Ring Contraction in an Arylcopper(I) Compound promoted by a Sulphur Donor Ligand: Penta[mesitylcopper(I)] forms a Tetra[mesitylcopper(I)] Compound

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Mesitylcopper(I) $(CuMes)_n$ was shown by an *X*-ray analysis to be a cyclic pentameric arylcopper(I) complex $(CuMes)_5$ in the solid state, which undergoes ring contraction with tetrahydrothiophene to the corresponding tetrameric species $[Cu_4Mes_4(C_4H_8S)_2]$, the structure of which has been found by *X*-ray crystallography.

Arylcopper(I) compounds form a variety of aggregates whose molecular complexity depends on the substituent on the aryl group, on the type of ancillary ligand attached to the metal, and on the nature of the reaction solvent.[1] Reported work has shown that structural changes in the aggregation depend on the solvent, or on a weak ligand acting as a molecule of solvent, from which the arylcopper(I) was isolated.[2] Recently, mesitylcopper(I), $(CuMes)_n$,[3] has been readily synthesized as a

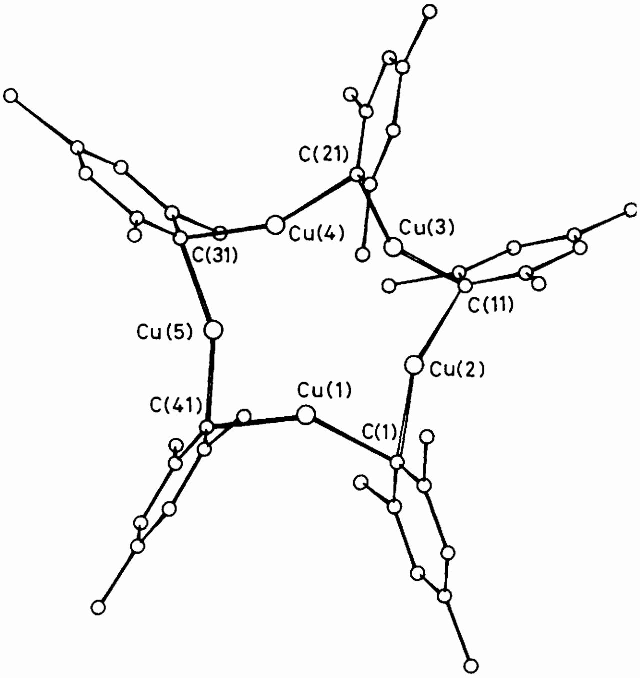

Figure 1. The structure of complex (**1**). The Cu–C distances and the C–Cu–C angles are in the range 1.96(2)—2.06(2) Å and 146(1)—158(1)°, respectively.

thermally stable and soluble arylcopper(I) species with a wide use in organic synthesis.[4] We report structural information on $(\mathrm{CuMes})_n$ in the solid state and on the product derived from its reaction with the weak ligand tetrahydrothiophene.

Tetrahydrothiophene, which contains a sulphur donor atom, has had little use in the organometallic chemistry of copper(I). Phosphorus and nitrogen donor ligands promote the breakdown of the polynuclear structure[4] or the decomposition of the Cu–C bond in arylcopper(I) compounds.[5] Formation of a diarylcuprate species occurred in the presence of a chelating phosphine ligand.[6]

Compound (**1**) was synthesized as reported,[3] and the resulting yellow solid was recrystallized from toluene to give light yellow crystals of $(\mathrm{CuMes})_5$, (**1**), suitable for an *X*-ray analysis. A tetrahydrofuran or toluene solution of (**1**) reacted with freshly distilled tetrahydrothiophene, $\mathrm{C_4H_8S}$, to give white crystals of $[\mathrm{Cu_4Mes_4(C_4H_8S)_2}]$, (**2**).† The tetrahydrothiophene promoted transformation of (**1**) into complex (**2**) is depicted in reaction (1).

$$\underset{(\mathbf{1})}{4\,(\mathrm{CuMes})_5} \xrightarrow{\mathrm{L}} \underset{(\mathbf{2})}{5\,(\mathrm{Cu_4Mes_4L_2})} \qquad (1)$$

$$\mathrm{L} = \mathrm{C_4H_8S}$$

Crystal data: complex (**1**), $\mathrm{C_{45}H_{55}Cu_5}$, monoclinic, space group $P2_1/n$, $a = 16.094(4)$, $b = 16.022(4)$, $c = 19.259(5)$ Å, $\beta = 97.49(4)°$, $U = 4924(2)$ Å^3, $Z = 4$, $D_c = 1.23$ g cm^{-3}, $F(000) = 1880$, Cu-K_α radiation ($\lambda = 1.5418$ Å), μ(Cu-K_α) = 25.2 cm^{-1}. The structure was solved by MULTAN[7] and refined anisotropically only for the copper atoms by full-matrix least-squares. The current R is 0.107 for 1629 reflections collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 110°$.‡ Complex (**2**), $\mathrm{C_{44}H_{60}Cu_4S_2}$, triclinic, space group $P\bar{1}$, $a = 12.907(3)$, $b = 20.624(5)$, $c = 8.708(2)$ Å, $\alpha = 102.14(3)$, $\beta = 107.38(3)$, $\gamma = 89.64(3)°$, $U = 2158(1)$ Å^3, $Z = 2$, $D_c = 1.40$ g cm^{-3}, $F(000) = 944$, Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) = 20.7 cm^{-1}. The structure was solved using MULTAN[7] and refined anisotropically for the non-hydrogen atoms by blocked full-matrix least-squares. For 3117 unique reflections collected at room temperature on a Philips PW 1100 diffractometer in the range $6 < 2\theta < 48°$ the current R is 0.069.‡

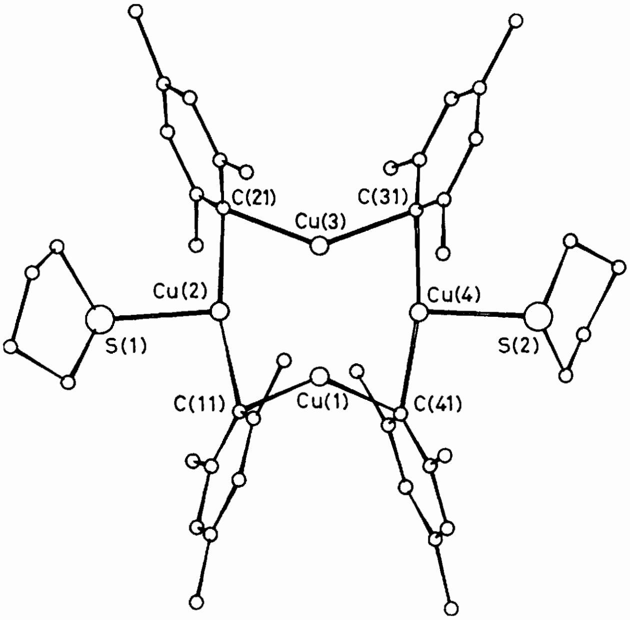

Figure 2. The structure of complex (**2**). Relevant bond distances (Å) and angles (°): Cu(1)–C(11), 2.054(7); Cu(1)–C(41), 2.055(8); Cu(2)–C(11), 2.101(6); Cu(2)–C(21), 2.097(6); Cu(3)–C(21), 2.072(9); Cu(3)–C(31), 2.056(8); Cu(4)–C(31), 2.084(9); Cu(4)–C(41), 2.093(7); Cu(2)–S(1), 2.369(4); Cu(4)–S(2), 2.407(6); C(11)–Cu(1)–C(41), 140.1(3); C(11)–Cu(2)–C(21), 166.9(4); S(1)–Cu(2)–C(21), 95.0(3); S(1)–Cu(2)–C(11), 98.0(2); C(21)–Cu(3)–C(31), 139.1(3); C(31)–Cu(4)–C(41), 168.4(4); S(2)–Cu(4)–C(41), 96.8(3); S(2)–Cu(4)–C(31), 94.5(3).

Figure 1 shows a unique pentameric cyclic structure for an arylcopper(I) compound. Crystallographic analysis is rather poor because of the low quality of crystals of complex (**1**). The structure consists of polynuclear molecules having a ten-membered ring where copper atoms are bridged by phenyl groups in a normal fashion.[1] The ring is puckered, with a total puckering amplitude of 1.53(3) Å,[8] and it has a *pseudo-C_s* symmetry with a mirror plane through the Cu(1) ⋯ C(21) line. The dihedral angles of the mesitylene groups about the best plane through the five copper atoms range from 91.0(5) to 105.0(4)°. The Cu–C [1.96(2)—2.06(2) Å] and Cu ⋯ Cu [2.437(8)—2.469(9) Å] distances and C–Cu–C angles [146(1)—158(1)°] are close to those found in complex (**2**), the structure of which is shown in Figure 2 with the most relevant bond distances and angles given in the caption. Complex (**2**) contains molecules having an eight-membered ring, which is puckered, the total puckering being $Q = 1.080(8)$ Å.[8] The four copper atoms lie in a plane bisecting the tetrahedron

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† Satisfactory analytical data have been obtained.

‡ 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.

formed by the carbon atoms. The phenyl groups are nearly perpendicular to the plane of copper atoms, the dihedral angles ranging from 92.1(2) to 94.7(2)°. The four Cu ··· Cu distances between adjacent coppers range from 2.441(3) to 2.449(2) Å and are significantly shorter than the distance between the opposite coppers [*e.g.* Cu(1) ··· Cu(3), 2.600(3) Å]. Copper–carbon distances involving the three-co-ordinated [Cu(2) and Cu(4)] copper atoms [mean value 2.094(8) Å] are slightly but significantly longer than those involving Cu(1) and Cu(3) [mean value 2.059(4) Å].

Conversion of (**1**) into (**2**) under the experimental conditions specified here can be related to the solid state isolation of these complexes. The solution–solid-state relationship is quite an intriguing problem in organocopper chemistry because of inter- and intra-aggregate exchange,[1] and solvent-dependent molecular complexity. The formation of (**2**) in a solvent containing tetrahydrothiophene is probably not due to an equilibrium between a hexa- and a tetra-copper compound as in reaction (2).

$$2\,(\mathrm{CuMes})_5 \underset{-\mathrm{L}}{\overset{\mathrm{L}}{\rightleftharpoons}} (\mathrm{L_2Cu_4Mes_4}) + (\mathrm{CuMes})_6 \qquad (2)$$

$$\mathrm{L} = \mathrm{C_4H_8S}$$

The yield of (**2**) from reaction (1) is higher than 80%. Conversely, cryoscopic measurements in a benzene solution of $(\mathrm{CuMes})_n$ gave a molecular weight independent of the concentration (485), indicating a value for *n* of *ca.* 2.5.

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