Journal of Organometallic Chemistry, 325 (1987) 293–309
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

8-(DIMETHYLAMINO)NAPHTHYLCOPPER(I), A NOVEL STABLE ORGANOCOPPER COMPOUND WITH UNUSUAL STRUCTURAL FEATURES. ITS SYNTHESIS, CRYSTAL STRUCTURE (X-RAY), AND REACTIVITY *

ERIK WEHMAN [a], GERARD VAN KOTEN [a]*, MARTIN KNOTTER [a], HANS SPELTEN [a], DICK HEIJDENRIJK [b], ADRIANUS N.S. MAK [b], and CASPER H. STAM [b]

Anorganisch Chemisch Laboratorium [a] *and Laboratorium voor Kristallografie* [b], *J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)*

(Received December 12th, 1986)

Summary

The synthesis and isolation of a hydrocarbon- and ether-insoluble organocopper compound containing the rigid 8-(dimethylamino)naphthyl group is described. An X-ray determination of its structure revealed a tetranuclear copper aggregate, in which the Cu atoms are arranged in a parallelogram (Cu... Cu 2.407(2) and 2.430(2) Å) and are three-center, two-electron bridged by C(*ipso*) (Cu–C 2.025(6) Å mean) of the naphthyl group. The amine ligands coordinate pairwise to opposite copper atoms. The copper aggregate thus contains two distinct types of Cu atoms, involving two nucleophilic two-coordinate and two electrophilic four-coordinate sites, pointing to a strong cuprate character. Reaction of the organocopper compound with several copper(I) salts resulted either in the formation of binaphthyl and dimethylaminonaphthalene or a stable mixed copper cluster, depending on the anion in the copper salt. With dimethyl acetylenedicarboxylate the copper compound, without added lithium or magnesium salts, gave the (*syn*) addition product 8-Me_2NnaphthylC(CO_2Me)=C(CO_2Me)Cu. These reactions are discussed in relation to the structural features of the tetranuclear organocopper compound.

Introduction

Structural knowledge of organocopper(I) compounds is of fundamental importance when considering mechanistic aspects of (organo)copper-mediated reactions [1]. A distinction in structural features can be drawn between alkyl- and aryl-copper compounds on the one hand and alkynylcopper compounds on the other. The

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* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

0022-328X/87/$03.50

structural components of the alkyl- and aryl-copper compounds, which show many similarities, are to a large extent determined by steric influence of the organic ligand, while for the alkynylcopper compounds the additional interaction of the alkyne triple bond with copper also plays an important role [1]. Because of the greater thermal stability of arylcopper compared to alkylcopper compounds, more attention has been paid to the former.

Common features for the structurally characterized organocopper compounds are: (i) a strong tendency to form aggregated species, and (ii) the presence of multi-center copper–carbon bonding, usually involving a three-center, two-electron bonding mode.

Studies on structures of arylcopper compounds have been mainly confined to phenylcopper and methyl-substituted phenylcopper derivatives [2], and to arylcopper derivatives with *ortho* substituents containing heteroatoms (e.g. NMe_2, CH_2NMe_2, OMe, oxazoline) [3], which make these substituents potentially coordinating. Although the heteroatom-substituted arylcopper compounds and the simple phenylcopper compounds have many common structural features, a distinct influence of the heteroatom group on the structure of the former type was observed. In this respect the type of chelation by the aryl C(*ipso*) atom and the heteroatom of the substituent was shown to be an especially important factor. Since much research in organocopper chemistry is directed to the synthesis of natural products [4], which often possess heteroatom containing substituents, knowledge of the influence of potentially coordinating groups built into the organocopper molecules is very relevant.

To examine the influence of the heteroatom containing substituent in more detail we have studied the synthesis, structural features and properties of 8-(dimethylamino)naphthylcopper. In this compound the NMe_2 group is in a fixed position relative to the copper–carbon bond (see Fig. 1b) and the nitrogen donor atom is

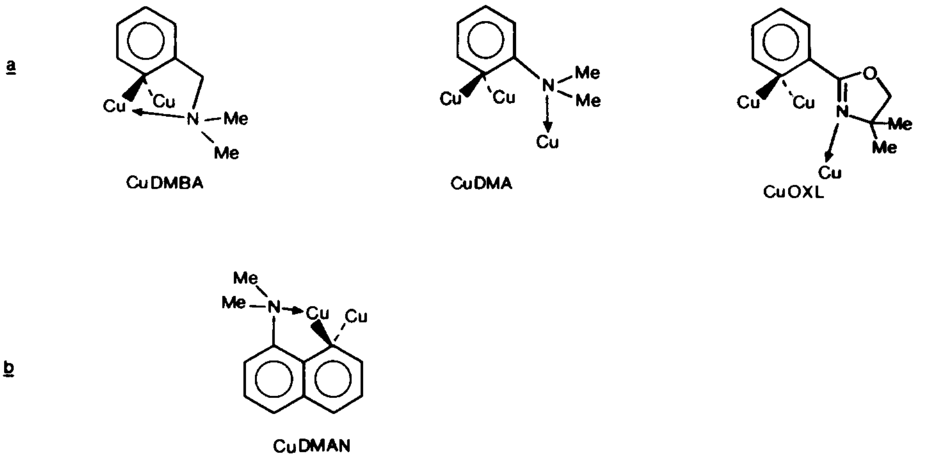


Fig. 1. Bonding modes of several aryl groups bearing heteroatom substituents. Note the differences between chelate rings formed (number and hybridisation of the chelate ring atoms). DMBA = 2-{(Dimethylamino)methyl}phenyl; DMA = 2-(Dimethylamino)phenyl; OXL = 2-(4,4-Dimethyl-2-oxazoline)phenyl; DMAN = 8-(Dimethylamino)naphthyl.

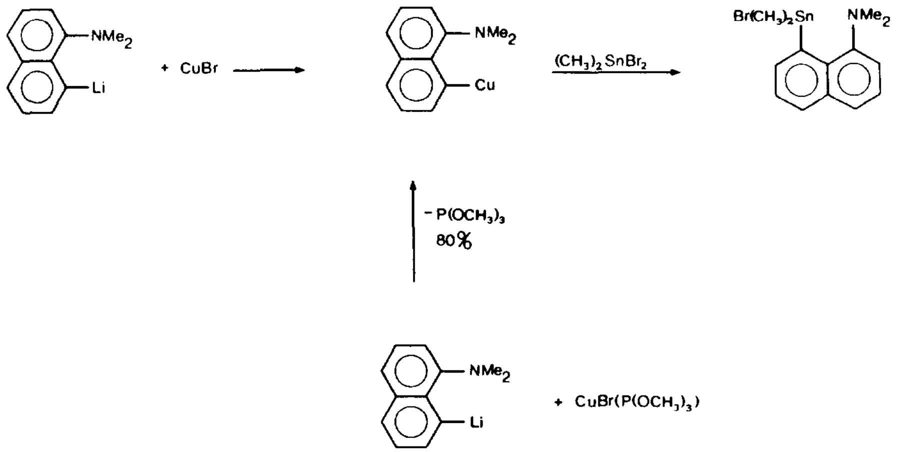
almost inevitably involved in coordination to the metal. This situation contrasts with the flexibility of the ligand systems shown in Fig. 1a, which leaves the heteroatom-containing substituent with the possibility of also acting as a non-coordinating *ortho* substituent. The results are discussed in relation to those for previously characterized arylcopper compounds and the structures of phenylcopper derivatives.

Results and discussion

Synthesis of 8-(dimethylamino)naphthylcopper(I)

The reaction of 8-(dimethylamino)naphthyllithium (**1**) (Li(DMAN)) * with one equivalent of CuBr in diethyl ether gave a diethyl ether insoluble, light-yellow compound **2**, which from elemental analysis appears to have the stoichiometry Cu(DMAN). The reaction of **2** with Me_2SnBr_2 afforded the white compound **3**, whose ^1H NMR spectrum was identical to that reported for $Me_2Sn(DMAN)Br$ [5]. This indicated that in compound **2** a copper–carbon bond is present at the 8 position of the naphthyl ring.

For the synthesis of Cu(DMAN) the order of mixing of the reactants is important, and a pure product could only be obtained when solid CuBr was slowly added to a suspension of Li(DMAN) (**1**) in diethyl ether. When Li(DMAN) (**1**) was added to a suspension of CuBr the mixture rapidly turned black and no Cu(DMAN) could be isolated. Moreover, the degree of success in the synthesis of **2** appeared to be very dependent on the scale of the reaction and the conditions; it was obtained in a yield of ca. 20% when the reaction was carried out starting from ca. 1 g of CuBr, but in larger scale reactions the yield of Cu(DMAN) was much lower, and it was impossible to obtain pure Cu(DMAN). Similar problems arose when the reaction time was too long, and with reaction times of more than 2 h it was not possible to isolate pure **2**. A much better synthesis of Cu(DMAN) involved the 1 : 1 reaction of



SCHEME 1

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* For the abbreviations used throughout this paper, see legend to Fig. 1.

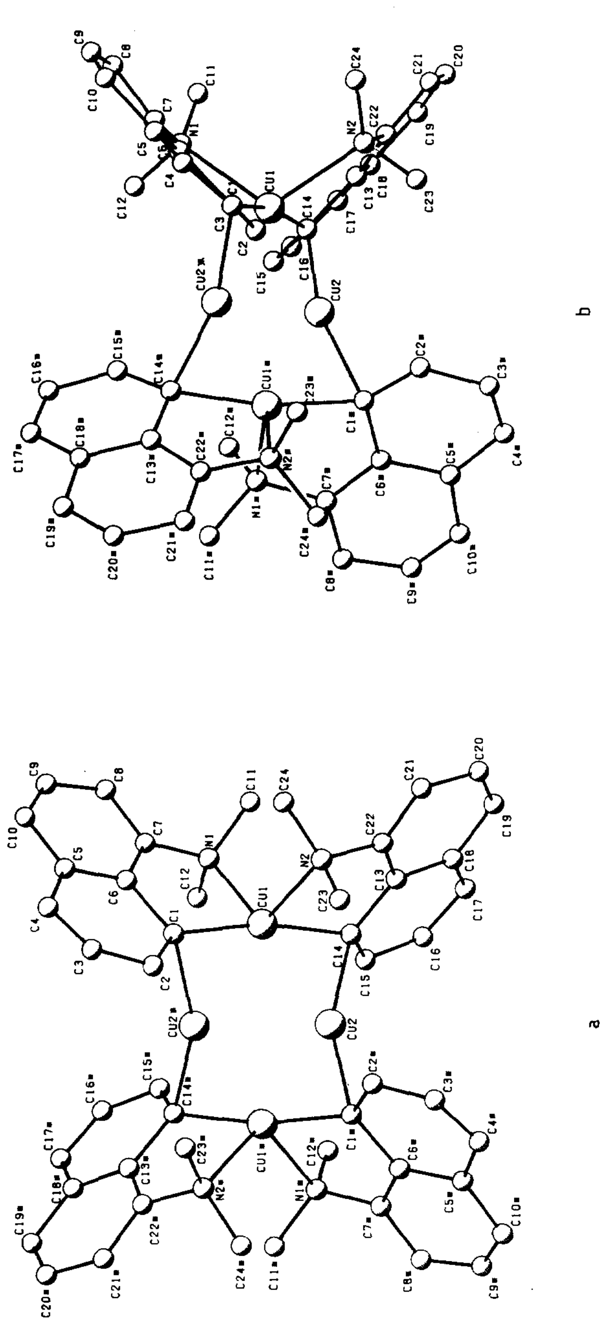


Fig. 2. Molecular structure of $Cu_4(DMAN)_4$; (a) projection at the Cu_4 parallelogram, (b) projection through the side of two naphthyl groups.

a suspension of Li(DMAN) in diethyl ether with a solution of CuBr{P(OMe)$_3$} in benzene; this procedure afforded Cu(DMAN) in yields of up to 80%, with the advantage that it could also be carried out on a much larger scale (e.g. starting from 10 g of Li(DMAN)). It is noteworthy that in this reaction (see eq. 1) P(OMe)$_3$ is

$$\mathrm{CuBr\{P(OMe)_3\} + Li(DMAN) \rightarrow Cu(DMAN) + P(OMe)_3 + LiBr} \tag{1}$$

liberated, and pure uncomplexed Cu(DMAN) is obtained, although it is known that arylcopper compounds can react with several kinds of donor ligands [6]. The better results obtained in this reaction are probably the result of the use of more homogeneous conditions. CuBr{P(OMe)$_3$} is added as a solution in benzene, which can also dissolve some of the organolithium reagent. In contrast, the reaction of CuBr with Li(DMAN) in diethyl ether, in which they are both insoluble, is completely heterogeneous; an additional factor in this case is the further reaction of the formed Cu(DMAN) with CuBr (vide infra).

Solid state structure of Cu(DMAN) (2)

Cu(DMAN) is insoluble in common organic solvents such as diethyl ether, THF, benzene and toluene, and because of this it was not possible to obtain an ^{1}H NMR spectrum of **2** or to crystallize it from one of these solvents. However, crystals of **2** were obtained by carrying out the reaction of Li(DMAN) with CuBr{P(OMe)$_3$} very slowly in benzene (see Experimental section). Unfortunately, attempted isolation of the dry crystals resulted in their rapid conversion into powders, probably as a result of loss of incorporated solvent. Mounting of a benzene-wetted crystal in a capillary which, filled with paraffin oil containing benzene enabled us to carry out the X-ray crystal structure determination.

The determined structure consists of a tetrameric organocopper cluster, Cu$_4$(DMAN)$_4$, the molecular geometry of which, along with the adopted numbering scheme, is shown in Fig. 2a. The tetramer has a crystallographic two-fold rotation axis. The four copper atoms are all in one plane and form a parallelogram, with the naphthylamine groups symmetrically bridging the copper–copper edges, via C(*ipso*) in a three-center two-electron bonding mode. The naphthyl groups point alternately above and below the plane of the copper atoms (see Fig. 2b). The copper–copper distances for adjacent copper atoms are 2.430(2) and 2.407(2) Å, respectively, while the copper–copper distances of opposite copper atoms are significantly longer, namely 2.708(2) and 3.988(2) Å. The distances found for the adjacent copper atoms are in the range expected for copper atoms bridged by one-electron organo groups [1]. The symmetrical bridging mode of the copper bonded carbon atoms is indicated by the almost equal copper–carbon bond distances of C(14) to Cu(1) and Cu(2) and of C(1) to Cu(1) and Cu(2*), which are in the range 2.019(9)–2.076(9) Å. Two different copper atom types can be distinguished in the tetramer. The first set of copper atoms (Cu(1) and Cu(1*)) is attached to C(*ipso*) of the naphthyl groups as well as to two dimethylamino substituents (Cu–N distances 2.243(8) and 2.269(7) Å). The second set is coordinated only to C(*ipso*) of the naphthyl groups, thus giving rise to a C(*ipso*)–Cu–C(*ipso*) coordination with a bond angle of 154.9(5)°, slightly deviating from the value of 164° expected for a copper center involved exclusively in two three-centre two-electron copper–carbon bonds [7].

TABLE 1

FRACTIONAL COORDINATES OF THE NON-HYDROGEN ATOMS [a]

Atom	x	y	z
Cu(1)	0.03766(7)	0.19433(5)	0.27098(10)
Cu(2)	−0.05494(8)	0.23227(5)	0.27011(11)
N(1)	0.1058(5)	0.1715(3)	0.1852(6)
N(2)	0.0146(5)	0.1439(3)	0.3566(6)
C(1)	0.1076(5)	0.2230(4)	0.3220(8)
C(2)	0.1103(6)	0.2444(4)	0.3925(8)
C(3)	0.1656(8)	0.2517(5)	0.4314(9)
C(4)	0.2188(7)	0.2382(5)	0.3990(9)
C(5)	0.2192(6)	0.2142(4)	0.3288(10)
C(6)	0.1632(6)	0.2062(4)	0.2903(8)
C(7)	0.1624(6)	0.1795(4)	0.2237(8)
C(8)	0.2149(6)	0.1612(5)	0.1973(10)
C(9)	0.2701(7)	0.1710(5)	0.2370(11)
C(10)	0.2723(6)	0.1969(5)	0.2981(10)
C(11)	0.0960(8)	0.1282(4)	0.1608(11)
C(12)	0.1003(7)	0.1984(5)	0.1133(8)
C(13)	−0.0540(5)	0.1360(4)	0.2431(8)
C(14)	−0.0393(5)	0.1770(4)	0.2168(7)
C(15)	−0.0601(6)	0.1887(4)	0.1422(8)
C(16)	−0.0978(6)	0.1633(4)	0.0951(8)
C(17)	−0.1124(6)	0.1252(5)	0.1205(9)
C(18)	−0.0915(6)	0.1105(4)	0.1946(9)
C(19)	−0.1040(8)	0.0696(5)	0.2230(11)
C(20)	−0.0801(9)	0.0540(5)	0.2891(11)
C(21)	−0.0392(8)	0.0782(4)	0.3372(10)
C(22)	−0.0270(6)	0.1187(4)	0.3131(8)
C(23)	−0.0171(7)	0.1628(4)	0.4239(8)
C(24)	0.0684(7)	0.1215(5)	0.3864(9)
C(25)★	0.210	0.070	−0.026
C(26)★	0.196	0.112	−0.035
C(27)★	0.236	0.141	−0.009
C(28)★	0.290	0.131	0.026
C(29)★	0.304	0.090	0.035
C(30)★	0.264	0.059	0.009
C(31)	0.132	−0.018	0.272
C(32)	0.185	−0.036	0.294
C(33)	0.239	−0.018	0.272
C(34)	0.238	0.054	0.463
C(35)	0.224	0.091	0.426
C(36)	0.238	0.128	0.463
C(37)	−0.057	0.512	−0.021
C(38)	−0.007	0.531	−0.056
C(39)	0.049	0.518	−0.034

[a] ★: Population parameter 0.5.

The arrangement of the copper atoms in a parallelogram is unprecedented in organocopper chemistry, and the presence of two two-coordinated and two four-coordinated copper(I) atoms is highly unusual. Previously reported tetrameric organocopper compounds viz. $Cu_4(CH_2SiMe_3)_4$ [8] and $Cu_4(C_6H_2Me_3)_4L_2$ [2a], show square-planar arrangements. Similar square-planar arrangements of the copper

TABLE 2

BOND DISTANCES (Å) WITH STANDARD DEVIATIONS IN PARENTHESES [a]

Cu(1)–Cu(2)	2.407(2)	C(3)–C(4)	1.38(2)
Cu(1)–Cu(1★)	3.988(2)	C(4)–C(5)	1.438(16)
Cu(1)–Cu(2★)	2.430(2)	C(5)–C(6)	1.436(13)
Cu(1)–N(1)	2.243(8)	C(5)–C(10)	1.413(14)
Cu(1)–N(2)	2.269(7)	C(6)–C(7)	1.440(13)
Cu(1)–C(1)	2.019(9)	C(7)–C(8)	1.389(14)
Cu(1)–C(14)	2.032(8)	C(8)–C(9)	1.444(16)
Cu(2)–Cu(2★)	2.708(2)	C(9)–C(10)	1.35(2)
Cu(2)–C(14)	2.055(8)	C(13)–C(14)	1.450(12)
Cu(2★)–C(1)	2.076(9)	C(13)–C(18)	1.444(13)
N(1)–C(7)	1.445(12)	C(13)–C(22)	1.459(14)
N(1)–C(11)	1.494(13)	C(14)–C(15)	1.414(13)
N(1)–C(12)	1.520(13)	C(15)–C(16)	1.431(13)
N(2)–C(22)	1.448(12)	C(16)–C(17)	1.359(15)
N(2)–C(23)	1.489(13)	C(17)–C(18)	1.437(15)
N(2)–C(24)	1.496(13)	C(18)–C(19)	1.452(15)
C(1)–C(2)	1.399(13)	C(19)–C(20)	1.35(2)
C(1)–C(6)	1.460(12)	C(20)–C(21)	1.46(2)
C(2)–C(3)	1.423(15)	C(21)–C(22)	1.413(14)

[a] ★: Symmetry operation $-x$, $1/2-y$, z.

atoms have been established in other copper compounds containing bridging anionic ligands, such as $Cu_4(NEt_2)_4$ [9], and $Cu_4(OtBu)_4$ [10]. Square-planar based structures have also been found for $[Cu_4(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}5)_4]$ [3b] and $[Cu_4\{(4\text{-}MeC_6H_4)MeC{=}C(C_6H_4NMe_2\text{-}2)\}_2(C_6H_4NMe_2\text{-}2)\}$ [11], which were shown to possess a butterfly arrangement of the Cu atoms. A planar arrangement can probably be regarded as the basic framework of most tetranuclear copper compounds and, deviations from this framework may result either from special steric requirements or from the presence of coordinating groups in the ligands attached to the copper atoms (vide infra). As a consequence, the structure of $Cu_4(DMAN)_4$ might be better described as a distorted planar arrangement of the copper atoms; the square plane being distorted by the presence of the coordinating groups at the aryl group towards formation of a parallelogram in **2** or towards a butterfly arrangement in $Cu_4(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}5)_4$ [3b].

The naphthyl ring is positioned perpendicular to the Cu–Cu edge, a feature commonly found in arylcopper compounds [1]. The Cu–N distances of 2.243(8) and 2.269(7) Å, are in the range found for related organocopper compounds containing a sp^3-N–Cu bond [3b,11,12]. The coordination of the dimethylamino groups to copper atoms Cu(1) and Cu(1★) is clearly revealed by the tetrahedral geometry of the nitrogen atoms; in related compounds containing non-coordinating dimethylamino groups it was observed that this group was coplanar with the aromatic ring [11]. A peculiar feature of this copper–nitrogen coordination is the observed pairwise coordination of the NMe_2 groups, which makes Cu(1) and Cu(1★) four-coordinate.

The structures of $Cu_4(DMAN)_4$ and of the organocuprate $Cu_2Li_2(DMBA)_4$ [3b] show striking similarities (see Fig. 3). In the cuprate structure the dimethylamino substituents are coordinated pairwise to the electrophilic sites of the mole-

TABLE 3

BOND ANGLES (°) WITH STANDARD DEVIATIONS IN PARENTHESES [a]

Cu(2)–C(1)–Cu(2★)	68.1(1)	Cu(2★)–C(1)–C(6)	125.7)7)
Cu(2)–Cu(1)–N(1)	138.4(2)	C(2)–C(1)–C(6)	118(1)
Cu(2)–Cu(1)–N(2)	100.6(3)	C(1)–C(2)–C(3)	122(1)
Cu(2)–Cu(1)–C(1)	115.2(3)	C(2)–C(3)–C(4)	120(1)
Cu(2)–Cu(1)–C(14)	54.4(3)	C(3)–C(4)–C(5)	121(1)
Cu(2★)–Cu(1)–N(1)	102.5(3)	C(4)–C(5)–C(6)	119(1)
Cu(2★)–Cu(1)–N(2)	139.2(2)	C(4)–C(5)–C(10)	122(1)
Cu(2★)–Cu(1)–C(1)	54.7(3)	C(6)–C(5)–C(10)	119(1)
Cu(2★)–Cu(1)–C(14)	114.0(3)	C(1)–C(6)–C(5)	120(1)
N(1)–Cu(1)–N(2)	109.7(4)	C(1)–C(6)–C(7)	121(1)
N(1)–Cu(1)–C(1)	85.2(5)	C(5)–C(6)–C(7)	119(1)
N(1)–Cu(1)–C(14)	100.3(5)	N(1)–C(7)–C(6)	119(1)
N(2)–Cu(1)–C(1)	103.3(5)	N(1)–C(7)–C(8)	120(1)
N(2)–Cu(1)–C(14)	84.4(5)	C(6)–C(7)–C(8)	121(1)
C(1)–Cu(1)–C(14)	168.5(4)	C(7)–C(8)–C(9)	118(1)
Cu(1)–Cu(2)–C(14)	53.4(3)	C(8)–C(9)–C(10)	122(1)
Cu(1)–Cu(2)–C(1★)	147.7(4)	C(5)–C(10)–C(9)	121(1)
Cu(1)–Cu(2)–Cu(1★)	111.9(1)	C(14)–C(13)–C(18)	119(1)
C(1★)–Cu(2)–Cu(1★)	52.6(4)	C(14)–C(13)–C(22)	121(1)
C(14)–Cu(2)–C(1★)	154.9(5)	C(18)–C(13)–C(22)	119(1)
C(14)–Cu(2)–Cu(1★)	147.6(3)	Cu(1)–C(14)–Cu(2)	72.2(5)
Cu(1)–N(1)–C(7)	103.3(7)	Cu(1)–C(14)–C(13)	107.8(7)
Cu(1)–N(1)–C(11)	113.6(8)	Cu(1)–C(14)–C(15)	127.9(7)
Cu(1)–N(1)–C(12)	107.6(7)	Cu(2)–C(14)–C(13)	129.4(7)
C(7)–N(1)–C(11)	115(1)	Cu(2)–C(14)–C(15)	96(1)
C(7)–N(1)–C(12)	110(1)	C(13)–C(14)–C(15)	117(1)
C(11)–N(1)–C(12)	108(1)	C(14)–C(15)–C(16)	123(1)
Cu(1)–N(2)–C(22)	102.9(7)	C(15)–C(16)–C(17)	119(1)
Cu(1)–N(2)–C(23)	108.0(7)	C(16)–C(17)–C(18)	121(1)
Cu(1)–N(2)–C(24)	113.3(7)	C(13)–C(18)–C(17)	120(1)
C(22)–N(2)–C(23)	110(1)	C(13)–C(18)–C(19)	117(1)
C(22)–N(2)–C(24)	114(1)	C(17)–C(18)–C(19)	123(1)
C(23)–N(2)–C(24)	109(1)	C(18)–C(19)–C(20)	124(1)
Cu(1)–C(1)–Cu(2★)	72.8(5)	C(19)–C(20)–C(21)	121(1)
Cu(1)–C(1)–C(2)	129.8(7)	C(20)–C(21)–C(22)	117(1)
Cu(1)–C(1)–C(6)	108.6(8)	N(2)–C(22)–C(13)	118(1)
Cu(2★)–C(1)–C(2)	92(1)	N(2)–C(22)–C(21)	120(1)
		C(13)–C(22)–C(21)	122(1)

[a] ★: Symmetry operation $-x$, $1/2-y$, z.

cule, i.e. the lithium atoms in *trans* positions. The copper atoms are primarily bonded to C(*ipso*) and are two-coordinate. The coordination pattern of $\mathrm{Cu_4(DMAN)_4}$, with four-coordinate Cu(1) and Cu(1★) sites and two-coordinate Cu(2) and Cu(2★) suggests a similar distribution of electrophilic (Cu(1) and Cu(1★)) and nucleophilic (Cu(2) and Cu(2★)) sites.

The predominant structural factors governing formation of the basic $\mathrm{C}(ipso)_n\mathrm{Cu}_n$ framework seem to be the Cu–Cu and Cu–C distances. Irrespective of the type of cluster formed and of the aggregation state of the cluster, the C-bridged Cu–Cu distances and the Cu–C distances show only minor variations (see Table 4). It has been pointed out previously that the Cu–Cu distances in organocopper compounds are relatively short [13], although calculations revealed only a weak interaction

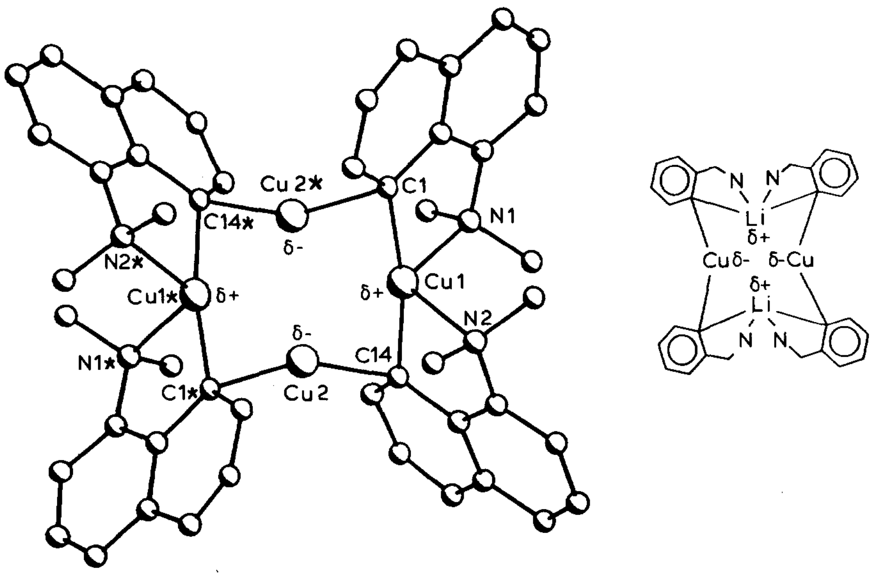


Fig. 3. Comparison of the structures of $Cu_4(DMAN)_4$ and $Cu_2Li_2(DMBA)_4$, with the electrophilic and nucleophilic sites indicated.

between the copper atoms [14]. The short Cu–Cu distances are mainly determined by the stereochemical demands of the bridging ligand, and can be best vizualized as a bridge-assisted Cu–Cu bond [13]. The bonding in organocopper compounds has been rationalized in terms of the MOs depicted in Fig. 4. MO I allows a weak interaction between the copper atoms, whereas II accounts for the perpendicular positioning of the aryl groups to the copper–copper edge. Special characteristics of

TABLE 4

MEAN C-BRIDGED Cu...Cu AND Cu–C DISTANCES FOR SOME REPRESENTATIVE ARYLCOPPER CLUSTERS

Compound [a]	Cu...Cu	Cu–C	Ref.
$Cu_5Ph_6^-$	2.452(4)	1.99(2)/2.19(2) [b]	[2b]
$Cu_4LiPh_6^-$	2.55(3)	1.96(4)/2.33(3) [b]	[2c]
$Cu_3Li_2Ph_6^-$		1.929(6)	[2d]
CuPh(triphos) [c]		2.020(4)	[6c]
Cu_5Mes_5	2.437(8)–2.469(9)	1.96(2)–2.06(2)	[2a]
$Cu_4Mes_4(THP)_2$ [c]	2.441(3)–2.449(2)	2.094(8)	[2a]
$CuMes_2^-$		1.915(9)	[6b]
$Cu_4(DMBA)_4$	2.383	1.97(2)–2.16(2)	[3b]
$Cu_4(DMAN)_4$	2.418(1)	2.045(4)	
$Cu_6(DMA)_4Br_2$	2.48	1.97–2.08	[3c]
$Cu_6(OXL)_4Br_2$	2.436(3)	2.031(3)	[3e]
$Cu_8(C_6H_4OCH_3)_8$	2.472(5)	2.04	[3f]

[a] For the abbreviations used in the Table, see legend to Fig. 1. [b] Phenyl groups are asymmetrically bridging a Cu...Cu side. [c] Triphos = 1,1,1-tris[(diphenylphosphino)methyl]ethane, THP = tetrahydrothiophene.

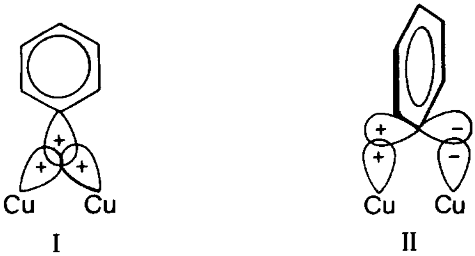


Fig. 4. Molecular orbitals involved in the 3c-2e copper carbon bonding.

the ligands, such as steric bulk or the presence of coordinating groups in the *ortho* position, then determine the actual structure formed.

The insolubility of some arylcopper compounds has been ascribed to formation of polymeric chains of arylcopper units [6,15], or, less probably, to the formation of complex salts such as $Cu^+ [R_2Cu]^-$ [16]. As can be concluded from the results for $Cu_4(DMAN)_4$, this insolubility does not necessarily imply a polymeric structure. In view of the strong tendency of the organocopper compounds to form discrete aggregates it might be questioned whether, for example, phenylcopper does have the polymeric structure proposed for it. Furthermore, the tendency to form discrete aggregates has also been observed in compounds closely related to phenylcopper [2], and therefore it seems reasonable to expect that phenylcopper would show a similar behaviour. A striking difference between PhCu and TolCu is the dramatic change in solubility, the former being insoluble and the latter showing good solubility. Analogous changes in solubility have been observed for some aryllithium compounds, which show many structural similarities to the arylcopper compounds. [2-({Dimethylamino}methyl)phenyllithium] (Li(DMBA)) is insoluble in ethers and benzene, whereas [2-({dimethylamino}methyl)-5-methylphenyllithium] (Li(5-MeDMBA)) is very soluble in these solvents. A tetranuclear structure was established by X-ray crystallography for Li(DMBA) [17], and this geometry was indicated by ^{13}C NMR spectroscopy to be retained in solution for Li(5-MeDMBA). Taking all these observations together, suggests that it is unlikely that the insolubility of some organocopper compounds can be ascribed to the formation of polymeric chains, and therefore it is very likely that these species exist as aggregates, with the insolubility possibly caused by charge separation within the aggregates.

Properties of $Cu_4(DMAN)_4$

Although $Cu_4(DMAN)_4$ is insoluble in common organic solvents such as ethers and hydrocarbons it is markedly soluble in dichloromethane. The stability of $Cu_4(DMAN)_4$ in the latter solvent was checked by stirring a solution of $Cu_4(DMAN)_4$ in CH_2Cl_2 overnight. The elemental analysis of the product isolated after work up was still in good agreement with pure $Cu_4(DMAN)_4$. A 100 MHz ^1H NMR spectrum of **2** in CD_2Cl_2 showed a broad signal for the dimethylamino group at 2.45 ppm, which split into a doublet at lower temperatures (δ 2.98 and 1.75 ppm; coalescence temperature 283 K [18]). This phenomenon was also observed for similar arylcopper compounds containing the prochiral built-in ligand CH_2NMe_2

[19], and was ascribed in these complexes to the existence of an equilibrium between a coordinated and a non-coordinated heteroatom substituent. Owing to the chirality of the copper aggregate [20] the NMe_2 group becomes diastereotopic when coordinated to the aggregate, whereas the fast pyramidal inversion at N [21] leaves the NMe_2 methyl groups homotopic when the group is not coordinated. From Fig. 2b it is obvious that the methyl groups of the coordinated NMe_2 substituent in $Cu_4(DMAN)_4$ are diastereotopic, and a dynamic process between coordinated and free NMe_2 groups could therefore also account for the observed fluxional behaviour in the 100 MHz ^1H NMR spectra of **2**. It cannot be decided from these spectra whether this occurs with retention of the Cu_4 cluster, but if it does, this process would, as a result of the changing Cu–N coordination, also lead to an interesting shift of the $Cu^+Cu^-Cu^+Cu^-$ charge separation through the Cu_4 array.

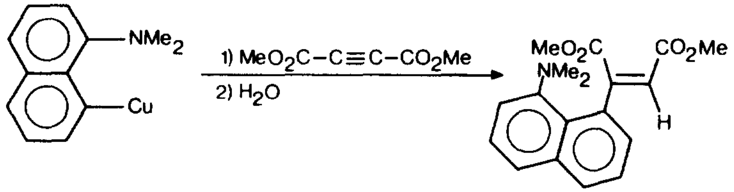
$Cu_4(DMAN)_4$ is a very stable organocopper compound which can be stored under nitrogen at room temperature for weeks. In the solid state it decomposes only slowly in air, but when suspended in a solvent the decomposition is much faster. Bubbling dry air through a suspension of $Cu_4(DMAN)_4$ in diethyl ether or benzene produced a mixture of $(DMAN)_2$ and DMAN-H. No indication of the presence of $8\text{-}Me_2NC_{10}H_6OH$ or the ether $8\text{-}Me_2NC_{10}H_6OC_{10}H_6NMe_2$ was found (cf. ref. 23).

Heating a solid sample of $Cu_4(DMAN)_4$ under N_2 (heating rate ca. 3°/min) revealed two distinct decomposition temperatures. At 145–150 °C black material was formed, and a second change, at 220 °C, produced a copper coloured residue. The enhanced stability of arylcopper compounds bearing heteroatom containing *ortho* substituents is reflected in the much higher decomposition temperatures of these species compared with those of phenylcopper and methyl-substituted phenylcopper compounds [1a]. The decomposition temperature of 145–150 °C is comparable with that reported for other organocopper compounds having a heteroatom-containing substituent in the *ortho* position [24]. Two distinct decomposition temperatures have been observed for some other organocopper compounds, and can be ascribed to a stepwise decomposition of the organocopper aggregate via a mixed valence cluster, as vizualized in eq. 2.

$$R_nCu^I_n \rightarrow R_{n-2}Cu^I_{n-2}Cu^0_2 + R_2 \tag{2}$$

Confirmation of the intramolecular C–C coupling process was obtained by heating **2** in mesitylene for 2 h, after which hydrolysis afforded a 1/2 mixture of RR and RH. Since no coupling products with mesitylene were found, a free radical mechanism for the coupling reaction can be excluded, and the product DMAN-H can be assumed to originate from hydrolysis of undecomposed $R_2Cu^I_2Cu^0_2$. Earlier examples of the proposed pathway depicted in eq. 2 are the isolation of a mixed Cu^ICu^0 cluster after thermolysis of $[\{3\text{-}(CF_3)C_6H_4\}_8Cu_8]$ [25] and the stepwise degradation of $[Cu_6(C_6H_4NMe_2\text{-}2)_4(C{\equiv}C(p\text{-}Tol))_2]$ [26].

Arylcopper compounds are known to react with phosphines, with cluster breakdown and formation of phosphine-complexed arylcopper compounds in a variety of stoichiometries [6]. For example, for $Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4$ complexation with DPPE was observed, followed by P–C bond cleavage of DPPE to give $Cu(PPh_2)(DPPE)$ and $Ph_2PCH{=}CH_2$ [27]. In contrast $Cu_4(DMAN)_4$ is unreactive towards PPh_3 and DPPE, probably because of the cuprate character of the copper tetramer. In this case the two-coordinate nucleophilic Cu sites do not have enough Lewis acid character for phosphine coordination, and it is evident that phosphine



SCHEME 2

coordination also cannot compete with the intramolecular coordination at the electrophilic sites. It is noteworthy that organocuprates are also unreactive towards phosphines [17].

$Cu_4(DMAN)_4$ shows a rather unusual reactivity for an organocopper reagent in its reaction with dimethyl acetylenedicarboxylate (DMADC). This reaction gave, after hydrolytic work up, a light-yellow oil of which the ^1H NMR spectrum indicated the presence of the DMAN moiety as well as showing two peaks for carboxylate methyl groups. At 6.20 ppm a single signal was observed, suggesting the presence of an olefinic proton. These observations point to addition of $Cu_4(DMAN)_4$ to the acetylene triple bond, and this was confirmed by the FD-mass spectrum of the isolated olefinic compound after hydrolysis (see Scheme 2). This reactivity is normally only observed for cuprate reagents or copper reagents to which lithium halides or magnesium halides have been added [28]. In such reactions, however, cuprate species are thought to be the reactive species [29]. In the light of the general pattern of reaction of cuprate reagents it is suggested that the reaction of $Cu_4(DMAN)_4$ with DMADC is a *syn* addition.

The reaction of $Cu_4(DMAN)_4$ with Cu^I salts either resulted in biaryl coupling or gave a stable mixed organo/organic copper cluster, depending on the anion. For example, reaction of $Cu_4(DMAN)_4$ with CuBr, CuBrL (L = $P(OMe)_3$, Me_2S) or CuOTf in benzene followed by hydrolysis of the product mixture gave $(DMAN)_2$ and DMAN-H. The ratio of RR/RH was influenced by the solvent used for the reaction; in benzene a mixture of RR and RH was obtained, whereas the reaction in dichloromethane afforded only RR (see Table 5). RR was also formed in 80% yield by an independent route involving the reaction of Li(DMAN) with $CuCl_2$. Reaction of $Cu_4(DMAN)_4$ with copper tolylcarboxylates yielded stable copper compounds,

TABLE 5

RATIO OF RR vs. RH FROM THE REACTION OF $Cu_4(DMAN)_4$ WITH COPPER(I) SALTS IN BENZENE [a] AFTER HYDROLYSIS

Reagent	%RR [b]	%RH [b]
CuO_2Ctolyl-*m* [c]	0	0
CuBr	76	24
$\frac{1}{2}$CuBr	58	42
CuBr (in CH_2Cl_2)	100	0
$CuBr[P(OMe)_3]$	68	32
$CuBr(SMe_2)$	85	15
CuOTf	50	50

[a] Unless stated otherwise. [b] Calculated on R (= DMAN) in $Cu_4(DMAN)_4$. [c] Resulted in the formation of a stable complex $Cu_3(DMAN)_2(O_2C$tolyl-*m*), see Fig. 5.

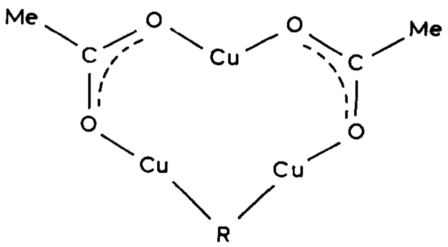


Fig. 5. Proposed general structure for aryl/carboxylatocopper clusters with a three-centre, two-electron bonded aryl group and bridging carboxylate groups.

but these could not be characterized spectroscopically owing to their insolubility after isolation. An elemental analysis carried out on the product obtained from the reaction of $Cu_4(DMAN)_4$ with Cu-*m*-tolylcarboxylate corresponded to a carboxylate to DMAN ratio of 2/1. On the basis of the crystal structure of an analogous organo/organic copper cluster [30], the general structure shown in Fig. 5 can be proposed. It is important to note, that these reactions do not result in C–C coupled and reduced products, but instead afford new stable copper aggregates.

The formation of biaryls upon reaction of RCu with CuX has been reported previously for $[Cu_4(C_6H_4Me\text{-}3)_4]$ with CuOTf [31]. The C–C coupling in this reaction was suggested to proceed via $(p\text{-Tol})_4Cu_4Cu(OTf)$ clusters in which valence disproportionation to Cu^0 and Cu^{II} biaryl centers occurs. This valence disproportionation is triggered by the presence of electron accepting anions and promoted by aryl groups containing substituents with hard donor atoms that can stabilize the Cu^{II} state by coordination. From the Cu^{II} biaryl centers, biaryls are formed by subsequent reductive elimination. The structural features of $Cu_4(DMAN)_4$, with the electrophilic four-coordinate and nucleophilic two-coordinate Cu sites (see Fig. 3) suggest that a process of the type described above leads to oxidative coupling at the electrophilic site, even when there is only a weak interaction of the cluster with copper salts. It must be noted, however, that the formation of stable clusters from the reaction of several arylcopper compounds with CuBr is documented [3c,3e]. The reaction of $Cu_4(DMAN)_4$ with copper carboxylates produces new cluster structures in which the features of $Cu_4(DMAN)_4$ which lead to easy binaphthyl formation are no longer present (see Fig. 5). In this reaction no binaphthyl is formed, confirming the important role of the anion in the Cu^I salts when these interact with organocopper cluster compounds.

The reaction of two equivalents of Li(DMAN) with CuBr or CuCN gave pale yellow compounds, which, according to their elemental analysis, were the organocuprate compounds. Owing to the insolubility of both compounds, they were not further characterized. Surprisingly, the R_2CuLi cuprate could not be synthesized from the reaction of $Cu_4(DMAN)_4$ with Li(DMAN) in benzene; this unusual behaviour is probably a result of the insolubility of the reactants, which prevents the interaggregate exchange (c.f. the formation of $Cu_2Li_2(DMBA)_4$ via such an exchange between $Li_4(DMBA)_4$ and $Cu_4(DMBA)_4$ [17]).

Experimental

Syntheses were carried out by use of standard Schlenk techniques and an atmosphere of purified nitrogen. The solvents were dried before use. The following compounds were prepared by published methods: [Li(DMAN)(OEt$_2$)] [32], CuBr [33], Cu(O$_2$CR) [34], CuBr{P(OMe)$_3$} [35].

The ^{1}H NMR spectra were recorded on a Bruker AC 100 spectrometer. Elemental analyses were carried out at the section for Elemental Analysis of ITC/TNO Zeist, The Netherlands.

Synthesis of Cu(DMAN) with CuBr

To a suspension of 1.4 g of Li(DMAN)(OEt$_2$) (5.6 mmol) in diethyl ether (100 ml) at −20 °C was slowly added (in 1 h) 0.8 g of CuBr (5.6 mmol). The yellow suspension was stirred for a further 30 min at −20 °C and then 1 h at room temperature. The yellow precipitate was filtered off, washed with 5 portions of diethyl ether (25 ml each), and dried in vacuo, to give 0.25 g of a yellow solid. Yield: 20%. ^{1}H NMR CD_2Cl_2, 296 K: δ 8.50 (1H, dd, ^3J(HH) 6.2 Hz, ^4J(HH) 1.3 Hz; H(7)), 7.86 (5H, m, Ar–H), 2.45 (6H, b, NMe$_2$) ppm. CD_2Cl_2, 233 K: δ 8.50 (1H, dd, ^3J(HH) 6.2 Hz), 7.51–7.20 (5H, m, Ar–H), 2.98 (3H, s, NMe), 1.75 (3H, s, NMe) ppm. Elemental analysis: found: C, 60.26; H, 5.19; N, 5.50; Cu, 26.40. $C_{12}H_{12}NCu$ calcd.: C, 61.65; H, 5.19; N, 5.99; Cu, 27.17%.

Synthesis of Cu(DMAN) with CuBr{P(OMe)$_3$}

To a suspension of 14 g of Li(DMAN)(OEt$_2$) (56 mmol) in diethyl ether (500 ml) was added dropwise a solution of 15 g of CuBr{P(OMe)$_3$} (56 mmol) in benzene (120 ml). The yellow suspension was stirred for 2 h at room temperature and the light-yellow precipitate then filtered off, washed with diethyl ether (5 × 50 ml), and dried in vacuo, to give 10.5 g of a yellow solid. Yield: 80%.

Reaction of Cu(DMAN) with Me_2SnBr_2

To a suspension of 620 mg of Cu(DMAN) (2.66 mmol) in benzene (50 ml) was added 820 mg of Me_2SnBr_2 (2.66 mmol) in diethyl ether (5 ml). The white suspension was stirred for 30 min and subsequently evaporated to dryness to give 900 mg of a white solid. Yield SnMe$_2$(DMAN)Br: 85%. ^{1}H NMR ($C_6D_5CD_3$): δ 6.6–7.6 (6H, Ar), 1.89 (s, 6H, NMe$_2$), 0.61 (s, 6H, SnMe$_2$: ^2J(^{117,119}Sn, H) 66, 63 Hz) ppm (cf. ref. 5).

Reaction of Cu(DMAN) with CuX (X = Br, OTf) and CuBr (L = P(OMe)$_3$ and Me$_2$S)

To a suspension of 0.5 g of Cu(DMAN) (2.14 mmol) in benzene (50 ml) was added 1 equiv. of CuX or CuBrL. The mixture was stirred overnight and then poured into a solution of 10% of NH_4Cl/NH_4OH (ca. 50 ml). The organic layer was washed with two 50 ml portions of 10% NH_4OH/H_2O and dried over Na_2SO_4. Evaporation of the solvent left an oily residue. Yield: for all the reactions 95–100% calculated on Cu(DMAN). The RH/RR ratio was established from the integrals in the ^{1}H NMR spectra (in $CDCl_3$) of the crude residue.

Reaction of Cu(DMAN) with Cu(O$_2$CR); R = C_6H_5, 2-,3-,4-MeC_6H_4

To a solution of 0.5 g of Cu(DMAN) (2.14 mmol) in benzene (50 ml) was added 1 equiv. of solid Cu(O$_2$CR). The suspension immediately turned dark red, and the Cu(DMAN) dissolved. The solution was stirred for 30 min and then filtered. The filtrate was evaporated to dryness and the residue washed with one portion of hexane (20 ml) to give a dark red solid. Yield: ca. 45% (calculated on Cu(DMAN).

Elemental analyses Cu_3(DMAN)(*m*-tolylcarboxylate)$_2$. Found: C, 53.44; H, 4.66; N, 2.13; O, 9.60; Cu, 29.63. $C_{28}H_{26}NO_4Cu_3$ calcd.: C, 53.28; H, 4.16; N, 2.22; O, 10.14; Cu. 30.20%.

Reaction of Cu(DMAN) and MeO_2C-C≡C-CO_2Me (DMADC)

To a suspension of 0.5 g of Cu(DMAN) (2.14 mmol) in benzene (50 ml) was added 304 mg of DMADC (2.14 mmol), upon which the suspension turned light brown almost immediately and all the Cu(DMAN) dissolved. The solution was stirred for 1 h and then poured into 10% NH_4Cl/NH_4OH (ca. 50 ml). The organic layer was washed with two portions of 10% NH_4OH/H_2O (ca. 50 ml) and dried over Na_2SO_4. Evaporation of the solution left a dark yellow oil, which was flash-chromatographed on a silica column with CH_2Cl_2 as eluant. Evaporation of the solution left a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.90–7.10 (6H, Ar), 6.20 (1H, olefinic), 3.83 + 3.53 (2 × 3H, DMADC-CH_3), 2.50 (6H, NMe_2) ppm. FD-mass spectrum (emitter current: 0 mA): 313 (calcd. for DMAN(MeO_2C)C=C(H)CO_2Me: 313).

Synthesis of (DMAN)$_2$

To a suspension of 725 mg of Li(DMAN)(OEt_2) (2.9 mmol) in diethyl ether (50 ml) was added at 0 °C 195 mg of $CuCl_2$ (1.45 mmol). The black solution was stirred for 1 h then poured into 10% NH_4Cl/NH_4OH (ca. 50 ml). The organic layers were washed with two portions of 10% NH_4OH/H_2O (ca. 50 ml) and dried over Na_2SO_4. Evaporation of the solvent left a colourless oil, which was recrystallized from hexane to give 400 mg of crystalline (DMAN)$_2$. Yield: 80%. ^{1}H NMR (C_6D_6): δ 7.71–7.14 (5H; m; Ar-H), 6.81 (1H; d, ^3J(HH) 7.2 Hz; H2); 2.63 + 2.59 (6H; 2s; NMe_2) ppm. FD-mass spectrum: *m/e* 340 (calcd. for (DMAN)$_2$: 340).

Production of crystals of Cu_4(DMAN)$_4$

A solution of 260 mg of CuBr{P(OMe)$_3$} (1 mmol) in benzene (15 ml) in a 200 ml Schlenk tube was frozen in a dry-ice/acetone bath (−78 °C). A layer of benzene (15 ml) containing 250 mg of Li(DMAN)(OEt_2) (1 mmol) was introduced over the frozen benzene and this upper layer was also frozen. The solid benzene layers were allowed to warm very slowly to room temperature (during about 20 h) and this afforded yellow needles of Cu_4(DMAN)$_4$. Some 80% of the solution was removed with a syringe in such a manner that the crystals remained under benzene. The crystals were washed by vigorously spraying benzene (10 ml) into the Schlenk tube followed by removal of 80% of the benzene with a syringe. This washing was repeated 4 times. A crystal suitable for an X-ray analysis was selected and placed quickly in paraffin oil. The crystal was then mounted in a capillary which already contained paraffin oil. Subsequently the capillary was filled with the benzene motherliquor. The X-ray data were collected at 6 °C to prevent thermal decomposition of the crystal.

X-ray structure determination

Crystal data. $Cu_4C_{48}H_{48}N_4(C_6H_6)_4$ orthorhombic, space group *Ibca*, *a* 22.279(2), *b* 32.688(2), *c* 17.175(1) Å, *Z* 8, *V* 12508(3) Å^3, D_{calc} 1.33 g cm^{-3}. 2506 independent intensities with $I > 2.5\sigma(I)$ were measured on a Nonius CAD-4 diffractometer using graphite monochromatized Cu-K_α (μ(Cu-K_α) 18.2 cm^{-1}) radiation.

The structure was solved by means of the heavy-atom technique. From an E^2-Patterson synthesis it became apparent that two Cu atoms were contained in the asymmetric unit. Fourier syntheses based on the Cu contributions to the structure factors revealed the rest of the complex, while in 4 places benzene molecules were visible, 3 at two-fold axes and one at the origin. During the block-diagonal least-squares refinement the positions of the benzene atoms were kept fixed and one isotropic thermal parameter per benzene ring was allowed to vary while the rest of the structure was treated anisotropically. An empirical absorption correction [36] was applied and a weighting scheme $w = 1/(10 + F_0)$ was used. The anomalous dispersion of Cu was taken into account. In this way R converged to 0.074 ($R_w = 0.077$). The programs used were from XRAY76 [37].

Tables of thermal parameters and lists of structure factors can be obtained from the authors on request.

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