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Preliminary communication

Synthesis and crystal structure of $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(\mu\text{-dppm})_3][BF_4]_2$, a tricopper(I) complex containing a μ_3-η^1 acetylide group and three bis(diphenylphosphino)methane (dppm) bridging ligands

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Abstract

The synthesis of the cationic trinuclear copper(I) complex $[Cu_3(C{\equiv}CPh)(dppm)_3][BF_4]_2$ is described. An X-ray structure determination shows a triangular array of copper atoms with three diphosphine ligands $Ph_2PCH_2PPh_2$ (dppm) bridging each edge of the triangle and a μ_3-η^1 phenyl acetylide group bound to the Cu_3 unit.

There is an increasing interest in the synthesis of organocopper derivatives owing to their versatility and selectivity in organic synthesis [1]. However, the structures of the active species are generally unknown.

We recently reported [2] the synthesis of tetranuclear copper(I) complexes (A) containing μ_3-η^1-acetylide bridging ligands, showing the structural analogies between the alkynyl group and carbon monoxide to act as triple bridging systems in polynuclear complexes. Although the "$Cu_3C{\equiv}CR$" moiety is formally an electron deficient system (4c-2e$^-$), it evidently shows significant stability since the bidentate phosphines of the molecule **A** act only as monodentate ligands. This seems to be in accord with the well known resistance to transfer of alkynyl groups ("dummy" ligands) in reactions of mixed organocuprate derivatives [3]. Most alkynyl copper derivatives are polymeric solids and their insolubility prevents a full structural characterization. In this context we are making a systematic study of the chemistry

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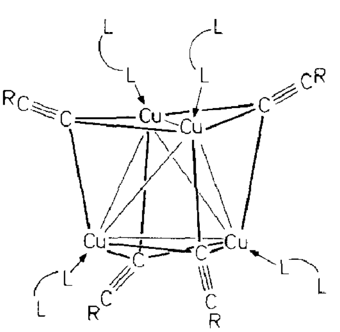

(A)

L-L = $C_5H_4NPPh_2$-$\underline{P}$, R = C_6H_5, ${}^tBu$; L-L = $Ph_2PCH_2PPh_2$-$\underline{P}$, R = C_6H_5

of acetylide copper complexes in order to determine the chemical and structural features of these unusual derivatives. We report here the synthesis and structural studies of a trinuclear copper(I) complex in which the phenyl acetylide group also acts as a μ_3-η^1 bridging ligand, showing the same structural entity as the skeletal faces found in the previously reported tetranuclear complexes [2].

A THF solution of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2$ (dppm = $Ph_2PCH_2PPh_2$) [4] was found to react with LiC≡CPh (prepared 'in situ" from HC≡CPh and $LiBu^n$) to give complex I, which was isolated as a white air stable crystalline solid (eq. 1)

$$3[Cu_2(\mu\text{-dppm})_2(MeCN)_2][BF_4]_2 + 2LiC{\equiv}CPh \rightarrow$$
$$2LiBF_4 + \underset{(I)}{2[Cu_3(C{\equiv}CPh)(dppm)_3][BF_4]_2} \quad (1)$$

Conductivity data (in Me_2CO) show that I behaves as a typical 2/1 electrolyte. The IR spectrum (Nujol mull) exhibits the expected ν(B-F) broad band at 1060 cm^{-1} but not ν(C≡C) band. ${}^{31}P\{{}^1H\}$ NMR spectrum in $CDCl_3$ shows a singlet at δ -7.67 ppm, indicating that all the phosphorus atoms are chemically equivalent.

In order to establish the bonding features of the phenylacetylide ligand the crystal structure of I was determined by X-ray diffraction. The structure is shown in Fig. 1, the legend to which gives selected bond distances and angles.

The molecule, which crystallizes with one molecule of H_2CCl_2, consists of a triangular arrangement of the copper atoms, with each edge bridged by a dppm ligand and with one of the faces of the triangle bearing a μ_3-η^1-phenylacetylide ligand. Two of the edges of the triangle are significantly shorter than the third, with copper-copper distances of Cu(2)-Cu(3) 2.904(3), Cu(1)-Cu(2) 2.813(3) and Cu(1)-Cu(3) 3.274(3) Å, as in the related compound $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-OH})][BF_4]_2$ (3.120(2), 3.127(2) and 3.322(2) Å) [5], suggesting negligible metal-metal bonding interactions [6]. The atoms in the Cu_3P_6 moiety are not coplanar (deviations from Cu_3 plane are as follows P(1) $-0.088(4)$; P(2) 0.177(4); P(3) 0.494(4); P(4) $-0.549(4)$; P(5) 1.117(4); P(6) 0.446 (4) Å). The Cu_2P_2C rings adopt envelope conformations with the methylene carbon atoms on the flap, one of them, C(4), folded towards the bridging acetylide ligand and the other two away from it.

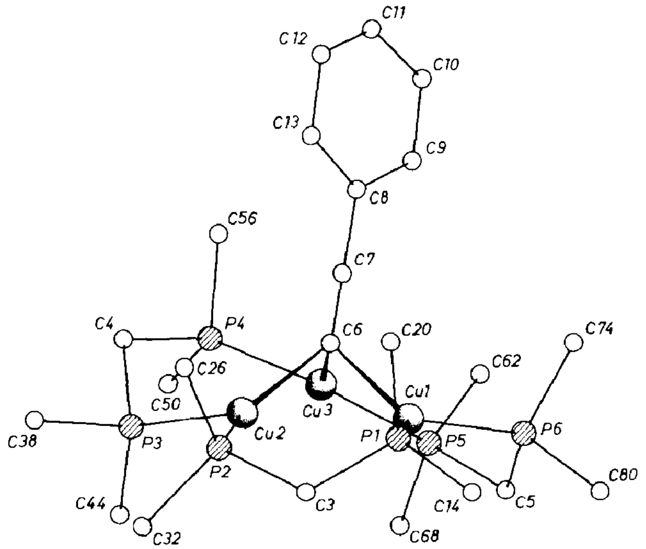

Fig. 1. View of the cation $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(dppm)_3]^{2+}$; main bond distances (Å) and angles (°) Cu(1)–C(6) 2.038(14), Cu(2)–C(6) 1.964(14), Cu(3)–C(6) 2.081(13), C(6)–C(7) 1.22(2), Cu–P in the range 2.257(4)–2.279(4). Cu(1)–C(6)–C(7) 125(1), Cu(2)–C(6)–C(7) 138(1), Cu(3)–C(6)–C(7) 100(1), C(6)–C(7)–C(8) 176(2).

Thus, each copper atom is three-coordinate, with two phosphorus atoms occupying two coordination sites (one from each of two bridging dppm ligands) and the acetylide carbon atom occupying the third site. The Cu–P distances are in the range 2.257(4)–2.279(4) Å. The copper–acetylide triple bridge is slightly asymmetric, with Cu(3)–C(6)–C(7), Cu(1)–C(6)–C(7), Cu(2)–C(6)–C(7) bond angles of 100(1), 125(1) and 138(1)°, respectively, and with Cu–C bond lengths of 2.038(14) (Cu(1)), 1.964(14) (Cu(2)) and 2.081(13)(Cu(3)) Å, which are a little shorter than those shown in the similar framework "$Cu_3C{\equiv}CPh$" of the complex $[Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)(Ph_2Ppy\text{-}P)]_4$ (in the range 2.053(8)–2.345(8) Å) [2]. The phenylacetylide ligand is approximately linear with a bond angle of 176(2)°, and a C≡C distance of 1.22(2) Å (typical of a triple bond). Although these deviations from a symmetric triple bridging mode could indicate a C≡C "side on" π-bonding and/or metal-to-ligand π-back bonding, the linearity of the phenylacetylide ligand and the short C≡C distance indicate a negligible π-interaction. The Cu–C(7) distances are 2.914(15) Cu(1), 2.988(15) Cu(2) and 2.580(14) Cu(3) Å, which are also consistent with pure σ-type bonding. Thus the moiety "$Cu_3C{\equiv}CPh$" is electron deficient, and the bonding can be described, as suggested for complex **A** [2], as that of a typical four centre two electron system. Presumably skeletal distortions are determinated by the irregular arrangement of the Cu_3 triangle and/or packing requirements in the solid state.

The methylene resonances of dppm appear in the proton NMR spectrum as two multiplets at δ 3.55 and 3.15 ppm, typical of a ABX_2 or AA'XX' spin system. This non-equivalence of the CH_2P_2 protons shows that there is no plane of symmetry containing the $[Cu_2P_2C]$ framework which arises from the presence of the $\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh$ ligand on one side of the Cu_3 triangle. Structurally related cationic trinuclear complexes of palladium and platinum, $[M_3(\mu_3\text{-}X)(\mu\text{-}dppm)_3]^{n+}$, $n = 2$. M = Pd, Pt; X = CO [7], $n = 1$. M = Pt; X = H [8], are known.

Crystal data. $C_{83}H_{71}B_2F_8P_6Cu_3 \cdot CH_2Cl_2$, yellowish crystal, 0.50 × 0.50 × 0.10 mm. size, $M_r = 1703.49$, monoclinic, space group $P2_1/c$, a 25.020(10), b 13.752(1), c 24.207(1) Å, β 93.375(4), V 8315(3) $Å^3$, $Z = 4$, D_x 1.36 Mg/m^3. Mo-K_α radiation (graphite crystal monochromator, λ 0.71073 Å), μ(Mo-K_α) 9.99 cm^{-1}, $F(000) = 3480$, T 293 K, 15666 reflections measured, 14616 unique reflections. Final conventional R-factor = 0.08 for 5751 'observed', $I > 3\sigma(I)$, reflections and 865 variables. Structure solved by Patterson using SHELX86 [9], expanded using DIRDIF [10] and refined with SHELX76 [11]. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [12]. All geometrical calculations were made with PARST [13]. The atomic coordinates and the thermal parameters are available on request from authors or from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

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