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Bis-Ortho-Chelated Arylcopper Compounds. Synthesis and X-ray Crystal Structure of $Cu_4Br_2[C_6H_3(CH_2NMe_2)_2\text{-}o,o']_2$†

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A novel arylcopper(I) compound has been prepared from the reaction of lithiated $C_6H_4(CH_2NMe_2)_2\text{-}o,o'$ with CuBr. An X-ray crystal structure determination on this new compound revealed it not to be $[Cu\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ but its 1:1 CuBr adduct ($Cu_4Br_2C_{24}H_{38}N_4$; orthorhombic; *Pcab*; $a = 18.167$ (3), $b = 19.462$ (3), $c = 17.036$ (2) Å; $Z = 8$). The determined molecular structure shows a highly asymmetric $[Cu_4\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2Br_2]$ molecule containing four differently coordinated copper atoms. The copper atoms, which are all three-coordinate, are in a butterfly arrangement which is kept together by two bridging C ipso atoms of the aryl ligands [Cu–C distance 2.074 (5) Å (mean)] and two bridging bromine atoms [Cu–Br distance 2.397 (1) Å (mean)]. The Cu–Cu distances for the two adjacent C-bridged bonds are 2.412 (2) and 2.406 (2) Å and for the Br-bridged bonds are 2.429 (2) and 2.737 (2) Å. The coordination pattern of the CH_2NMe_2 side arms is such that each of the copper atoms is N-coordinated [Cu–N distance 2.176 (4) Å (mean)], thus making them all three-coordinate. Variable-temperature ^1H NMR measurements in the temperature range 233–373 K show that this asymmetric structure is not retained in solution and that a more symmetric molecule is formed. These spectra also show the existence of complex fluxional processes. Reaction of $[Li_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2]$ with $CuBr\{P(OMe)_3\}$ afforded an arylcopper compound whose formulation based on elemental analysis and ^1H NMR data is $[Cu_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}Br\{P(OMe)_3\}_2]$.

Introduction

During the last decade considerable progress has been made in the structural elucidation of arylcopper compounds.[2] Important factors determining the structure of these compounds appear to be the presence of bulky groups near the Cu–C bond and of either "inter"- or intramolecular coordinating groups. As a common property arylcopper compounds show a strong propensity to form aggregated species involving electron-deficient three-center, two-electron copper–carbon bonds.

To examine the influence that intramolecular coordinating groups have on the structures of arylcopper compounds,[3-7] we have studied phenylcopper derivatives with various nitrogen-containing ortho substituents. It was found that there was a strong tendency of the copper atom to coordinate to the nitrogen atom and the adopted structure appeared to be determined by the chelating properties of the amino aryl group. These latter properties depend on the orientation of the N lone pair substituent relative to the copper atom as well as on the flexibility of the chelate ring formed. These factors are reflected, for example, in the different structures of $[Cu_4(C_6H_3(CH_2NMe_2)\text{-}2\text{-}Me\text{-}5)_4]$[3] and $[Cu_4(\text{naphthylNMe}_2\text{-}8)_4]$[4] in which the aryl NMe_2 group acts as a chelating group and of $[Cu_6(C_6H_4NMe_2\text{-}2)_4Br_2]$[5] and $[Cu_2(5\text{-}MeC_6H_3\text{-oxazoline-}2)_2]$[6] containing bridging aryl heteroatom groups. When, on the other hand, the ortho substituents CH_2NMe_2, NMe_2 and oxazoline are not coordinated, they function as sterically demanding bulky groups.

In the course of these studies on arylcopper complexes we were prompted to investigate the effect of heteroatom-containing substituents in both ortho positions of the aryl ligand. Interest in these species[3] arises because there is a model system, comprising of a Cu(I) complex of a 1,3-disubstituted aryl ligand which mimics the dioxygen reactivity found in copper monooxygenases.[8] In this system the Cu(I) complex (see Scheme I) readily reacts with O_2 to give a phenoxocopper(II) complex. The intermediate stages of this aromatic hydroxylation reaction, involving the copper-mediated conversion of an aromatic C–H bond with O_2 into an aromatic C–OH bond, are not known. The question then arises as to whether similar systems with an aromatic C–Cu instead of a C–H bond could readily undergo oxygenation to phenoxocopper(I) derivatives. To help answer this the $\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}^-$ group was selected since it has already often been shown to be very well suited for bis-ortho chelation of the metal that is σ-bound to the aryl ring.[9] In the present study we have reinvestigated the synthesis and structure of $Cu[C_6H_3(CH_2NMe_2)_2\text{-}o,o']$ (1).[3] On the basis of previous structural studies of the related arylcopper compound $[Cu\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}Me\text{-}5\}]_4$[3] and the lithium compounds $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}]_4$[10] and $[Li\{C_6H\text{-}$

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† Bis[*o,o'*-bis{(dimethylamino)methyl}phenyl]tetracopper dibromide.

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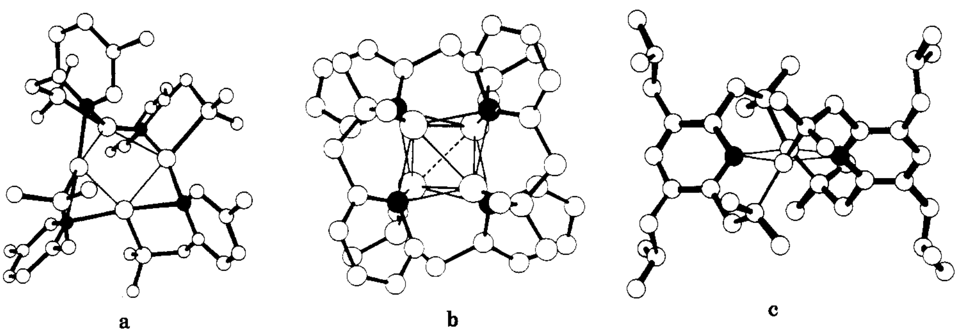
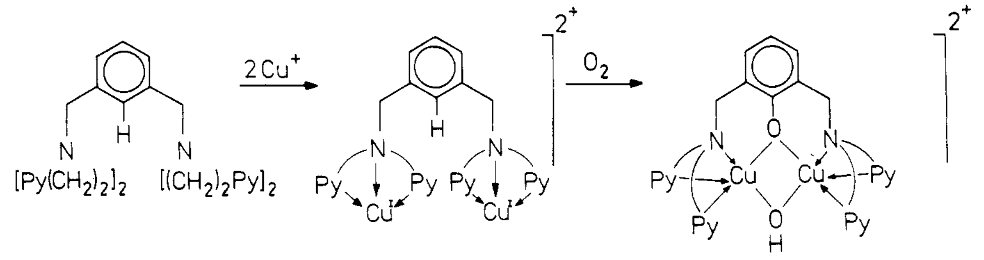
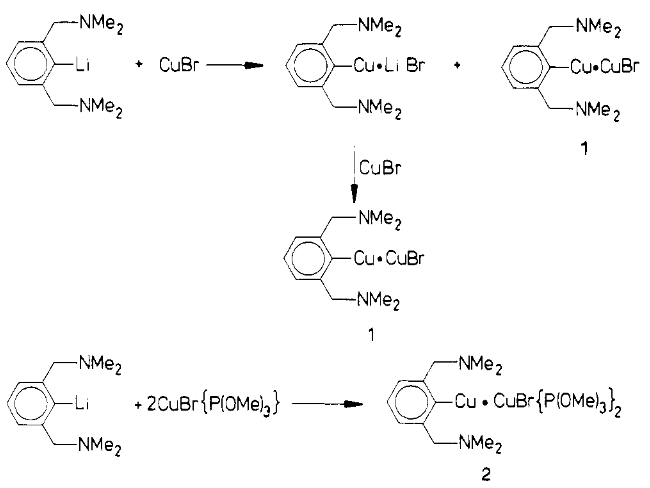


Figure 1. Solid-state structures of $[\mathrm{Cu}\{\mathrm{C_6H_3(CH_2NMe_2)\text{-}2\text{-}Me\text{-}5}\}]_4$ (a), $[\mathrm{Li}\{\mathrm{C_6H_4(CH_2NMe_2)\text{-}2}\}]_4$ (b), and $[\mathrm{Li}\{\mathrm{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6}\}]_2$ (c).

Scheme I



Scheme II



$(\mathrm{CH_2NMe_2})_4\text{-}2,3,5,6\}]_2$,[11] it is anticipated that the second ortho substituent will have a large effect on the structural features of this compound.

Results and Discussion

The 1:1 reaction of $\mathrm{Li}\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}o,o'\}$ with CuBr in diethyl ether afforded a solid yellow product which, according to its elemental analysis, still contained bromide even after washing with diethyl ether and other organic solvents. Elemental analyses on samples from several different reactions showed variable amounts of bromide, and the formation and isolation of a mixture of LiBr and CuBr adducts of $\mathrm{Cu}\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}o,o'\}$ in varying ratios were suspected. However, a yellow complex, 1, with a well-defined $[\mathrm{Cu_2Br}\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}o,o'\}]$ stoichiometry was isolated when the aryllithium compound was reacted with an excess of CuBr.

Pure 1 could, furthermore, only be obtained when the $[\mathrm{Li_2}\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}o,o'\}_2]$ used was prepared via the lithium bromide exchange reaction of o,o'-$(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3Br}$ with n-BuLi in diethyl ether and not when it was prepared from the metalation reaction of the aryl bromide with metallic lithium. In the latter case (extra) LiBr is present and this appears to interfere with the isolation of the 1:1 organocopper–copper bromide adduct.

Reaction of 1 with $\mathrm{Me_2SnBr_2}$ resulted in formation of known $[\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}o,o'\}\mathrm{SnMe_2}]^+\mathrm{Br}^-$ (characterized by ^{1}H NMR[12]), consistent with the presence of a copper–carbon bond at the aryl 1-position in 1.

Reaction of $\mathrm{Li_2}\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}o,o'\}_2$ with $\mathrm{CuBr}\{\mathrm{P(OMe)_3}\}$ afforded a white product which, on the basis of its ^{1}H NMR spectrum and its elemental analysis, is formulated as the copper bromide adduct $[\mathrm{Cu}\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}o,o'\}\cdot\mathrm{CuBr}\{\mathrm{P(OMe)_3}\}_2]$ (2) (see Scheme II). Both 1 and 2 (vide infra) react with $\mathrm{O_2}$, though solid 1 can be handled in air for short periods. They are stable in a nitrogen atmosphere to at least 100 °C.

The formation of CuBr adducts is a well-established feature of the chemistry of arylcopper compounds[5,7,13] and strongly depends on the ortho substituents present. Normally this adduct formation can be prevented by careful addition of CuBr to the corresponding aryllithium compound.[14] However, in the reaction of $\mathrm{Li_2}\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}o,o'\}_2$ with CuBr this procedure is not successful. Apparently, the arylcopper compound formed reacts faster with any metal halide (LiBr or CuBr) present than the unreacted aryllithium reagent. Moreover, the arylcopper–copper bromide adduct is almost unreactive to further reaction with the aryllithium reagent. This lack of reactivity of the 1:1 CuBr adduct with excess lithium reagent resembles that reported earlier for the vinyl-

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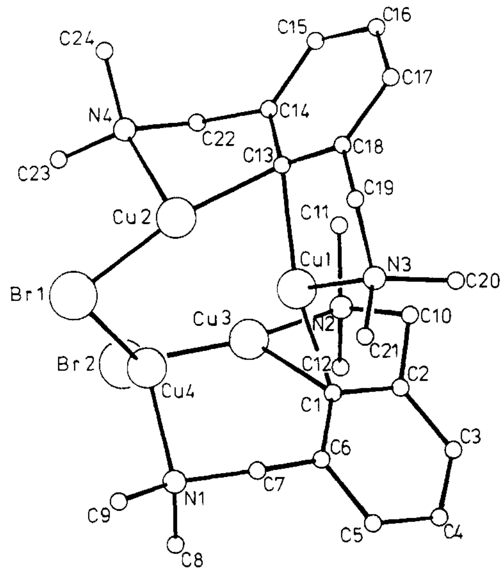

Figure 2. Molecular structure of $[Cu_4Br_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2]$ (1) along with the adopted numbering scheme. Note that Br(2) is bridging the Cu(3)···Cu(4) edge and that each of the copper atoms is three-coordinate. For an ORTEP figure, see supplemantary material.

copper–copper bromide compound $[Vi_2Cu_4Br_2]$ (Vi = (2-$Me_2NCH_2C_6H_4$)C=C(Me)C_6H_4Me-4),[13] which contains a potentially coordinating NMe_2 group. In this case the steric hindrance of the bulky vinyl group is thought to prevent the formation of a pure ViCu aggregate and to favor the complexation of CuBr, so forming the less hindered mixed aggregate. This explanation is also likely to be valid for the formation of our $[ArCu_2Br]_n$ complex. Here the aryl group contains two bulky substituents ortho to the Cu–C bond that would hamper the formation of stable $(ArCu)_n$ aggregates. The binding of metal halides (LiBr or CuBr) is then favored to form discrete, stable aggregates. Furthermore, when the copper atoms in organocopper compounds are involved in coordination with heteroatoms, they prefer to be three-coordinated, which can only be achieved in this bis-ortho-substituted arylcopper species by complexation of CuBr or LiBr. This view is supported by the fact that the copper species containing only one CH_2NMe_2 substituent ortho to the Cu–C bond does form a stable ArCu aggregate in which each of the copper atoms is three-coordinate.[3]

Arylcopper compounds often have complicated structures. In the case of 1 a complex solution structure was indicated by its ^1H NMR spectrum (vide infra). An X-ray structure determination was therefore undertaken to establish the nature of $[Cu\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}CuBr]$ in the solid state. Crystals suitable for analysis were obtained by crystallizing 1 from a mixture of diethyl ether and hexane at −20 °C. The molecular structure with the adopted numbering scheme is shown in Figure 2, while fractional coordinates and relevant bond distances and angles are compiled in Tables I and II, respectively.

The structure of 1 consists of four copper atoms positioned in a butterfly arrangement (Cu(2) and Cu(3) at the "wing tips"). In this aggregate two adjacent copper edges, Cu(1)···Cu(2) and Cu(1)···Cu(3), are each bridged by C_{ipso} of an aryl group with three similar copper–carbon distances of 2.003 (8), 2.029 (10), and 2.090 (10) Å whereas the fourth distance Cu(1)–C(13) is somewhat longer, namely, 2.172 (9) Å. These Cu–C distances are consistent with those usually found for three-center, two-electron bonded aryl groups in arylcopper species. The two remaining copper edges Cu(3)···Cu(4) and Cu(2)···Cu(4) are bridged by two bromine atoms (Cu–Br distances varying from 2.322 (2) to 2.533 (2) Å). The C(1)–Cu(1)–C(13) angle is 155.8 (4)°, somewhat smaller than predicted for a three-center, two-electron Cu–C bond (164°)[15] but similar compared to that in $[Cu_4\{(4\text{-}MeC_6H_4)MeC{=}C(C_6H_4NMe_2)\}_2(C_6H_4NMe_2\text{-}$

Table I. Fractional Coordinates of the Non-Hydrogen Atoms of $[Cu_4Br_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2]$ with the Standard Deviation in Parentheses

atom	x	y	z	U_{eq}, Å^2
Cu(1)	0.42798 (9)	0.14117 (9)	0.31129 (10)	0.0436 (9)
Cu(2)	0.49188 (10)	0.16193 (10)	0.18948 (11)	0.0489 (10)
Cu(3)	0.38027 (10)	0.03300 (9)	0.26558 (11)	0.0469 (10)
Cu(4)	0.35089 (14)	0.11725 (13)	0.16516 (16)	0.0789 (16)
Br(1)	0.41650 (9)	0.20285 (9)	0.09025 (9)	0.0653 (9)
Br(2)	0.35391 (8)	−0.01131 (7)	0.14220 (8)	0.0542 (8)
N(1)	0.2455 (5)	0.1544 (5)	0.1986 (7)	0.049 (6)
N(2)	0.4131 (7)	−0.0384 (6)	0.3550 (7)	0.061 (7)
N(3)	0.4398 (6)	0.2307 (6)	0.3880 (7)	0.055 (7)
N(4)	0.5720 (6)	0.0879 (6)	0.1352 (6)	0.054 (7)
C(1)	0.3338 (7)	0.0970 (7)	0.3507 (8)	0.052 (8)
C(2)	0.3402 (8)	0.0505 (7)	0.4165 (9)	0.058 (8)
C(3)	0.2819 (9)	0.0444 (9)	0.4714 (8)	0.068 (10)
C(4)	0.2208 (10)	0.0847 (9)	0.4622 (9)	0.078 (11)
C(5)	0.2125 (8)	0.1286 (9)	0.3970 (10)	0.071 (10)
C(6)	0.2702 (7)	0.1357 (6)	0.3412 (8)	0.051 (7)
C(7)	0.2598 (7)	0.1850 (8)	0.2773 (9)	0.061 (9)
C(8)	0.1890 (9)	0.1049 (9)	0.2020 (10)	0.074 (11)
C(9)	0.2257 (10)	0.2109 (9)	0.1425 (14)	0.095 (13)
C(10)	0.4047 (8)	0.0052 (8)	0.4252 (9)	0.066 (9)
C(11)	0.4849 (11)	−0.0719 (11)	0.3499 (12)	0.097 (14)
C(12)	0.3581 (12)	−0.0946 (8)	0.3566 (12)	0.091 (13)
C(13)	0.5458 (7)	0.1486 (7)	0.2909 (7)	0.044 (7)
C(14)	0.5947 (8)	0.0949 (7)	0.2766 (8)	0.055 (8)
C(15)	0.6562 (8)	0.0863 (7)	0.3210 (9)	0.061 (9)
C(16)	0.6735 (8)	0.1293 (8)	0.3830 (11)	0.069 (10)
C(17)	0.6256 (8)	0.1841 (7)	0.3979 (7)	0.057 (8)
C(18)	0.5613 (7)	0.1948 (7)	0.3525 (7)	0.048 (7)
C(19)	0.5137 (8)	0.2561 (7)	0.3668 (8)	0.054 (8)
C(20)	0.4387 (9)	0.2041 (9)	0.4685 (9)	0.072 (10)
C(21)	0.3842 (9)	0.2856 (8)	0.3806 (12)	0.083 (12)
C(22)	0.5824 (8)	0.0473 (7)	0.2091 (9)	0.059 (9)
C(23)	0.5450 (8)	0.0470 (9)	0.0703 (9)	0.070 (10)
C(24)	0.6428 (8)	0.1212 (9)	0.1120 (10)	0.068 (9)

Table II. Relevant Bond Distances (Å) and Angles (deg) of the Non-Hydrogen Atoms of $[Cu_4Br_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2]$ with the Standard Deviation in Parentheses

Cu(1)–Cu(2)	2.412 (2)	Cu(3)–Br(2)	2.322 (2)
Cu(1)–Cu(3)	2.406 (2)	Cu(3)–N(2)	2.146 (9)
Cu(1)–Cu(4)	2.894 (2)	Cu(3)–C(1)	2.090 (10)
Cu(1)–N(3)	2.188 (8)	Cu(4)–Br(1)	2.414 (2)
Cu(1)–C(1)	2.029 (9)	Cu(4)–Br(2)	2.533 (2)
Cu(1)–C(13)	2.172 (8)	Cu(4)–N(1)	2.124 (7)
Cu(2)–Cu(4)	2.737 (2)	C(1)–C(2)	1.446 (14)
Cu(2)–Br(1)	2.317 (2)	C(1)–C(6)	1.388 (13)
Cu(2)–N(4)	2.247 (8)	C(13)–C(14)	1.393 (13)
Cu(2)–C(13)	2.003 (8)	C(13)–C(18)	1.409 (12)
Cu(3)–Cu(4)	2.429 (2)		

N(3)–Cu(1)–C(1)	102.8 (5)	Cu(3)–N(2)–C(10)	100.0 (9)
N(3)–Cu(1)–C(13)	86.9 (4)	Cu(3)–N(2)–C(11)	119.7 (9)
C(1)–Cu(1)–C(13)	155.8 (4)	Cu(3)–N(2)–C(12)	107.7 (9)
Br(1)–Cu(2)–N(4)	107.7 (3)	Cu(1)–N(3)–C(19)	102.1 (7)
Br(1)–Cu(2)–C(13)	164.3 (2)	Cu(1)–N(3)–C(20)	106.0 (8)
N(4)–Cu(2)–C(13)	87.4 (5)	Cu(1)–N(3)–C(21)	117.3 (8)
Br(2)–Cu(3)–N(2)	117.3 (3)	Cu(2)–N(4)–C(22)	94.3 (8)
Br(2)–Cu(3)–C(1)	140.0 (3)	Cu(2)–N(4)–C(23)	116.5 (8)
N(2)–Cu(3)–C(1)	90.2 (5)	Cu(2)–N(4)–C(24)	112.9 (7)
Br(1)–Cu(4)–Br(2)	126.12 (10)	Cu(1)–C(1)–Cu(3)	71.5 (5)
Br(1)–Cu(4)–N(1)	110.6 (3)	Cu(1)–C(1)–C(2)	116.9 (8)
Br(2)–Cu(4)–N(1)	113.4 (3)	Cu(1)–C(1)–C(6)	115.7 (8)
Cu(2)–Br(1)–Cu(4)	70.66 (10)	C(2)–C(1)–C(6)	119.8 (10)
Cu(3)–Br(2)–Cu(4)	59.85 (8)	Cu(1)–C(13)–Cu(2)	70.4 (5)
Cu(4)–N(1)–C(7)	102.8 (7)	Cu(1)–C(13)–C(14)	127.3 (7)
Cu(4)–N(1)–C(8)	115.8 (8)	Cu(1)–C(13)–C(18)	96.9 (8)
Cu(4)–N(1)–C(9)	107.1 (8)	C(14)–C(13)–C(18)	118.8 (10)

2)$_2$].[15] Two copper atoms, Cu(2) and Cu(3), are coordinated to one bridging C_{ipso} atom of an aryl group, one bridging bromine atom, and one nitrogen atom. Of the other two copper atoms, Cu(1) is only coordinated to two bridging C_{ipso} atoms and a nitrogen substituent and Cu(4) is bonded to two bromine atoms and a nitrogen substituent, thus making each of the copper atoms three-coordinate. The Cu–N distances vary from 2.124 (7) to 2.247 (8) Å and fall in the range for Cu–N(sp^3) bond lengths.[2] The copper–copper distances within the Cu_4 core show great variation. The C_{ipso}-bridged Cu–Cu distances of 2.412 (2) and 2.406 (2) Å, are compatible with previously established values for such distances in polynuclear arylcopper compounds,[2] whereas the two bromine-bridged Cu···Cu edges have widely differing separations of 2.429 (2) and 2.737 (2) Å comparable with those in polynuclear arylcopper copper bromide complexes.[5,7,13b] The copper atoms positioned at the wing tips, Cu(2) and Cu(3), have a separation of 3.475 (4) Å.

The structure of the present compound reflects certain features expected for arylcopper compounds, i.e., a strong tendency to aggregate and to form three-center, two-electron copper–carbon bonds.[2] However, whereas previously established structures were all highly symmetrical,[2a] an interesting feature of this structure is the asymmetry of the aggregate; see Figure 2. There is only one aryl C_{ipso} center (C(13)) which bridges two Cu atoms that are also coordinated to the two ortho CH_2NMe_2 substituents. This structural feature resembles the situation found in the corresponding bis-ortho-chelated aryllithium compound $Li_2\{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6\}_2$[11] (see Figure 1c). In principle a second aryl group could also coordinate to this $Cu_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}$ unit in the same way to afford a dimeric structure as in Figure 1c. However, this is unlikely because it would produce four-coordinate copper sites, and this situation has only been achieved so far by ligands with special requirements as in $[Cu(naphthylNMe_2\text{-}8)]_4$ tetramer.[4] Another possible aggregate bonding involves three coordination at each Cu center as has been found in $[Cu_4\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}Me\text{-}5\}_4]$.[2] This can be only realized for $[Cu_n\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_n]$ when other CuX species are involved in the cluster. In 1 it is in fact a combination of two CuBr units with two bis-ortho-chelated (aryl)Cu units that is observed (Figures 2 and 4).

The butterfly arrangement for the copper atoms was also observed previously in $[Cu_4\{C_6H_3(CH_2NMe_2\text{-}2)\text{-}Me\text{-}5\}_4]$.[3] It can be regarded as a distorted square-planar arrangement, which seems to be the general geometry for Cu_4 aggregates,[4] as a result of the coordinating properties of the CH_2NMe_2 substituents to form a butterfly.

Furthermore, it shows an interesting structural resemblance to the $[Vi_2CuBr_2]$ (Vi = $(2\text{-}Me_2NCH_2C_6H_4)C{=}C(Me)C_6H_4Me\text{-}4$) complex reported before.[13] Herein the alkenyl groups and the bromine atoms are also mutually cis positioned. Until now two structural types of CuBr organocopper compounds have been characterized, namely, a $[(RCu)_2CuBr]$ complex (R = $C_6H_4NMe_2\text{-}2$, $C_6H_4(oxazoline)\text{-}2$)[7] having a 2:1 RCu:CuBr stoichiometry and a [(RCu)CuBr] complex (R = $(2\text{-}Me_2NCH_2C_6H_4)C{=}C(Me)C_6H_4Me\text{-}4$),[13b] $C_6H_3(CH_2NMe_2)_2\text{-}o,o'$) having a 1:1 RCu:CuBr stoichiometry. A possible explanation for these different stoichiometries is the steric bulkiness of the organic group, favoring a 1:1 stoichiometry with increasing bulkiness.

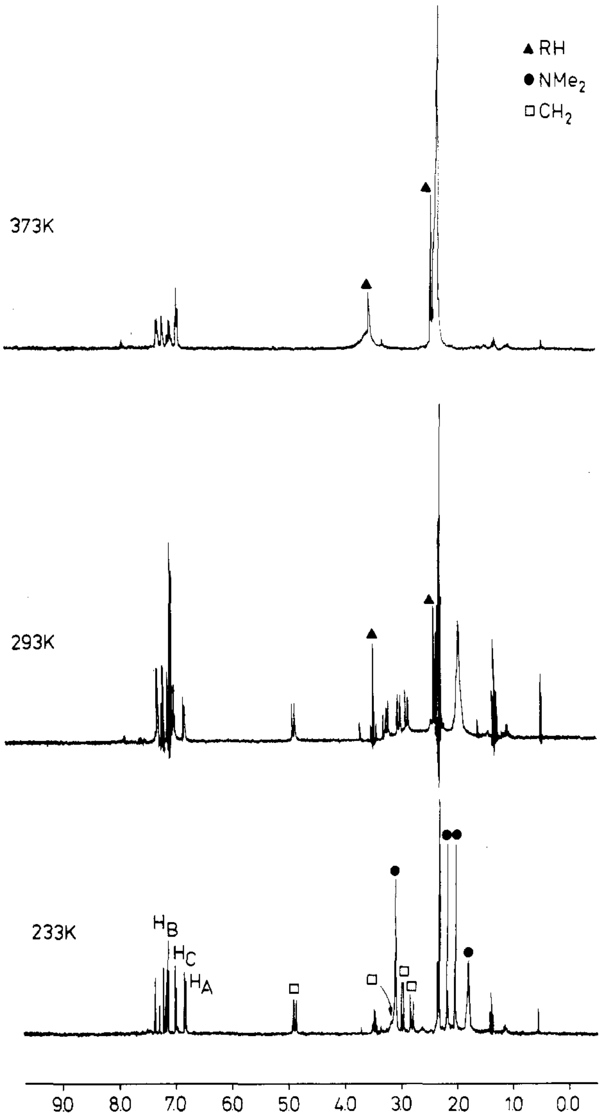

Figure 3. Temperature-dependent ^1H NMR spectra in toluene-d_8.

Solution Studies. A cryoscopic molecular weight determination of 1 in benzene afforded a molecular weight of 823 which corresponds to a dimeric $[(RCu)CuBr]_2$ composition. Variable-temperature ^1H NMR measurements (see Figure 3) in toluene-d_8 (250 MHz) indicate that the asymmetry found in the solid is most probably not retained in solution and that fluxional processes are operative. At 233 K the spectrum shows four signals for the NMe_2 groups and two AB patterns for the CH_2 protons, while the aryl protons give rise to a single ABC pattern (Figure 3a). These data exclude, at this temperature, the structure found in the solid state since this would give rise to eight NMe_2 signals, four AB patterns, and two aryl patterns owing to the inequivalence of all the CH_2NMe_2 substitutents. To explain this experimental data, it is possible to propose the more symmetric structure, schematically shown in Figure 4, when the following assumptions and restrictions are made. (i) The dimeric structure is retained in solution at 233 K. (ii) There is only one species present in solution. (iii) Possible compounds in which triangular Cu_3 faces are bridged by one aryl ligand (for which there are no precedents) are not considered. The proposed solution geometry consists of four copper atoms, in a distorted square-planar arrangement,[4] kept together by two adjacent bridging aryl units and two bridging bromide atoms. Two CH_2NMe_2 substituents are

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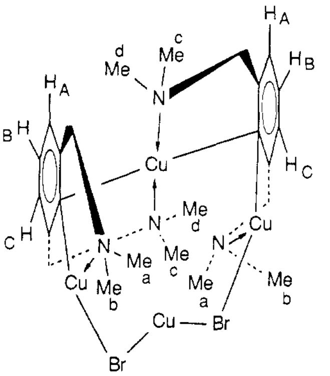


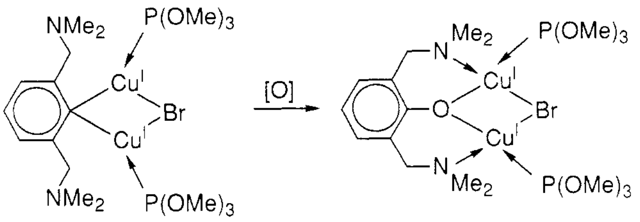
Figure 4. Schematic representation of the proposed structure in solution at 233 K on the basis of 250-MHz ^1H NMR spectra.

coordinated to the same copper atom, so making it four-coordinate, whereas the other two substituents are coordinated to two opposite copper atoms. Owing to the coordination pattern at the copper atoms, the aggregate is chiral.[17] This molecule can be attained from the solid-state structure by a change in coordination of one CH_2NMe_2 substituent. When the CH_2NMe_2 substituents are coordinated, pyramidal inversion at the N atom, that is normally a fast process, is blocked.[18] This leads to inequivalence of the methyl groups on each N atom (see Figure 4), i.e., Me_a and Me_b, on one hand, and Me_c and Me_d, on the other, thus providing four NMe_2 signals. Similarly, this structure would give rise to the two AB patterns for the CH_2 protons and the magnetically inequivalent aryl protons observed.

When the temperature is raised, the spectrum begins to change and at 239 K the spectrum shows two, somewhat broadened, signals for the NMe_2 group though still two AB patterns for the CH_2 protons. The most likely explanation for this is a fluxional process involving coordinated and uncoordinated CH_2NMe_2 groups. When uncoordinated fast pyramidal inversion at the N atoms is possible making Me_a, Me_b and Me_c, Me_d, respectively, equivalent, but $Me_{a,b}$ and $Me_{c,d}$ remain inequivalent. Because the chiral aggregate is still rigid at this temperature, the CH_2 protons are observed as two AB patterns and H_A and H_C are inequivalent.

On further warming to 373 K both the NMe_2 and the CH_2 protons afford singlet resonances and the aryl protons are now seen as a single AB_2 pattern. These observations are consistent with fluxionality of the entire aggregate, for example, involving rotation of the aryl groups around the Cu_2C(ipso) bonds. Such a process has also been proposed to occur in (*p*-tolyl)Cu[19] and $[Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4]$.[17] The variable-temperature behavior of this cluster is fully reversible.

The molecular weight of $[Cu\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}CuBr\{P(OCH_3)_3\}_2]$ (2), determined by cryoscopy in benzene, was 594 (concentration independent), corresponding to the monomeric unit. The ^1H NMR spectrum of 2 (C_6D_6, 293 K) shows singlets for the CH_2 and NMe_2 protons whose chemical shifts are consistent with the presence of uncoordinated CH_2NMe_2 substituents. On the basis of these data the structure depicted in Figure 5 is proposed for this compound. During attempts to crystallize this compound crystals of the interesting phenoxocopper(I) compound $[Cu\{OC_6H_3(CH_2NMe_2)_2\text{-}o,o'\}CuBr\{P(OCH_3)_3\}_2]$ originating from a reaction of 2 with oxygen were formed. This phenoxo compound, which is the first example of a phenoxocopper(I) complex, has a structure very similar to that of the model copper(II) cationic compound for the aromatic hydroxylation, shown in Scheme I, is published elsewhere.[20] The isolation of this compound, which has a $Cu^I\cdots Cu^I$ distance of 2.853 (5) Å, nicely supports the proposed reaction route by Karlin et al. (see Scheme I and Introduction) involving a copper-mediated oxygenation of an aromatic C–H bond. However, particularly interesting of this compound is the simplicity of the organic system, whereas it was thought that the oxygenation reaction could only be achieved with copper complexes containing special ligand systems.[21]



2 3

Figure 5. The reaction of $[Cu_2Br\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}\{P(OMe)_3\}_2]$ (2) (proposed structure) with O_2 yielding the phenoxocopper(I) complex (50% yield; for X-ray structure determination see ref 20).

Experimental Section

Syntheses were carried out by using standard Schlenk techniques in an atmosphere of purified nitrogen. The solvents were dried prior to use. The following compounds were prepared according to the literature methods: CuBr,[22] $CuBr\{P(OMe)_3\}$,[23] $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Br$.[24]

^1H NMR spectra were obtained on a Bruker WM 250 spectrometer. Elemental analyses were carried out by the section Elemental Analyses of ITC/TNO, Zeist, The Netherlands.

Synthesis of $[Cu_4Br_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2]$ (1). To a solution of freshly distilled $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Br$ (1.23 g, 4.54 mmol) in diethyl ether (25 mL) was added a solution of *n*-BuLi in hexane (7.3 mL, 1.6 M, 4.54 mmol). The solution was stirred for 1 h, and then CuBr (1.29 g, 9 mmol) was slowly added portionwise. The resulting suspension was stirred for 1 h and subsequently filtered. The yellow solution was concentrated in vacuo. Addition of hexane afforded 1.40 g of yellow crystalline $[Cu_4Br_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2]$ (1) (yield 55%). Analysis. Calcd for $C_{12}H_{19}N_2BrCu_2$: C, 36.29; H, 4.58; N, 7.06; Br, 20.12; Cu, 31.95. Found: C, 36.03; H, 4.93; N, 6.75; Br, 19.97; Cu, 31.46. FD-MS (C_6H_6, 20 mA): *m/e* 795 (calcd for $[Cu_4Br_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2$ *m/e* 794). Molecular weight determination: 823 (cryoscopic in benzene concentration independent in the range 0.04–0.13 mol/L).

Synthesis of $[Cu_2Br\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}\{P(OMe)_3\}_2]$ (2). To a solution of $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Br$ (5.13 g, 19 mmol) in diethyl ether (25 mL) was added a solution of *n*-BuLi in hexane (12 mL, 1.6 M, 19 mmol). The resulting solution was stirred for 1 h, and subsequently a solution of $CuBr\{P(OMe)_3\}$ (2.35 g, 19 mmol) in benzene (100 mL) was slowly added. After additional stirring for 1 h the volume of the suspension was concentrated to one-third of the initial volume. The resulting white precipitate was filtered off, washed with diethyl ether, and dried in vacuo to give 3.0 g of white $[Cu_2Br\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}\{P(OMe)_3\}_2]$,

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(2) (yield 20%). Anal. Calcd for $C_{18}H_{36}BrN_2P_2O_6Cu_2$: C, 33.50; H, 5.63; N, 4.34; P, 9.60; Br, 12.38; Cu, 19.66. Molecular weight determination: 594 (cryoscopic in benzene, concentration independent in the range 0.026–0.08 mol/L); calcd 645. Found: C, 32.71; H, 5.73; N, 3.96; P, 9.20; Br, 12.52; Cu, 18.87.

Reaction of $[Cu_4\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2Br_2]$ with Me_2SnBr_2. To a solution of $[Cu\{C_6H_3(CH_2NMe_2)\text{-}o,o'\}CuBr]$ (0.5 g, 1.25 mmol) in diethyl ether (15 mL) was added Me_2SnBr_2 (0.38 g, 0.5 mmol). The resulting suspension was stirred at room temperature for 1.5 h and filtered. The filtrate was evaporated to dryness to afford white $[\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}SnMe_2]^+Br^-$ which was characterized by comparing its ^1H NMR spectrum with that of an authentic sample. Yield: 0.42 g, 80%.

Crystal Structure Determination. Transparent yellow crystals of the title compound $Cu_4Br_2C_{24}H_{38}N_4$ are orthorhombic, space group *Pcab* with eight molecules in a unit cell of dimensions $a = 18.167$ (3) Å, $b = 19.462$ (3) Å, and $c = 17.036$ (2) Å. A total of 5655 independent intensities ($2\theta < 130°$) were measured on a Nonius CAD4 diffractometer, at 25 °C, using graphite-monochromated Cu Kα radiation (λ(Cu Kα) = 1.5418 Å. A total of 2587 reflections were below the $3\sigma(I)$ level and were treated as unobserved.

The Cu and Br positions were located by means of the symbolic addition program set SIMPEL.[25] The positions of the C and N atoms were obtained by standard difference Fourier techniques. After isotropic block–diagonal least-squares refinement an empirical absorption correction (DIFABS[26]) was applied (crystal dimensions 0.25 × 0.33 × 0.33 mm; $\mu = 64.3$ cm^{-1}).

Continued anisotropic refinement converged to $R = 0.066$ (H atoms were introduced at calculated positions). Continued refinement, anisotropic for Cu, Br, C, and N (the H atoms were kept at their idealized positions) converged to $R = 0.065$ ($R_w = 0.112$). An extinction correction was applied and a weighting scheme, $w = 1/(9.3 + F_o + 0.012F_o^2)$, was employed. The anomalous dispersion of Cu and Br were taken into account. The scattering factors were taken from ref 27 and were corrected for anomalous dispersion.[28]

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Registry No. 1, 116926-17-1; 2, 116926-18-2; o,o'-$(Me_2NCH_2)_2C_6H_3Br$, 66479-06-9; CuBr, 7787-70-4; CuBr{P(OMe)$_3$}, 34836-54-9; Me_2SnBr_2, 2767-47-7; $[\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}SnMe_2]^+Br^-$, 66484-01-3.

Supplementary Material Available: Tables of fractional coordinates of the hydrogen atoms (Table 2), anisotropic thermal parameters (Table 3), bond distances of the non-hydrogen atoms (Table 4) and of the hydrogen atoms (Table 5), and bond angles of the non-hydrogen atoms (Table 6) and of the hydrogen atoms (Table 7) and an ORTEP view of 1 (9 pages); a listing of observed and calculated structure factors (Table 1) (24 pages). Ordering information is given on any current masthead page.

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Aliphatic versus Aromatic C–H Activation and the X-ray Crystal Structure of $[IrH(H_2O)(7,8\text{-benzoquinolinato})(PPh_3)_2]SbF_6$

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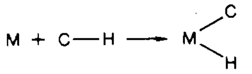
The crystal structure of $[(bq)IrH(H_2O)(PPh_3)_2]SbF_6$ (2, bq = 7,8-benzoquinolato) shows that benzoquinoline cyclometalates under conditions which give only a C–H···M bridged system with 8-methylquinoline. 2, a rare example of an organometallic aqua hydride complex, crystallizes in space group $P2_1/c$ with $a = 13.330$ (4) Å, $b = 18.131$ (5) Å, $c = 21.777$ (7) Å, $\beta = 98.86$ (3)°, and $Z = 4$. The possible intermediacy of η^2-arene species is considered and rejected, and a transition state (7) for the C–H oxidative addition is proposed.

The question of aromatic versus aliphatic C–H bond activation has aroused considerable interest over the last few years.[1-3] It is generally agreed that examples of C–H bond oxidative addition (eq 1) are much more numerous for aromatic than for aliphatic or benzylic C–H groups.



$$\mathrm{M} + \mathrm{C{-}H} \longrightarrow \mathrm{M}\genfrac{}{}{0pt}{}{\diagup\mathrm{C}}{\diagdown\mathrm{H}} \qquad (1)$$

Two types of explanations have been advanced to account for this observation. One suggestion, based on kinetic arguments, is that the arene group can bind to the metal, for example, in an η^2 fashion and that this binding leads to oxidative addition.[2] A second explanation is thermodynamic. On this idea, the deciding factor is the greater bond strength for an M–C(aryl) over an M–C(alkyl) or M–C(benzyl) bond in eq 1.[1,3] Part of our motivation for this study was an attempt to throw some light on this problem by using a ligand for which the first of these explanations would be unlikely to hold. We had already shown that 8-methylquinoline (mq) reacts with [Ir-

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