

Article

Synthesis and Structural Characterization of
 $[\text{Ir}_4(\mu\text{-CO})(\text{CO})_7\{\mu_4\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{C}(\text{Ph})\text{PCBu}^t\}(\mu\text{-PPh}_2)]$:
Alkyne-Phosphaalkyne Coupling and Formation of a Novel
2-phosphabutadienylphosphine Ligand

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A reação de $[\text{Ir}_4(\mu\text{-H})(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$ **1** com $\text{P}\equiv\text{CBu}^t$ em CH_2Cl_2 a 35 °C por 4 h leva à formação do composto inédito $[\text{Ir}_4(\mu\text{-CO})(\text{CO})_7\{\mu_4\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{C}(\text{Ph})\text{PCBu}^t\}(\mu\text{-PPh}_2)]$ **2**, que contém a cadeia 2-fosfabutadienilfosfina. O composto **2** forma-se também quando $[\text{Ir}_4(\text{CO})_{10}(\text{Ph}_2\text{PC}\equiv\text{CPh})(\text{PPh}_2\text{H})]$ **3** é aquecido na presença de $\text{P}\equiv\text{CBu}^t$, em thf, a 40 °C, por 48 h. Essas duas reações também produzem pequenas quantidades de $[\text{Ir}_4(\mu\text{-CO})(\text{CO})_7(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$ **4**, porque as velocidades das transformações de **1** e de **3** em **4** e das reações desses compostos com $\text{P}\equiv\text{CBu}^t$ são semelhantes. O composto **2** foi caracterizado por dados analíticos e espectroscópicos, espectrometria de massas usando fonte de FAB e experimentos de RMN de ^1H , ^{31}P , ^{13}C , 2D ^{31}P - ^1H HETCOR, diferença de nOe e DEPT que levaram à sua formulação e estabeleceram que havia ocorrido o acoplamento entre o ligante $\text{Ph}_2\text{PC}\equiv\text{CPh}$ e o $\text{P}\equiv\text{CBu}^t$ e a migração do hidreto para o C α do $\text{Ph}_2\text{PC}\equiv\text{CPh}$. Entretanto, esses dados não permitiram decidir se a clivagem da ligação P-C_{sp} do $\text{Ph}_2\text{PC}\equiv\text{CPh}$ havia ocorrido e nem definir o modo de interação da cadeia organofosforada. A estrutura molecular do composto **2**, determinada por uma análise de difração de raios-X, mostrou que o cluster exibe um arranjo metálico na forma de uma borboleta e que a cadeia organofosforada, corretamente formulada por dados espectroscópicos, interage com o poliedro metálico através de quatro ligações σ .

Reaction of $[\text{Ir}_4(\mu\text{-H})(\text{CO})_9(\text{Ph}_2\text{PC}\equiv\text{CPh})(\mu\text{-PPh}_2)]$ **1** with $\text{P}\equiv\text{CBu}^t$ in CH_2Cl_2 , at 35 °C, for 4 h yields the novel compound $[\text{Ir}_4(\mu\text{-CO})(\text{CO})_7\{\mu_4\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{C}(\text{Ph})\text{PCBu}^t\}(\mu\text{-PPh}_2)]$ **2**, which contains the 2-phosphabutadienylphosphine chain. Compound **2** is also formed upon thermolysis of $[\text{Ir}_4(\text{CO})_{10}(\text{Ph}_2\text{PC}\equiv\text{CPh})(\text{PPh}_2\text{H})]$ **3** in the presence of $\text{P}\equiv\text{CBu}^t$ in thf, at 40 °C, for 48 h. Small amounts of $[\text{Ir}_4(\mu\text{-CO})(\text{CO})_7(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$ **4** are always obtained from both reactions, because of the competing rates of the transformations of **1** and **3** into **4** and of their reactions with $\text{P}\equiv\text{CBu}^t$. Compound **2** was characterized by analytical and spectroscopic studies such as FAB ms, ^1H , ^{31}P , ^{13}C , 2D ^{31}P - ^1H HETCOR, nOe difference and DEPT NMR experiments, which led to its formulation and established the coupling between the coordinated $\text{Ph}_2\text{PC}\equiv\text{CPh}$ and $\text{P}\equiv\text{CBu}^t$ and the migration of the hydride to the C α of the $\text{Ph}_2\text{PC}\equiv\text{CPh}$ ligand. However, it was impossible to establish unambiguously if cleavage of the P-C_{sp} bond of the $\text{Ph}_2\text{PC}\equiv\text{CPh}$ ligand had occurred and the mode of interaction of the organophosphorus chain. An X-ray diffraction study of compound **2** established

a butterfly arrangement of iridium atoms with the new ligand interacting with the metal framework via four σ bonds and the PPh₂ phosphorus lone pair.

Keywords: iridium cluster, phosphalkyne, alkyne, coupling reaction

Introduction

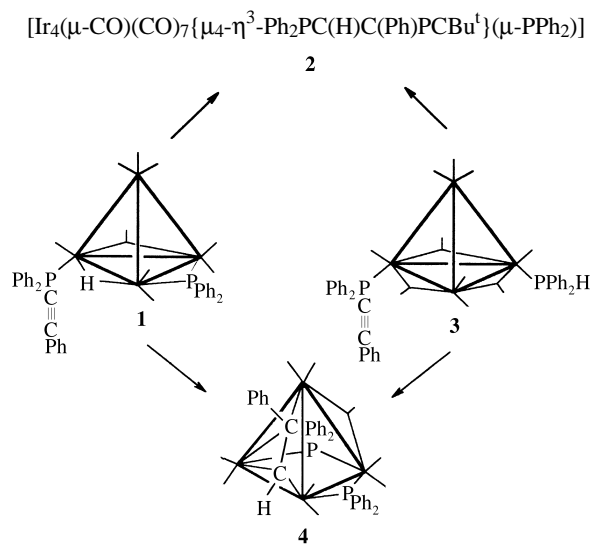
There are relatively few examples of alkyne-alkyne coupling reactions at polynuclear carbonyl clusters¹, one example being the reaction between [Ir₄(μ -H)(CO)₉-(Ph₂PC \equiv CPh)(μ -PPh₂)] and HC \equiv CPh, which led to [Ir₄(CO)₇(μ_4 - η^3 -PhCC(H)CCPh)(μ -PPh₂)₃]². The coordination chemistry of phosphalkynes, P \equiv CR, has been of great interest and its similarity to alkynes has been discussed previously, and various publications and reviews have been written³. Published examples of codimerization between a phosphalkyne and an alkyne are relatively few. For example, the reaction between [Co₂(Cp)₂-(Me₃SiCCSiMe₃)] and P \equiv CBu^t resulted in the desired η^4 -1-phosphacyclobutadiene complex [Co(Cp)(η^4 -PC(Bu^t)C(SiMe₃)C(SiMe₃))] and the reaction of [Zr(Cp)₂(PMe₃)(η^2 -PCBu^t)] with alkynes led to the 1-phospha-3-zircona cyclopentadiene complexes⁴. The only published attempt to couple similar molecules on a cluster compound involved the reaction between [Fe₃(CO)₉Se(PBu^t)-(Bu^tC \equiv CH)] and P \equiv CBu^t with led to the unexpected [Fe₃(CO)₇Se(PBu^t)(Bu^tC \equiv CH)(μ_3 -P-C(=C=O)(Bu^t)] compound⁵. Although a number of 2-phosphabutadienes are known⁶, none have previously been obtained by the alkyne-phosphalkyne coupling route. We recently reported that [Ir₄(μ -H)(CO)₉(Ph₂PC \equiv CPh)(μ -PPh₂)] **1** containing a terminally bound diphenylphosphinoacetylene undergoes a facile rearrangement into [Ir₄(μ -CO)(CO)₇(μ_3 - η^2 -HCCPh)(μ -PPh₂)₂] **4** which was proposed to occur *via* CO loss, P-C_{sp} bond cleavage and hydride migration to the α -carbon of the acetylide fragment⁷. Cluster coordinated acetylides have been shown to undergo nucleophilic attack of alkynes at the α -carbon^{8,9} and, in an attempt to trap the proposed hydrido-acetylido intermediate in the transformation of **1** into **4**, this reaction was carried out in the presence of P \equiv CBu^t. We report herein the first example of a phosphalkyne-alkyne coupling reaction in the coordination sphere of a cluster compound, and describe the synthesis and characterization of [Ir₄(μ -CO)(CO)₇{ μ_4 - η^3 -Ph₂PC(H)C(Ph)PCBu^t}(μ -PPh₂)] **2**, which contains the 2-phosphabutadienylphosphine chain. A preliminary communication of this work has appeared elsewhere¹⁰.

Results and Discussion

The reaction of the orange compound [Ir₄(μ -H)(CO)₉(Ph₂PC \equiv CPh)(μ -PPh₂)] **1** with P \equiv CBu^t in CH₂Cl₂, at 35 °C, for 4 h resulted in a dark brown solution, from which the brown compound [Ir₄(μ -CO)(CO)₇{ μ_4 - η^3 -Ph₂PC(H)C(Ph)PCBu^t}(μ -PPh₂)] **2** was isolated in up to 48% yield, after purification by TLC, besides unreacted **1** and small amounts of [Ir₄(μ -CO)(CO)₇(μ_3 - η^2 -HCCPh)(μ -PPh₂)₂] **4**. Formation of **2** in 10% yield was also observed when [Ir₄(CO)₁₀(Ph₂PC \equiv CPh)(PPh₂H)] **3** was heated with P \equiv CBu^t in thf at 40 °C for 48 h. In both cases, heating for longer periods of time only resulted in additional formation of **4** and decomposition. Small amounts of compound **4** were unavoidably obtained, because of the competing rates of the two reactions illustrated in Scheme 1.

The reaction of **4** with P \equiv CBu^t was also investigated. All attempts led to an immediate color change from orange to dark brown, but *in situ* ³¹P{¹H} NMR showed no phosphorus signals, which indicated that the reaction had occurred, but the product underwent decomposition. Similar behavior was observed when the reaction of **4** with PR₃ was investigated¹¹.

Compound **2** was formulated on the basis of analytical and spectroscopic data discussed below. The coupling reaction between the Ph₂PCCPh ligand and the PCBu^t molecule, and the hydride migration to the resulting new phosphorus carbon chain were established by ¹H, ³¹P and



Scheme 1.

^{13}C -NMR spectroscopy. In spite of the detailed spectroscopic studies undertaken, it was impossible to establish unambiguously whether the diphenylphosphino-alkyne had undergone P-C_{sp} bond cleavage and the geometry of the metal polyhedron in **2**, therefore an X-ray diffraction study had to be carried out.

Solution characterization of $[\text{Ir}_4(\mu\text{-CO})(\text{CO})_7\{\mu_4\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{C}(\text{Ph})\text{PCBu}^t\}(\mu\text{-PPh}_2)]$ **2**

The solution infrared spectrum of compound **2**, between 2200-1600 cm⁻¹, only showed absorptions due to terminal and bridging carbonyl ligands. This result suggested that the triple bond of the Ph₂PC≡CPh ligand was interacting with the metal framework, because of the absence of the ν_{C=C} band at 2172 cm⁻¹ which is observed in both starting materials **1** and **3**. In the FAB mass spectrum of **2**, a molecular ion at *m/z* 1568 and sequential loss of eight CO ligands were observed. The mass difference between **1** and **2** clearly indicated the incorporation of one PCBu^t molecule and loss of a CO group, resulting in a complex having the formula “Ir₄H(CO)₈(Ph₂PCCPh)(PPh₂)(PCBu^t)”, with which the elemental analysis agreed perfectly.

The ^1H -NMR data for **2** were consistent with the presence of both PPh₂ and Bu^t groups. The absence of a hydride signal and the presence of a doublet of doublets at δ 5.4 (*J*_{H-P} = 55 and 13 Hz) suggested that the hydride ligand had migrated to one of the carbon atoms of the Ph₂PCCPh (Cα or Cβ) or of the PCBu^t (Cγ) ligands, because migration of the hydride to one of the phosphorus atoms would have led to a much larger one-bond H-P coupling constant, typically between 300 and 500 Hz¹². A nOe difference experiment established to which of the ligands Ph₂PCCPh or PCBu^t the hydride had migrated. This experiment consisted of continuous irradiation of the resonance at δ 5.4 (CH), which resulted in a nOe of some of the phenyl proton resonances, but did not affect the Bu^t signal [Fig. 1a]. Likewise, when the Bu^t resonance at δ 1.1 was irradiated, only nOe of some of the phenyl proton resonances was observed [Fig. 1b]. Thus, the spacial proximity of the CH and the phenyl protons indicated that migration of the hydride had occurred either to Cα or Cβ of the Ph₂PCCPh ligand.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** showed three sets of pseudo-triplets at δ 16.1, 28.0 and 116.5 with *J*_{P-P} = 5 Hz. The 2D ^1H - ^{31}P shift correlation spectrum established that the lowest frequency peak could be assigned to the phosphorus atom of the PCBu^t (P_A) group, and the other two resonances at higher frequency were due to the PPh₂ groups (P_B and P_C) [Fig. 2]. This experiment also indicated that the strong P-H coupling of 55 Hz was to the P_A nucleus (δ 16.1), whilst the 13 Hz P-H coupling was to the PPh₂ phosphorus P_B (δ 28.0). The signal at δ 116.5 (P_C), was

confidently attributed to the bridging phosphido nucleus, on the basis of previous work⁷. The second PPh₂ (P_B) appeared at δ 28.0 and it is indicative of a phosphine¹², however the breaking of the P-C_{sp} bond cannot be excluded, since the μ-PPh₂ phosphorus nuclei have been shown to span a wide chemical shift range, depending on the distance between the metal atoms they bridge¹².

The coupling of the diphenylphosphinoalkyne with the phosphaalkyne was strongly suggested by the $^{13}\text{C}\{^1\text{H}\}$ and ^{13}C -NMR spectra and a DEPT experiment. These experiments made it possible to identify the Cβ (C_{quat}) resonance as a doublet of doublets at δ 54.2, with *J*_{C-P} = 37 and 28 Hz, and the Cα (CH), also as a dd, at δ 126.0, *J*_{C-P} = 57 and 35 Hz, and $^1J_{\text{C-H}}$ = 164 Hz. The chemical shifts of Cα and Cβ and the P-C and C-H coupling constants are in agreement

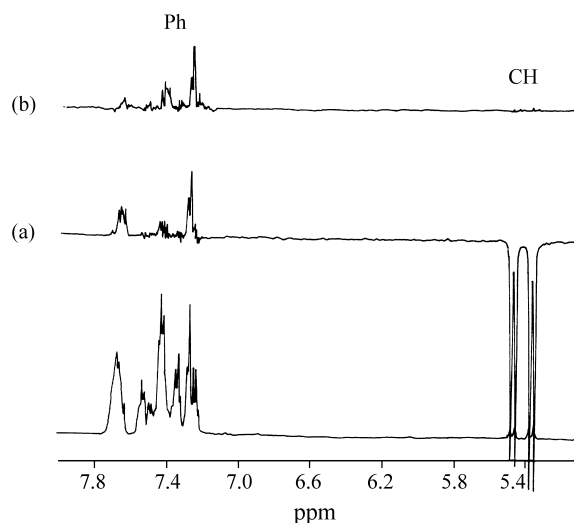


Figure 1. nOe difference spectrum of compound **2** in CDCl₃ at 25 °C resulting from: (a) irradiation of the resonance at δ 5.4 (CH) and (b) irradiation of the Bu^t at δ 1.1.

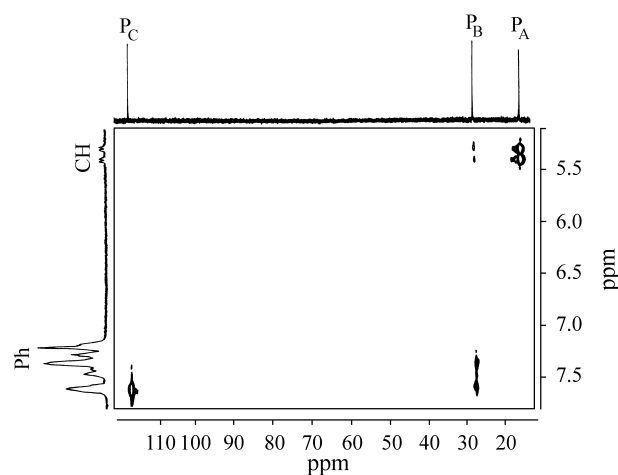


Figure 2. ^{31}P - ^1H heteronuclear correlation spectrum of compound **2** in CDCl₃ at 25 °C.

with those normally observed for sp^2 hybridized carbon atoms which are coordinated to organometallic compounds¹³. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** it was possible to identify all eight CO groups and to assign the bridging CO resonance at δ 191.2, which is shifted to high frequency, in comparison with the terminal CO groups¹⁴. This result was in agreement with the IR and mass spectra data and the elemental analysis. It was also possible to identify five quaternary carbons and the CH carbon atom of the phenyl groups, in the aromatic carbon region between δ 141.7 and 128.3. The two C_{quat} resonances at δ 38.5 and 29.6, were assigned to C_γ and C^* or *vice versa*.

On the basis of these results two possible structures **A** and **B** were proposed for the new 2-phosphabutadienyl chain, as shown in Scheme 2. In **A** the coupling between Ph_2PCCPh and PCBu^t would have occurred without cleavage of the $\text{Ph}_2\text{P}-\text{C}$ bond, and in **B** cleavage would have occurred, leading to a $\mu\text{-PPh}_2$ coordinated fragment. The *trans*-H to phospho-alkene P_A arrangement would result in the large $^3J_{\text{H-P}} = 55$ Hz observed.

The mode of interaction of the proposed 2-phosphabutadienyl fragments **A** or **B** to the Ir_4 metal frame could only be speculated upon based on the above analytical and spectroscopic data. Because the $^{13}\text{C}\{^1\text{H}\}$ NMR data do not suggest interaction of the $\text{C}=\text{C}$ bond with the metal frame, fragment **A** would be a potential 7 electron donor to the 55 electron " $\text{Ir}_4(\text{CO})_8(\text{PPh}_2)$ " fragment, whereas in **B** it could donate 6 electrons to the 58 electron " $\text{Ir}_4(\text{CO})_8(\text{PPh}_2)_2$ " fragment. Compound **2** would therefore have 62 (**A**) or 64 (**B**) valence electrons and, therefore would exhibit a butterfly or a spiked triangle arrangements of metal atoms according to Wade rules¹⁵. Similar metal arrangements were previously observed for $[\text{Ir}_4(\text{CO})_8(\eta^1\text{-COPh})(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$ (62 electrons)¹⁶ and $[\text{Ir}_4(\mu\text{-H})(\text{CO})_9(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PCCPh})(\mu\text{-PPh}_2)]$ (64 electrons) clusters.

Crystal Structure of **2**

The molecular structure of **2** in the solid state is shown in Fig. 3, together with the atomic labeling scheme, and confirmed the geometry shown in **A**. Selected bond distances (\AA) and angles ($^\circ$) are in Table 1. The structure consists of a butterfly arrangement of iridium atoms with metal-metal bond mean value of 2.785 \AA . This arrangement of iridium atoms was previously observed for other 62-electron Ir_4 clusters for which Ir-Ir bond mean values are comparable *e.g.* $[\text{Ir}_4(\text{CH}_3)(\text{CO})_8(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PCCPh})(\mu\text{-PPh}_2)]$ ¹⁷, [2.773 \AA], $[\text{Ir}_4(\text{CO})_8(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC(H)CPh})(\mu\text{-PPh}_2)(\text{PCy}_3)]$ ¹⁸, [2.749 \AA] and $[\text{Ir}_4(\text{CO})_8(\eta^1\text{-COPh})(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$ ¹⁶, [2.788 \AA]. Complex **2** possesses seven terminal CO ligands, distributed one on Ir(4) and two on each remaining Ir atoms, and one bridging carbonyl, which spans asymmetrically the shortest edge of the metal

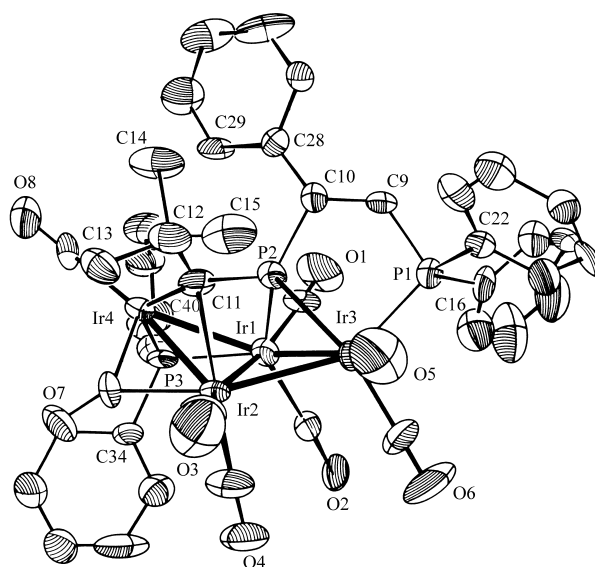
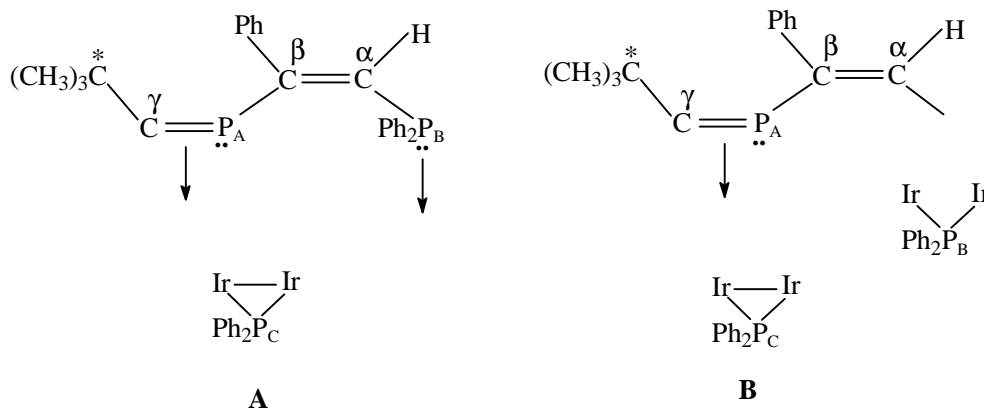


Figure 3. Molecular Structure of $[\text{Ir}_4(\mu\text{-CO})(\text{CO})_7(\mu_4\text{-}\eta^3\text{-Ph}_2\text{PC(H)-C(Ph)PCBu}^t)(\mu\text{-PPh}_2)]$ **2**.



Scheme 2.

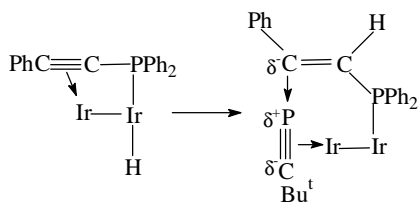
Table 1. Selected bond distances (Å) and angles (deg) for **2**.

Ir(1)-Ir(2)	2.798(1)	Ir(1)-Ir(3)	2.795(1)
Ir(1)-Ir(4)	2.838(1)	Ir(2)-Ir(3)	2.790(1)
Ir(2)-Ir(4)	2.704(1)	Ir(1)-P(2)	2.352(5)
Ir(1)-P(3)	2.390(6)	Ir(2)-P(2)	2.734(5)
Ir(3)-P(1)	2.299(6)	Ir(3)-P(2)	2.277(5)
Ir(4)-P(3)	2.264(5)	Ir(1)-C(1)	1.95(2)
Ir(1)-C(2)	1.89(2)	Ir(2)-C(3)	1.84(2)
Ir(2)-C(4)	1.91(2)	Ir(2)-C(7)	2.14(2)
Ir(2)-C(11)	2.25(2)	Ir(3)-C(5)	1.85(3)
Ir(3)-C(6)	1.95(2)	Ir(4)-C(7)	1.95(2)
Ir(4)-C(8)	1.85(2)	Ir(4)-C(11)	2.05(2)
P(1)-C(9)	1.79(2)	P(1)-C(16)	1.78(2)
P(1)-C(22)	1.78(2)	P(2)-C(10)	1.87(2)
P(2)-C(11)	1.70(2)	P(3)-C(34)	180(2)
P(3)-C(40)	1.78(2)	C(9)-C(10)	1.32(3)
C(10)-C(28)	1.44(2)		
Ir(1)-P(2)-Ir(2)	66.3(1)	Ir(1)-Ir(3)-P(2)	54.1(1)
Ir(1)-Ir(4)-P(3)	54.5(2)	Ir(1)-P(3)-Ir(4)	75.1(2)
Ir(1)-P(2)-Ir(3)	74.3(2)	Ir(2)-Ir(1)-P(3)	91.0(1)
Ir(2)-Ir(1)-P(2)	63.4(1)	Ir(2)-Ir(3)-P(2)	64.4(1)
Ir(2)-Ir(4)-P(3)	96.3(1)	Ir(3)-Ir(1)-P(2)	51.7(1)
Ir(4)-Ir(1)-P(3)	50.5(1)	Ir(4)-Ir(1)-P(2)	65.1(1)
Ir(4)-Ir(2)-P(2)	62.5(1)	P(1)-Ir(3)-P(2)	84.4(2)
Ir(1)-C(1)-O(1)	176(2)	Ir(1)-C(2)-O(2)	178(2)
Ir(2)-C(3)-O(3)	174(3)	Ir(2)-C(4)-O(4)	172(3)
Ir(3)-C(5)-O(5)	177(2)	Ir(3)-C(6)-O(6)	178(3)
Ir(2)-C(7)-O(7)	135(2)	Ir(2)-C(7)-Ir(4)	82.8(7)
Ir(4)-C(7)-O(7)	142(2)	Ir(4)-C(8)-O(8)	177(2)
Ir(3)-Ir(1)-P(3)	150.5(1)		
Ir(1)-Ir(3)-P(1)	103.6(1)		
Ir(1)-Ir(4)-C(11)	81.6(6)		
Ir(1)-Ir(2)-C(11)	79.3(6)		
Ir(1)-P(2)-C(11)	105.4(7)		
Ir(1)-P(2)-C(10)	115.8(5)		
Ir(2)-Ir(3)-P(1)	148.7(1)		
Ir(2)-C(11)-P(2)	86.2(8)		
Ir(2)-C(11)-Ir(4)	77.6(6)		
Ir(3)-P(2)-C(10)	110.5(6)		
Ir(3)-P(2)-C(11)	114.2(6)		
Ir(4)-C(11)-P(2)	97.0(10)		
P(1)-C(9)-C(10)	125(2)		
P(2)-C(11)-C(12)	129(2)		
P(2)-Ir(1)-P(3)	113.6(2)		
P(2)-C(10)-C(9)	113.0(14)		
P(2)-C(10)-C(28)	121(2)		
P(3)-Ir(4)-C(11)	136.0(6)		
Ir(2)-C(11)-C(12)	125.1(14)		
Ir(4)-C(11)-C(12)	127(2)		
C(9)-C(10)-C(28)	126(2)		
C(10)-P(2)-C(11)	125.3(9)		
C(16)-P(1)-C(22)	107.6(10)		

framework Ir(2)-Ir(4) [2.704(1) Å, Ir(4)-C(7) 1.95(2) and Ir(2)-C(7) 2.14(2) Å]. The Ir(1)-Ir(4) is the longest edge [2.838(1) Å] and is spanned by an asymmetric phosphido group [Ir(1)-P(3) 2.390(6) and Ir(4)-P(3) 2.265(5) Å] which donates, formally, three electrons to the cluster. The new phosphabutadienyl Ph₂PC(H)C(Ph)PCBu^t ligand donates formally seven electrons to the cluster: two from the P(1)-C(9)=C(10) moiety which is interacting with the metal framework *via* the phosphorus atom lone pair of the P(1)Ph₂ group [Ir(3)-P(1) 2.299(6) Å], five from the 2-phosphaalkenyl P(2)=C(11) moiety, which is essentially sp² [P(2)=C(11) 1.70(2) Å, C(10)-P(2)=C(11) 125.3(9)° and P(2)=C(11)-C(12) 129(2)°] and interacts with all four iridium atoms *via* four σ bonds [Ir(1)-P(2) 2.352(5), Ir(3)-P(2) 2.277(5), Ir(2)-C(11) 2.25(2) and Ir(4)-C(11) 2.05(2) Å]. The P=C and Ir-P bond distances are comparable with other complexes reported in the literature *e.g.* [W(CO)₅-(SiMe₃)₂C=P-C(OEt)=C(H)Ph]¹⁹, [P=C 1.65(10) Å], [Ru(MeP=CHBu^t)Cl(I)(CO)(PPh₃)₂]²⁰, [P=C 1.657(8) Å], [TiCp₂(Et₂BH)(P=C^tBu^t)]²¹, [1.666(2) Å], [Ir₄(CO)₈(η¹-COCH₃)(μ₄-η³-Ph₂P(1)CCPh)(μ-PPh₂)]¹⁷, [Ir-P(1) 2.307(9) Å], [Ir₄(μ-H)(CO)₉(μ₄-η³-Ph₂P(1)CCPh)(μ-PPh₂)]⁷, [Ir-P(1) 2.373(9) Å], [Ir₄(CO)₈(μ₃-η³-Ph₂P(1)C(H)CPh)(μ-PPh₂)(PCy₃)]¹⁸, [Ir-P(1) 2.270 Å]. A formal electron count in **2** results in 19 and 17 electrons on Ir(2) and Ir(4), respectively, and 18 electrons on the other two metal atoms. This has been previously observed for other Ir₄ clusters such as [Ir₄(CO)₈(η¹-COCH₃)-(μ₄-η³-Ph₂PCCPh)(μ-PPh₂)], [Ir₄(CO)₈(η¹-CH₃)(μ₄-η³-Ph₂PCCPh)(μ-PPh₂)] and [Ir₄(CO)₈(μ₃-η³-Ph₂P C(H)CPh)(μ-PPh₂)(PCy₃)].

Although the X-ray diffraction study has confirmed structure **A**, proposed in Scheme 2 for the novel chain, it is impossible to be sure that P-C bond cleavage was not involved in the process, considering the analogous transformation of [Ru₃(μ-H)(CO)₈(μ₃-η²-CCBu^t)(Ph₂PC≡CPh)] into [Ru₃(CO)₈{μ₃-η⁴-Ph₂PC(Ph)C(H)CC(Bu^t)}]²². In this case, the alkyne-alkyne condensation and migration of the hydride ligand resulted in a new organic chain, Ph₂PC(Ph)C(H)CC(Bu^t). It was suggested that a P-Cα bond cleavage had initially occurred, with formation of a μ-PPh₂ ligand, and after the condensation, insertion of the new carbon chain, "C(Ph)C(H)CC(Bu^t)", into the Ru-PPh₂ occurred leading to the observed P-Cβ(Ph); all these proposed steps had been previously observed.

No information regarding the detailed mechanism of the formation of compound **2** is available, but one can speculate the following steps: (i) CO loss and interaction of the acetylene moiety with an electron poor Ir center with a Ir-Ir bond cleavage, (ii) hydride migration to the Cα of the Ph₂PCCPh ligand, and (iii) nucleophilic attack of the



C β at the δ^+ P of the PCBu^t ligand with formation of the 2-phosphabutadienylphosphine observed experimentally.

Experimental

General procedures

All manipulations and reactions were performed under an atmosphere of argon, unless otherwise specified, using standard Schlenk techniques. CH₂Cl₂ was dried over CaH₂, hexane and thf over sodium wire. Solvents were freshly distilled under N₂ from Na/K alloy (hexane and thf) or from CaH₂ (CH₂Cl₂) prior to use. P \equiv CBu^t, ³ [Ir₄(μ -H)(CO)₉(Ph₂PC \equiv CPh)(μ -PPh₂)], **1** and [Ir₄(CO)₁₀(Ph₂PC \equiv CPh)(PPh₂H)]⁷, **3** were prepared by literature methods.

Preparative TLC was carried out in air by using *ca.* 2 mm thickness glass-backed silica plates (20 x 20 cm) prepared from silica gel type GF₂₅₄ (Fluka) and CH₂Cl₂-hexane (3:7) as eluent and the compounds were extracted from silica with CH₂Cl₂.

IR spectra were obtained on a Bomem MB series IR instrument scanning between 2200 and 1600 cm⁻¹, using CaF₂ cells. Microanalyses were performed at the Instituto de Química, Unicamp, Brazil. Fast atom bombardment mass spectra (FAB MS) were obtained on a Kratos MS50, operating at 8 keV. Xenon was used as the source of fast atoms. 3-Nitrobenzylalcohol, purchased from Aldrich, and distilled under *vacuo*, was used as a matrix. CH₂Cl₂ was used as solvent. All *m/z* values are referred to ¹⁹³Ir and were obtained at the University Chemical Laboratories, University of Cambridge, UK. ¹H, ¹³C and ³¹P-NMR studies were carried out using CDCl₃ solutions and a Bruker AMX 500 spectrometer. Standard pulse sequences were used for the NMR experiments²³. Chemical shifts are given in ppm using deuterated solvents as lock and reference (¹H and ¹³C, SiMe₄; ³¹P 85 % H₃PO₄, external) and coupling constants (*J*) are given in Hz.

Preparation of [Ir₄(CO)₈{ μ - η^3 -Ph₂PC(H)C(Ph)PCBu^t}(μ -PPh₂)] **2**

Method 1

An orange solution of [Ir₄(μ -H)(CO)₉(Ph₂PC \equiv CPh)(μ -PPh₂)] **1** (100 mg, 0.08 mmol) and P \equiv CBu^t (8 μ L, 0.08 mmol) in CH₂Cl₂ (10 mL) was heated at 35 °C for 4 h, after which time a color change from orange to dark brown was observed. The solution was concentrated under *vacuo* to about 1 mL and the mixture purified by TLC to afford

[Ir₄(CO)₈{ μ - η^3 -Ph₂PC(H)C(Ph)PCBu^t}(μ -PPh₂)] **2** (60 mg, 48%, R_f 0.30, brown), [Ir₄(CO)₈{ μ - η^2 -HCCPh)(μ -PPh₂)₂] **4** (15 mg, 12%, R_f 0.55, orange) and starting material **1** (15 mg, 15%, R_f 0.41, orange).

Method 2

To a yellow solution of [Ir₄(CO)₁₀(Ph₂PC \equiv CPh)(PPh₂H)] **3** (53 mg, 0.035 mmol) in thf (10 mL) P \equiv CBu^t (7 μ L, 0.07 mmol) was added and the reaction mixture was heated at 40 °C for 48 h. The resulting brown solution was concentrated under *vacuo* to about 1 mL. Separation of the mixture by TLC afforded [Ir₄(CO)₈{ μ - η^3 -Ph₂PC(H)C(Ph)PCBu^t}(μ -PPh₂)] **2** (5 mg, 10%, R_f 0.58, brown), [Ir₄(CO)₈{ μ - η^2 -HCCPh)(μ -PPh₂)₂] **4** (2 mg, 4%, R_f 0.67, orange), and unreacted **3** (27 mg, 50%, R_f 0.62, yellow), along with some decomposition products (base line on the TLC plates).

Reaction of [Ir₄(CO)₈{ μ - η^2 -HCCPh)(μ -PPh₂)₂] **4** with P \equiv CBu^t

(a) To a solution of [Ir₄(CO)₈{ μ - η^2 -HCCPh)(μ -PPh₂)₂] **4** (27 mg, 0.018 mmol) in CH₂Cl₂ (10 mL) was added P \equiv CBu^t (5.2 μ L, 0.046 mmol) and the reaction mixture heated at 35 °C for 5 h. After *ca.* 10 min the color of the solution slowly began to change from orange to brown and after 5 h the solution was dark brown. Purification by preparative TLC afforded unreacted starting material **4** along with decomposition on the base line of the TLC plates.

(b) A solution of **4** (70 mg, 0.047 mmol) and P \equiv CBu^t (10 μ L, 0.095 mmol) in benzene (20 mL) in a closed Schlenk fitted with Young tap, was heated under reflux for 4 h, a slowly color change from orange to dark brown was observed. The solvent was removed under reduced pressure and separation by preparative TLC afforded the starting material **4**, along with decomposition products on the base line of the TLC plates.

Characterization of **2**

Anal. Calcd. for C₄₅H₃₅O₈P₃Ir₄: C, 34.5; H, 2.2. Found: C, 34.7; H, 1.9%. IR (hexane, ν_{CO}): 2068 w, 2058 w, 2030vs, 2014w (sh), 2006s, 1985w, 1956s, 1836m cm⁻¹. FAB MS: *m/z* 1568 (*M*)⁺, 1540 (*M*-CO)⁺, 1512 (*M*-2CO)⁺, 1484 (*M*-3CO)⁺, 1456 (*M*-4CO)⁺, 1428 (*M*-5CO)⁺, 1400 (*M*-6CO)⁺, 1372 (*M*-7CO)⁺ and 1344 (*M*-8CO)⁺. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 1.1 (s, 9H, C(CH₃)₃), 5.4 (dd, 1H, *J*_{H-P} 55 and 13 Hz), 6.9-7.5 (m, 25H, C₆H₅). ¹³C {¹H} NMR (125.721 MHz, CDCl₃, 25 °C): δ 191.2 (d, *J*_{C-P} 6 Hz, CO), 183.3 (d, *J*_{C-P} 73 Hz, CO), 175.5 (t, *J*_{C-P} 35 Hz, CO), 173.8 (d, *J*_{C-P} 49 Hz, CO), 170.4 (s, CO), 168.0 (d, *J*_{C-P} 25 Hz, CO), 165.8 (d, *J*_{C-P} 111 Hz, CO), 161.8 (br, CO), 141.7 (d, *J*_{C-P} 33 Hz, C_{quat.}, Ph), 138.4 (d, *J*_{C-P} 30 Hz, C_{quat.}, Ph),

136.0 (d, J_{C-P} 57 Hz, $C_{quat.}$, Ph), 134.8 (dd, J_{C-P} 21 and 8 Hz, $C_{quat.}$, Ph), 133.7 (d, J_{C-P} 13 Hz, CH, Ph), 132.6 (d, J_{C-P} 11 Hz, CH, Ph), 132.1 (d, J_{C-P} 13 Hz, CH, Ph), 131.7 (s, CH, Ph), 130.5 (s, CH, Ph), 130.1 (s, $C_{quat.}$, Ph), 130.0 (s, CH, Ph), 129.6 (t, J_{C-P} 8, CH, Ph), 129.1 (d, J_{C-P} 11 Hz, CH, Ph), 128.6 (d, J_{C-P} 12 Hz, CH, Ph), 128.3 (t, J_{C-P} 11 Hz, CH, Ph), 126.0 (dd, J_{C-P} 57 and 35 Hz, CH), 54.2 (dd, J_{C-P} 37 and 28 Hz, $C_{quat.}$), 38.5 (s, $C_{quat.}$), 36.6 (d, J_{C-P} 8 Hz, CCH₃), 29.6 (s, $C_{quat.}$). $^{31}P\{^1H\}$ NMR (202.404 MHz, CDCl₃, 25 °C): δ 16.1 (P₁, t, J_{P-P} 5 Hz), 28.0 (P₂, t, J_{P-P} 5 Hz), 116.5 (P₃, t, J_{P-P} 5 Hz).

X-ray structure determination of 2

X-ray quality crystals were grown by slow evaporation of a very concentrated CHCl₃ solution of 2. Data were collected at 293 K on an Enraf-Nonius CAD4 diffractome-

ter. Crystal and refinement details are given in Table 2. Non-H atoms were located by heavy atom methods and the structure refined using SHELXS-86²⁴ and refined on F² with all reflections using SHELXS-93²⁴. Hydrogen atoms were included in rigid mode.

Atomic coordinates, thermal parameters and a full list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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Table 2. Crystal data and details of measurements for compound 2.

Empirical formula	C ₄₅ H ₃₅ Ir ₄ O ₈ P ₃ ·CHCl ₃
Formula weight	1684.8
Crystal system	Monoclinic
Space group	C2/c (N. 15)
a	41.913 (8) (Å)
b	12.747 (4) (Å)
c	18.522 (5) (Å)
β	95.17 (deg)
Volume	9855 Å ³
Z	8
Density (calculated)	2.27 (Mg m ⁻³)
Absorption coefficient	110.8 (cm ⁻¹)
F(000)	6240
Crystal size	0.4 x 0.2 x 0.1 (mm)
Wavelength	0.71073 (Å)
Temperature	293(2) K
θ range	2 to 25 (deg)
Index ranges	0 ≤ h ≤ 49, 0 ≤ k ≤ 15, -22 ≤ l ≤ 21
Reflections collected	9198
Independent reflections	8654 [R _{int} = 0.04]
Reflections with I > 2 σ (I)	5449
Structure solution	Direct methods
Refinement method	Full-matrix on all F ²
Data/restraints/parameters	8641/0/577
Goodness-of-fit on F ²	1.072
Final R indices [I > 2 σ (I)]	R ₁ = 0.064, wR ₂ = 0.126
R indices (all data)	R ₁ = 0.121, wR ₂ = 0.158
Largest diff. peak and hole	1.62 and -2.34 e.Å ⁻³
Abs. correction from psi scans	T _{max} = 1.00, T _{min} = 0.46
Maximum shift/e.s.d	0.002

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