Synthesis and Structural Characterization of

\[ \text{[Ir}_4(\mu\text{-CO})_7(\mu_4-\eta^2\text{Ph}_2\text{PC}(\text{H})\text{C(Ph)}\text{PCBu}_1)(\mu_3\text{PPh}_2)] } \]

Alkyne-Phosphaalkyne Coupling and Formation of a Novel 2-phosphabutadienylphosphine Ligand

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A reaction of [Ir(μ-H)(CO)₉(Ph₂PC=CPh)(μ-PPh₂)] \textit{1} with P=CBu\textit{t} in CH₂Cl₂ at 35 °C for 4 h leads to the formation of the new compound [Ir(μ-H)(CO)₉(μ₃-η²-Ph₂PC(H)C(Ph)PCBu₁)(μ-PPh₂)] \textit{2}, which contains the 2-phosphabutadienylphosphine chain. Compound \textit{2} is also formed by thermolysis of [Ir(μ-H)(CO)₉(Ph₂PC=CPh)(μ-PPh₂)] \textit{3} in the presence of P=CBu\textit{t} in ethyl formate, at 40 °C for 48 h. Small amounts of [Ir(μ-H)(CO)₉(μ₃-η²-HCCPh)(μ-PPh₂)] \textit{4} are always obtained from both reactions, because of the competing rates of the transformations of \textit{1} and \textit{3} into \textit{4} and of their reactions with P=CBu\textit{t}. Compound \textit{2} was characterized by analytical and spectroscopic studies such as FAB ms, \textit{¹H}, \textit{³¹P}, \textit{¹³C}, 2D-\textit{³¹P}-\textit{¹H} HETCOR, nOe difference and DEPT NMR experiments, which led to its formulation and established the coupling between the coordinated Ph₂PC=CPh and P=CBu\textit{t} and the migration of the hydride to the Cα of the Ph₂PC=CPh ligand. However, it was impossible to establish unambiguously if cleavage of the P-Cσ bond of the Ph₂PC=CPh ligand had occurred and the mode of interaction of the organophosphorus chain. An X-ray diffraction study of compound \textit{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, phosphaalkyne, alkyne, coupling reaction

**Introduction**

There are relatively few examples of alkyne-alkyne coupling reactions at polynuclear carbonyl clusters, one example being the reaction between \([\text{Ir}_4(\mu-\text{H})(\text{CO})_7(\text{PPh}_2\text{PC-cppPh})(\mu-\text{PPh}_2)]\) and \(\text{HC}≡\text{CPh}\), which led to \([\text{Ir}_4(\text{CO})_7(\mu_4-\eta^1-\text{PCCC}(\text{H})\text{CPPh})(\mu-\text{PPh}_2)]\)\(^2\). The coordination chemistry of phosphaalkynes, \(\text{P}≡\text{C} \text{R}\), has been of great interest and its similarity to alkynes has been discussed previously, and various publications and reviews have been written. Published examples of codimerization between a phosphaalkyne and an alkyne are relatively few. For example, the reaction between \([\text{Co}_2(\text{Cp})_2-(\text{Me}_3\text{SiCCSiMe}_3)]\) and \(\text{P}≡\text{CBu}^1\) resulted in the desired \(\eta^1\)-1-phosphacyclobutadiene complex \([\text{Co}(\text{Cp})(\eta^1-\text{P}(\text{Bu}^1)\text{C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)]\) and the reaction of \([\text{Zr}(\text{Cp}_2)(\text{PMe}_3)(\eta^2-\text{PCBu}_1)]\) 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 \([\text{Fe}_3(\text{CO})_9\text{Se}(\text{PBu}_1)-(\text{Bu}^1\text{C}=\text{CH})]\) and \(\text{P}≡\text{CBu}_1\) with led to the unexpected \([\text{Fe}_3(\text{CO})_7\text{Se}(\text{PBu}_1)(\text{Bu}^1\text{C}=\text{CH})(\mu_3-\text{P}(=\text{C}=\text{O})(\text{Bu}^1)]\) compound.\(^5\) Although a number of 2-phosphabuta- dienes are known, none have previously been obtained by the alkyne-phosphaalkyne coupling route. We recently reported that \([\text{Ir}_4(\mu-\text{H})(\text{CO})_7(\text{PBPh}_2\text{PC-cppPh})(\mu-\text{PPh}_2)]\) containing a terminally bound diphenylphosphinoacetylene undergoes a facile rearrangement into \([\text{Ir}_4(\mu-\text{CO})(\text{CO})_7(\mu_4-\eta^2-\text{HCCPph})(\mu-\text{PPh}_2)]\) which was proposed to occur via CO loss, P-C₉ bond cleavage and hydride migration to the α-carbon of the acetylido fragment.\(^6\) Cluster coordinated acetylenes have been shown to undergo nucleophilic attack of alkynes at the α-carbon 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 \(\text{P}≡\text{CBu}^1\). 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 \([\text{Ir}_4(\mu-\text{CO})(\text{CO})_7(\mu_4-\eta^3-\text{PhPh}_2\text{PC}(\text{H})\text{C}(\text{Ph})\text{PCBu}_1)(\mu-\text{PPh}_2)]\) which contains the 2-phosphabuta dialenylphosphine chain.

**Results and Discussion**

The reaction of the orange compound \([\text{Ir}_4(\mu-\text{H})(\text{CO})_7(\text{Ph}_2\text{PC-cppPh})(\mu-\text{PPh}_2)]\) with \(\text{P}≡\text{CBu}_1\) in \(\text{CH}_2\text{Cl}_2\), at 35 °C, for 4 h resulted in a dark brown solution, from which the brown compound \([\text{Ir}_4(\mu-\text{CO})(\text{CO})_7(\mu_4-\eta^3-\text{PhPh}_2\text{PC}(\text{H})\text{C}(\text{Ph})\text{PCBu}_1)(\mu-\text{PPh}_2)]\) was isolated in up to 48% yield, after purification by TLC, besides unreacted 1 and small amounts of \([\text{Ir}_4(\mu-\text{CO})(\text{CO})_7(\mu_3-\eta^2-\text{HCCPph})(\mu-\text{PPh}_2)]\) 4. Formation of 2 in 10% yield was also observed when \([\text{Ir}_4(\text{CO})_{10}(\text{Ph}_2\text{PC-cppPh})(\text{PPh}_2\text{H})]\) 3 was heated with \(\text{P}≡\text{CBu}_1\) 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 \(\text{P}≡\text{CBu}_1\) was also investigated. All attempts led to an immediate color change from orange to dark brown, but \textit{in situ} \(^{31}\text{P}[\text{H}]\) 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 \(\text{PR}_3\) was investigated.\(^11\)

Compound 2 was formulated on the basis of analytical and spectroscopic data discussed below. The coupling reaction between the \(\text{Ph}_2\text{PC-cppPh}\) ligand and the \(\text{PCBu}_1\) molecule, and the hydride migration to the resulting new phosphorus carbon chain were established by \(^1\text{H}, \text{ }^{31}\text{P}\) and

\[
[\text{Ir}_4(\mu-\text{CO})(\text{CO})_7(\mu_4-\eta^3-\text{PhPh}_2\text{PC}(\text{H})\text{C}(\text{Ph})\text{PCBu}_1)(\mu-\text{PPh}_2)]
\]
13C-NMR spectroscopy. In spite of the detailed spectroscopic studies undertaken, it was impossible to establish unambiguously whether the diphenylphosphino-alkyne had undergone P-Csp 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 [Ir₄(µ-CO)(CO)₇{µ₄-η³-Ph₂PC(H)C(Ph)PCBu]}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 νC≡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 PCBu¹ molecule and loss of a CO group, resulting in a complex having the formula “Ir₄H(CO)₈(Ph₂PCCPh)(PPh₂)(PCBu)”, with which the elemental analysis agreed perfectly.

The ¹H-NMR data for 2 were consistent with the presence of both PPh₂ and Bu' 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 PCBu¹ (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. A NOE difference experiment established to which of the ligands Ph₂PCCPh or PCBu¹ 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' signal [Fig. 1a]. Likewise, when the Bu' resonance at δ 1.1 was irradiated, only NOE of some of the phenyl proton resonances was observed [Fig. 1b]. Thus, the spatial 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 ³¹P{¹H} 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-³¹P shift correlation spectrum established that the lowest frequency peak could be assigned to the phosphorus atom of the PCBu¹ (Pₐ) group, and the other two resonances at higher frequency were due to the PPh₂ groups (Pₐ and Pₐ) [Fig. 2]. This experiment also indicated that the strong P-H coupling of 55 Hz was to the Pₐ nucleus (δ 16.1), whilst the 13 Hz P-H coupling was to the PPh₂ phosphorus Pₐ (δ 28.0). The signal at δ 116.5 (Pₐ), was confidently attributed to the bridging phosphido nucleus, on the basis of previous work. The second PPh₂ (Pₐ) appeared at δ 28.0 and it is indicative of a phosphine, however the breaking of the P-Csp 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 bridge.

The coupling of the diphenylphosphinoalkyne with the phosphaalkyne was strongly suggested by the ¹³C{¹H} and ¹³C-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 J_C-H = 164 Hz. The chemical shifts of Cα and Cβ and the P-C and C-H coupling constants are in agreement.
with those normally observed for sp\(^2\) hybridized carbon atoms which are coordinated to organometallic compounds\(^{13}\). In the \(^{13}\)C\([\text{\{}{\text{H}}\text{]}\) NMR spectrum of 2 it was possible to identify all eight CO groups and to assign the bridging CO resonance at \(\delta\) 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 \(\delta\) 141.7 and 128.3. The two C\(_{\text{quat}}\) resonances at \(\delta\) 38.5 and 29.6, were assigned to C\(\gamma\) and C\(\alpha\) 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\(_2\)PCCPh and PCBu\(^t\) would have occurred without cleavage of the Ph\(_2\)P-C bond, and in B cleavage would have occurred, leading to a \(\mu\)-PPh\(_2\) coordinated fragment. The \(\text{trans}\) to phospha-alkene P\(_A\) arrangement would result in the large \(J_{\text{H-P}}\) = 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 \(^{13}\)C\([\text{\{}{\text{H}}\text{]}\) 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\(_2\))” 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)\(_8\)(\(\mu\)-\(\eta^3\)-PhPC(H)CPh)(\(\mu\)-PPh\(_2\))] (62 electrons)\(^{16}\) and [Ir\(_4\)(\(\mu\)-H)-(CO)\(_6\)(\(\mu\)-\(\eta^3\)-Ph\(_2\)PCCPh)(\(\mu\)-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\(_3\))\(_3\)(CO)\(_8\)(\(\mu\)-\(\eta^3\)-Ph\(_2\)PCCPh)(\(\mu\)-PPh\(_2\))]\(^{17}\), [2.773 Å], [Ir\(_4\)(CO)\(_8\)(\(\mu\)-\(\eta^3\)-Ph\(_2\)PCC(H)CPh)(\(\mu\)-PPh\(_2\))(PCy\(_3\))]\(^{18}\), [2.749 Å] and [Ir\(_4\)(CO)\(_8\)(\(\eta^3\)-COPh) (\(\mu\)-\(\eta^3\)-PhPC(H)CPh)(\(\mu\)-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.
Table 1. Selected bond distances (Å) and angles (deg) for 2.

| Bond/Distance | Value     | Bond/Distance | Value     |
|---------------|-----------|---------------|-----------|
| 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)-Ir(5)   | 2.795(1)  |
| Ir(1)-P(3)    | 2.390(6)  | Ir(2)-Ir(6)   | 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)-Ir(4)   | 2.838(1)  | Ir(1)-C(2)    | 1.89(2)   |
| Ir(2)-Ir(4)   | 2.704(1)  | Ir(2)-C(3)    | 1.84(2)   |
| Ir(2)-Ir(5)   | 2.734(5)  | Ir(3)-C(4)    | 1.85(3)   |
| Ir(1)-Ir(6)   | 2.838(1)  | Ir(4)-C(5)    | 1.85(3)   |
| Ir(1)-P(3)    | 2.390(6)  | Ir(2)-C(6)    | 2.14(2)   |

framework Ir(2)-Ir(4) [2.704(1) Å, Ir(4)-Ir(5) 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)(C₆H₄)PCBu₃ 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)Ir₂ group [Ir(3)-P(1) 2.299(6) Å], five from the 2-phosphaalkeny1 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(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]⁺: [Ir(1)-P(2) 2.352(5), Ir(3)-P(2) 2.277(5), Ir(1)-P(3) 2.390(6) and Ir(4)-P(3) 2.265(5) Å].

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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)₆(μ₃-η^1-CCBu')₃(PC₆H₆)(μ₃-η^1-CC₆H₄)₃] into [Ru₃(CO)(μ₃-η²-CC₆H₄)(PC₆H₆)(μ₃-η²-CC₆H₄)₃] in the case of the alkyne-alkyne condensation and migration of the hydride ligand resulting in a new organic chain, Ph₃PC(Ph)(C₆H₄)(PC₆H₆)(μ₂-P₃Ph₃)], [Ir(1)-Ir(4)](CO)₅(μ₃-η²-Ph₃PC(C₆H₄)PC₆H₆)(μ₂-P₃Ph₃)] and [Ir(1)-Ir(4)](CO)₅(μ₃-η²-Ph₃PC(C₆H₄)(PC₆H₆)(μ₂-P₃Ph₃)]. 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 Cβ of the Ph₃PC(C₆H₄)PC₆H₆ ligand, and (iii) nucleophilic attack of the
Preparation of \([\text{Ir}(CO)_6(\mu-\eta^3-H_2\text{PC}(H)C(Ph)\text{PCBu}^1)(\mu-\text{PPh}_2)])\) 2

Method 1

An orange solution of \([\text{Ir}(\mu-\text{H})(CO)_6(\text{PPh}_2\text{PC}=\text{CPh})(\mu-\text{PPh}_2)]) 1\) (100 mg, 0.08 mmol) and \(\text{P}=\text{CBu}^1\) (8 \(\mu\)L, 0.08 mmol) in \(\text{CH}_2\text{Cl}_2\) (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 \(\text{vacuo}\) to about 1 mL and the mixture purified by TLC to afford \([\text{Ir}(\mu-\text{H})(\text{CO})_6(\text{PPh}_2\text{PC}(H)C(Ph)\text{PCBu}^1)(\mu-\text{PPh}_2)])\) 2 (60 mg, 48%, \(R_f\) 0.30, brown), \([\text{Ir}(\mu-\eta_2-H_2\text{CPC}(\mu-\text{PPh}_2)])\) 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 \([\text{Ir}(\mu-\eta_2-H_2\text{CPC})\text{PPh}_2])\) \(P=\text{CBu}^1\) (53 mg, 0.035 mmol) in \(\text{thf}\) (10 mL) \(\text{P}=\text{CBu}^1\) (7 \(\mu\)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 \(\text{vacuo}\) to about 1 mL. Separation of the mixture by TLC afforded \([\text{Ir}(\mu-\eta_2-H_2\text{PC}(H)C(Ph)\text{PCBu}^1)(\mu-\text{PPh}_2)])\) 2 (5 mg, 10%, \(R_f\) 0.58, brown), \([\text{Ir}(\mu-\eta_2-H_2\text{CPC})(\mu-\text{PPh}_2)])\) 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 \([\text{Ir}(\mu-\eta^3-H_2\text{CPC})\text{PPh}_2])\) 4 with \(P=\text{CBu}^1\)

(a) To a solution of \([\text{Ir}(\mu-\eta^3-H_2\text{CPC})\text{PPh}_2])\) 4 (27 mg, 0.018 mmol) in \(\text{CH}_2\text{Cl}_2\) (10 mL) was added \(\text{P}=\text{CBu}^1\) (5.2 \(\mu\)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 products on the base line of the TLC plates.

(b) A solution of 4 (70 mg, 0.047 mmol) and \(\text{P}=\text{CBu}^1\) (10 \(\mu\)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 \(\text{C}_{38}\text{H}_{35}\text{O}_{35}\text{P}_{14}\): C, 34.5; H, 2.2. Found: C, 34.7; H, 1.9%. IR (hexane, \(\nu_{\text{CO}}\)): 2068 w, 2058 w, 2030 vs, 2014 w (sh), 1985s, 1956s, 1836m cm\(^{-1}\).

FAB MS: \(m/z\) 1568 (\(M^+\)), 1540 (\(M-\text{CO}^+\)), 1512 (\(M-2\text{CO}^+\)), 1484 (\(M-3\text{CO}^+\)), 1456 (\(M-4\text{CO}^+\)), 1428 (\(M-5\text{CO}^+\)), 1400 (\(M-6\text{CO}^+\)), 1372 (\(M-7\text{CO}^+\)) and 1344 (\(M-8\text{CO}^+\)) \(\text{P}^+\). \(\text{H}\) NMR (500 MHz, \(\text{CDCl}_3\), 25 °C): \(\delta\) 1.1 (s, 9H, C(\(\text{CH}_3\))), 5.4 (dd, 1H, \(J_{\text{H-p}}\) 55 and 13 Hz), 6.9-7.5 (m, 25H, C-Ph), 138.4 (d, \(J_{\text{C-p}}\) 30 Hz, C-Ph), 175.5 (t, \(J_{\text{C-p}}\) 1540 Hz, external) and coupling constants \((J)\) are given in Hz.
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-86 and refined on F² with all reflections using SHELXS-93. 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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References

1. Sappa, E.; Tiripicchio, A.; Braunstein, P. Chem. Rev. 1983, 83, 203; Shapley, J.R.; McAttee, 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.; Fijiiwara, 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 Göttingen Germany. Sheldrick, G.M. (1993) SHELXL-93. Program for Crystal Structure Refinement. University of Göttingen, Germany. Watkin, D.J. and Pearce, L.J., 1993 CAMERON. An Interactive Graphics Editor. University of Oxford, England.

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