J. Braz. Chem. Soc., Vol. 9, No. 6, 563-570, 1998.
Printed in Brazil.

0103 – 5053 \$6.00 + 0.00

Article

Synthesis and Structural Characterization of $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$: Alkyne-Phosphaalkyne Coupling and Formation of a Novel 2-phosphabutadienylphosphine Ligand

Maria Helena Araujo[a,b]***, Peter B. Hitchcock***[b]***, John F. Nixon****[b]***,***
and Maria D. Vargas*[a]

[a]*Instituto de Química, Universidade Estadual de Campinas, C.P. 6154,*
13081-970 Campinas - SP, Brazil
[b]*School of Chemistry, Physics and Environmental Science, University of Sussex,*
Brighton, BN1 9QJ, UK

Received: August 26, 1998

A reação de $[Ir_4(\mu\text{-}H)(CO)_9(Ph_2PC\equiv CPh)(\mu\text{-}PPh_2)]$ **1** com $P\equiv CBu^t$ em CH_2Cl_2 a 35 °C por 4 h leva à formação do composto inédito $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ **2**, que contem a cadeia 2-fosfabutadienilfosfina. O composto **2** forma-se também quando $[Ir_4(CO)_{10}(Ph_2PC\equiv CPh)(PPh_2H)]$ **3** é aquecido na presença de $P\equiv CBu^t$, em thf, a 40 °C, por 48 h. Essas duas reações também produzem pequenas quantidades de $[Ir_4(\mu\text{-}CO)(CO)_7(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2]$ **4**, porque as velocidades das transformações de **1** e de **3** em **4** e das reações desses compostos com $P\equiv CBu^t$ 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 $^{31}P\text{-}^1H$ HETCOR, diferença de nOe e DEPT que levaram à sua formulação e estabeleceram que havia ocorrido o acoplamento entre o ligante $Ph_2PC\equiv CPh$ e o $P\equiv CBu^t$ e a migração do hidreto para o $C\alpha$ do $Ph_2PC\equiv CPh$. Entretanto, esses dados não permitiram decidir se a clivagem da ligação $P\text{-}C_{sp}$ do $Ph_2PC\equiv CPh$ 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 $[Ir_4(\mu\text{-}H)(CO)_9(Ph_2PC\equiv CPh)(\mu\text{-}PPh_2)]$ **1** with $P\equiv CBu^t$ in CH_2Cl_2, at 35 °C, for 4 h yields the novel compound $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ **2**, which contains the 2-phosphabutadienylphosphine chain. Compound **2** is also formed upon thermolysis of $[Ir_4(CO)_{10}(Ph_2PC\equiv CPh)(PPh_2H)]$ **3** in the presence of $P\equiv CBu^t$ in thf, at 40 °C, for 48 h. Small amounts of $[Ir_4(\mu\text{-}CO)(CO)_7(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2]$ **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 $P\equiv CBu^t$. Compound **2** was characterized by analytical and spectroscopic studies such as FAB ms, ^1H, ^{31}P, ^{13}C, 2D $^{31}P\text{-}^1H$ HETCOR, nOe difference and DEPT NMR experiments, which led to its formulation and established the coupling between the coordinated $Ph_2PC\equiv CPh$ and $P\equiv CBu^t$ and the migration of the hydride to the $C\alpha$ of the $Ph_2PC\equiv CPh$ ligand. However, it was impossible to establish unambiguously if cleavage of the $P\text{-}C_{sp}$ bond of the $Ph_2PC\equiv CPh$ 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 PPh_2 phosphorus lone pair.

Keywords: *iridium cluster, phosphaalkyne, alkyne, coupling reaction*

Introduction

There are relatively few examples of alkyne-alkyne coupling reactions at polynuclear carbonyl clusters[1], one example being the reaction between $[Ir_4(\mu\text{-}H)(CO)_9\text{-}(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)]$ and $HC{\equiv}CPh$, which led to $[Ir_4(CO)_7(\mu_4\text{-}\eta^3\text{-}PhCC(H)CCPh)(\mu\text{-}PPh_2)_3]^2$. The coordination chemistry of phosphaalkynes, $P{\equiv}CR$, has been of great interest and its similarity to alkynes has been discussed previously, and various publications and reviews have been written[3]. Published examples of codimerization between a phosphaalkyne and an alkyne are relatively few. For example, the reaction between $[Co_2(Cp_2)\text{-}(Me_3SiCCSiMe_3)]$ and $P{\equiv}CBu^t$ resulted in the desired η^4-1-phosphacyclobutadiene complex $[Co(Cp)(\eta^4\text{-}PC(Bu^t)C(SiMe_3)C((SiMe_3)]$ and the reaction of $[Zr(Cp_2)(PMe_3)(\eta^2\text{-}PCBu^t)]$ with alkynes led to the 1-phospha-3-zircona cyclopentadiene complexes[4]. The only published attempt to couple similar molecules on a cluster compound involved the reaction between $[Fe_3(CO)_9Se(PBu^t)\text{-}(Bu^tC{\equiv}CH)]$ and $P{\equiv}CBu^t$ with led to the unexpected $[Fe_3(CO)_7Se(PBu^t)(Bu^tC{=}CH)(\mu_3\text{-}P\text{-}C({=}C{=}O)(Bu^t)]$ compound[5]. Although a number of 2-phosphabutadienes are known[6], none have previously been obtained by the alkyne-phosphaalkyne coupling route. We recently reported that $[Ir_4(\mu\text{-}H)(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)]$ **1** containing a terminally bound diphenylphosphinoacetylene undergoes a facile rearrangement into $[Ir_4(\mu\text{-}CO)(CO)_7(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2]$ **4** which was proposed to occur *via* CO loss, P-C_{sp} bond cleavage and hydride migration to the α-carbon of the acetylide fragment[7]. 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 phosphaalkyne-alkyne coupling reaction in the coordination sphere of a cluster compound, and describe the synthesis and characterization of $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)\ C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ **2**, which contains the 2-phosphabutadienylphosphine chain. A preliminary communication of this work has appeared elsewhere[10].

Results and Discussion

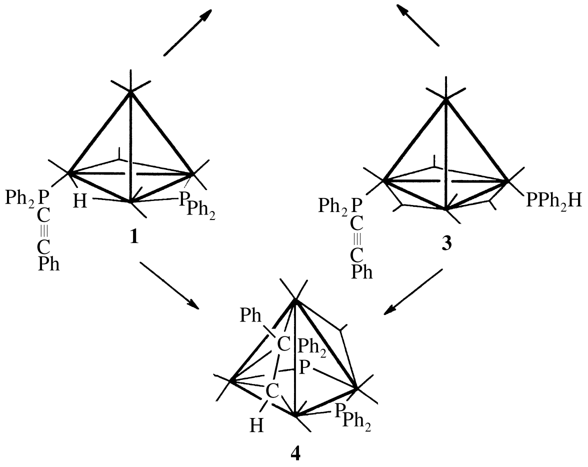
The reaction of the orange compound $[Ir_4(\mu\text{-}H)(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)]$ **1** with $P{\equiv}CBu^t$ in CH_2Cl_2, at 35 °C, for 4 h resulted in a dark brown solution, from which the brown compound $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ **2** was isolated in up to 48% yield, after purification by TLC, besides unreacted **1** and small amounts of $[Ir_4(\mu\text{-}CO)(CO)_7(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2]$ **4**. Formation of **2** in 10% yield was also observed when $[Ir_4(CO)_{10}(Ph_2PC{\equiv}CPh)(PPh_2H)]$ **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* $^{31}P\{^1H\}$ 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 PR_3 was investigated[11].

Compound **2** was formulated on the basis of analytical and spectroscopic data discussed below. The coupling reaction between the Ph_2PCCPh ligand and the $PCBu^t$ molecule, and the hydride migration to the resulting new phosphorus carbon chain were established by ^1H, ^{31}P and

$[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$

2



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 $[Ir_4(\mu\text{-}CO)(CO)_7\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ *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 $Ph_2PC{\equiv}CPh$ ligand was interacting with the metal framework, because of the absence of the $\nu_{C\equiv C}$ 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 "$Ir_4H(CO)_8(Ph_2PCCPh)(PPh_2)(PCBu^t)$", with which the elemental analysis agreed perfectly.

The ^{1}H-NMR data for **2** were consistent with the presence of both PPh$_2$ and Bu^t groups. The absence of a hydride signal and the presence of a doublet of doublets at δ 5.4 ($J_{H\text{-}P}$ = 55 and 13 Hz) suggested that the hydride ligand had migrated to one of the carbon atoms of the Ph$_2$PCCPh (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 Hz[12]. A nOe difference experiment established to which of the ligands Ph$_2$PCCPh 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 Ph$_2$PCCPh ligand.

The ^{31}P{^{1}H} NMR spectrum of **2** showed three sets of pseudo-triplets at δ 16.1, 28.0 and 116.5 with $J_{P\text{-}P}$ = 5 Hz. The 2D ^{1}H-^{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 PPh$_2$ 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 PPh$_2$ 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 work[7]. The second PPh$_2$ (P$_B$) appeared at δ 28.0 and it is indicative of a phosphine[12], however the breaking of the P-C$_{sp}$ bond cannot be excluded, since the μ-PPh$_2$ phosphorus nuclei have been shown to span a wide chemical shift range, depending on the distance between the metal atoms they bridge[12].

The coupling of the diphenylphosphinoalkyne with the phosphaalkyne was strongly suggested by the ^{13}C{^{1}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 $J_{C\text{-}P}$ = 37 and 28 Hz, and the Cα (CH), also as a dd, at δ 126.0, $J_{C\text{-}P}$ = 57 and 35 Hz, and $^1J_{C\text{-}H}$ = 164 Hz. The chemical shifts of Cα and Cβ and the P-C and C-H coupling constants are in agreement

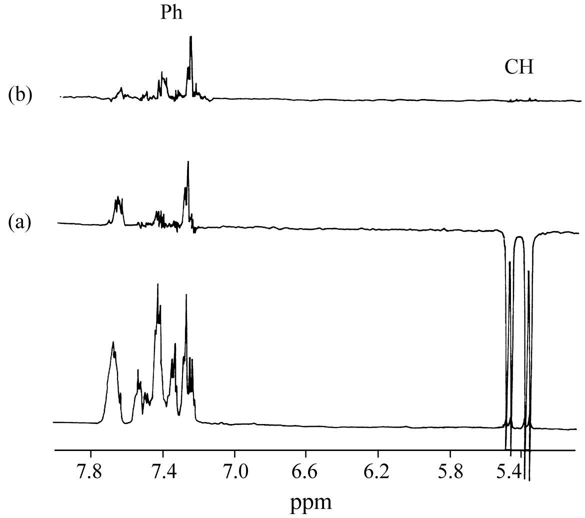


Figure 1. nOe difference spectrum of compound **2** in CDCl$_3$ at 25 °C resulting from: (a) irradiation of the resonance at δ 5.4 (CH) and (b) irradiation of the Bu^t at δ 1.1.

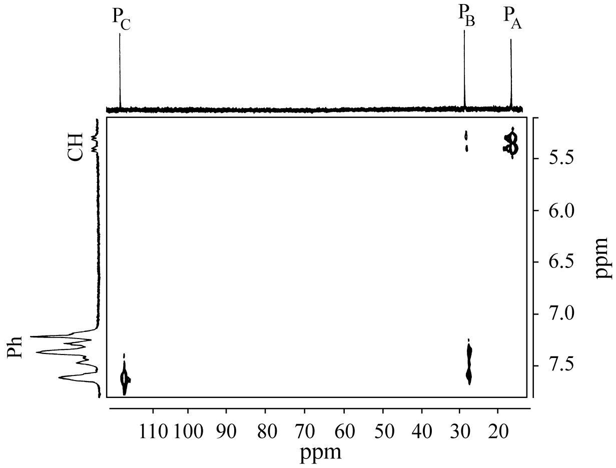


Figure 2. ^{31}P-^{1}H heteronuclear correlation spectrum of compound **2** in CDCl$_3$ at 25 °C.

with those normally observed for sp^2 hybridized carbon atoms which are coordinated to organometallic compounds[13]. In the $^{13}C\{^1H\}$ 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 groups[14]. 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 $C\gamma$ 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 Ph_2P-C bond, and in **B** cleavage would have occurred, leading to a μ-PPh_2 coordinated fragment. The *trans*-H to phospha-alkene P_A arrangement would result in the large $^3J_{H\text{-}P}$ = 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 $^{13}C\{^1H\}$ NMR data do not suggest interaction of the C=C bond with the metal frame, fragment **A** would be a potential 7 electron donor to the 55 electron "$Ir_4(CO)_8(PPh_2)$" fragment, whereas in **B** it could donate 6 electrons to the 58 electron "$Ir_4(CO)_8(PPh_2)_2$" 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 rules[15]. Similar metal arrangements were previously observed for $[Ir_4(CO)_8(\eta^1\text{-COPh})(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$ (62 electrons)[16] and $[Ir_4(\mu\text{-H})(CO)_9(\mu_4\text{-}\eta^3\text{-Ph}_2PCCPh)(\mu\text{-PPh}_2)]$ (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 (Å) and angles (°) are in Table 1. The structure consists of a butterfly arrangement of iridium atoms with metal-metal bond mean value of 2.785 Å. 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.* $[Ir_4(CH_3)(CO)_8(\mu_4\text{-}\eta^3\text{-Ph}_2PCCPh)(\mu\text{-PPh}_2)]$[17], [2.773 Å], $[Ir_4(CO)_8(\mu_3\text{-}\eta^3\text{-Ph}_2PC(H)CPh)(\mu\text{-PPh}_2)(PCy_3)]$[18], [2.749 Å] and $[Ir_4(CO)_8(\eta^1\text{-COPh})(\mu_4\text{-}\eta^3\text{-PhPC(H)CPh})(\mu\text{-PPh}_2)]$[16], [2.788 Å]. 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

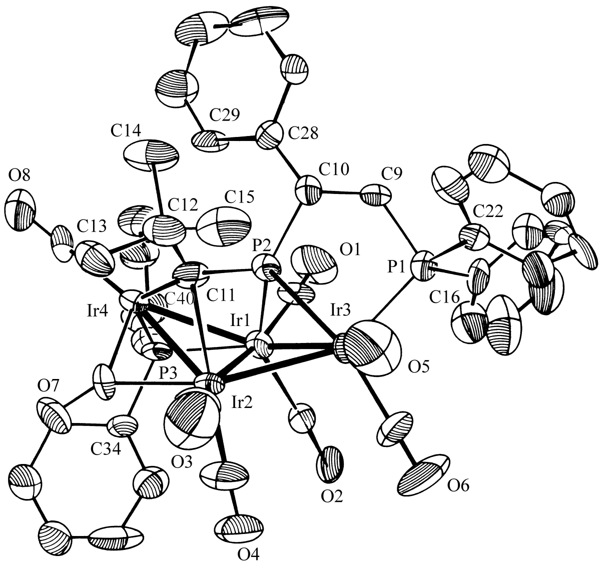
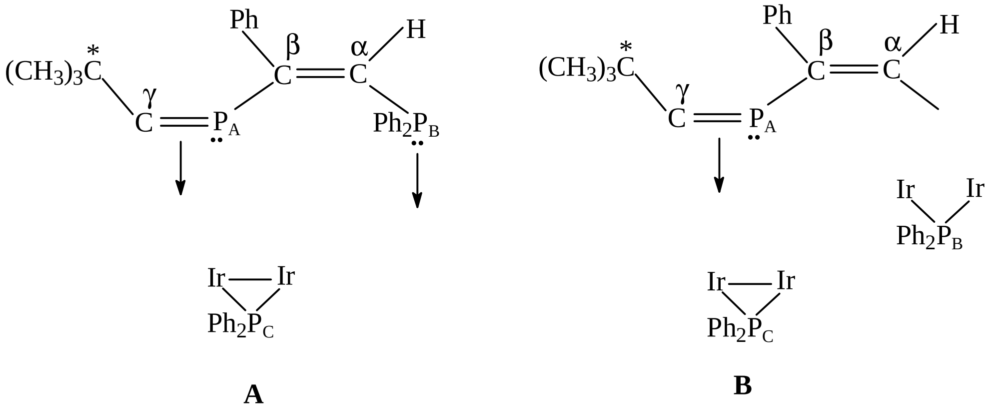


Figure 3. Molecular Structure of $[Ir_4(\mu\text{-CO})(CO)_7(\mu_4\text{-}\eta^3\text{-Ph}_2PC(H)\text{-}C(Ph)PCBu^t)(\mu\text{-PPh}_2)]$ **2**.



Scheme 2.

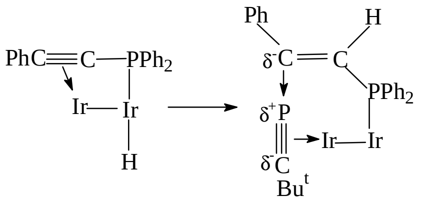
Table 1. Selected bond distances (Å) and angles (deg) for 2.

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 $Ph_2PC(H)C$ (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)Ph_2 group [Ir(3)-P(1) 2.299(6) Å], five from the 2-phosphaalkenyl P(2)=C(11) moiety, which is essentially sp^2 [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.* [$W(CO)_5$-{$(SiMe_3)_2C$=P-C(OEt)=C(H)Ph}][19], [P=C 1.65(10) Å], [Ru(MeP=CHBu^t)Cl(I)(CO)$(PPh_3)_2$][20], [P=C 1.657(8) Å], [$TiCp_2(Et_2BH)$(P=CBu^t)][21], [1.666(2) Å], [$Ir_4(CO)_8(\eta^1$-$COCH_3)(\mu_4$-η^3-$Ph_2P(1)CCPh)(\mu$-$PPh_2)$][17], [Ir-P(1) 2.307(9) Å], [$Ir_4(\mu$-$H)(CO)_9(\mu_4$-η^3-$Ph_2P(1)CCPh)$ (μ-$PPh_2)$][7], [Ir-P(1) 2.373(9) Å], [$Ir_4(CO)_8(\mu_3$-η^3-$Ph_2P(1)C(H)CPh)(\mu$-$PPh_2)(PCy_3)$][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 Ir_4 clusters such as [$Ir_4(CO)_8(\eta^1$-$COCH_3)$-$(\mu_4$-η^3-$Ph_2PCCPh)(\mu$-$PPh_2)$], [$Ir_4(CO)_8(\eta^1$-$CH_3)(\mu_4$-η^3-$Ph_2PCCPh)(\mu$-$PPh_2)$] and [$Ir_4(CO)_8(\mu_3$-η^3-Ph_2P C(H)CPh) (μ-$PPh_2)(PCy_3)$].

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 [$Ru_3(\mu$-$H)(CO)_8(\mu_3$-η^2-CCBu^t)($Ph_2PC\equiv$CPh)] into [$Ru_3(CO)_8${μ_3-η^4-Ph_2PC(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, Ph_2PC(Ph)C(H)CC(Bu^t). It was suggested that a P-Cα bond cleavage had initially occurred, with formation of a μ-PPh_2 ligand, and after the condensation, insertion of the new carbon chain, “C(Ph)C(H)CC(Bu^t)”, into the Ru-PPh_2 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 Ph_2PCCPh ligand, and **(iii)** nucleophilic attack of the



Cβ 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. CH_2Cl_2 was dried over CaH_2, hexane and thf over sodium wire. Solvents were freshly distilled under N_2 from Na/K alloy (hexane and thf) or from CaH_2 (CH_2Cl_2) prior to use. P≡CBu^t, [3] $[Ir_4(\mu\text{-}H)(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)]$[7], **1** and $[Ir_4(CO)_{10}(Ph_2PC{\equiv}CPh)(PPh_2H)]$[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 GF_{254} (Fluka) and CH_2Cl_2-hexane (3:7) as eluent and the compounds were extracted from silica with CH_2Cl_2.

IR spectra were obtained on a Bomen MB series IR instrument scanning between 2200 and 1600 cm^{-1}, using CaF_2 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. CH_2Cl_2 was used as solvent. All *m/z* values are referred to ^{193}Ir and were obtained at the University Chemical Laboratories, University of Cambridge, UK. ^{1}H, ^{13}C and ^{13}P-NMR studies were carried out using $CDCl_3$ solutions and a Bruker AMX 500 spectrometer. Standard pulse sequences were used for the NMR experiments[23]. Chemical shifts are given in ppm using deuterated solvents as lock and reference (^{1}H and ^{13}C, $SiMe_4$; ^{31}P 85 % H_3PO_4, external) and coupling constants (*J*) are given in Hz.

Preparation of $[Ir_4(CO)_8\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ 2

Method 1

An orange solution of $[Ir_4(\mu\text{-}H)(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)]$ **1** (100 mg, 0.08 mmol) and P≡CBu^t (8 μL, 0.08 mmol) in CH_2Cl_2 (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 $[Ir_4(CO)_8\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ **2** (60 mg, 48%, R_f 0.30, brown), $[Ir_4(CO)_8\{\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2]$ **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 $[Ir_4(CO)_{10}(Ph_2PC{\equiv}CPh)(PPh_2H)]$ **3** (53 mg, 0.035 mmol) in thf (10 mL) P≡CBu^t (7 μL, 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 $[Ir_4(CO)_8\{\mu_4\text{-}\eta^3\text{-}Ph_2PC(H)C(Ph)PCBu^t\}(\mu\text{-}PPh_2)]$ **2** (5 mg, 10%, R_f 0.58, brown), $[Ir_4(CO)_8\{\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2]$ **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 $[Ir_4(CO)_8\{\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2]$ 4 with P≡CBu^t

(a) To a solution of $[Ir_4(CO)_8\{\mu_3\text{-}\eta^2\text{-}HCCPh)\text{-}(\mu\text{-}PPh_2)_2]$ **4** (27 mg, 0.018 mmol) in CH_2Cl_2 (10 mL) was added P≡CBu^t (5.2 μL, 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≡CBu^t (10 μL, 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 $C_{45}H_{35}O_8P_3Ir_4$: 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 $(M\text{-}CO)^+$, 1512 $(M\text{-}2CO)^+$, 1484 $(M\text{-}3CO)^+$, 1456 $(M\text{-}4CO)^+$, 1428 $(M\text{-}5CO)^+$, 1400 $(M\text{-}6CO)^+$, 1372 $(M\text{-}7CO)^+$ and 1344 $(M\text{-}8CO)^+$. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.1 (s, 9H, $C(CH_3)_3$), 5.4 (dd, 1H, $J_{H\text{-}P}$ 55 and 13 Hz), 6.9-7.5 (m, 25H, C_6H_5). $^{13}C\{^1H\}$ NMR (125.721 MHz, $CDCl_3$, 25 °C): δ 191.2 (d, $J_{C\text{-}P}$ 6 Hz, *C*O), 183.3 (d, $J_{C\text{-}P}$ 73 Hz, *C*O), 175.5 (t, $J_{C\text{-}P}$ 35 Hz, *C*O), 173.8 (d, $J_{C\text{-}P}$ 49 Hz, *C*O), 170.4 (s, *C*O), 168.0 (d, $J_{C\text{-}P}$ 25 Hz, *C*O), 165.8 (d, $J_{C\text{-}P}$ 111 Hz, *C*O), 161.8 (br, *C*O), 141.7 (d, $J_{C\text{-}P}$ 33 Hz, $C_{quat.}$, Ph), 138.4 (d, $J_{C\text{-}P}$ 30 Hz, $C_{quat.}$, Ph), 136.0 (d, $J_{C\text{-}P}$ 57 Hz, $C_{quat.}$, Ph), 134.8 (dd, $J_{C\text{-}P}$ 21 and 8 Hz, $C_{quat.}$, Ph), 133.7 (d, $J_{C\text{-}P}$ 13 Hz, *C*H, Ph), 132.6 (d, $J_{C\text{-}P}$ 11 Hz, *C*H, Ph), 132.1 (d, $J_{C\text{-}P}$ 13 Hz, *C*H, Ph), 131.7 (s, *C*H, Ph), 130.5 (s, *C*H, Ph), 130.1 (s, $C_{quat.}$, Ph), 130.0 (s, *C*H, Ph), 129.6 (t, $J_{C\text{-}P}$ 8, *C*H, Ph), 129.1 (d, $J_{C\text{-}P}$ 11 Hz, *C*H, Ph), 128.6 (d, $J_{C\text{-}P}$ 12 Hz, *C*H, Ph), 128.3 (t, $J_{C\text{-}P}$ 11 Hz, *C*H, Ph), 126.0 (dd, $J_{C\text{-}P}$ 57 and 35 Hz, *C*H), 54.2 (dd, $J_{C\text{-}P}$ 37 and 28 Hz, $C_{quat.}$), 38.5 (s, $C_{quat.}$), 36.6 (d, $J_{C\text{-}P}$ 8 Hz, C*C*H_3), 29.6 (s, $C_{quat.}$). $^{31}P\{^1H\}$ NMR (202.404 MHz, $CDCl_3$, 25 °C): δ 16.1 (P_1, t, $J_{P\text{-}P}$ 5 Hz), 28.0 (P_2, t, $J_{P\text{-}P}$ 5 Hz), 116.5 (P_3, t, $J_{P\text{-}P}$ 5 Hz).

*X-ray structure determination of **2***

X-ray quality crystals were grown by slow evaporation of a very concentrated $CHCl_3$ solution of **2**. Data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer. Crystal and refinement details are given in Table 2. Non-H atoms were located by heavy atom methods and the structure refined using SHELXS-86[24] and refined on F^2 with all reflections using SHELXS-93[24]. Hydrogen atoms were included in rigid mode.

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

Empirical formula	$C_{45}H_{35}Ir_4O_8P_3.CHCl_3$
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	$0 \le h \le 49, 0 \le k \le 15, -22 \le l \le 21$
Reflections collected	9198
Independent reflections	8654 [$R_{int} = 0.04$]
Reflections with I > 2σ (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 > 2σ (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

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

Acknowledgements

We acknowledge financial support from the Commission of European Communities, Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq (M.H.A, M.D.V) and Fundação de Amparo à Pesquisa do Estado de São Paulo - FAPESP (M.H.A). We thank Dr. Anthony G. Avent for all his help with the NMR experiments.

References

1. Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203; Shapley, J.R.; McAteer, C.H.; Churchill, M.R.; Biondi, L.V. *Organometallics* **1984**, *3*, 1595; Riaz, V.; Curtis, M.D.; Rheingold, A.; Haggerty, B.S. *Organometallics* **1990**, *9*, 2647; Matsuzaka, H.; Mizobe, Y.; Nishio, M.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1011.
2. Pereira, R.M.S. Ph.D. Thesis, Universidade Estadual de Campinas, Brazil, 1996.
3. Nixon, J.F. *Chem. Rev.* **1988**, *88*, 1327; *Chem. Ind.* **1993**, 404; *Coord. Chem. Rev.* **1995**, *145*, 201; *Chem. Soc. Rev.* **1995**, 319; Dillon, K.B.; Mathey, F.; Nixon, J.F. *Phosphorus: The Carbon Copy* 1998, Ed. John Wiley.
4. Imhof, W.; Huttner, G. *J. Organomet. Chem.* **1993**, *447*, 31.
5. Binger, P.; Milczarek, R.; Mynott, R.; Regitz, M. *J. Organomet. Chem.* **1987**, *323*, C35; Regitz, M. In *Multiple Bond and Low Coordination in Phosphorus Chemistry*, Ed. Regitz, M.; Scherer, O.J., Georg Thieme Verlag, Stuttgart, 1990, Chapter 2.
6. Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Ed. Regitz, M.; Scherer, O.J., Georg Thieme Verlag, Stuttgart, 1990, Chapter 2.
7. Benvenutti. M.H.A.; Vargas, M.D.; Braga, D.; Grepioni, F.; Mann, B.E.; Naylor, S. *Organometallics* **1993**, *12*, 2947 and references therein.
8. Sappa, E.; Pasquinelli, G.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Soc., Dalton Trans.* **1989**, 601 and references therein.
9. Chi, Y.; Hwang, D.-K.; Chen, S.-F.; Liu, L.-K. *J. Chem. Soc., Chem. Commun.* **1989**, 1540; Chi, Y.; Huttner, G.; Imhof, W. *J. Organomet. Chem.* **1990**, *384*, 93.

10. Benvenutti, M.H.A.; Hitchcock, P.B.; Nixon, J.F.; Vargas, M.D. *J. Chem. Soc., Chem. Commun.* **1994**, 1869.
11. Araujo, M.H. *Ph.D. Thesis*, Universidade Estadual de Campinas, Brazil, 1995.
12. Verkade, J.G.; Mosbo, J.A. in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, Ed. Verkade, J.G. and Quin, L.D., 1987, VHC, Chapter 13.
13. Doherty, S.; Corrigan, J.F.; Carty, A.J.; Sappa, E. *Adv. Organomet. Chem. 37*, 39.
14. Mann, B.E.; Pickup, B.T.; Smith, A.K. *J. Chem. Soc., Dalton Trans.* **1989**, 889.
15. Mingos, D.M.P.; May, A.S. In *Structural and Bonding Aspects of Metal Cluster Chemistry*, Shriver, D.F.; Kaesz, H.D.; Adams, R.D., eds., VHC, 1990, 16, 4833.
16. Pereira, R.M.S.; Fijiwara, F.Y.; Vargas, M.D.; Braga, D.; Grepioni, F. *Organometallics* **1997**, *16*, 4833.
17. Vargas, M.D.; Pereira, R.M.S.; Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun.* **1993**, 1008.
18. Benvenutti. M.H.A.; Vargas, M.D.; Braga, D.; Grepioni, F.; Parisini, E.; Mann, B.E. *Organometallics* **1993**, *12*, 2955, and references therein.
19. Hobbold, M.; Streubel, R.; Benvenutti, M.H.A.; Hitchcock, P.B.; Nixon, J.F. *Organometallics* **1997**, *16*, 3726.
20. Bedford, R.B.; Hill, A.F.; Jones, C.; White, A.J.P.; Wilton-Ely, J.D.E.T. *J. Chem. Soc., Dalton Trans.* **1997**, 139.
21. Binger, P.; Sandmeyer, F.; Krüger, C.; Jörg, K.; Goddard, R.; Erker, G. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 197.
22. Sappa, E.; Pasquinelli, G.; Tiripichio, A.; Camellini, M.T. *J. Chem. Soc., Dalton Trans.* **1989**, 601 and references therein.
23. Mann, B.E. *Adv. Organomet. Chem.* **1988**, *28*, 397 and references therein.
24. Enraf-Nonius, CAD-4 Software. Version 5.0, 1989. Enraf-Nonius, The Netherlands. Sheldrick, G.M., 1985, SHELXS-86. Program for the Solution of Crystal Structures. University of Gottingen Germany. Sheldrick, G.M. (1993) SHELXL-93. Program for Crystal Structure Refinement. University of Gottingen, Germany. Watkin, D.J. and Pearce, L.J., 1993 CAMERON. An Interactive Graphics Editor. University of Oxford, England.

FAPESP helped in meeting the publication costs of this article