

# Synthesis and characterization of the organocopper–copper halide complex $[\text{CuMes}^*\{\text{Cu}_2\text{Br}_2(\text{SMe}_2)_3\}]$ ( $\text{Mes}^* = \text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6}$ )

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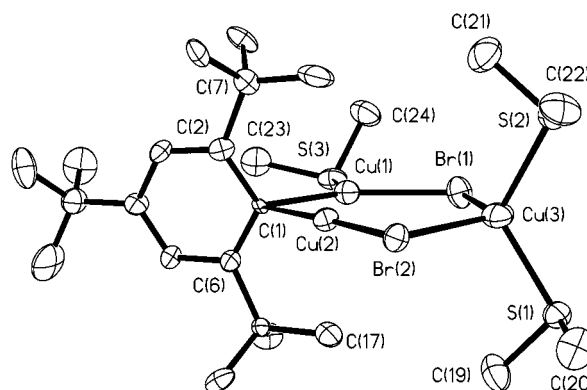
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Treatment of 3 equivalents of  $\text{CuBr}$  with  $\text{LiMes}^*$  ( $\text{Mes}^* = \text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6}$ ) in  $\text{Et}_2\text{O}$  at *ca.*  $-78^\circ\text{C}$  afforded, upon treatment with  $\text{SMe}_2$ , the organocopper–copper halide complex  $[\text{CuMes}^*\{\text{Cu}_2\text{Br}_2(\text{SMe}_2)_3\}]$  **1** which has the previously unobserved  $\text{CuR}:\text{CuX}$  ratio of 1:2; it is a very rare example of a structurally characterized  $\text{CuR}:\text{CuX}$  complex without chelating R groups.

Organocopper–copper halide aggregates are an important and growing class of organocopper compounds.<sup>1</sup> They are characterized by different organocopper to copper halide ratios. To date, well defined, aggregates with the  $\text{CuR}/\text{CuX}$  (R = alkyl or aryl; X = halide) ratios of 2:1,<sup>2</sup> 2:2,<sup>2,3</sup> 2:3,<sup>4</sup> 4:2<sup>5</sup> have been characterized. In many instances chelating aryl ligands such as  $\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)\text{-2}^6$  have played a key role in stabilizing these complexes. During investigations of the reaction of  $\text{LiMes}^*$  ( $\text{Mes}^* = \text{C}_6\text{H}_2\text{Bu}^t\text{-2,4,6}$ )<sup>7</sup> with copper bromide in diethyl ether solution, it was observed that most of the copper bromide appeared to have reacted when less than 0.5 equivalent of  $\text{LiMes}^*$  was added. This observation suggested that an organocopper–copper halide, possibly of previously unobserved 1:2 stoichiometry, had formed. In this paper the synthesis and characterization of this new complex  $[\text{CuMes}^*\{\text{Cu}_2\text{Br}_2(\text{SMe}_2)_3\}]$  **1** are now reported.

Compound **1** was synthesized<sup>†</sup> by the addition of  $\text{LiMes}^*$  to  $\text{CuBr}$  in  $\text{Et}_2\text{O}$  at *ca.*  $-78^\circ\text{C}$ . Warming to room temperature and the addition of dimethyl sulfide, followed by filtration and cooling in a  $-20^\circ\text{C}$  freezer, afforded colorless crystals of **1** in moderate yield. Proton NMR spectroscopy of **1** in  $\text{C}_6\text{D}_6$  solution indicated a 3:1 ratio of  $\text{SMe}_2$  to  $\text{Mes}^*$  groups. The  $\text{Cu}-\text{Mes}^*$  bonding was indicated by the appearance of an *ipso* carbon resonance at  $\delta$  167.50 in the  $^{13}\text{C}-\{^1\text{H}\}$  NMR spectrum which is within the known range for *ipso* carbon shifts in arylcopper/arylcuprate solutions in  $\text{SMe}_2$ .<sup>8</sup> However, the exact

structure of **1** was established by X-ray crystallography.<sup>‡</sup> The illustration in Fig. 1 indicates that one  $\text{CuMes}^*$  unit is associated with two copper bromides to form a very unusual six-membered ring composed of three coppers, two bromides and an *ipso* carbon from the  $\text{Mes}^*$  group. The  $\text{Cu}_3\text{Br}_2\text{C}$  array is almost planar (average deviation = 0.009 Å), but there are gross variations in the angles within the ring. There is an almost perpendicular angle of  $88.2^\circ$  between the plane of the  $\text{Mes}^*$  ring and the  $\text{Cu}_3\text{Br}_2\text{C}$  core. The ring distances are also quite variable; the shortest involve the  $\text{C}(1)-\text{Cu}(2)-\text{Br}(2)$  unit where  $\text{Cu}(2)-\text{C}(1)$  and  $\text{Cu}(2)-\text{Br}(2)$  bond lengths of 1.972(14) and 2.295(3) Å, respectively are observed. These may be compared to the much longer  $\text{Cu}(1)-\text{C}(1)$  and  $\text{Cu}(3)-\text{Br}(2)$  distances of 2.09(2) Å and 2.558(4) Å. These structural data as well as the near linear co-ordination at  $\text{Cu}(2)$  [ $\text{C}(1)-\text{Cu}(2)-\text{Br}(2)$   $170.6(4)^\circ$ ] suggest that the compound can be viewed as a contact ion pair composed of a  $[\text{BrCuMes}^*]^-$  anion and a  $[(\text{Me}_2\text{S})_2\text{Cu}(\mu\text{-Br})\text{Cu}(\text{SMe}_2)]^+$  cation. This view is further supported by the fact that the deviation of the  $\text{Cu}(2)-\text{C}(1)$  vector from the  $\text{Mes}^*$  ring plane is  $27.5^\circ$  whereas the deviation for the  $\text{Cu}(1)-\text{C}(1)$  vector is  $47.4^\circ$ . In the anion, the  $\text{Cu}-\text{C}$  and  $\text{Cu}-\text{Br}$  bond lengths are just slightly longer than those observed in the solvent separated anion  $[\text{Cu}(\text{Br})\{\text{CH}(\text{SiMe}_3)_2\}]^-$  in which  $\text{Cu}-\text{C} = 1.920(0)$  Å and  $\text{Cu}-\text{Br} = 2.267(2)$  Å.<sup>9</sup> The longer distances in



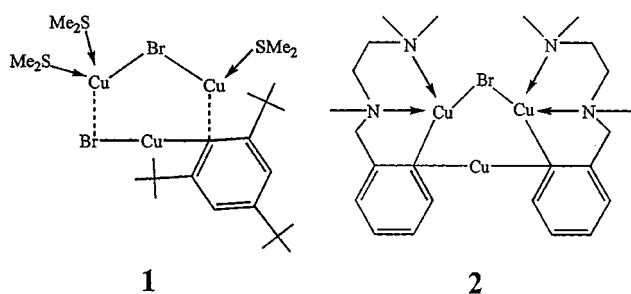
**Fig. 1** Computer generated drawing of **1** with H atoms not shown. Selected bond distances (Å) and angles ( $^\circ$ ):  $\text{Cu}(1)-\text{C}(1)$  2.09(2),  $\text{Cu}(1)-\text{S}(3)$  2.306(6),  $\text{Cu}(1)-\text{Br}(1)$  2.420(4),  $\text{Cu}(2)-\text{C}(1)$  1.972(14),  $\text{Cu}(2)-\text{Br}(2)$  2.295(3),  $\text{Cu}(3)-\text{Br}(1)$  2.510(3),  $\text{Cu}(3)-\text{Br}(2)$  2.558(4),  $\text{Cu}(3)-\text{S}(1)$  2.278(5),  $\text{Cu}(3)-\text{S}(2)$  2.267(5);  $\text{C}(1)-\text{Cu}(1)-\text{S}(3)$   $111.5(4)^\circ$ ,  $\text{C}(1)-\text{Cu}(1)-\text{Br}(1)$   $142.6(4)^\circ$ ,  $\text{S}(3)-\text{Cu}(1)-\text{Br}(1)$   $105.7(2)^\circ$ ,  $\text{Cu}(1)-\text{C}(1)-\text{Cu}(2)$   $50.4(4)^\circ$ ,  $\text{C}(1)-\text{Cu}(2)-\text{Br}(2)$   $170.6(4)^\circ$ ,  $\text{Cu}(2)-\text{Br}(2)-\text{Cu}(3)$   $88.95(11)^\circ$ ,  $\text{Br}(1)-\text{Cu}(3)-\text{Br}(2)$   $113.8(2)^\circ$ ,  $\text{Cu}(1)-\text{Br}(1)-\text{Cu}(3)$   $110.6(2)^\circ$ ,  $\text{S}(1)-\text{Cu}(3)-\text{S}(2)$   $119.8(2)^\circ$ ,  $\text{C}(2)-\text{C}(1)-\text{C}(6)$   $115.5(13)^\circ$ .

<sup>†</sup> Under anaerobic and anhydrous conditions  $\text{LiMes}^*$  (0.504 g, 2 mmol) in  $\text{Et}_2\text{O}$  (20 mL) was added to a well-stirred suspension of  $\text{CuBr}$  (0.86 g, 6 mmol) in  $\text{Et}_2\text{O}$  (20 mL) with cooling in a dry ice bath. After *ca.* 1 h, the mixture was allowed to come to room temperature whereupon *ca.* 2 mL of  $\text{SMe}_2$  was added. Stirring was continued for *ca.* 3 h and the pale yellow solution was filtered. The volume of the solution was reduced to *ca.* 10 mL and it was then stored in a  $-20^\circ\text{C}$  freezer for 24 h to afford the product **1** as colorless crystals. Yield 0.75 g, 0.96 mmol, 48%; mp  $127^\circ\text{C}$  (decomp.). It has not been possible to obtain a satisfactory combustion analysis of **1** owing to desolvation of the crystals. However, atomic absorption spectroscopy indicates an approximate Cu:Br ratio of 3:2.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  7.59 (br s, 2 H, *m*- $\text{C}_6\text{H}_2$ ); 1.92 (br s, 18 H,  $\text{SMe}_2$ ); 1.71 [s, 18 H, *o*- $\text{C}(\text{CH}_3)_3$ ]; 1.56 [s, 9 H, *p*- $\text{C}(\text{CH}_3)_3$ ].  $^{13}\text{C}-\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  167.50 (*i*- $\text{C}_6\text{H}_2$ ), 150.33 (*o*- $\text{C}_6\text{H}_2$ ); 120.37 [*p*- $\text{C}(\text{CH}_3)_3$ ]; 119.66 (*m*- $\text{C}_6\text{H}_2$ ); 38.53 [*o*- $\text{C}(\text{CH}_3)_3$ ], 35.09 [*p*- $\text{C}(\text{CH}_3)_3$ ]; 33.38 [*o*- $\text{C}(\text{CH}_3)_3$ ]; 30.65 [*p*- $\text{C}(\text{CH}_3)_3$ ]; 18.78 ( $\text{SMe}_2$ ). The broad singlet obtained for the  $\text{SMe}_2$  signal is probably due to rapid exchange of  $\text{SMe}_2$  between the copper sites. Cooling the spectrum to  $-60^\circ\text{C}$  did not result in splitting of the signal.

<sup>‡</sup> Crystal data at 130 K with Mo-K $\alpha$  ( $\lambda = 0.71073$ ) radiation for  $\text{C}_{24}\text{H}_{47}\text{Br}_2\text{Cu}_3\text{S}_3$ :  $M = 782.24$ ,  $a = 14.510(5)$ ,  $b = 18.993(5)$ ,  $c = 11.448(3)$  Å,  $U = 3155(2)$  Å<sup>3</sup>, orthorhombic, space group  $Pca2_1$ ,  $\mu = 4.747$  mm<sup>-1</sup>,  $Z = 4$ ,  $R1 = 0.085$  for 2048 [ $I > 2\sigma(I)$ ] data,  $wR2 = 0.1874$  for all 3831 data, full-matrix least squares based on  $F^2$ . CCDC reference number 186/1079.

the anion of **1** can be attributed to the increased co-ordination numbers as a result of its association with the cation. The Cu–S distances observed in **1** lie in the middle of the currently known range [*ca.* 2.185(1)<sup>10</sup>–2.383(2) Å<sup>11</sup>] for SMe<sub>2</sub> complexes of organocopper species. The Cu(1)–S(3) bond length in **1** is 2.306(6) Å, which is longer than the 2.267(5) and 2.278(5) Å Cu–S distances observed for Cu(3). The longer Cu(1)–S(3) distance is surprising in view of the fact that the Cu(1) co-ordination number is lower than that of Cu(3). Part of the explanation may be that, since Cu(1) is also bound to the Mes\* ligand, its environment may be more crowded which leads to a lengthened Cu–S bond.

The structural arrangement of **1** bears some resemblance to that of the chelated trimetallic species Cu<sub>3</sub>(Br){C<sub>6</sub>H<sub>4</sub>[CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]-2}<sub>2</sub>.<sup>2</sup> In this molecule the anion has the formula [Cu{C<sub>6</sub>H<sub>4</sub>[CH<sub>2</sub>N(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>]}]<sup>–</sup> with Cu–C distances that average 1.967(11) Å which is very similar to the Cu(2)–C(1) distance in **1**. Two further Cu<sup>+</sup> ions are complexed by the two N donors in each ‘arm’ of the ligand. These metals also interact with an *ipso* carbon on each aryl ring and have Cu–C distances that average 2.095(14) Å, which is identical to the Cu(1)–C(1) length in **1**. The structure is completed by a Br<sup>–</sup> ion which bridges the two amine complexed coppers to afford Cu–Br distances that average 2.435(8) Å. This length is very like the 2.420(4) Å seen for the Cu(1)–Br(1) bond in **1**. Longer bond lengths are seen for Cu(3) where distances of 2.510(3) and 2.558(4) Å were observed. This is probably a result of the higher co-ordination number at Cu(3).



The structure of **1** is also characterized by a relatively short Cu(1)⋯Cu(2) distance of 2.471(4) Å. This is longer than the corresponding average of 2.406(3) Å in **2**<sup>2</sup> but close to the 2.443(1) Å seen in the unusual dimer [(Me<sub>2</sub>S)<sub>2</sub>Cu(μ-C<sub>6</sub>H<sub>2</sub>Ph<sub>3</sub>-

2,4,6)CuC<sub>6</sub>H<sub>2</sub>Ph<sub>3</sub>-2,4,6].<sup>10</sup> These Cu–Cu distances are indicative of a weak d<sup>10</sup>–d<sup>10</sup> interaction between the metals.<sup>12</sup>

In summary, compound **1** represents the highest ratio (2:1) copper halide–organocopper complex that has been isolated to date. The structure of **1** provides further evidence that such complexes can be isolated in the absence of chelating ligands as well as underlining the importance of SMe<sub>2</sub> as ligand or solvent in organocopper chemistry.<sup>13</sup>

## Acknowledgements

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