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GROUP IB ORGANOMETALLIC CHEMISTRY

XVI*. COMPLEX FORMATION BETWEEN 2-(DIMETHYLAMINO)-PHENYLCOPPER WITH COPPER(I) OR SILVER HALIDES. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF HEXANUCLEAR $(2\text{-}Me_2NC_6H_4)_4Cu_{6-n}M_nX_2$ (M = Cu OR Ag) CLUSTER COMPOUNDS

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Summary

The 2/1 complexes (2RCu · MX) between 2-(dimethylamino)phenylcopper (RCu) and CuX (X = Cl, Br or I) or AgBr have been prepared in two ways (*i*) from the 2/3 reaction of 2-(dimethylamino)phenyllithium with cuprous halide and (*ii*) from the reaction of RCu with excess of the metalIB halide.

The structure of bis[(2-dimethylamino)phenylcopper] cuprous bromide, which is dimeric ($R_4Cu_6Br_2$) in the solid state, has been determined by X-ray analysis. The bonding in this hexanuclear cluster (Cu—Cu ranging from 2.48 to 2.70 Å, multicenter bonded aryl groups) is discussed. Molecular weight determinations and ^1H NMR spectroscopy reveal a similar hexanuclear structure for the $R_4Cu_6X_2$ complexes in benzene solution. NMR spectroscopy indicates that in solution the mixed-metal cluster compounds $R_4Cu_{6-n}Ag_nBr_2$ are not stable but enter into interaggregate exchange reactions. A possible pathway involving trinuclear species $R_2Cu_{3-n}Ag_nX$ as intermediates is proposed.

Introduction

In research on GroupIB organometallic compounds we observed that arylcopper and arylsilver compounds can form complexes with metal halides [2,3]. Examples of stable compounds are $2\text{-}Me_2NCH_2C_6H_4M \cdot MBr$ (M = Cu [2-4] or Ag [5]) and $4\text{-}Me_2NC_6H_4Cu \cdot CuBr$ [2,6]. In general these complexes are insoluble in common organic solvents.

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* For Part XV see ref. 1.

Complex formation between organocopper compounds and metal halides (LiX or MgX_2 [3,7], CuX_n [4] etc.) plays an important role in their synthesis and isolation. In addition, it is well-known that the chemical reactivity of organocopper compounds is strongly influenced by metal halides [1,3,8]. This has been ascribed to the presence in solution of organocopper—metal halide complexes (the so-called heterocuprates; e.g. $Li^+CuBrPh^-$) [8]. However, nothing is known with certainty about the nature of these complexes.

During a detailed study of the synthesis of 2-(dimethylamino)phenylcopper it was found that this compound forms a benzene-soluble 2/1 complex with cuprous bromide [6]. The availability of a well-defined organocopper—cuprous bromide complex possessing favourable physical properties (good solubility, high thermal stability) offered the possibility of studying the nature of the complex formation between arylmetalIB compounds and metal halides in greater detail.

In this paper the synthesis and structural characterization of cluster compounds of the type $(2\text{-}Me_2NC_6H_4)_4Cu_{6-n}M_nX_2$ will be discussed. The influence of complex formation of organocopper compounds with metal halides on the reactivity of organocopper intermediates in organic synthesis will be dealt with in a later paper [3,9].

Results and discussion

Synthesis of bis[2-(dimethylamino)phenylcopper] metalIB halide complexes

2RCu · CuX complexes. The 2/1 complex of 2-(dimethylamino)phenylcopper (I) with cuprous bromide, 2RCu · CuBr (II), is formed in the 1/1 reaction of 2-(dimethylamino)phenyllithium (III) with cuprous bromide (addition of RLi to the CuBr suspension) [6]. A closer examination of this reaction revealed that II can be synthesized in two ways:

a. Starting from 2-(dimethylamino)phenyllithium (RLi; III):

$$2\,RLi + 4\,CuBr \xrightarrow[-CuBr\ (excess)]{Et_2O\,;\ -20^\circ C\,;\ 2\ h} \underset{(II)}{2RCu \cdot CuBr} + 2\,LiBr \qquad (1)$$

Slow addition of a solution of III in ether at —20°C to a suspension of CuBr in ether (III/CuBr molar ratio 1/2) affords the 2/1 complex II (elemental analysis, see Table 1) in 90% yield based on the amount of III.

b. Starting from 2-(dimethylamino)phenylcopper (RCu; I):

$$2\,RCu + 2\,CuBr \xrightarrow[-CuBr\ (excess)]{Et_2O;\ 25^\circ C;\ 7\ days} \underset{(II)}{2RCu \cdot CuBr} \qquad (2)$$

The reaction of I with an equimolar amount of cuprous bromide in ether, which proceeds very slowly, affords the 2/1 complex II in 71% yield.

The corresponding chloro complex 2RCu · CuCl (IV) and iodo complex 2RCu · CuI (V) have been obtained by route *b* (eqn. 3).

$$2\ \mathrm{RCu} + 2\ \mathrm{CuX} \xrightarrow[\text{—CuX (excess)}]{C_6H_6;\ 25^\circ C} 2\mathrm{RCu}\cdot\mathrm{CuX} \qquad (3)$$

$$\begin{array}{l}(\mathrm{IV}, \mathrm{X} = \mathrm{Cl})\\(\mathrm{V}, \mathrm{X} = \mathrm{I})\end{array}$$

Attempts to synthesize the chloro derivative via route *a* (eqn. 1) unexpectedly afforded the bromo compound 2RCu · CuBr (II) contaminated with the chloro derivative (according to IR spectroscopy and elemental analysis; at. ratio Br/Cl ≈ 8.41). The overall yield of this product was rather low (30%).

$$2\ \mathrm{RBr} + 4\ \mathrm{Li} \rightarrow [2\ \mathrm{RLi} + 2\ \mathrm{LiBr}] \qquad (4)$$

The organolithium reagent III used in this reaction had been prepared in situ and therefore contained an equivalent amount of LiBr (see eqn. 4). Possible explanations for the isolation of the bromo compound II instead of the chloro derivative IV are given in the following reaction sequences:

(*1.*) $2\ \mathrm{RLi}(2\ \mathrm{LiBr}) + 3\ \mathrm{CuCl} \rightarrow 2\mathrm{RCu}\cdot\mathrm{CuCl} + 2\ \mathrm{LiBr} + 2\ \mathrm{LiCl}$

$2\mathrm{RCu}\cdot\mathrm{CuCl} + \mathrm{LiBr} \rightarrow 2\mathrm{RCu}\cdot\mathrm{CuBr} + \mathrm{LiCl}$

(*2.*) $2\ \mathrm{LiBr}(2\ \mathrm{RLi}) + 2\ \mathrm{CuCl} \rightleftharpoons 2\ \mathrm{LiCl}(2\ \mathrm{RLi}) + 2\ \mathrm{CuBr}$

$3\ \mathrm{CuBr} + 2\ \mathrm{RLi} \rightarrow 2\mathrm{RCu}\cdot\mathrm{CuBr}$

Sequence *1.* involves the primary formation of a 2RCu · CuCl complex which in a second step undergoes halogen-exchange with the LiBr present in solution, affording the organocopper—cuprous bromide complex. In sequence *2.* halogen-exchange between CuCl and LiBr occurs prior to the arylating reaction. This reaction sequence implies that CuCl does not react with the arylating lithium compound, or does so only very slowly, to give the organocopper. The first explanation is supported by the observation that the reaction of 2RCu · CuCl with LiI affords quantitatively the 2RCu · CuI complex (V)*.

$$\underset{(\mathrm{IV})}{2\mathrm{RCu}\cdot\mathrm{CuCl}} + 2\ \mathrm{LiI} \xrightarrow[120\ h]{Et_2O;\ 25^\circ C} \underset{(\mathrm{V})}{2\mathrm{RCu}\cdot\mathrm{CuI}} + 2\ \mathrm{LiCl} \qquad (5)$$

The iodo complex 2RCu · CuI (V) was synthesized without complications via the organolithium route, and pure V was isolated in 64% yield (elemental analysis, see Table 1).

$$2\ \mathrm{RLi}(2\ \mathrm{LiBr}) \xrightarrow[\text{—CuI (excess)}]{+4\ \mathrm{CuI};\ -2\ \mathrm{LiI}} \underset{(\mathrm{V})}{2\mathrm{RCu}\cdot\mathrm{CuI}} \qquad (6)$$

The orange bis[(2-dimethylamino)phenylcopper] cuprous halide compounds II, IV and V decompose between 181 and 202°C (II, 198—202°C; IV, 181—183°C and V, 195—197°C). Complex II does not undergo visible decomposition upon exposure to the atmosphere for seven days. 2RCu · CuBr dissolved in benzene reacts very slowly with D_2O. After 13 days 2-deuterio-*N*,*N*-dimethylaniline (VI) had been formed in only 55% yield. This indicates that complex II is very stable

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* Based on the hexanuclear structure of both IV and V this exchange reaction has been formulated as a ligand substitution reaction with retention of the hexanuclear cluster structure [10].

TABLE 1

ANALYTICAL AND MOLECULAR WEIGHT DATA FOR BIS[2-(DIMETHYLAMINO)PHENYLCOPPER]-METALIB HALIDE COMPLEXES

Compound	Analysis found (calcd.) %					Mol.wt.[a]	
	C	H	N	X	Cu	Found (calcd.)	n
II; $C_{16}H_{20}N_2Cu_3Br$	37.5	4.0	5.4	Br, 15.6	37.2	984	1.92 A
	(37.62)	(3.95)	(5.48)	(15.64)	(37.31)	1027	2.01 B
						(510.5)	
IV; $C_{16}H_{20}N_2Cu_3Cl$[b]	40.4	4.5	5.7	Cl, 7.9	39.4	469,618,	1.01 B
	(40.59)	(4.26)	(5.92)	(8.01)	(41.21)	761(466)	1.33
							1.63
V; $C_{16}H_{20}N_2Cu_3I \cdot 0.45C_6H_6$[c]	37.7	3.8	4.7	I, 19.7	31.7	1150	2.06 B
	(37.87)	(3.89)	(4.72)	(21.40)	(32.14)	(557.5)	
VII; $C_{16}H_{20}N_2Cu_2AgBr$	34.8	3.8	4.9		23.1		
	(34.61)	(3.63)	(5.05)		(22.89)		

[a] Concentration independent unless stated otherwise. In benzene, by A cryometry, and B by ebulliometry. [b] Elemental data calculated for $2RCu \cdot CuCl \cdot 0.07CuCl$. [c] IR spectroscopy confirmed the presence of benzene in the complex (absorption band at 685 cm^{-1}).

towards hydrolysis [compare, e.g., the parent organocopper I which gives 86% VI after 7 days [6] and phenylcopper [7] or fluorinated phenylcopper [11] compounds which undergo rapid hydrolysis with H_2O].

The 2RCu · AgBr complex. The reaction of 2-(dimethylamino)phenylcopper (I) with AgBr in benzene (exact 1/1 molar ratio of I and AgBr) afforded a benzene-soluble compound of stoichiometry 2RCu · AgBr (see Table 1) in about 70% yield:

$$2\,RCu + 2\,AgBr \xrightarrow[\text{21 days; —AgBr (excess)}]{C_6H_6} \underset{\text{(VII)}}{2RCu \cdot AgBr} \qquad (7)$$

Complex VII decomposes between 182 and 185°C.

Structural investigation of bis[2-(dimethylamino)phenylcopper] metalIB halide compounds

Molecular weights of the complexes 2RCu · CuX. The molecular weights of the complexes 2RCu · CuX (X = Cl, Br or I) in benzene were determined by cryometry (X = Br) and by ebulliometry (X = Cl, Br or I). The results are given in Table 1. Both the Br- and the I-derivative exist in benzene solution as stable hexanuclear species with the stoichiometry $R_4Cu_6X_2$. In contrast, the hexanuclear structure of the chloro derivative is less stable as revealed by its concentration-dependent molecular weight (n increases from 1.01 to 1.63 with increasing concentration).

Solid state structure of $R_4Cu_6Br_2$ (II).* Attempts to grow single crystals were successful in the case of the CuBr complex II. The complex crystallizes from benzene as $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2 \cdot 1.5C_6H_6$**. An X-ray study has been carried

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* For a preliminary account, see ref. 12.

** Recrystallization of II from benzene affords $R_4Cu_6Br_2 \cdot 1.5C_6H_6$. When these crystals are suspended in pentane $R_4Cu_6Br_2$ can be isolated (see Experimental).

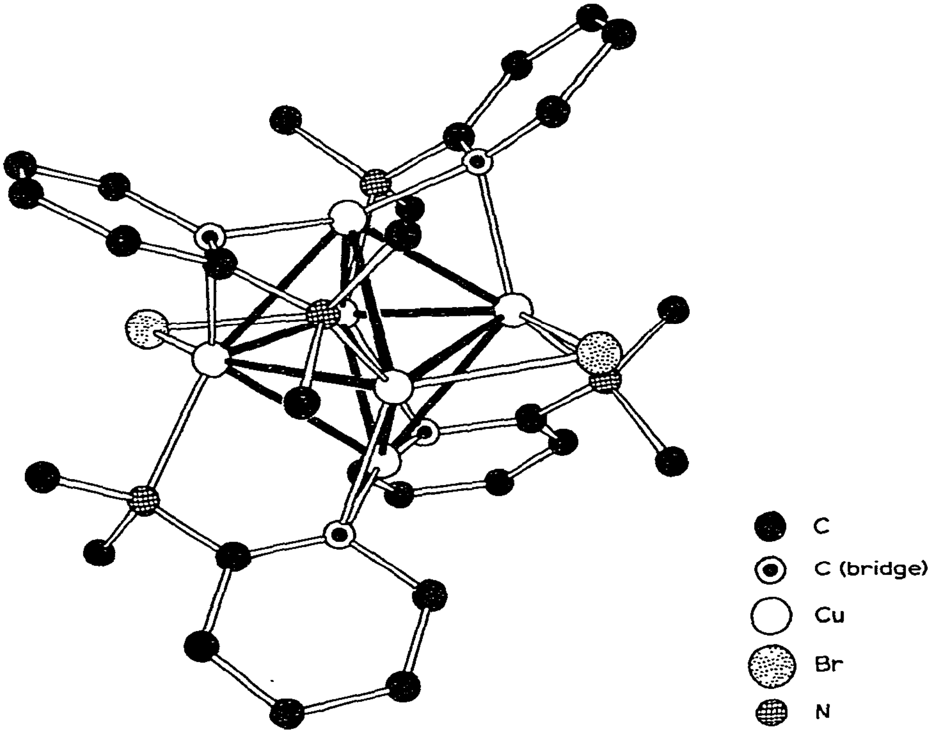

Fig. 1. Structure of hexanuclear bis[2-(dimethylamino)phenylcopper] cuprous bromide [12].

out by the group of Prof. R. Mason at the University of Sussex, England [12].

The structure of $R_4Cu_6Br_2$, which is shown in Fig. 1, has the following main features:

1. The six copper atoms are positioned in an octahedral arrangement. A similar arrangement of the copper atoms has been found in $Cu_6H_6(PPh_3)_6 \cdot$ DMF (mean Cu—Cu distances of 2.54 and 2.65 Å [13].

2. Each aryl ligand bridges two copper atoms (Cu_{ap}—C 1.967 and Cu_{eq}—C 2.085 Å). By analogy with the bonding situation in the R'_4Cu_4 compounds ($R' = 2\text{-}Me_2NCH_2C_6H_4$— [14]), two electron-three center bonding is assumed for the aryl ligands. The equal C—C distances in each of the aryl nuclei is in agreement with this view [sp^2-hybridization occurs at the bridging C(Phenyl) atom]. The bromine atoms bridge trans-equatorial edges of the octahedron. Each dimethylamino-nitrogen atom is coordinated to a third copper atom, so that each anilino ligand "bridges" a triangular face of the copper octahedron.

3. The Cu—Cu distances in II depend on the nature of the bridging ligands [15]. The mean separation of the aryl bridged (2e—3c) copper atoms is 2.48 Å, which is appreciably shorter than the Cu—Cu distance of 2.56 Å in copper metal. The bromine-bridged (4e—3c) copper atoms are separated by 2.70 Å. The remaining copper—copper distances are 2.64 Å.

4. There is a distinct difference between the coordination geometries of the apical and equatorial copper atoms. When direct copper-to-copper bonding is excluded [14], then the coordination geometry of the equatorial atoms is roughly trigonal (bond angles Br—Cu—C 117°, Br—Cu—N 106°, N—Cu—C 120°) whereas that around the apical copper atoms is digonal (C—Cu—C 164°). It is noteworthy that in electron deficient $(Me_3SiCH_2)_4Cu_4$ (2e—3c bonded Me_3SiCH_2 ligands) exactly the same C—Cu—C angle of 164° has been found for the digonal copper atoms [16], whereas in electron precise $[Me_2P(CH_2)_2]_2Cu_2$ a C—Cu—C angle of 176° has been observed [7]. In case of 2e—3c aryl-to-copper bonding linear hybridization (*ds* or *sp*)* at the apical copper atom implies an angle between the internuclear Cu—C axes which is smaller than 180°.

IR and NMR spectra of $R_4Cu_6X_2$ (II, IV and V). The IR spectra of $R_4Cu_6Br_2$ and $R_4Cu_6I_2$ are superimposable in the 1600-200 cm^{-1} region, whereas the spectrum of $R_4Cu_6Cl_2$ contains some additional bands in the C—H binding region (770-715 cm^{-1}). The observation that the vibrations are insensitive to the bridging halogen atoms X indicates a similar structure for the R_4Cu_6 skeleton in the $R_4Cu_6X_2$ compounds (Fig. 2 shows the IR spectrum of $R_4Cu_6Br_2$).

NMR data for the various compounds are given in Table 2. In Fig. 3 the NMR spectrum of the bromo derivative II recorded at different temperatures is shown. At room temperature the respective proton resonances of each of the three compounds II, IV and V appear at almost the same chemical shift positions, which indicates an identical magnetic environment for each of the R groups in the various $R_4Cu_6X_2$ compounds and therefore an identical structure.

The most informative part of the spectrum is the aliphatic region which shows two broadened singlets (at 1.84 and 2.92 ppm) for the NCH_3 protons. The presence of these two singlets is interpreted in terms of a rather inert (i.e. within the NMR time scale) Cu ← $N(Me_2)$ coordination bond.

Inspection of the $R_4Cu_6Br_2$ compound reveals that as a consequence of the Cu—N coordination the two methyl groups in the same NMe_2 grouping are in different environments; one Me group points away from the cluster whereas the other lies near a triangular face of the cluster. At higher temperatures the

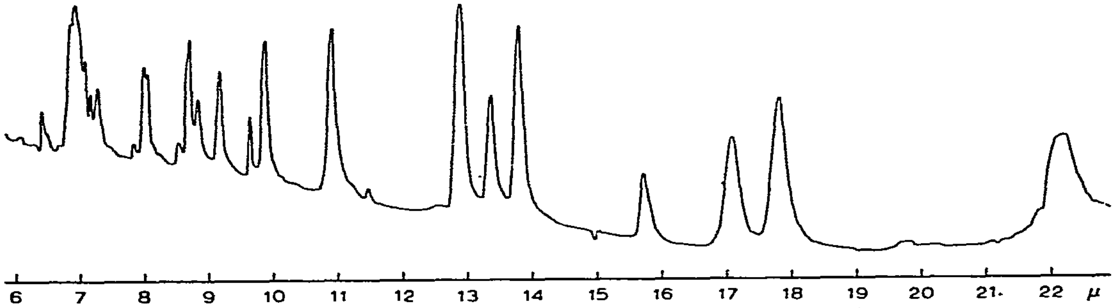

Fig. 2. IR spectrum (Nujol) of hexanuclear bis[2-(dimethylamino)phenylcopper] cuprous bromide (II; $R_4Cu_6Br_2$).

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* In organic-GroupIB metal chemistry a variety of linear complexes is known. In all these complexes the metal ions have the d^{10} electronic configuration. Examples are $CuCl_2^-$ and $Ag(CN)_2^-$. Orgel [18] and Jørgensen and Pouradier [19] have pointed out that a small difference between the excited d^9s and the d^{10} ground state is the essential condition for the formation of such linear complexes. However, NQR investigations by Bowmaker et al. [20] did not provide conclusive data about the state of hybridization, i.e. whether *ds* or *sp*, of the copper atom in linear CuX_2^- complexes.

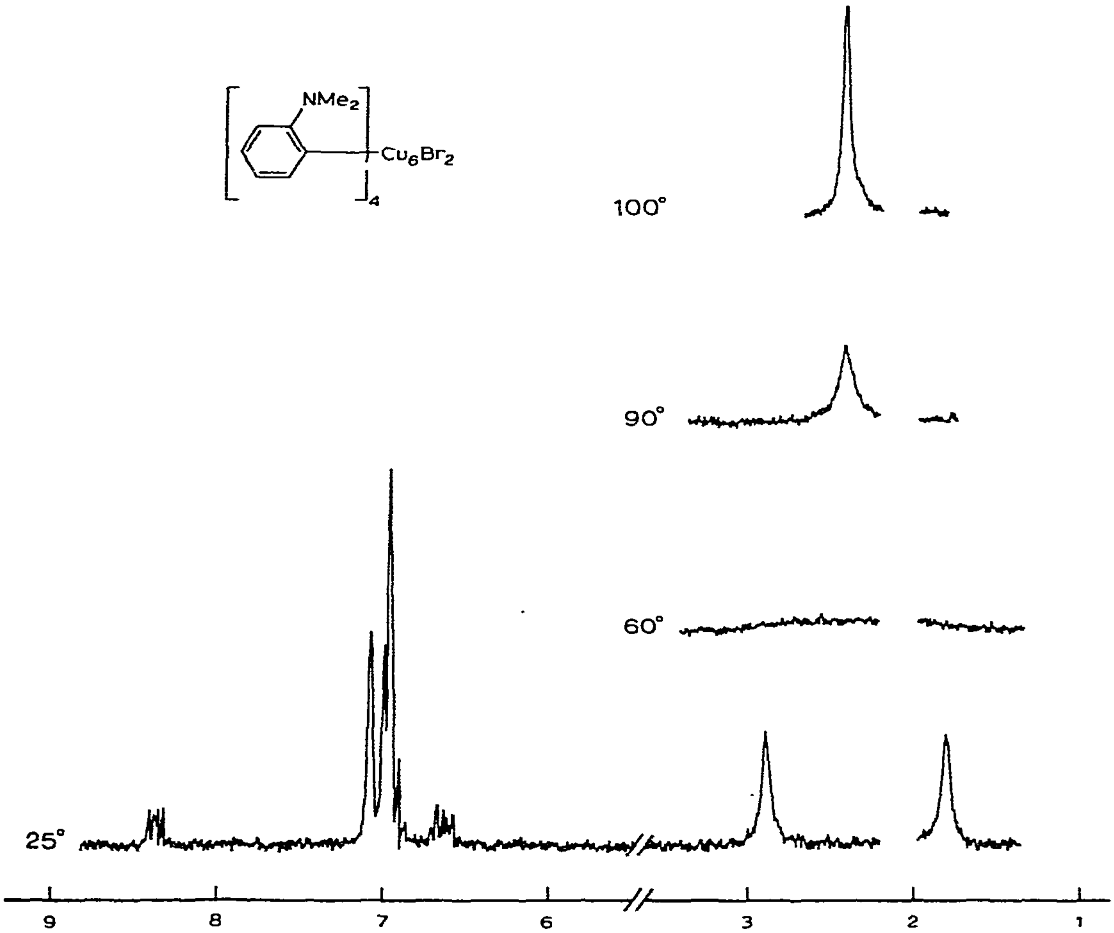


Fig. 3. NMR spectrum (δ ppm) of $R_4Cu_6Br_2$ (II) in toluene-d_8 (CH_xD_{3-x} resonances are not shown). see also Table 2.

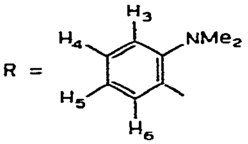
equilibrium between non-coordinated and coordinated NMe_2 groups shifts to the non-coordinated situation. That the cluster structure remains intact at higher temperatures is apparent from the molecular weight data for the bromo and iodo derivative at 80°C (see Table 1). In the non-coordinated situation the methyl groups become equivalent by rotation around the C(Ph)—N bond and inversion at the nitrogen atom, which explains the coalescence of the doublet to one singlet (at 2.42 ppm) at about 90°C.

The spectrum of the chloro derivative recorded at 110° shows two broadened singlets at 2.42 and 2.35 ppm (peak area ratio about 3/1) suggesting that the dimer is in equilibrium with another aggregate, most probably the monomer (cf. the concentration dependence of the molecular weight at 80°C, Table 1). The dimerization of two monomers R_2ClCu_3 can be explained by a change from intra- into inter-molecular coordination of the chloro atom as depicted in Fig. 4.

Structures of the bis[2-(dimethylamino)phenylcopper] silver bromide complexes $R_4Ag_{6-n}Cu_nBr_2$ (n = 0, 2, 4). The 2/1 complex of 2-(dimethylamino)-

TABLE 2

NMR DATA FOR THE HEXANUCLEAR COPPER COMPOUNDS $R_4Cu_6X_2$

Compound	T (°C)	δ (ppm)[a]		
		NCH_3	H_3	H_6
N,N-dimethylaniline[b] (RH)	25	2.50 (s)	6.59 (m)	7.20 (m)
R = 				
II: $R_4Cu_6Br_2$[c]	25	1.84 and 2.94(br)[d]	6.64 (m)	8.48 (m)
	90	2.42 s, sharp		
IV: $R_4Cu_6Cl_2$[c]	25	1.84 and 2.92(br)[d]	6.64 (m)	8.3 (m)
	110	2.42 s, sharp and 2.35(br)		8.24 (m)
V: $R_4Cu_6I_2$[c]	25	1.78 and 2.87(br)[d]	6.62 (m)	8.46 (m)
	110	2.42 s, sharp	6.74 (m)	8.42 (m)

[a] Downfield from TMS; s, singlet; m, multiplet; (br), broad. [b] In C_6D_6. [c] In $CD_3C_6D_5$. [d] 1/1 peak area ratio.

phenylsilver (RAg; VIII) with silver bromide has been isolated as a yellow, benzene-soluble solid from the 2/3 reaction of 2-(dimethylamino)phenyllithium (III) with silver bromide [5].

$$\underset{(III)}{2\,RLi} + 3\,AgBr \xrightarrow[60°C\,;\,0°C\,;\,16\ h]{Et_2O\ ;\ C_6H_6} \underset{(IX)}{2RAg \cdot AgBr \cdot 0.33C_6H_6} + 2\,LiBr \qquad (8)$$

The molecular weight in benzene shows that this complex exists as a dimer, and thus has $R_4Ag_6Br_2$ stoichiometry.

A mixed copper—silver complex has been obtained from the 1/1 reaction of (in situ prepared) 2-(dimethylamino)phenylsilver (VIII) with cuprous bromide [5].

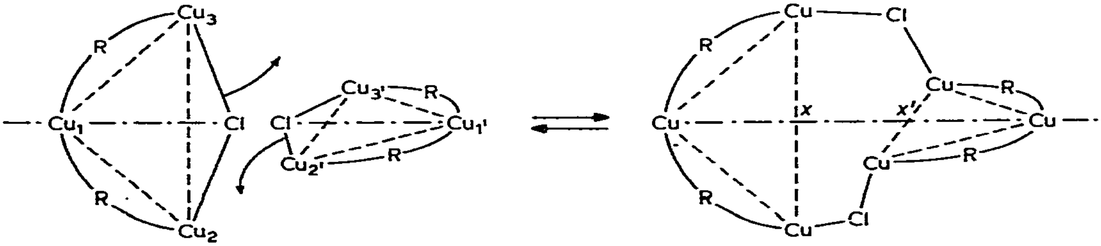


Fig. 4. Proposed mechanism for the dimerization of two monomers R_2ClCu_3 to hexanuclear $R_4Cu_6Cl_2$ ($x = x'$). R represents the bridging 2-(dimethylamino)phenyl group.

$$\underset{\text{(VIII)}}{2\,RAg} + CuBr \rightarrow \underset{\text{(X)}}{2RAg \cdot CuBr} \qquad (9)$$

The benzene-soluble light-brown complex X, isolated from this reaction in 80% yield, analysed correctly for a 2/1 complex. Again, the complex was found to be dimeric [5] and thus has the overall stoichiometry $R_4Ag_4Cu_2Br_2$. This compound then can be considered to be the counterpart of compound VII which has been isolated from the 1/1 reaction of 2-(dimethylamino)phenylcopper (I) with silver bromide (eqn. 7). From the analysis, VII can be formulated as $R_4Ag_2Cu_4Br_2$. For all these complexes a hexanuclear structure similar to that of $R_4Cu_6Br_2$ (cf. Fig. 1), but with copper atoms replaced by silver atoms, seems likely.

NMR data for the complexes $R_4Ag_6Br_2$ (IX), $R_4Ag_4Cu_2Br_2$ (X) and $R_4Ag_2Cu_4Br_2$ (VII) are listed in Table 3. The observation that the spectra of both VII and X consist of a sharp resonance pattern, which is identical to that of $R_4Cu_6Br_2$ (see Table 2), superimposed on a broad resonance pattern, indicates the presence of several species in solution. Most probably in solution the complexes $R_4Ag_4Cu_2Br_2$ and $R_4Ag_2Cu_4Br_2$ are not stable, but enter into interaggregate exchange reactions giving rise to an equilibrium mixture of hexanuclear species of the type $R_4Cu_mAg_nBr_2$ [$m + n = 6$].

One of the possible pathways for interaggregate exchange involves dissociation into trinuclear species followed by association, as shown in eqns. 10—12 (see also Fig. 4 for the equilibrium $R_4Cu_6Cl_2 \rightleftharpoons 2\,R_2Cu_3Cl$).

$$\underset{\text{(VII)}}{R_4Ag_2Cu_4Br_2} \rightleftharpoons R_2Ag_2CuBr + R_2Cu_3Br \qquad (10)$$

$$2\,R_2Cu_3Br \rightleftharpoons \underset{\text{(II)}}{R_4Cu_6Br_2} \qquad (11)$$

$$2\,R_2Ag_2CuBr \rightleftharpoons \underset{\text{(X)}}{R_4Ag_4Cu_2Br_2} \text{ ..... etc.} \qquad (12)$$

An alternative mechanism, involving monomeric species RCu or RAg, seems unlikely in view of the tendency of these species to form coordination polymers which are highly insoluble [3,6].

In the dissociation step (e.g. eqn. 10), M—N and M—Br coordination bonds must be broken. In the case of $R_4Cu_6Br_2$, dissociation (eqn. 11) will be very slow on the NMR time-scale, resulting in a sharp resonance pattern for H_6 and two singlets for the methyl protons in one and the same dimethylamino group*. The subsequent exchange processes involving the mixed species $R_4Ag_mCu_nBr_2$ [e.g. eqn. 12] then account for the additional broad resonance pattern.

Conclusions

This study reveals that the interaction of polymeric 2-(dimethylamino)-phenylcopper (RCu [6]) with metalIB halides results in the formation of com-

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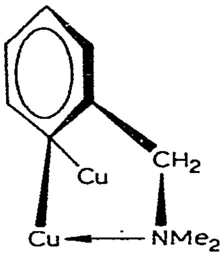
* In the case of $R_4Ag_6Br_2$ the $CH_3(N)$ protons as well as the H_6 proton appear at ambient temperature as broadened resonances which can be attributed to rapid interaggregate exchange (e.g. via $R_4Ag_6Br_2 \rightleftharpoons 2\,R_2Ag_3Br_2$).

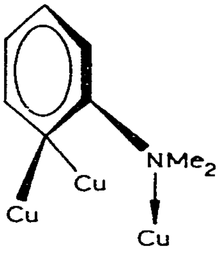
plexes which have a discrete cluster structure consisting of $2\text{-}Me_2NC_6H_4$ groups bonded to a $Cu_{6-n}M_n$ core (M = Cu or Ag) by 2e—3c bonds. Earlier we had observed that complex formation of 2-[(dimethylamino)methyl]phenylcopper, which has a discrete R_4Cu_4 cluster structure, with metalIB halides gives organocopper—metal halide complexes which are insoluble and probably have a polymeric structure [4]. These two observations indicate that the type of built-in ligand attached to the phenyl nucleus of phenylcopper has a pronounced influence on the type of aggregates formed.

Both in the Me_2NCH_2 - and Me_2N-substituted arylcopper compounds the $Me_2NCH_2C_6H_4$ and the $Me_2NC_6H_4$ group can act as a bidentate ligand (carbon—copper 2e—3c interaction and nitrogen—copper coordination bond). However, the modes of coordination of these ligands will be different. In the Me_2NCH_2 - substituted phenylcopper compound, the $2\text{-}Me_2NCH_2C_6H_4$ group can coordinate to the same copper atom leading to a 5-membered chelate ring (see A). For the Me_2N-substituted phenylcopper steric factors require that N—Cu coordination takes place with a different copper atom to which the aryl group is not bonded (see B*).



(A, R'_4Cu_4, $R'_4Me_2Li_2$

$R = 2\text{-}Me_2NCH_2C_6H_4$—)



(B, $R_4Cu_6X_2$, R_nCu_n

$R = 2\text{-}Me_2NC_6H_4$—)

Structural unit A occurs in the discrete clusters R'_4Cu_4 [14] and in the mixed metal clusters $R'_4M_2Li_2$ (M = Cu, Ag or Au) [21]. Structural unit B, which occurs in $R_4Cu_6X_2$, accounts for the polymeric nature of the organocopper R_nCu_n [6].

The fact that electronic effects (mesomeric and inductive), as well as the strength of the Cu—built-in ligand coordination bond, influence the aggregation state, is demonstrated by the fact that upon substitution of MeO for NMe_2 structural unit B is less stable. From the reaction of $2\text{-}MeOC_6H_4Cu$ with CuBr solids with different stoichiometries (e.g. mRCu • nCuBr**; m/n = 2/1, 3/1, 5/1) have been isolated [9] instead of a complex with $R_4Cu_6Br_2$ stoichiometry.

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* In $Cu_4[(i\text{-}C_3H_7O)_2PS_2]_4$ the $(i\text{-}C_3H_7O)_2PS_2^-$ ligand acts similarly as a bidentate; i.e. one of the sulphur atoms bridges almost symmetrically two copper atoms of the central copper tetrahedron while the other sulphur atom forms a bond with a third copper atom [22].

** NMR spectroscopy of these solids indicates that in solution different aggregates, which are in equilibrium via interaggregate exchange, are present.

Experimental (with Mr. C.A. Schaap)

General

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use under nitrogen.

^{1}H NMR spectra, which were run by Mrs. L. van der Grift-Veldstra, were recorded on a Varian Associates HA-100 NMR spectrometer. IR spectra which were run by Mrs. H. de Ridder-Alberda and Mrs. G.M. Bijlsma-Kreuger, were recorded on a Grubb—Parsons Spectromaster. Elemental analyses were carried out under the supervision of Mr. W.J. Buis in the Analytical Department of this Institute.

Bis[2-(dimethylamino)phenylcopper] cuprous bromide (II)

Via RLi (III) with CuBr. A solution of 2-(dimethylamino)phenyllithium [6] (III; 19.8 mmol) was added at —20°C to a suspension of cuprous bromide (39.6 mmol) in ether (40 ml). The mixture was stirred for ½ h at —20°C and for 2½ h at room temperature. The bright-red precipitate was filtered off and washed with ether (removal of LiBr). The resulting solid was recrystallized from hot (60°C) benzene. The crystals contained crystal-benzene when isolated directly from the benzene solution. (Found: Cu, 34.1; Br, 13.9. 2RCu · CuBr · 0.75 C_6H_6 calcd.: Cu, 33.50; Br, 14.04%.)

When the benzene solution was decanted from the crystals, and the crystals extracted with pentane (2 × 15 ml) complex II was isolated. Elemental analysis see Table 1. NMR data see Table 2. IR spectrum see Fig. 2.

Via RCu (I) with CuBr. A mixture of 2-(dimethylamino)phenylcopper [6] (I; 1.85 mmol) and CuBr (1.85 mmol) in ether (20 ml) was stirred for 170 h at room temperature. The ether was removed by evaporation at low pressure. The resulting red solid was extracted with benzene to give a grey-coloured residue (unreacted CuBr) and a red benzene extract. From this benzene extract a red, crystalline solid was obtained, which was indicated by its IR spectrum and copper analysis (found: Cu, 36.6. 2RCu · CuBr calcd.: Cu, 37.31%) to be almost pure II (71% yield).

Reaction of (II) with D_2O. The reaction of II (1.22 mmol) in benzene (10 ml) with D_2O (1 ml) at room temperature for 13 days afforded a yellow solution and red precipitate; the solution contained 55% of VI. After standing for 4 days in the atmosphere the content of VI rose to 70%. Subsequent treatment of the yellow-coloured solution with a 4 *N* HCl solution, followed by neutralization of the acidic layer and extraction of this layer with ether, gave a yellow oil. IR spectroscopy showed [6] this oil to be a mixture of 2-deuterio-*N*,*N*-dimethylaniline and *N*,*N*-dimethylaniline (absorption at 692 cm^{-1}).

Bis[2-(dimethylamino)phenylcopper] cuprous iodide (V)

The synthesis of complex V was carried out as described for the CuBr complex II.

Bis[2-(dimethylamino)phenylcopper] cuprous chloride (VI)

Via RLi (III) with CuCl. A solution of 2-(dimethylamino)phenyllithium (III; 18.5 mmol) in ether was added at —20°C to a suspension of CuCl (37 mmol)

TABLE 3

NMR DATA FOR THE $R_4Cu_{6-n}Ag_nBr_2$ COMPLEXES VII, IX and X

Compound	Chemical shift δ (ppm)[a]	
	NMe	H_6[b]
VII; $R_4Ag_2Cu_4Br_2$	1.83[d] (s, br) 2.1-2.7 (vbr) 2.94[d] (s, br)	8.4-8.55 (m)
IX; $R_4Ag_6Br_2$[c]	2.42 (s, 6H)	8.15-8.35 (vbr, 1H)
X; $R_4Ag_4Cu_2Br_2$[c]	1.94[d] (s, br) 2.1-2.8 (vbr) 2.42[e] (s) 2.94[d] (s, br)	8.2-8.4[e] (vbr) 8.4-8.6 (m)

[a] TMS internal; C_6D_6; room temperature. [b] Proton *ortho* with respect to the M—C bond. [c] See ref. 5. [d] Peak area ratio of singlets ≈1/1. [e] Weak signals.

in ether (50 ml). The black-coloured mixture was stirred for 2 h at —20°C and for 6 h at room temperature. The precipitate was filtered off, washed with ether (3 × 20 ml; removal of LiBr) and dried in vacuo and gave a red-brown solid. This solid was extracted with benzene (2 × 100 ml). Concentration of the benzene filtrate gave an orange solid which was washed with pentane (2 × 15 ml) and dried in vacuo (yield 30%). Elemental analysis indicated that the product was a mixture of the CuBr and the CuCl complex. (Found: C, 36.9; H, 4.0; N, 5.4; Br, 15.4; Cl, 0.8; Cu, 36.3. 2RCu · CuBr/2RCu · CuCl molar ratio 8.4/1 calcd.: C, 37.97; H, 3.98; N, 5.54; Br, 14.11; Cl, 0.74; Cu, 37.66%.) Decomposition starts at 191—193°C; total dec. at 204°C.

Via RCu (I) with CuCl. The reaction of *pure* 2-(dimethylamino)phenylcopper (I; 5.22 mmol) with cuprous chloride (5.22 mmol) in benzene (50 ml) gave in 80% yield IV as an orange crystalline solid. Reaction time 14 days. Elemental analysis see Table 1. NMR data see Table 2. IV decomposes at 181—183°C.

Bis[2-(dimethylamino)phenylcopper] silver bromide (VII)

In a typical experiment a mixture of pure I (2.29 mmol) and silver bromide (2.29 mmol) in benzene (15 ml) was stirred at room temperature (in the dark) for 21 days. The light-brown precipitate was filtered off and washed with benzene (25 ml). The remaining brown solid was recrystallized from benzene (2 × 60 ml). The benzene extract was concentrated to about 10 ml; addition of pentane (10 ml) gave light-brown VII in 70% yield. Elemental analysis see Table 1. NMR data see Table 3.

Exchange reaction of 2RCu · CuCl (IV) with LiI

Solid lithium iodide [23] (0.815 mmol) was added to a suspension of 2RCu · CuCl (IV) (0.815 mmol) in ether (25 ml). This mixture was stirred at room temperature during 120 h. The ether was evaporated and the residue extracted with benzene (45 ml). The benzene extract was concentrated to give orange, crystalline 2RCu · CuI (V) in quantitative yield. (Found: C, 35.4; H, 3.7; N, 5.1; I, 22.1. $C_{16}H_{20}N_2Cu_3I$ calcd.: C, 34.45; H, 3.61; N, 5.02; I, 22.75.)

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