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Preliminary communication

COPPER(I)—ALKYL BONDING IN THE DINUCLEAR COPPER(I) COMPOUND $[(CH_3)_2P(CH_2)_2]_2Cu_2$

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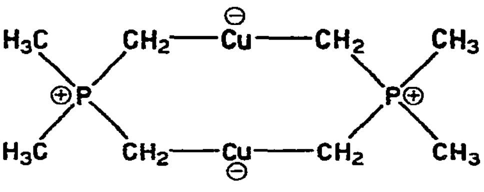
Summary

The complex of empirical formula $Cu^I[(CH_3)_2(CH_2)_2P]$ has been found to be dimeric with two digonal copper(I) atoms bridged by two ligand molecules through copper—carbon σ-bonds, resulting in a centrosymmetric eight-membered heterocycle.

X-ray analyses of two stable copper(I) aryls [1] and one alkyl [2] compound have revealed that a common feature is the presence of bridging carbon atoms between copper atoms. It has been [1, 2] suggested that such a geometry may be explained in terms of three-centre two electron bonds. In addition the alkyl compound [2] $(Me_3SiCH_2Cu)_4$, is characterized by having digonal copper atoms with a C—Cu—C angle of 164°.

A digonal arrangement with an angle at Cu atoms of 158° has been found [3] in the trinuclear complex, $[Cu(Ph_2P)_2CH]_3$. On the other hand the copper atoms were assumed to have a +2 oxidation state and no bridging carbon atom was found.

Recently Schmidbaur et al. reported [4] that the stabilization of organocopper compounds by the $(CH_3)_3SiCH_2$ group [5] is greatly exceeded by that of the isoelectronic phosphonium group $(CH_3)_3P^+—CH_2$. These authors isolated a stable ylide under inert gas at room temperature, and on the basis of ^1H and ^{31}P NMR, IR and mass spectra they attributed to it the dimeric structure (I) having a linear C—Cu—C group.



We describe below the results of an X-ray analysis of this compound, and we show that in the solid state the proposed structure is fully confirmed.

The colourless crystals, although stable in inert atmosphere, were extremely difficult to handle under the usual conditions of diffraction data collection as the crystals loose crystallinity after a few days. We collected a set of photographic data as quickly as possible using a crystal sealed under nitrogen, in a thin-walled glass capillary. The need for speed ruled out the collection of an "ideal" set of data, but those obtained were sufficient for the crystal structure analysis.

The crystals are monoclinic with cell parameters a 10.17(8), b 9.72(7), c 13.19(9)Å, β 94.0(5)°, space group $C2/c$ (from Patterson analysis and refinement). The density of 1.58 g/cm^3, determined by flotation is only of diagnostic value, because of the difficulty of the measurement, the calculated density being 1.65 g/cm^3 with eight formula units, $CuMe_2P(CH_2)_2$, in a cell.

The structure based on 775 independent reflections, collected on equi-inclination Weissenberg photographs with Cu-K_α radiation, was solved by the heavy-atom method and refined by anisotropic least-squares refinement to a conventional R-index 0.11.

The crystal is built up of discrete dimeric units $[Cu^I\{(CH_3)_2P(CH_2)_2\}]_2$ arranged on the crystallographic symmetry centres forming an eight-membered heterocycle. The dimer is shown in Fig. 1 together with the distances of interest. The coordination around the copper atom is digonal with the CH_2—Cu—CH_2 angle of 175.8(8)° and Cu—C bond lengths of 1.962(15) and 1.953(17)Å. The geometry around the P atom is characterized by P—C bond lengths ranging from 1.78(2) to 1.83(2)Å, whereas the CH_3—P—CH_3 and CH_2—P—CH_2 bond angles are 103.0(9) and 112.1(8)°, the others ranging from 108.9(9) to 112.2(8)°. Finally the Cu—C—P bond angles are 109.7(7) and 107.1(9)°. The copper and carbon atoms of the cycle are quite coplanar, the deviations of these atoms from their mean plane being ±0.012 Å. The P atoms lie 0.79 Å above and below

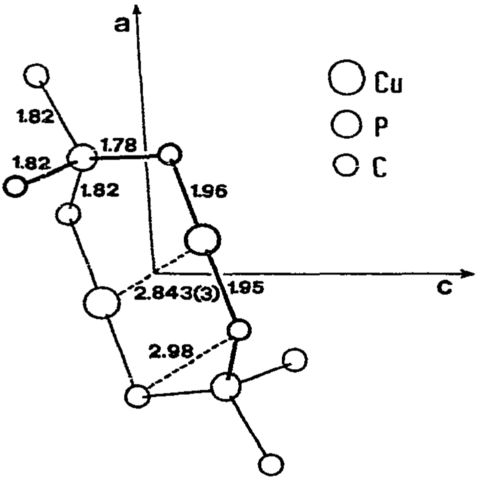


Fig. 1. A view of the molecule viewed along the crystallographic b axis. The estimated standard deviations of the Cu—C and Cu—P distances are 0.02 Å.

this plane. One methyl group of each ligand molecule is axially bonded, the other being in equatorial position.

The Cu—Cu distance of 2.843(3)Å is significantly shorter than CH_2—CH_2 (2.98(2)Å) of the bridging ligand. We suggest that this small distortion arises from a weak interaction between the copper atoms.

It is worthwhile to compare such a structure with that of the tetranuclear copper(I) complex $(Me_3SiCH_2Cu^I)_4$ [2]. The ability of the $(CH_3)_3PCH_2$ group to act as a bidentate ligand when it looses one hydrogen atom permits the formation of two Cu—C σ-bonds. In contrast, the monodentate $(CH_3)_3SiCH_2$ group can give only three-centre bonds to form 1/1 complexes containing digonal copper atoms. Since a tetranuclear species is observed, it seems that the digonal C—Cu—C arrangement is particularly stable.

Acknowledgement

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