

Preliminary communication

FUNCTIONALLY SUBSTITUTED ARYLCOPPER COMPOUNDS; CRYSTAL STRUCTURE OF THE COPPER BROMIDE COMPLEX OF [2-(4,4-DIMETHYL-2-OXAZOLINE)-4-METHYLPHENYL]COPPER]

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Summary

Arylcopper compounds containing a reactive oxazoline substituent in the *ortho* position to the Cu—C bond were synthesized. They react with CuBr to form complexes, and the structure of one of these, $[\text{Cu}_6(\text{oxl})_4\text{Br}_2]$ (oxl = 4,4-dimethyl-2-oxazoline-4-methylphenyl) was determined by X-ray diffraction. The six copper atoms form a distorted octahedron with four two-electron, three-center bonded bridging aryl groups and two bridging bromine atoms. The aryloxazoline substituent is coordinated via the *ipso* carbon to two copper atoms, and the imine-N atom is bonded to a third copper atom.

Organocopper compounds are of importance as reagents for organic syntheses [1]. Consideration of mechanistic aspects of these copper-mediated reactions often requires knowledge of the structures of the organocopper compounds, but structural information is limited to rather simple non-functionalized organocopper species or compounds bearing inert substituents, e.g. CH_2NMe_2 , NMe_2 or OMe [2]. Arylcopper compounds containing reactive aryl substituents have never previously been isolated and characterized, although it is just this group of compounds which is of particular importance for the syntheses of large molecules [3]. We have therefore embarked on a study of the synthesis and characterization of this type of compound.

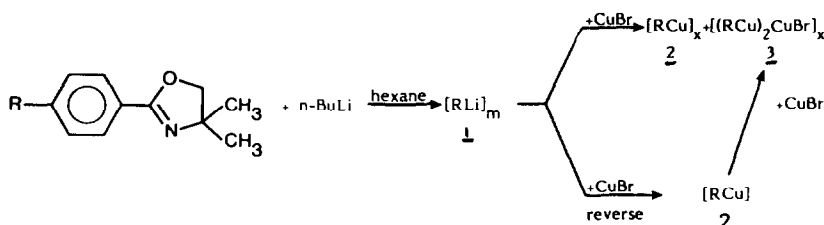
Our attention was especially attracted by the aryloxazoline compounds because the oxazoline group appears to be a very useful protecting group for the carboxylic acid function [4]. Studies by Meyers et al. have led to a very

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versatile organic chemistry of *ortho*-lithiated aryloxazoline compounds [5], while, Ziegler et al. have recently shown that aryloxazoline-copper intermediates can undergo asymmetric Ullmann-type coupling reactions with high selectivity [6].

A series of arylcopper compounds with C=N-bond containing substituents have been synthesized [7], of which the aryloxazoline compounds are reported herein. An interesting feature of these compounds is their ready complexation with copper bromide, a reaction [8] which has received little attention in mechanistic discussions of coupling reactions of organocopper intermediates.

The organolithium compound **1** was obtained as a crystalline solid by direct metallation of the arene compound with *n*-BuLi in hexane [7] (see scheme 1)*. Addition of a solution of **1** in diethyl ether to a CuBr suspension in diethyl ether in a 1/1 ratio gave a bright orange compound, which was indicated by elemental analyses to be a mixture of $[(RCu)_2(CuBr)]_x$ (**3**) and $[RCu]_y$ (**2**). However, use of the reverse mode of addition, i.e. slow addition of solid CuBr to the diethyl ether solution of the organolithium compound [7], gave pure **2**. Addition of another equivalent of CuBr to a solution of pure **2** in benzene, gave



SCHEME 1

the 2/1 complex $[(RCu)_2(CuBr)]_x$ (**3**). Crystals of **3** suitable for a X-ray structure determination were obtained by slow distillation of hexane into a toluene solution of **3**.

Crystal data. $\text{Cu}_6\text{Br}_2\text{C}_{44}\text{N}_4\text{O}_4\text{H}_{48}$, triclinic, space group $P\bar{1}$, a 13.661(3), b 19.154(4), c 11.666(5) Å, α 95.46(3)°, β 92.49(3)° and γ 110.49(3)°, $Z = 2$. 2103 independent intensities with $I > 3\sigma(I)$ measured on a Nonius CAD-4 diffractometer using graphite monochromated Mo- K_α radiation were used. The Cu and Br positions were derived from a Patterson synthesis and C, N, and O were found from a subsequent ΔF synthesis. After isotropic block-diagonal least squares refinement an empirical absorption correction (DIFABS) [9] was applied (crystal dimensions $0.3 \times 0.4 \times 0.5$ mm; $\mu = 36.5 \text{ cm}^{-1}$). Continued anisotropic refinement converged to $R = 0.063$. At this stage apart from hydrogen atoms a ΔF synthesis showed additional electron density in the region $x = -0.048$ to 0.19 , $y = 0.07$ to 0.22 and $z = 0.11$ to 0.34 . This electron density is probably due to the presence of toluene. The electron count was 21.7, implying about 0.4 molecules of toluene per formula unit, which moreover showed disorder. Since the toluene was not of direct interest no attempts were made to find a satisfactory model for it. Instead, the effect of the solvent

*The synthesis of the lithium compound described by Gschwend [12] has the disadvantage that side reactions involving additions to the C=N bond occur even at -70°C , preventing isolation of the pure organolithium compound. Reaction in hexane results in precipitation of the organolithium compound, which can be isolated pure.

was eliminated by correcting the structure factors for its contributions which were obtained by direct Fourier inversion of its electron density**. Hydrogen atoms were introduced at calculated positions and continued refinement, anisotropic for Cu, Br, C, N, O and isotropic for H converged to $R = 0.045$ (R_w 0.078). The anomalous dispersions of Cu and Br were taken into account. An extinction correction was applied and a weighting scheme $\omega = 1/(13.2 + F_o + 0.005F_o^2)$ was employed***.

The overall structure of **3**, which is shown in Fig. 1, consists of a distorted octahedron with stoichiometry $[\text{Cu}_6\text{R}_4\text{Br}_2]$. The main structural features of **3** are: (i) There are two types of Cu atoms with different numbers of interactions with the ligands: the apical ones (Cu(1) and Cu(3)) are coordinated exclusively

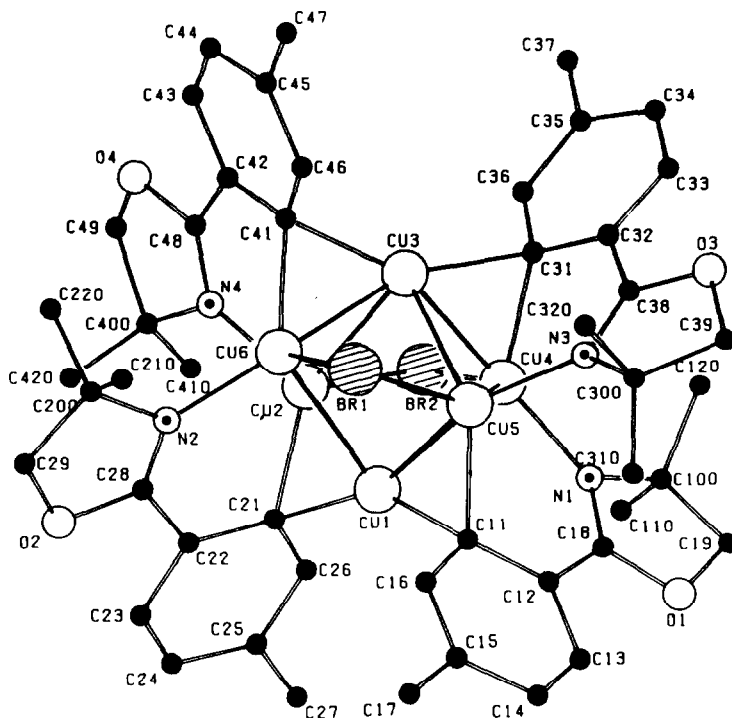


Fig. 1. Molecular structure of **3**. Relevant bond lengths (Å) and angles ($^\circ$): Cu(1)—Cu(2) 2.434(5), Cu(1)—Cu(4) 2.678(5), Cu(1)—Cu(5) 2.451(5), Cu(1)—Cu(6) 2.728(5), Cu(2)—Cu(3) 2.763(6), Cu(2)—Cu(4) 3.012(6), Cu(2)—Cu(6) 2.600(5), Cu(3)—Cu(4) 2.432(6), Cu(3)—Cu(5) 2.694(5), Cu(3)—Cu(6) 2.426(5), Cu(4)—Cu(5) 2.634(5), Cu(5)—Cu(6) 3.033(5), Cu(1)—C(11) 1.952(9), Cu(1)—C(21) 1.985(9), Cu(2)—C(21) 2.079(9), Cu(3)—C(31) 1.993(9), Cu(3)—C(41) 2.011(9), Cu(4)—C(31) 2.090(10), Cu(5)—C(11) 2.068(8), Cu(6)—C(41) 2.071(8), Cu(2)—N(4) 1.980(8), Cu(4)—N(1) 1.948(9), Cu(5)—N(3) 1.972(8), Cu(6)—N(2) 1.974(8), Cu(2)—Br(2) 2.493(5), Cu(4)—Br(2) 2.70(7), Cu(5)—Br(1) 2.470(4), Cu(6)—Br(1) 2.565(5), C(11)—Cu(1)—C(21) 143.9(4), C(41)—Cu(3)—C(31) 147.1(4).

**The contributions of the solvent electron density to the scattering is calculated as $F_{hkl}^{\text{sol}} = \sum_i \sum_j \sum_k \Delta V \cos 2\pi(hx_i + ky_j + lz_k)$. The summation is over all grid points i, j, k within the area of solvent electron density. (i, j, k) is the electron density ($1/\text{Å}^3$) at the grid point i, j, k . x_i, y_j, z_k are the fractional grid point coordinates. ΔV is the grid unit volume.

***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 (Great Britain). Any request should be accompanied by a full literature citation for this communication.

to *C-ipso* atoms while the equatorial Cu atoms (Cu(2), Cu(4), Cu(5) and Cu(6)) are bonded to *C-ipso*, Br, and N atoms; (ii) two-electron, three-center bonded aryl groups bridge a copper atom pair. The aryl rings are almost perpendicular to the copper-copper axis.

Each aryl group bridges a Cu_3 face of the octahedron, as can be clearly seen in Fig. 1 for the aryloxazoline ligand bridging the Cu(3), Cu(4), Cu(5) face. The bromine atoms are symmetrically bridging two copper atoms in the equatorial plane of the octahedron, and the oxazoline group is coordinated via the nitrogen to the equatorial Cu atoms. The Cu-N distance (1.968(7) Å mean) is in the range found for $\text{Cu}^{\text{I}}-\text{sp}^2\text{N}$ bonds [10], but is significantly shorter than the Cu-N distances in compounds we previously examined [11] (about 2.2 Å). The Cu-C bond distance, 2.031(3) Å (mean), agrees well with values for other organocopper compounds.

Noteworthy differences between the present structure and those observed previously for arylcopper-copper bromide complexes [2] are the significantly longer bromine-bridged Cu-Cu distances (3.02 Å, compared with 2.70 Å in $[\text{Cu}_6\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2)_4]$ (4)) and the more acute C-Cu(1)-C and C-Cu(3)-C bond angles of $143.9(4)^\circ$ and $147.1(4)^\circ$, respectively, compared with 164° in 4. A possible explanation for these differences is that the chelating properties of the aryloxazoline group differ from those of the previously studied *ortho*-substituted aryl ligands, $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ and $\text{C}_6\text{H}_4\text{NMe}_2$ (see Fig. 2). An important additional factor is the planarity of the $\text{C}_6\text{H}_4\text{C}(\text{O})=\text{N}$ part of the aryl-

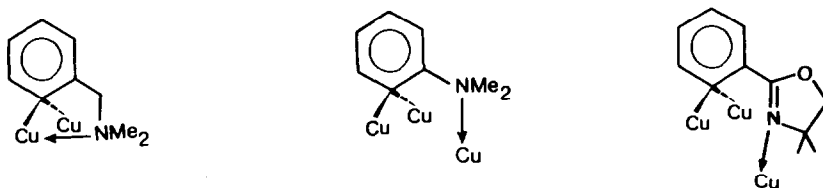


Fig. 2.

oxazoline ligand, which arises from electron delocalization (see e.g. the rather short C(12)-C(18) distance of 1.449(11) Å).

The formation of complex 3 illustrates: (i) The strong ability of organocopper compounds to react with metal halides to form mixed complexes. This observation is relevant to the understanding of the product formation in the coupling reactions of organic groups via organocopper intermediates; this aspect (see also ref. 2) will be studied in more detail for the aryloxazoline compound. (ii) The importance of the correct mode of addition of the reactants when synthesizing organocopper compounds.

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