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Preliminary communication

SYNTHESIS AND X-RAY STRUCTURE OF $[CuPPh_3C{\equiv}CPh]_4$, AN ELECTRON DEFICIENT MOLECULE WITH μ_3-BRIDGING PHENYLACETYLIDE LIGANDS

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Summary

The $[CuPPh_3C{\equiv}CPh]_4$ tetramer, obtained by treatment of $[Cu(PPh_3)_2BH_4]$ with phenylacetylene and KOH (molar ratio 1/1/1) in 1/1 benzene/benzyl alcohol, consists of a tetrahedral skeleton of metal atoms bonded to four terminal phosphine molecules and to four μ_3-bridging phenylacetylide ligands which behave essentially as 2*e* donors.

Substituted acetylides are versatile ligands which have been shown to coordinate to metal polyhedra in a variety of bonding modes, i.e. μ_1-η^1 (terminal), μ_2-η^1 (double bridging), and a number of μ_x-η^2 patterns ($x = 2, 3, 4$) in which both the acetylenic carbons are at bond distance from one or more metal atoms [1–5]. However, no metal complex containing μ_3-η^1 bridging acetylides has been isolated so far. We report here the synthesis and X-ray structure determination of the first example of such a compound, the copper tetramer $[CuPPh_3\text{-}\mu_3\text{-}C{\equiv}CPh]_4$ (1).

Compound 1 can be obtained by treating tetrahydrogenoboratebis(triphenylphosphine)copper(I) with phenylacetylene and KOH (in the molar ratio 1/1/1) in a benzene/benzyl alcohol 1/1 solution. Yellow crystals of 1 suitable for X-ray analysis were obtained by slow diffusion of hexane into the solution. When the solution of 1 is stirred for several days an insoluble fluorescent

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yellow-green compound 2 separates (melting point and analysis unchanged), which can be reconverted into 1 by refluxing in CH_3CN.

Crystal data. $C_{104}H_{80}Cu_4P_4$, M=1707.85, monoclinic, space group $C2/c$, a 14.866(4), b 24.552(4), c 23.345(9) Å, β 95.89(2)°, U 8476 Å^3, $Z = 4$, $D_{\mathrm{calc.d}}$ 1.338 g cm^{-3}, μ(Mo-K_α) 11.54 cm^{-1}. 6625 intensity data were collected on a Nonius-CAD-4 automated diffractometer by the ω-scan technique in the 2θ range 6—50°. The structure was solved by use of the MULTAN program and refined using 3769 independent absorption-corrected reflections having $I > 3\sigma(I)$. The final full-matrix least-squares refinement led to conventional R and R_w values of 0.054 and 0.065 respectively.

The $[CuPPh_3\text{-}\mu_3\text{-}C{\equiv}CPh]_4$ molecule, of crystallographic C_2 symmetry, consists of an essentially tetrahedral metal skeleton bearing four terminally

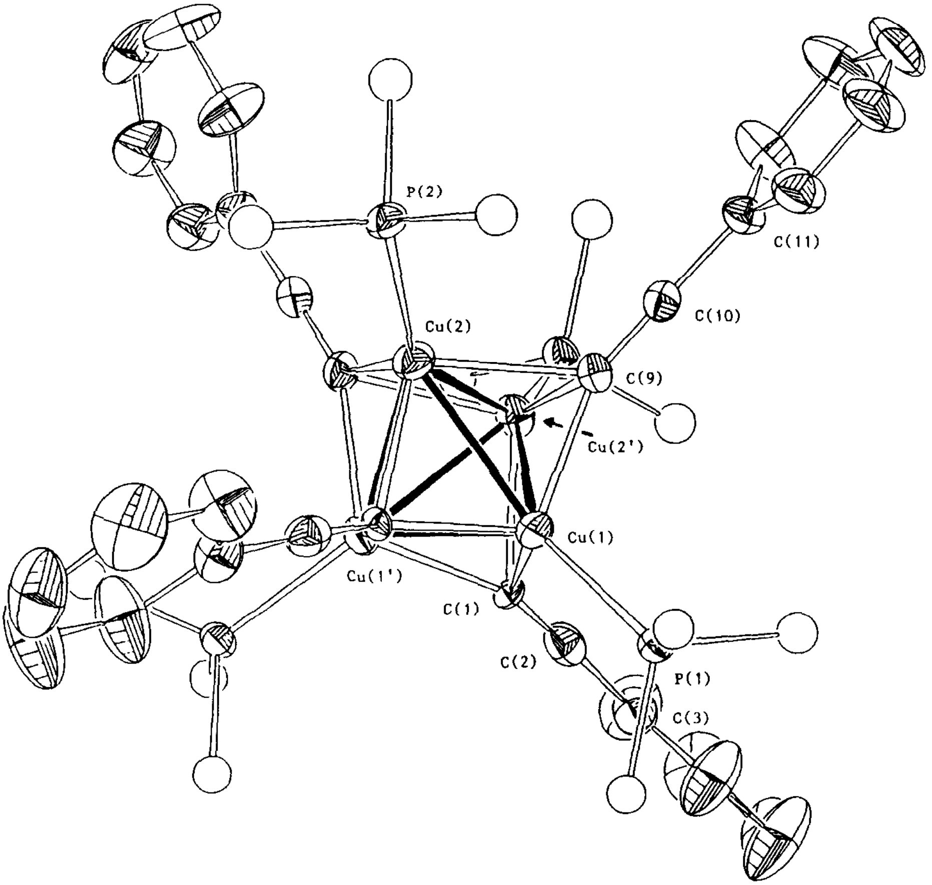

Fig. 1. ORTEP view of the $[CuPPh_3\text{-}\mu_3\text{-}C{\equiv}CPh]_4$ molecule. Only the first carbon atoms of the triphenylphosphine ligands are shown for clarity. Principal bond parameters are: Cu(1)—Cu(1′) 2.600(1), Cu(1)—Cu(2) 2.523(1), Cu(1)—Cu(2′) 2.676(1), Cu(2)—Cu(2′) 2.620(1), Cu(1)—P(1) 2.234(1), Cu(2)—P(2) 2.221(1), Cu(1)—C(1) 2.380(4), Cu(1′)—C(1) 2.072(4), Cu(2′)—C(1) 2.214(4), Cu(1)—C(9) 2.096(5), Cu(2)—C(9) 2.232(4), Cu(2′)—C(9) 2.115(4), C(1)—C(2) 1.154(6), C(9)—C(10) 1.193(6) Å, P—Cu—$C_{(av.)}$ 113.7, C—Cu—$C_{(av.)}$ 104.6°.

bonded triphenylphosphine molecules and four μ_3-η^1 phenylacetylide ligands (see Fig. 1). Principal bond parameters are listed in the caption of Fig. 1. Important average distances are: Cu—Cu 2.603, Cu—P 2.228, Cu—C 2.185 and C≡C 1.174 Å. The copper-acetylide triple bridges are markedly asymmetric, with Cu—C contacts in the range 2.072(4)—2.380(4) Å. The observed very short C≡C distances are indicative of a typical triple bond (cf. for instance 1.20 Å in the free acetylene [6] and 1.174 Å in $Cu_6(C_6H_4NMe_2\text{-}2)_4(C{\equiv}CC_6H_4Me\text{-}4)_2$ [1]) and of the absence of π back-donation from the metals to the ligand $\pi^\star$ orbitals. The C(1)—C(2)—C(3) and C(9)—C(10)—C(11) fragments are strictly linear (average angle 178°), and the interactions of atoms C(2) and C(10) with metal triangles Cu(1)—Cu(1′)—Cu(2′) and Cu(1)—Cu(2)—Cu(2′), respectively, are negligible (average C. . .Cu distance 3.104 Å): both these features are in contrast with the substantial ligand-to-metal π-donation (which is known, for instance, in molecule 2 of $[(MeC{\equiv}C)_2BeNMe_3]_2$ [3], and in a number of metalacetylide complexes [2]) and indicate that in the present case the acetylide ligands behave as essentially 2 electron donors.

Although direct metal—metal bonds in organocopper clusters is considered to be unimportant [1], EHMO calculations performed by Hoffmann et al. on polynuclear copper(I) complexes of various geometries [7] have shown that Cu(I)—Cu(I) distances in the range of those observed here are indicative of a soft metal—metal attraction. Consistently, the Cu. . .Cu distances in the topologically similar halogen-bridged cubane-like tetramers $[CuLX]_4$ (L = substituted phosphine, X = Cl, Br, I) are all longer [8] (shortest Cu. . .Cu distance 2.927(2) Å for L = PEt_3 and X = I [9]) and definitely non bonding, in keeping with the presence of bridging halide ligands which are generally believed to function as 4 electron donors. We conclude, therefore, that the description of the bonding in each Cu_3C fragment of the electron-deficient $[CuPPh_3\text{-}\mu_3\text{-}C{\equiv}CPh]_4$ tetramer should refer to a four-centre two-electron σ-bond as providing the major contribution, with a minor supporting role played by metal—metal attraction.

IR spectra of **1** show a single C≡C absorption at 2020m cm^{-1} (Nujol phase or spread on NaCl discs), whereas compound **2** shows two absorption bands at 2060m and 1935w cm^{-1}. It seems likely that the yellow-green isomer **2** may contain differently bonded phenylacetylide ligands, as previously found for instance in $[(MeC{\equiv}C)_2BeNMe_3]_2$ [3].

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References

1 J.G. Noltes, Phil. Trans. R. Soc. Lond. A, 308 (1982) 35.
2 G.E. Coates, and C. Parkin, J. Inorg. Nucl. Chem., 22 (1961) 59.
3 N.A. Bell, I.W. Nowell, and H.M.M. Shearer, J. Chem. Soc., Chem. Commun., (1982) 147.
4 A.J. Carty, S.A. MacLaughlin, and N.J. Taylor, J. Organomet. Chem., 204 (1981) C27.
5 M. Lanfranchi, A. Tiripicchio, E. Sappa, S.A. MacLaughlin, and A.J. Carty, J. Chem. Soc., Chem. Commun., (1982) 538; A.J. Carty, S.A. MacLaughlin, and N.J. Taylor, J. Am. Chem. Soc., 103 (1981) 2456.
6 Interatomic distances Spec. Publ. No. 11, London, The Chem. Soc., 1958.
7 P.K. Mehrotra, and R. Hoffmann, Inorg. Chem., 17 (1978) 2187.
8 R.G. Goel, A.L. Beauchamp, Inorg. Chem., 22 (1983) 395 and ref. therein.
9 M.R. Churchill, and K.L. Kalra, Inorg. Chem., 13 (1974) 1899.