

Preliminary communication

NOVEL TRANSITION METAL PHOSPHA-ALKYNE COMPLEXES: ${}^t\text{BuC}\equiv\text{P}$ ACTING AS A 6 ELECTRON DONOR LIGAND. SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE OF $[\text{Co}_2(\text{CO})_6(\mu\text{-}{}^t\text{BuCP})\text{W}(\text{CO})_5]$

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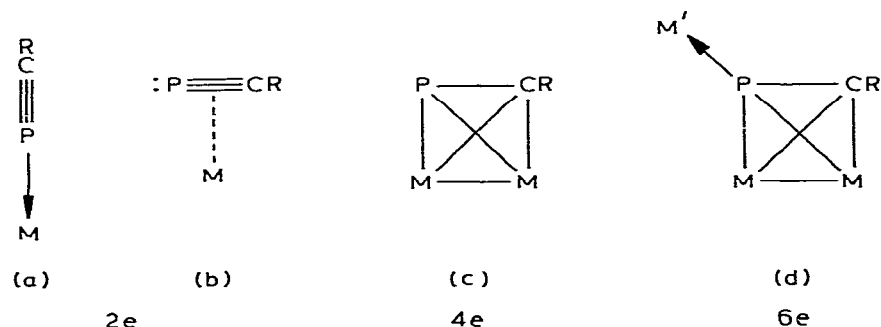
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Summary

A single crystal X-ray diffraction study of $[\text{Co}_2(\text{CO})_6(\mu\text{-}{}^t\text{BuCP})\text{W}(\text{CO})_5]$ establishes that phospho-alkyne behaves as a 6e donor. Synthesis of the related $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}{}^t\text{BuCP})\text{W}(\text{CO})_5]$ complex is reported.

There is current interest in the synthesis and ligating properties of phospho-alkenes $\text{R}_2\text{C}=\text{PR}$ [1–5] and phospho-alkynes, $\text{RC}\equiv\text{P}$ [6,7]. In suitable transition metal complexes the phospho-alkynes might be envisaged to act as either 2e, 4e or 6e donors by making use of the $\text{P}\equiv\text{C}$ π -system and the lone pair on phosphorus (see Scheme 1, (a) \rightarrow (d)). Recently we reported the first examples of complexes in which the phospho-alkyne, ${}^t\text{BuC}\equiv\text{P}$ acts as a 2e donor in $[\text{Pt}(\text{PPh}_3)_2(\text{P}\equiv\text{CBu}^t)]$ as in (b) and as a 4e donor in $[\text{Co}_2(\text{CO})_6\text{-}$

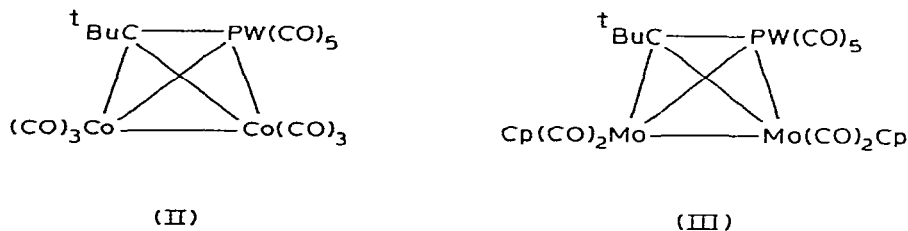


SCHEME 1

($\text{P}\equiv\text{C}\text{Bu}^t$) as in (c). [6] We now describe the synthesis and first fully structurally characterised complex in which the $\text{tBuC}\equiv\text{P}$ acts as a 6e donor.

Treatment of $\text{tBuC}\equiv\text{P}$ with $[\text{Co}_2(\text{CO})_8]$ in toluene readily affords the deep red, light and air-sensitive, liquid complex $[\text{Co}_2(\text{CO})_6(\text{P}\equiv\text{C}\text{Bu}^t)]$ (I), which reacts with $[\text{W}(\text{CO})_5\text{THF}]$ to give light- and air-stable, wine-red crystals of the complex $[\text{Co}_2(\text{CO})_6(\mu\text{-tBuCP})\text{W}(\text{CO})_5]$ (II), m.p. $109\text{--}110^\circ\text{C}$, $\nu(\text{CO})$ in n-hexane: 2116w , 2075ms , 2065s , 2046m , 2038w , 1977vs cm^{-1} . Similarly $\text{tBuC}\equiv\text{P}$ reacts with $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}\equiv\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ followed by $[\text{W}(\text{CO})_5(\text{THF})]$ to give $[\eta^5\text{-}(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\mu\text{-tBuCP})\text{W}(\text{CO})_5]$ (III).

Hitherto the synthesis of derivatives of type (c) has not been achieved directly from the free phospho-alkynes. Previously Seyferth et al. [7] reported partial characterisation of analogues of II which result in low yield



from successive reactions of $[\text{Co}_2(\text{CO})_8]$ with $\text{RCCl}_2\text{PCl}_2$ and $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{Cr}, \text{W}$).

In order to determine the bonding mode a single crystal X-ray structure determination of II was carried out.

Crystal data: monoclinic space group, $P2_1/n$, a 9.391(1), b 15.866(1), c 15.460(1) Å, β $99.48(1)^\circ$, $Z = 4$. Least squares refinement based on 3014 reflections measured on a CAD 4 diffractometer converged at $R = 0.028$.

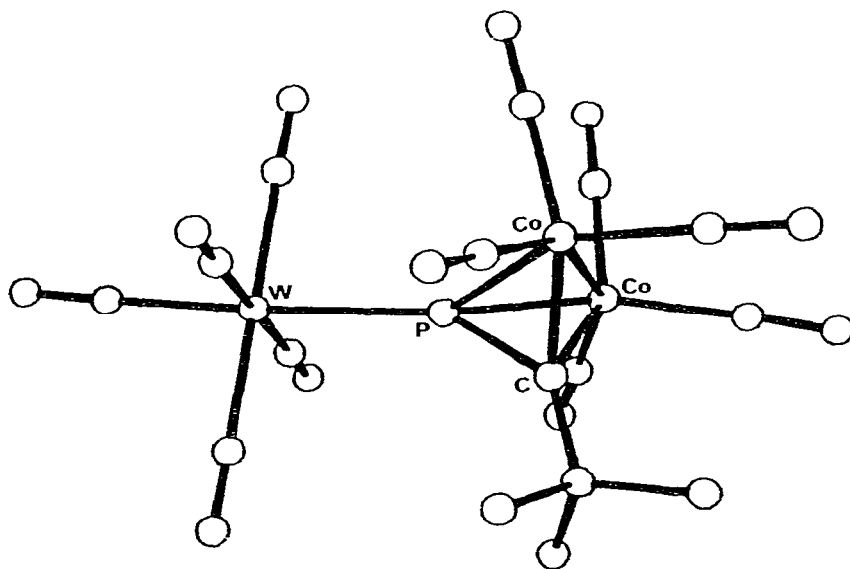


Fig. 1. Molecular structure of II. Some important bond lengths and angles are W-P 2.465(1) Å, P-C 1.695(6) Å, W-P-C $148.1(2)^\circ$, P-C-C $139.4(4)^\circ$.

The molecular structure is shown in Fig. 1. The phospho-alkyne is bonded to the cobalt atoms in a side-on fashion characteristic of related alkyne complexes [8] and is attached to the tungsten via the phosphorus lone pair. The C—P bond length, 1.695(6) Å, is much longer than that found for free phospho-alkynes [9–11] (1.544 Å), but interestingly is closer to that expected for a phospho-alkene than for a formal P—C single bond. The ^tBu group attached to the C≡P unit is bent back by 41° and the C—P—W bond angle is 148°. The W—P bond length of 2.465(1) Å is rather short, (compare 2.502 Å in *cis*-[W(CO)₄(PMe)₆] [12], 2.480 Å in [W(CO)₃(NO)(P(OPh)₃)HW(CO)₅] [13], reflecting the unusual hybridisation of the phosphorus atom.

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