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Preliminary communication

A new type of stable organometallic copper complex; properties and structure of the product of the reaction of arylcopper compounds with bis(diphenylphosphino)methane

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SUMMARY

The complex of empirical formula $Cu(Ph_2PCH_2PPh_2)$ is formed from bis(diphenylphosphino)methane and arylcopper compounds, the structure of $[Cu(Ph_2PCH_2PPh_2)\cdot\frac{2}{3}(PhCH_3)]$ has been determined.

Previous researches on the stabilization of organocopper compounds have revealed differences in the behaviour of 1,2-bis(diphenylphosphino)ethane (DPE) and bis(diphenylphosphino)methane (DPM) in their reactions with phenyl- and *o*-, *m*-, or *p*-tolylcopper.. Complexes of the formula $(CuR)_2(DPE)_3$ (R = aryl) were isolated[1] with the DPE ligand. In contrast, with the DPM ligand, the same product was always obtained whichever arylcopper compound was taken, and the aryl group was present quantitatively in the mother liquor as the corresponding arene. We describe below the characterization and the solid state structure of this compound, the elemental composition of which corresponds to the empirical formula $Cu(Ph_2PCH_2PPh_2)$.

The product is a yellow diamagnetic solid, stable at room temperature in an inert atmosphere. When prepared in toluene, it crystallizes with 0.66 molecules of solvent for each copper atom. It reacts with most of the common organic solvents. For example, chloro derivatives of the type $(CuCl)_n(DPM)_m$[2] (where n/m = 1 or 4/3) were isolated together with vinyl chloride from dichloroethane solution, whereas dissolution in carbon disulfide occurs through reaction of two molecules of solvent per three copper atoms.

In a structural investigation, the prismatic crystals were found to be monoclinic, with cell parameters $a = 14.021 \pm 0.007$, $b = 23.366 \pm 0.009$, $c = 23.335 \pm 0.009$ and β 110.9°, space group $P2_1/c$. The density of 1.29 ± 0.01 g/cm^3, determined by flotation, was in agreement with the calculated value of 1.29 g/cm^3 with twelve formula units, assumed to be $[CuDPM\cdot\frac{2}{3}$ toluene$]$, in a cell. The 2926 independent reflections, with

$I/\sigma(I) \geqslant 3$, were collected on a Siemens automatic diffractometer using Mo-K_α radiation. The structure, solved by the conventional Patterson and Fourier method, was refined by the block-diagonal least-squares method to a conventional R factor of 0.075.

The crystal is built up from trimeric copper units and toluene molecules of crystallization. As shown in Fig. 1, the trimeric unit consists of copper atoms arranged at the vertices of a nearly regular isosceles triangle, with the base Cu(1)—Cu(2) of length 2.836(4) Å and sides of length 3.146(3) and 3.112(4) Å. The basal copper atoms, which are bridged by the three ligand molecules through their phosphorus atoms (average Cu—P 2.317(5) Å), assume a nearly trigonal geometry, the sum of P—Cu—P angles around each copper atom being 359.8 and 359.7° respectively. In contrast, Cu(3) bridges the methine carbon atoms of two ligand molecules with an angle at Cu(3) of 158.0(8)° and Cu—C bond lengths of 1.96(2) and 2.00(2) Å respectively. The overall molecule, stabilized by efficient phenyl—phenyl interactions (see Fig. 1), has a rough C_{2v} symmetry, the three P atoms coordinated to Cu(1) being slightly skewed with respect to those coordinated to Cu(2), as shown in Fig. 2. Two of the phosphine ligands are geometrically equivalent, with a mean P—C distance of 1.84(2) Å and a mean P—C—P angle of 107.8(8)°. The Cu—C—P angles range from 93.4(7) to 96.7(9)°. Furthermore each carbon atom is displaced by 0.83 and 0.87 Å out of the plane containing the two metal atoms and the two corresponding phosphorus atoms (coplanar within ± 0.09 and ± 0.12 Å, respectively), as found in the

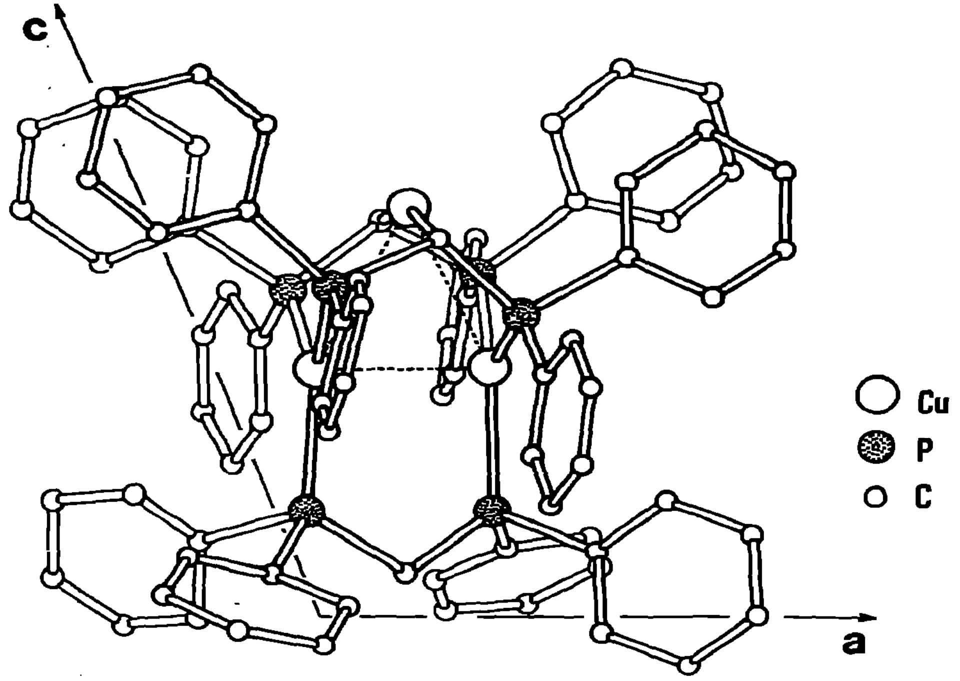

Fig. 1. The trimeric molecule viewed along the crystallographic b axis.

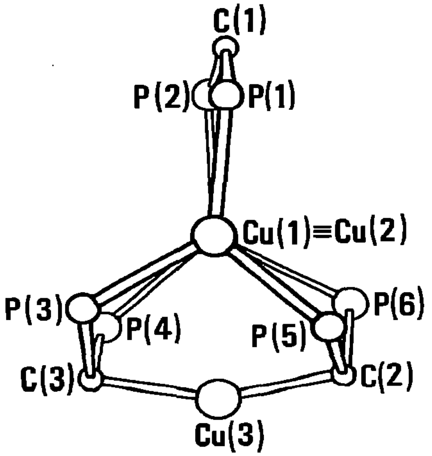

Fig. 2. The backbone structure projected along the base of the copper atom triangle, together with the atom numbering scheme.

tetranuclear $[(\mathrm{CuI})_2\mathrm{DPM}]_2$[3], in which DPM acts as a neutral ligand. Assuming a nearly tetrahedral geometry for the methine carbon atoms, the calculated position of their hydrogen atoms occurs in a sharp maximum of positive electron density on the Fourier difference map. In contrast, the third phosphine exhibits a different geometry, with a mean P—C distance of 1.74(2) Å and a P(1)—C(1)—P(2) angle of 121(1)°. Furthermore the C(1) atom is nearly in the plane passing through Cu(1)P(1)P(2)Cu(2) atoms (coplanar within 0.06 Å) being displaced of 0.12 Å. These geometrical parameters are in agreement with the presence of an amount of double bond character in the P—C bonds, suggesting for the third ligand formulation as the monoanion $[\mathrm{Ph_2P}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{PPh_2}]^-$[4]. Previously reported values for P—C bond lengths range from 1.629 (ref. 5) to 1.748 Å (ref. 6), depending on the amount of double bond character in the P—C bond. The position of the methine hydrogen atom, located on the Fourier difference map, is easily explained in terms of trigonal hybridization of the C(1) carbon atom.

The simplest mode of formation of the compound, remembering that it can also be obtained by reaction of copper bromide with bis(diphenylphosphino)methyllithium, is:

$$3\,\mathrm{Cu^IR} + 3\,\mathrm{Ph_2PCH_2PPh_2} \rightarrow 3\,\mathrm{RH} + [\mathrm{Cu^I}(\mathrm{Ph_2P}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{PPh_2})]_3$$

where in the trimeric copper(I) compound, two phosphines are acting as Lewis bases, donating a pair of electrons from the carbon to the copper atom. However the structural non-equivalence of the phosphine ligands favours the following scheme:

$$3\,\mathrm{Cu^IR} + 3\,\mathrm{Ph_2PCH_2PPh_2} \rightarrow 3\,\mathrm{RH} + [\mathrm{Cu^{II}}(\mathrm{Ph_2P}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{PPh_2})\cdot\mathrm{Cu^{1/2}}_2(\mathrm{Ph_2P}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{PPh_2})]$$

which shows a dismutation reaction taking place, with formation of a trimeric compound in which the copper(II) atom is σ-bonded to two carbon atoms. The occurrence of copper(II) in association with phosphine ligands is unusual, but our example is not unique[7].

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