

**Novel Transition Metal Phospha-alkyne Complexes.
X-Ray Crystal and Molecular Structure of a Side-bonded
Bu^tC≡P Complex of Zerovalent Platinum, Pt(PPh₃)₂(Bu^tCP)**

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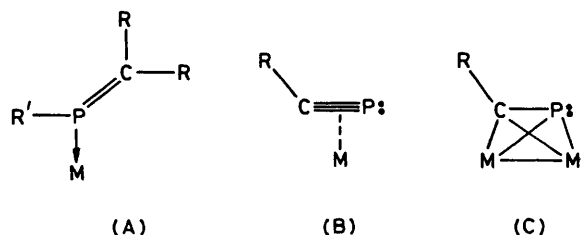
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Summary A single crystal X-ray diffraction study of the novel complex Pt(PPh₃)₂(Bu^tCP) indicates that the phospha-alkyne is co-ordinated in a side-on manner to platinum and its near-normal Pt-P bond length (2.320 Å) is discussed in relation to its exceptionally small platinum-phosphorus coupling constant ¹J(PtP) (62 Hz); Co₂(CO)₈

reacts with Bu^tCP to give the dinuclear complex Co₂(CO)₆(Bu^tCP).

RECENTLY¹ we reported syntheses of a number of novel transition metal complexes of phospha-alkenes, R₂C=PR'. N.m.r. spectroscopic studies established that co-ordination

to the metal atom was *via* the phosphorus lone pair as shown in (A), and this mode of bonding has subsequently been confirmed in the case of *cis*-PtCl₂(PEt₃)[P(mesityl)=CPh₂]² and Cr(CO)₅[P(mesityl)=CPh₂]³ by single crystal *X*-ray diffraction studies.



We now report the first examples of syntheses of phospho-alkyne, RC≡P, complexes of transition metals directly from the free ligand. An excess of Bu^tC≡P⁴ reacted quantitatively with Pt(C₂H₄)(PPh₃)₂ in benzene at room temperature to give translucent cream-coloured crystals of Pt(PPh₃)₂(Bu^tC≡P), (1) isolated as the benzene solvate. Complex (1) was characterised by elemental analysis and i.r. and ³¹P n.m.r. spectroscopy, and a single crystal *X*-ray structure determination has been carried out on the benzene solvate.

Crystal data: monoclinic, space group *C*2/*c*, *a* = 32.971(10), *b* = 9.650(7), *c* = 26.022(5) Å, β = 90.82(2)°, *Z* = 8. Least-squares refinement based on 2698 observed independent reflections measured on a CAD 4 diffractometer converged at *R* = 0.077. The molecular structure is shown in Figure 1.†

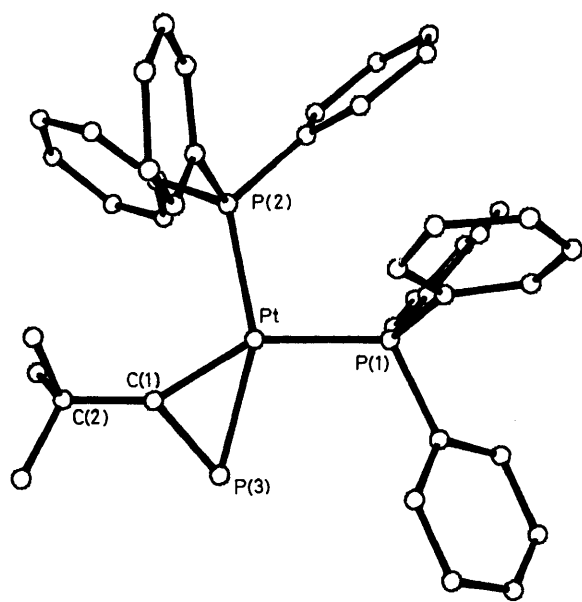
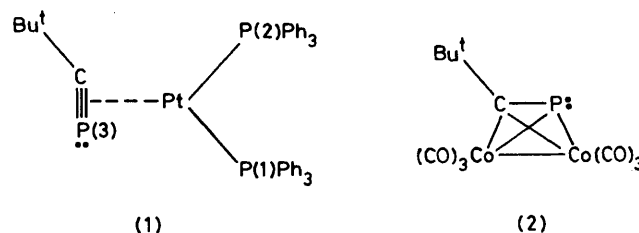


FIGURE 1. Molecular structure of (1). Some important bond lengths and angles are Pt-P(1) 2.292(5), Pt-P(2) 2.285(5), Pt-P(3) 2.320(6), Pt-C(1) 1.973(21), and P(3)-C(1) 1.672(17) Å, P(1)-Pt-P(2) 101.6(2), P(2)-Pt-C(1) 109.1(5), P(1)-Pt-P(3) 104.6(2), C(1)-Pt-P(3) 45.0(5), Pt-C(1)-P(3) 78.6(8), Pt-P(3)-C(1) 56.5(7), Pt-C(1)-C(2) 149(1), and P(3)-C(1)-C(2) 132(2)°.

The phospho-alkyne ligand is bonded to platinum in a side-on fashion, (B), similar to that known for several mononuclear alkyne-metal complexes⁵ and it appears that the phosphorus lone pair does not interact significantly with the metal. The environment around platinum is approximately planar, the dihedral angle between the planes Pt-P(1)-P(2) and Pt-P(3)-C(1) being only 6.7°. The platinum-phosphorus distances to the PPh₃ ligands lie in the usual range and are not significantly different, while the platinum-phosphorus distance for the co-ordinated phospho-alkyne is only slightly longer. The platinum-carbon bond length (1.973 Å) in (1) may be compared with values of *ca.* 2.02 Å in related alkyne complexes.⁵ The *t*-butyl group attached to the C≡P unit is bent away from platinum with a bend-back angle of 48.02°.



A noteworthy feature of the structure is the considerable lengthening of the C-P bond length, 1.672(17) Å, in co-ordinated Bu^tCP compared with the typical values of 1.544 Å found for the related free ligands FCP,⁶ MeCP,⁷ and PhCP.⁸ This presumably reflects the effect of back-bonding from the zerovalent platinum.

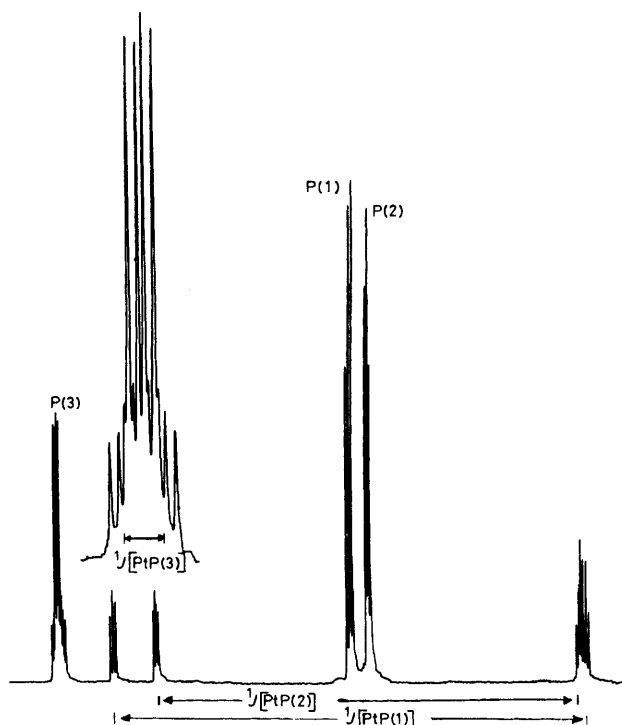


FIGURE 2.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum of (1) shown in Figure 2 is in accord with the solid-state structure, consisting of three distinct resonances for the non-equivalent phosphine ligands each exhibiting a doublet of doublets pattern with ^{195}Pt satellites evident: δ [P(1)] = 112.2, δ [P(2)] = 114.7, and δ [P(3)] = 56.9 p.p.m., 1J [PtP(1)] 3587, 1J [PtP(2)] 3206, and 1J [PtP(3)] 62, 2J [P(1)P(2)] 20, 2J [P(2)P(3)] 15, and 2J [P(1)P(3)] 24 Hz. The spectrum indicates that there is no rotation of the phospho-alkyne about the metal-ligand axis at ambient temperature.

Although all the platinum-phosphorus bond lengths are similar and the magnitude of 1J (PtP) for the PPh_3 ligands is close to that found in a number of $\text{Pt}(\text{PPh}_3)_2(\text{RC}\equiv\text{CR})$ complexes,⁹ 1J (PtP) for the co-ordinated phospho-alkyne is remarkably low (62 Hz) and is easily the smallest one-bond platinum-phosphorus coupling constant so far recorded. As discussed in detail elsewhere¹⁰ the magnitude of 1J (PM) in metal-phosphine complexes reflects the importance of the s-character term in the coupling expression. The low value of 1J (PtP) for the Bu^tCP ligand in (1) is a consequence of

the lone pair on the co-ordinated phospho-alkyne being in a hybrid orbital which is not directed towards the metal atom.

A solution of $\text{Co}_2(\text{CO})_8$ in tetrahydrofuran reacted with 1 equiv. of Bu^tCP at or below room temperature to give the volatile air- and light-sensitive blood-red oil formulated as $\text{Co}_2(\text{CO})_6\text{Bu}^t\text{CP}$, (2), [$\nu(\text{CO}) = 2090, 2050, \text{ and } 2020 \text{ cm}^{-1}$] which exhibited the parent ion in the mass spectrum together with ions corresponding to $[\text{M} - (\text{CO})_x]^+$, ($x = 1-6$), $[\text{H}_2\text{CC}(\text{Me})\text{CPCo}_2]^+$, and $[\text{HCPCo}_2]^+$ ions. The spectroscopic data strongly suggest a structure based on type (C) which is well known for alkyne complexes of the type $\text{Co}_2(\text{CO})_6(\text{RC}\equiv\text{CR})$. Interestingly, the physical and i.r. data for (2) are similar to those of products reported by Seyferth and Henderson¹¹ from the dechlorination of $\text{RCCl}_2\text{PCl}_2$ by $\text{Co}_2(\text{CO})_8$ and support their formulation as phospho-alkyne complexes.

We thank the S.R.C. for financial support for the work.

(Received, 27th July 1981; Com. 902.)

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