr<sup>i</sup><sub>2</sub>NH<sub>2</sub>] [Ru<sub>4</sub>(CO)<sub>12</sub>( $\mu_3$ -P=O]], possibly via formation of the hydroxyphosphinidene cluster [Ru<sub>4</sub>(CO)<sub>12</sub>( $\mu_3$ -POH)] [13].

The transformation of 3a into 5 and 6 has not been investigated under conditions that would discount the importance of the water and oxygen in their formation, so we can only speculate about the possible reactions of 3a on the silica gel surface that might be involved in the formation of these species. Thus, electrophilic attack of the silanol group at the P—Cl bond of the PPh<sub>2</sub>Cl coordinated ligand in 3a and elimination of HCl would result in the formation of the [Ir<sub>4</sub>(CO)<sub>11</sub>(PPh<sub>2</sub>OSi≡)] species. Also, oxidative addition of surface silanol groups at an Ir—Ir bond, as with [M<sub>3</sub>(CO)<sub>12</sub>] (M = Ru and Os), from which [( $\mu$ -H)M<sub>3</sub>(CO)<sub>10</sub>OSi≡] are formed on silica surface [14], would result in species such as [( $\mu$ -H)Ir<sub>4</sub> (CO)<sub>10</sub>(OSi≡)(PPh<sub>2</sub>CI)]. Both reactions are favoured on highly hydroxilated surfaces. In addition, oxidation of these species and of **3a** (and possibly **4**) may also occur, with the generation of reactive fragments, whose combination would be favoured by the high cluster concentration on the plates, to generate the hexanuclear cluster **6**.

#### Characterisation of [Ir<sub>4</sub>(CO)<sub>11</sub>(PPh<sub>2</sub>OH)], **3b**

The formulation of compound **3b** was based on spectroscopic and analytical data (see Table 1), as crystals suitable for an X-ray analysis could not be obtained. The hydroxil proton of **3b** appears at  $\delta$  3.1,  $J_{P-H} = 13$  Hz in the <sup>1</sup>H NMR spectrum, at 233 K. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3b** in CD<sub>2</sub>Cl<sub>2</sub>, at 295 K, consists of a broad singlet at  $\delta$  72.3. On cooling to 233 K, two signals are resolved at  $\delta$  68.8 and 65.5 in the

2867

Compounds	$^{31}\mathbf{P}\left\{ ^{1}\mathrm{H} ight\}$	$^{1}\mathrm{H}$
$[\mathrm{Ir}_4(\mathrm{CO})_{11}(\mathrm{PPh}_2\mathrm{OH})] \; \mathbf{3b}^a$	68.8, 65.2 (s, 1:0.03)	3.1 (d, <i>J</i> <sub>P-H</sub> 13) 7.6–7.5 (Ph, m)
$[Ir_6(\mu-CO)(CO)_{12}(\mu-PPh_2)_2]$ <b>6</b> <sup>b</sup>	127.7 s	7.6–7.2 (Ph, m)
$[Ir_7(\mu-CO)(CO)_{13}(\mu-PPh_2)(\mu_3-PPhC_6H_4)]$ 7 <sup>c</sup>	152.7 d, 253.6 d, <sup>3</sup> J <sub>P-P</sub> 4	7.6–6.7 (Ph, m)
$[Ir_{8}(\mu\text{-CO})_{2}(CO)_{14}(\eta^{1}\text{-Ph})(\mu\text{-PPh}_{2})(\mu_{4}\text{-PPh})] 8^{c}$	191.1 d, 47.0 d, ${}^{3}J_{P-P}$ 63	7.7–6.9 (Ph, m)

Table 1. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of compounds **3b** and **6–8** 

Chemical shifts in ppm, coupling constants in Hz.

 $a - 40^{\circ}$ C in CD<sub>2</sub>Cl<sub>2</sub>,

 ${}^{b}25 \text{ to } -90^{\circ}\text{C in } \text{CD}_{2}\text{Cl}_{2},$ 

<sup>c</sup> 25°C in CDCl<sub>3</sub>.

intensity ratio 1:0.03. These data indicate that **3b** exists in solution in the form of two inter-converting isomers which, by analogy with the  $[Ir_4(CO)_{11}L]$  (L = PPh<sub>3</sub>, PPh<sub>2</sub>Me, PMe<sub>3</sub>), compounds, are the C<sub>3v</sub>axial and C<sub>3v</sub>radial isomers [15].

Although to our knowledge this is the first report of a phosphinous acid derivative  $R_2POH$  stabilized by a carbonyl cluster,  $PH_2OH$  itself and some of its derivatives have been stabilized previously by P-complexation to "W(CO)<sub>5</sub>" [16].

*X-ray molecular structure of*  $[Ir_6(\mu-CO)(CO)_{12}(\mu-PPh_2)_2]$ , **6** 

Compound **6** was characterized by analytical and spectroscopic methods (see Table 1 and Experimental) and by an X-ray analysis. Crystals of **6** suitable for X-

ray crystallography were obtained from CH2Cl2/hexane. A perspective view of 6 is shown in Fig. 1, together with the labeling scheme. Selected bond distances and angles of 6 are listed in Table 2. The molecule contains an Ir<sub>6</sub> octahedral core, with eleven Ir—Ir bond distances falling in a fairly narrow range [from 2.729(1) to 2.791(1) Å]. Two diphenylphosphido ligands symmetrically bridge two non-consecutive edges belonging to two different equators of the octahedral frame. P-Ir bond distances average to 2.294(4) and 2.281(4) Å for the P(1)Ph<sub>2</sub> and P(2)Ph<sub>2</sub> ligands, respectively. Interestingly, the Ir-Ir edge, which is bridged by the closest PPh2 group also shows the shortest metal-metal bond distance in the octahedron frame. Twelve CO ligands are terminally bound, two on each metal vertex, while the thirteenth CO group symmetrically bridges one edge of the octahedron equator not substituted by the PPh<sub>2</sub> ligands.



Fig. 1. Molecular structure of  $[Ir_6(\mu$ -CO)(CO)<sub>12</sub>( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>], 6.

6		7		8	
Ir(1)— $Ir(2)$	2.736(1)	Ir(1)— $Ir(4)$	2.728(4)	Ir(1)— $Ir(2)$	2.755(2)
Ir(1) - Ir(3)	2.756(1)	Ir(1) - Ir(3)	2.788(4)	Ir(1) - Ir(3)	2.845(2)
Ir(1)— $Ir(4)$	2.792(1)	Ir(1)— $Ir(7)$	2.792(5)	Ir(1)— $Ir(4)$	2.797(2)
Ir(1)— $Ir(6)$	2.781(1)	Ir(1)— $Ir(6)$	2.811(5)	Ir(1)— $Ir(5)$	2.735(2)
Ir(2)— $Ir(4)$	2.751(1)	Ir(1)— $Ir(2)$	2.840(4)	Ir(1)— $Ir(7)$	2.770(2)
Ir(2)— $Ir(5)$	2.839(1)	Ir(2)— $Ir(7)$	2.712(5)	Ir(1)— $Ir(8)$	2.820(2)
Ir(2)—Ir(6)	2.791(1)	Ir(2)— $Ir(5)$	2.747(5)	Ir(2)— $Ir(3)$	2.799(2)
Ir(3)— $Ir(4)$	2.775(1)	Ir(2)— $Ir(3)$	2.817(4)	Ir(2)—Ir(5)	2.746(2)
Ir(3)— $Ir(5)$	2.778(1)	Ir(2)— $Ir(4)$	2.828(4)	Ir(3)— $Ir(4)$	2.787(2)
Ir(3)—Ir(6)	2.782(1)	Ir(3)—Ir(7)	2.632(5)	Ir(4)—Ir(5)	2.810(2)
Ir(4)— $Ir(5)$	2.762(1)	Ir(3)— $Ir(5)$	2.721(5)	Ir(4)—Ir(6)	2.711(2)
Ir(5)—Ir(6)	2.729(1)	Ir(3)— $Ir(6)$	2.729(5)	Ir(4)— $Ir(7)$	2.752(2)
		Ir(4)—Ir(6)	2.758(4)	Ir(5)—Ir(6)	2.752(2)
Ir(1) - P(1)	2.291(4)	Ir(4)— $Ir(5)$	2.866(4)	Ir(5)—Ir(8)	2.743(2)
Ir(3) - P(1)	2.297(4)	Ir(5)—Ir(6)	2.741(4)	Ir(6)—Ir(7)	2.817(2)
Ir(5)—P(2)	2.282(4)			Ir(6)—Ir(8)	2.752(2)
Ir(6) - P(2)	2.279(4)	Ir(2) - P(1)	2.27(2)	Ir(7)—Ir(8)	2.763(2)
		Ir(5) - P(1)	2.28(2)		
P(1)—C(70)	1.811(9)	Ir(1) - P(2)	2.33(2)	Ir(2) - P(1)	2.400(9)
P(1)—C(76)	1.830(9)	Ir(6)—P(2)	2.26(2)	Ir(3) - P(1)	2.408(9)
P(2)—C(82)	1.838(9)	Ir(4)—C(117)	2.17(3)	Ir(4) - P(1)	2.261(10)
P(2)—C(88)	1.818(10)			Ir(5) - P(1)	2.346(9)
		P(1)—C(100)	1.80(4)	Ir(6)—P(2)	2.277(9)
mean Ir—C(t)	1.86(2)	P(1)—C(106)	1.80(4)	Ir(8)—P(2)	2.266(9)
mean Ir—C(b)	2.06(2)	P(2)—C(112)	1.76(3)	Ir(3)—C(90)	2.06(4)
mean C—O	1.13(2)	P(2)—C(118)	1.79(4)		
				P(1)—C(96)	1.80(2)
		mean Ir—C(t)	1.84(4)	P(2)—C(102)	1.80(2)
		mean Ir—C(b)	1.99(10)	P(2)—C(108)	1.82(2)
		mean C—O	1.18(4)	C(90)—C(95)	1.41(5)
				C(90)—C(91)	1.44(5)
				C(91)—C(92)	1.28(6)
				C(92)—C(93)	1.50(6)
				C(93)—C(94)	1.31(6)
				C(94)—C(95)	1.37(6)
				mean Ir—C(b)	2.03(3)
				mean Ir—C(t)	1.87(3)
				mean C—O	1.13(4)

Table 2. Relevant bond lengths [Å] for 6, 7 and 8

Cluster 6 possesses 86 valence electrons, and exhibits a remarkably similar molecular geometry to those of the dianionic  $[Ir_6(\mu-CO)_3(CO)_{12}]^{2-}$  [17] and the monoanionic  $[Ir_6(\mu-CO)_2(CO)_2(\mu-PPh_2)]^-$  [18] clusters. The latter compound was recently obtained from the oxidation of  $[Ir_6(\mu-CO)_3(CO)_{12}]^{2-}$  with  $[FeCp_2]^+$ in the presence of PPh<sub>2</sub>H, followed by deprotonation of the coordinated phosphine. Two of the three bridging CO ligands in the dianionic compound are formally replaced by two 3-electron donor PPh<sub>2</sub> groups in 6, whilst  $[Ir_6(\mu-CO)_2(CO)_{12}(\mu-PPh_2)]^-$  results, formally, from the replacement of one  $\mu$ -CO in the dianion by a  $\mu$ -PPh<sub>2</sub> fragment. The steric arrangement of the remaining twelve CO ligands does not differ substantially in the three species. Average Ir-Ir bond distances compare well in 6,  $[Ir_6(\mu-CO)_2(CO)_{12}(\mu-CO)_{12}(\mu$  $PPh_2)]^-$  and  $[Ir_6(\mu-CO)_3(CO)_{12}]^{2-}$  [av. Ir—Ir

2.776(1), 2.776(1) and 2.773(1) Å, respectively] and so do the metal-carbon bond lengths [av. Ir— $C_{(COt)}$  1.86(2), 1.87(2) and 1.86(2); Ir— $C_{(COb)}$  2.06(2), 2.05(2) and 2.04(2), respectively].

In spite of the lack of symmetry of compound **6** in the solid state, the <sup>31</sup>P {<sup>1</sup>H} NMR spectrum showed a singlet at  $\delta$  127.7 from 295 to 183 K which indicates that it is fluxional at those temperatures.

#### Thermolysis of $[HIr_4(CO)_{10}(\mu-PPh_2)]$ , 5

In order to find out whether compound 6 would also be formed under thermolytic conditions, compound 5was heated in THF under reflux. After 12 h, three compounds were isolated in sufficient yields to be fully characterized by analytical and spectroscopic data and by X-ray analyses : compound **6** (40%),  $[Ir_7(\mu-CO)_2(CO)_{12}(\mu-PPh_2)(\mu_3-PPhC_6H_4)]$ , **7** (10%) and  $[Ir_8(\mu-CO)(CO)_{15}(\eta^1-Ph)(\mu-PPh_2)(\mu_4-PPh)]$  **8**, (18%), in addition to starting material **5** (18%). Heating compound **5** for an additional 12 h period did not lead to the formation of other products, but resulted in an increase in the yield of the octanuclear cluster **8** (40%) and a decrease in that of the hexanuclear compound **6** (14%), whilst that of **7** (10%) remained unchanged ; some starting material **5** (9%) was also recovered under these conditions. Furthermore, thermolysis of **5** in THF for longer periods of time, or in refluxing toluene for 12 h led to larger amounts of decomposition material on the base line of the TLC plates.

Formation of **6** might be rationalized in terms of condensation of **5** with a reactive unsaturated hydrido-phosphido fragment with loss of  $H_2$  and CO (See Scheme 2). Considering that heating compound **6** under reflux in THF for 12 h does not lead to cluster build up, it is possible that compounds **7** and **8** might result from further condensation of a monomeric and a dimeric unsaturated fragments, respectively, with **6**, accompanied by orthometallation and cleavage of a P—C<sub>Ph</sub> bond, respectively.

Formation of high nuclearity clusters from other phosphido compounds, such as  $[HRu_3(CO)_{10}(\mu-PPh_2)]$ ,  $[HRu_3(CO)_9(\mu-PPh_2)]$  [19,20],  $[H_2Ru_3(CO)_8(\mu-PPh_2)_2]$  [20] and  $[H_3Ru_3(CO)_7(\mu-PPh_2)_3]$ [20], has been shown to occur previously. Also in these cases, products resulting from the activation of P—C<sub>Ph</sub> and orthometallation were isolated. It is interesting, however, that heating  $[HM_3(CO)_{10}(\mu-PPh_2)]$ (M = Ru [20] and Os [21]) under mild conditions leads to the formation of the unsaturated compound  $[HRu_3(CO)_9(\mu-PPh_2)]$  and of the orthometallated product  $[H_2Os_3(CO)_9(\mu-PPhC_6H_4)]$ , respectively, whilst even under mild conditions, compound **5** undergoes cluster build up.

# *X-ray molecular structure of* $[Ir_7(\mu-CO)(CO)_{13}(\mu-PPh_2)(\mu_3-PPhC_6H_4)]$ , 7

The molecular structure of **7** is shown in Fig. 2. Selected bond distances are listed in Table 2. The molecule possesses 98 valence electrons, and exhibits a capped octahedron arrangement of iridium atoms, with fifteen Ir—Ir bond distances falling in the range



Scheme 2.



Fig. 2. Molecular structure of  $[Ir_7(\mu$ -CO)(CO)<sub>13</sub>( $\mu$ -PPh<sub>2</sub>)( $\mu_3$ -PPhC<sub>6</sub>H<sub>4</sub>)], 7.

from 2.632(5) to 2.866(4) Å. A diphenylphophido and a phenyl orthometallated phosphido ligands bridge two opposite equatorial edges of the octahedron. Thirteen CO ligands are terminally bound, two on six metal vertex and one on the seventh metal atom, while the fourteenth CO group symmetrically bridges the edge formed by the capping iridium atom and the iridium atom bearing only one terminal CO. The only other known heptanuclear iridium cluster,  $[Ir_7(\mu CO)(CO)_{11}(C_8H_{12})(C_8H_{11})(C_8H_{10})],$ which was obtained from the reaction of 1 with 1,5-cyclooctadiene in refluxing chorobenzene [22], exhibits a similar metal framework arrangement. The steric arrangement of the thirteen CO ligands does not differ substantially in the two species. Average Ir-Ir bond distances compare well in 7 and  $[Ir_7(\mu-CO)(CO)_{11}]$  $(C_8H_{12})(C_8H_{11})(C_8H_{10})$ ] [av. Ir—Ir 2.767(5), and 2.763(1) Å, respectively] and the same can be said for the metal-carbon bond lengths [av. Ir-C<sub>(COt)</sub> 1.84(4) and 1.86(5); Ir-C<sub>(COb)</sub> 1.99(10) and 2.04(4), respectively].

# *X-ray molecular structure of* $[Ir_8(\mu-CO)_2(CO)_{14}(\eta^1-Ph)(\mu-PPh_2)(\mu_4-PPh)]$ , **8**

Compound **8** was formulated on the basis of analytical and spectroscopic data (see Table 1 and Experimental) but an X-ray analysis experiment was necessary to establish its structure unambiguously. The molecular structure of **8** is shown in Fig. 3, together with the labeling scheme. Selected bond distances are listed in Table 2. The metal arrangement can be described as a fused polyhedron, formed by an octahedron and a square based pyramid (atoms

Ir1-Ir5) sharing a triangular face. Ir-Ir bond distances range from 2.711(2) to 2.845(2) Å. The  $\mu$ -PPh<sub>2</sub> ligand symmetrically bridges one of the edges of the octahedron. A second PPh<sub>2</sub> ligand has undergone P-C bond cleavage; the two resulting fragments, viz the phenyl ligand and the phenyl phosphinedene, bind in  $\eta^1$ -fashion to one of the basal atoms and in  $\mu_4$ fashion the four basal atoms of the square based pyramid, respectively. A similar kind of  $\mu_4$ -coordination of a PPh ligand, which donates four electrons to the metal frame, has previously been observed in the pentanuclear iridium compounds  $[Ir_5(\mu-CO)_2(CO)_7L(\eta^5 C_5Me_5(\mu_4-PPh)$ ] (L = CO, PPh<sub>3</sub>) [23]. Fourteen carbonyls are terminally bound to the iridium atoms, while the remaining two CO ligands symmetrically bridge one of the basal square pyramids and one of the octahedron edges. The only two other octanuclear iridium clusters whose structures have been determined to date are  $[Ir_8(CO)_{22}]^-$  [24] and  $[Ir_8Au_2$ (CO)<sub>20</sub>(PhPPPh)(PEt<sub>3</sub>)] [25], which exhibit bis-tetranuclear frameworks linked by an Ir-Ir bond and by the PhPPPh ligand, respectively.

#### EXPERIMENTAL

#### General procedures and materials

Iridium trichloride (Johnson and Matthey), PPNCl and Bu<sub>4</sub>NBr (Aldrich), diphenyl phosphine and chlorodiphenyl phosphine (Strem Chemicals) were used as purchased. The compounds  $[Ir_4(CO)_{12}]$  **1** [26],  $[Ir_4(CO)_{11}(PPh_2H)]$  **3c**,  $[HIr_4(CO)_{10}(\mu$ -PPh<sub>2</sub>)] **5** [12], Bu<sub>4</sub>N[Ir<sub>4</sub>(CO)<sub>11</sub>Br] **2a** and PPN[Ir<sub>4</sub>(CO)<sub>11</sub>Cl] **2b** [9] were prepared by literature methods. Manipulations



M. H. de Araujo et al.

Fig. 3. Molecular structure of  $[Ir_8(\mu-CO)_2(CO)_{14}(\eta^1-Ph)(\mu-PPh_2)(\mu_4-PPh)]$ , 8.

were performed in Schlenk tubes, under an atmosphere of dry Ar, unless otherwise specified. Solvents were dried as previously described [12] and freshly distilled under Ar and degassed before use. Preparative TLC was carried out in air by using ca 2 mm thick glass-backed silica gel plates  $(20 \times 20 \text{ cm})$ prepared from silica GF<sub>254</sub> Type 60, Fluka, and the compounds extracted from the silica with dichloromethane. All substituted Ir<sub>4</sub> cluster compounds were stored under an inert atmosphere for they were found to be slightly air sensitive in the solid state. FAB-MS were obtained on a VG AutoSpec using pnitrobenzyl alcohol as a matrix at the University of Sussex, U.K. IR spectra on a JASCO IR 700 between 2200 and 1600 cm<sup>-1</sup> using CaF<sub>2</sub> cells. <sup>1</sup>H and <sup>31</sup>P  $\{^{1}H\}$  NMR data were obtained on a Bruker AC 300 instrument, using deuterated solvents as lock and reference [<sup>1</sup>H SiMe<sub>4</sub>; <sup>31</sup>P 85% H<sub>3</sub>PO<sub>4</sub> (external)]. Microanalyses were performed at the Instituto de Química, UNICAMP, Brazil.

#### Preparation of [Ir<sub>4</sub>(CO)<sub>11</sub>(PPh<sub>2</sub>Cl)], **3a**

An orange solution of PPN[Ir<sub>4</sub>(CO)<sub>11</sub>Cl] **2b** (37.1 mg, 0.023 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) was cooled to  $-30^{\circ}$ C and treated with PPh<sub>2</sub>Cl (4.1  $\mu$ l, 0.023 mmol). The yellow reaction mixture was warmed to 25°C. Quick purification of the reaction mixture by TLC, using CH<sub>2</sub>Cl<sub>2</sub>/hexane (3:7) as eluent, taking care to load each plate with a maximum of 3 mg of **3a**, and extracting the yellow compound from the plates, just after it had separated out from the base line, gave pure **3a** (17.3 mg, 60%), IR ( $v_{CO}$  hexane) : 2084 s, 2052 vs, 2040 vs, 2030 vs, 1955 m, 1885 w, 1845 m and 1824

m, cm<sup>-1</sup>. Use of Bu<sub>4</sub>N[Ir<sub>4</sub>(CO)<sub>11</sub>Br] **2a**, instead of **2b**, gave similar yields of **3a**, under the same conditions.

Investigation of the stability of 3a in the presence of PPNCl or  $Bu_4NBr$ 

An orange solution of PPN[Ir<sub>4</sub>(CO)<sub>11</sub>Cl] **2b** (148.5 mg, 0.09 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was cooled to  $-30^{\circ}$ C and treated with PPh<sub>2</sub>Cl (16.6  $\mu$ l, 0.09 mmol). Quick warming of the reaction mixture to  $20^{\circ}$ C was followed by addition of 0.5 cm<sup>3</sup> of CDCl<sub>3</sub>. A <sup>31</sup>P {<sup>1</sup>H} NMR spectrum was recorded immediately, and every 30 min thereafter. After 10 min stirring at room temperature **1** started to precipitate, and was decanted, before each sampling. Same procedure was followed in the reaction of Bu<sub>4</sub>N[Ir<sub>4</sub>(CO)<sub>11</sub>Br], **2a** with PPh<sub>2</sub>Cl.

Investigation of the stability of 3a in the absence of PPNCl or  $Bu_4NBr$ 

Solutions of pure **3a** (20 mg, 0.016 mmol) in  $CH_2Cl_2:CDCl_3$  (0.8 cm<sup>3</sup>:0.5 cm<sup>3</sup>) were left stirring under Ar and under CO for 4 h. No precipitation of **1** was observed and the <sup>31</sup>P {<sup>1</sup>H} NMR spectra of both solutions showed only the presence of **3a**.

### Reaction of [Ir<sub>4</sub>(CO)<sub>11</sub>(PPh<sub>2</sub>Cl)] **3a** on TLC plates

*Method* 1: Low cluster loading (10 mg/plate), CH<sub>2</sub>Cl<sub>2</sub>/hexane (1.5:8.5), yielded the orange species **5** (83.5 mg, 75%), the yellow compound [Ir<sub>4</sub>(CO)<sub>11</sub> (PPh<sub>2</sub>OH)] **3b** (11.5 mg, 10%); R<sub>f</sub> 0.79, IR ( $\nu_{CO}$ hexane): 2084 s, 2052 vs, 2014 vs, 1974 vs, 1880 w, 1845 m and 1823 m cm<sup>-1</sup> and the brown compound  $[Ir_6(\mu$ -CO)(CO)<sub>12</sub>( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>] **6** (8.5 mg, 5%) R<sub>f</sub> 0.64, IR ( $v_{CO}$  hexane): 2078 s, 2050 vs, 2040 vs, 2020 wsh, 2010 s, 1993 s, 1957 w and 1842 s cm<sup>-1</sup>. Found: C, 23.2; H, 0.8. Calc. for  $C_{37}H_{20}O_{13}P_2Ir_6$ : C, 23.5; H, 1.0%. *Method* 2: High cluster loading (40 mg/plate), CH<sub>2</sub>Cl<sub>2</sub>/hexane (3:7), resulted in the separation of compounds **5** (11 mg, 10%), **3b** (11.5 mg, 10%) and **6** (68 mg, 40%).

## Reactions of 3a with silica gel

The following reactions were monitored by <sup>31</sup>P {<sup>1</sup>H} NMR spectroscopy, after stirring for 1 h at 25°C under (a) Ar and (b) air. Addition of silica gel for TLC (excess, approximately 50 mg) to three solutions containing **3a** (20 mg, 0.016 mmol) and PPNCl (1 equiv.), **3a** and Bu<sub>4</sub>NBr (1 equiv.) or pure **3a** in CH<sub>2</sub>Cl<sub>2</sub>: CDCl<sub>3</sub> (2 cm<sup>3</sup>: 1 cm<sup>3</sup>) led to the formation of compounds **3b**, **5** and **6** in trace amounts.

### Reaction of 3a with $H_2O$

Addition of H<sub>2</sub>O (50  $\mu$ l, 2.85 mmol) to a solution of **3a** (10 mg, 0.008 mmol) in CH<sub>2</sub>Cl<sub>2</sub>: CDCl<sub>3</sub> (4 cm<sup>3</sup>: 1 cm<sup>3</sup>) led to quantitative formation of [Ir<sub>4</sub>(CO)<sub>11</sub> (PPh<sub>2</sub>OH)] **3b**, confirmed by  ${}^{31}P \{{}^{1}H\}$  NMR spectroscopy.

#### Thermolysis of 5

A solution of compound 5 (100 mg, 0.08 mmol) in THF (20 cm<sup>3</sup>) was heated under reflux for 12 h. The solvent was evaporated, the mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) and purified by TLC with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5) as eluent, to yield : compounds 6 ( $R_f 0.51, 60$ mg, 40%);  $[Ir_7(\mu-CO)_2CO)_{12}(\mu-PPh_2)(\mu_3-PPhC_6H_4)]$  7  $(R_f 0.58, 17 \text{ mg}, 10\%), IR (v_{CO} \text{ hexane}) : 2074 \text{ m}, 2046$ s, 2040 vs, 2022 m, 2006 w, 1993 w and 1850 w, cm<sup>-1</sup>; and  $[Ir_8(\mu-CO)(CO)_{15}(\eta^1-Ph)(\mu-PPh_2)(\mu_4-PPh)]$  8 (R<sub>f</sub> 0.40, 28 mg, 15%): IR ( $v_{CO}$  hexane): 2076 s, 2048 vs, 2038 vs, 2008 m, 1991 m, 1955 m and 1840 s, cm<sup>-1</sup>; Found: C, 20.2; H, 0.6. Calc. for C<sub>40</sub>H<sub>20</sub>O<sub>16</sub>P<sub>2</sub>Ir<sub>8</sub>: C, 20.4; H, 0.8%. FAB-MS m/z = 2362 (=M) [Mn(CO)] (n = 1-16); three brown species ( $R_f 0.24, 0.29$ , 0.62) in minute amounts and unreacted 5 (18 mg, 18%).

The thermolysis of compound **5** was repeated (a) under the same conditions but for 24 h, and gave the same three products, **6** (10 mg, 14%), **7** (8 mg, 10%) and **8** (37 mg, 40%), and unreacted **5** (4 mg, 9%); (b) in toluene under reflux for 12 h, and produced the

Compound	6	7	8
Formula	$C_{37}H_{20}Ir_6O_{13}P_2$	$C_{38}H_{19}Ir_7O_{14}P_2$	$C_{40}H_{20}Ir_8O_{16}P_2$
Formula weight	1875.67	2092.87	2340.10
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	$P2_1/c$
<i>a</i> (Å)	13.090(2)	9.874 (8)	19.394 (7)
b (Å)	15.707 (3)	11.347 (4)	13.427 (5)
<i>c</i> (Å)	10.665(3)	19.332 (6)	20.681 (9)
α (°)	103.52(2)	93.88 (3)	90
β(°)	92.19(2)	92.66 (4)	117.06(3)
γ (°)	77.420 (10)	90.10(4)	90
$V(Å^3)$	2080.6 (8)	2159 (2)	4796 (3)
T (K)	293 (2)	293 (2)	293 (2)
$D_{\text{calcd}} (\text{mg m}^{-3})$	2.994	3.220	3.241
Z	2	2	4
F (000)	1676	1856	4136
$\lambda$ (Mo- $K_{\alpha}$ ), Å	0.71069	0.71069	0.71069
Absorption coefficient (mm <sup>-1</sup> )	18.59	20.88	21.47
Psi-scan correction			
minmax. transmission	0.61-1.00	0.48 - 1.00	0.56-1.00
$\theta$ range (°)	3–25	3–25	3–25
Reflections collected	6922	7767	7935
Independent reflections	6290	7525	7673
Independent reflections	4439	3146	4547
with $I > 2\sigma(I)$			
No. of refined parameters	356	315	360
$R_1$ (on $F, I > 2\sigma(I)$ )	$R_1 = 0.0459$	$R_1 = 0.1195$	$R_1 = 0.0703$
$wR_2$ (on $F^2$ , all data)	$wR_2 = 0.1474$	$wR_2 = 0.3704$	$wR_2 = 0.2264$

Table 3. Crystal data and details of measurements for compounds 6, 7 and 8

same products **6** (23 mg, 30%), **7** (5 mg, 6%) and **8** (27 mg, 32%), and unreacted **5** (4 mg, 9%).

Thermolysis of  $[Ir_6(\mu$ -CO)(CO)\_{12}(\mu-PPh<sub>2</sub>)<sub>2</sub>], **6**. A solution of compound **6** (20 mg, 0.01 mmol) in THF (10 cm<sup>3</sup>) was heated under reflux for 12 h. The reaction was monitored by IR spectroscopy, which showed no changes in the  $v_{CO}$  region. The solvent was evaporated, the mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>) and purified by TLC with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1.5 : 8.5) as eluent. Only compound **6** (16 mg, 84%) was recovered from the plates, which showed also some decomposition material on the base line.

Crystal structure determination. Crystal data and details of measurements for compounds 6, 7 and 8 are summarized in Table 3. Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo– $K_{\alpha}$ ,  $\lambda = 0.71069$  Å). Intensity data were reduced to  $F_{o}^{2}$ . Crystals were obtained from  $CH_2Cl_2$ /hexane by slow evaporation. The structures were solved by direct methods, followed by least-squares refinements. For all calculations the crystallographic programs SHELX86 [27a] and SHELXL93 [27b] were used. Empirical absorption correction was applied for the three compounds by azimuthal scanning of reflections with  $\chi > 80^{\circ}$ . Ir and P atoms and CO groups in 6, Ir, P and O atoms in 7 and 8 were refined anisotropically. All phenyl rings (except for the orthometallated ring in 8) were refined as rigid groups. Due to the scarce quality of data, constraints were applied for compound 7 on refining Ir—C<sub>co</sub> and C—O distances. The hydrogen atoms were added in calculated positions ( $C_{sp}^2$ —H 0.93 Å) and refined "riding" on the corresponding C atoms. graphical representations the For program SCHAKAL92 [27c] was used.

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*Supplementary material available*—Complete listings of fractional atomic coordinates, anisotropic thermal parameters and bond lengths and angles.

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