Isolation and Crystal and Molecular Structure of a Rare Example of a Mononuclear Organo-cuprate

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The reaction of mesitylcopper(I), CuAr, with 1,2-bis(diphenylphosphino)ethane, dppe, gives $[(dppe)_2Cu_2Ar_2]$, whose molecular structure, determined by a single-crystal *X*-ray study, consists of a linear mononuclear $[CuAr_2]^-$ unit with a tetrahedral $[Cu(dppe)_2]^+$ unit as counter-ion.

Organocopper reagents are of basic importance in organic synthesis[1] and the variety of reactions which they undergo has proven to be an invaluable tool for the formation of carbon–carbon bonds.[2] They have not usually been isolated and it is believed that the nature of the species present in solution depends on the solvent and on the ratio of LiR to CuR′.[3] Recently Bau *et al.*[4] reported the first structural characterization of the binary copper–phenyl organometallic compound $[Li(thf)_4]^+$ $[Cu_5Ph_6]^-$ (thf = tetrahydrofuran), in which the $[Cu_5Ph_6]^-$ anion has a trigonal bipyramidal metal framework. All previous structure determinations[5,6] on copper–aryl compounds involved bidentate aryl ligands with ring-substituents containing donor atoms. Common aspects of these structurally characterized copper–aryl organometallic compounds are: (i) their metal cluster structures, (ii) the two electron-three centre bonding mode displayed by the aryl ligand.

We report here the synthesis and structure determination of a rare example of a mononuclear copper–aryl compound. The reaction of mesitylcopper(I),[7] CuAr, with 1,2-bis(diphenylphosphino)ethane, dppe, carried out in toluene, gave a pale yellow solution from which precipitated compound (**1**) [reaction (1)].† Recrystallization of (**1**) from tetrahydrofuran, thf, gave crystals suitable for *X*-ray analysis. Its molecular structure has been established by a single-crystal *X*-ray diffraction study.

$$2\,CuAr + 2\,dppe \xrightarrow{\text{toluene}} \underset{(\mathbf{1})}{[Cu(dppe)_2]^+\,[CuAr_2]^-} \qquad (1)$$

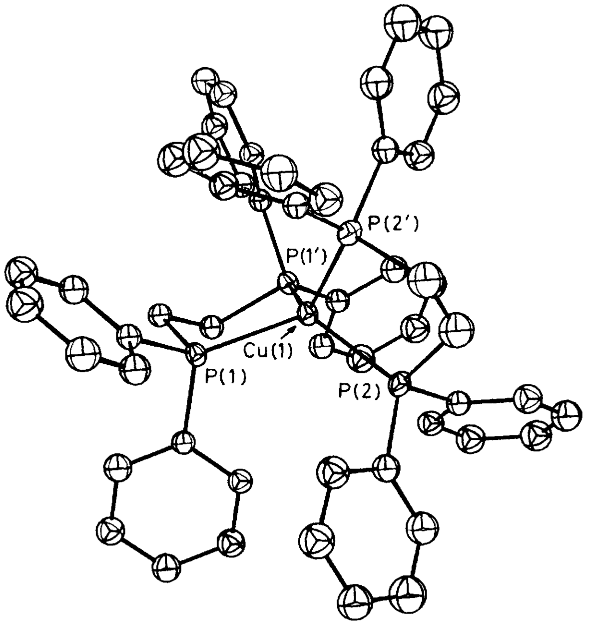

Figure 1. Perspective view of the $[Cu(dppe)_2]^+$ cation. The C_2 axis is horizontal, bisecting the central C–C bond of the dppe ligands. Relevant bond distances (Å) and angles (°): Cu(1)–P(1) 2.320(4), Cu(1)–P(2) 2.305(4); P(1)–Cu(1)–P(1′) 88.3(1), P(2)–Cu(1)–P(2′) 88.6(1), P(1)–Cu(1)–P(2) 120.9(1).

Crystal data: $C_{70}H_{70}Cu_2P_4$, $M = 1162.3$, monoclinic, space group $C2/c$, $a = 29.096(15)$, $b = 13.075(8)$, $c = 20.315(12)$ Å, $\beta = 128.07(3)°$, $U = 6084.3$, $Z = 4$, $D_c = 1.268$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 8.4$ cm^{-1}. The crystal used was coated in paraffin to prevent air decomposition. Intensity data were collected on a Philips computer-controlled PW 1100 diffractometer using the ω–2θ scan technique and graphite-monochromated Mo-K_α radiation. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares methods using anisotropic thermal parameters for the copper and phosphorus atoms only. The phenyl rings of the dppe ligand were treated as rigid groups. The final R and R_w factors for the 2060 reflections ($2\theta \leqslant 40°$) having $I \geqslant 3\sigma(I)$ are 0.078 and 0.083, respectively. The molecular structure consists of discrete $[Cu(dppe)_2]^+$ cations and $[CuAr_2]^-$ anions.‡

Figures 1 and 2 show the two units with important bond distances and angles. The metal atoms, which lie on a crystallographic two-fold axis, display two different co-ordination geometries. In the cation the copper atom is surrounded by two dppe ligands in a distorted tetrahedral geometry while in the anion the metal is linearly bonded to two mesityl groups. In the cation, whose distorsions are mainly due to the requirement of the bidentate dppe ligand, the Cu–P distances are fully comparable with those reported for copper(I) tertiary

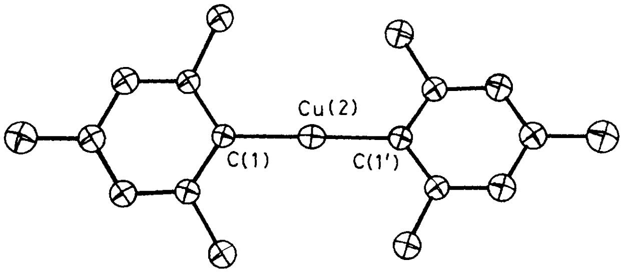

Figure 2. Perspective view of the $[CuAr_2]^-$ anion. The C_2 axis is approximately perpendicular to the drawing. Important bond distances (Å) and angles (°): Cu(2)–C(1) 1.915(9); C(1)–Cu(2)–C(1′) 180.0(7).

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† Satisfactory elemental analytical data were obtained for complex (**1**); ^{1}H n.m.r. (CD_3COCD_3) δ 7.2 (m, 20H, Ph of dppe), 6.7 (s, 2H, mesityl-ArH), 2.65 (m, 4H, CH_2 of dppe), and 2.25 (s, 9H, mesityl-Me).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

phosphine complexes.[8] In the anion the Cu–C distance of 1.915(9) Å is significantly shorter than those reported for complexes containing aryl groups bound to copper through a two-electron-three centre bonding.[4–6] This distance, taking the different covalent radius into account, can be compared with the values of 2.04(2) and 2.06(2) Å reported for the isostructural $[Au(C_6F_5)_2]^-$ anion.[9] It is noteworthy that the $CuAr_2$ moiety significantly deviates from planarity, the angle between the planes containing the two mesityl groups being 26.3°.

The structure reported is unique because it contains: (a) two aryl groups σ-bound to a single copper(I) centre; (b) a second co-ordinatively saturated copper(I) centre with distorted tetrahedral geometry acting as the counter-ion. The influence of the counter-ion on the reactivity of (**1**) towards organic substrates, compared to that of polynuclear lithium organocuprates, is now under investigation.

Tertiary phosphines have often been used as additional ligands in organocopper reagents used in syntheses.[10] Earlier work on the stabilization of arylcopper compounds such as phenylcopper and *o*-, *m*-, and *p*-tolylcopper have suggested that the reaction with diphosphine ligands results in the formation of smaller aggregates with $Ar_xCu_xL_y$ stoicheiometry.[11] However, to the best of our knowledge, structural determinations of products obtained by treatment of arylcopper compounds with diphosphine ligands only concern cases in which loss of the aryl group occurs.[12]

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