

The Direct Electrochemical Synthesis of Metal–Diphenylphosphido Complexes, and the Crystal Structure of $\text{Cu}_4(\mu\text{-PPh}_2)_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$

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The electrochemical oxidation of metal anodes in an acetonitrile solution of Ph_2PH yields $\text{M}(\text{PPh}_2)$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) or $\text{M}(\text{PPh}_2)_2$ ($\text{M} = \text{Co}, \text{Zn}, \text{Cd}$); with a solution of Ph_2PH and bis(diphenylphosphino)methane (dppm), this method gives $\text{Cu}_4(\text{PPh}_2)_4(\text{dppm})_2$ whose structure is found to be very similar to that of $\text{Cu}_4(\text{SC}_5\text{H}_{11})_4(\text{dppm})_2$.

The electrochemical oxidation of a sacrificial anode in a non-aqueous solution of thiol has been shown to be a convenient one-step room-temperature route to the thiolato complexes of metals such as zinc, cadmium, mercury,^{1,2} tin,³ lead,³ copper,^{4,5} silver,⁵ gold,⁴ cobalt,⁶ and nickel.⁶ The products are the metal thiolates, their adducts, or anionic cage

complexes, depending on the composition of the electrolyte phase. We now report the use of similar techniques to prepare diphenylphosphido derivatives of both main group and transition metal elements. The synthetic routes reported in the literature for the preparation of $\text{M}(\text{PR}_2)_n$ compounds include alkane elimination between MR and HPR_2 ,⁷ the elimination

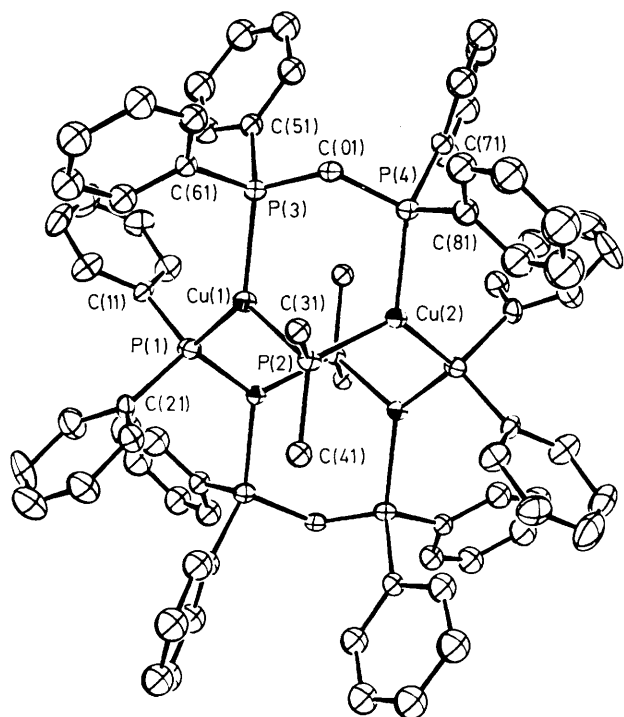


Figure 1. The molecular structure of $\text{Cu}_4(\mu\text{-PPh}_2)_4(\text{dppm})_2$; ORTEP diagram, 30% probability ellipsoids. The numbering system is shown.

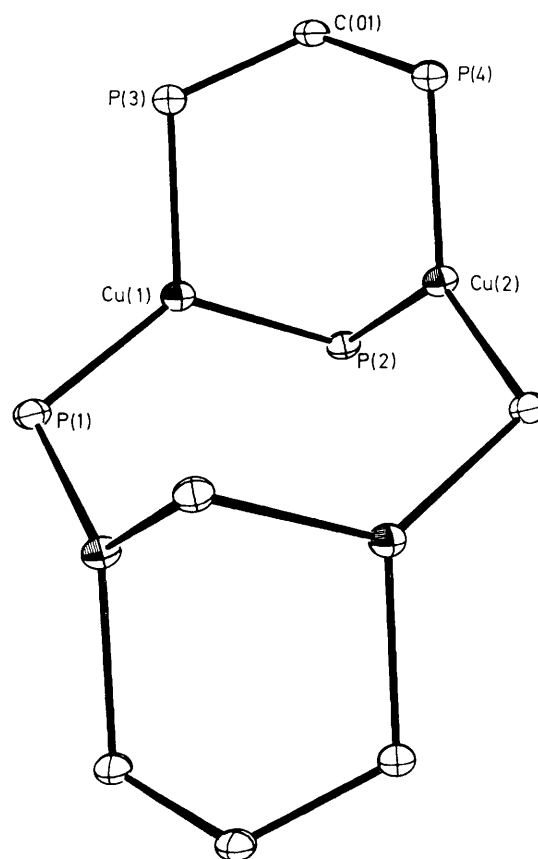


Figure 2. The core Cu_4P_4 ring with its capping $\text{Cu}_2\text{PCP}'_2$ rings.

of Me_3SiCl between NiCl_2 and $\text{Me}_3\text{SiPPh}_2$,⁸ the reaction of MR with $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$,⁹ and transmetallation using R_2PLi .^{10,11} We believe that the direct electrochemical preparation has the advantages of simplicity and high yield compared with the methods described previously.

When a metal anode (e.g. Zn) was oxidized in a solution of Ph_2PH (2 ml, 2.14 g, 50 ml MeCN), using the cell $\text{Zn}|\text{MeCN} + \text{Ph}_2\text{PH}|\text{Pt}$, an applied voltage of 35 V produced a current of 20 mA. A white precipitate formed immediately at the anode and hydrogen was evolved at the cathode. The precipitate was collected, washed (MeCN), dried *in vacuo*, and identified by elemental analysis and i.r. spectroscopy as $\text{Zn}(\text{PPh}_2)_2$, which is insoluble in all common organic solvents. All experimental work was carried out under dry nitrogen. The yield of $\text{Zn}(\text{PPh}_2)_2$ was >90%, based on metal dissolved (0.215 g) after 8 h; the electrochemical efficiency, E_F , was 0.55 mol F^{-1} . Similar experiments with Cd and Co yielded $\text{M}(\text{PPh}_2)_2$, while with Cu, Ag, and Au the products were the insoluble MPPH_2 (E_F 1.00 mol F^{-1}). Yields were >90% in each case.

The solubilities of these Ph_2P derivatives are similar to those of the corresponding thiolato compounds, implying that the two ligands have similar co-ordination and/or bridging properties. This correspondence has been shown to hold in the copper(I) adduct $\text{CuPPH}_2 \cdot 0.5 \text{ dppm}$ [dppm = bis(diphenylphosphino)methane]. Electrochemical oxidation of copper in a solution of Ph_2PH (2 ml, 2.14 g) and dppm (2 g) in a mixture of MeCN (45 ml) and toluene (25 ml) for 8 h (15 V, 20 mA) caused 0.37 g Cu to dissolve; E_F 0.98 mol F^{-1} . After electrolysis, the yellow-orange solution was allowed to stand overnight with a slow stream of N_2 bubbling through the mixture; a large quantity of yellow-orange crystals was then isolated as before. This material analysed as $\text{CuPPH}_2 \cdot 0.5 \text{ dppm} \cdot 0.5 \text{ PhMe}$, but crystals grown from hot toluene-MeCN (50:20) for X-ray crystallography were found to have the composition $\text{CuPPH}_2 \cdot 0.5 (\text{dppm}) \cdot \text{MeCN}$. The crystal struc-

ture analysis^{3,12†} identified the structure of the adduct (Figure 1) as that of the tetrameric $\text{Cu}_4(\mu\text{-PPh}_2)_4(\text{dppm})_2$ (1) with four molecules of MeCN in the unit cell but apparently playing no role in determining the stereochemistry of the adduct. The adduct consists essentially of a Cu_4P_4 ring involving the Ph_2P ligands, capped by two six-membered boat-form $\text{Cu}_2\text{PCP}'_2$ rings with dppm bridging two copper atoms. All the phosphorus atoms have essentially tetrahedral co-ordination. Figure 2 shows the skeleton of the three fused rings. This structure is almost identical to that found⁵ for $\text{Cu}_4(\mu\text{-SC}_5\text{H}_{11})_4(\text{dppm})_2$ (2) which also contains an eight-membered Cu_4S_4 ring and two capping $\text{Cu}_2\text{SCP}'_2$ rings in the boat form. Table 1 summarizes some of the important features of these two unusual molecules. One significant difference is that the stereochemistry at phosphorus in the Cu_4P_4 ring is tetrahedral, while sulphur is almost trigonal in Cu_4S_4 , but otherwise the ring dimensions and angles are remarkably similar. The Cu_4S_4 ring is apparently unique⁴ amongst the rich variety of Cu(I)-thiolate cage structures presently known,^{13,14} and it seems reasonable to

† Crystal data for (1): $\text{Cu}_4(\mu\text{-PPh}_2)_4(\text{dppm})_2 \cdot 4\text{MeCN}$, $M = 1928$, space group $P\bar{1}$, $a = 14.719(4)$, $b = 13.649(5)$, $c = 17.112(5)$ Å, $\alpha = 112.4(3)$, $\beta = 106.2(2)$, $\gamma = 115.4(2)^\circ$, $Z = 1$, $D_c = 1.26$, $D_x = 1.28$ g cm^{-3} , Mo- K_α radiation, data collected at 21 °C, $R = 0.0632$ for 3622 reflections. The structure was refined in two blocks during the least-squares analysis, with Cu, P, and the CH_2 of dppm in one block, and the carbon atoms of all phenyl groups in the second; 351 variables. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Comparison of important steric parameters in $\text{Cu}_4(\mu\text{-PPh}_2)_4(\text{dppm})_2$ (**1**) and $\text{Cu}_4(\mu\text{-SC}_5\text{H}_{11})_4(\text{dppm})_2$ (**2**).^a

	(1)	(2)
8-Membered ring		
$r(\text{Cu-P, Cu-S})/\text{\AA}$ (av.)	2.268	2.246
Σ angles at Cu/ $^\circ$ (av.)	367	359
Deviations from Cu_4 plane/ \AA		
	P(1), P(1)* -0.095	S(1), S(1)* -1.52
	P(2), P(2)* -1.55	S(2), S(2)* -0.42
6-Membered rings		
$r(\text{Cu-P}')/\text{\AA}$ (av.)	2.290	2.274
$r(\text{C-P}')/\text{\AA}$ (av.)	1.861	1.846
$\text{Cu-P}'\text{-C}'/\text{\AA}$ (av.)	113.5	113.6
$\text{P}'\text{-C-P}'/\text{\AA}$ (av.)	115.4	116.7
$\text{Cu-P, S-Cu}'/\text{\AA}$	86.4(1), 112.9(2)	85.9(1), 98.5(1)

^a $\text{SC}_5\text{H}_{11} = \text{-SCMe}_2\text{CH}_2\text{Me}$.

suggest from the present results that there may well be a corresponding range of Cu(I)-phosphido ligand structures to be identified.

In addition to the potential use of $\text{M}(\text{PR}_2)_n$ compounds in the synthesis of other phosphido species, these molecules have a chemistry as yet largely unexplored. Thus we find that $\text{M}(\text{PPh}_2)_n$ compounds react with CS_2 to give $\text{M}(\text{S}_2\text{CPh}_2)_n$ by insertion into the M-P bond. Another set of related compounds can easily be prepared electrochemically. Oxidation of a zinc anode in a solution of Ph_2PH (1 ml, 1.07 g) and sulphur (0.30 g) in MeCN-toluene (30:20) for 3 h (15 V, 30 mA) caused 0.110 g of metal to dissolve (E_F 0.51 mol F^{-1}). The white precipitate was collected, washed (MeCN then tolu-

ene), and dried *in vacuo*. This material was identified as $\text{Zn}(\text{S}_2\text{PPh}_2)_2$, identical with the compound described by McCleverty *et al.*¹⁵ Similar techniques have given the corresponding Cd^{II} , Ni^{II} , and Co^{II} complexes in yields exceeding 90%.

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