

## A Heterometallic 'Super-sandwich' containing a Novel Hexagonal $\text{Cu}_6$ Unit at the Centre: Synthesis and X-Ray Structure Determination of $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{CoP}_3](\text{CuBr})_6[\text{P}_3\text{Co}\{(\text{Ph}_2\text{PCH}_2)_3\text{CMe}\}]\cdot 2\text{CH}_2\text{Cl}_2$

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The reaction of  $\text{CuBr}$  with  $[(\text{triphos})\text{CoP}_3]$  [ $\text{triphos} = 1,1,1$ -tris(diphenylphosphinomethyl)ethane] gives  $[(\text{triphos})\text{CoP}_3](\text{CuBr})_6[\text{P}_3\text{Co}(\text{triphos})]$ , which has been shown by a single crystal X-ray study to consist of two  $(\text{triphos})\text{CoP}_3$  units held together by a hexagonal  $\text{Cu}_6$  fragment.

The co-ordinating ability of the  $\text{P}_4$  molecule has been poorly investigated. Indeed the strong reactivity of white phosphorus seldom allows the isolation of metal complexes in which  $\text{P}_4$  acts as a ligand.<sup>1,2</sup> The comparative chemical inertness of the derivative  $[(\text{triphos})\text{CoP}_3]$ ,<sup>3,4</sup> (**1**), [ $\text{triphos} = 1,1,1$ -tris(diphenylphosphinomethyl)ethane,  $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ] makes this complex a useful model for  $\text{P}_4$  molecular reactivity.

We have recently reported that (**1**) can bind  $[\text{M}(\text{triphos})]^{2+}$  moieties ( $\text{M} = \text{Co}, \text{Ni}, \text{Fe}$ ),<sup>5,6</sup> and metal carbonyl fragments such as  $\text{Cr}(\text{CO})_5$ ,<sup>4,7</sup> and  $\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_2$ ,<sup>8</sup> to form heterometallic polynuclear derivatives in which the  $\text{P}_3$  unit acts as a  $3\pi$  ligand and as a Lewis base.

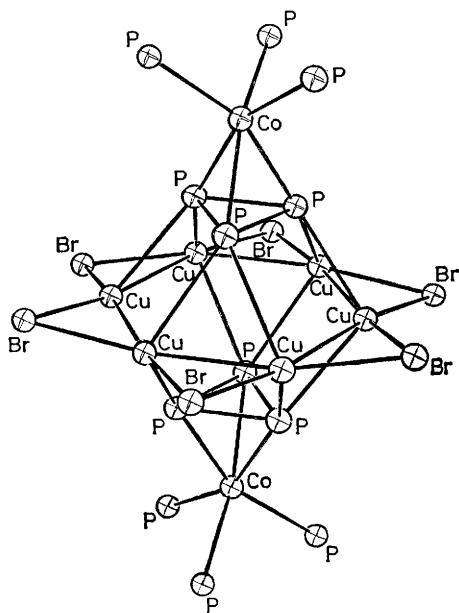
We have now found that the complex (**1**) reacts with copper(I) bromide to form the 'sandwich' derivative  $[(\text{triphos})\text{CoP}_3](\text{CuBr})_6[\text{P}_3\text{Co}(\text{triphos})]$ , (**2**), containing an unusual hexagonal  $\text{Cu}_6$  core. A suspension of  $\text{CuBr}$  (0.9 mmol) in a solution of  $[(\text{triphos})\text{CoP}_3]$  (0.3 mmol) in dichloromethane (or chloroform-tetrahydrofuran) was stirred for 3 h at 30 °C under a nitrogen atmosphere. After filtration, addition of n-butanol to the resultant dark brown solution, and concentration under

a flow of nitrogen, red-brown crystals of stoichiometric composition  $[(\text{triphos})\text{CoP}_3](\text{CuBr})_3$  were precipitated.† The complex, which decomposes very slowly in air, is not very soluble in the common polar organic solvents. Its molecular structure has been established by a single-crystal X-ray diffraction study.

*Crystal data:*  $\text{C}_{84}\text{H}_{82}\text{Br}_6\text{Cl}_4\text{Co}_2\text{Cu}_6\text{P}_{12}$ ,  $M = 2583.6$ , monoclinic, space group  $P2_1/n$ ,  $a = 19.019(8)$ ,  $b = 16.431(7)$ ,  $c = 14.940(7)$  Å,  $\beta = 91.40(5)^\circ$ ,  $U = 4667.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.838$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 45.9$  cm<sup>-1</sup>.

Intensity data were collected on a Philips PW 1100 diffractometer using the  $\omega$ - $2\theta$  scan technique and graphite-monochromated Mo- $K_\alpha$  radiation in the  $2\theta$  range 5–40°. An absorption correction giving transmission factors ranging from 0.80 to 0.44 was applied. The structure was solved by the

† The reaction of (**1**) and  $\text{CuBr}$  in the molar ratio 2:3 by an analogous method yielded another derivative of stoichiometric composition  $[(\text{triphos})\text{CoP}_3]_2(\text{CuBr})_3$  whose characterization is in progress.



**Figure 1.** Inner core of  $[(\text{triphos})\text{CoP}_3](\text{CuBr})_6[\text{P}_3\text{Co}(\text{triphos})]$ . For the sake of clarity all the atoms were assigned the same temperature factor. Mean values of important bond distances: Cu–Cu = 2.61(2), Cu–Br = 2.400(5), Cu–P = 2.54(5), Co–P(triphos) = 2.20(1), Co–P( $\text{P}_3$ ) = 2.26(1), P–P( $\text{P}_3$ ) = 2.03(1) Å.

heavy atom technique. The phenyl rings of the triphos ligand were treated as rigid groups. A solvent molecule of  $\text{CH}_2\text{Cl}_2$ , detected in a difference Fourier map, appeared to be highly disordered, the chlorine atoms being statistically distributed in two positions each with 50% occupancy. The present  $R$  and  $R_w$  values for 1885 reflections with  $I > 3\sigma(I)$  are 0.091 and 0.094 respectively.‡

The inner core of the  $[(\text{triphos})\text{CoP}_3](\text{CuBr})_6[\text{P}_3\text{Co}(\text{triphos})]$  molecule which possesses crystallographic  $\bar{1}$  symmetry is

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

shown in Figure 1. The molecule consists of two symmetry-related  $(\text{triphos})\text{Co}(\text{P}_3)$  units held together by a hexagonal  $\text{Cu}_6$  fragment, whose edges are all symmetrically bridged by bromine atoms lying approximately in the  $\text{Cu}_6$  plane. The phosphorus atoms of the two cyclotriphosphorus groups and the copper atoms are at the vertices of a cuboctahedron; the inner core may therefore be described as a cuboctahedron of copper and phosphorus atoms with two centrosymmetric triangular  $\text{P}_3$  faces, each capped by a  $(\text{triphos})\text{Co}$  group. Assuming negligible Cu–Cu interactions<sup>9</sup> each copper atom is surrounded by two bromine and two phosphorus atoms in a nearly tetrahedral geometry. However, the presence of only one lone pair on each phosphorus atom of the  $\text{P}_3$  fragment as well as the mutual arrangement of the  $\text{P}_3$  and  $\text{Cu}_6$  rings (the two  $\text{P}_3$  triangles, each staggered with respect to the other, point alternately to the middle of the edges of the  $\text{Cu}_6$  hexagon) are indicative that the bonding must be considered essentially delocalized.

The  $\text{Co}(\text{P}_3)$  fragment shows some differences in bond distances in comparison with the starting  $[(\text{triphos})\text{Co}(\text{P}_3)]$  complex;<sup>4</sup> these differences however have not been rationalized because the distances in the present compound are uncorrected for the high thermal motion which affects the phosphorus atoms of the cyclotriphosphorus group.

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