

Metal vapour synthesis of phospha-organometallic compounds via reaction of cobalt atoms with the phospha-alkyne  $t\text{BuC}\equiv\text{P}$ : synthesis and structural characterisation of the sandwich compounds  $[\text{Co}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$ ,  $[\text{Co}(\eta^5\text{-P}_2\text{C}_3^t\text{Bu}_3)(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$  and the protonated tetraphospha-barrelene complex  $[\text{Co}(\eta^4\text{-P}_4\text{C}_4^t\text{Bu}_4\text{H})(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$ , the latter as its  $[\text{W}(\text{CO})_5]$  adduct

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This paper is dedicated to the memory of Professor Michael J.S. Dewar, FRS, in recognition of his pioneering theoretical studies concerning the nature of the bonding between unsaturated hydrocarbons and transition metals. Our metal vapour synthetic route to novel polyphospha-organocobalt(I) complexes, no doubt initially involves an analogous interaction of the phospha-alkyne,  $t\text{BuC}\equiv\text{P}$ , with the cobalt centre

## Abstract

The reaction of cobalt atoms with  $t\text{BuC}\equiv\text{P}$  gives the sandwich compounds  $[\text{Co}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$  and  $[\text{Co}(\eta^5\text{-P}_2\text{C}_3^t\text{Bu}_3)(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$ , which have both been structurally characterised by single crystal X-ray diffraction studies. The novel protonated tetraphospha-barrelene complex  $[\text{Co}(\eta^4\text{-P}_4\text{C}_4^t\text{Bu}_4\text{H})(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$  is also formed in the reaction and has been structurally characterised as its  $[\text{W}(\text{CO})_5]$  adduct. Variable temperature NMR spectra of these complexes are reported and discussed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Metal vapour synthesis; Cobalt; Phospha-alkyne; Sandwich compounds

## 1. Introduction

The past decade has seen the rapid development of a rich new area of organometallic chemistry in which phosphorus atoms replace  $\text{CH}^-$  fragments in the more familiar unsaturated organic ligands. There is now an extensive range of phospha-organometallic compounds containing phospha-alkynes, phospha-alkenes, phospha-dienes, phospha-allyls, phosphacyclobutadienes, phosphacyclopentadienyls and phospha-arenes as well as tetraphosphacubanes and tetraphospha-barrelenes. The area has recently been comprehensively reviewed [1–12].

One of the more developed systems involves cyclopentadienyl ring anions in which one or more CR units are replaced by phosphorus atoms, in particular the 1,3-di- and 1,2,4-tri-phospholyl anions,  $\text{P}_2\text{C}_3^t\text{Bu}_3^-$  and  $\text{P}_3\text{C}_2^t\text{Bu}_2^-$  which show interesting electronic and co-ordinating properties. Both  $\text{P}_2\text{C}_3^t\text{Bu}_3^-$  and  $\text{P}_3\text{C}_2^t\text{Bu}_2^-$  rings can exhibit  $\eta^5$ -ligation through their delocalised  $6\pi$ -aromatic systems and hence can mimic the bonding of the well-known cyclopentadienyl ligand in the formation of metallocene-like sandwich compounds. A wide range of such polyphospholyl compounds is now known, typified by the tetra-phosphametallocenes  $[\text{M}(\text{P}_2\text{C}_3^t\text{Bu}_3)_2]$  ( $\text{M} = \text{Sc}, \text{Fe}, \text{Ni}, \text{Pd}, \text{Pt}, \text{Yb}$ ), penta-phosphametallocenes  $[\text{M}'(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^5\text{-P}_2\text{C}_3^t\text{Bu}_3)]$  ( $\text{M}' = \text{V}, \text{Cr}, \text{Fe}, \text{Ru}$ ),  $[\text{M}'(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^3\text{-P}_2\text{C}_3^t\text{Bu}_3)]$

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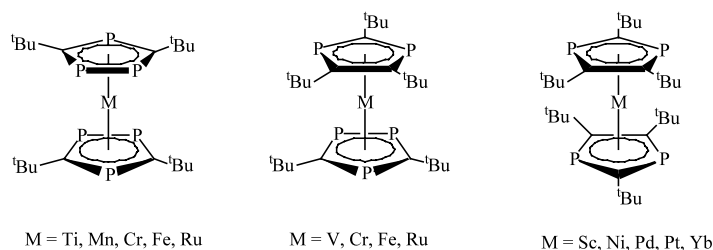


Fig. 1. Some transition metal  $P_3C_2Bu_2$  and  $P_2C_3Bu_3$  complexes.

( $M'' = Ni$ ), and the hexa-phosphametalloenes [ $M''(\eta^5-P_3C_2Bu_2)_2$ ] ( $M'' = Ti, V, Cr, Mn, Fe, Ru$ ) [13–24] (see Fig. 1). Very recently photoelectron spectroscopic measurements and density functional calculations have revealed details about the electronic structures of [ $M(P_3C_2Bu_2)_2$ ] ( $M = Ti, Fe$ ) [25,26].

Two major synthetic routes have been developed namely: (i) by treatment of the appropriate metal halide with the alkali metal salts of the  $P_2C_3Bu_3^-$  and  $P_3C_2Bu_2^-$  anions; or (ii) via metal vapour synthesis directly from the appropriate transition metal and the phosphalkyne  $P\equiv C^tBu$ . The recent synthesis of the pure potassium salt of the  $P_2C_3Bu_3$  anion, via the remarkable reaction involving phosphorus extrusion from the 1,3,5 triphosphabenzene  $P_3C_3Bu_3$  on treatment with potassium [27], offers further synthetic potential for the former route, while Zenneck and coworkers [28–30] have recently reported that  $Ph_3SnP_3C_2Bu_2$  is also a useful ring transfer reagent and have used it to synthesise the paramagnetic hexaphosphamanganocene, [ $Mn(\eta^5-P_3C_2Bu_2)_2$ ], which interestingly has a low spin  $^2A_1$  electronic ground state.

The most commonly occurring rings in co-condensation experiments with  $^tBuC\equiv P$  are the 1,3-di- and 1,2,4-tri-phosphorus analogues of the cyclopentadienyl ligand  $P_2C_3Bu_3$  and  $P_3C_2Bu_2$ . More recently, main group metal phospholyl derivatives, typified by the In(I) compounds shown in Fig. 2, have also been prepared by the MVS approach [31,32] as well as the [ $M(\eta^5-P_3C_2Bu_2)_2$ ] compounds ( $M = Sr, Pb, Zn, Cd$ ) which were made more conventionally directly from the  $P_3C_2Bu_2^-$  anion [33–35].

Co-condensation experiments with transition metal vapours have also afforded  $\pi$ -complexes in which the metal is complexed to another ring system as well as the phosphorus substituted cyclopentadienyl. These include the novel aromatic phosphirenyl cation ( $PC_2^tBu_2^+$ ) in [ $Ni(\eta^5-P_3C_2Bu_2)(\eta^3-PC_2^tBu_2)$ ] [36] and the rarely observed  $\eta^6$ -ligated 1,3,5-triphosphabenzene ( $P_3C_3Bu_3$ ) in the novel triple decker sandwich compound [ $(\eta^5-P_3C_2Bu_2)Sc(\mu-\eta^6:\eta^6-P_3C_3Bu_3)Sc(\eta^5-P_3C_2Bu_2)$ ] [37] (see Fig. 3).

Much less common in the co-condensation reactions of  $^tBuC\equiv P$  with transition metals are  $\pi$ -complexes solely containing the 4-membered 2,4-di-*tert*-butyl-1,3-diphos-

phacyclobutadiene ( $P_2C_2Bu_2$ ) ring. Two such compounds which we have previously reported [18,36] are shown in Fig. 4.

In this paper, we describe new phospho-organometallic products which are formed via the co-condensation reaction of  $^tBuC\equiv P$  with cobalt atoms.

## 2. Results and discussion

Co-condensation of electron beam generated cobalt atoms with an excess of  $^tBuCP$  produces a black petrol-soluble solid. Chromatographic work up in hexane on deactivated alumina affords the three compounds 1–3 albeit in very low overall yield (typically 5–10%) (Scheme 1).

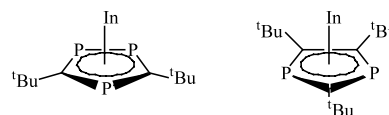


Fig. 2.  $\eta^5-P_3C_2Bu_2$  and  $\eta^5-P_2C_3Bu_3$  complexes of indium (I).

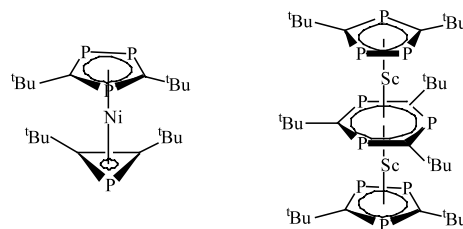


Fig. 3. Some mixed-ring phospho-organometallic compounds synthesised via metal vapour synthesis from  $^tBuC\equiv P$ .

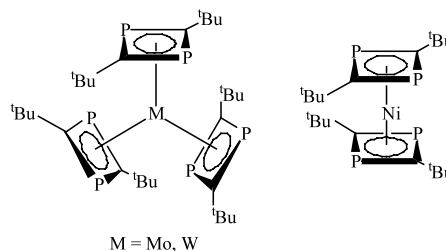
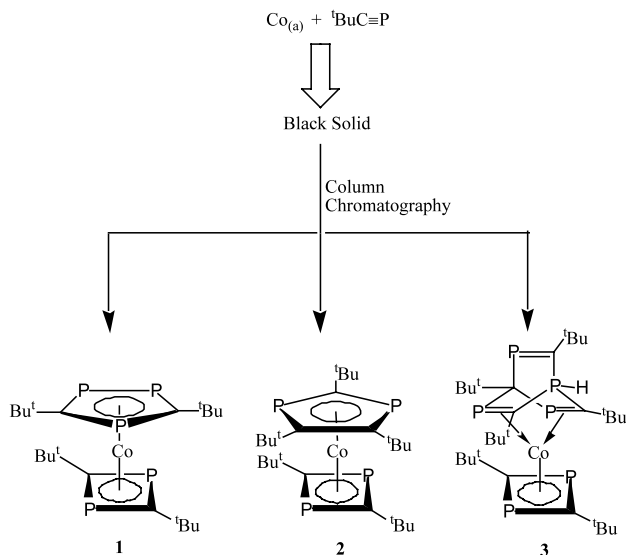


Fig. 4. Homoleptic  $\eta^4-P_2C_2Bu_2$  complexes synthesised via MVS.



Scheme 1.

The red crystalline compound [Co( $\eta^5$ -P<sub>3</sub>C<sub>2</sub>Bu<sub>2</sub>)( $\eta^4$ -P<sub>2</sub>C<sub>2</sub>Bu<sub>2</sub>)] (**1**) was isolated by fractional crystallisation from pentane at  $-50$  °C. The mass spectrum of **1** shows the parent ion at  $m/z$  490 and a base peak at  $m/z$  290 corresponding to  $M^+ - (P_2C_2Bu_2)$ .

The <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum of **1** gave further structural information, consisting of: (i) a doublet and a triplet ( $\delta_A$  102.2 ppm,  $\delta_B$  99.0 ppm,  $^2J_{(PP)} = 44.8$  Hz) representing the [AB<sub>2</sub>] spin system of the 1,2,4-triphosphacyclopentadienyl ring (the P<sub>B</sub> resonance exhibiting further small doublet coupling  $^2J_{(PP)} = 8.1$  Hz from coupling to the two phosphorus atoms of the 1,3-diphosphacyclobutadiene ring; and (ii) a broad singlet ( $\delta$  60.9 ppm) attributed to the two equivalent phospho-

rus atoms of the  $\eta^4$ -1,3-diphosphacyclobutadiene ring, which however, showed no resolvable additional interfering coupling perhaps because of line broadening effects of the quadrupolar cobalt-59 nucleus. Although the <sup>31</sup>P resonance of the  $\eta^5$ -P<sub>3</sub>C<sub>2</sub>Bu<sub>2</sub> ring shows no temperature dependence, a variable temperature <sup>1</sup>H-NMR spectroscopic study on **1** gave evidence for fluxional behaviour in solution. At 348 K the <sup>1</sup>H-NMR spectrum of **1** consists of two sharp singlets corresponding to the two types of <sup>t</sup>Bu groups of the P<sub>3</sub>C<sub>2</sub>Bu<sub>2</sub> and P<sub>2</sub>C<sub>2</sub>Bu<sub>2</sub> rings. Cooling the solution causes one of the singlets to collapse into two signals at  $\delta$  1.04 and 1.06 ppm, respectively (see Fig. 5) which can be assigned to the two <sup>t</sup>Bu groups of the P<sub>2</sub>C<sub>2</sub>Bu<sub>2</sub> ring which are in a staggered conformation with respect to the <sup>t</sup>Bu groups of the P<sub>3</sub>C<sub>2</sub>Bu<sub>2</sub> ring. The sharp singlet of the P<sub>3</sub>C<sub>2</sub>Bu<sub>2</sub> ring remains unchanged over this temperature range.

The projection of **1** viewed down the ligand–metal–ligand axis shown below, reveals the expected staggered conformer and the equivalence of both <sup>t</sup>Bu groups of the P<sub>3</sub>C<sub>2</sub>Bu<sub>2</sub> ring. The two non-equivalent <sup>t</sup>Bu groups of the P<sub>2</sub>C<sub>2</sub>Bu<sub>2</sub> ring lie on different sides of the P<sub>3</sub>C<sub>2</sub>Bu<sub>2</sub> ring. Because the phosphorus atoms of the P<sub>2</sub>C<sub>2</sub>Bu<sub>2</sub> ring lie on either side of the mirror plane which bisects the molecule they remain equivalent in the <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum at all temperatures.

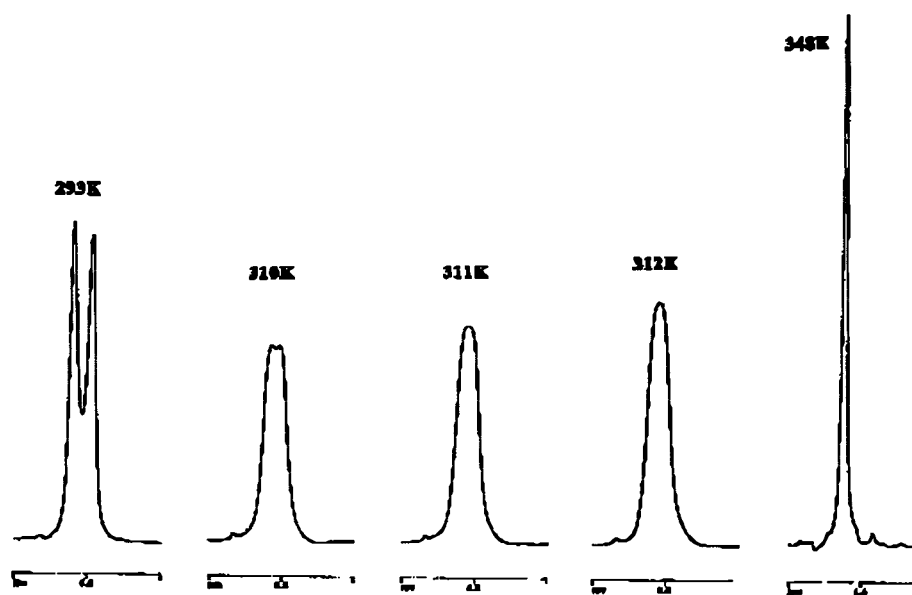
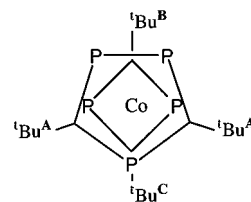


Fig. 5. Variable temperature <sup>1</sup>H-NMR spectra of **1** showing the <sup>t</sup>Bu resonance of the  $\eta^4$ -ligated 1,3-P<sub>2</sub>C<sub>2</sub>Bu<sub>2</sub> ring.

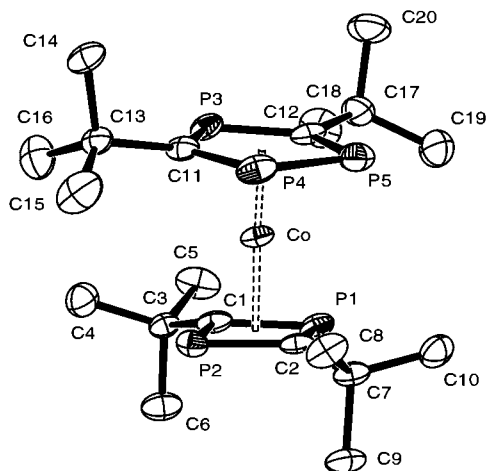


Fig. 6. Molecular structure of  $[\text{Co}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_2)(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$  (**1**).

$^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopic data for **1** are also fully consistent with the proposed staggered conformation. The two ring quaternary carbons of the  $\text{P}_3\text{C}_2\text{Bu}_2$  ring give rise to one signal, however, the quaternary carbons of the  $\text{P}_2\text{C}_2\text{Bu}_2$  ring are present as two distinct triplets ( $\delta$  116.6 and 120.3 ppm,  $^1J_{\text{P-C}} = 54.6$  and 57.0 Hz) and this behaviour is also repeated by the  $^t\text{Bu}$  quaternary and  $^t\text{Bu}$  methyl carbon resonances for both rings. The resonances of the quaternary carbons for both rings give rise to the expected splitting patterns. The  $\text{P}_3\text{C}_2\text{Bu}_2$  ring carbons appear as the A part of an [AMXY] spin system {X<sup>-</sup>, Y and M are the ring phosphorus atoms of the  $\text{P}_3\text{C}_2\text{Bu}_2$  ring in the 1, 2 and 4 positions, respectively} and the spectrum has been successfully simulated ( $\delta_{\text{A}}$  166.8 ppm,  $J_{\text{AM}} = 80.3$  Hz,  $J_{\text{AX}} + J_{\text{AY}} = 100$  Hz).

A single crystal X-ray crystallographic structural determination of **1** was carried out and the molecular structure is shown in Fig. 6. The structure confirms that the complex contains a central cobalt atom sandwiched between an  $\eta^5$ -1,3,4-triphosphacyclopentadienyl ring and an  $\eta^4$ -1,3-diphosphacyclobutadiene ring. Both rings lie essentially parallel to each other (dihedral angle 3.1°). Bond lengths within the  $\text{P}_2\text{C}_2\text{Bu}_2$  ring of **1** are essentially identical, ranging from 1.778 to 1.798 Å, consistent with a fully delocalised ring system similar to that previously observed in the complex  $[\text{Co}(\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$  (R = H, Me) [38,39] but very different from the long-(1.820) short-(1.748) long-(1.836) short-(1.749 Å) P–C distances which are exhibited by  $[\text{Ti}(\eta^8\text{-C}_8\text{H}_8)(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$  [40]. In the latter complex the localised 1,3-diphosphacyclobutadiene ring exhibits a marked shift to higher frequency of  $\delta$  213 ppm in sharp contrast to the value of  $\delta$  60.9 ppm observed for the delocalised ring in complex **1**.

The metal to phosphorus bond lengths of 2.26 and 2.25 Å and metal to carbon bond lengths of 2.09 and 2.13 Å in the four-membered ring of **1** are essentially

the same as those reported for  $[\text{Co}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$  (Co–P bond lengths 2.24 and 2.25 Å and Co–C bond lengths 2.09 and 2.08 Å, respectively) [39] indicating that replacement of the pentamethylcyclopentadienyl ring with a triphosphacyclopentadienyl ring has very little effect upon the overall molecular geometry. The 1,3-diphosphacyclobutadiene ring undergoes the expected rhomboidal distortions with an average P–C–P angle of 98.6° and an average C–P–C angle of 81.3°.

The identity of the red crystalline compound  $[\text{Co}(\eta^5\text{-P}_2\text{C}_3\text{Bu}_3)(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$  (**2**) was readily predicted on the basis of mass spectroscopic data. A strong molecular ion is observed at  $m/z$  528 amu (70% intensity) and the expected fragmentation patterns were observed: viz.  $m/z$  390 (50%) [ $M^+ - ^t\text{BuCC}^t\text{Bu}$ ],  $m/z$  328 (32%) [ $M^+ - \text{P}_2\text{C}_2\text{Bu}_2$ ] and 290 (100%) [ $M^+ - \text{P}_2\text{C}_3\text{Bu}_3$ ]. The  $^1\text{H}$ -NMR spectrum of **2** consists of the expected three singlets in a 2:1:2 ratio which is consistent with a staggered conformation of the rings with respect to the *tert*-butyl groups. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **2** is simple consisting of two singlets. No inter-ring coupling is observed and the lines appear broad owing to the close proximity of the cobalt nucleus. The availability of only a very small quantity of material precluded recording a meaningful  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum. A single crystal X-ray diffraction study of **2** confirmed the expected sandwich structure shown in Fig. 7. As in complex **1** the two rings lie essentially parallel to one another, with a dihedral angle of 5.9°. As expected, steric repulsions between the *tert*-butyl groups of the two different rings cause the molecule to adopt the staggered configuration. Bond lengths around the 1,3-diphosphacyclobutadiene ring in **2** are essentially identical, indicative of a fully delocalised ring system. The average C–P bond length of 1.78 Å is similar to that of **1** and to the reported value of 1.80 Å for  $[\text{Co}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$  [38]. Similarities between compounds **1** and **2** also exist with respect to both Co–C and Co–P distances and also in the rhomboidal distortion angles within the  $\text{P}_2\text{C}_2\text{Bu}_2$  ring.

The third product **3** from the co-condensation reaction of cobalt atoms with  $^t\text{BuC}\equiv\text{P}$  was a purple–red oil, after chromatographic work up of the crude product, which could not be successfully isolated in a pure form. Mass spectra data, however, showed the major sublimable component had the formula  $^t\text{Co}(^t\text{BuCP})_6\text{H}$  from the observation of the a parent ion peak at  $m/z$  660 amu. No successful interpretation of the fragmentation pattern could be made and although extensive NMR spectroscopic studies were undertaken structural interpretations were ambiguous. However, subsequent derivatisation of **3** by treatment with  $[\text{W}(\text{CO})_5\text{THF}]$  (Fig. 8), readily led to its characterisation as the purple crystalline  $[\text{W}(\text{CO})_5]$  adduct **4**. We have previously successfully applied this technique of adding a  $[\text{W}(\text{CO})_5]$

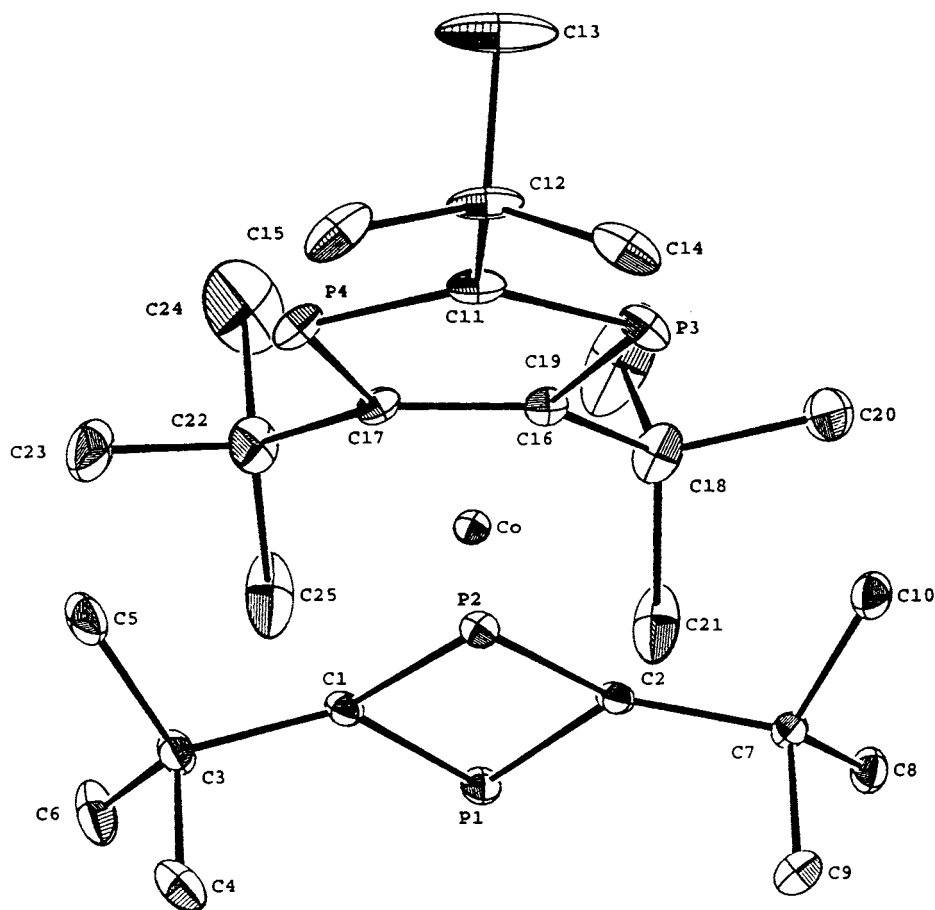


Fig. 7. Molecular structure of  $[\text{Co}(\eta^5\text{-P}_2\text{C}_2\text{Bu}_3)(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$  (**2**).

fragment to afford crystalline material in the structural characterisation of the phosphirenyl cationic complex  $[\text{Ni}(\eta^5\text{-P}_3\text{C}_2\text{Bu}_2)(\eta^3\text{-PC}_2\text{Bu}_2)]$  [36].

The resulting single crystal X-ray diffraction study on **4** (see Fig. 9) established that **3** is  $[\text{Co}(\eta^4\text{-P}_4\text{C}_4\text{Bu}_4\text{H})(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$ , containing the novel protonated 1,3,5,7-tetraphosphabarrelene (Fig. 9a).

$\eta^1$ -Ligation of the  $[\text{W}(\text{CO})_5]$  fragment is to the  $\text{P}_2\text{C}_2\text{Bu}_2$  ring rather than to the more sterically encumbered protonated 1,3,5,7-tetraphosphabarrelene ligand. The H atom in the P–H bond, was successfully located on a difference map and refined isotropically as part of the overall crystal structure determination. Both ligands relieve steric strain within the molecule by adopting a staggered conformation and the  $[\text{W}(\text{CO})_5]$  fragment causes a slight twist of the  $\text{P}_2\text{C}_2\text{Bu}_2$  ring relative to the plane described by P3, P4 and H3.

Although no comparable structural data exist for 1,3,5,7-tetraphosphabarrelene complexes, the geometry around the  $\text{P}_2\text{C}_2\text{Bu}_2$  ring gives some information on this ligand relative to cyclopentadienyl and phosphorus substituted cyclopentadienyl ligands in both **1** and **2** and  $[\text{Co}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)]$  [39]. The Co–C and Co–P bond lengths within the  $\eta^4\text{-P}_2\text{C}_2\text{Bu}_2$  ring in **4** lie within the expected ranges 2.09–2.03 and 2.25–2.26 Å,

respectively. Steric strain around the  $[\text{W}(\text{CO})_5]$  unit is also apparent with *cis* CO ligands bending away from idealised octahedral geometry by  $6^\circ$  from the rest of the molecule. Interestingly a reduction in the rhomboidal distortion of the  $(\text{P}_2\text{C}_2\text{Bu}_2)$  ring is observed compared with **1** and **2**. Average CPC and PCP ring angles in **4** are closer to  $90^\circ$  ( $84.1$  and  $96.1^\circ$ , respectively, cf. **1** and **2**  $81.3$  and  $98.6^\circ$  (for **1**) and  $81.2$  and  $98.8^\circ$  (for **2**)).

Compounds **3** and **4** represent rare examples of complexes containing the protonated form of the 1,3,5,7-tetraphosphabarrelene ligand. Recently Binger et al. [41,42] obtained zirconium(0) and hafnium(0) com-

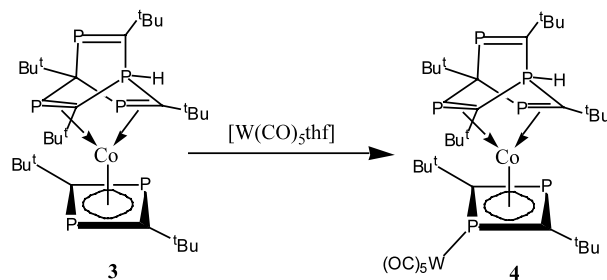


Fig. 8. Preferential ligation of  $[\text{W}(\text{CO})_5]$  to the  $\eta^4$ -ligated 1,3- $\text{P}_2\text{C}_2\text{Bu}_2$  ring of **3**.

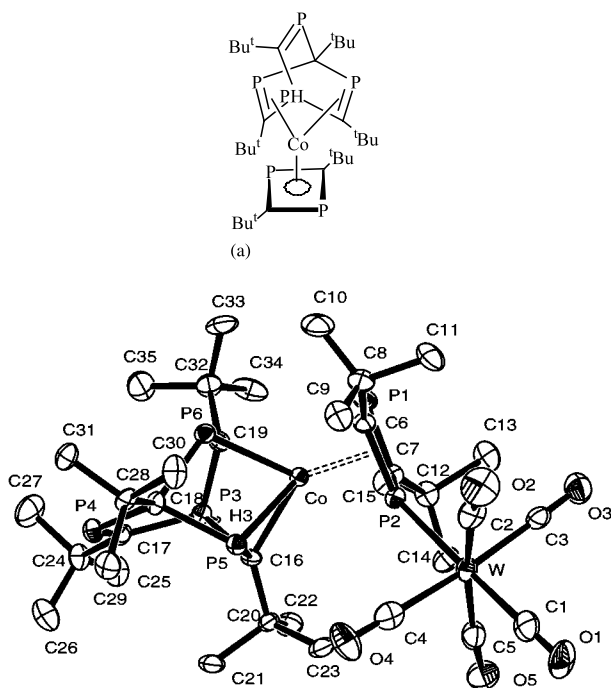


Fig. 9. Molecular structure of  $[\text{Co}(\eta^4\text{-P}_4\text{C}_4\text{Bu}_4\text{H})(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2)\text{W}(\text{CO})_5]$ , **4**.

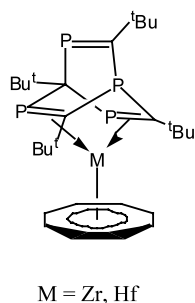


Fig. 10. 1,3,5,7-Tetraphosphabarrelene complexes of zerovalent Zr and Hf.

plexes of 1,3,5,7-tetraphosphabarrelene,  $[\text{M}(\eta^8\text{-C}_8\text{H}_8)(\text{Bu}_4\text{C}_4\text{P}_4)]$  (M = Zr, Hf), shown in Fig. 10, by treatment of the corresponding cyclo-octatetraene complexes  $[\text{M}(\eta^8\text{-C}_8\text{H}_8)_2]$  (M = Zr, Hf) with  $\text{tBuC}\equiv\text{P}$ . Subsequent reaction of these compounds with hexachloroethane yields the uncoordinated 1,3,5,7-tetraphosphabarrelene, which has also been fully structurally characterised.

The solution  $^1\text{H-NMR}$  spectrum of **4** at room temperature was in accord with the solid state structure, giving the expected four singlets in a 2:1:2:1 ratio for the four different types of *tert*-butyl groups and most significantly a doublet of relative intensity 1 at  $\delta$  7.80 ppm attributable to a P–H hydrogen ( $^1J_{\text{P-H}} = 454.4$  Hz). At 253 K the  $^1\text{H-NMR}$  spectrum, in the *tert*-butyl region (Fig. 11), consists of six singlets indicative of a molecular conformation of very low symmetry in which all the *tert*-butyl groups become non-equivalent.

The  $^{31}\text{P-NMR}$  spectrum contains a doublet of the same  $^1J_{\text{P-H}}$  coupling at  $\delta$  –31.6 ppm which in the proton-decoupled  $^{31}\text{P-NMR}$  spectrum reverts to a singlet. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **4** contains six separate signals reflecting the low overall symmetry of the complex. NMR evidence was obtained of rapid exchange of the two pairs of *tert*-butyl groups at room temperature. Unfortunately quadrupolar effects of the cobalt-59 nucleus results in broad  $^{31}\text{P}$  line widths and precluded any determination of P–P coupling constants. Some structural information can be obtained, however, from the *pseudo* quartet observed at  $\delta$  421.8 ppm, strongly characteristic of the 1,3,5,7-tetraphosphabarrelene ligand, which is assigned to the apical phosphorus atom P<sub>4</sub>. Likewise the doublet at  $\delta$  26.3 ppm clearly exhibits tungsten satellites ( $^1J_{\text{P-W}} = 214.5$  Hz). The free rotation of the 1,3,5,7-tetraphosphabarrelene and 1,3-diphosphacyclobutadiene ligands at room temperature, may be stopped at low temperature.

### 2.1. Preparation of

#### $[\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2\text{W}(\text{CO})_5)(\eta^5\text{-P}_3\text{C}_2\text{Bu}_2)]$ (**5**)

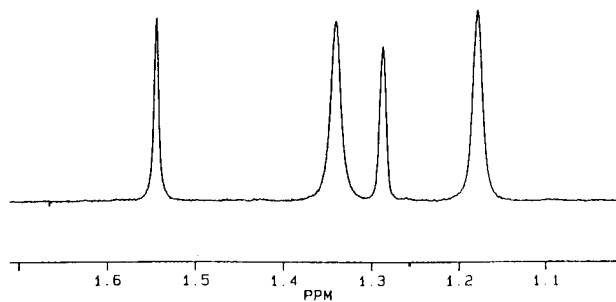
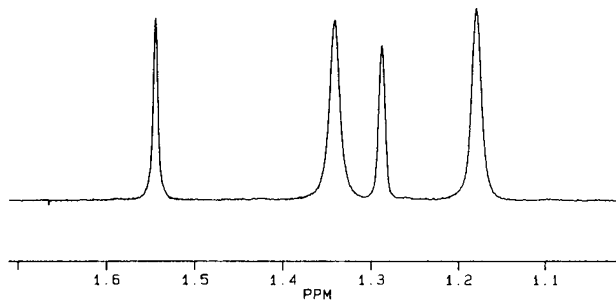
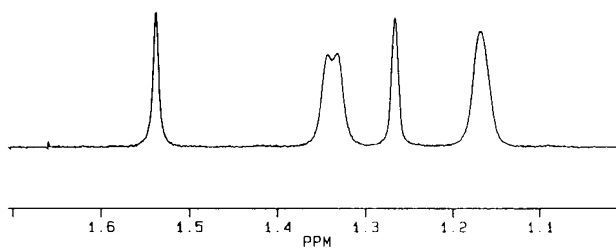
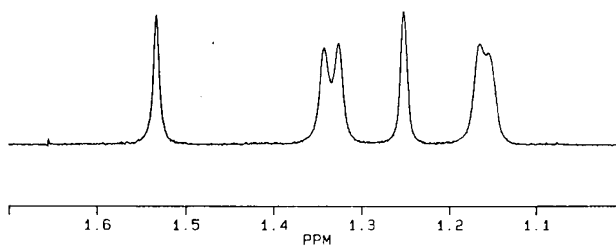
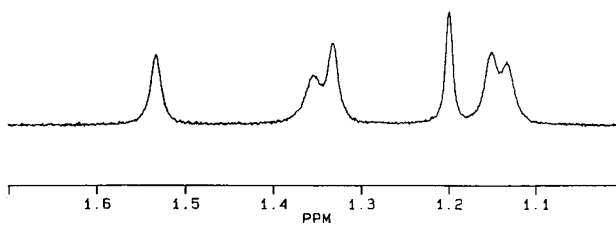
Treatment of **1** with  $[\text{W}(\text{CO})_5\text{THF}]$  in THF solution (Fig. 12) yields a dark oil. Chromatographic work-up on deactivated alumina with hexane eluant affords a red crystalline solid which mass spectroscopic data show to be  $[\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{Bu}_2\text{W}(\text{CO})_5)(\eta^5\text{-P}_3\text{C}_2\text{Bu}_2)]$  (**5**).

The mass ion for **5** at  $m/z$  814 amu shows the expected isotopic ratios and also shows losses of 28 amu corresponding to sequential loss of five CO molecules from the parent ion. The expected site of ligation to the  $[\text{W}(\text{CO})_5]$  fragment [1,2], namely via one of the P–P bonded phosphorus atoms of the  $\text{P}_3\text{C}_2\text{Bu}_2$  ring did not occur, instead the metal bonds to one of the P atoms of the 1,3-diphosphacyclobutadiene ring. This is clearly shown by the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **5**, shown in Fig. 13, which consists of four resonances: the doublet and triplet representing the three phosphorus atoms of the  $\text{P}_3\text{C}_2\text{Bu}_2$  ring and two separate singlets at  $\delta$  20.1 and 53.0 ppm for the two phosphorus atoms of the  $\text{P}_2\text{C}_2\text{Bu}_2$  ring only the latter resonance showing  $^{183}\text{W}$  satellites ( $^1J_{\text{P-W}} = 226.7$  Hz). Several examples are known of secondary  $\eta^1$ -ligation of complexes containing  $\eta^1$ -bonded 1,3-diphosphacyclobutadiene rings to transition metal centres [43–46].

The  $^1\text{H-NMR}$  spectrum of **5** consists of two singlets and remain unchanged on cooling the solution, suggesting either rapid ring rotation or a symmetrical structure containing a mirror plane.

## 3. Experimental

All manipulations, unless otherwise stated, were conducted in an inert atmosphere of Ar or dinitrogen using

**328K****298K****289K****283K****253K**Fig. 11. Variable temperature  $^1\text{H-NMR}$  spectra of **4**.

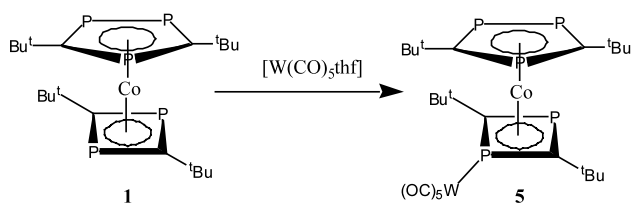


Fig. 12. Reaction of **1** with  $[\text{W}(\text{CO})_5\text{THF}]$ .

a dual vacuum/Ar (or dinitrogen) line, employing conventional Schlenk line techniques, or by use of either a Miller–Howe or mBraun glove box under an atmosphere of dinitrogen. Solvents were pre-dried by distillation under dinitrogen over the appropriate drying agent and subsequently degassed and stored in glass ampoules under Ar in the presence of a sodium (or potassium) mirror. All glassware, cannulae and Celite were stored in an oven ( $> 373 \text{ K}$ ) and glassware and Celite were flame-dried in vacuo immediately prior to use. Cobalt for the electrongun vaporisation MVS experiment was degassed prior to use. Deuteriated solvents were purchased from M.S.D. Isotopes, Ltd. and Goss Scientific. They were degassed by the freeze–thaw method, refluxed in vacuo over molten potassium or sodium (according to boiling point) and then vacuum transferred to a glass ampoule fitted with a Young's tap prior to storage in the glove box. Solution NMR spectra were recorded on Brüker ACP250, WM360, DMX300, DMX400 or AMX500 instruments at ambient temperature unless otherwise stated. Coupling constants are given in Hz, and chemical shift ( $\delta$ ) in ppm is relative to the residual proton chemical shift of the deuteriated solvent ( $^1\text{H}$ ), the carbon chemical shift of the deuteriated solvent ( $^{13}\text{C}$ ), and  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). Electron

impact (EI) mass spectra were recorded in a Kratos MS80RF instrument in the School of Chemistry at the University of Sussex by Dr A. Abdul-Sada. Microanalyses were performed by Medac Ltd (UK) or Canadian Microanalytical Services Ltd (Canada).

### 3.1. Reaction of cobalt atoms with $^t\text{BuCP}$

Co-condensation at 77 K of electron beam vaporised (500 W) cobalt (0.96 g, 16 mmol) with an excess of  $^t\text{BuCP}$  over 2 h resulted in the formation of a deep red matrix which was allowed to warm to room temperature under vacuum. The apparatus was then opened to an external trapping system and unreacted  $^t\text{BuCP}$  was collected in an external trap at 77 K. After 4 h the reaction vessel was refilled with dinitrogen and the matrix washed into a Schlenk receiver with petrol (40–60). The crude reaction mixture was then filtered through a flame-dried bed of Celite to remove colloidal metal and solvent removed in vacuo. The resultant black solid yielded three products following chromatographic workup (deactivated alumina {4% m/m  $\text{H}_2\text{O}$ }, petrol eluant). The primary fraction (red band) yielded two compounds  $[\text{Co}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$  (**1**) and  $[\text{Co}(\eta^5\text{-P}_2\text{C}_3^t\text{Bu}_3)(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$  (**2**), subsequently purified by fractional crystallisation. In order to obtain sufficient quantities of material, the chromatographic stages of the preparation were repeated up to five times.

**1**: MS (70 eV); 490 (100,  $[\text{M}^+]$ ), 290 (63,  $[\text{M}^+ - (\text{P}_2\text{C}_2^t\text{Bu}_2)]$ )

$^1\text{H-NMR}$  ( $d^8$ -toluene) {298 K}:  $\delta = 1.02$  (s, 18H,  $^t\text{Bu}$ ), 1.48 (s, 18H,  $^t\text{Bu}$ ), { $-35^\circ\text{C}$ }:  $\delta = 1.04$  (s, 9H,  $^t\text{Bu}$ ), 1.06 (s, 9H,  $^t\text{Bu}$ ), 1.51 (s, 18H,  $^t\text{Bu}$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $d^8$ -toluene) { $-35^\circ\text{C}$ }:  $\delta = 60.9$  (s,  $\text{P}^{\text{C}}$ ), 99.0

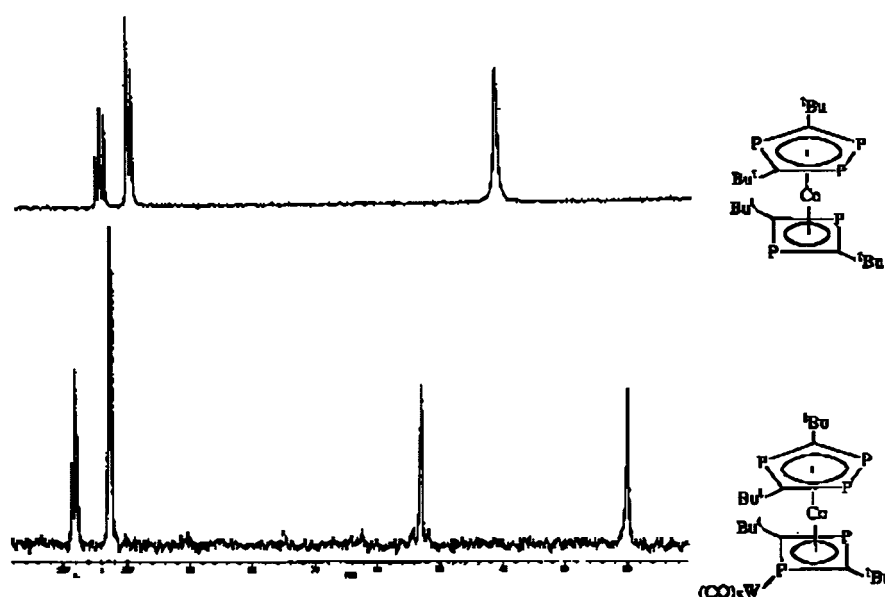
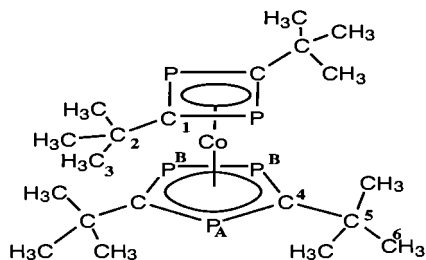


Fig. 13. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **1** and **5**.



(dt,  $^2J(\text{PP}) = 44.8$  Hz,  $^2J(\text{PP}) = 8.1$  Hz,  $\text{P}^{\text{B}}$ ), 102.2 (t,  $^2J(\text{PP}) = 44.8$  Hz  $\text{P}^{\text{A}}$ ).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $d^8$ -toluene)  $\{-30$  °C $\}$ :  $\delta = 32.0$  (s,  $\text{C}^3\text{H}_3$ ), 32.7 (s,  $\text{C}^3\text{H}_3$ ), 35.6 (t,  $^2J(\text{CP}) = 7.05$  Hz,  $\text{C}^2$ ), 36.2 (t,  $^2J(\text{CP}) = 6.6$  Hz,  $\text{C}^2$ ), 36.7 (s,  $\text{C}^6\text{H}_3$ ), 39.7 (a part of AMXX' spin system,  $J_{\text{AM}} = 17.5$  Hz,  $J_{\text{AX}} + J_{\text{AX}'} = 26.0$  Hz,  $\text{C}^5$ ), 116.5 (t,  $^1J(\text{CP}) = 54.6$  Hz,  $\text{C}^1$ ), 120.2 (t,  $^1J(\text{CP}) = 57.0$  Hz,  $\text{C}^1$ ), 166.83 (a part of AMXY spin system  $J_{\text{AM}} = 80.3$  Hz,  $J_{\text{AX}} + J_{\text{AY}} = 100$  Hz,  $\text{C}^4$ ). Anal. Found: C, 49.24; H, 7.25; Calc. for C, 48.99; H, 7.40%.



**2:** MS (70 eV); 528 (65,  $[M^+]$ ), 390 (50,  $[M^+ - 2'\text{Bu}]$ ), 328 (32,  $[M^+ - (\text{P}_2\text{C}_2'\text{Bu}_2)]$ ), 290 (100,  $[M^+ - 2'\text{Bu} - (\text{PC}'\text{Bu})]$ ).

$^1\text{H}$ -NMR ( $d^6$ -benzene)  $\{298$  K $\}$ :  $\delta = 1.28$  (s, 18H, 'Bu), 1.56 (s, 9H, 'Bu), 1.63 (s, 18H, 'Bu).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $d^6$ -benzene):  $\delta = 46.6$  (s), 60.3 (s).

**3:** Red oil. Attempts at purification by recrystallisation, sublimation ( $10^{-6}$  mbar 20–200 °C) and column chromatography were unsuccessful. Interpretation of complex data is inferred by analysis of characterising data of derivatives (vide infra).

MS 70 eV; 660 (30,  $[\text{Co}(\text{Me}_3\text{CCP})_6\text{H}]^+$ ).

$^{31}\text{P}\{^1\text{H}\}$ -NMR ( $d^6$ -benzene):  $\delta = -148$  (m),  $-34.5$  (m), 59.4 (m).

### 3.2. Reaction of $[\text{Co}(\text{tBuCP})_6\text{H}]$ (**3**) with $[\text{W}(\text{CO})_5\text{THF}]$

To  $[\text{W}(\text{CO})_5\text{THF}]$  generated in situ from  $[\text{W}(\text{CO})_6]$  (0.10 g) in THF (25 ml) was added a THF solution of  $[\text{Co}(\text{tBuCP})_6\text{H}]$  (**3**) (approximately 0.03 g) and the mixture stirred for 4 h. The solvent was removed in vacuo to yield a dark red oil. Extraction of the oil into petrol (40–60) followed by chromatographic work up on Kieselgel 60 GF<sub>254</sub> with petrol (40–60) as eluant afforded  $[\text{Co}(\text{tBuCP})_6\text{H}(\text{W}(\text{CO})_5)]$  (**4**) as a micro-crystalline powder on removal of solvent. Recrystallisation from pentane ( $-50$  °C) afforded analytically pure red–purple crystals. (0.025 g, 60%), which were suitable for an X-ray crystal structure determination.

$^1\text{H}$ -NMR ( $d^8$ -toluene)  $\{298$  K $\}$ :  $\delta = 1.14$  (s, 18H, 'Bu), 1.24 (s, 9H, 'Bu), 1.30 (s, 18H, 'Bu), 1.50 (s, 9H, 'Bu), 7.80 (d,  $^1J(\text{P,H}) = 454.4$  Hz, H–P).  $\{253$  K $\}$ :  $\delta = 1.13$  (s, 9H, 'Bu), 1.15 (s, 9H, 'Bu), 1.20 (s, 9H, 'Bu), 1.33 (s, 9H, 'Bu), 1.35 (s, 9H, 'Bu), 1.53 (s, 9H, 'Bu).

$^{31}\text{P}\{^1\text{H}\}$ -NMR ( $d^8$ -toluene)  $\{253$  K $\}$ :  $\delta = -157.5$  (m, P5 or P6),  $-144.4$  (m, P5 or P6),  $-31.6$  (m, P3),

26.3 (m,  $^1J(\text{PW}) = 214.5$  Hz, P2), 28.1 (s, P1), 421.8 (m, P4).

$^{31}\text{P}$ -NMR ( $d^8$ -toluene)  $\{253$  K $\}$ :  $\delta = -157.5$  (m, P5 or P6),  $-144.4$  (m, P5 or P6),  $-31.6$  (d,  $^1J(\text{PH}) = 454.4$  Hz, P3), 26.3 (m,  $^1J(\text{PW}) = 214.5$  Hz, P2), 28.1 (s, P1), 421.8 (m, P4).

MS (70 eV); 984 (5,  $[M^+]$ ), 956(3,  $[M^+ - \text{CO}]$ ), 660 (20,  $[M^+ - \text{W}(\text{CO})_5]$ ). Anal. Found: C 42.86, H 5.54; Calc. for C 42.7, H 5.6%.

### 3.3. Reaction of $[\text{Co}(\eta^5\text{-P}_3\text{C}_2'\text{Bu}_2)(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2)]$ with $[\text{W}(\text{CO})_5\text{THF}]$

To  $[\text{W}(\text{CO})_5\text{THF}]$  generated in situ from  $[\text{W}(\text{CO})_6]$  (0.10 g) in THF (25 ml) was added a THF solution of  $[\text{Co}(\eta^5\text{-P}_3\text{C}_2'\text{Bu}_2)(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2)]$  (**1**) (60 mg, 0.12 mmol) and the mixture stirred for 4 h. The solvent was removed in vacuo to yield a red solid. Extraction of the oil into petrol (40–60) followed by chromatographic work up on Kieselgel 60 GF<sub>254</sub> with petrol (40–60) as eluant, afforded  $[\text{Co}(\eta^5\text{-P}_3\text{C}_2'\text{Bu}_2)(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2\text{W}(\text{CO})_5)]$  (**5**) as a micro-crystalline powder on removal of solvent. Recrystallisation from pentane ( $-50$  °C) afforded red crystals.

MS (70 eV); 814 (7,  $[M^+]$ ), 758 (2,  $[M^+ - 2\text{CO}]$ ), 730 (4,  $[M^+ - 3\text{CO}]$ ), 674 (4,  $[M^+ - 5\text{CO}]$ ), 490 (100,  $[M^+ - \text{W}(\text{CO})_5]$ ).

$^1\text{H}$ -NMR ( $d^8$ -toluene),  $\{298$  K $\}$ :  $\delta = 1.07$  (s 18H, 'Bu), 1.44 (s, 18H, 'Bu).

$^{31}\text{P}\{^1\text{H}\}$ -NMR ( $d^8$ -toluene),  $\{298$  K $\}$ :  $\delta = 20.1$  (s,  $\text{P}^{\text{D}}$ ), 53.0 (s,  $^1J(\text{PW}) = 227$  Hz,  $\text{P}^{\text{C}}$ ), 102.7 (d,  $^2J(\text{PP}) = 42.8$  Hz,  $\text{P}^{\text{B}}$ ), 108.2 (t,  $^2J(\text{PP}) = 42.8$  Hz,  $\text{P}^{\text{A}}$ ).

## 4. Crystallography

Intensity data were measured on an Enraf–Nonius CAD4 using Mo– $\text{K}_\alpha$  radiation.

*Crystal data* for **1**:  $\text{C}_{20}\text{H}_{36}\text{P}_5\text{Co}$ ,  $M = 490.3$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 10.428(3)$ ,  $b = 11.846(3)$ ,  $c = 19.778(4)$  Å,  $\beta = 95.95(2)^\circ$ ,  $V = 2430.0(11)$  Å<sup>3</sup>,  $T = 173(2)$  K,  $Z = 4$ ,  $\mu = 1.039$  mm<sup>-1</sup>,  $\lambda = 0.71073$  Å,  $F(000)$  1032; 4516 reflections collected, 4276 independent ( $R_{\text{int}} = 0.0601$ ), 3094 reflections with  $I > 2\sigma I$ ,  $R_1 = 0.0760$ ,  $wR_2 = 0.1953$ ;  $R_1 = 0.1062$ ,  $wR_2 = 0.2227$  for all data.

*Crystal data* for **2**:  $\text{C}_{25}\text{H}_{45}\text{P}_4\text{Co}$ ,  $M = 528.5$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 14.152(4)$ ,  $b = 10.902(3)$ ,  $c = 18.527(11)$  Å,  $\beta = 103.46(3)^\circ$ ,  $V = 2780(2)$  Å<sup>3</sup>,  $T = 173(2)$  K,  $Z = 4$ ,  $\lambda = 0.71073$  Å,  $F(000)$  1128.5365 reflections collected, 5166 independent ( $R_{\text{int}} = 0.02$ ), 3655 reflections with  $I > 2\sigma I$ ,  $R_1 = 0.045$ ,  $wR_2 = 0.091$  for  $I > 2\sigma I$ ,  $R_1 = 0.054$ ,  $R^1 = 0.061$ .

*Crystal data* for **3**:  $\text{C}_{35}\text{H}_{55}\text{O}_5\text{P}_6\text{CoW}$ ,  $M = 984.4$ , monoclinic, space group  $P2_1/n$  (non-standard. 14),  $a = 12.903(2)$ ,  $b = 19.556(4)$ ,  $c = 16.651(5)$  Å,  $\beta = 91.52(2)^\circ$ ,

$V = 4200(2) \text{ \AA}^3$ ,  $T = 173(2) \text{ K}$ ,  $Z = 4$ ,  $\mu = 3.40 \text{ mm}^{-1}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $F(000) 1984$ ; 7712 reflections collected, 7373 independent ( $R_{\text{int}} = 0.0345$ ), 5830 reflections with  $I > 2\sigma I$ ,  $R_1 = 0.040$ ,  $wR_2 = 0.087$ ;  $R_1 = 0.061$ ,  $wR_2 = 0.096$  for all data.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 162997, 162998 and 162999 for compounds **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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