

# X-ray molecular structures and multinuclear NMR studies of the tetranuclear iridium clusters $[\text{Ir}_4(\text{CO})_7(\mu_4\text{-}\eta^3\text{-PhCC(H)CCPh})(\mu\text{-PPh}_2)_3]$ and $[\text{Ir}_4(\text{CO})_7(\mu_3\text{-}\eta^2\text{-HCCPh})(\eta^1\text{-CCPh})(\mu\text{-PPh}_2)_3]$

Maria Helena Araujo <sup>a,1</sup>, Regina M.S. Pereira <sup>a,2</sup>, Maria D. Vargas <sup>a,\*,3</sup>  
Dario Braga <sup>b</sup>, Fabrizia Grepioni <sup>b</sup>

<sup>a</sup> Instituto de Química, Universidade Estadual de Campinas, CP 6154, Campinas, 13081-970 SP, Brazil

<sup>b</sup> Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna, Via Selmi 2, 40126 Bologna, Italy

Received 5 July 2005; accepted 8 July 2005

Available online 19 August 2005

## Abstract

The reaction of  $[\text{HIr}_4(\text{CO})_{10}(\mu\text{-PPh}_2)]$  with two equiv. of  $\text{Ph}_2\text{PC}\equiv\text{CPh}$  produced  $[\text{HIr}_4(\text{CO})_8(\text{Ph}_2\text{PC}\equiv\text{CPh})_2(\mu\text{-PPh}_2)]$  (**1**) in quantitative yield. Mild thermolysis of **1** gave  $[\text{Ir}_4(\text{CO})_7(\mu_4\text{-}\eta^3\text{-PhCC(H)CCPh})(\mu\text{-PPh}_2)_3]$  (**2**) and  $[\text{Ir}_4(\text{CO})_7(\mu_3\text{-}\eta^2\text{-HCCPh})(\eta^1\text{-CCPh})(\mu\text{-PPh}_2)_3]$  (**3**) in good yields. These compounds were characterized with analytical and spectroscopic data including  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR (1 and 2D) spectroscopy, and their molecular structures were established by X-ray diffraction studies. The metal frameworks of **2** and **3** are similarly constituted of a spiked metal triangle; in both clusters the seven CO ligands are terminally bound and the three  $\text{-PPh}_2$  ligands span two consecutive Ir–Ir bonds and an open edge. The difference between the two structures is that compound **2** contains a butadienic chain,  $\mu_4\text{-}\eta^3\text{-PhCC(H)CCPh}$ , interacting with all four iridium atoms, whereas compound **3** bears two fragments of this ligand, i.e. a phenylacetylene capping a triangular face and a terminally bound phenylacetylide bonded to the fourth atom of the cluster. Although these two fragments are directed in the appropriate fashion to interact further and generate the chain of compound **2**, they do not undergo condensation under thermolytic conditions.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Tetrairidium clusters; Acetylide; C–C coupling; X-ray molecular structure

## 1. Introduction

Examples of acetylide ligand coupling reactions in the coordination sphere of late transition metal clusters to generate polyene ligands are relatively scarce in the literature [1–6]. In most cases, the acetylide fragments are generated in  $\text{R}_2\text{PC}\equiv\text{CR}'$  containing dimers or clusters via  $\text{P-C}_{\text{sp}}$  bond cleavage under thermolytic conditions. Coupling of these fragments occurs either under the same conditions or at higher temperatures necessary for the cluster further activation, and results in the formation of several products, frequently of different nucleicities, due to cluster fragmentation and recombination of the reactive fragments. For example, from the

\* Corresponding author. Fax: +55 21 26292129.

E-mail addresses: [mharaujo@ufmg.br](mailto:mharaujo@ufmg.br) (M.H. Araujo), [rpereira02@hotmail.com](mailto:rpereira02@hotmail.com) (R.M.S. Pereira), [mdvargas@vm.uff.br](mailto:mdvargas@vm.uff.br) (M.D. Vargas), [grepioni@ciam.unibo.it](mailto:grepioni@ciam.unibo.it) (F. Grepioni).

<sup>1</sup> Present address: Departamento de Química, ICEX, Universidade Federal de Minas Gerais, Belo Horizonte – MG 31270-901, Brazil.

<sup>2</sup> Present address: Departamento de Farmácia, Universidade Bandeirante de São Paulo, rua Maria Cândida 1813, São Paulo – SP 02071-013, Brazil.

<sup>3</sup> Present address: Instituto de Química, Universidade Federal Fluminense, Outeiro de São João Batista s/n, Campus do Valonguinho, Centro, Niterói, RJ 24020-150, Brazil.

thermolysis of  $[\text{Ru}_2(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_2\text{'Bu})(\mu\text{-PPh}_2)(\text{CO})_6]$  [4,7] in refluxing toluene the diacetylide complex  $[\text{Ru}_4(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_2\text{'Bu})(\mu_3\text{-}\eta^2\text{-C}_2\text{'Bu})(\mu\text{-PPh}_2)_2(\text{CO})_9]$  was isolated and shown to react further to yield the diyne tetranuclear cluster  $[\text{Ru}_4(\mu_4\text{-}^1\text{BuC}_4\text{'Bu})(\mu\text{-PPh}_2)_2(\text{CO})_8]$  resulting from *head-to-head* coupling of the two acetylide ligands. Generally, the outcome of the reaction is sensitive to the substituent on the acetylide, e.g. heating  $[\text{Ru}_2(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_2\text{Ph})(\mu\text{-PPh}_2)(\text{CO})_6]$  [8] resulted in the formation of the *head-to-head* condensation (acetylide +  $\text{Ph}_2\text{PCPh}$  from P to C bond re-formation),  $[\text{Ru}_4(\text{CO})_{10}(\mu\text{-PPh}_2)(\mu_4\text{-Ph}_2\text{PC(Ph)CCC(Ph)})]$ , and other minor products.

Only two examples have been described in the literature involving the thermolysis of clusters containing two phosphinoalkynes, viz.  $[\text{M}_3(\text{CO})_{10}(\text{Ph}_2\text{PC}\equiv\text{CR})(\text{Ph}_2\text{PC}\equiv\text{CR}')] ]$  (M = Ru [9] R = Ph, R' = 'Bu and R = R' = Ph, 'Bu, and M = Os [10], R = R' = Ph, 'Pr). Whereas the only products obtained from the thermolysis at 125 °C of the osmium clusters were  $[\text{Os}_3(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CR})_2(\mu\text{-PPh}_2)_2]$  (R = Ph and 'Pr), the nature of the products formed from the analogous ruthenium clusters depended both on the thermolysis temperature and on the substituent on the phosphinoalkyne [9]. For example, when heated at 110 °C, the compound containing two  $\text{Ph}_2\text{PC}\equiv\text{C}'\text{Bu}$  ligands yielded a mixture of tetranuclear products similar to that formed from the thermolysis of  $[\text{Ru}_2(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}_2\text{'Bu})(\mu\text{-PPh}_2)(\text{CO})_6]$ , but at lower temperature (67 °C) the cluster nuclearity stayed intact and the P–C bond activation product,  $[\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C}'\text{Bu})_2(\mu\text{-PPh}_2)_2]$ , was isolated instead. Furthermore, from the reaction of the cluster containing two different phosphinoalkyne ligands, both  $[\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C}'\text{Bu})(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)_2]$  and the product from acetylide *head-to-head* condensation,  $[\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^2\text{-PhCCC}\equiv\text{C}'\text{Bu})(\mu\text{-PPh}_2)_2]$ , were isolated.

Other sources of acetylide fragments for condensation in the coordination sphere of late transition metal clusters include: (i) the  $\text{P}(\text{C}\equiv\text{C}'\text{Bu})_3$  ligand in  $[\text{Ru}_3(\text{CO})_{11}\{\text{P}(\text{C}\equiv\text{C}'\text{Bu})_3\}]$ , whose mild thermolysis led to the formation of  $[\text{Ru}_3(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C}'\text{Bu})_2\{\mu\text{-P}(\text{C}\equiv\text{C}'\text{Bu})_2\}(\text{CO})_9]$  and then to the diyne tetranuclear compound  $[\text{Ru}_4(\mu_4\text{-}\eta^4\text{'BuC}_4\text{'Bu})(\text{CO})_{10}]$  [11]; (ii)  $\text{RC}\equiv\text{CSEt}$  (R = Me, Ph) that was heated in the presence of  $[\text{Ru}_3(\text{CO})_{12}]$ , leading to several products of various nuclearities containing  $\text{C}_4$  ligands, e.g.  $[\text{Ru}_5(\mu_5\text{-}\eta^4\text{-CPhCCPhC})(\mu\text{-SEt})_2(\text{CO})_{13}]$  and  $[\text{Ru}_6(\mu_6\text{-}\eta^4\text{-MeC}_4\text{-Me})(\mu\text{-SEt})_2(\text{CO})_{10}]$  as the result of *head-to-tail* and *head-to-head* couplings, respectively, of two acetylide units [1] and (iii) mononuclear metal acetylide compounds that were shown to undergo condensation with cluster compounds, e.g.  $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3(\text{C}\equiv\text{CPh})]$  and  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{C}\equiv\text{CPh})]$  (M = Mo or W) with  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-E})_2]$  (E = S, Se or Te) under thermolytic conditions to yield high nuclearity heterometallic clus-

ters containing  $\text{C}_4$  ligands, including that resulting from the rare *head-to-head* acetylide condensation process [12,13].

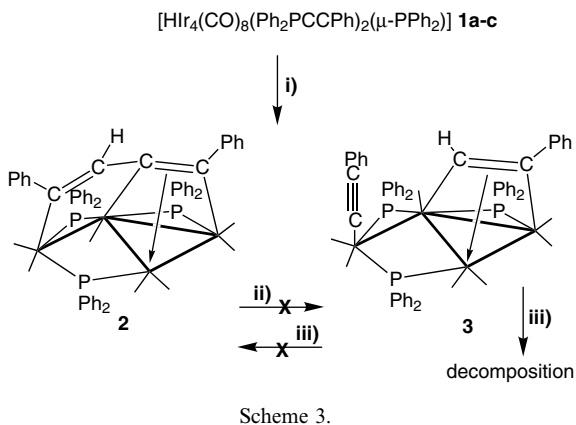
Activation of the P–C<sub>sp</sub> bond of the  $\text{Ph}_2\text{PC}\equiv\text{CPh}$  ligand in the iridium cluster  $[\text{HIr}_4(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$  (**A**) is an extremely facile process that occurs in refluxing  $\text{CH}_2\text{Cl}_2$  for 5 h, in the absence of CO, to give  $[\text{HIr}_4(\text{CO})_8(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$  (**B**) in yields above 70% [14]. Considering that the reactions of both clusters with  $\text{HC}\equiv\text{CPh}$  result in selective formation of two isomeric compounds,  $[\text{Ir}_4(\text{CO})_6(\mu_3\text{-}\eta^2\text{-HCCPh})\{\mu_2\text{-}\eta^4\text{-}(\text{H})\text{CC}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\}(\mu\text{-PPh}_2)_2]$  and  $[\text{Ir}_4(\text{CO})_6(\mu_3\text{-}\eta^2\text{-HCCPh})\{\mu_2\text{-}\eta^4\text{-}(\text{H})\text{CC}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{H})\}(\mu\text{-PPh}_2)_2]$ , containing  $\text{C}_4$  ligands, as the result of *head-to-tail* and *tail-to-tail* condensations of two HCCPh molecules, respectively [15], we decided to investigate the behavior of the di-substituted cluster  $[\text{HIr}_4(\text{CO})_8(\text{Ph}_2\text{PC}\equiv\text{CPh})_2(\mu\text{-PPh}_2)]$  (**1**) under mild thermolytic conditions. As described herein this reaction led to high yield formation of two products:  $[\text{Ir}_4(\text{CO})_7(\mu_4\text{-}\eta^3\text{-PhCC}(\text{H})\text{CCPh})(\mu\text{-PPh}_2)_3]$  (**2**), which contains a butadienic chain resulting formally from *head-to-head* condensation of two acetylide fragments and incorporation of the cluster hydride, and  $[\text{Ir}_4(\text{CO})_7(\mu_3\text{-}\eta^2\text{-HCCPh})(\eta^1\text{-CCPh})(\mu\text{-PPh}_2)_3]$  (**3**), bearing the two fragments of the butadienic ligand directed in the appropriate fashion to generate the chain of compound **2**.

## 2. Results and discussion

### 2.1. Preparation and characterization of $[\text{HIr}_4(\text{CO})_8(\text{Ph}_2\text{PC}\equiv\text{CPh})_2(\mu\text{-PPh}_2)]$ (**1**)

The reaction between  $[\text{HIr}_4(\text{CO})_{10}(\mu\text{-PPh}_2)]$  [16] and two equiv. of  $\text{Ph}_2\text{PC}\equiv\text{CPh}$  in  $\text{CH}_2\text{Cl}_2$ , at 25 °C, for 1 h (Scheme 1, i), afforded the dark orange di-substituted cluster **1** in 90% yield, in addition to the mono-substituted species  $[\text{HIr}_4(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$  (**A**, 10%). Compound **1** was isolated previously as a by product of the reaction of  $[\text{HIr}_4(\text{CO})_{10}(\mu\text{-PPh}_2)]$  with one equiv. of  $\text{Ph}_2\text{PC}\equiv\text{CPh}$  in the same solvent, at 30 °C, for 4 h that gives the mono-substituted product **A** in 70% yield (Scheme 1, ii) [14]. Addition of one equiv. of  $\text{Ph}_2\text{PC}\equiv\text{CPh}$  to pure **A** under the same reaction conditions (Scheme 1, iii) also led to cluster **1** albeit in lower yield (50%), together with  $[\text{HIr}_4(\text{CO})_8(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$  (**B**), the product from the rearrangement of **A** (Scheme 1, iv), isolated in about 30% yield. Conversion of **A** into **B** has been shown to be hampered by the presence of 1 atm of CO [14]. The selectivity of reaction i, therefore, must be due to the presence of dissolved CO in solution, after the first CO substitution, which inhibits P–C bond activation, but not substitution of a second CO ligand to give cluster **1**.





the yield of **3** (<10%) and **4–6**, as well as extensive decomposition material on the base line of the TLC plates. Furthermore, compound **2** was stable when heated in toluene under reflux for 3 h (Scheme 3, ii), whereas heating compound **3** at 80 °C for 12 h (Scheme 3, iii) led to extensive decomposition without formation of compounds **2** or **4–6**. Thus, although structurally similar (vide infra) these compounds do not inter-convert under thermolysis conditions.

### 2.3. X-ray diffraction studies of [Ir<sub>4</sub>(CO)<sub>7</sub>(μ<sub>4</sub>-η<sup>3</sup>-PhCC(H)CCPh)(μ-PPh<sub>2</sub>)<sub>3</sub>] (**2**) and [Ir<sub>4</sub>(CO)<sub>7</sub>(μ<sub>3</sub>-η<sup>2</sup>-HCCPh)(η<sup>1</sup>-CCPh)(μ-PPh<sub>2</sub>)<sub>3</sub>] (**3**)

The molecular structures of compounds **2** and **3** and the atomic labeling schemes are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are shown in Table 1.

The molecular structures of compounds **2** and **3** are very similar (see Scheme 3) and therefore will be described together. The metal frameworks can be described either as constituted of a flat butterfly with an

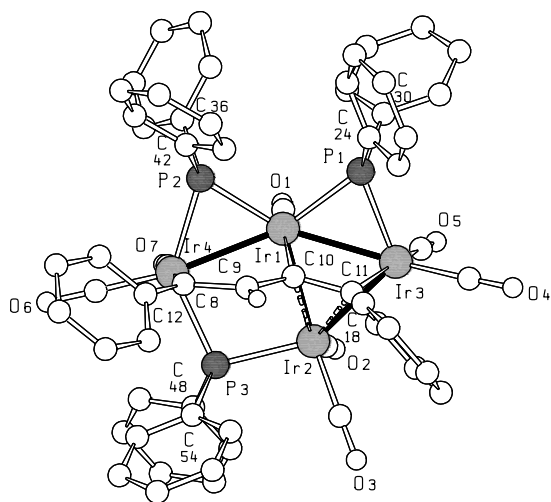


Fig. 1. Molecular structure of [Ir<sub>4</sub>(CO)<sub>7</sub>(μ<sub>4</sub>-η<sup>3</sup>-PhCC(H)CCPh)(μ-PPh<sub>2</sub>)<sub>3</sub>] (**2**).

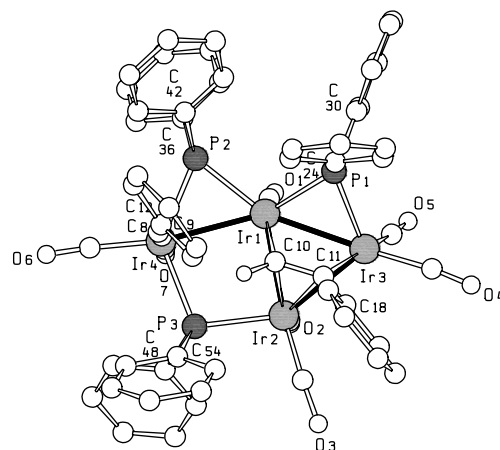


Fig. 2. Molecular structure of [Ir<sub>4</sub>(CO)<sub>7</sub>(μ<sub>3</sub>-η<sup>2</sup>-HCCPh)(η<sup>1</sup>-CCPh)(μ-PPh<sub>2</sub>)<sub>3</sub>] (**3**).

open edge, or as a spiked metal triangle (dihedral angles 172° and 175°, respectively). Metal–metal bond distances range from 2.679(2) to 2.790(2) Å for **2** and from 2.685(1) to 2.799(1) Å for **3**, the longest bond corresponding to the spike [Ir(1)–Ir(4)]. The separation between Ir atoms along the open edge is 3.663(1) and 3.730(1) Å, respectively. Seven CO ligands are terminally bound, except for Ir(1) which carries only one terminal ligand; each iridium atom carries two terminal ligands, one bound in radial and one bound in axial position with respect to the metal frame. Three diphenylphosphido ligands span two consecutive Ir–Ir bonds [P(1) and P(2)] along the butterfly wings [Ir(1)–Ir(3) and Ir(1)–Ir(4)] and the open edge [P(3) along Ir(2)–Ir(4)]. This is an interesting aspect of this structure because it shows the great structural flexibility of this ligand. In fact, the angles at the P-atoms range from 73.3(1)° and 73.9(1)° to 101.5(1)° for **2** and from 73.0(2)° and 74.1(2)° to 103.9(2)° for **3** along the “closed” and “open” bonds, respectively. Ir–P distances are fairly comparable, although those corresponding to P(3) are slightly longer in both clusters [2.347(4) and 2.383(3) Å, **2** and 2.353(6) and 2.383(6) Å, **3**] than those of P(1) [2.319(4) and 2.293(3) Å, **2** and 2.302(6) and 2.312(6) Å, **3**] and P(2) [2.320(3) and 2.325(3) Å, **2** and 2.313(6) and 2.331(6) Å, **3**]. Each phosphido ligand donates three electrons to the cluster.

The marked difference between the two compounds is that cluster **2** exhibits a PhCC(H)CCPh butadienyl chain that interacts with the four metal atoms, whereas compound **3** contains this chain's precursor fragments, HCCPh and CCPh, interacting with three and one iridium atoms, respectively, and oriented similarly to the butadienyl chain in **2**, as if ready for a *head-to-tail* coupling. The PhC(H)CCPh chain in compound **2** is bonded to the cluster via a π- and three σ-interactions (vide Fig. 1) and as such gives formally five electrons to the metal frame. Carbons C(10) and C(11) (that



Table 1  
Selected intramolecular distances (Å) and angles (°) for compounds **2** and **3**

	<b>2</b>	<b>3</b>
<i>Distances (Å)</i>		
Ir(1)–Ir(2)	2.720(1)	2.685(1)
Ir(1)–Ir(3)	2.751(2)	2.746(1)
Ir(1)–Ir(4)	2.790(2)	2.799(1)
Ir(2)–Ir(3)	2.679(2)	2.717(1)
Ir(2)–Ir(4)	3.663(1)	3.730(1)
Ir(1)–P(1)	2.319(4)	2.302(6)
Ir(1)–P(2)	2.320(3)	2.313(6)
Ir(2)–P(3)	2.347(4)	2.353(6)
Ir(3)–P(1)	2.293(3)	2.312(6)
Ir(4)–P(2)	2.325(3)	2.331(6)
Ir(4)–P(3)	2.383(3)	2.383(6)
Ir(1)–C(10)	2.06(1)	2.10(2)
Ir(2)–C(10)	2.29(1)	2.15(2)
Ir(2)–C(11)	2.31(1)	2.29(2)
Ir(3)–C(11)	2.07(1)	2.12(2)
Ir(4)–C(8)	2.13(1)	1.99(2)
C(8)–C(9)	1.44(2)	1.25(3)
C(9)–C(10)	1.52(2)	
C(10)–C(11)	1.42(2)	1.32(3)
<i>Angles (°)</i>		
Ir(1)–P(1)–Ir(3)	73.2(1)	73.0(2)
Ir(1)–P(2)–Ir(4)	73.9(1)	74.1(2)
Ir(2)–P(3)–Ir(4)	101.5(1)	103.9(2)
P(2)–Ir(4)–P(3)	138.0(1)	135.6(2)
P(2)–Ir(1)–P(1)	107.5(1)	106.5(2)
C(9)–C(8)–C(12)	115.6(14)	173(2)
C(8)–C(9)–C(10)	125.5(16)	
C(11)–C(10)–C(9)	128.0(12)	
C(10)–C(11)–C(18)	124.6(10)	127.2(18)
Ir(1)–C(10)–C(9)	122.2(10)	
Ir(1)–C(10)–C(11)	109.7(8)	112.6(13)
Ir(2)–C(10)–C(11)	72.7(6)	78.5(15)
Ir(2)–C(11)–C(10)	122.2(7)	67.2(13)
Ir(2)–C(11)–Ir(3)	75.2(4)	76.0(7)
Ir(3)–C(11)–C(10)	107.8(8)	106.8(13)
Ir(4)–C(8)–C(9)	110.5(11)	176(2)
C(11)–Ir(2)–Ir(3)	48.4(3)	49.2(5)
C(11)–Ir(3)–Ir(1)	71.5(3)	71.0(6)
C(11)–Ir(3)–Ir(2)	56.4(3)	54.8(5)
C(8)–Ir(4)–Ir(1)	89.6(5)	91.0(6)

constitute the alkyne portion of the chain) interact with the Ir(1)–Ir(2)–Ir(3) triangular face in a  $\mu_3\text{-}\eta_2\text{-}\parallel$  manner, parallel to the Ir(1)–Ir(3) edge via a  $\pi$  [Ir(2)–C(10) 2.29(1) Å and Ir(2)–C(11) 2.31(1) Å] and two  $\sigma$  interactions [Ir(1)–C(10) 2.06(1) Å and Ir(3)–C(11) 2.07(1) Å]. The C(10)–C(11) bonding distance [1.42(2) Å] is similar to those encountered in other clusters containing alkynes coordinated in the same mode [14,20]. The alkenyl portion of the chain [C(8)–C(9) 1.44(2) Å] interacts uniquely with Ir(4) via a  $\sigma$  bond [Ir(4)–C(8) 2.13(1) Å]. The three  $\sigma$ -interactions are all comparable in length [Ir(4)–C(8) 2.13(1) Å, Ir(1)–C(10) 2.06(1) Å, and Ir(3)–C(11) 2.07(1) Å] while they are expectedly shorter than those from the ethylenic system [Ir(2)–C(10) 2.29(1) Å, Ir(2)–C(11) 2.31(1) Å]. The bonding pattern within the PhCC(H)CCPh system is in agreement with an alterna-

tion of double and single C–C bonds along the chain interacting with the cluster, starting with C(11)–C(10) [1.42(2) Å], via C(10)–C(9) 1.52(2) Å, and ending with C(9)–C(8) 1.44(2) Å. The angles distribution is also in agreement with the presence of a sequence of  $\text{sp}^2$  hybridized C-atoms (see Table 1).

The structure of compound **2** shows some similarity with those of cluster  $[\text{Ir}_4(\text{CO})_8(\eta^1\text{-Ph})(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$ , obtained from the thermolytic activation of a P–C<sub>Ph</sub> bond of  $[\text{Ir}_4(\text{CO})_8(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PC(H)CPh})(\mu\text{-PPh}_2)]$ , and of its CO insertion product,  $[\text{Ir}_4(\text{CO})_8\{\eta^1\text{-C(O)Ph}\}(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$  [21].

In compound **3**, the HCCPh molecule interacts with the cluster in a similar fashion as the alkyne portion of the C<sub>4</sub> chain, with the Ir(1)–Ir(2)–Ir(3) triangular face, via a  $\pi$ - [Ir(2)–C(10) 2.15(2) Å and Ir(2)–C(11) 2.29(2) Å] and two  $\sigma$ - [Ir(1)–C(10) 2.10(2) Å and Ir(3)–C(11) 2.12(2) Å] interactions, formally acting as a four electron donor. Although these bonding distances are similar in the two clusters, the C(10)–C(11) distance is markedly shorter in cluster **3** [1.32(3) Å] than in cluster **2** [1.42(2) Å].

The C≡CPh acetylide fragment interacts terminally with the cluster via a  $\sigma$  bond [Ir(4)–C(8) 1.99(2) Å], and exhibits C≡C [1.25(3) Å] bond distance and Ir(4)–C(8)–C(9) [176(2)°] bond angle that are typical of metal acetylides. This ligand acts formally as a one-electron donor. To the best of our knowledge, there is not a single example of an iridium cluster containing a  $\eta^1$ -coordinated acetylide; furthermore, this coordination mode has been reported only for the following osmium clusters:  $[\text{Os}_3\text{Pt}(\mu_4\text{-}\eta^2\text{-CCPh})(\eta^1\text{-C}\equiv\text{CPh})\text{L}(\text{CO})_9]$  (L = bipyridines) [22],  $[\text{Os}_3(\mu\text{-}\eta^2\text{-CCPh})(\eta^1\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)_2(\text{NH}_2\text{Et})_2(\text{CO})_6]$  [10], and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{W}(\text{O})(\mu\text{-O})\text{Os}_3(\eta^1\text{-CCPh})(\text{CO})_{11}]$  [23]. The stabilization of this coordination mode only in third row transition metal clusters is probably associated to the high activation energies necessary to induce metal–CO and/or metal–metal bond cleavage for the generation of a vacant coordination site and further interaction of the acetylide via the C≡C bond.

The structure of compound **3** is somewhat related to those of the two flat-butterfly cluster species  $[\text{Ir}_4(\text{CO})_8(\eta^1\text{-Ph})(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$  and  $[\text{Ir}_4(\text{CO})_8(\eta^1\text{-C(O)Ph})(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$  [21] that carry a  $\mu_4\text{-}\eta^3\text{-PhPC(H)CPh}$  unit bound to the cluster frame via two P–Ir interactions and one  $\sigma$  and one  $\pi$ -interactions from the ethylenic system. This latter interaction is the same as in the title complex.

#### 2.4. Solution characterization of compounds **2** and **3**

The IR, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR data of compounds **2** and **3** are in agreement with the solid-state structures. Only bands due to terminal CO ligands are observed in the IR spectra. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of

compounds **2** and **3** showed three sets of doublets of doublets at  $\delta$ -47.80, 70.60 and 235.70 and  $\delta$ -37.60, 80.00 and 215.40, respectively. The low frequency resonances at  $\delta$ -47.80 ( $J_{P3-P2}$  138.0 Hz,  $J_{P3-P1}$  18.0 Hz) and at  $\delta$ -37.60 ( $J_{P3-P2}$  141.0 Hz,  $J_{P3-P1}$  18.0 Hz) were attributed to P(3) that bridges the two iridium atoms that do not interact [Ir(2)–Ir(4) 3.663(1), **2** and 3.730(1) Å, **3**]. The other two sets of doublets of doublets at  $\delta$  70.60 and  $\delta$  235.70 [ $J_{P2-P1}$  20.0 Hz, **2**] and  $\delta$  80.00 and 215.40 [ $J_{P2-P1}$  12.0 Hz, **3**] were attributed to P(2) and P(1), respectively. The assignments of P(1), P(2) and P(3) were based on the empirical rules previously discussed [24]. However, the relatively small difference in the Ir(1)–Ir(3) and Ir(1)–Ir(4) distances [2.751(2), 2.790(2) Å, **2** and 2.746(1), 2.799(1) Å, **3**] bridged by P(1) and P(2), respectively, contrasts with a large  $\Delta\delta$  of 165.10 ppm, **2** and 135.40 ppm, **3**, and therefore the assignments of P(1) and P(2) were further confirmed by correlations between the observed coupling constants and P–Ir–P angles. Thus, the large  $^2J_{P2-P3}$  [138.0 Hz, **2** and 141.0 Hz, **3**] result from the wide P(2)–Ir(4)–P(3) angle [138.0(1)°, **2** and 135.6(2)°, **3**], whilst the small  $^2J_{P1-P2}$  [20.0 Hz, **2** and 12.0 Hz, **3**] were associated to the narrow P(2)–Ir(1)–P(1) angle [107.5(1)°, **2** and 106.5(2)°, **3**]. The room temperature,  $^1\text{H}$  NMR spectra of compounds **2** and **3** in  $\text{CDCl}_3$  exhibit the expected phenyl resonances. In compound **3**, the aliphatic proton ( $\mu_3$ - $\eta^2$ -HCCPh) appears as a doublet of doublets at  $\delta$  8.76 (dd,  $J_{P-P}$  9.4 and 10.6 Hz), whereas in compound **2** the aliphatic proton of the chain ( $\mu_4$ - $\eta^3$ -PhCC(H)CCPh) was hidden under the aromatic signals; it was identified at  $\delta$  6.33 (m) in the  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$ . This is in agreement with other  $^1\text{H}$  chemical shifts observed for hydrogens bonded to  $\text{sp}^2$ carbons of  $\text{Ir}_4$  coordinated olefinic chains, e.g. in  $[\text{Ir}_4(\text{CO})_9(\eta^1\text{-Ph})(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$  [two isomers: A,  $\delta$  5.70, and B,  $\delta$  6.50] [21] and  $[\text{Ir}_4(\text{CO})_7(\mu\text{-CO})\{\mu_4\text{-}\eta^3\text{-Ph}_2\text{PC(H)C(Ph)PCBu}^1\}(\mu\text{-PPh}_2)]$  [ $\delta$  5.4] [25]. These assignments, for compounds **2** and **3**, were confirmed by a 2D-HSQC experiment, which showed the correlation between the signal at  $\delta$  125.21 (s) and that at  $\delta$  6.33 (m), for **2**, and the correlation between the signal at  $\delta$  110.98 (s) and that at  $\delta$  8.76 (dd), for **3**. The CH carbons were assigned in both compounds using DEPT-90 experiments (see Section 4).

*2.5. Mechanistic considerations on the formation of clusters  $[\text{Ir}_4(\text{CO})_7(\mu_4\text{-}\eta^3\text{-PhCC(H)CCPh})(\mu\text{-PPh}_2)_3]$  (**2**) and  $[\text{Ir}_4(\text{CO})_7(\mu_3\text{-}\eta^2\text{-HCCPh})(\eta^1\text{-CCPh})(\mu\text{-PPh}_2)_3]$  (**3**)*

The di-substituted cluster **1** is far more stable than the derivative containing a single  $\text{Ph}_2\text{PC}\equiv\text{CPh}$  ligand,  $[\text{H}\text{Ir}_4(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$  (**A**), since the temperature needed to induce rearrangement to **2** and **3** is about 40 °C higher than that needed to form **B** from

**A**. The relative stability of cluster **1** can be associated, on the one hand to the presence of an additional phosphine ligand leading to an increase in the electron density on the metal frame, which is transferred to the CO ligands via  $\pi$  back-bonding, thus strengthening the Ir–CO bonds, and on the other, to the steric hindrance of the phosphinoalkyne phenyl substituents that makes P–C<sub>sp</sub> bond activation a more difficult process than for the mono-substituted cluster.

It has been shown for analogous ruthenium clusters that activation via CO dissociation involves higher energies than those necessary for the subsequent C–C and C–H bond formations. Indeed, the chemically activated cluster  $[\text{HRu}_3(\mu_3\text{-}\eta^2\text{-CC}^t\text{Bu})(\text{CO})_8(\text{MeCN})]$ , for example, has been shown to react with alkynes at room temperature due to facile MeCN loss. This low energy path has allowed characterization of reaction intermediates and the understanding of subsequent processes on the way to C<sub>4</sub> chain formation [26]. Unfortunately, attempts to activate cluster **1** via reaction with 1 equiv. of Me<sub>3</sub>NO in MeCN (1:1) at –10 °C only led to decomposition of the starting material.

Any attempt to propose a reasonable sequence of events responsible for the formation of compounds **2** and **3** is mere speculation. It is note worthy however, that compound **3** is not converted into **2** under thermolytic conditions, considering that formation of the PhCC(H)CCPh chain in **2** formally involves an alkyne + acetylide ligands coupling, and that both ligands are not only present in the coordination sphere of **3**, but also oriented in the appropriate way to couple. Since the starting cluster **1** exists in solution in the form of three isomers that may interconvert in solution under the thermolysis conditions, as do the isomers of the related dppm containing cluster  $[\text{H}\text{Ir}_4(\text{CO})_8(\text{dppm})(\mu\text{-PPh}_2)]$  [18], compounds **2** and **3** may come from a common species formed after cluster **1** activation via CO dissociation (or Ir–Ir bond cleavage) and cleavage of a phosphinoalkyne P–C bond. Compound **3** could be formed after: (i) migratory insertion of the acetylide fragment into the H–Ir bond with formation of a  $\mu_3\text{-}\eta^2\text{-HCCPh}$  ligand and (ii) activation of the second phosphinoalkyne P–C bond after further Ir–Ir bond cleavage, with formation of the stable  $\eta^1\text{-C}\equiv\text{CPh}$  ligand. Formation of cluster **2** would occur instead, if the activation of the two phosphinoalkyne P–C bonds occurred simultaneously or at least if the migratory insertion of the first acetylide into the H–Ir bond occurred more slowly than the generation of the second acetylide fragment. An intermediate species: (i) would couple in the *head-to-head* fashion and (ii) insert into the H–Ir bond. In other words, we propose that formation of **2** or **3** depends on the relative rates of formation of the second acetylide and migratory insertion of the first acetylide into the H–Ir bond. Since com-

pounds **2** and **3** are formed in similar yields, these two processes seem to compete under the thermolytic conditions investigated herein.

### 3. Conclusion

Although the thermolysis reaction of the di-substituted cluster **1** is not as selective as that of the cluster containing a single phosphinoalkyne,  $[\text{HIr}_4(\text{CO})_9(\text{Ph}_2\text{PCCPh})(\mu\text{-PPh}_2)]$  (**A**), the fact that it only yields two products in good yields and of the same nuclearity as the starting cluster is a good illustration of the versatility of the iridium metal frame in studies involving unsaturated molecules activation and C–C bond formation processes. As anticipated, the acetylide fragments generated from the activation of two phosphinoalkynes in cluster **1** can undergo condensation with formation of a C<sub>4</sub> chain, as previously observed for analogous ruthenium and osmium clusters described in the literature, however, the presence of a hydride ligand in this cluster makes other pathways available that compete with the condensation process, leading also to a product in which the coupling has not occurred.

### 4. Experimental

#### 4.1. General procedures

All manipulations and reactions were carried out under dry argon, unless otherwise specified, using standard Schlenk techniques. CH<sub>2</sub>Cl<sub>2</sub> was dried over CaH<sub>2</sub>, hexane and toluene over sodium.  $[\text{HIr}_4(\text{CO})_{10}(\mu\text{-PPh}_2)]$  [16] and Ph<sub>2</sub>PC≡CPh [27] were prepared as described in the literature. Solvents were freshly distilled under argon and freed from dissolved oxygen, where compatible, by freeze degassing before use.

The progress of the reactions was monitored by analytical TLC (pre-coated plates, silica gel F 254, 0.25 mm thick; Merck) and IR spectroscopy. The separation and purification of the reaction products were carried out in air by preparative TLC (2 mm thick glass-backed silica plates, 20 × 20 cm, prepared from silica gel GF 254, Fluka) and the compounds were extracted from silica with CH<sub>2</sub>Cl<sub>2</sub>.

Infrared spectra were recorded on a Bomen (FT-IR Michelson) spectrophotometer scanning between 2200 and 1600 cm<sup>-1</sup> (ν<sub>CO</sub>) using CaF<sub>2</sub> liquid cells. Microanalyses were performed on a Perkin–Elmer 2401 Elemental Analysis Instrument. Solution NMR spectra were recorded on a Varian Inova-500, Bruker AMX 500, AC 300P or AC 200 spectrometers. Signals were attributed based on the following NMR experiments: <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, NOE, DEPT-90, 2D-HSQC; standard pulse sequences were used for the experiments. Hydrogen, car-

bon and phosphorus atoms were labeled as in the crystal structures. The phenyl groups were identified by the first quaternary carbon bonded to the phosphorus of the phosphido groups or to the carbons of the organic chains and labeled as in the crystal structure. Deuterated solvents were used as locks and references: <sup>1</sup>H relative to the proton resonance resulting from incomplete deuteration of the CDCl<sub>3</sub> (δ 7.27), C<sub>6</sub>D<sub>6</sub> (δ 7.16) or CD<sub>2</sub>Cl<sub>2</sub> (δ 5.32); <sup>13</sup>C relative to the carbon of the CDCl<sub>3</sub> (δ 77.23) or CD<sub>2</sub>Cl<sub>2</sub> (δ 54.00) and for <sup>31</sup>P, external 85% H<sub>3</sub>PO<sub>4</sub>.

#### 4.2. Preparation of $[\text{HIr}_4(\text{CO})_8(\text{Ph}_2\text{PC}\equiv\text{CPh})_2(\mu\text{-PPh}_2)]$ (**1**)

An orange solution of  $[\text{HIr}_4(\text{CO})_{10}(\mu\text{-PPh}_2)]$  (100 mg, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was stirred with Ph<sub>2</sub>PC≡CPh (46 mg, 0.16 mmol) for 1 h at 30 °C, after which time the solvent was concentrated in vacuo and the reaction mixture separated by TLC (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 3:7 as eluent) affording compounds **1** (R<sub>f</sub> 0.25, 126 mg, 90%) and  $[\text{HIr}_4(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$  (**A**) (R<sub>f</sub> 0.57, 10 mg, 10%). Anal. Calc. for C<sub>60</sub>H<sub>41</sub>O<sub>8</sub>P<sub>3</sub>Ir<sub>4</sub> (**1**): C, 43.5; H, 3.4. Found: C, 43.7; H, 3.2% [14]. IR (hexane): ν<sub>C≡C</sub> 2172 w, ν<sub>CO</sub> 2068 m, 2052 m, 2022 s, 1987 mbr, 1805 wbr, cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>, 25 °C): <sup>1</sup>H (200 MHz), δ 8.00–6.74 (m, Ph) and the hydride signal for the three isomers: **1a** (major isomer) δ –11.00 (ddd, J<sub>P–H</sub> 5.3, 9.6 and 70.0 Hz, 1H), **1b** δ –10.78 (double pseudo triplet, J<sub>P–H</sub> 10.0 and 56.0 Hz, 1H) and **1c** (minor isomer) δ –11.54 (br m, J<sub>P–H</sub> 56.0 Hz, 1H); <sup>31</sup>P{<sup>1</sup>H} (121.49 MHz): **1a** (major isomer) δ 270.99 (s, μ-PPh<sub>2</sub>), –44.14 (d, J<sub>P–P</sub> 37.0 Hz, Ph<sub>2</sub>P≡CPh), –63.79 (d, Ph<sub>2</sub>P≡CPh), **1b** δ 256.87 (s, μ-PPh<sub>2</sub>), –27.58 (s, Ph<sub>2</sub>P≡CPh), –47.68 (s, Ph<sub>2</sub>P≡CPh) and **1c** (minor isomer) δ 271.85 (s, μ-PPh<sub>2</sub>), –41.62 (s, Ph<sub>2</sub>P≡CPh), –35.57 (s, Ph<sub>2</sub>P≡CPh).

#### 4.3. Reaction of $[\text{HIr}_4(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$ (**A**) with **1** equiv. Ph<sub>2</sub>PC≡CPh

Pure  $[\text{HIr}_4(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$  (**A**) (60 mg, 0.04 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) was stirred with Ph<sub>2</sub>PC≡CPh (12 mg, 0.04 mmol), as described above. After TLC separation using the same solvent system, compounds **1** (42 mg, 60%) and  $[\text{Ir}_4(\text{CO})_8(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$  (**B**) (20 mg, 35%) were isolated.

#### 4.4. Preparation of $[\text{Ir}_4(\text{CO})_7(\mu_4\text{-}\eta^3\text{-PhCC(H)CCPh})(\mu\text{-PPh}_2)_3]$ (**2**) and $[\text{Ir}_4(\text{CO})_7(\mu_3\text{-}\eta^2\text{-HCCPh})(\eta^1\text{-CCPh})(\mu\text{-PPh}_2)_3]$ (**3**)

A solution of **1** (150 mg, 0.08 mmol) in toluene (20 mL) was heated at 80 °C for 3 h, after which time a color change from dark orange to dark red was observed. The solvent was evaporated in vacuo and the

mixture was dissolved in  $\text{CH}_2\text{Cl}_2$  (2 mL). Purification by preparative TLC ( $\text{CH}_2\text{Cl}_2$ /hexane, 1:4 as eluent) afforded very little starting material **1** ( $R_f$  0.60), the dark red compound **3** ( $R_f$  0.49, 44 mg, 32%), the red compound **2** ( $R_f$  0.45, 62 mg, 45%) and a mixture of three red compounds **4**, **5** and **6**, that could not be separated with a variety of solvent systems ( $R_f$  0.41, 12 mg, 10%). Some decomposition material was noted in the base line. Compounds **2** and **3** have very similar  $R_f$  in a variety of solvents and needed to be re-purified by TLC and crystallized from  $\text{CH}_2\text{Cl}_2$ /hexane.

Anal. Calc. for  $\text{C}_{59}\text{H}_{41}\text{O}_7\text{P}_3\text{Ir}_4 \cdot 0.5\text{C}_6\text{H}_6$ : C, 42.8; H, 2.5. Found: C, 42.7; H, 2.6%. IR  $\nu_{\text{CO}}(\text{CH}_2\text{Cl}_2)$ : 2068 s, 2045 vs, 2018 m, 1997 m, 1966 w,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C, 300 MHz),  $\delta$  6.33 (m, 1H, CH), 6.67 (d,  $J_{\text{H-H}}$  7.1 Hz, 2H, *ortho*-H), 7.38 (d,  $J_{\text{H-H}}$  7.9 Hz, 2H, *ortho*-H), 6.45 (t,  $J_{\text{H-H}}$  7.7 Hz, 2H, *ortho*-H), 7.48 (dd,  $J_{\text{H-H}}$  7.1 and 12.3 Hz, 2H, *ortho*-H), 7.96–7.66 (m, Ph), 7.11–6.77 (m, Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25 °C, 125.69 MHz),  $\delta$  181.5 (m, CO), 176.1 (s, CO), 175.6 (m, CO), 175.0 (s, CO), 170.0 (s, CO), 162.2 (s, CO), 156.6 (d,  $J_{\text{C-P}}$  31.4 Hz, CO), 148.46 (s,  $C_{\text{quat}}$ , Ph), 143.62 (dd,  $J_{\text{C-P}}$  32.0 and 54.2 Hz,  $C_{\text{quat}}$ , Ph), 139.48 (dd,  $J_{\text{C-P}}$  31.5 and 74.5 Hz,  $C_{\text{quat}}$ , Ph), 139.51 (s,  $C_{\text{quat}}$ , Ph), 135.24 (s,  $C_{\text{quat}}$ , Ph), 135.00 (s,  $C_{\text{quat}}$ , Ph), 130.66 (s,  $C_{\text{quat}}$ , Ph), 130.66 (s,  $C_{\text{quat}}$ , Ph), 135.04 (d,  $J_{\text{C-P}}$  10.8 Hz, CH, Ph), 134.10 (d,  $J_{\text{C-P}}$  10.8 Hz, CH, Ph), 133.58 (d,  $J_{\text{C-P}}$  10.8 Hz, CH, Ph), 132.59 (m, CH, Ph), 131.86 (d,  $J_{\text{C-P}}$  9.8 Hz, CH, Ph), 130.10 (s, CH, Ph), 129.79 (s, CH, Ph), 129.61 (s, CH, Ph), 129.09 (s, CH, Ph), 128.60–127.87 (m, CH, Ph), 127.26–127.10 (m, CH, Ph), 126.49 (s, CH, Ph), 125.94 (s, CH, Ph), 125.21 (m, CH);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25 °C, 121.49 MHz),  $\delta$  235.70 (dd,  $J_{\text{P1-P2}}$  20.0 Hz and  $J_{\text{P1-P3}}$  18.0 Hz,  $\mu$ -P1Ph<sub>2</sub>), 70.60 (dd,  $J_{\text{P2-P3}}$  138.0 Hz and  $J_{\text{P2-P1}}$  20.0 Hz,  $\mu$ -P2Ph<sub>2</sub>) and –47.80 (dd,  $J_{\text{P3-P1}}$  18.0 Hz and  $J_{\text{P3-P2}}$  138.0 Hz,  $\mu$ -P3Ph<sub>2</sub>).

Anal. Calc. for  $\text{C}_{59}\text{H}_{41}\text{O}_7\text{P}_3\text{Ir}_4$  (**3**): C, 41.1; H, 2.4. Found: C, 40.7; H, 2.1%. IR  $\nu_{\text{CO}}(\text{CH}_2\text{Cl}_2)$ : 2065 m, 2044 vs, 2011 s, 1993 s, 1965 w,  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ , 25 °C):  $^1\text{H}$  (300 MHz),  $\delta$  6.03 (d,  $J_{\text{H-H}}$  8.0 Hz, 2H, *ortho*-H), 8.03 (dd,  $J_{\text{H-H}}$  8.0 and 11.7 Hz, 2H, *ortho*-H), 7.61–6.78 (m, Ph), 8.76 (dd,  $J_{\text{P-H}}$  10.6 and 9.4 Hz, 1H, CH),  $^{13}\text{C}\{^1\text{H}\}$  (125.69 MHz), 149.51 (s,  $C_{\text{quat}}$ , Ph), 140.32 (s,  $C_{\text{quat}}$ , Ph), 137.19 (d,  $J_{\text{P-C}}$  30.8 Hz,  $C_{\text{quat}}$ , Ph), 134.88 (d,  $J_{\text{C-P}}$  11.7 Hz, CH, Ph), 134.56 (d,  $J_{\text{C-P}}$  12.3 Hz, CH, Ph), 133.99 (d,  $J_{\text{C-P}}$  12.3 Hz, CH, Ph), 133.26 (d,  $J_{\text{C-P}}$  12.3 Hz, CH, Ph), 132.97 (d,  $J_{\text{C-P}}$  11.7 Hz, CH, Ph), 131.13 (s, CH, Ph), 129.91 (d,  $J_{\text{C-P}}$  8.3 Hz, CH, Ph), 129.71 (s, CH, Ph), 128.92 (s, CH, Ph), 128.78 (s, CH, Ph), 128.59 (d,  $J_{\text{C-P}}$  9.8 Hz, CH, Ph), 128.34 (s, CH, Ph), 128.25 (s, CH, Ph), 128.15 (s, CH, Ph), 127.83 (s, CH, Ph), 127.62 (s, CH, Ph), 127.18 (dd,  $J_{\text{C-P}}$  11.7 and 7.3 Hz, CH, Ph), 126.62 (s, CH, Ph), 125.11 (s, CH, Ph), 110.98 (s, CH);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.49 MHz),  $\delta$  215.40 (dd,  $J_{\text{P1-P2}}$

12.0 Hz and  $J_{\text{P1-P3}}$  18.0 Hz,  $\mu$ -P1Ph<sub>2</sub>), 80.00 (dd,  $J_{\text{P2-P3}}$  141.0 Hz and  $J_{\text{P2-P1}}$  12.0 Hz,  $\mu$ -P2Ph<sub>2</sub>) and –37.60 (dd,  $J_{\text{P3-P1}}$  18.0 Hz and  $J_{\text{P3-P2}}$  141.0 Hz,  $\mu$ -P3Ph<sub>2</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121.49 MHz) for **4**:  $\delta$  224.30 (t,  $J_{\text{P-P}}$  12.5 and 15.4 Hz,  $\mu$ -PPh<sub>2</sub>), 66.05 (dd,  $J_{\text{P-P}}$  12.5 and 138.9 Hz,  $\mu$ -PPh<sub>2</sub>) and –36.11 (dd,  $J_{\text{P-P}}$  15.4 and 138.9 Hz,  $\mu$ -PPh<sub>2</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.49 MHz) for **5**:  $\delta$  246.31 (d,  $J_{\text{P-P}}$  10.7 Hz,  $\mu$ -PPh<sub>2</sub>), 26.81 (d,  $J_{\text{P-P}}$  141.7 Hz,  $\mu$ -PPh<sub>2</sub>) and –25.00 (dd,  $J_{\text{P-P}}$  10.7 and 141.8 Hz,  $\mu$ -PPh<sub>2</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.49 MHz) for **6**:  $\delta$  215.48 (t,  $J_{\text{P-P}}$  13.8 and 17.4 Hz,  $\mu$ -PPh<sub>2</sub>), 94.17 (dd,  $J_{\text{P-P}}$  13.8 and 156.1 Hz,  $\mu$ -PPh<sub>2</sub>) and 3.12 (dd,  $J_{\text{P-P}}$  17.4 and 156.1 Hz,  $\mu$ -PPh<sub>2</sub>).

#### 4.5. Investigation of the thermolyses of compounds **2** and **3**

Compounds **2** and **3** (30 mg) were heated separately in toluene at the following temperatures: 80, 90 °C and under reflux for 3 h, after which time the solvent was evaporated under vacuum, the residues were taken in  $\text{CH}_2\text{Cl}_2$  and chromatographed on TLC plates, using  $\text{CH}_2\text{Cl}_2$ /hexane, 1:4 as eluent. Compound **2** was recovered unchanged according to the  $^{31}\text{P}$  NMR spectrum, and no decomposition was noted on the TLC plates. Dark red compound **3** underwent extensive decomposition, even at 80 °C and was partly recovered from the TLC plates.

#### 4.6. Reaction of compound **1** with $\text{Me}_3\text{NO}/\text{MeCN}$

A solution of freshly sublimed  $\text{Me}_3\text{NO}$  (1.5 mg, 0.02 mmol in 1 mL of  $\text{CH}_2\text{Cl}_2$ ) was added slowly to an orange solution of **1** (38 mg, 0.02 mmol) in MeCN (10 mL), cooled to –10 °C. The reaction mixture was stirred at this temperature for 1 h, after which time darkening of the solution was observed, and then left to warm to 25 °C. The solvents were evaporated in vacuo and the brown residue, dissolved in  $\text{CH}_2\text{Cl}_2$  (1 mL). Preparative TLC ( $\text{CH}_2\text{Cl}_2$ /hexane, 1:4 as eluent) afforded only the starting material **1** (10 mg). A large amount of decomposition material was left on the base line.

#### 4.7. X-ray structural analyses of compounds **2** and **3**

The compounds were obtained as red crystals by slow diffusion of hexane in a very concentrated solution of the respective compound in  $\text{CH}_2\text{Cl}_2$ /benzene (**2**) and  $\text{CH}_2\text{Cl}_2$  (**3**) at 25 °C. Diffraction intensities were collected at 293 K on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo  $K\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ). Crystal data and details of measurements for compounds **2** and **3** are summarized in Table 2. Psi-scan absorption correction was applied to all compounds. The computer program SHELXL97 [28] was used for structure solution and refinement. All non-H atoms



Table 2  
Crystallographic data for compounds **2** and **3**

	<b>2</b> · 0.5(C <sub>6</sub> H <sub>6</sub> )	<b>3</b>
Formula	C <sub>62</sub> H <sub>44</sub> Ir <sub>4</sub> O <sub>7</sub> P <sub>3</sub>	C <sub>59</sub> H <sub>41</sub> Ir <sub>4</sub> O <sub>7</sub> P <sub>3</sub>
<i>M</i>	1762.68	1723.63
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	15.204(4)	11.956(2)
<i>b</i> (Å)	17.420(8)	19.788(3)
<i>c</i> (Å)	12.131(9)	22.688(3)
$\alpha$ (°)	94.54(2)	90
$\beta$ (°)	109.00(1)	91.75(1)
$\gamma$ (°)	81.27(1)	90
<i>U</i> (Å <sup>3</sup> )	3001(3)	5365(1)
<i>Z</i> , <i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	2, 1.951	4, 2.134
$\mu$ (mm <sup>-1</sup> )	8.970	10.032
Independent reflections	9198	7290
<i>R</i> <sub>1</sub> (on <i>F</i> [ <i>I</i> > 2σ( <i>I</i> )])	0.0431	0.0524
<i>wR</i> <sub>2</sub> (on <i>F</i> <sup>2</sup> , all data)	0.1288	0.1535

were refined anisotropically. H atoms bound to C atoms were added in calculated positions. The computer program SCHAKAL99 [29] was used for all graphical representations. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 243735 and CCDC 243736. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

### Acknowledgements

We thank FAPESP and CNPq (M.H.A., R.M.S.P. and M.D.V) and FAPERJ of Brazil (M.D.V.) and the Ministero della Università e della Ricerca Scientifica e Tecnologica of Italy (D.B. and F.G.) for research grants.

### References

- [1] S. Jeannin, F. Robert, C. Rosenberger, *Inorg. Chem.* 33 (1994) 243.
- [2] M.I. Bruce, G.A. Koutsantonis, E.R.T. Tiekink, *J. Organomet. Chem.* 407 (1991) 391.
- [3] A.J. Carty, G. Hogarth, G. Enright, G. Frapper, *Chem. Commun.* (1997) 1883.
- [4] J.E. Davies, M.J. Mays, P.R. Raithby, K. Sarveswaran, *Angew. Chem. Int., Ed. Engl.* 36 (1997) 2668.
- [5] Y. Chi, A.J. Carty, P. Blenkiron, E. Delgado, G.D. Enright, W. Wang, S.-M. Peng, G.-H. Lee, *Organometallics* 15 (1996) 5269.
- [6] B.J. Bobbie, N.J. Taylor, A.J. Carty, *J. Chem. Soc., Chem. Commun.* (1991) 1511.
- [7] A.A. Cherkas, L.H. Randall, S.A. MacLaughlin, G.N. Mott, N.J. Taylor, A.J. Carty, *Organometallics* 7 (1988) 969.
- [8] E. Delgado, Y. Chi, W. Wang, G. Horgath, P.J. Low, G.D. Enright, S.-M. Peng, G.-H. Lee, A.J. Carty, *Organometallics* 17 (1998) 2936.
- [9] P.J. Low, T.M. Haynes, K.A. Udachin, A.E. Goeta, J.A.K. Howard, G.D. Enright, A.J. Carty, *J. Chem. Soc., Dalton Trans.* (2002) 1455.
- [10] A.A. Cherkas, N.J. Taylor, A.J. Carty, *J. Chem. Soc., Chem. Commun.* (1990) 385.
- [11] B.J. Bobbie, N.J. Taylor, A.J. Carty, *J. Chem. Soc., Chem. Commun.* (1991) 151.
- [12] P. Mathur, M.O. Ahmed, A.K. Dash, M.G. Walawalkar, *J. Chem. Soc., Dalton Trans.* (1999) 1795.
- [13] P. Mathur, M.O. Ahmed, A.K. Dash, M.G. Walawalkar, V.G. Puranik, *J. Chem. Soc., Dalton Trans.* (2000) 2916.
- [14] M.H.A. Benvenuti, M.D. Vargas, D. Braga, F. Grepioni, B.E. Mann, S. Naylor, *Organometallics* 12 (1993) 2947.
- [15] M.H. Araujo, A.G. Avent, M.D. Vargas, D. Braga, F. Grepioni, *J. Organomet. Chem.* 689 (2004) 3513.
- [16] F.S. Livotto, P.R. Raithby, M.D. Vargas, *J. Chem. Soc., Dalton Trans.* (1993) 1797.
- [17] P.B. Hitchcock, J.F. Nixon, M.D. Vargas, C.M. Ziglio, *J. Chem. Soc., Dalton Trans.* (2000) 2916.
- [18] C.M. Ziglio, M.D. Vargas, D. Braga, F. Grepioni, J.F. Nixon, *J. Organomet. Chem.* 656 (2002) 188.
- [19] R. Ros, A. Scrivanti, V.G. Albano, D. Braga, L. Garlaschelli, *J. Chem. Soc., Dalton Trans.* (1986) 2411.
- [20] A. Ceriotti, R. Della Pergola, F. Demartin, L. Garlaschelli, M. Manassero, N. Masciocchi, *Organometallics* 11 (1992) 756.
- [21] R.M.S. Pereira, F.Y. Fujiwara, M.D. Vargas, D. Braga, F. Grepioni, *Organometallics* 16 (1997) 4833.
- [22] W.-Y. Wong, F.-L. Ting, W.-L. Lam, *Eur. J. Chem.* (2001) 623.
- [23] A.A. Cherkas, N.J. Taylor, A.J. Carty, *J. Chem. Soc., Chem. Commun.* (1990) 385.
- [24] A.J. Carty, S.A. Mac Laughlin, D. Nucciaroni, in: J.G. Verkade, L.D. Quin (Eds.), *Phosphorus-31-NMR Spectroscopy in Stereochemical Analysis of Organic Compounds and Metal Complexes*, VCH, 1987 (Chapter 16).
- [25] M.H. Araujo, P.B. Hitchcock, J.F. Nixon, M.D. Vargas, *J. Braz. Chem. Soc.* 9 (1998) 563.
- [26] J.P.H. Charmant, G. Davies, P.J. King, J.R. Wigginton, E. Sappa, *Organometallics* 19 (2000) 2330.
- [27] A. Hengefelt, R. Nast, *Chem. Ber.* 116 (1983) 2025.
- [28] G.M. Sheldrick, *SHELX-97*, Program for Crystal Structure Determination, University of Göttingen, Göttingen, Germany, 1997.
- [29] E. Keller, *SCHAKAL99 Graphical Representation of Molecular Models*, University of Freiburg, Germany, 1999.