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SYNTHESIS AND CHARACTERIZATION  
OF POLYNUCLEAR  
ORGANOCOPPER COMPOUNDS

PROEFSCHRIFT

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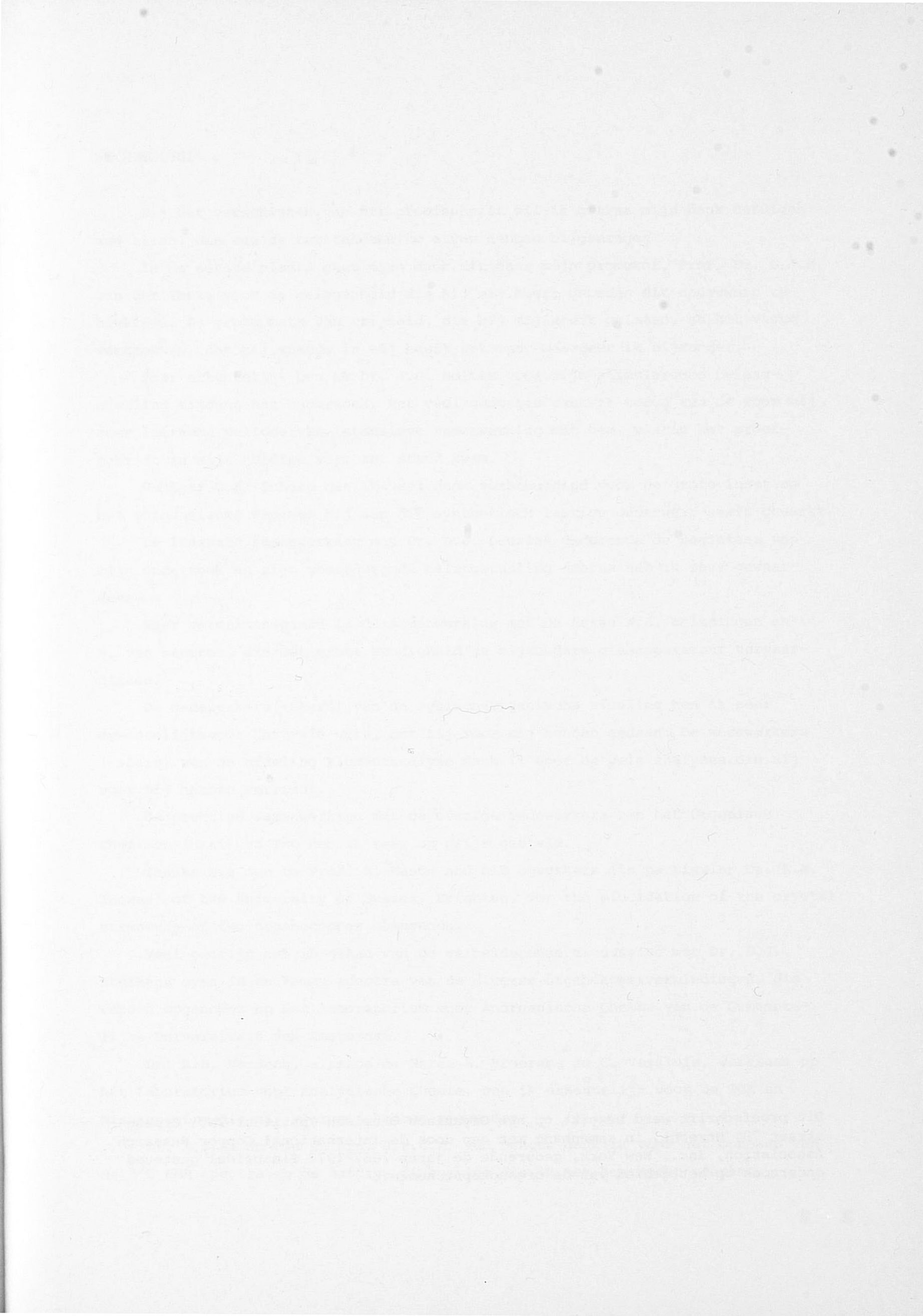
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PROMOTOR: PROF. DR. G.J.M. VAN DER KERK

Dit proefschrift kwam tot stand onder leiding van Dr. J.G. Noltes, Hoofd van de  
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## CHAPTER I

### GENERAL INTRODUCTION

The first reports dealing with the synthesis and isolation of organocopper compounds date back to 1859 [1]. Attempts to synthesize an alkylcopper compound via the reaction of  $\text{Et}_2\text{Zn}$  with cuprous halides [1, 2]\* as well as via the reaction of  $\text{Et}_2\text{Hg}$  with metallic copper at  $150^\circ$  [3] were unsuccessful. It was not until 1923 that the first organocopper compound was isolated, when Reich obtained phenylcopper as an air-sensitive white solid which decomposed slowly at room temperature [5]. Experiments by Reich aiming at the isolation of alkylcopper compounds failed although he made it plausible that these compounds were formed at low temperatures [5]. Apart from a report by Gilman and Straley in 1936 on organocopper compounds [6] further papers dealing with the synthesis and isolation of alkyl- and arylcopper compounds did not appear until 1957 [7]. Even to-day the number of well characterized organocopper compounds is very limited. This is undoubtedly connected with experimental difficulties encountered in the isolation of organocopper compounds which usually have limited oxidative, hydrolytic and thermal stability. The general low solubility of organocopper compounds and their tendency to form complexes with metal salts [7, 8] formed as by-products in their preparation (e.g.  $\text{MgX}_2$ ,  $\text{LiX}$ ) hamper the isolation of pure products. The difficulties are well illustrated by the report of Costa et al. on the preparation of phenylcopper [9].

Major efforts have been directed to the use of in situ prepared organocopper compounds and complexes as intermediates in organic synthesis. Already long ago speculations were made about the transient formation of organocopper compounds in a variety of copper-promoted reactions such as the symmetric coupling reactions of  $\text{RMgX}$  to  $\text{R-R}$  under the influence of copper salts [10]. Gilman and coworkers were the first to report that organocopper compounds display a very specific reactivity [6]. For example, phenylcopper reacts with benzoyl chloride to give benzophenone whereas addition across the carbonyl group (as observed for e.g. Grignard reagents) does not occur.

The discovery of the so-called organocuprate compounds (e.g.  $\text{R}_2\text{CuLi}$ ,

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\*As late as 1968 Thiele established that in fact alkylcopper compounds can be isolated at low temperatures from the reaction of dialkylzinc compounds with copper salts [4].

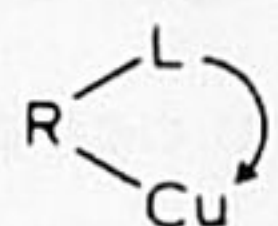


RXCuLi etc.) has caused a spectacular growth of the applications of organocopper compounds in organic synthesis. These compounds are more soluble and display higher thermal stabilities than the parent organocopper compounds RCu. Examples illustrating the versatility of the cuprate reagents are presented in recent reviews by Posner [11], Normant [7] and by Bähr and Burba [12]. In spite of the wide interest in these compounds until recently [13] nothing was known concerning their structural features such as aggregation state, bonding relation between the organic groups and the metals [11]. This is not too surprising in view of the extreme hydrolytic and oxidative lability of the organocuprate compounds.

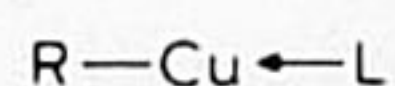
In recent years interest in the isolation and characterization of organocopper compounds, with the aim to obtain more structural information, has steadily increased [14-18]. Cairncross and Sheppard observed that introduction of fluoro atoms or of trifluoromethyl substituents into the aryl nucleus of phenylcopper results in strongly increased thermal stability [14]. E.g.,  $C_6F_5Cu$  decomposes at  $210-220^\circ$  [14] as compared with slow decomposition of phenylcopper at room temperature [19]. However, these compounds are still very sensitive towards oxidation and hydrolysis. Also for alkylcopper compounds introduction of suitable substituents can result in a considerable increase of thermal stability [15, 20-22].  $Me_3SiCH_2Cu$ , recently reported by Lappert et al. [21], decomposes at  $79^\circ$  whereas  $MeCu$  is unstable above  $-15^\circ$  [12]. Schmidbauer et al. observed that replacement of  $Me_3SiCH_2-$  by isoelectronic  $Me_3P^+CH_2-$  resulted in alkylcopper compounds which thermally are even more stable [22].

It is of interest to note that Costa and Camus in their extensive research on arylcopper compounds observed that complexation of phenyl-, tolyl- and 2-anisylcopper [15] with mono- and bidentate phosphine ligands does not notably influence the stability of the Cu-C bond [23, 24].

In this thesis investigations are described aiming at the stabilization of the Cu-C bond in arylcopper compounds by adding an internal (built-in) ligand, rather than an external ligand\*, i.e. by attaching the complexing ligand L to the aryl nucleus:



Internal ligand L



External ligand L

\*This principle was first applied for the stabilization of the chromium-carbon bond by Bähr et al. [25].



This approach has resulted in the isolation of stable arylcopper compounds, for some of which the structure has been elucidated. The structural characterization of a representative of the "organocuprate" compounds has been included in this thesis.

The work described in the following Chapters forms part of a more extensive research program dealing with the preparation, properties and applications of organocopper compounds which has been going on since 1967 at the Institute for Organic Chemistry TNO on behalf of the International Copper Research Association, Inc., New York.

Chapter II deals with the synthesis and properties of arylcopper compounds containing the 2-(dimethylamino)methyl group as a built-in ligand.

Chapter III describes the structural characterization of some 2-(dimethylamino)methyl-substituted arylcopper compounds.

In Chapter IV the nature of the reaction of aryllithium and arylcopper(I) compounds with cuprous and cupric halides is discussed in greater detail.

Chapter V contains a description of the synthesis, characterization and thermal behaviour of compounds  $\text{RCu}^{\text{I}}_2$  in which R is a bifunctional group.

Chapter VI covers the synthesis and characterization of arylcopper compounds containing the methoxy or dimethylamino group as a built-in ligand.

In Chapter VII the synthesis and structural characterization of hexanuclear bis[2-(dimethylamino)phenylcopper]metalIB halide compounds  $\text{R}_4\text{Cu}_{6-n}\text{M}_n\text{X}_2$  are described.

Chapter VIII deals with the synthesis, characterization and thermal behaviour of some organocopper compounds of the type  $\text{R}_4\text{R}'_2\text{Cu}_6$ .

Chapter IX covers the synthesis and characterization of bis{2-[(dimethylamino)methyl]phenyl}copperlithium compounds of the type  $\text{R}_4\text{Cu}_2\text{Li}_2$ .

In Chapter X an attempt has been made to place published data and the results presented in this thesis into a broader perspective.

## REFERENCES

- 1 G. BUCKTON, Justus Liebigs Ann.Chem., 109 (1859) 225.
- 2 J.A. WANKLYN and L. CARIUS, Justus Liebigs Ann.Chem., 120 (1861) 70.
- 3 E. FRANKLAND and D.F. DUPPA, J.Chem.Soc., 17 (1864) 31.
- 4 K.H. THIELE and J. KÖHLER, J.Organometal.Chem., 12 (1968) 225.
- 5 R. REICH, C.R. Acad.Sci., 177 (1923) 322.
- 6 H. GILMAN and J.M. STRALEY, Recl.Trav.Chim.Pays-Bas, (1936) 821.



- 7 J.F.NORMANT, *Synthesis*, (1972) 63.
- 8 This thesis, Chapters IV and VII.
- 9 G.COSTA, A.CAMUS, L.GATTI and N.MARSICH, *J.Organometal.Chem.*, 5 (1966) 568.
- 10 H.GILMAN and H.H.PARKER, *J.Amer.Chem.Soc.*, 46 (1924) 2823 and ref. cited therein; H.GILMAN and J.E.KIRBY, *Recl.Trav.Chim.Pays-Bas*, 48 (1929) 155.
- 11 G.H.POSNER, *Org.Reactions*, Vol. 19, Wiley, New York, 1972, p. 2; *ibid.*, 1974, to be published.
- 12 G.BÄHR and P.BURBA, in HOUBEN-WEYL (Eds.), *Organo-Kupfer Verbindungen Methoden der Organischen Chemie*, Vol. 13/1, 1970, p. 747.
- 13 G.VAN KOTEN and J.G.NOLTES, *J.Chem.Soc., Chem.Comm.*, (1972) 940.
- 14 A.CAIRNCROSS and W.A.SHEPPARD, *J.Amer.Chem.Soc.*, 93 (1971) 247; A.CAIRNCROSS, H.OMURA and W.A.SHEPPARD, *ibid.*, 93 (1971) 248.
- 15 A.CAIRNCROSS and W.A.SHEPPARD, *J.Amer.Chem.Soc.*, 90 (1968) 2186.
- 16 A.CAMUS and N.MARSICH, *J.Organometal.Chem.*, 14 (1968) 441.
- 17 A.YAMAMOTO, A.MIYASHITA, T.YAMAMOTO and S.IKEDA, *Bull.Chem.Soc. Jap.*, 45 (1972) 1583.
- 18 E.g.: G.VAN KOTEN, A.J.LEUSINK and J.G.NOLTES, *Chem.Comm.*, (1970) 1107; G.VAN KOTEN, A.J.LEUSINK and J.G.NOLTES, *Inorg.Nucl.Chem. Lett.*, 7 (1971) 227.
- 19 G.E.COATES, M.L.H.GREEN and K.WADE, *Organometallic Compounds*, Vol. II, 3rd ed., Methuen, London, 1968, p. 253.
- 20 G.VAN KOTEN and J.G.NOLTES, *J.Chem.Soc., Chem.Comm.*, (1972) 59.
- 21 M.F.LAPPERT and R.PEARCE, *J.Chem.Soc., Chem.Comm.*, (1973) 24.
- 22 M.SCHMIDBAUER, J.ADLKOFER and W.BUCHNER, *Angew.Chem.*, (1973) 448.
- 23 G.COSTA, A.CAMUS, N.MARSICH and L.GATTI, *J.Organometal.Chem.*, 8 (1967) 339.
- 24 A.CAMUS and N.MARSICH, *J.Organometal.Chem.*, 21 (1970) 249.
- 25 G.BÄHR and H.ZOHM, *Angew.Chem.*, 75 (1963) 94.

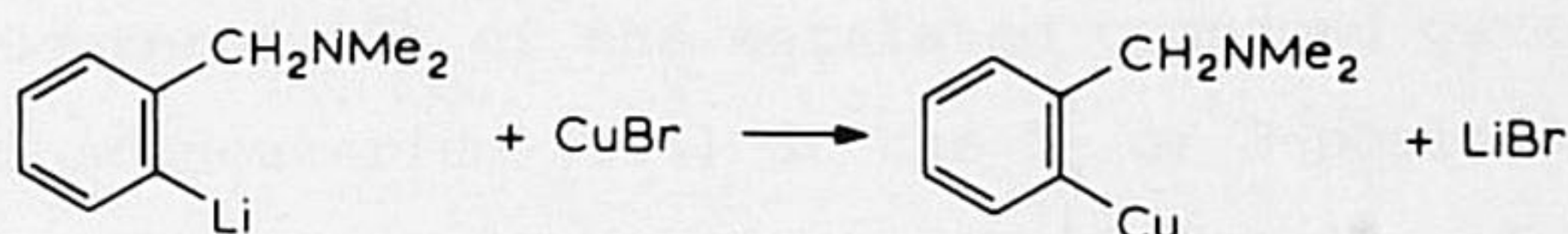


## CHAPTER II

### SYNTHESIS AND PROPERTIES OF ARYLCOPPER COMPOUNDS CONTAINING THE 2-(DIMETHYLAMINO)METHYL GROUP AS A BUILT-IN LIGAND

#### INTRODUCTION

Our efforts aiming at the stabilization of the Cu-C bond in arylcopper compounds by introduction of a built-in ligand (cf. Chapter I) were started with the synthesis of 2-[(dimethylamino)methyl]phenylcopper:



Already at an early stage two observations were made which largely determined the course of our further studies, viz.:

*i.* 2-[(Dimethylamino)methyl]phenylcopper\* appeared to be surprisingly stable (dec. at 170-180°). Moreover, the compound showed good solubility in hydrocarbon and ether solvents which enabled its isolation in the pure state and the determination of its molecular weight.

This result led to the synthesis of other arylcopper compounds containing the Me<sub>2</sub>NCH<sub>2</sub> group as a built-in ligand as described in this Chapter. The structural characterization of these compounds, made possible by their favourable physical properties, is presented in Chapter III.

*ii.* It appeared that only if cuprous bromide is added to a suspension of the organolithium compound and if the reagents are used in an exact 1/1 molar ratio the arylcopper compound can be isolated in the pure state.

"Reversed addition", i.e. addition of the organolithium compound to cuprous bromide, under all circumstances afforded inseparable combinations of the organocopper compound with cuprous bromide.

In fact, these observations strongly contrasted with the conclusions reached by Camus et al. [2] who recommended "reversed addition" of the reagents and an RLi/CuBr molar ratio  $\leq 1$ .

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\*For a preliminary account see ref. 1.

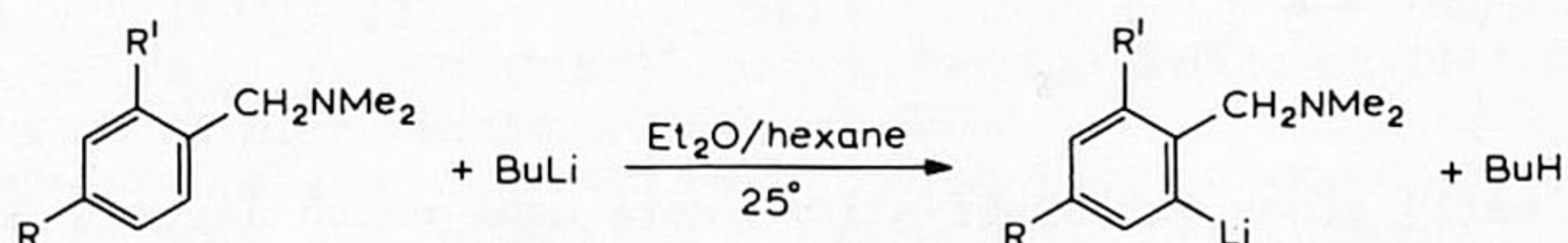


The results of a closer study of the reaction of aryllithium compounds with copper halides will be the subject of Chapter IV.

## RESULTS AND DISCUSSION

### *Preparation of the organolithium starting materials*

The 2-(dimethylamino)methyl-substituted aryllithium starting materials (Ib)-(Vb) have been prepared via Li-H-exchange reactions\* of the corresponding arenes (Ia)-(Va) with butyllithium.



(Ia,b), R = R' = H

(IIa,b), R = Me, R' = H

(IIIa,b), R = MeO, R' = H

(IVa,b), R = Cl, R' = H

(Va,b), R = H, R' = Cl

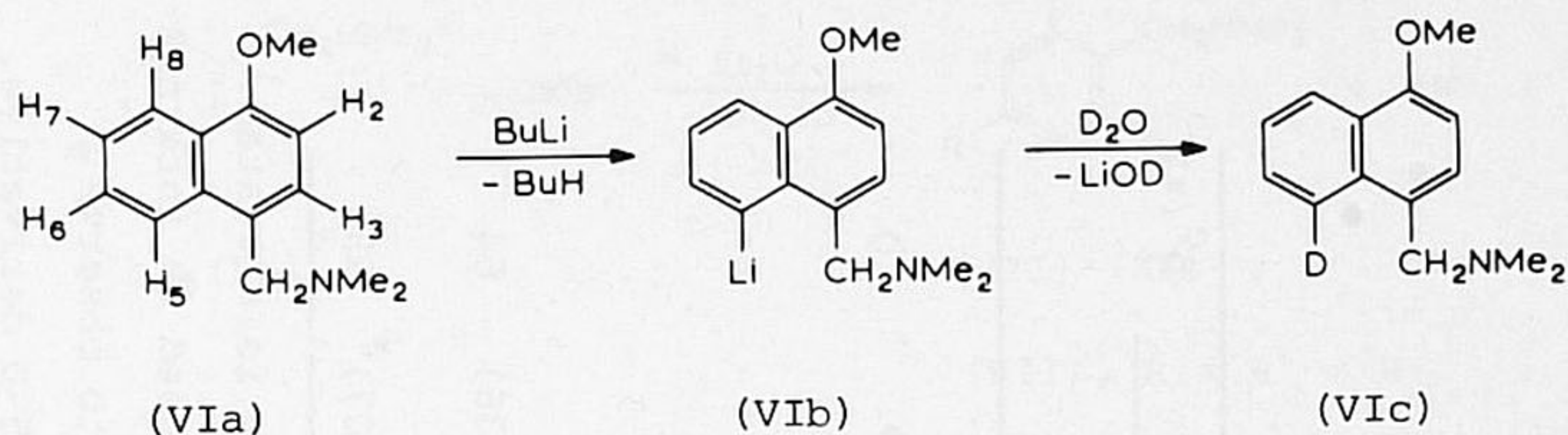
Although a 1/2 molar ratio of arene and butyllithium has been applied by Hauser et al. [4], we have observed that the 1/1 reaction of a series of substituted benzylamines (Ia)-(Va) results in almost quantitative lithiation (90-100%) at the *ortho*-position\*\* as shown by deuterolysis experiments (see Experimental part of this Chapter).

The metalation of 1-methoxy-4-[(dimethylamino)methyl]naphthalene (VIa) with butyllithium might be expected to take place at the 2-, 3-, 5- or 8-position. This can be concluded from separate studies of the metalation of 1-methoxynaphthalene [5] and 1-[(dimethylamino)methyl]naphthalene [6] with butyllithium. Actually metalation of (VIa) occurs at the 5-position.

\*During the past five years several excellent reviews, dealing with this subject, have appeared in the literature [3].

\*\*The isolation and characterization of several of these 2-[(dimethylamino)methyl]phenyllithium compounds is described in Chapter IX.





The NMR spectrum of (VIa) in  $\text{CCl}_4$  shows an aromatic pattern which, on the basis of the results of proton-spin decoupling experiments and by comparison with the patterns found in the NMR spectra of other 1,4-disubstituted naphthalene compounds [7], has been tentatively assigned (see Table 1). In this spectrum the low field multiplet belongs to  $\text{H}_5$  and  $\text{H}_8$ , whereas  $\text{H}_2$  and  $\text{H}_3$  appear as a doublet of doublets.

Deuterolysis of the metalated compound gave a naphthalene derivative which contained deuterium (64%) at the 5- or 8-position as deduced from its NMR spectrum in  $\text{CCl}_4$ . In this spectrum the intensity of several peaks in the  $\text{H}_{5,8}$  multiplet was strongly reduced. The approximate peak area ratios appeared to be  $1.36(\text{H}_{5,8})/2(\text{H}_{6,7})/1(\text{H}_2)/1(\text{H}_3)/3(\text{OCH}_3)/2(\text{NCH}_2)/6(\text{NCH}_3)$ , which excludes metalation at the 2- or 3-position.

The deuterated naphthalene derivative obtained upon deuterolysis of the corresponding organocopper compound\* (XIII) with  $\text{CH}_3\text{COOD}$  contained 93% deuterium at the 5- or 8-position. Now the  $\text{H}_{5,8}$  multiplet was reduced to a doublet of doublets which confirms that metalation had occurred exclusively at only one position. Since the  $\text{CH}_2\text{NMe}_2$  group is a better directing group for the metalation than the OMe group [4], it seems plausible to conclude that metalation of (VIa) with butyllithium affords the 5-lithiated compound (VIb) as the major product.

#### *Synthesis of 2-[(dimethylamino)methyl]phenylcopper compounds*

2-[(Dimethylamino)methyl]phenylcopper as well as its 3- or 5-substituted methyl, methoxy and chloro derivatives were synthesized via metathesis of the corresponding organolithium compounds with cuprous bromide\*\*, using diethyl ether as a solvent.

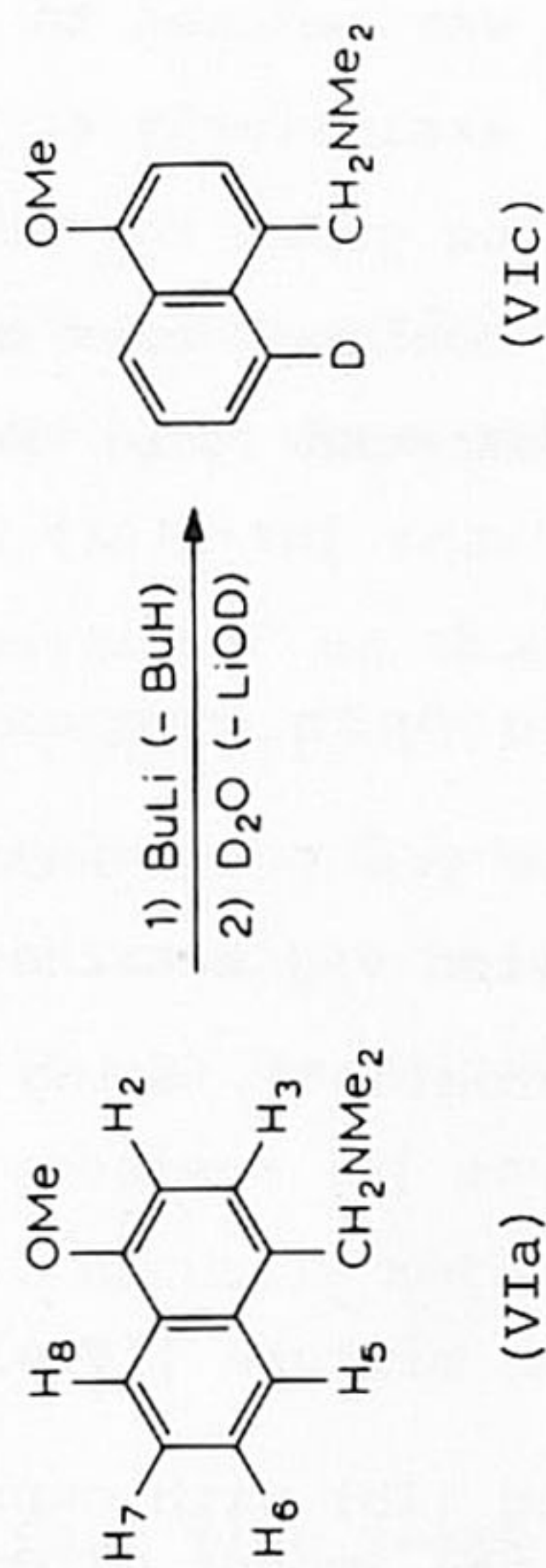
\*Obtained from the reaction of the metalated reaction mixture [(VIa)+BuLi] with cuprous bromide.

\*\*From the 2/1 reaction of the organolithium compound (Ib) with cupric bromide pure (VII) was isolated in 47% yield (calculated on the amount of  $\text{CuBr}_2$  used). The relative merits of the use of cuprous or cupric bromide as a starting material will be discussed in Chapter IV.



TABLE 1

NMR SPECTRA (IN  $\text{CCl}_4$ ) OF NON-DEUTERATED AND DEUTERATED  
1-METHOXY-4-[(DIMETHYLAMINO)METHYL]NAPHTHALENE (VI)



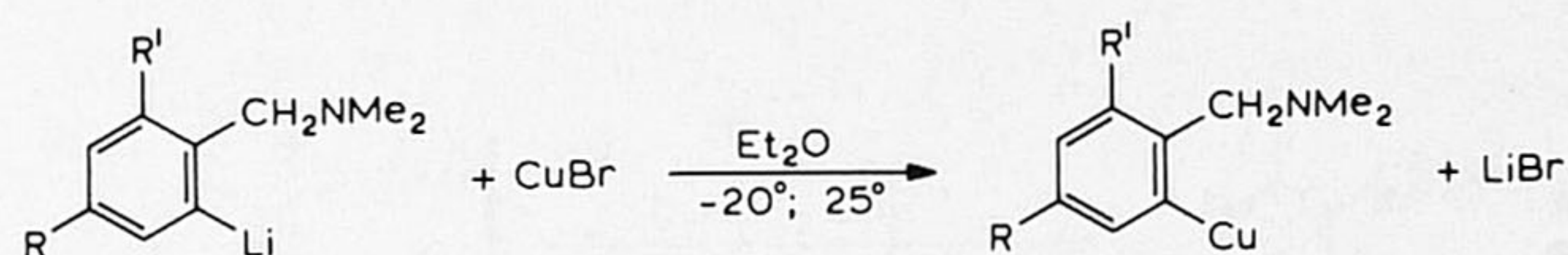
| Compound                        | $\delta$ (ppm; TMS internal) |                |                |                |                        |                          | $D^c$ (%)                 |
|---------------------------------|------------------------------|----------------|----------------|----------------|------------------------|--------------------------|---------------------------|
|                                 | $\text{NCH}_3$               | $\text{NCH}_2$ | $\text{OCH}_3$ | $\text{H}_2^a$ | $\text{H}_3^a$         | $\text{H}_{5,8}^b$       |                           |
| (VIa)                           | 2.14(s,6)                    | 3.60(s,2)      | 3.78(s,3)      | 6.47(d,1)      | 7.09(d,1) <sup>d</sup> | 7.38(m,2)                | 8.16(m,2)                 |
| Irradiation at $\text{H}_{5,8}$ |                              |                |                |                |                        | 7.38(2xd) <sup>e,f</sup> |                           |
| Irradiation at $\text{H}_{6,7}$ |                              |                |                |                |                        | 8.16 <sup>g</sup>        |                           |
| (VIC) <sup>h</sup>              | 2.16(s,6)                    | 3.61(s,2)      | 3.81(s,3)      | 6.49(d,1)      | 7.11(d,1) <sup>d</sup> | 7.38(m,2)                | 8.15(m,1.36)              |
| (VIC) <sup>h,i</sup>            | 2.16(s,6)                    | 3.60(s,2)      | 3.80(s,3)      | 6.48(d,1)      | 7.10(d,1) <sup>d</sup> | 7.38(m,2)                | 8.18(m,1.07) <sup>j</sup> |

<sup>a</sup>Tentatively assigned as  $\text{H}_2$  and  $\text{H}_3$ , respectively. <sup>b</sup>Position at which the centre of the multiplet is situated.

<sup>c</sup>Calcd. for substitution of 1 D for 1 H. The peak areas of the  $\text{OCH}_3$ ,  $\text{NCH}_2$  and  $\text{NCH}_3$  protons are used as internal standards. <sup>d</sup> $J_{2,3}$  7.9 Hz. <sup>e</sup> $J_{6,7}$  7.5 Hz. <sup>f</sup>AB pattern with a very small  $\Delta\delta$ . <sup>g</sup>It has been possible to observe separate singlets for  $\text{H}_5$  and  $\text{H}_8$  but  $\Delta[\delta(\text{H}_5) - \delta(\text{H}_8)]$  is very small. <sup>h</sup>Tentatively assigned to the 5-D derivative.

<sup>i</sup>Obtained upon deuterolysis of the organocopper compound (XII). <sup>j</sup> $J_{7,8}$  6.9;  $J_{6,8}$  3.0 Hz.





(Ib) - (Vb)

(VII) - (XI)

(VII), R = R' = H

(VIII), R = Me, R' = H

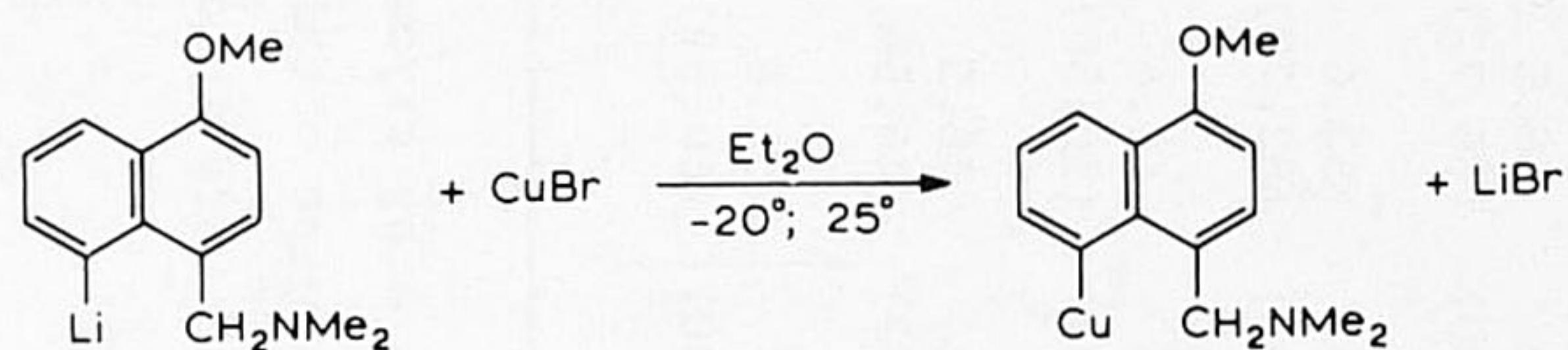
(IX), R = MeO, R' = H

(X), R = Cl, R' = H

(XI), R = H, R' = Cl

These benzene soluble organocopper compounds were isolated as yellow- to green-coloured crystalline solids in 25-66% yield after recrystallization from benzene or ethers.

Via a similar reaction the 4-(dimethylamino)methyl substituted naphthyl-copper compound (XII) was synthesized:



(VIb)

(XII)

This yellow compound was isolated in 50% yield. Because of its very low solubility in hydrocarbon and ether solvents this compound could not be recrystallized and, therefore, the isolated product was not completely pure.

The formation of 2-(dimethylamino)methyl-substituted arylcopper compounds (VII)-(XII) in these reactions was established by elemental analysis (correct C, H, N, Cu and Cl analyses, see Table 2), by IR spectroscopy (correct aromatic substitution patterns) and by NMR spectroscopy (correct resonance patterns). As additional proof for the site and degree of metalation of the aromatic ring, the organocopper compounds were treated with D<sub>2</sub>O. The respective deuterolysis products formed were compared with those obtained upon deuterolysis of the corresponding organolithium compounds.



TABLE 2

 PHYSICAL AND ANALYTICAL DATA OF THE 2-[(DIMETHYLAMINO)METHYL]PHENYLCOPPER COMPOUNDS  
 (VII) - (XII)

| Compound         | Yield (%) | Colour       | Dec. temp. <sup>a</sup> (°C) | Analysis, found (calcd.) (%) |                 |               |               |                 | Mol. wt. <sup>b</sup> found (calcd.) <sup>c</sup> |
|------------------|-----------|--------------|------------------------------|------------------------------|-----------------|---------------|---------------|-----------------|---|
|                  |           |              |                              | Cu                           | C               | H             | N             | Cl              |   |
| (VII) RCu        | 44        | Yellow       | 175-185                      | 31.6<br>(32.13)              | 54.9<br>(54.66) | 6.3<br>(6.12) | 7.0<br>(7.08) |                 | 792, $n = 4.0$ ; A<br>(197.5)                     |
| (VIII) (5-MeR)Cu | 66        | Yellow       | 170-210                      | 29.8<br>(30.00)              | 56.5<br>(56.72) | 6.7<br>(6.66) | 6.4<br>(6.61) |                 | 863, $n = 4.1$ ; B<br>(211.5)                     |
| (IX) (5-MeOR)Cu  | 38        | Yellow-green | 140-145<br>(fast 170)        | 27.8<br>(27.90)              | 52.6<br>(52.73) | 6.3<br>(6.20) | 6.0<br>(6.15) |                 | 921, $n = 4.0$ ; A<br>(227.8)                     |
| (X) (5-ClR)Cu    | 41        | Green        | 140-142                      | 27.5<br>(27.37)              | 46.6<br>(46.56) | 4.9<br>(4.78) | 5.9<br>(6.03) | 15.2<br>(15.27) | <sup>d</sup>                                      |
| (XI) (3-ClR)Cu   | 25        | Yellow       | 108-109                      | 27.2<br>(27.37)              | 46.5<br>(46.56) | 4.6<br>(4.78) | 5.9<br>(6.03) | 15.3<br>(15.27) | <sup>e</sup>                                      |
| (XII) (Naphth)Cu | 50        | Yellow       | 162-165                      | 21.7<br>(22.88)              | 55.8<br>(60.52) | 5.7<br>(5.80) | 5.2<br>(5.04) |                 | <sup>f</sup>                                      |

<sup>a</sup>Determined in a capillary under N<sub>2</sub> atm. <sup>b</sup>In benzene; A by cryometry ( $\pm 5^\circ$ ); B by ebulliometry ( $\approx 80^\circ$ ).

<sup>c</sup>Calcd. for the monomer ( $n = 1$ ). <sup>d</sup>No reliable results were obtained by method B, most probably as a result of slow decomposition of the solution. <sup>e</sup>See Chapter III. <sup>f</sup>Very insoluble.



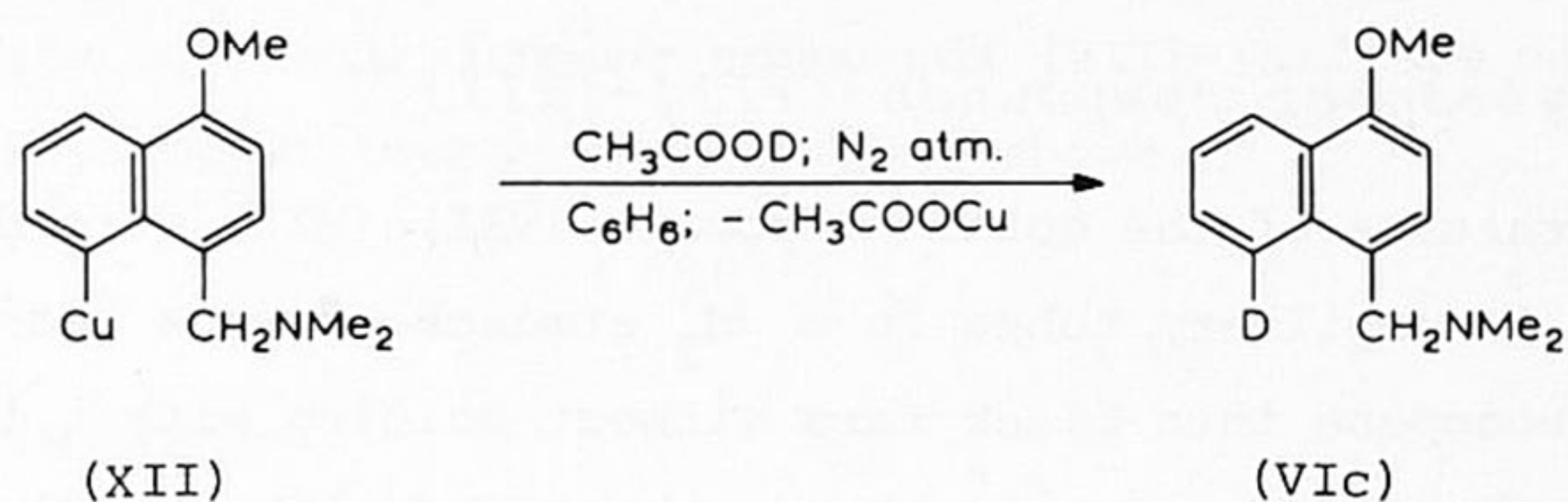
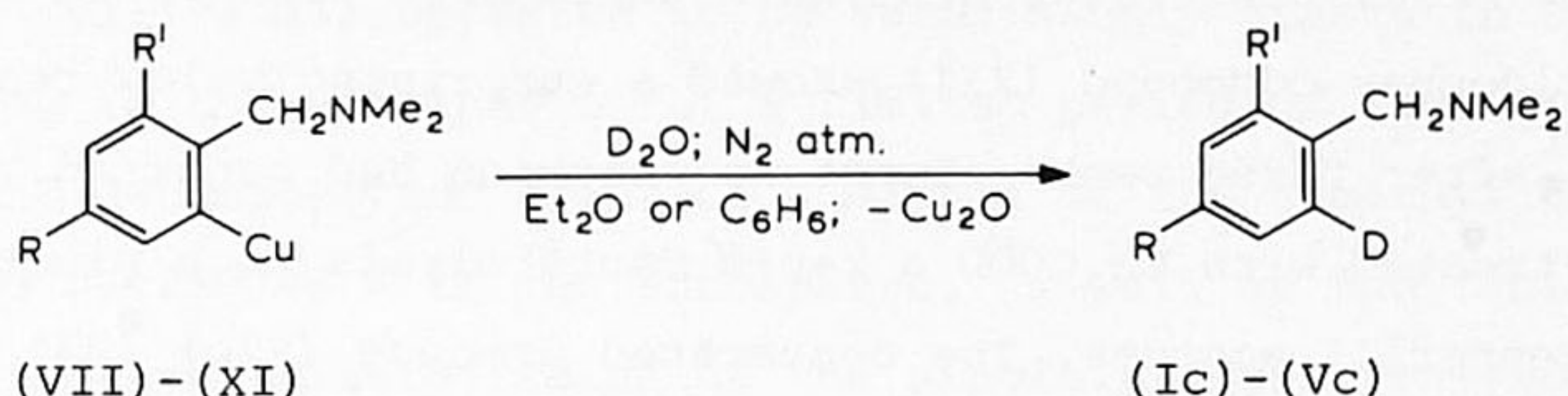
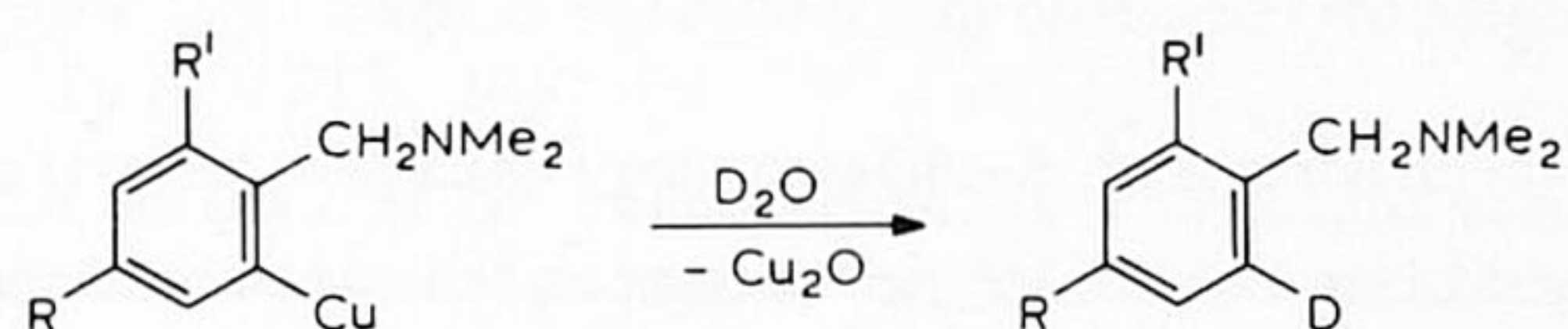


TABLE 3

DEUTEROLYSIS OF THE ARYL COPPER COMPOUNDS (VII)-(XI) AT ROOM TEMPERATURE<sup>a</sup>



| Compound               | Reaction time (h) | Solvent | Yield of RD (%) <sup>b</sup> |
|------------------------|-------------------|---------|------------------------------|
| (VII), R = R' = H      | 66                | Ether   | 90                           |
| (VIII), R = Me, R' = H | 140               | Benzene | 63                           |
| (IX), R = MeO, R' = H  | 140               | Ether   | 45                           |
| (X), R = Cl, R' = H    | 264               | Benzene | 74                           |
| (XI), R = H, R' = Cl   | 30                | Benzene | 80                           |

<sup>a</sup>For a discussion of the deuterolysis of the naphthylcopper compound (XII) see text. <sup>b</sup>The % D in the deuterated amines, isolated from these deuterolysis reactions, was at least 95%. The yield of RD has been determined by GLC using decane as an internal standard.



In all cases, the same *ortho*-deuterated benzyldimethylamines were isolated (see Table 3). The naphthylcopper compound (XII) showed a surprisingly low reactivity towards deuterolysis; after three weeks almost no reaction had occurred. However, when (XII) was treated with  $\text{CH}_3\text{COOD}$  a rapid deuterolysis took place, affording (VIc) and copper(I) acetate. The deuterated product (VIc) (93% D; see Table 1) was isolated in 76% yield.

#### *Properties of the arylcopper compounds (VII)-(XII)*

Decomposition temperatures of the solid compounds (VII)-(XII) were determined by heating samples in capillary tubes in a  $\text{N}_2$  atmosphere at a rate of  $5^\circ/\text{min}^*$ . The compounds decompose into black tars without melting within the range of  $110\text{--}210^\circ$ , see Table 2. It appears, that as compared with phenylcopper\*\* (slow decomposition at  $25^\circ$  [9]) introduction of the (dimethylamino)-methyl group increases thermal stability considerably. Introduction of other substituents may increase or decrease thermal stability. Heating of (VII) at  $131\text{--}133^\circ$  during 5 h caused almost no decomposition. This was concluded from the isolation of (2-deuteriobenzyl)dimethylamine in about 90% yield after deuterolysis of the heated sample.

With the exception of the 3-chloro and 5-chloro derivatives the organocopper compounds are stable in boiling benzene. No decomposition products were detected in the NMR spectrum of a benzene- $d_6$  solution of (VII) which had been heated at  $80^\circ$  for 4 h.

The unsubstituted (VII) and 3-chloro-substituted (XI) derivatives are very soluble in benzene and show a moderate solubility in ether and pentane. These compounds are also soluble in pyridine, acetonitrile and dioxane without forming isolable complexes with these solvents. The 5-substituted derivatives are less soluble, while the naphthylcopper compound is very insoluble in the solvents mentioned.

In contrast to the high sensitivity towards hydrolysis and oxidation of phenylcopper [9], *ortho*-, *meta*- and *para*-tolylcopper [1], perhalogenated phenylcopper [10] and of 4-(dimethylamino)phenylcopper\*\*\*, the solid organocopper com-

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\*TGA analysis of 5-methyl-2-[(dimethylamino)methyl]phenylcopper (5-MeRCu): conditions; 2.372 mg as a powder, platinum pan used, flow rate of  $\text{N}_2$  gas 32 ml/min, heating rate  $5^\circ/\text{min}$ ; results, weight loss starts at  $170^\circ$ , at  $215^\circ$  50% loss of weight and at  $240^\circ$  100% loss of weight (calculated on the amount of 5-MeR-).

\*\*The decomposition temperature of phenylcopper depends very much on the purity of the sample. Very pure phenylcopper decomposes at about  $100^\circ$  [8].

\*\*\*See Chapter VI.



pounds (VII)-(XII) appeared to be surprisingly stable in air. This allows their handling in the atmosphere for a limited period of time. The unchanged IR spectrum and decomposition point of a sample of the 5-methyl derivative, after being exposed during 48 h to the atmosphere, as well as the isolation of (4-methyl-2-deuteriobenzyl)dimethylamine as the single product from subsequent deuterolysis of the exposed sample, support this view. However, in solution the oxidative stability of the arylcopper compounds (VII)-(XII) is comparable with that of the other arylcopper compounds mentioned above.

#### EXPERIMENTAL\*

##### *Metalation of the tertiary benzylamines (Ia)-(Va)*

The following standard procedure was used. The tertiary benzylamine (10 mmol) was added at room temperature to a solution of 10 mmol of butyllithium in ether/hexane (50 ml). The reaction mixture was stirred at room temperature until a test on the presence of butyllithium (Gilman test II) [11] was negative.

##### *Reaction of the 2-[(dimethylamino)methyl]phenyllithium compounds (Ib)-(Vb) with D<sub>2</sub>O*

The solution or suspension of the lithiated benzyldimethylamine was added portionwise with stirring to a cold (0°) mixture of 50 ml of diethyl ether and 2 ml of deuterium oxide (D<sub>2</sub>O). This mixture was stirred for 2 h and then filtered. The filtrate was dried over MgSO<sub>4</sub>, filtered and analysed by GLC [% yield of (2-deuteriobenzyl)dimethylamine]. The ether solution was extracted with 2 N HCl. The water layer was extracted with ether and then made alkaline with solid sodium hydroxide. The resulting solution was extracted with ether. The ether layer was dried over MgSO<sub>4</sub>, filtered and concentrated, yielding the pure (2-deuteriobenzyl)dimethylamine. NMR spectroscopy (in CCl<sub>4</sub>) afforded the amount of D (see Table 1), while IR spectroscopy revealed that exclusively 2-deuterated benzylamines were present (substitution pattern of the aromatic ring in the 830-690 cm<sup>-1</sup> region). Reaction time for the metalation, yield of RH/RD, % D; (Ia), 24, 90, 100; (IIa), 66, 86, 80; (IIIa), 66, 90, 96; (IVa), 24, 75, 97; (Va), 24, 80, 90.

##### *Reaction of the 2-[(dimethylamino)methyl]phenylcopper compounds (VII)-(XI) with D<sub>2</sub>O*

1-5 Mmol of the respective organocopper compounds (VI)-(XI), dissolved or suspended in Et<sub>2</sub>O or benzene (10 ml) and 1 ml of D<sub>2</sub>O, was stirred at room temperature until no further change was observed. The cuprous oxide formed was filtered off and the filtrate was analysed by GLC [% of (2-deuteriobenzyl)dimethylamine, see Table 3]. The isolation and purification of the benzylamines was carried out as described above. The resulting (2-deuteriobenzyl)dimethyl-

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\*General directions regarding solvents, apparatus and reaction conditions are presented in Chapter IX.



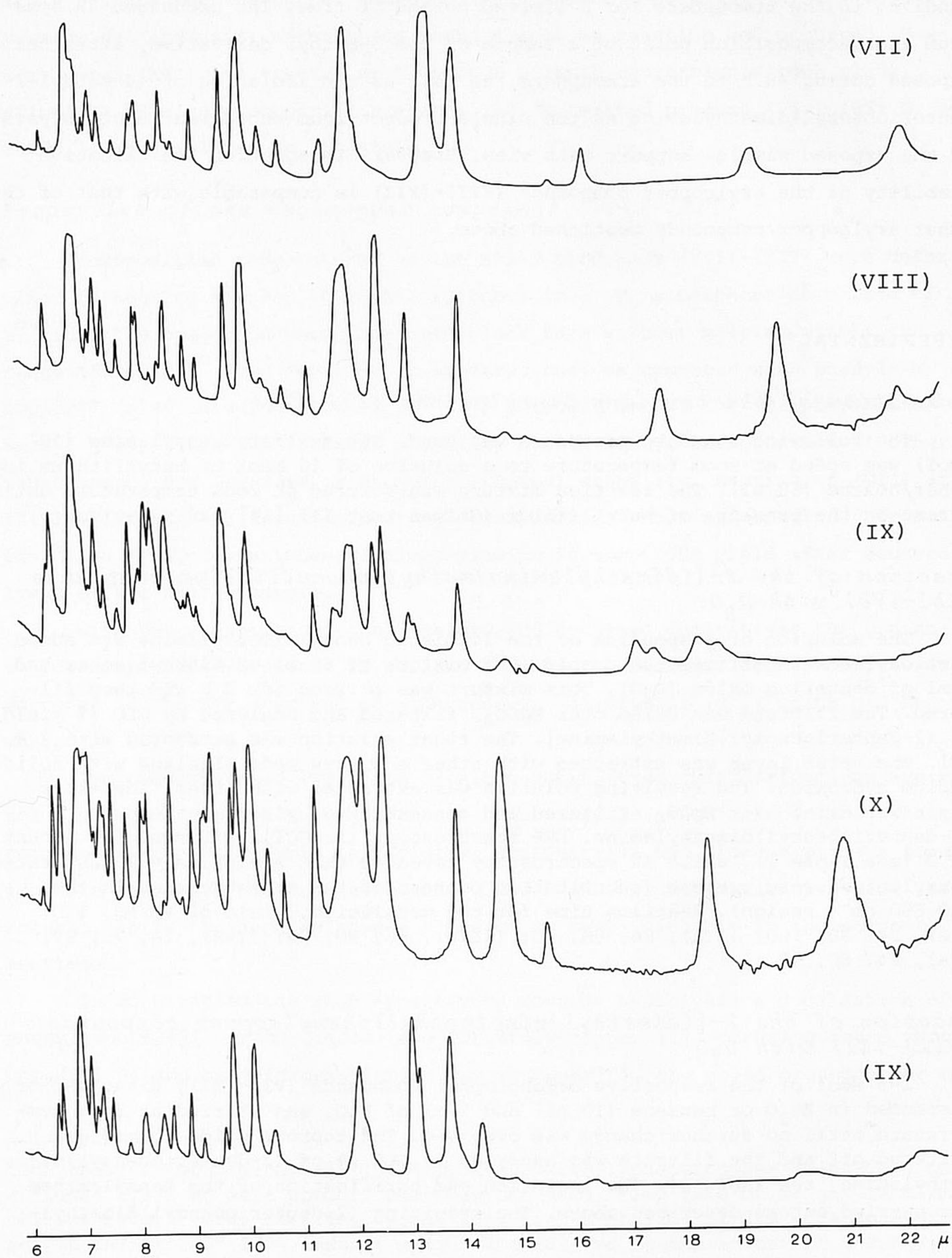


Fig. 1. IR spectra (nujol) of the 2-[(dimethylamino)methyl]phenylcopper compounds (VII)-(XI).



amines were identical with the respective samples obtained from the benzylamine/BuLi/D<sub>2</sub>O route (NMR and IR spectroscopy).

#### *Synthesis of 2-[(dimethylamino)methyl]phenylcopper (VII)*

*Addition of CuBr to RLi (Ib).* Solid CuBr (60 mmol) was slowly added (in about 1½ h) at -20° to a freshly prepared suspension of 2-[(dimethylamino)methyl]phenyllithium\* (Ib) (60 mmol) in ether (160 ml). Initially a black solid was formed, followed by the precipitation of a white solid (R<sub>2</sub>CuLi) the colour of which slowly turned yellow (RCu) when the RLi/CuBr ratio decreased from 2 to 1. The mixture was stirred at -20° for 1 h, warmed up to room temperature and then stirred for another 2 h. The yellow-green solid was filtered off and extracted with cold ether until a test for the presence of Br<sup>-</sup> (from LiBr) in the filtrate (vide infra) was negative.

The yellow-green solid was dried in vacuo and subsequently extracted with ether (4 x 80 ml; removal of Cu<sup>0</sup>). Concentration of this ether extract by low temperature distillation at diminished pressure (LTD) afforded yellow crystalline (VII) which was filtered off, washed with pentane and then dried in vacuo.

Physical data, see Table 2; IR spectrum, see Fig. 1; NMR and mass spectrum, see Chapter III.

*Addition of CuBr<sub>2</sub> to RLi (Ib).* Solid CuBr<sub>2</sub> (15 mmol) was added at -40° in about 3 h to a solution of 30 mmol of (Ib) in Et<sub>2</sub>O (125 ml). The resulting mixture was stirred at -40° for 2 h and at 0° for 1½ h. During the reaction the organocopper compound (VII) precipitated. For the isolation and purification of (VII) (47% yield) vide supra. (Found: Cu, 31.8. C<sub>9</sub>H<sub>12</sub>NCu calcd.: Cu, 32.13%.) IR spectrum, identical to that of a sample of (VII) obtained via the CuBr/RLi route.

#### *Synthesis of 3-chloro-2-[(dimethylamino)methyl]phenylcopper (XI)*

Solid cuprous bromide (20 mmol) was added at -20° to a red solution of (Vb). During the reaction a black solid separated. After stirring for an additional hour yellow (XI) precipitated. The solids were filtered off and subsequently washed with cold ether (removal of LiBr). The residue was extracted with benzene. The benzene extract upon concentration yielded a yellow solid (XI) which was recrystallized from benzene/pentane.

Physical data, see Table 2; IR spectrum, see Fig. 1; NMR spectrum, see Chapter III.

#### *Synthesis of the 5-substituted 2-[(dimethylamino)methyl]phenylcopper compounds (VIII)-(X)*

Solid cuprous bromide was added at -20° to a solution of the concerning organolithium compound (1/1 molar ratio). The mixture was stirred at -20° for 2 h, warmed up to room temperature (1 h) and stirred at room temperature for an additional 2 h. The precipitate was filtered off and extracted with Et<sub>2</sub>O (removal of LiBr). The remaining solid was recrystallized from benzene.

Physical data of (VIII)-(X), see Table 2; IR spectra, see Fig. 1; NMR [of (VIII)-(X)] and mass spectra [of (VIII)], see Chapter III.

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\*Stirring during the reaction of (Ia) with BuLi is essential.



*Synthesis of 1-methoxy-4-[(dimethylamino)methyl]-5-cuprionaphthalene (XII)*

A mixture of 20 mmol of butyllithium and 20 mmol of 1-methoxy-4-[(dimethylamino)methyl]naphthalene (VIa) was stirred at room temperature for 24 h.

The resulting purple suspension of (VIb) in ether was cooled to  $-20^{\circ}$  and 20 mmol of solid cuprous bromide were slowly added. The yellow suspension was stirred at  $-20^{\circ}$  for 2 h, warmed up to room temperature and then stirred for another 1 h. The precipitate was filtered off and extracted with ether. The residue was suspended in benzene and stirred during 2 h. Filtration afforded yellow (XII). The filtrate contained a small amount of a very finely divided black solid.

Physical data, see Table 2.

*Reaction of (XII) with  $\text{CH}_3\text{COOD}$ .* Solid (XII) (2.7 mmol) was added to a mixture of benzene (15 ml)/ $\text{CH}_3\text{COOD}$  (2 ml 10 N in  $\text{D}_2\text{O}$ ) and stirred for 24 h. The resulting mixture was made alkaline with 6 N  $\text{NH}_4\text{OH}$  solution, stirred for 1 h and subsequently filtered. The precipitate was extracted with benzene and with 6 N  $\text{NH}_4\text{OH}$  (2 x 5 ml). The water layer was extracted with benzene. The combined benzenic extracts were dried. GLC analysis indicated the presence of 2.07 mmol (67%) of the amine. The amine was purified by an acid/base work-up procedure (see above) using ether as a solvent. The resulting oil appeared to be pure 1-methoxy-4-[(dimethylamino)methyl]-5-deuterionaphthalene (VIc) (see Table 1).

REFERENCES

- 1 G.VAN KOTEN, A.J.LEUSINK and J.G.NOLTES, *Chem.Comm.*, (1970) 1107.
- 2 A.CAMUS and N.MARSICH, *J.Organometal.Chem.*, 14 (1968) 441.
- 3 E.g., J.M.MALLAN and R.L.BEBB, *Chem.Rev.*, 69 (1969) 693; H.GILMAN and J.W.MORTON, *Org.Reactions*, Vol. 8, 1954, p. 258; U.SCHÖLLKOPF, in HOUBEN-WEYL (Eds.), *Methoden der Organischen Chemie*, Vol. 13/1, 1970, p. 87; D.J.PETERSON, *Organometal.Chem.Rev. A*, 7 (1972) 295.
- 4 E.g., F.N.JONES and C.R.HAUSER, *J.Org.Chem.*, (1962) 4389; K.P.KLEIN and C.R.HAUSER, *J.Org.Chem.*, 32 (1967) 1479.
- 5 D.A.SHIRLEY and C.FONG CHENG, *J.Organometal.Chem.*, 20 (1969) 251.
- 6 R.L.GAY and C.R.HAUSER, *J.Amer.Chem.Soc.*, 89 (1967) 2297.
- 7 E.g., W.BRÜGEL, *Nuclear Magnetic Resonance Spectra and Chemical Structure*, Vol. 1, Academic Press, New York, 1967.
- 8 G.VAN KOTEN and J.G.NOLTES, unpublished results.
- 9 G.COSTA, A.CAMUS, L.GATTI and N.MARSICH, *J.Organometal.Chem.*, 5 (1966) 568.
- 10 A.CAIRNCROSS and W.A.SHEPPARD, *J.Amer.Chem.Soc.*, 93 (1971) 247; A.CAIRNCROSS, H.OMURA and W.A.SHEPPARD, *J.Amer.Chem.Soc.*, 93 (1971) 248.
- 11 G.E.COATES and K.WADE, *Organometallic compounds*, Vol. 1, The Main Group Elements, 3rd ed., Methuen, London, 1967, p. 31.

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\*A gift of a sample of (VIa) by Dr. W.H. Dekker is gratefully acknowledged.



## CHAPTER III

### STRUCTURAL CHARACTERIZATION OF SOME 2-(DIMETHYLAMINO)METHYL-SUBSTITUTED PHENYLCOPPER COMPOUNDS

#### INTRODUCTION

Until recently, the structures of only a few organocopper compounds had been established unambiguously via X-ray analysis, viz.: the structures of a few acetylenic copper compounds and complexes [1] and of two complexes of *penta-hapto*-cyclopentadienylcopper(I) with triphenylphosphine [2] and triethylphosphine [3]. The structure of simple alkyl\*- and arylcopper compounds is unknown. The general insolubility of these compounds, which suggests a polymeric structure, has hampered the application of the available physico-chemical techniques (e.g. X-ray analysis, NMR spectroscopy, mol.wt. determinations, etc.). Green [5] envisaged three possible structures for organocopper compounds. For alkylcopper compounds a metal cluster structure with bridging alkyl groups or, less likely, ionic structures of the type  $\text{Cu}^+(\text{CuR}_2)^-$ , whereas for phenylcopper the possibility of  $\pi$ -bonding by the phenyl nucleus was suggested. Indications for a metal cluster structure were found by Cairncross et al. [6] for octameric *m*-(trifluoromethyl)phenylcopper(I), but this was not confirmed by an X-ray structure determination.

The favourable physical properties (good solubility, and relatively high thermal stability) of the pure arylcopper compounds described in Chapter II has allowed the characterization of their structures by physico-chemical techniques\*\*.

#### RESULTS AND DISCUSSION

##### *Molecular weights*

Cryometric and ebulliometric molecular weight determinations indicated that

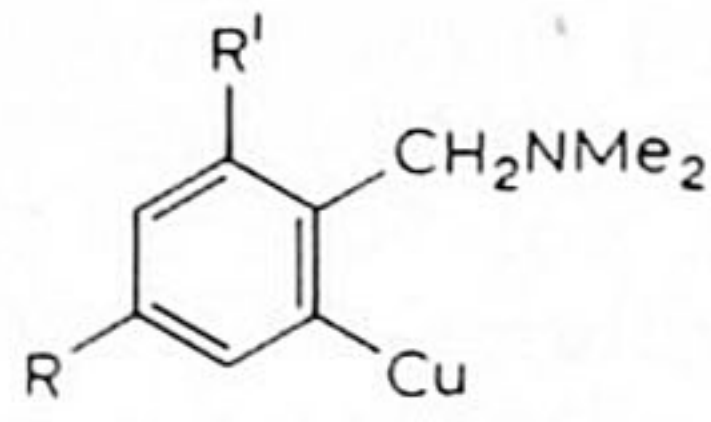
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\*Very recently a preliminary communication on the structure of  $\text{Me}_3\text{SiCH}_2\text{Cu}$  has appeared [4].

\*\*A preliminary account of the X-ray structure determination of 5-methyl-2-[(dimethylamino)methyl]phenylcopper tetramer has appeared in print, see ref. 7.



the 2-[(dimethylamino)methyl]phenylcopper compounds (I)-(III) and (V) exist in benzene solution as tetrameric species  $R_4Cu_4$ .

|  | Mol.wt. found (calcd.) |
|---|------------------------|
| (I), R = R' = H   | 792(197.5) $n = 4.0$   |
| (II), R = Me, R' = H  | 863(211.5) $n = 4.1$   |
| (III), R = OMe, R' = H  | 921(227.8) $n = 4.0$   |
| (IV), R = Cl, R' = H  | See text               |
| (V), R = H, R' = Cl   | See text               |

The molecular weight of the 5-chloro-derivative (IV) could not be determined as a result of its low solubility (at  $+5^\circ$ ) and low stability (at  $80^\circ$ ) in benzene. For the 3-chloro-derivative (V) values for  $n$  of about 3.6 were found; the molecular weight was found to be concentration independent. Impurities could not be detected (see elemental data, Chapter II; NMR spectroscopy, this Chapter).

Since the molecular weights of (I)-(III) appeared to be concentration independent these tetramers  $R_4Cu_4$  must be of considerable stability. With respect to their structure, it seemed plausible to postulate that the four RCu-units are held together by *intermolecular* Cu-N coordination. In the absence of other molecular interactions *intramolecular* Cu-N coordination can not explain the formation of these tetranuclear  $R_4Cu_4$  species.

### Structure and bonding

On the basis of their solubility properties, (I) and (II) were singled out for further study. Crystallization\* of 5-methyl-2-[(dimethylamino)methyl]phenylcopper (II) from benzene afforded single crystals suitable for X-ray analysis\*\*.

The yellow crystals are monoclinic with:  $a$  18.02;  $b$  11.35;  $c$  19.58 Å;  $\beta$   $97.6^\circ$ ; space group  $C2/c$ ;  $Z$  4. The compound has  $C_2$  symmetry in the crystal. The overall structure of compound (II) is shown in Fig. 1.

As appears from this Figure the organocopper compound (II) is also tetranuclear in the solid. The main features of this structure are:

\*Details are given in the experimental part of this Chapter.

\*\*The X-ray analysis of (II) was carried out by Prof. R. Mason and his co-workers at the University of Sussex, England.



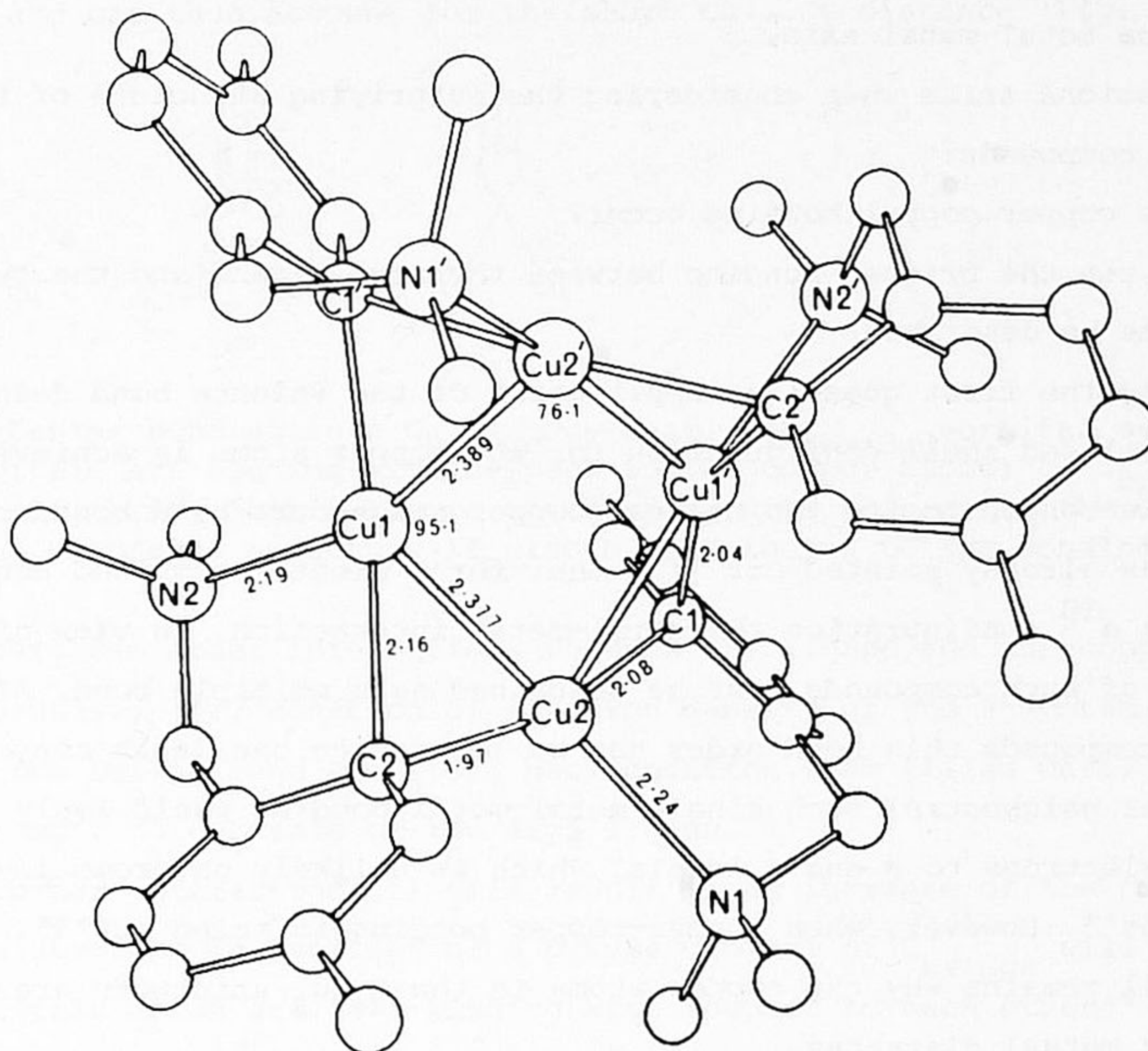


Fig. 1. Structure of tetranuclear 5-methyl-2-[(dimethylamino)methyl]phenyl-- copper (II).

1. The Cu-N distances of 2.21 Å (mean) as well as the observed stereochemistry around copper suggests that Cu-N coordination occurs.

2. The four copper atoms are positioned in a butterfly arrangement intermediate between a square planar and a tetrahedral situation. The Cu-Cu distances, which average 2.38 Å, are very short. For example in copper metal the Cu-Cu distance is 2.56 Å.

3. The most remarkable feature is the presence of bridging phenyl groups. The bonds from the aryl ligands to the respective copper atoms are either almost symmetric, 2.04 and 2.08 Å, or asymmetric, 2.16 and 1.97 Å (e.s.d.'s in the Cu-C bond average 0.015 Å).

For transition metals bridging phenyl groups have a precedent only in osmium trinuclear clusters, as recently observed by Mason et al. [8]. So far, as the main group metals are concerned the occurrence of bridging phenyl groups in the arylaluminium dimers is well known [9]. The phenyl ligands bridging the metals in the Os, Al and Cu compounds have their plane oriented about perpen-



dicular to the metal-metal axis.

Two questions arise when considering the surprising structure of these organocopper compounds:

- i. Does copper-copper bonding occur?
- ii. How can the bridged bonding between the aryl ligand and the two copper atoms be described?

Regarding the first question, application of the valence bond description shows that a closed shell configuration for the copper atoms is achieved if each copper atom is bonded to its two nearest copper neighbours by a bond order of two\*. Lewis has already pointed out [10] that for a dimetal compound containing metals with a  $d^{10}$  configuration the metal-metal interaction, in view of the diamagnetism of such compounds must be described as a multiple bond. Although for the  $Cu_4$  compounds this bond order can be lowered to one (each copper atom has two copper neighbours) such single metal-metal bonding would imply promotion of  $d$  electrons to  $s$  and  $p$  levels, which is unlikely on promotion energy considerations\*\*. However, when copper-copper bonding is ruled out\*\*\*, the question still remains why the copper atoms in the  $R_4Cu_4$  structure are placed at such short mutual distances.

A better approach to both questions seems the use of the qualitative symmetry-based theory of the stereochemistry of polynuclear complexes given by Mason and Mingos [13]. This theory provides an explanation for the observed correlation between the magnitude of the bridged bond angle and the value of the metal-metal separation found in a series of polynuclear complexes.

In the absence of metal-metal bonding the copper atoms in the  $R_4Cu_4$  compound have a distorted trigonal planar stereochemistry. The aryl-copper bonding can then be discussed in terms of a localized three center-two electron bond, resulting from overlap of  $sp^2$  hybrid orbitals (one on each of the two Cu atoms and one on the  $C_{bridge}$  atom of the phenyl group). In this electron-deficient bond the bridge orbitals are *bonding* with respect to the *copper* atoms. When other bonding interactions are absent, only this bridge-molecular orbital will

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\*The four aryl groups, four amine ligands and the four copper(I) atoms contribute a total of 56 electrons to the  $Cu_4$  cluster, leaving it 16 electrons short of achieving the noble gas configuration around each copper atom.

\*\*Promotion energy of  $Cu^+$ :  $3d^{10} \rightarrow 3d^9 4s^1 = 2.72$  eV and  $3d^{10} \rightarrow 3d^9 4p^1 = 8.25$  eV, see ref. 11.

\*\*\*This conclusion is corroborated by the absence in the Raman spectrum of (I) of a strong absorption in the region where metal-metal vibrations are expected [12].



be filled and can thus account for the short Cu...Cu distance (Fig. 2a).

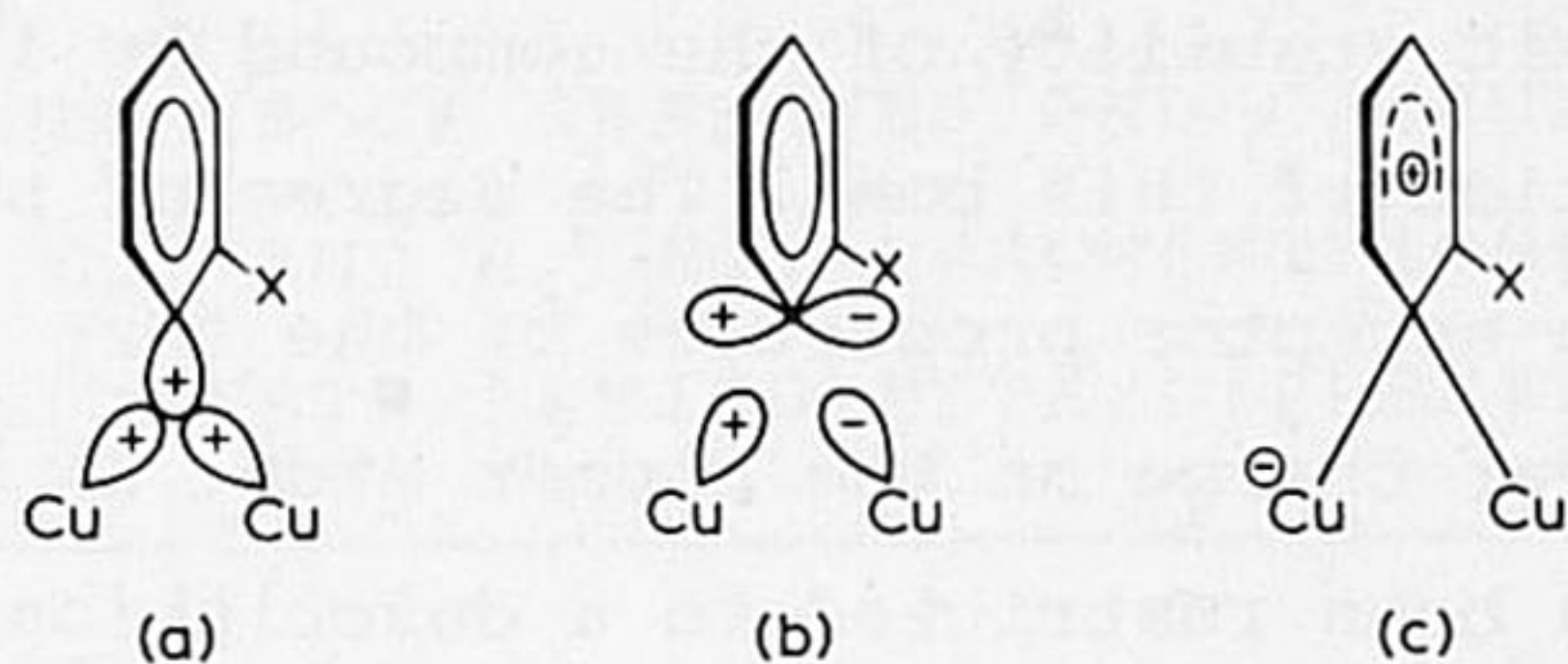


Fig. 2. 3-Center bonding in a  $C_{\text{bridge}}\text{Cu}_2$ -unit: a,  $C_{\text{bridge}}$ -orbital symmetric, bridge orbitals are bonding with respect to the copper atoms; b,  $C_{\text{bridge}}$ -orbital antisymmetric, bridge orbitals are antibonding with respect to the copper atoms; c, possible resonance structure if also b contributes to the bonding.

However, two other interactions between the ligand and the copper atoms may be operative: (i), donation of electron density of the  $\pi$  system of the aryl ligand to the bridge bond and (ii), back donation from filled metal orbitals of copper to empty  $\pi^*$  orbitals of the aryl ligand.

The former interaction (i) will result in an increase of the copper-copper separation, because an overlap\* of a  $p$  type orbital of  $C_{\text{bridge}}$  will involve copper orbitals which are *anti*-bonding with respect to each other\*\* (see Fig. 2b). This release of  $\pi$ -electron density from the ligand to the bridge bond will result in a contribution of the resonance structure depicted in Fig. 2c. As a consequence, this contribution will influence the intramolecular bond lengths\*\*\* as well as bond angles of the aromatic ring. In view of the very short Cu-Cu distance found in the  $R_4\text{Cu}_4$  compound as well as the absence of distortions in the aryl rings, interactions of this type are probably not important.

On the basis of the second interaction (ii) a rationalization of the observed higher thermal stability of the 2-(dimethylamino)methyl substituted phenylcopper compounds, as compared with that of phenylcopper, seems possible\*\*\*\*.

\*Such an overlap will be maximal when the phenyl ring is placed perpendicular to the metal-metal vector.

\*\*Examples in  $\text{Cu}^{\text{I}}$ -organic chemistry where such MO's are occupied by 2 electrons are;  $\text{Cu}_2[\text{SC}(\text{NCH}_3)_2]_6^{2+}$ , Cu-Cu 2.828 Å, Cu-S-Cu' 72.3° [14] and  $\text{Diphos}\cdot\text{CuPPh}_2$ , Cu-Cu 3.34 Å, Cu-P-Cu' 89.7° [17].

\*\*\*Malone and McDonald [9] observed that the bridging phenyl groups in the  $\text{AlPh}_3$ -dimer are considerably distorted from a regular hexagon, viz. the  $\text{C-C}_{\text{bridge}}\text{-C}$  angle is 113.7° and the two  $\text{C-C}_{\text{bridge}}$  bonds are longer (by 0.02 Å) than the mean bond lengths in the ring. Although they suggested a contribution of a resonance structure like that depicted in Fig. 2c, it appeared that also the terminal (non-bridging) phenyl rings are somewhat distorted.

\*\*\*\*Moreover, back donation of this type will reduce the possibility of non-bonding interactions between the neighbouring copper atoms. The observed short Cu-Cu distance is in line with this view.



Back donation from copper to the aryl ligand enhances the strength of the copper-aryl bond, thus increasing the kinetic stability of the compound by increasing the energy necessary for dissociation of this bond. The degree of back donation will be determined by the electron acceptor properties of the surrounding ligands and by the effective nuclear charge on the copper atom. In this respect the foregoing discussion, which has been restricted to a description of the bonding in an isolated  $C_{\text{bridge}}Cu_2$ -unit, is an oversimplification with regard to the total bonding in the  $R_4Cu_4$  cluster; each copper atom takes part in *two* electron deficient bonds and also in one  $\sigma$ -type bond with the  $NMe_2$  ligand\*. Such a Cu-N coordination decreases the effective nuclear charge on copper thereby causing an increase of the donor capacity of the  $Cu^I$  atom which results in an enhanced back bonding. Exactly this interaction, which strengthens the copper-aryl bond, distinguishes the 2- $CH_2NMe_2$  substituted phenylcopper compounds from the parent phenylcoppers.

In this connection it is of interest that fluoro-substituted arylcopper compounds display high thermal stability. Here, enhanced back donation, brought about by the better electron acceptor properties\*\* of the fluoro-substituted aryl groups as compared with the phenyl group, may be operative.

#### Mass spectrometry

The mass spectra of two tetrameric 2-[(dimethylamino)methyl]phenylcopper compounds, viz. (I) and its 5-methyl-substituted derivative (II) have been recorded. Two types of ions were present in these spectra: those containing exclusively C, H and/or N atoms and those containing in addition to these elements also  $n$  ( $n = 1$  to 4) copper atoms. The discussion will be restricted to the copper-containing ions which are readily singled out because they show patterns corresponding to the natural abundance of the  $^{63}Cu$  and  $^{65}Cu$  isotopes. Examples of the observed and calculated patterns of the various ions  $R_nCu_n^+$  are given in Table 1. In Table 2 all ions which could be assigned in both spectra\*\*\* are compiled. For comparison the mass spectra of two tetrameric fluoro-substituted arylcopper compounds, reported by Cairncross, Omura and Sheppard [16], have been included.

\*The  $NMe_2$ -ligand has no  $\pi$  bonding capacity.

\*\*For a discussion concerning this matter, see ref. 15.

\*\*\*Several patterns in the region below  $m/e$  413 (I) and 441 (II) were difficult to interpret. However, their relative intensity [calculated on  $I(R_3Cu_4^+)$ ] does not exceed 10%.



TABLE 1

EXAMPLES OF OBSERVED AND CALCULATED PATTERNS<sup>a</sup> FOR THE  $R_4^{63}\text{Cu}_4^+$  AND  $R_3^{63}\text{Cu}_4^+$  FRAGMENT-IONS IN THE MASS SPECTRUM OF 2-[(DIMETHYLAMINO)METHYL]PHENYLCOPPER TETRAMER (I)

| $R_4^{63}\text{Cu}_4^+$<br>$\text{C}_{36}\text{H}_{48}\text{N}_4^{63}\text{Cu}_4$ |                                  | $R_3^{63}\text{Cu}_4^+$<br>$\text{C}_{27}\text{H}_{36}\text{N}_3^{63}\text{Cu}_4$ |                    |
|---|----------------------------------|---|--------------------|
| <i>m/e</i>  | Found (calcd. <sup>b</sup> ) (%) | <i>m/e</i>  | Found (calcd.) (%) |
| 788   | 15.2 (14.93)                     | 654   | 16.9 (16.60)       |
| 789   | 6.5 (6.34)                       | 655   | 5.4 (5.29)         |
| 790   | 27.7 (28.04)                     | 656   | 29.5 (30.51)       |
| 791   | 11.8 (11.53)                     | 657   | 9.6 (9.55)         |
| 792   | 19.7 (20.30)                     | 658   | 21.3 (21.39)       |
| 793   | 7.6 (7.94)                       | 659   | 6.2 (6.50)         |
| 794   | 7.4 (6.96)                       | 660   | 7.4 (6.93)         |
| 795   | 2.7 (2.49)                       | 661   | 2.1 (1.99)         |
| 796   | 1.3 (1.09)                       | 662   | 1.2 (0.96)         |
|   |                                  | 663   | 0.4 (0.24)         |

<sup>a</sup> $I(x)/I(\text{total}) \times 100\%$ , in which  $I(x)$  represents the intensity of a peak at  $m/e$   $x$  and  $I(\text{total})$  the sum of all peaks belonging to the pattern ( $R_4\text{Cu}_4^+$  or  $R_3\text{Cu}_4^+$ ). <sup>b</sup>Thanks are due to Dr. L.C. Willemsens for calculation of these patterns.

The following conclusions are drawn from these data:

*i.* Substitution at the 5-site of 2-[(dimethylamino)methyl]phenylcopper does not influence the fragmentation pattern.

*ii.* No other fragments at higher mass units than that of the tetrameric species are found.

*iii.* The  $\text{Cu}_4$ -cluster in both compounds has considerable stability. This appears from the high relative abundance of the  $\text{Cu}_4$ -containing species. In this respect it is of interest that the ligand R can fragmentate while the  $\text{Cu}_4$ -skeleton remains intact. A similar fragmentation of R occurs in  $\text{Cu}_3$ - and  $\text{Cu}_2$ -containing species.

*iv.* Although the  $R_4\text{Cu}_4^+$  ions in both spectra are very abundant, the  $R_3\text{Cu}_4^+$



TABLE 2

MASS SPECTRAL DATA FOR SOME ARYL COPPER COMPOUNDS  $R_4^{63}\text{Cu}_4$ 

| Ion   | Relative abundance, % <sup>a</sup> |                   |  |  |
|---|------------------------------------|-------------------|--|--|
|   | (I) <sup>b</sup>                   | (II) <sup>c</sup> | R = <i>o</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>d</sup> | R = F <sub>5</sub> C <sub>6</sub> <sup>d</sup> |
| R <sub>4</sub> Cu <sub>4</sub>                                  | 59 (788)                           | 54 (844)          | 100 (832)  | 100 (920)                                      |
| R <sub>3</sub> Cu <sub>4</sub>                                  | 100 (654)                          | 100 (696)         |  | 15 (735)                                       |
| R <sub>3</sub> Cu <sub>4</sub> -CH <sub>4</sub>                 | 15 (638)                           | 15 (680)          |  |  |
| R <sub>3</sub> Cu <sub>4</sub> -C <sub>2</sub> H <sub>6</sub> N | 3 (610)                            | 2 (652)           |  |  |
| R <sub>3</sub> Cu <sub>4</sub> -C <sub>3</sub> H <sub>9</sub> N | 5 (595)                            | 4 (637)           |  |  |
| R <sub>2</sub> Cu <sub>4</sub> H                                | 6 (521)                            | 4 (549)           |  |  |
|   |                                    |                   | 20 (435) <sup>e</sup>  |  |
| R <sub>3</sub> Cu <sub>3</sub>                                  | 6 (591)                            | 7 (633)           | < 1 (624)  | 85 (690)                                       |
| R <sub>2</sub> Cu <sub>3</sub>                                  | 26 (457)                           | 22 (485)          |  | 85 (523)                                       |
| R <sub>2</sub> Cu <sub>3</sub> -CH <sub>4</sub>                 | 4 (441)                            | 3 (469)           |  |  |
| R <sub>2</sub> Cu <sub>3</sub> -C <sub>2</sub> H <sub>6</sub> N | 4 (413)                            | 2 (441)           |  |  |
| R <sub>2</sub> Cu <sub>2</sub>                                  | 16 (394)                           | 12 (422)          | < 1 (435)  | 40 (460)                                       |
| R <sub>2</sub> Cu <sub>2</sub> -C <sub>2</sub> H <sub>6</sub> N |                                    | 5 (378)           |  |  |
| RCu <sub>2</sub>  | 16 (260)                           |                   |  |  |
|   |                                    |                   | < 0.1 (208) <sup>f</sup>   |  |
| R <sub>2</sub> Cu   | 6 (331)                            | 7 (359)           |  |  |
| RCu-H   | 20 (196)                           | 19 (210)          |  |  |

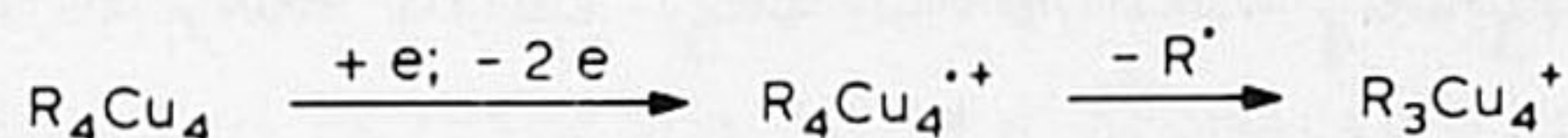
<sup>a</sup>*m/e* value between brackets. <sup>b</sup>R = 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub><sup>-</sup>. <sup>c</sup>R = 5-Me-2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>3</sub><sup>-</sup>.

<sup>d</sup>See ref. 16. <sup>e</sup>RCu<sub>4</sub>F<sub>2</sub><sup>+</sup>. <sup>f</sup>RCu.

species forms the base peak in the R<sub>*n*</sub>Cu<sub>*n*</sub> part of the mass spectrum\*. Moreover, no ions were detected in the range between *m/e*(R<sub>4</sub>Cu<sub>4</sub><sup>+</sup>) and *m/e*(R<sub>3</sub>Cu<sub>4</sub><sup>+</sup>), which suggests that the following fragmentation occurs exclusively:

\*In other words removal of one electron from the R<sub>4</sub>Cu<sub>4</sub> cluster reduces the bonding between R and Cu. This suggests that in spite of copper having *d* electrons, a valence-electron (from the bridge-bond MO) is removed.





These observations point to a higher stability of the  $R_3Cu_4^+$  species (even-electron system) than of the parent ion  $R_4Cu_4^{\cdot+}$  (odd-electron system).

The high abundance of ions of the type  $R_{n-1}Cu_n^+$  (even-electron system) may be a general feature in the mass spectra of polynuclear compounds containing bridging aryl or alkyl groups. Examples are:  $R_2Cu_3^+$  in the spectrum of (I) and (II) and of  $(C_6F_5Cu)_4$ ;  $R_3Cu_4^+$  ( $R = C_6F_5$ ), but also  $RCu_4F_2^+$  ( $R = o-CF_3C_6H_4$ ), and  $R_2Cu_4H^+$  in (I) and (II); in the spectra of ethyllithium even-electron  $Et_5Li_6^+$  and  $Et_3Li_4^+$  species have been observed [24].

v. Worthy of note are the species found at  $m/e$  331 (I) and  $m/e$  359 (II) which have been assigned to the  $R_2Cu^+$  ion. Obviously in this ion the copper atom has a formal oxidation state of two.

A striking difference with the spectra of  $(C_6F_5Cu)_4^*$  and  $(o-CF_3C_6H_4Cu)_4$  is the absence of fragment ions R-R in the spectra of (I) and (II). Most abundant species of the C, H and N-containing fragments in the spectra of (I) and (II) are  $RH^+$ ,  $R^+$  and  $R-2H^+$  \*\*.

It would seem that if  $(RCu)_n$  compounds are volatile and thermally stable, mass spectrometry may provide information concerning the degree of association in the solid. Moreover, mass spectra may supply qualitative information concerning the stability of the  $Cu_n$ -skeleton.

Mass spectrometry may also provide information about the occurrence of interaggregate exchange reactions of organocopper compounds. For example, when 2-[(dimethylamino)methyl]phenylcopper tetramer (I) and its 5-methyl derivative (II) were dissolved in benzene in a 1/1 molar ratio, a mass spectrum of the solution, recorded after 24 h, showed five patterns in the parent peak region separated by 14 mass units ranging from  $m/e$  844 [ $(5-MeR)_4^{63}Cu_4$ ] to 788 [ $R_4^{63}Cu_4$ ]. This observation indicates that intercluster exchange between  $(5-MeR)_4Cu_4$  and  $R_4Cu_4$  has taken place\*\*\* with the formation of the three possible mixed species

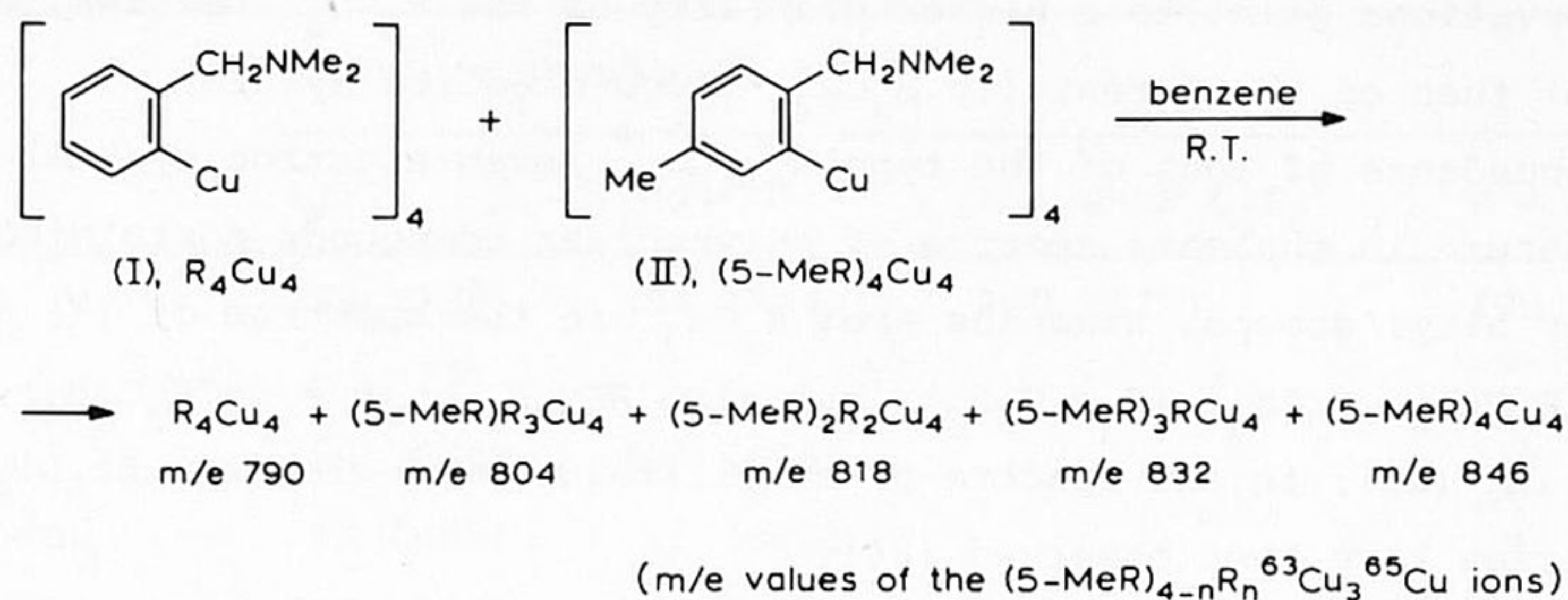
\*Decafluorobiphenyl is an abundant species in the spectrum of  $(C_6F_5Cu)_4$ . It is not clear whether this species results from fragmentation or arises from thermal decomposition [16].

\*\*Since the mass spectra are recorded at  $150^\circ$  it is believed that these ions result from fragmentation. It is interesting, however, that the observation of these ions parallels the decomposition pattern of solid (I) at  $210^\circ$ .  $RH$  is the major product whereas  $R-R$  is a minor product [17].

\*\*\*It seems unlikely that this exchange occurs in the gas phase in view of the very low pressures (about  $10^{-7}$  mm) used.



$(5\text{-MeR})\text{R}_3\text{Cu}_4$ ,  $(5\text{-MeR})_2\text{R}_2\text{Cu}_4$ , and  $(5\text{-MeR})_3\text{RCu}_4$  with  $m/e$   $^{63}\text{Cu}_3^{65}\text{Cu}$  of 804, 818 and 832, respectively.



This exchange reaction may be postulated to proceed through an octanuclear intermediate  $\text{R}_4(5\text{-MeR})_4\text{Cu}_8$  formed by association of two tetramers. Other examples of intercluster exchange reactions are presented in Chapter IX.

### $^1\text{H}$ NMR spectroscopy

The  $^1\text{H}$  NMR spectra of the tetrameric 2-[(dimethylamino)methyl]phenylcopper compounds (I)-(V) show the expected resonance patterns as well as correct peak area ratios. As an example the spectrum of 2-[(dimethylamino)methyl]phenylcopper (I) in benzene- $d_6$  is shown in Fig. 3, while the chemical shift data of

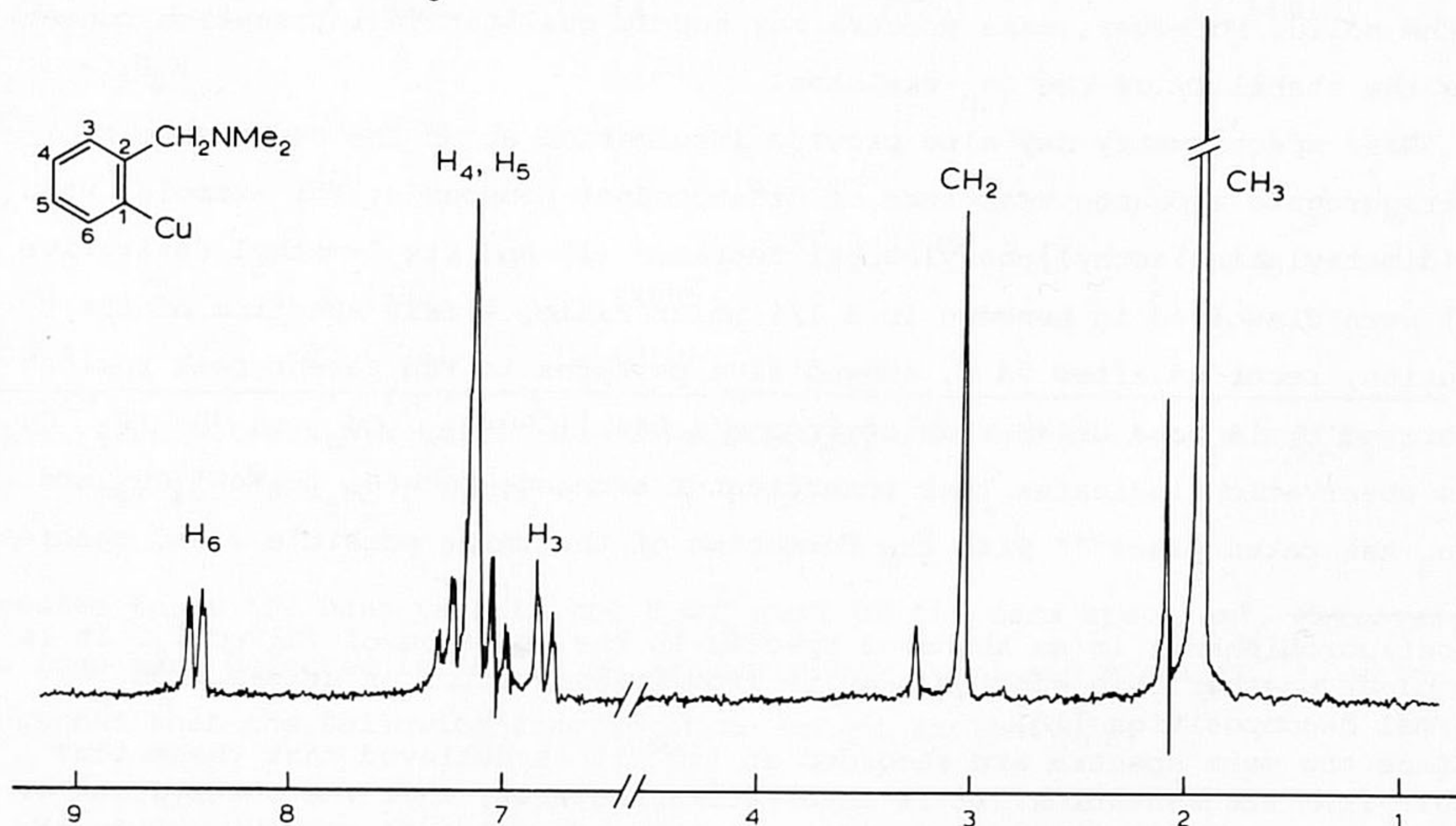


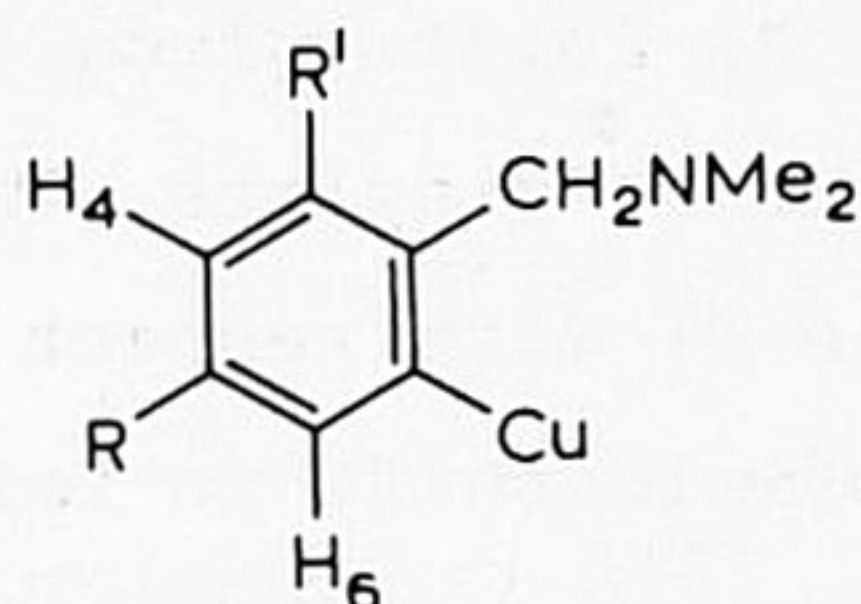
Fig. 3. NMR spectrum ( $\delta$  ppm) of 2-[(dimethylamino)methyl]-phenylcopper (I) in benzene- $d_6$ . (The resonances at 2.08 and 3.28 ppm are due to  $N,N$ -dimethylbenzylamine.)



this and the other compounds are compiled in Table 3. The assignment of the respective multiplets in the aromatic region is based upon their multiplicity as well as on their relative peak areas.

TABLE 3

$^1\text{H}$  NMR DATA<sup>a</sup> OF THE 2-[(DIMETHYLAMINO)METHYL]PHENYLCOPPER COMPOUNDS (I)-(V)



| Compound                                  | $\delta$ (ppm)   |                  |                     |  |  |   |  |
|---|------------------|------------------|---------------------|--|--|---|--|
|   | NCH <sub>3</sub> | NCH <sub>2</sub> | R(CH <sub>3</sub> ) | H <sub>6</sub>   | H <sub>3</sub>   | H <sub>4,5</sub>                            |  |
| (I)<br>R = R' = H                         | 1.90<br>(s)      | 3.02<br>(s)      |                     | 8.45<br>(d of d)<br>$J_{5,6} \approx 6$ Hz<br>$J_{4,6} \approx 2$ Hz     | 6.80<br>(d of d)<br>$J_{3,4} \approx 7$ Hz<br>$J_{3,5} \approx 1.5$ Hz | 7.0-7.35<br>(m)                             |  |
| (II)<br>R = 5-Me<br>R' = H <sub>3</sub>   | 1.98<br>(s)      | 3.06<br>(s)      | 2.44<br>(s)         | 8.37<br>(d)<br>$J_{4,6} \approx 1$ Hz <sup>b</sup>                       | 6.78<br>(d)<br>$J_{3,4} \approx 8$ Hz <sup>b</sup>                     | $\approx 6.95$<br>(H <sub>4</sub> , d of d) |  |
| (III)<br>R = 5-OMe<br>R' = H <sub>3</sub> | 1.99<br>(s)      | 3.04<br>(s)      | 3.64<br>(s)         | 8.20<br>(d)<br>$J_{4,6} \approx 2.5$ Hz                                  | 6.76<br>(d)<br>$J_{3,4} \approx 8$ Hz                                  | 6.58<br>(H <sub>4</sub> , d of d)           |  |
| (IV)<br>R = 5-Cl<br>R' = H <sub>3</sub>   | 1.86<br>(s)      | 2.80<br>(s)      |                     | 8.43<br>(d)<br>$J_{4,6} \approx 2.5$ Hz                                  | 6.50<br>(d)<br>$J_{3,4} \approx 8$ Hz                                  | 7.02<br>(H <sub>4</sub> , d of d)           |  |
| (V)<br>R = H <sub>6</sub><br>R' = 3-Cl    | 1.81<br>(s)      | 3.37<br>(s)      |                     | 8.10<br>(d of d)<br>$J_{5,6} \approx 6.5$ Hz<br>$J_{4,6} \approx 1.5$ Hz |  | 6.85-7.1<br>(m)                             |  |

<sup>a</sup>In benzene-*d*<sub>6</sub> at ambient temperature; TMS internal standard. <sup>b</sup>Values taken from the spectrum recorded at 90°.



The NMR spectra are remarkably simple. This implies that they reveal no *positive* information, neither on the arrangement of the aryl ligands around the  $\text{Cu}_4$  cluster, nor about the interaction of the (dimethylamino)methyl ligand with copper\*. However, it is assumed that the main structural features for the compounds (I)-(V) (multicenter bonded aryl groups; tetranuclear  $\text{Cu}_4$  cluster) are retained in solution. This view seems justified, (*i*) by the observation that both in the solid and in solution the compounds are tetranuclear and (*ii*) by the positive proof ([18,19] and Chapter IX) for multicenter-bonded aryl groups in the related  $\text{R}_4\text{Cu}_2\text{Li}_2$  and  $\text{R}_4\text{Ag}_2\text{Li}_2$  compounds in solution. As follows from Table 3 and Fig. 3, the benzylic and the *N*-methyl protons appear as singlets. These singlets are shifted upfield (by 0.09-0.27 ppm, see Table 4) with respect to those of the parent arenes. An interpretation of this upfield shift in terms of absence of Cu-N coordination is doubtful because in the NMR spectra of the 2-[(dimethylamino)methyl]phenyl-palladium [20], -platinum [20], -cobalt [21], -copperlithium and -lithium compounds both upfield (Co, CuLi and Li) as well as downfield shifts (Pd and Pt) for the  $\text{NCH}_3$  and  $\text{NCH}_2$  proton resonances have been observed. For all these compounds M-N coordination is assumed to take place. In contrast with the Co, CuLi and Li compounds the NMR spectra of the organocopper derivatives (I) and (V) (3-Cl) are temperature independent. Also at low temperatures ( $-80^\circ$ ) the  $\text{CH}_2$  and  $\text{CH}_3$  protons appear as singlets. It does not seem unreasonable to assume that in solution the "hard"  $\text{CH}_2\text{NMe}_2$ -ligand will only weakly coordinate with the "soft" copper(I) atom, as predicted by the HSAB principle.

In Table 4  $\Delta\delta$  ( $= \delta_{\text{RH}} - \delta_{\text{RCu}}$ ) for the respective protons are given. From this Table it appears that large downfield shifts (about 1.2 to 1.4 ppm) are found for the protons ( $\text{H}_6$ ) *ortho* to the C(1)-Cu bond, whereas the protons ( $\text{H}_3$ ) *ortho* to the  $\text{CH}_2\text{NMe}_2$ -ligand are shifted slightly upfield (0.3-0.6 ppm). The influence of the solvent on  $\delta$  is small (about 0.2 ppm) as appears from Table 5 in which the spectra of (I) recorded in  $\text{C}_6\text{D}_6$ ,  $\text{C}_5\text{D}_5\text{N}$  and  $\text{c-C}_6\text{H}_{12}$  are compiled. The origin of the large  $\Delta\delta$  values for the protons  $\text{H}_3$  and  $\text{H}_6$  has been discussed for aryl-copper [22], -lithium [23] and -magnesium halide [23] compounds in terms of

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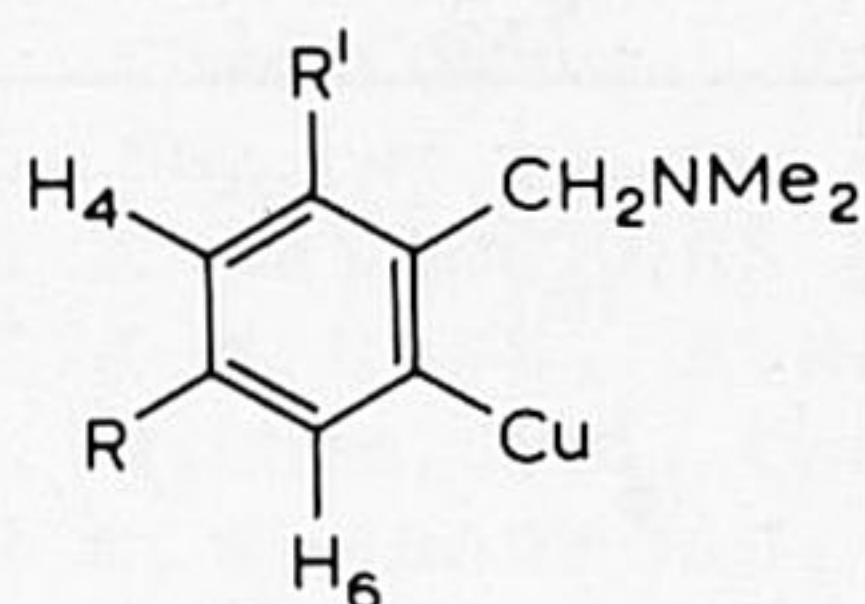
\*In contrast, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the organo-lithium, -copperlithium and silverlithium compounds described in Chapter IX provide direct information about the structures concerned (bridging aryl groups and Li-N coordination).



the magnetic anisotropy of C(1)\*.

TABLE 4

EFFECT ON  $\delta$  OF INTRODUCING A COPPER ATOM INTO DIMETHYLBENZYL-AMINES *ortho* WITH RESPECT TO THE (DIMETHYLAMINO)METHYL GROUP



| Organocopper compound                     | $\Delta(\delta_{\text{arene}} - \delta_{\text{RCu}})^a$ (ppm) |                  |                            |                |                  |               |
|---|---|------------------|----------------------------|----------------|------------------|---------------|
|   | NCH <sub>3</sub>  | NCH <sub>2</sub> | H <sub>6</sub>             | H <sub>3</sub> | H <sub>4,5</sub> | 5-Substituent |
| (I)<br>R = R' = H                         | 0.18  | 0.14             | -1.30                      | 0.35           | $\approx 0$      |               |
| (II)<br>R = 5-Me<br>R' = H <sub>3</sub>   | 0.10  | 0.18             | -1.38                      | 0.46           | 0.04             | Me, -0.33     |
| (III)<br>R = 5-OMe<br>R' = H <sub>3</sub> | 0.09  | 0.18             | -1.43                      | 0.46           | 0.19             | MeO, -0.31    |
| (IV)<br>R = 5-Cl<br>R' = H <sub>3</sub>   | 0.12  | 0.25             | -1.44                      | 0.60           | $\approx 0$      |               |
| (V)<br>R = H <sub>6</sub><br>R' = 3-Cl    | 0.27  | 0.05             | $\approx -1.16 \pm 0.10^b$ |                | $c$              |               |

<sup>a</sup>Arene = *N,N*-dimethylbenzylamine or its *para*- or *ortho*-substituted derivatives; RCu = the corresponding organocopper compound. <sup>b</sup>Estimated value. <sup>c</sup>Not determined since the H<sub>4</sub>- and H<sub>5</sub>-multiplets are partly matching each other.

\*The large downfield shifts for C(1) and to a lesser extent of C(2) and C(6) in the <sup>13</sup>C NMR spectra (see Chapter IX) of R<sub>4</sub>Cu<sub>4</sub> (I) and the corresponding copper-lithium R<sub>4</sub>Cu<sub>2</sub>Li<sub>2</sub> and lithium (5-MeR)<sub>4</sub>Li<sub>4</sub> derivatives are in accord with this view: about 25 ppm for C(1) in R<sub>4</sub>Cu<sub>4</sub>, 40 ppm in R<sub>4</sub>Cu<sub>2</sub>Li<sub>2</sub> and 47 ppm in (5-MeR)<sub>4</sub>Li<sub>4</sub> relative to benzene; for C(2,6) values of 15, 16-20 and 10-12 ppm, respectively, are found.



TABLE 5

<sup>1</sup>H NMR DATA<sup>a</sup> OF 2-[(DIMETHYLAMINO)METHYL]PHENYLCOPPER (I)  
IN VARIOUS SOLVENTS

| Solvent  | $\delta$ (ppm)   |                  |                  |                  |                  |
|--|------------------|------------------|------------------|------------------|------------------|
|  | NCH <sub>3</sub> | NCH <sub>2</sub> | H <sub>6</sub>   | H <sub>3</sub>   | H <sub>4,5</sub> |
| Benzene- <i>d</i> <sub>6</sub>   | 1.90<br>(s)      | 3.02<br>(s)      | 8.45<br>(d of d) | 6.80<br>(d of d) | 7.0 -7.35<br>(m) |
| Benzene- <i>d</i> <sub>6</sub> /<br>pyridine- <i>d</i> <sub>5</sub><br>(0.4 ml/30 $\mu$ l) | 1.91<br>(s)      | 3.03<br>(s)      | <i>b</i>         | <i>b</i>         | <i>b</i>         |
| Pyridine- <i>d</i> <sub>5</sub>  | 1.98<br>(s)      | 3.12<br>(s)      | 8.48<br>(d of d) | 6.94<br>(d of d) | 7.1 -7.5<br>(m)  |
| Cyclohexane  | <i>b</i>         | 3.03<br>(s)      | 8.24<br>(d of d) | 6.68<br>(d of d) | 6.80-7.15<br>(m) |

<sup>a</sup>At ambient temperature; TMS internal standard. <sup>b</sup>Masked by solvent resonances.

## EXPERIMENTAL\*

The synthesis of the 2-(dimethylamino)methyl-substituted phenylcopper compounds (I)-(V) has been described in Chapter II.

The <sup>1</sup>H NMR spectra were recorded using a Varian Associates HA-100 NMR spectrometer. The mass spectra were recorded on an AEI Ms 9 mass spectrometer (70 eV, ionization chamber temp. 150-170°).

*Preparation of single crystals of 5-methyl-2-[(dimethylamino)-methyl]phenylcopper (II)*

An ampoule was charged with about 0.2 g of (II). At 60° benzene was added until a saturated solution was obtained. The ampoule was sealed off, placed in a thermostated waterbath and then continuously cooled down from 60 to 20° at a rate of 2°/24 h.

*Interaggregate exchange reaction between (I) and (II)*

A mixture of equimolar amounts (0.18 mmole) of (I) and (II) was dissolved in benzene (1 ml). The resulting solution was stirred at room temperature for 24 h. A sample of this solution was transferred to the direct-insertion probe of the mass spectrometer.

\*General directions dealing with solvents, apparatus and reaction conditions are presented in Chapter IX.



## REFERENCES

- 1 G.E.COATES, M.L.H.GREEN and K.WADE , Organometallic Compounds, Vol. II, 3rd ed., Methuen, London, 1968, pp. 275 and 278.
- 2 F.A.COTTON and J.TAKATS , J.Amer.Chem.Soc., 92 (1970) 2353.
- 3 L.T.J.DELBAERE, D.W.McBRIDE and R.B.FERGUSON , Acta Crystallogr., Sect. B, 26 (1970) 515.
- 4 J.A.JARVIS, B.T.KILBOURN, R.PEARCE and M.F.LAPPERT , J.Chem.Soc., Chem.Comm., (1973) 475.
- 5 See ref. 1, p. 254.
- 6 A.CAIRNCROSS and W.A.SHEPPARD , J.Amer.Chem.Soc., 93 (1971) 247.
- 7 J.M.GUSS, R.MASON, I.SOTOFTE, G.VAN KOTEN and J.G.NOLTES , J.Chem.Soc., Chem.Comm., (1972) 446.
- 8 C.W.BRADFORD, R.S.NYHOLM, G.J.GAINSFORD, J.M.GUSS, P.IRELAND and R.MASON , J.Chem.Soc., Chem.Comm., (1972) 87; *ibid.*, J.Organometal.Chem., 40 (1972) C 70.
- 9 J.F.MALONE and W.S.McDONALD, Chem.Comm., (1967) 444 and (1970) 280.
- 10 J.LEWIS, Pure Appl.Chem., 10 (1965) 11.
- 11 R.S.NYHOLM , Proc.Chem.Soc., (1961) 273.
- 12 D.J.STUFKENS, private communication.
- 13 R.MASON and D.M.P.MINGOS , J.Organometal.Chem., 50 (1973) 53.
- 14 M.S.WEININGER, I.F.TAYLOR and E.L.AMMA, Inorg.Nucl.Chem.Lett., 9 (1973) 737.
- 15 D.HOLTZ, Chem.Rev., 71 (1971) 139 and references cited therein.
- 16 A.CAIRNCROSS, H.OMURA and W.A.SHEPPARD, J.Amer.Chem.Soc., 93 (1971) 248.
- 17 G.VAN KOTEN and J.G.NOLTES , to be published.
- 18 G.VAN KOTEN and J.G.NOLTES , J.Chem.Soc., Chem.Comm., (1972) 940.
- 19 A.J.LEUSINK, G.VAN KOTEN and J.G.NOLTES , J.Organometal.Chem., 55 (1973) 419.
- 20 G.LONGONI, P.FANTUCCI, P.CHINI and F.CANZIANI, J.Organometal.Chem., 39 (1972) 413.
- 21 A.C.COPE and R.N.GOURLEY, J.Organometal.Chem., 8 (1967) 527.
- 22 A.BAICI, A.CAMUS and G.PELLIZER, J.Organometal.Chem., 26 (1971) 431.
- 23 J.A.LADD and J.PARKER, J.Chem.Soc., Dalton Trans., (1972) 930.
- 24 M.Y.DARENSBOURG, B.Y.KIMURA, G.E.HARTWELL and T.L.BROWN, J.Amer.Chem.Soc., 92 (1970) 1236 and references cited therein.







## CHAPTER IV

### THE REACTIONS OF 2-[(DIMETHYLAMINO)METHYL]PHENYL-COPPER AND -LITHIUM TETRAMER WITH CUPROUS AND CUPRIC HALIDES

#### INTRODUCTION

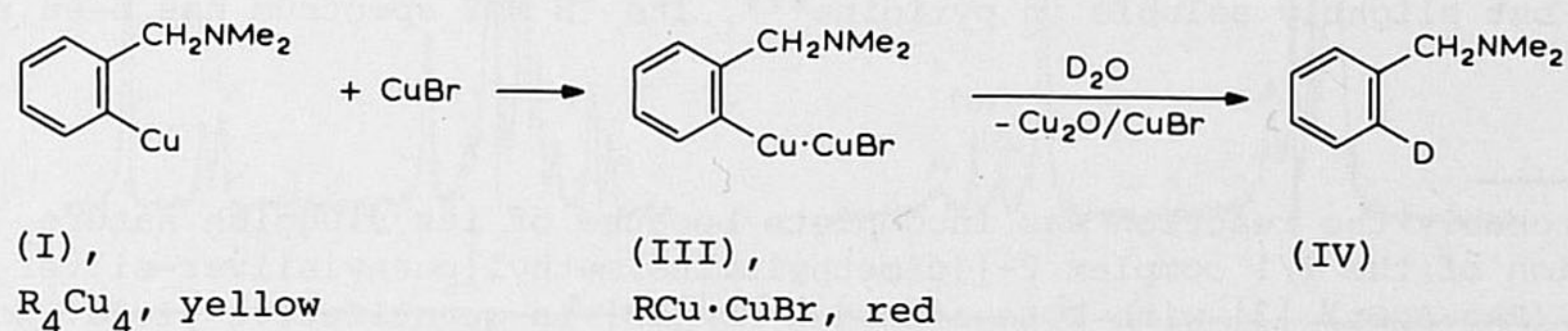
Among the reported arylcopper compounds only relatively few have been isolated in the pure state. This is mainly ascribed to their general low solubility, which hampers their purification, as well as to the tendency to form complexes with metal salts formed as by-products in their preparation (e.g.  $MgX_2$  or  $LiX$ ) [1,2]. During the present study it has been observed that arylcopper compounds can form complexes with copper(I) halides and that this type of complex formation often interferes severely with attempts to isolate pure, well-defined species\*.

To gain a better insight in the course of the reactions of organolithium compounds with copper halides the reactions of 2-[(dimethylamino)methyl]phenyl-copper [RCu, (I)] and -lithium [RLi, (II)] with cuprous as well as with cupric halides have been investigated in greater detail.

#### RESULTS AND DISCUSSION

##### *The reaction of 2-[(dimethylamino)methyl]phenylcopper (I) with cuprous bromide*

Slow addition of solid cuprous bromide to a benzene solution of an equimolar amount of (I) afforded a red precipitate and a red solution.



\*See, for example, the synthesis of the dimethylamino-substituted phenylcopper compounds, Chapter VI.



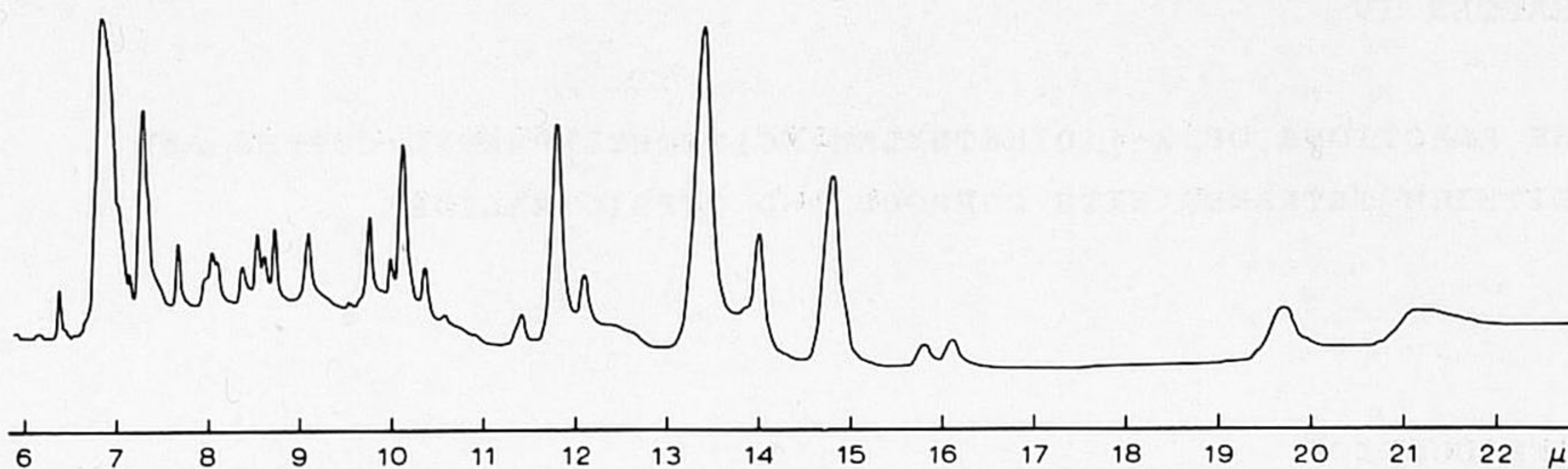


Fig. 1. IR spectrum (nujol) of 2-[(dimethylamino)methyl]phenylcopper-cuprous bromide (III).

Elemental analysis of the hydrocarbon- and ether-insoluble precipitate pointed to the isolation of a complex (IIIa) consisting of the organocopper (I), CuBr and benzene (IR absorption at  $674\text{ cm}^{-1}$ ) in a 1/1.4/0.2 molar ratio. When a slight *excess* of the organocopper (I) was used in this reaction (molar ratio RCu/CuBr 1.02/1) a red solid (IIIb) was isolated (68% yield) with an RCu/CuBr/ $\text{C}_6\text{H}_6$  molar ratio of 1/1.2/0.2. The IR spectra of (IIIa) and (IIIb) (see Fig. 1) were identical in the  $2000\text{-}400\text{ cm}^{-1}$  region which suggests that in both cases a mixture of a discrete complex — most probably the 1/1 complex RCu·CuBr (III) — with cuprous bromide had been formed\*.

As compared with the parent organocopper (I) (dec. at  $175\text{-}185^\circ$ ) the 1/1 complex has a considerably decreased thermal stability [e.g. (IIIa), dec. at  $96\text{-}98^\circ$ ].

The deuterolysis of (III), which required prolonged reaction times (96 h with  $\text{D}_2\text{O}$ ; 24 h with DOAc), gave (2-deuteriobenzyl)dimethylamine [RD, (IV)] in 72 and 90% yield, respectively. Not a trace of the dimer 2,2'-bis[(dimethylamino)methyl]biphenyl [RR, (V)] could be detected in the reaction mixtures\*\*.

The 1/1 complex RCu·CuBr (III) is insoluble in hydrocarbon solvents and ethers, but slightly soluble in pyridine\*\*\*. Its  $^1\text{H}$  NMR spectrum has been re-

\*Most probably the reaction was incomplete because of its sluggish nature.

\*\*Reaction of the 1/1 complex 2-[(dimethylamino)methyl]phenylsilver-silver bromide ( $\text{RAg}\cdot\text{AgBr}$ ) [3] with DOAc afforded RD (IV) in quantitative yield. However, deuterolysis with  $\text{D}_2\text{O}$  resulted in the formation of the biaryl RR (V) (100% yield).

\*\*\*The insolubility in non-complexing solvents suggests a polymeric structure  $(\text{RCu}\cdot\text{CuBr})_n$  rather than a discrete cluster structure as has been established by X-ray analysis for the 2/1 complex of 2-(dimethylamino)phenylcopper with cuprous bromide, see Chapter VII.



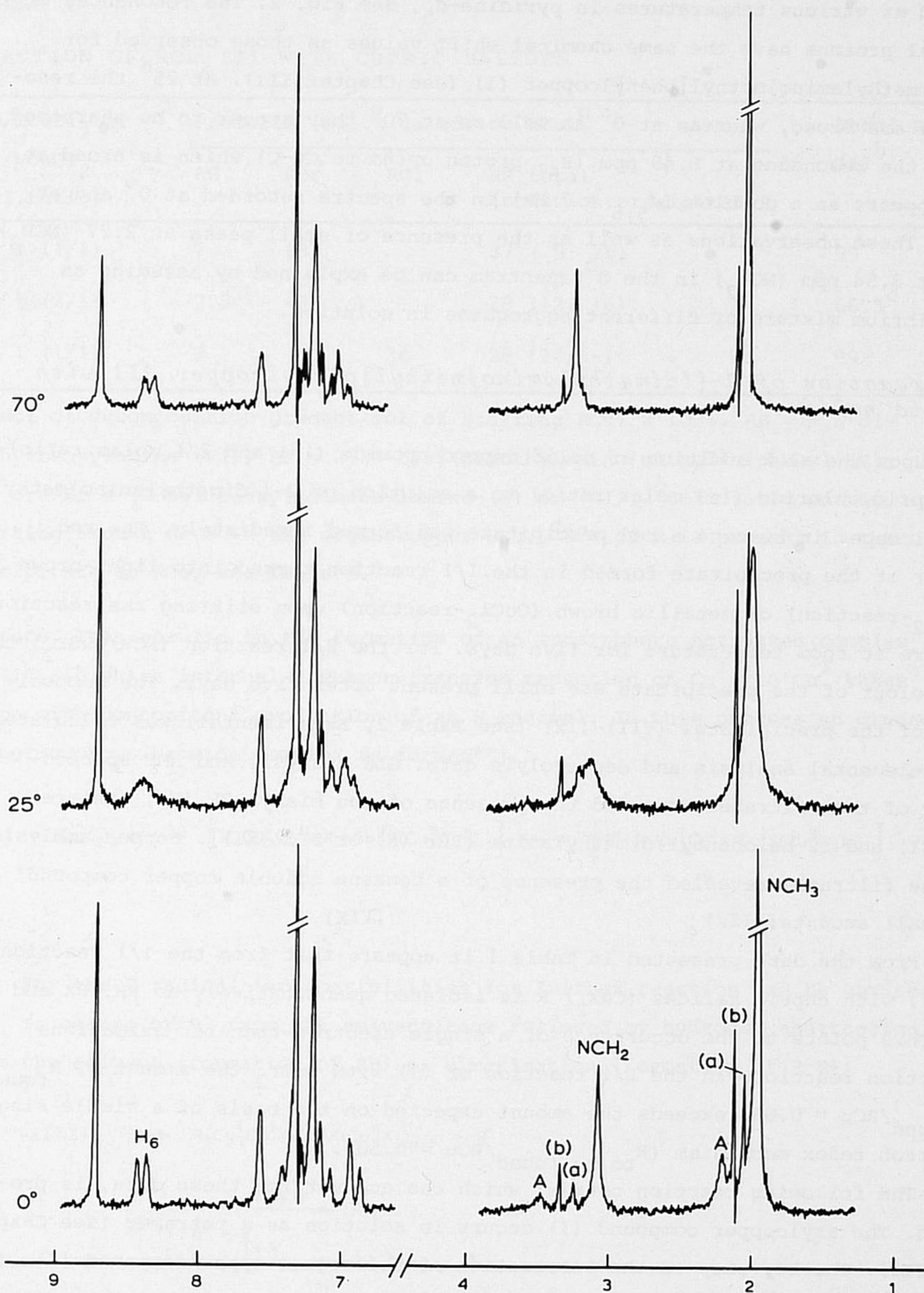


Fig. 2.  $^1\text{H}$  NMR spectra ( $\delta$  ppm) of (III) in pyridine- $d_5$  at different temperatures. RR (V) [resonances marked with (a)] and RH (VI) [resonances marked with (b)] are present as impurities.



corded at various temperatures in pyridine- $d_5$ , see Fig. 2. The resonances of the several protons have the same chemical shift values as those observed for 2-[(dimethylamino)methyl]phenylcopper (I) (see Chapter III). At 25° the resonances are broad, whereas at 0° as well as at 70° they appear to be sharpened [e.g. the resonance at 8.40 ppm ( $H_6$ , proton *ortho* to Cu-C) which is broad at 25° appears as a doublet ( $J_{5,6} \approx 7$  Hz) in the spectra recorded at 0° and at 70°]. These observations as well as the presence of small peaks at 2.27 (NCH<sub>3</sub>) and at 3.54 ppm (NCH<sub>2</sub>) in the 0° spectrum can be explained by assuming an equilibrium mixture of different aggregates in solution.

*The reaction of 2-[(dimethylamino)methyl]phenylcopper (I) with cupric halides*

Upon the slow addition of solid cupric bromide (1/1 and 2/1 molar ratio) or cupric chloride (1/1 molar ratio) to a solution of 2-[(dimethylamino)methyl]phenylcopper in benzene a red precipitate was formed immediately. The red colour of the precipitate formed in the 1/1 reaction turned into light-brown (CuBr<sub>2</sub>-reaction) or metallic brown (CuCl<sub>2</sub>-reaction) upon stirring the reaction mixture at room temperature for five days. For the 2/1 reaction (RCu/CuBr<sub>2</sub>) the red colour of the precipitate was still present after five days. The composition of the precipitates (VII)-(IX) (see Table 2, Experimental) was calculated from elemental analysis and deuterolysis data. GLC analysis and NMR spectroscopy of the filtrates revealed the presence of the biaryl RR (V), the arene RH (VI) and (2-halobenzyl)dimethylamine [RBr (X) or RCl (XI)]. Copper analysis of the filtrates revealed the presence of a benzene soluble copper compound\* in small amounts.

From the data presented in Table 1 it appears that from the 1/1 reactions of (I) with cupric halides (CuX<sub>2</sub>) R is isolated quantitatively as RR, RX and RH. This points to the occurrence of a single electron-transfer oxidation-reduction reaction. In the 2/1 reaction of (I) with CuBr<sub>2</sub> the amount of R<sub>found</sub> ( $R_{\text{found}}/RCu \approx 0.66$ ) exceeds the amount expected on the basis of a simple single electron redox mechanism ( $R_{\text{to be found}}/RCu = 0.50$ ).

The following reaction course, which can account for these data, is proposed. The arylcopper compound (I) occurs in solution as a tetramer (see Chapter III). The key step in the interaction of the organocopper compound (I) with the benzene-insoluble cupric halides involves complex formation at the crystal

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\*This is most probably a complex of a copper(I) halide with one of the amines RH, RR or RX present in the filtrates.



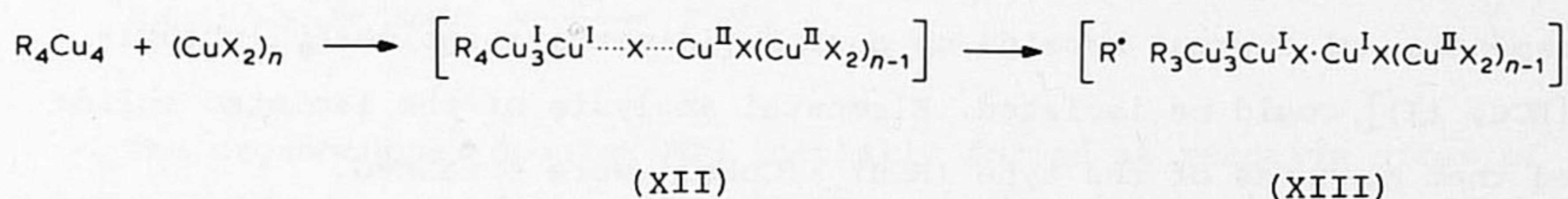
TABLE 1

## REACTION OF RCu (I) WITH CUPRIC HALIDES

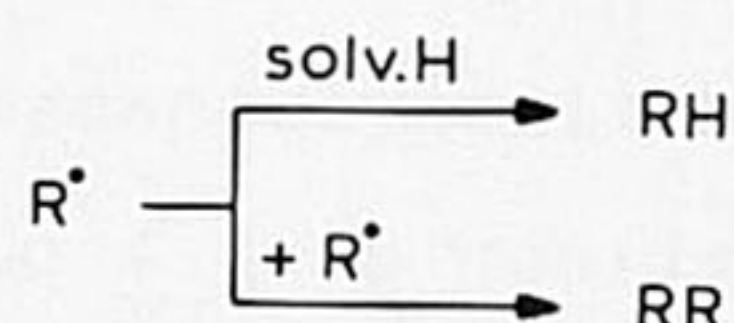
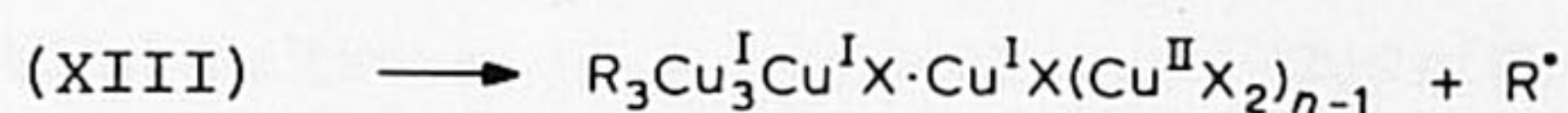
| RCu/ $x$ CuBr <sub>2</sub> or<br>RCu/ $y$ CuCl <sub>2</sub><br>(mol.ratio) | Products (mol.% calcd. on RCu) <sup>a</sup> |     |     |                                    | Total R<br>(%) <sup>b</sup> |
|--|---|-----|-----|------------------------------------|-----------------------------|
|  | RH  | RBr | RCl | RR total<br>(solution;precipitate) |                             |
| $x = 1$ (1/1)  | 7   | 18  |     | 37 ( 9; 28)                        | 99                          |
| $x = \frac{1}{2}$ (2/1)  | 2.5   | 8   |     | 28 (12; 16)                        | 66.5 <sup>c</sup>           |
| $y = 1$ (1/1)  | 9   |     | 34  | 28 (28; -)                         | 99                          |

<sup>a</sup>(Mol of decomposition product/mol of starting RCu) x 100%. RH = *N,N*-dimethylbenzylamine (VI); RR = 2,2'-bis[(dimethylamino)methyl]biphenyl (V); RCl or RBr = (2-halobenzyl)dimethylamine (X) or (XI). <sup>b</sup>Calculated on the starting amount of R in the organocopper RCu. <sup>c</sup>37% of R is present in the precipitate as RCu, see Table 2.

surface. This results in the formation of an innersphere activated complex (XII)\*, in which internal electron-transfer reduction of Cu<sup>II</sup> to Cu<sup>I</sup> takes place with concomitant production of an R radical. In this process an organo-copper-cuprous bromide complex is formed\*\*:



For the R radical two possibilities for further reaction can be envisaged: *i*, escape of R<sup>·</sup> from the solvent cage followed by hydrogen abstraction from the solvent (formation of RH) or dimerization (formation of R-R):

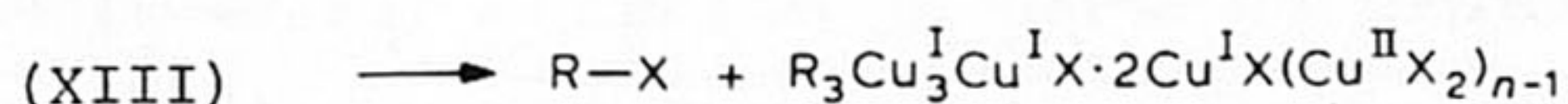
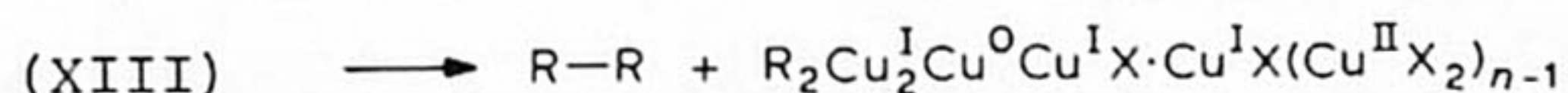


\*A similar complex has been proposed as a possible intermediate in the reaction of trialkylboranes and copper(I) halides [4].

\*\*The precipitate formed in the early stage of the reaction has a red colour [cf. red colour of RCu·CuX (III)].



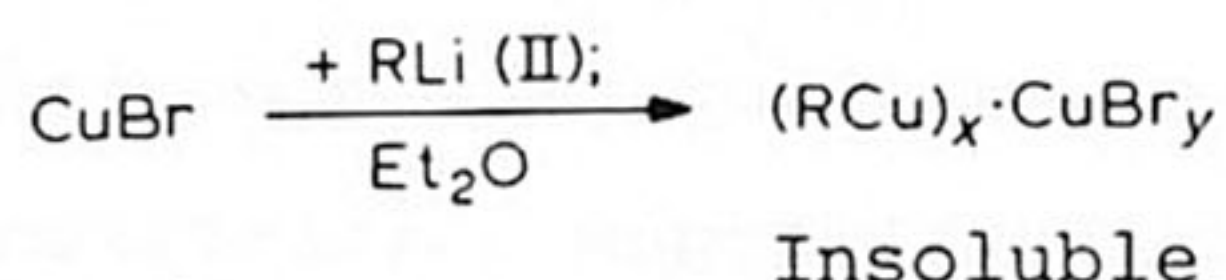
*ii*, intramolecular reaction of R· with a Cu<sup>I</sup>-R or with a Cu<sup>II</sup>-X bond:



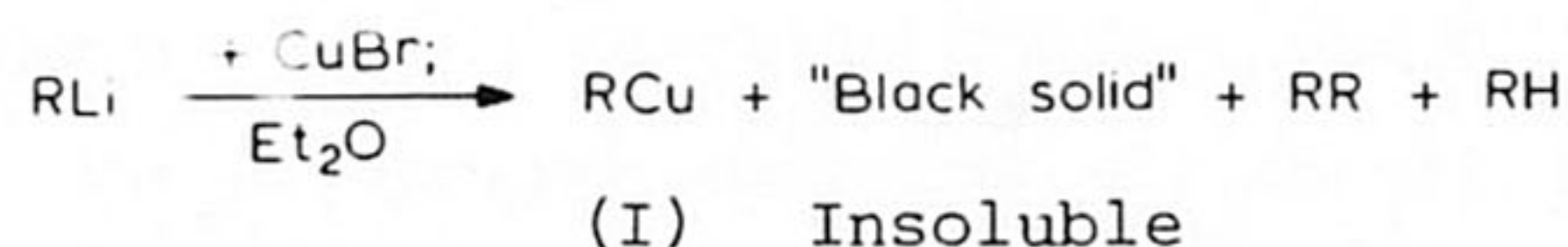
In view of the low yield of RH (see Table 1) possibility (*i*) seems to represent the less probable reaction path. Obviously, intramolecular trapping of the R radical by the Cu<sup>I</sup>-R bond (to give Cu<sup>0</sup> and RR) or by the Cu<sup>II</sup>-X bond\* (to give Cu<sup>I</sup> + RX) is preferred. The latter two reactions are competitive, the RR/RX ratio depending on the type of cupric halide used (see Table 1). These reactions also provide an explanation for the  $R_{\text{found}}/RCu$  ratio of 0.66 as well as for the lower yield of RBr in the 2/1 as compared with the 1/1 reaction of (II) with cupric bromide. The "concentration" of Cu<sup>I</sup>-R bonds in the innersphere complex will be twice that in the complexes formed in the 1/1 reactions. This makes the intramolecular trapping of the R radical in the first case more probable.

*The reactions of 2-[(dimethylamino)methyl]phenyllithium (II) with cuprous and cupric halides*

Organocopper compounds have generally been prepared by the slow addition of the arylating reagent to an ether suspension of the copper salt (reversed addition) [1,2,6]. However, when the organolithium compound (II) was added to an ether suspension of cuprous bromide no pure 2-[(dimethylamino)methyl]phenylcopper [RCu, (I)] could be isolated. Elemental analysis of the isolated solids indicated that mixtures of the type  $(RCu)_x \cdot (CuBr)_y$  were obtained.



It appeared that only the addition of cuprous bromide to the organolithium solution allows the isolation of pure RCu (I).



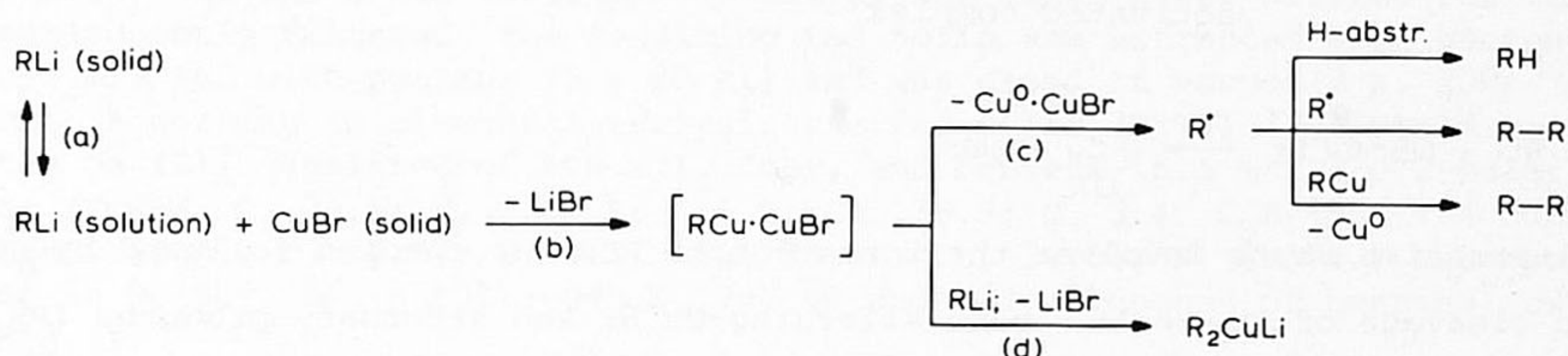
\*Recently Snider [5] reported the oxidative coupling of *trans*-CF<sub>3</sub>CF=C(CF<sub>3</sub>)Ag (R'Ag) with CuBr<sub>2</sub> to yield 48% of the bromo derivative (R'Br) and 42% of the dimer (R'-R'). Most probably also this reaction proceeds through an innersphere complex of type (XII).



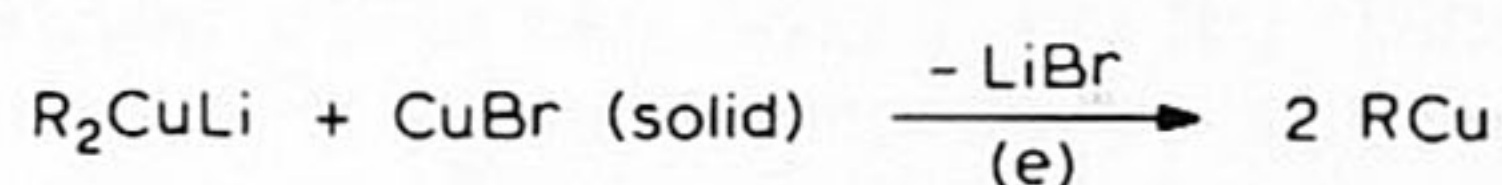
In this reaction during the early stages of the addition of the cuprous bromide the formation of a "black solid" (Cu-content 70-80%) was observed (see below). According to NMR spectroscopy the dimer RR (V) and the arene RH (VI) are present as side products\*. As pointed out below, these observations are connected with complex formation of 2-[(dimethylamino)methyl]phenylcopper with cuprous bromide. Interestingly, when cupric halides were used instead of cuprous bromide in this reaction (ratio RLi/CuBr<sub>2</sub> 2/1) the formation of the "black solid" did not occur.

Based on our results derived from the reactions of the organocopper (I) with cuprous and cupric halides the following picture may be presented for the course of the metathesis reaction of 2-[(dimethylamino)methyl]phenyllithium (II) with cuprous halides (addition of CuBr to RLi):

i.  $\text{CuBr/Li} \leq \frac{1}{2}$



ii.  $\frac{1}{2} < \text{CuBr/Li} \leq 1$



The organocopper species RCu initially formed at reactive sites of the highly insoluble cuprous bromide coordination polymer gives rise to the formation of complexes of the type  $(\text{RCu})_x \cdot (\text{CuBr})_y$  (step b). Several of these complexes are thermally unstable and decompose via homolytic cleavage of the Cu-C bond to give  $\text{Cu}^0 \cdot (\text{CuBr})_y$  (the so-called "black solid") and products originating from R<sup>•</sup> (step c). If an *excess* of the organolithium compound is present in the reaction mixture (i.e. addition of CuBr to RLi), the more stable complexes react further yielding ether-soluble organocopperlithium species (step d). That the formation of the organocopperlithium compound (R<sub>2</sub>CuLi) is a predominant reaction at a CuBr/LiR ratio  $\leq \frac{1}{2}$  is confirmed by the isolation of bis{2-[(dimethylamino)-methyl]phenyl}copperlithium from the 1/2 reaction (CuBr/LiR; CuBr added to RLi, see Chapter IX). When the CuBr/LiR ratio exceeds 1/2, reaction (e) occurs,

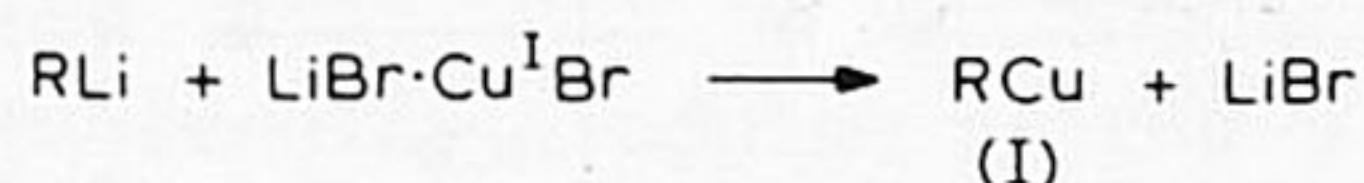
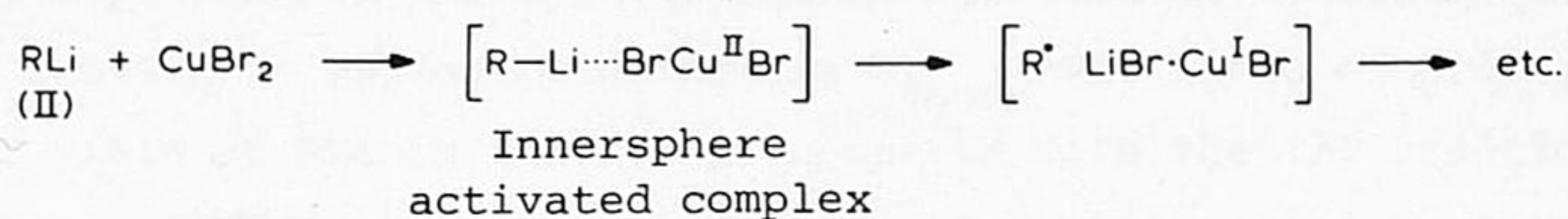
\*See Experimental, synthesis of (I); work-up of the filtrate.



yielding the organocopper compound (I) and lithium bromide.

For the successful preparation of 2-[(dimethylamino)methyl]phenylcopper (I) it is essential that during the 1/1 reaction of RLi with CuBr the organolithium compound RLi is always present in excess. The addition of CuBr to RLi prevents inactivation of the CuBr surface by the presence of insoluble CuR·CuBr complexes via reaction (d). Moreover, a highly active RLi suspension should be used and the addition of CuBr must be sufficiently slow to maintain a high RLi-concentration [eqn. (a)] during the early stages of the reaction ( $\text{CuBr/Li} \leq \frac{1}{2}$ ).

The course of the reaction of RLi with  $\text{CuBr}_2$  is much more complicated. Redox reactions involving electron transfer reduction of  $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$  will be followed by reaction of the  $\text{Cu}^{\text{I}}$  salt formed with RLi\*.



An alternative route involves the formation of  $\text{RCu}^{\text{II}}\text{Br}$  species followed by homolytic cleavage of the  $\text{R-Cu}^{\text{II}}$  bond affording  $\text{Cu}^{\text{I}}\text{Br}$  and secondary products (RH, RR and RBr) originating from  $\text{R}^{\cdot}$ .

## EXPERIMENTAL\*\*

### *Synthesis of 2-[(dimethylamino)methyl]phenylcopper (I)*

*Addition of CuBr to RLi (II).* Solid cuprous bromide (60 mmol) was slowly added (in about 1½ h) at  $-20^{\circ}$  to a freshly prepared suspension of 60 mmol of 2-[(dimethylamino)methyl]phenyllithium [(II): see Chapter II] in ether (160 ml). The mixture was stirred at  $-20^{\circ}$  for 1 h, warmed up to room temperature and then stirred for another 2 h. The yellow-green solid was filtered off and was extracted with cold ether until a test on the presence of  $\text{Br}^-$  (from LiBr) in the filtrate (vide infra) was negative. From the residue pure (I) was isolated (see Chapter II).

Work-up of the filtrate included removal of the ether by low temperature distillation at diminished pressure, followed by extraction of the residue with pentane. The insoluble fraction appeared to be LiBr which was obtained in nearly quantitative yield. The pentane extract was concentrated yielding an oil containing *N,N*-dimethylbenzylamine (VI) and 2,2'-bis[(dimethylamino)methyl]biphe-

\*The course of this reaction will be similar to that described for the reaction of RCu (I) with  $\text{CuX}_2$  salts.

\*\*General directions dealing with solvents, apparatus and reaction conditions are presented in Chapter IX.



nyl (V). NMR ( $C_6D_6$ , TMS internal,  $\delta$  ppm): (VI), 2.12 (s, 6 H,  $NCH_3$ ), 3.32 (s, 2 H,  $NCH_2$ ); (V), 2.02 (s, 12 H,  $NCH_3$ ), 3.01 and 3.06 (2 x d, 2 H,  $J_{gem} \approx 13$  Hz).

*Addition of RLi (II) to CuBr: "reversed addition"*. A solution of 30 mmol of (II) was added at  $-20^\circ$  to a well-stirred suspension of CuBr in ether. As distinct from the reaction described above a black-brown solid precipitated from the reaction mixture, the colour of which turned slowly red-brown upon continued stirring at  $-20^\circ$  for 1 h. This mixture was filtered. Both the precipitate and the benzene-soluble brown solid obtained from the filtrate gave a positive test on the presence of Br. Elemental analysis of the major amount of brown solid isolated (20% yield) pointed to a Cu/R ratio of 2/1. (Found: C, 31.2; H, 3.9; N, 3.8; Cu, 36.4.  $C_9H_{12}NCu_2Br$  (RCu·CuBr) calcd.: C, 31.68; H, 3.55; N, 4.10; Cu, 37.25%.) During the work-up procedure the colour of several of the isolated fractions turned black upon standing at  $-18^\circ$  for 24 h.

#### *Reaction of 2-[(dimethylamino)methyl]phenylcopper (I) with CuBr*

*Run 1*. Solid cuprous bromide (4.91 mmol) was added slowly to a solution of 4.91 mmol of (I) in benzene (35 ml). The yellow colour of the solution turned immediately red and a red solid precipitated. The mixture was stirred for 72 h and subsequently filtered. The resulting red solid was extracted with benzene (2 x 20 ml) and with pentane (2 x 20 ml) and was dried in vacuo (3 h,  $20^\circ/0.2$  mm). According to elemental analysis the red solid (IIIa) [70% yield calculated on (I)] consisted of RCu (I), CuBr, and benzene in a 1/1.4/0.2 molar ratio. (Found: C, 29.5; H, 3.6; Br, 26.9; Cu, 36.3; N, 3.4.  $C_9H_{12}NCu \cdot 1.4$  CuBr  $\cdot$  0.2  $C_6H_6$  calcd.: C, 29.57; H, 3.21; Br, 27.02; Cu, 36.81; N, 3.38%.) Decomposition at  $96-68^\circ$ . IR (nujol): 848 s, 747 vs and 674 (presence of benzene)  $cm^{-1}$ , see Fig. 1.

*Run 2*. The same experiment was carried out using CuBr (4.88 mmol) and a slight excess (5.00 mmol) of (I). The reaction mixture was stirred for 24 h. Following a similar work-up procedure as described above (*run 1*) resulted in the isolation of a red solid (IIIb) [80% yield calculated on (I)] which decomposed at  $100-101^\circ$ . (Found: C, 30.9; H, 3.4; Br, 24.9; Cu, 34.3; N, 3.5.  $C_9H_{12}NCu \cdot 1.2$  CuBr  $\cdot$  0.2  $C_6H_6$  calcd.: C, 31.78; H, 3.45; Br, 24.87; Cu, 36.26; N, 3.63 %). IR (nujol): identical to that of (IIIa).

#### *Deuterolysis of (IIIa)*

*With  $D_2O$* . A mixture of (IIIa) (0.5 g) and 1 ml of  $D_2O$  in benzene (10 ml) was stirred for 4 days at room temperature. The resulting orange-yellow precipitate was filtered off. The filtrate contained (2-deuteriobenzyl)dimethylamine (IV) as the single product (GLC, internal standard decane): 72% yield. IR (neat): identical to an analytically pure sample of (IV).

*With  $CH_3COOD$* . (IIIa) (0.5 g) in 11 ml benzene/10 N  $CH_3COOD$  in  $D_2O$  10/1 v/v, 24 h, room temperature: 90% yield of (IV).

#### *Reaction of 2-[(dimethylamino)methyl]phenylcopper (I) with cupric halides*

##### *With cupric bromide (1/1 reaction)*

Solid  $CuBr_2$  (6.58 mmol) was slowly added to a yellow solution of (I) (6.58 mmol) in benzene (30 ml). An immediate red colouration of the solution and the formation of a red precipitate were observed. After stirring the resulting reaction mixture during 5 days a red coloured solution with a light-brown precipitate was obtained. The precipitate [(VII): 2.21 g] was filtered off, washed



TABLE 2

## STOICHIOMETRY OF THE PRECIPITATES (VII)-(IX)

| Precipitate                                   | Colour            | NMR data of the deuterolyzed reaction mixture |    |                    | Stoichiometry <sup>b</sup>   |
|---|-------------------|---|----|--------------------|--|
|   |                   | RR  | RD | RD/RR <sup>a</sup> |  |
| (VII)<br>(From RCu/CuBr <sub>2</sub><br>1/1)  | Light-<br>brown   | +   | -  | -                  | C <sub>9</sub> H <sub>12</sub> NCu <sub>3.1</sub> Br <sub>3.1</sub> ·0.3<br>C <sub>6</sub> H <sub>6</sub><br>(Composition: 0.5 RR,<br>3.1 CuBr, 0.3 C <sub>6</sub> H <sub>6</sub> )  |
| (VIII)<br>(From RCu/CuBr <sub>2</sub><br>2/1) | Red               | +   | +  | 2.37/1             | C <sub>9</sub> H <sub>12</sub> NCu <sub>2.0</sub> Br <sub>1.3</sub> ·0.03<br>C <sub>6</sub> H <sub>6</sub><br>(Composition: 0.23 RR,<br>0.54 RCu, 1.3 CuBr, 0.16<br>Cu <sup>0</sup> , 0.03 C <sub>6</sub> H <sub>6</sub> ) |
| (IX)<br>(From RCu/CuCl <sub>2</sub><br>1/1)   | Metallic<br>brown |   |    |                    | <sup>c</sup>   |

<sup>a</sup>Mol. ratio calculated from the peak area ratios, see Experimental. <sup>b</sup>Deduced from the combined data as obtained from elemental analysis, NMR spectroscopy of the deuterolyzed reaction mixture and from IR spectroscopy. <sup>c</sup>Ratio Cu/Cl is 1.45/1, see elemental analysis.

with benzene and dried in vacuo (1 mm/25°). [Found: C, 21.2; H, 2.7; Br, 40.0; Cu, 33.2; N, 2.3. C<sub>9</sub>H<sub>12</sub>NCu<sub>3.1</sub>Br<sub>3.1</sub>·0.3 C<sub>6</sub>H<sub>6</sub> (see Table 2) calcd.: C, 21.54; H, 2.31; Br, 41.12; Cu, 32.70; N, 2.33%.] IR spectroscopy confirmed the presence of benzene (vide supra). Quantitative GLC analysis of the filtrate (decane internal standard): 0.45 mmol of RH (VI); 1.18 mmol of RBr (X); 0.612 mmol of RR (V). Cu analysis of the filtrate: 0.81 mmol Cu. NMR spectrum (C<sub>6</sub>H<sub>6</sub>; TMS internal, δ ppm): RH, 2.13 (s, 6 H, NCH<sub>3</sub>), 3.36 (s, 2 H, NCH<sub>2</sub>); RBr, 2.10 (s, 6 H, NCH<sub>3</sub>), 3.46 (s, 2 H, NCH<sub>2</sub>); RR, 2.05 (s, 12 H, NCH<sub>3</sub>), 3.05 (d, 2 H) and 3.35 (d, 2 H, J<sub>gem</sub> ≈ 13 Hz).

*Deuterolysis of (VII).* (VII) (0.5 g) was suspended in a mixture of benzene (10 ml) and DOAc/D<sub>2</sub>O (1 ml, 10 N) was added; 19 h, room temperature. NMR spectroscopy of the reaction mixture confirmed the presence of RR (V) as



the single product.

*With cupric bromide (2/1 reaction)*

Addition of cupric bromide (3.01 mmol) to a solution of (I) (6.02 mmol) in benzene (30 ml) afforded a red precipitate (VIII) and a red solution (reaction time 5 days; room temperature). Elemental analysis of the *precipitate* (VIII) (red solid; 1.48 g); found: C, 30.2; H, 3.3; Br, 28.0; Cu, 34.2; N, 3.9.  $C_9H_{12}NCu_{2.0}Br_{1.3} \cdot 0.03 C_6H_6$  (see Table 2) calcd.: C, 30.00; H, 3.34; Br, 28.27; Cu, 34.58; N, 3.81%. The IR spectrum of (VIII) (nujol, 2000-400  $cm^{-1}$  region) appeared to be a superposition of the spectrum of (VII) and of  $RCu \cdot CuBr$  (IIIa). Quantitative GLC analysis of the *filtrate* (decane internal standard): 0.154 mmol of RH (VI); 0.476 mmol of RBr (X); 0.728 mmol of RR (V). Copper analysis: 0.58  $\mu$ mol Cu. NMR spectrum ( $C_6H_6$ ; TMS internal,  $\delta$  ppm): RH, 2.08 (s, 6 H,  $NCH_3$ ), 3.28 (s, 2 H,  $NCH_2$ ); RBr, 2.07 (s, 6 H,  $NCH_3$ ), 3.42 (s, 2 H,  $NCH_2$ ); RR, 2.01 (s, 12 H,  $NCH_3$ ), 3.07 (d, 2 H) and 3.28 (d, 2 H,  $J_{gem} \approx 13$  Hz).

*Deuterolysis of (VIII)*. (VIII) (0.44 g) in benzene (10 ml) was deuterolized with 1 ml 10 N  $CH_3COOD$  solution in  $D_2O$ . Reaction time 19 h; room temperature, work-up of the reaction mixture resulted in a benzene extract which on evaporation afforded a green-black coloured oil. Treatment of this oil, dissolved in ether, with a KCN solution (400 mg in 5 ml  $H_2O$ ) resulted in a colourless ether solution. Evaporation of the ether afforded a yellow oil. NMR spectrum ( $CCl_4$ , TMS internal): RD/RR in a 2.37/1 molar ratio.

*With cupric chloride (1/1 reaction)*

Solid cupric chloride (6.58 mmol) was slowly added to a yellow solution of (I) (6.58 mmol) affording a red precipitate which became (upon continued stirring for 5 days) metallic brown coloured. The *precipitate* was filtered off and washed with benzene. The resulting metallic-brown coloured solid (IX) (1.07 g) was dried in vacuo. (Found: Cu, 62.5; Cl, 24.2%. Cu/Cl 1.45/1.) The red *filtrate* was analysed by GLC; 0.615 mmol of RH (VI), 2.23 mmol of RCl (XI); 1.83 mmol of RR (V).

#### REFERENCES

- 1 G.COSTA, A.CAMUS, L.GATTI and N.MARSICH, *J.Organometal.Chem.*, 5 (1966) 568.
- 2 J.F.NORMANT, *Synthesis*, (1972) 63.
- 3 A.J.LEUSINK, G.VAN KOTEN and J.G.NOLTES, *J.Organometal.Chem.*, 56 (1973) 379.
- 4 C.F.LANE, *J.Organometal.Chem.*, 31 (1971) 421 and references cited therein.
- 5 R.H.SNIDER, Thesis, Cornell University, 1972; *Chem.Abstr.*, 77 (1972) 126811y.
- 6 A.CAMUS and N.MARSICH, *J.Organometal.Chem.*, 14 (1968) 441.





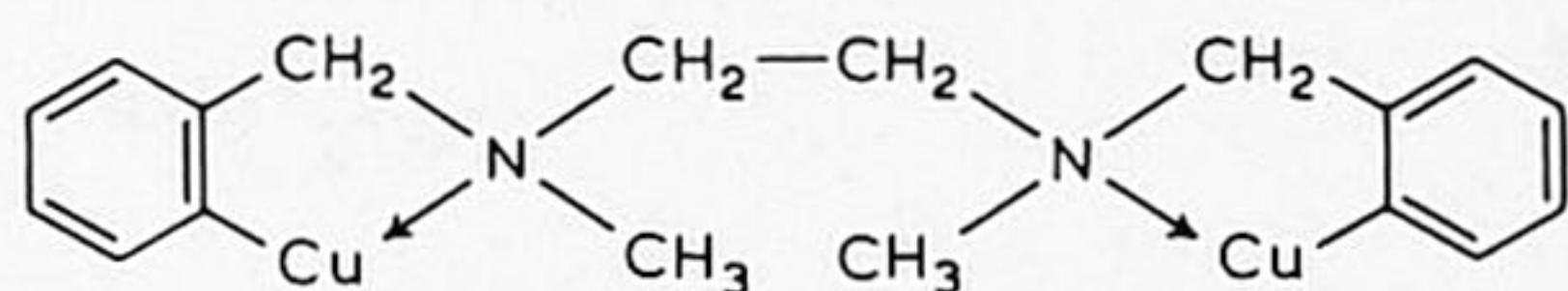


## CHAPTER V

### SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF ARYLCOPPER COMPOUNDS $\text{RCu}^{\text{I}}_2$

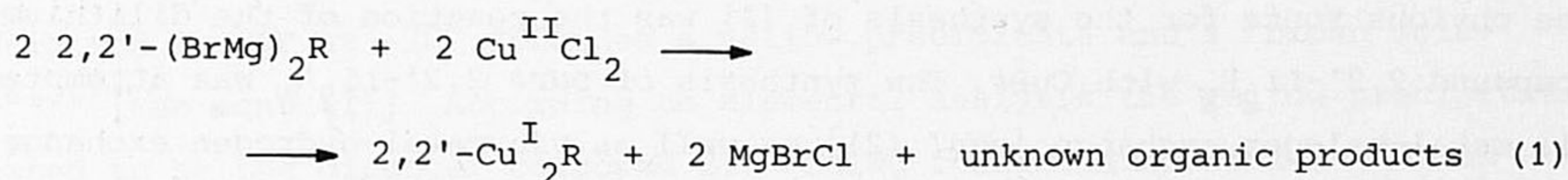
#### INTRODUCTION

Towards the end of 1970 Bähr and Burba published a review [1] dealing with the synthesis and reactivity of organocopper compounds. In this review the authors referred to the work of Weidemüller in which the isolation of an aryl-copper compound containing *two* copper atoms in the organic ligand is described\*.



(I);  $2,2'\text{-Cu}_2\text{R}_N$

(I) had been synthesized via the 1/1 reaction of the corresponding di-Grignard  $2,2'\text{-(BrMg)}_2\text{R}_N$  with cupric chloride\*\*.



The observed relatively high thermal and hydrolytic stability of (I) was ascribed to the stabilization of the copper-aryl bond by intramolecular Cu-N complex formation. On the basis of molecular weight measurements\*\*\*, it was concluded that the compound exists in benzene as a monomer. These considerations led Weidemüller to suggest the structure depicted above.

In view of our own results on the synthesis and structure of 2-(dimethyl-

\*We kindly thank Dr. P. Burba for making available a copy of the Diplom-Arbeit of Dr. W. Weidemüller [2].

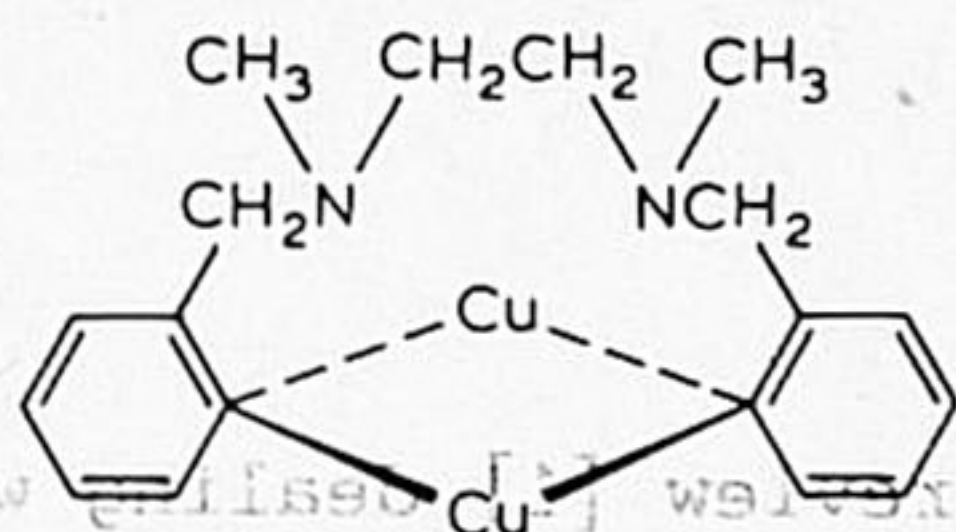
\*\*The  $2,2'$ -disubstituted organic group R is abbreviated as  $2,2'\text{-X}_2\text{R}_N$  in which X represents Br-, BrMg-, Cu-, H-, or D- and  $\text{R}_N$  denotes that the group R carries nitrogen-containing built-in ligands.

\*\*\*The data were not very convincing (see ref. 2). Two independent series of measurements (by cryometry in benzene) were carried out affording the following values: 426, 581, 1275 and 469, 531, 562, respectively. The calculated value for the monomer is 393.5.



amino)methyl-substituted arylcopper compounds (Chapter III), a reinvestigation of (I) seemed of interest with regard to the following questions:

i. The nature of the aryl-copper bond (two electron-two centre bond, structure I) or the presence of bridging organic ligands (two electron-three centre bond, e.g. structure II).

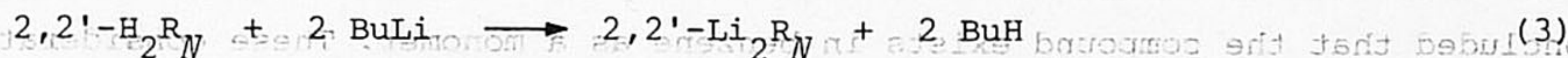
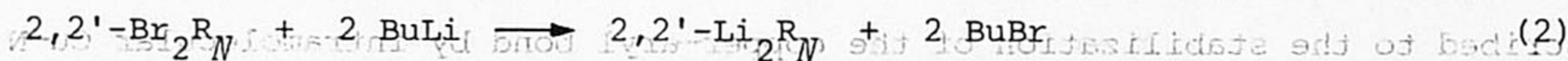


ii. The nature of the "unknown" organic products formed in this reaction. The results of our investigation are discussed below.

## RESULTS AND DISCUSSION

### Synthesis of the starting organolithium(magnesium) compound

As discussed in Chapters II and IV arylcopper compounds containing the 2-(dimethylamino)methyl group can be readily synthesized via the reaction of appropriate organolithium compounds with cuprous or cupric halides. Consequently, the obvious route for the synthesis of (I) was the reaction of the dilithium compound  $2,2'\text{-Li}_2\text{R}_N$  with CuBr. The synthesis of *pure*  $2,2'\text{-Li}_2\text{R}_N$  was attempted via metal-halogen exchange [eqn. (2)] as well as via metal-hydrogen exchange [eqn. (3)]:



**Metal-halogen exchange.** Addition of butyllithium to a solution of  $2,2'\text{-Br}_2\text{R}_N$  in ether in a 2/1 molar ratio afforded a yellow-coloured reaction mixture. NMR spectroscopy of a sample of this mixture indicated that *ortho*-metalation had indeed occurred [cf. broadened resonance at 8.32 ppm ( $\text{H}_3$ )]. Subsequent hydrolysis of the reaction mixture revealed (according to GLC and NMR) that in addition to  $2,2'\text{-H}_2\text{R}_N$  (60% yield; originating from hydrolysis of  $2,2'\text{-Li}_2\text{R}_N$ ) yet unidentified organolithium compounds had been present.

**Metal-hydrogen exchange.** A 2/1 mixture of butyllithium and  $2,2'\text{-H}_2\text{R}_N$



was stirred at room temperature during 64 h. The resulting red-coloured reaction mixture was deuterolyzed with  $D_2O$ . The ratio of the several proton resonances for the deuterated amines formed, showed that metal-hydrogen exchange had taken place for about 95% (calculated for the exchange of two protons), viz. 65% exchange of the *ortho*-hydrogen atoms and 30% exchange of the benzylic hydrogen atoms ( $\alpha$ -lithiation)\*. IR spectroscopy confirmed this view: 1,2- as well as mono-substituted phenyl rings,  $\nu[C-(2-D)]$  2250 br\*\* and  $\nu[C-(\alpha-D)]$  2053 br  $cm^{-1}$ .

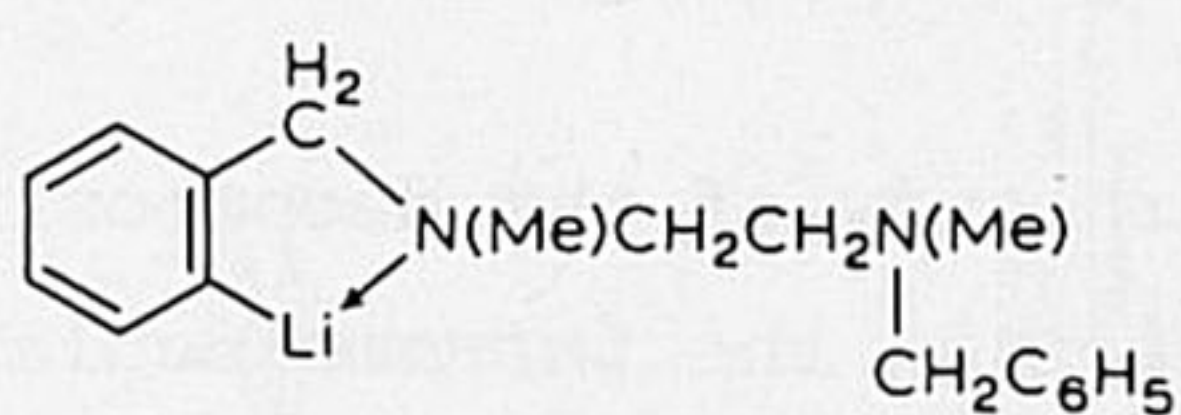
The formation of unwanted metalated products does not occur when the  $2,2'-Br_2R_N$  compound is converted into the corresponding di-Grignard reagent  $2,2'-(BrMg)_2R_N$  by reaction with magnesium in THF. Although Grignard reagents in general are inferior starting materials for the preparation of arylcopper compounds we therefore have attempted the synthesis of (I) starting from  $2,2'-(BrMg)_2R_N$ .

#### Synthesis of the organocopper compound $2,2'-Cu_2R_N$

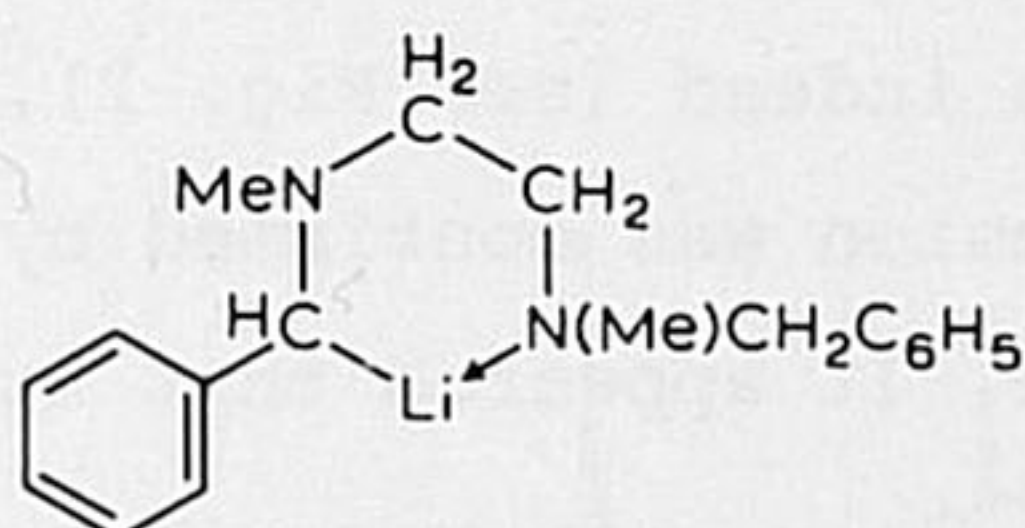
Since we did not succeed in isolating pure  $2,2'-Cu_2R_N$  from the reaction of  $2,2'-(BrMg)_2R_N$  with cuprous bromide, our attention was focussed on using cupric chloride as a starting material.

Addition of cupric chloride to a solution of an equivalent amount of the di-Grignard in THF at  $-20^\circ$  afforded a yellow precipitate and a "brown solution"\*\*\* [see eqn. (1)]. According to elemental analysis the yellow precipitate appeared to be the dicopper compound  $2,2'-Cu_2R_N$  contaminated with magnesium

\*The higher stability of (*ortho*-lithiated benzyl)dimethylamine as compared with the  $\alpha$ -lithiated product has been ascribed [3] to stabilization of the former isomer by intramolecular Li-N coordination. The lithiation reaction of  $2,2'-H_2R_N$  with BuLi can be expected to occur both at the *ortho*- and at the  $\alpha$ -site because the two lithio derivatives can both be stabilized by intramolecular Li-N coordination:



*ortho*-lithio- $R_N$



$\alpha$ -lithio- $R_N$

\*\* (2-Deuteriobenzyl)dimethylamine:  $\nu(C-D)$  2252  $cm^{-1}$  [4].

\*\*\*The identification of the organic products present in this solution is described below.



halides. The latter impurity could be removed almost quantitatively by recrystallization of the yellow product from dioxane or a dioxane/benzene mixture. The total yield of  $2,2'\text{-Cu}_2\text{R}_N$  (I) was about 25% (calculated on the amount of  $\text{CuCl}_2$  used).

The identity of (I) was established by elemental analysis\*, IR spectroscopy (1,2-substitution pattern for the aryl nucleus, see Fig. 1) and NMR spectroscopy (see below).

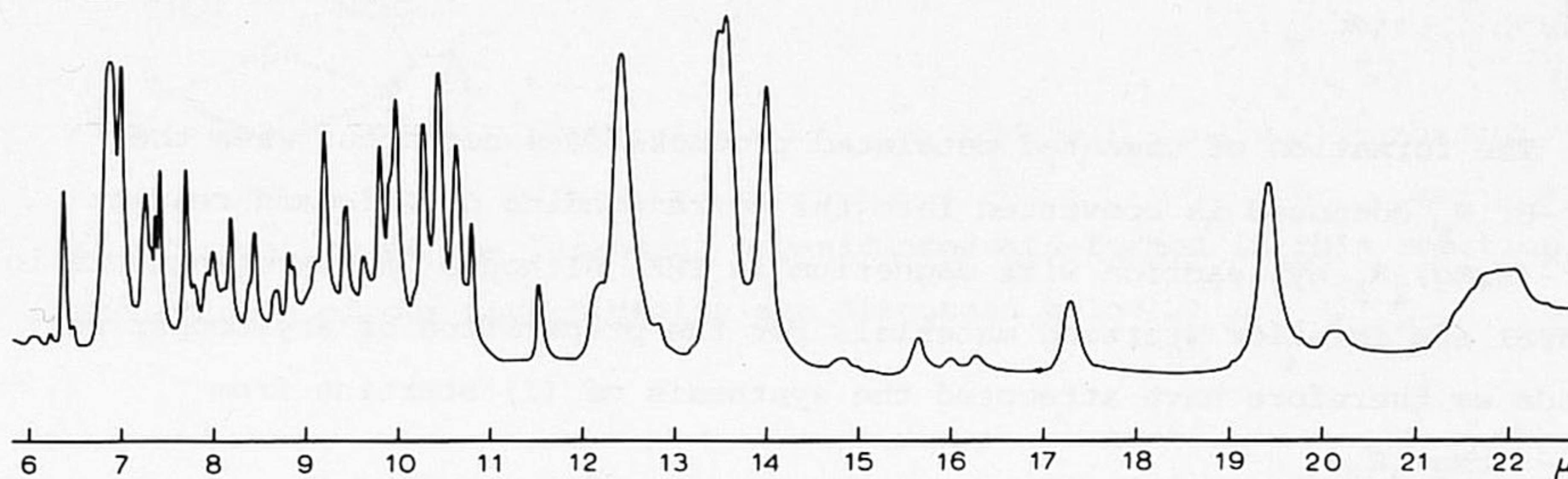


Fig. 1. IR spectrum (nujol) of  $2,2'\text{-Cu}_2\text{R}_N$  (I).

Cryometric molecular weight measurements proved this compound to exist in benzene as discrete dimeric units  $(2,2'\text{-Cu}_2\text{R}_N)_2$  (independent of concentration).

Compound (I) is rather stable in air and shows a high stability towards hydrolysis. When heated in a capillary tube under nitrogen (I) decomposes slowly at  $125\text{-}130^\circ$  and fast at  $133^\circ$ .

NMR spectroscopy\*\* at different temperatures provided information about the thermal stability of (I) in solution. Upon heating a benzene solution to  $80^\circ$  a black solid precipitated and the solution which had turned from yellow to colourless showed a totally different NMR spectrum (see Fig. 2). The complete disappearance of the doublet of doublets at  $\delta$  8.61 ppm, belonging to the proton *ortho* with respect to the copper-carbon bond, pointed to a total decomposition of (I). The NMR spectrum of this solution clearly showed that the decomposition reaction is very clean indeed (see Fig. 2).

The latter conclusion was confirmed by a closer study of the decomposition on a preparative scale. It appeared that in this reaction the *intramolecular*

\*Elemental analysis indicated that even after two recrystallizations the product still contained some halogen (see Experimental) as well as dioxane. The presence of the latter contamination was also confirmed by NMR spectroscopy (see Fig. 2, resonance at  $\delta$  3.33 ppm).

\*\*For a discussion of the NMR spectrum of (I) see next section.



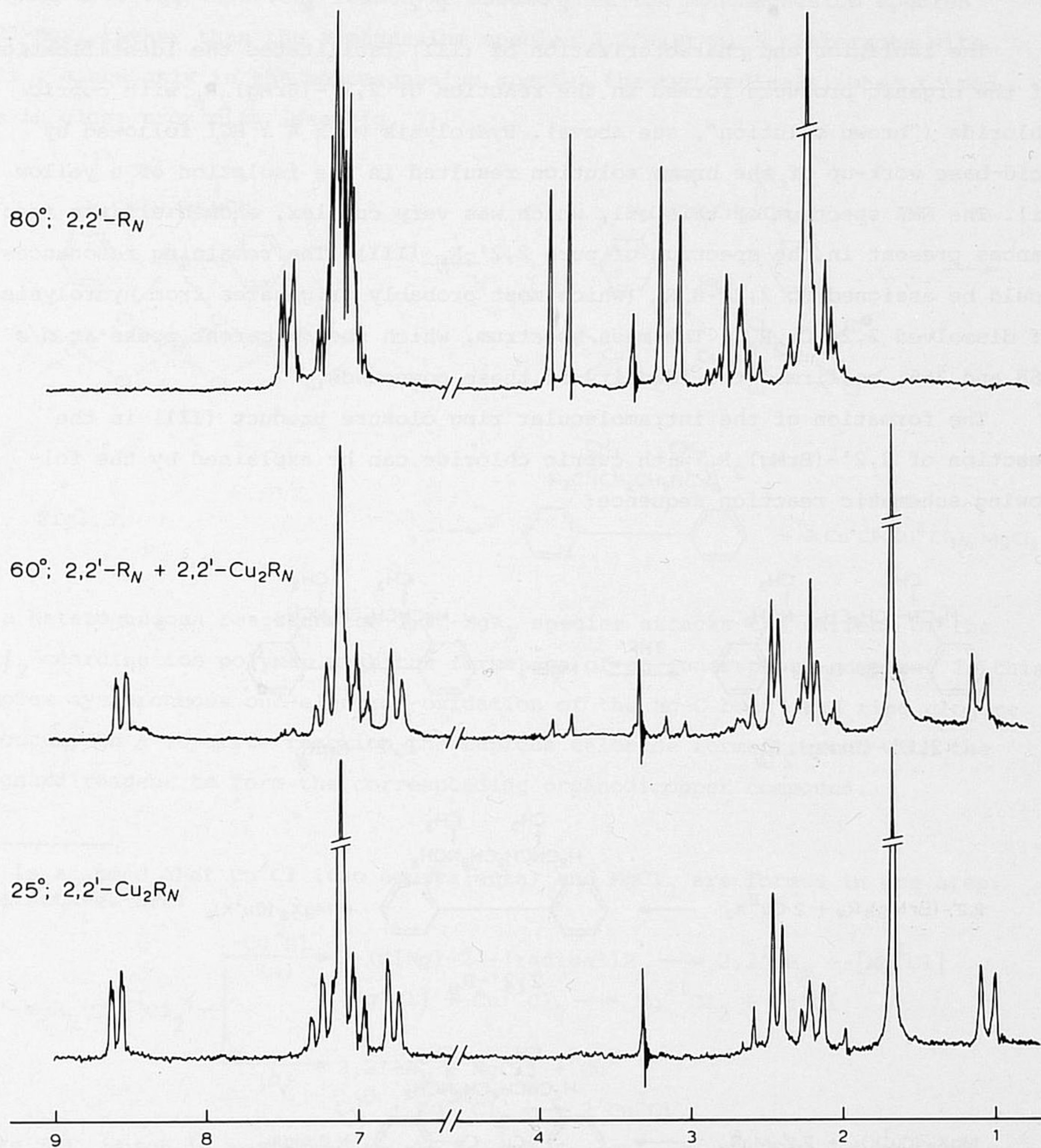
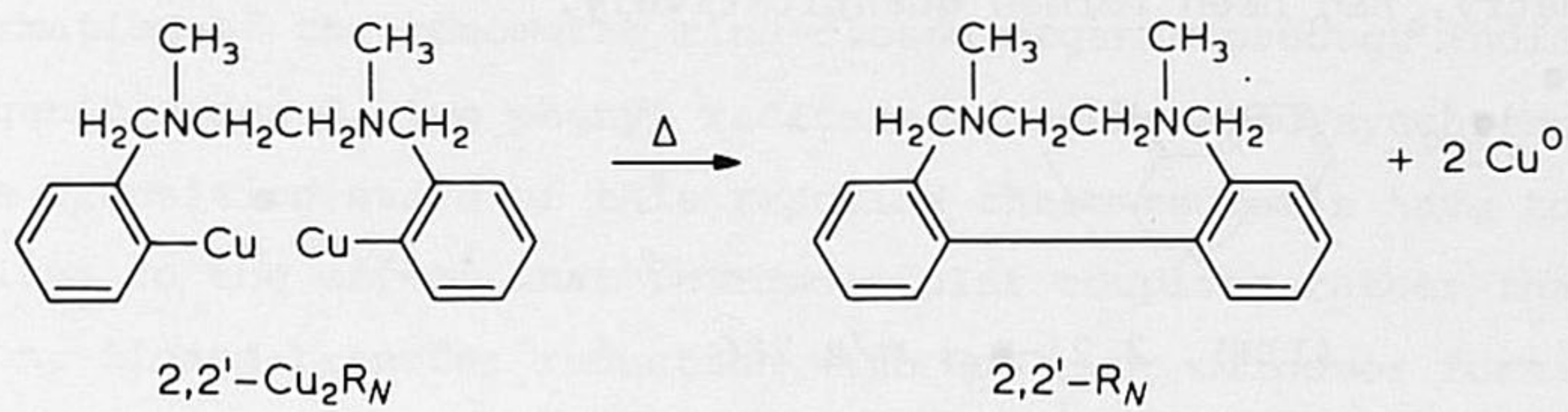
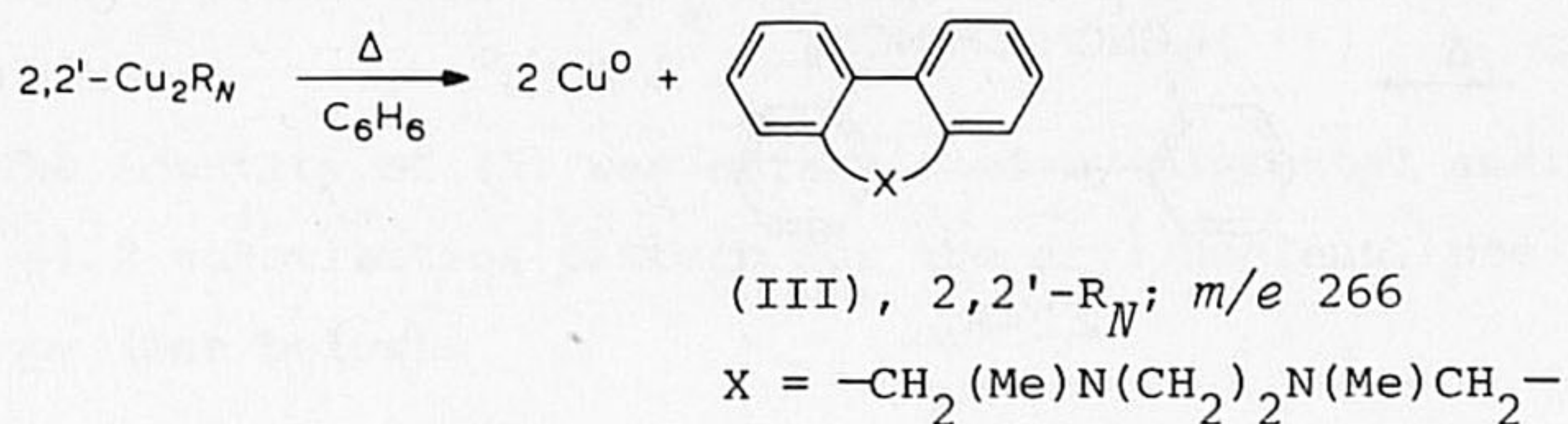


Fig. 2. NMR spectra ( $\delta$  ppm) showing the thermal decomposition of a solution of 2,2'-Cu<sub>2</sub>R<sub>N</sub> (I) in benzene-*d*<sub>6</sub> (see also Table 2).

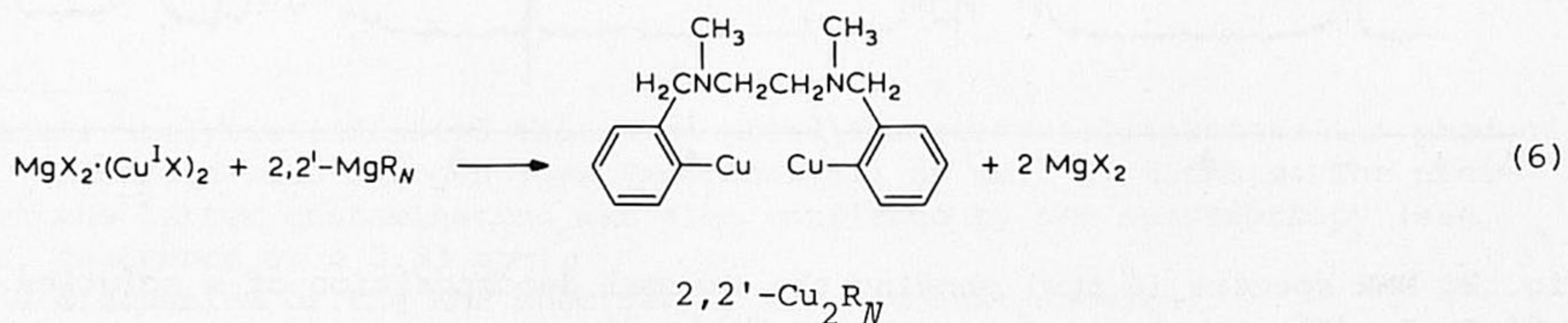
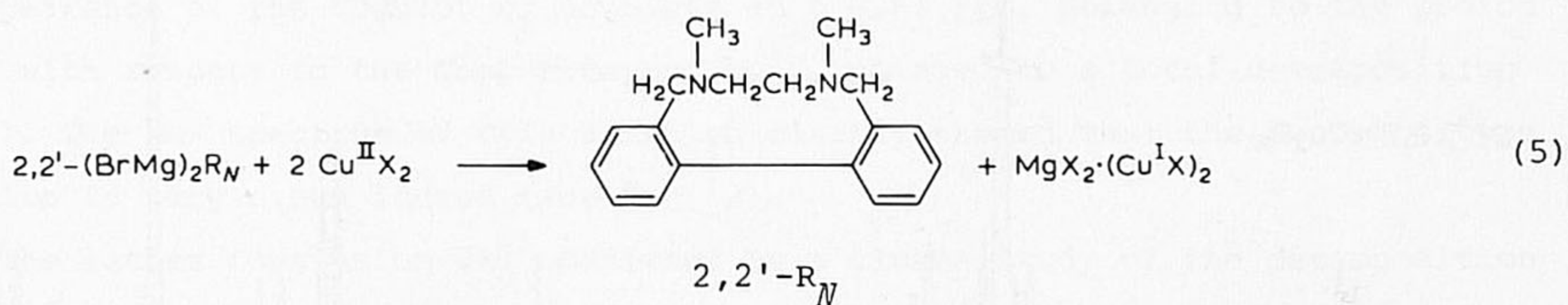
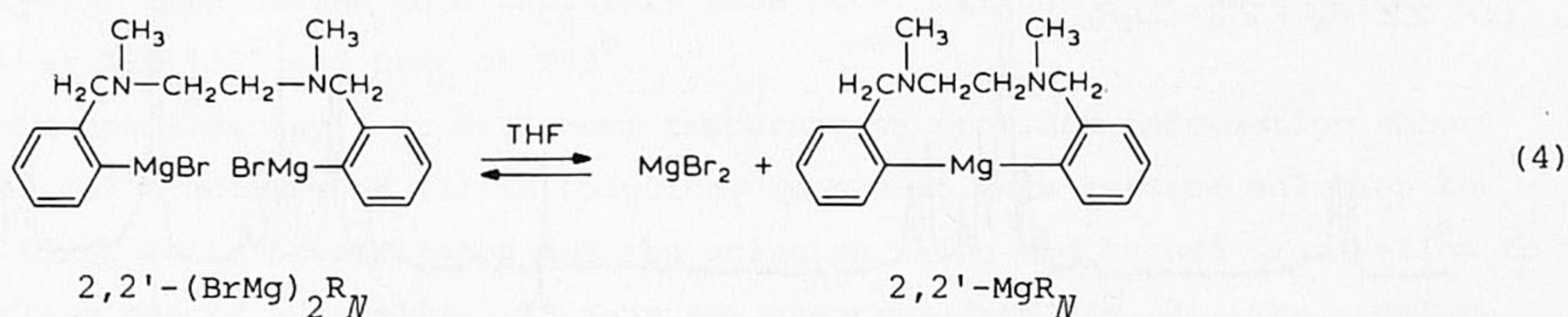


ring closure product 2,2'-R<sub>N</sub> (III), which was characterized by means of IR, NMR and mass spectrometry, had been formed quantitatively.



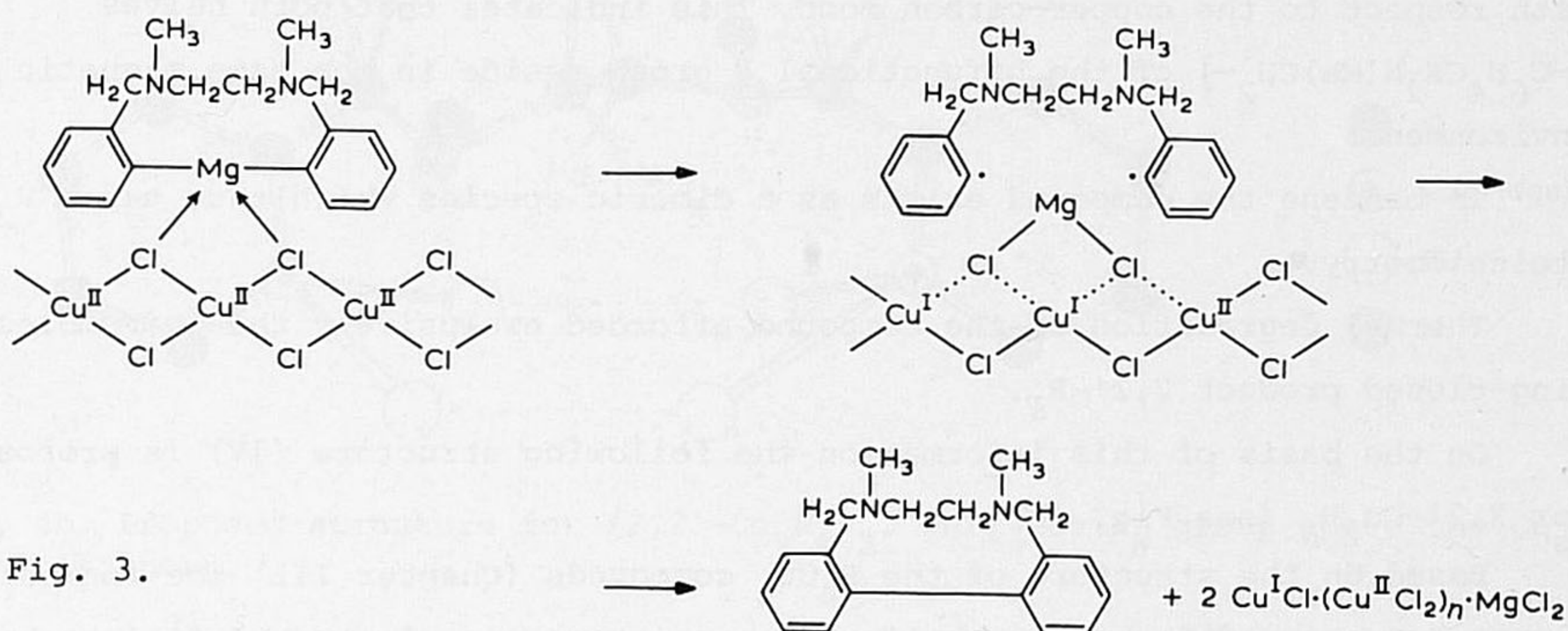
The isolation and characterization of (III) facilitated the identification of the organic products formed in the reaction of 2,2'-(BrMg)<sub>2</sub>R<sub>N</sub> with cupric chloride ("brown solution", see above). Hydrolysis with 4 *N* HCl followed by acid-base work-up of the brown solution resulted in the isolation of a yellow oil. The NMR spectrum of this oil, which was very complex, showed all the resonances present in the spectrum of pure 2,2'-R<sub>N</sub> (III). The remaining resonances could be assigned to 2,2'-H<sub>2</sub>R<sub>N</sub> (which most probably originates from hydrolysis of dissolved 2,2'-Cu<sub>2</sub>R<sub>N</sub>). The mass spectrum, which showed parent peaks at *m/e* 268 and 266, confirmed the identity of these compounds.

The formation of the intramolecular ring closure product (III) in the reaction of 2,2'-(BrMg)<sub>2</sub>R<sub>N</sub> with cupric chloride can be explained by the following schematic reaction sequence:



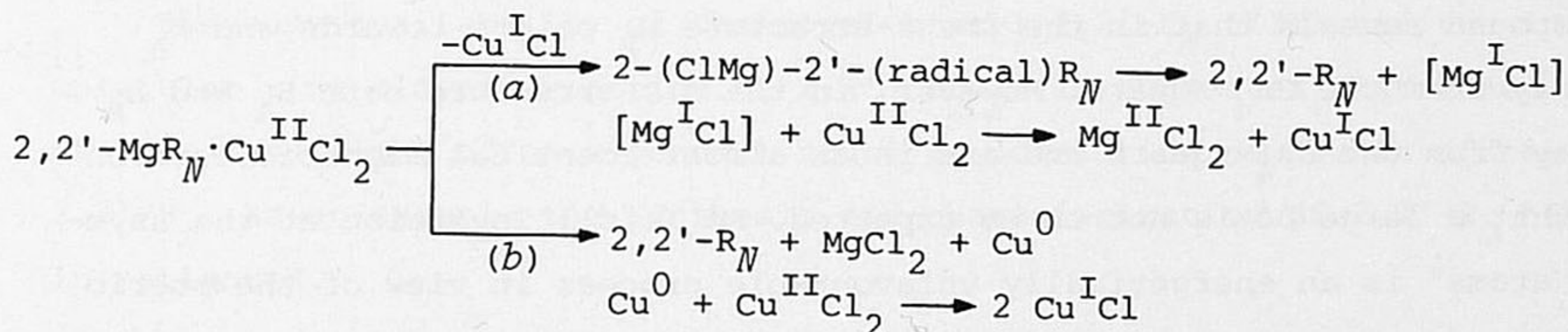


Not a trace of oligomeric or polymeric products could be detected. The exclusive formation of the monomeric ring-closed organic product indicates that within *one* organic group  $R_N$  two phenyl radicals are generated synchronously. Moreover, in the transition state of this reaction these radicals have to be at close proximity, to the effect that *intramolecular* coupling rather than hydrogen abstraction, ligand-transfer reduction with  $\text{CuCl}_2$  or oligomer formation does occur (see Chapter IV). For this very reason we assume that the monomagnesium species  $2,2'\text{-MgR}_N$  rather than the dimagnesium species  $2,2'\text{-(BrMg)}_2\text{R}_N$  interacts with  $\text{CuCl}_2$ , since only in the monomagnesium species the two radicals, when formed, are in close proximity (see Fig. 3):



In a heterogeneous reaction the  $2,2'\text{-MgR}_N$  species attacks the surface of the  $\text{CuCl}_2$ -coordination polymer with the formation of an innersphere complex. In this complex synchronous one-electron oxidation of the  $\text{Mg-C}$  bond\* and ring closure do occur. In a separate reaction the cuprous chloride formed reacts with the Grignard reagent to form the corresponding organodicopper compound.

\*It is assumed that  $\text{Cu}^{\text{I}}\text{Cl}$  (two equivalents) and  $\text{MgCl}_2$  are formed in one step. Alternatives are:



Route (a), which is analogous to the biaryl formation mechanism put forward by Russell [5], suggests that a  $\text{Mg-C}$  bond is a better radical trap than  $\text{Cu}^{\text{II}}\text{Cl}_2$ . This is, however, not very likely (see Chapter IV). The second route (b) differs not essentially from the one given in eqn. (5). In fact it offers an alternative for what is happening in the  $\text{Cu}^{\text{I}}\text{Cl}_2$  coordination polymer.



### Structure of the organocopper compound $(2,2'-\text{Cu}_2\text{R}_N)_2$ (I)

Only indirect evidence for the structure of the dimeric organodicycopper compound  $(2,2'-\text{Cu}_2\text{R}_N)_2$  (I) is available.

The NMR spectrum of (I) in benzene is shown in Fig. 2 (see also Table 2). At room temperature all protons show sharp resonances. The assignment of the resonances in the aromatic region parallels that given in Chapter III for the 2-(dimethylamino)methyl-substituted arylcopper compounds. The aliphatic region shows sharp AB patterns both for the benzylic and the ethylenic protons. Cooling down does not change the spectrum. Moreover, only *one* pattern is observed for the methyl protons (singlet) and for the protons *ortho* (doublet of doublets) with respect to the copper-carbon bond. This indicates that both halves  $[-\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{Me})\text{CH}_2-]$  of the bifunctional R group reside in the same magnetic environment.

In benzene the compound exists as a dimeric species which thus has a  $\text{R}_2\text{Cu}_4$  stoichiometry.

Thermal degradation of the compound afforded exclusively the *intramolecular* ring-closed product  $2,2'-\text{R}_N$ .

On the basis of this information the following structure (IV) is proposed for  $2,2'-\text{Cu}_2\text{R}_N$  (see Fig. 4b).

Based on the structure of the  $\text{R}_4\text{Cu}_4$  compounds (Chapter III) the four aryl groups are assumed to bridge the four copper atoms via electron-deficient bonds. The two  $\text{R}_N$ -ligands reside on different sides of the copper square. The two phenyl groups of each of the  $\text{R}_N$  groups are placed in a *trans* geometry as shown in the figure under A.

This structure is in accordance with the observed NMR spectrum in that it offers an explanation for (i) the equivalence of the two  $-\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{Me})\text{CH}_2-$  moieties, (ii) the large  $\Delta\delta$  (1.12 ppm) for the ethylenic protons  $\text{H}_A$  and  $\text{H}_B$  and (iii) the sharp AB pattern for the benzylic protons. Ad (i): a two-fold axis through the  $\text{CH}_A\text{H}_B-\text{CH}_A\text{H}_B$  bond is present. Ad (ii): inspection of a model of the  $\text{R}_2\text{Cu}_4$  compound reveals that in the *trans*-structure  $\text{H}_B$  points towards and  $\text{H}_A$  points away from the  $\text{Cu}_4$  square. However, in the *cis*-structure both  $\text{H}_A$  and  $\text{H}_B$  point away from the  $\text{Cu}_4$ -square and are in an almost identical magnetic environment so that a large  $\Delta\delta$  is not to be expected. Ad (iii): Inversion at the asymmetric N atoms\* is an energetically unfavourable process in view of the steric requirements of the  $-\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2-$ bridge.

\*When the rate of this process is fast enough with respect to the NMR timescale the AB pattern will collapse.



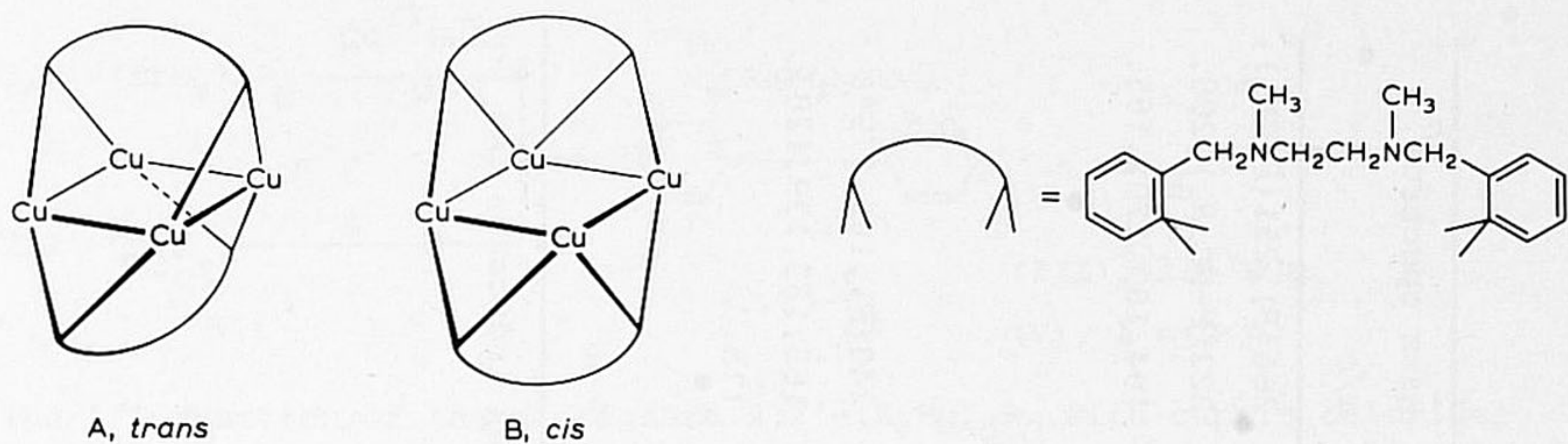


Fig. 4a. Arrangement of the bifunctional group  $R_N$  in  $(2,2'-Cu_2R_N)_2$  in a *trans* (A) and in a *cis* (B) manner.

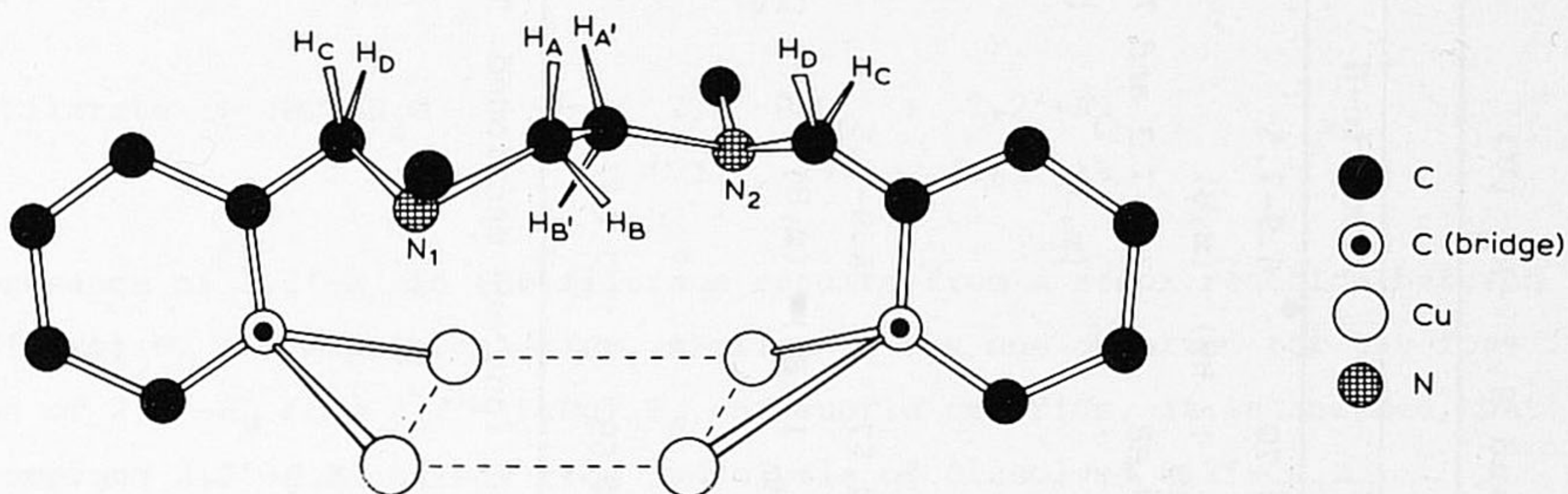


Fig. 4b. Proposed structure for  $(2,2'-Cu_2R_N)_2$ . Only the  $R_N$  group above the  $Cu_4^-$  plane is shown.

Furthermore, the proposed structure accounts for the clean thermal decomposition of  $R_2Cu_4$  to  $2,2'-R_N$ . Concerted homolytic Cu-C bond cleavage results in the formation of intramolecular pairs of radicals which are positioned such, that intramolecular coupling occurs to the exclusion of other possible reactions. The copper square acts as a template for this reaction.

*Thermolysis of  $2,2'-Cu_2R_0$ ; characterization of the novel ring-closed product  $2,2'-R_0^*$*

The easy availability of the novel biaryl  $2,2'-R_N$  (III) via the intramolecular ring closure reaction of  $2,2'-Cu_2R_N$  (I) suggested that other reactions of this type might offer a general route to novel ring compounds of the type  $2,2'-R_x$ . As an example the synthesis and characterization of  $2,2'-R_0$  has been investigated.

\* $R_0$  stands for  $-C_6H_4CH_2O(CH_2)_2OCH_2C_6H_4-$ .



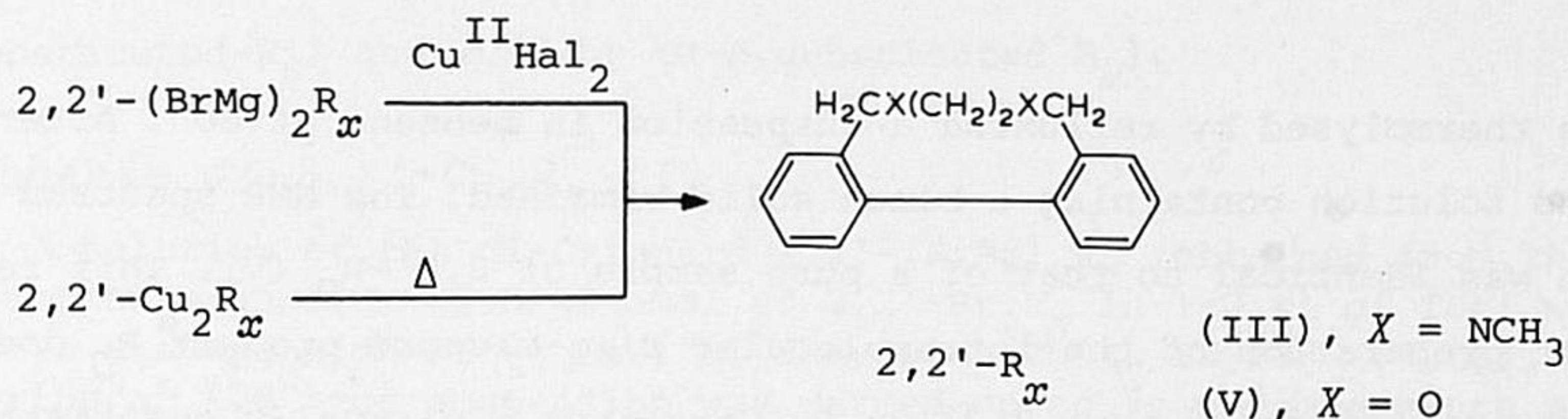
TABLE 1

NMR AND MASS SPECTROSCOPIC DATA OF 2,2'-R<sub>N</sub> (III) and 2,2'-R<sub>O</sub> (V)

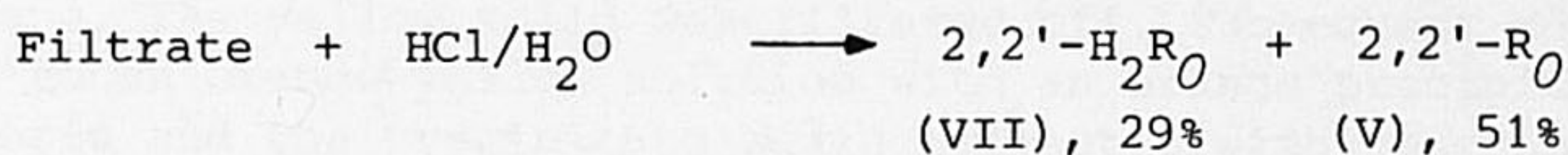
| Compound                      | Solvent                       | δ (ppm) <sup>a</sup> |   |   | PhCH <sub>2</sub> Y                  | Aromatic-H   | Mass spectrum <sup>b</sup> |
|-------------------------------|-------------------------------|----------------------|---|---|--------------------------------------|--|----------------------------|
|                               |                               | NCH <sub>3</sub>     | YCH <sub>2</sub> CH <sub>2</sub> Y  |   |                                      |  |                            |
| (III),<br>2,2'-R <sub>Y</sub> | CCl <sub>4</sub>              | 2.30<br>(s,4)        |   | 3.11 and 3.70<br>(2xd,4,J <sub>gem</sub> 12 Hz) | 6.9-7.5<br>(m,8)                     | 266(P), 251(P-CH <sub>3</sub> ),<br>222(P-NC <sub>2</sub> H <sub>6</sub> ), 208, |                            |
|                               | C <sub>6</sub> D <sub>6</sub> | 2.22                 | 1.90-2.40 and<br>2.40-2.90<br>(2xm,4,AA'BB')  | 3.12 and 3.88                                   | 7.0-7.3 and 7.45-7.65<br>(m,3) (m,1) | 194, 180, 179*, 165.   |                            |
| (V),<br>2,2'-R <sub>O</sub>   | CCl <sub>4</sub>              |                      | 3.33 and 3.54<br>(2xm,4,J <sub>AA'</sub> 7.40<br>J <sub>AB</sub> 2.16, J <sub>BB'</sub> 5.20,<br>J <sub>AB'</sub> -12.69 Hz) <sup>c</sup> | 4.24 and 4.57<br>(2xd,4,J <sub>gem</sub> 12 Hz) | 6.9-7.6<br>(m,8)                     | 240(P), 195, 179*,<br>165, 152, 139, 128,<br>115.                                |                            |
|                               | C <sub>6</sub> D <sub>6</sub> |                      |   | 4.21 and 4.69                                   | 7.0-7.6                              |  |                            |

<sup>a</sup>TMS internal standard; room temperature. <sup>b</sup>Some very abundant ions are mentioned. The asterisk indicates the base peak in the spectrum. <sup>c</sup>See ref. 6.





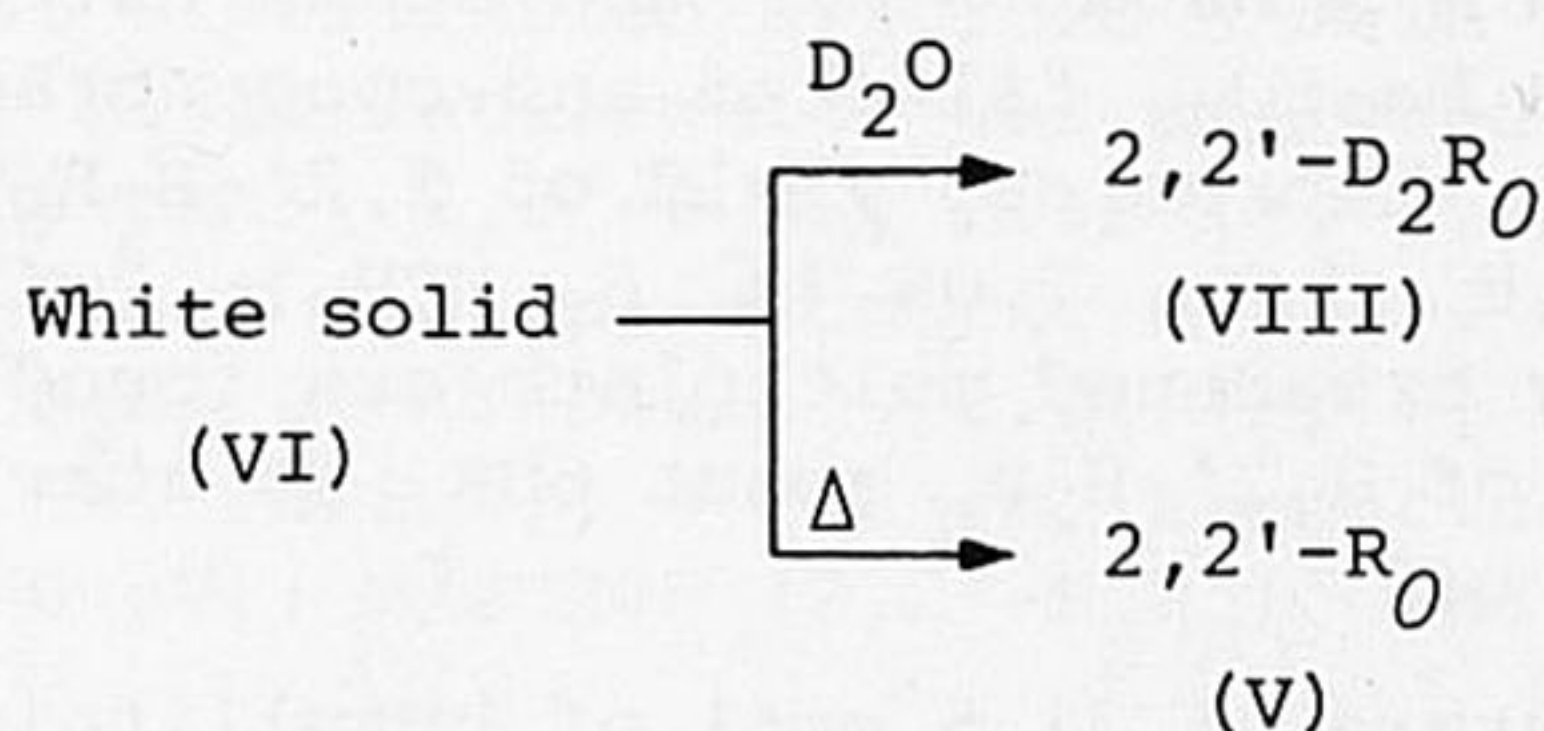
The 1/1 reaction of the diGrignard  $2,2'-(\text{BrMg})_2\text{R}_0$  with cupric chloride afforded a white precipitate (VI) (see below), which was removed by filtration:



The presence of  $2,2'-\text{R}_0$  in the filtrate results from a redox reaction between  $2,2'-(\text{BrMg})_2\text{R}_0$  and cupric chloride, similar to the one observed for the formation of  $2,2'-\text{R}_N$  from  $2,2'-(\text{BrMg})_2\text{R}_N$  and cupric chloride. It is assumed that the compound  $2,2'-\text{H}_2\text{R}_0$  arises from hydrolysis of dissolved  $2,2'-\text{Cu}_2\text{R}_0$ .

The ring-closed product  $2,2'-\text{R}$  was separated from  $2,2'-\text{H}_2\text{R}_0$  by crystallization. Its identity was established by IR and NMR spectroscopy\* as well as by mass spectrometry (see Table 1).

Elemental analysis indicated that the white solid (VI) consisted of  $2,2'-\text{Cu}_2\text{R}_0$  contaminated with magnesium halides. This view was confirmed by formation of  $2,2'-\text{D}_2\text{R}_0$  (VIII) upon deuterolysis of a sample of (VI).



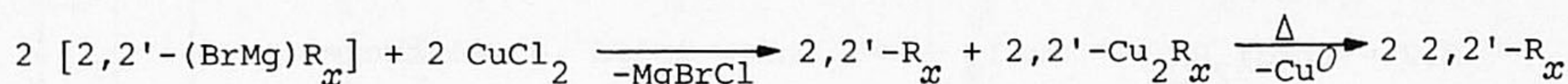
Because in this case we were primarily interested in the synthesis of the ring-closed biaryl  $2,2'-\text{R}_0$  it has not been attempted to isolate  $2,2'-\text{Cu}_2\text{R}_0$  in the

\*Molecular models of the ring-closed products  $2,2'-\text{R}_N$  and  $2,2'-\text{R}_0$  reveal that these molecules are conformationally rigid, the phenyl rings being held in a fixed position by the aliphatic bridge. In fact the NMR spectra of these compounds are perfect examples of AA'BB' patterns for the ethylenic protons. A full analysis of the spectra has been undertaken [6].



pure state.

(VI) was thermolysed by refluxing a suspension in benzene at 80°. After 24 h a colourless solution containing a black solid remained. The NMR spectrum of this solution was identical to that of a pure sample of 2,2'-R<sub>0</sub> (V). This result indicates that preparation of the intramolecular ring-closure product R<sub>0</sub> does not require the isolation of pure 2,2'-Cu<sub>2</sub>R<sub>0</sub>, but that a virtually quantitative synthesis of 2,2'-R<sub>0</sub> can be realized by combining the redox and thermolysis reactions:



#### EXPERIMENTAL\*

The starting compounds 2,2'-Br<sub>2</sub>R<sub>N</sub>, 2,2'-Br<sub>2</sub>R<sub>0</sub> and the respective di-Grignard reagents were synthesized by methods already reported in the literature [7]. The NMR data of the respective 2,2'-X<sub>2</sub>R<sub>N</sub> and 2,2'-X<sub>2</sub>R<sub>0</sub> derivatives (X = Br, H, Cu) are compiled in Table 2.

#### Attempts to synthesize pure 2,2'-Li<sub>2</sub>R<sub>N</sub>

*Via metal-halogen exchange.* A solution of 4 mmol of butyllithium in hexane (2.15 ml) was added at room temperature to a solution of 2 mmol of 1,2-bis[*N*-(2-bromobenzyl)-*N*-methylamino]ethane (2,2'-Br<sub>2</sub>R<sub>N</sub>) in ether (20 ml). The resulting mixture was stirred during 1 h at room temperature. A sample of the yellow solution was taken apart and concentrated. The resulting light yellow crystalline residue was dissolved in C<sub>6</sub>D<sub>6</sub>. An NMR spectrum of this solution showed broadened resonances at (δ ppm): 8.32 (d, H<sub>3</sub> of 2-lithiated-R<sub>N</sub>), 7.5-6.7 (aromatic-H), 4.2 and 2.88 (2 x d, *J* ≈ 11 Hz, assigned to benzylic-H of 2-lithiated-R<sub>N</sub>), 2.6-0.6 various broad resonances. The main solution was hydrolyzed with H<sub>2</sub>O (5 ml) followed by addition of 4 ml of 4 *N* HCl. The water layer was extracted with ether, made alkaline with 4 *N* NaOH (5 ml) and again extracted with ether. The ether extracts were dried on Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated, affording 0.35 g of a yellow oil (72% of the theoretical yield of 2,2'-H<sub>2</sub>R<sub>N</sub>). NMR spectrum (C<sub>6</sub>D<sub>6</sub>, TMS internal, δ ppm): 2,2'-H<sub>2</sub>R<sub>N</sub>, 2.08 (s, 6, NCH<sub>3</sub>), 2.47 (s, 4, NCH<sub>2</sub>CH<sub>2</sub>N), 3.35 (s, 4, PhCH<sub>2</sub>N); other broadened multiplets are found at 0.9, 1.3, 2.1, 2.5 and 3.4. Estimated yield of 2,2'-H<sub>2</sub>R<sub>N</sub> about 60%. No starting product 2,2'-Br<sub>2</sub>R<sub>N</sub> could be detected in the oil.

*Via metal-hydrogen exchange.* A mixture of 31.5 mmol of butyllithium and 15.7 mmol of 1,2-bis(*N*-benzyl-*N*-methylamino)ethane 2,2'-H<sub>2</sub>R<sub>N</sub> was stirred at room temperature during 48 h. The resulting dark-red solution was added to a mixture of D<sub>2</sub>O and benzene (10/50 v/v). The benzene/ether layer was dried over MgSO<sub>4</sub>, filtered and concentrated affording a yellow oil (75% yield). This oil was distilled affording pure (GLC) D<sub>2</sub>R<sub>N</sub>. B.p. 140°/0.3 mm. NMR spectrum (CCl<sub>4</sub>, TMS internal, δ ppm): 2.13 (s, 6, NCH<sub>3</sub>), 2.50 (s, 4, NCH<sub>2</sub>CH<sub>2</sub>N), 3.44 (s, 3.4, PhCH<sub>2</sub>N), 7.22 (m, 8.7, aromatic H). IR (neat, cm<sup>-1</sup>): ν(C-D) 2250 br\*\* (*ortho*-

\*General directions with respect to solvents, reaction conditions and apparatus, see Chapter IX.

\*\*IR (2-deuteriobenzyl)dimethylamine (neat, cm<sup>-1</sup>): ν(C-D) 2252 cm<sup>-1</sup>, see Chapter II.



D substituted  $R_N$ ) and 2053 br ( $\alpha$ -D substituted  $R_N$ ).

### Synthesis of $2,2'-Cu_2R_N$ (I)

A solution of the di-Grignard  $2,2'-(BrMg)_2R_N$  (obtained from the reaction of 150 mat of magnesium with 42 mmol of  $2,2'-Br_2R_N$  in 180 ml of THF) was added at  $-20^\circ$  to a suspension of 36 mmol of anhydrous  $CuCl_2$  in THF (60 ml). After 2 h stirring at  $-20^\circ$  the suspension was warmed-up to room temperature and then stirred for another 16 h. The light-yellow precipitate was filtered off, extracted with ether (2 x 20 ml) and dried in vacuo (3.55 g).

The work-up of the filtrate has been described below.

*Work-up of the precipitate.* In one preparation the addition of dioxane to the yellow solid afforded a yellow-orange solution with a white precipitate. This mixture was filtered and the filtrate concentrated yielding orange crystalline  $2,2'-Cu_2R_N$  (Ia) in 24% yield.

In a second preparation the yellow solid did not dissolve upon addition of dioxane. The yellow solid was filtered off. Subsequent addition of benzene gave rise to an orange-yellow solution with an orange precipitate. The solution was filtered and the precipitate again extracted with benzene (2 x 40 ml). From the combined benzene extracts orange crystalline  $2,2'-Cu_2R_N$  (Ib) was isolated (2.05 g; 25% yield). [Found (Ia): C, 55.1; H, 5.8; N, 7.0; Cu, 30.6; Hal\*, 0.9; (Ib): C, 54.5; H, 5.7; N, 7.0; Cu, 30.8; Hal\*, 0.9.  $C_{18}H_{22}N_2Cu_2$  calcd.: C, 54.95; H, 5.63; N, 7.12; Cu, 32.34; Br, 0.0%]. The presence of dioxane ( $\approx 5.6$  mol %) in (Ia) and (Ib) was confirmed by NMR spectroscopy (see Fig. 2). The IR spectra (nujol, see Fig. 1) of (Ia) and (Ib) were identical. Mol.wt. (cryometric in benzene): mean 790,  $\bar{n}$  2.0 (concentration independent).

*Work-up of the filtrate.* The filtrate was hydrolysed with 4 N HCl (oxygen-free) solution. The resulting mixture was made alkaline with 4 N  $NH_4OH$  solution (removal of copper). The THF-layer was extracted several times with  $NH_4OH$  solution and then with water. The THF was removed at low pressure affording a yellow oil which subsequently was dissolved in ether. The ethereal solution was extracted with 4 N HCl. The acidic water layer was made alkaline with 4 N NaOH. Extraction of the water layer with ether afforded ether extracts which contained exclusively the amine containing products. The combined ether extracts were dried over  $Na_2SO_4$ , filtered and concentrated yielding a yellow oil. Fractional distillation afforded a main fraction (b.p.  $145-147^\circ/1.5$  mm; 70% of the total distillate) which was analysed by NMR spectroscopy. NMR ( $CCl_4$ , TMS internal,  $\delta$  ppm);  $2,2'-H_2R_N$ , 2.12 (s, 6,  $NCH_3$ ), 2.47 (s, 4,  $NCH_2CH_2N$ ), 3.42 (s, 4,  $PhCH_2N$ ),  $\approx 7.2$  (m, aromatic-H);  $2,2'-R_N$  (III), 2.0-2.9 (AA'BB'-pattern of  $NCH_2CH_2N$ , see Table 1), 2.31 (s, 6,  $NCH_3$ ), 3.11 and 3.71 (2 x d, 4 H,  $J_{gem} \approx 12.0$  Hz,  $PhCH_2N$ ),  $\approx 7.2$  (m, aromatic-H); mol.ratio  $2,2'-H_2R_N/2,2'-R_N \approx 1/0.9$ . MS (70 eV):  $m/e$  268 ( $2,2'-H_2R_N$ )<sup>+</sup> and  $m/e$  266 ( $2,2'-R_N$ )<sup>+</sup>.

### Thermolysis of $2,2'-Cu_2R_N$ (I); isolation of $2,2'-R_N$ (III)

A solution of  $2,2'-Cu_2R_N$  (2.24 mmol) in benzene (10 ml; partly dissolved) was refluxed for 2 h. An immediate decomposition of the mixture was observed (formation of black precipitate). After 2 h a colourless solution with a metallic brown precipitate was obtained. NMR spectroscopy of the solution revealed the exclusive formation of  $2,2'-R_N$  (III), see Fig. 2. The precipitate was filtered off. The filtrate was concentrated and then worked-up, following the acid-base procedure as described above. Pure  $2,2'-R_N$  (III) (according to GLC;

\*Calcd. for halogen is Br.



TABLE 2

NMR SPECTRA OF 2,2'-X<sub>2</sub>R<sub>y</sub> COMPOUNDS

| Compound   | $\delta$ (ppm) <sup>a</sup> in benzene-d <sub>6</sub> (CCl <sub>4</sub> ) |  |   |   |
|--|---|--|---|---|
|  | NCH <sub>3</sub>  | YCH <sub>2</sub> CH <sub>2</sub> Y                             | PhCH <sub>2</sub> Y   | Aromatic-H  |
| $R_N = \begin{array}{c} -CH_2N(Me)CH_2 \\   \\ -CH_2N(Me)CH_2 \end{array}$ |   |  |   |   |
| 2,2'-H <sub>2</sub> R <sub>N</sub>   | 2.10(2.13)<br>(s, 6)  | 2.50(2.49)<br>(s, 4)   | 3.36(3.44)<br>(s, 4)  | 7.0-7.4(7.0-7.4)<br>(m, 10)   |
| 2,2'-Br <sub>2</sub> R <sub>N</sub>  | 2.08<br>(s, 6)  | 2.47<br>(s, 4)   | 3.54<br>(s, 4)  | 6.6-7.6<br>(m, 8)   |
| 2,2'-Cu <sub>2</sub> R <sub>N</sub>  | 1.69<br>(s, 6)  | 1.07 and 2.19<br>(2 x d, 4,<br><i>J</i> <sub>gem</sub> ≈ 9 Hz) | 2.36 and 2.54<br>(2 x d, 4 H,<br><i>J</i> <sub>gem</sub> 12.5 Hz) | H <sub>3</sub> 8.61<br>( <i>J</i> <sub>3,4</sub> 7,<br><i>J</i> <sub>3,5</sub> 1.5 Hz)<br>H <sub>6</sub> 7.78<br>( <i>J</i> <sub>5,6</sub> 7,<br><i>J</i> <sub>4,6</sub> 1 Hz)<br>H <sub>4,5</sub> 6.7-7.4 (m) <sup>b</sup> |
| $R_O = \begin{array}{c} -CH_2OCH_2 \\   \\ -CH_2OCH_2 \end{array}$         |   |  |   |   |
| 2,2'-H <sub>2</sub> R <sub>O</sub>   |   | 3.46(3.50)<br>(s, 4)   | 4.36(4.42)<br>(s, 4)  | (7.0-7.5)<br>(m, 10)  |
| 2,2'-Br <sub>2</sub> R <sub>O</sub>  |   | 3.43(3.72)<br>(s, 4)   | 4.49(4.55)<br>(s, 4)  | 6.6-7.7(6.9-7.6)<br>(m, 8)  |

<sup>a</sup>TMS internal standard: room temperature. <sup>b</sup>Masked by C<sub>6</sub>D<sub>x</sub>H<sub>6-x</sub>.



one peak) was isolated as a colourless oil in 85% yield. Spectroscopic data, see Table 1.

### Reaction of $2,2'-(\text{BrMg})_2\text{R}_0$ with cupric chloride

*Run 1.* A solution of the di-Grignard  $2,2'-(\text{BrMg})_2\text{R}_0$  [from 88.3 mat of magnesium and 30 mmol of 1,2-bis(2-bromobenzyloxy)ethane  $2,2'-\text{Br}_2\text{R}_0$  in THF (80 ml)] was added at  $-20^\circ$  to a suspension of cupric chloride (25.7 mmol) in THF (40 ml). The reaction mixture was stirred at  $-20^\circ$  for 2 h and then at room temperature for 16 h. The white precipitate was filtered off, extracted with THF (2 x 20 ml) and dried in vacuo (3.9 g). This product is insoluble in dioxane, benzene and pentane. (Found: Cu, 11.0%).

The filtrate was hydrolysed with 20 ml of 4 N HCl. Subsequent work-up with  $\text{NH}_4\text{OH}$  solution (vide supra, removal of copper) afforded a light-brown oily residue (5.8 g). According to NMR spectroscopy this oil consisted of  $2,2'-\text{H}_2\text{R}_0$  (VIII) (29% calculated on the starting amount of  $2,2'-\text{Br}_2\text{R}_0$ ) and of  $2,2'-\text{R}_0$  (V) (51% yield). Molar ratio  $2,2'-\text{H}_2\text{R}_0/2,2'-\text{R}_0 \approx 1/1.8$ . NMR data see Table 2. Fractional distillation of the oil afforded a main fraction (b.p.  $133-140^\circ/0.35$  mm) which partly solidified. Extraction with pentane (3 x 2.5 ml) afforded white crystalline  $2,2'-\text{R}_0$  (V). M.p.  $99-100^\circ$ . Spectroscopic data of (V), see Table 1.

*Run 2.* Exactly the same amounts of starting materials were used (see Run 1). The white precipitate was filtered off and then extracted with THF (2 x 20 ml). The filtrate was concentrated affording a white residue. This residue was extracted with dioxane (60 ml), followed by extraction with benzene (60 ml). The dioxane- and benzene-insoluble residue (VI) was dried in vacuo (21.9 g). The dioxane/benzene extract was concentrated affording a residue which was extracted with ether. From the ether extracts a colourless oil was obtained. NMR spectroscopy in  $\text{C}_6\text{D}_6$  revealed the isolation of a mixture of  $2,2'-\text{R}_0$  (V) and  $2,2'-\text{H}_2\text{R}_0$  in a 5/1 molar ratio, i.e. 24% yield of  $2,2'-\text{R}_0$  (V) and 4.7% yield of  $2,2'-\text{H}_2\text{R}_0$ .

The dioxane- and benzene-insoluble residue (VI) was deuterolyzed with  $\text{D}_2\text{O}$  (see *i*) and heated in benzene (see *ii*).

*i.* A suspension of (VI) (2.22 g) in ether/ $\text{D}_2\text{O}$  (20/1) was stirred for 24 h. The ether layer was separated, extracted with water (2 x 5 ml) and then dried over  $\text{Na}_2\text{SO}_4$ . The  $\text{Na}_2\text{SO}_4$  was filtered off and the filtrate concentrated, which afforded an oily residue (0.34 g). NMR ( $\text{CCl}_4$ , TMS internal,  $\delta$  ppm):  $2,2'-\text{R}_0/2,2'-\text{D}_2\text{R}_0$  1/4.5 molar ratio (calcd. from the peak area ratio of the AB pattern due to  $\text{PhCH}_2\text{O}$  of  $2,2'-\text{R}_0$  and the singlet resonance due to  $\text{PhCH}_2\text{O}$  of  $2,2'-\text{D}_2\text{R}_0$ ); the amount of D in  $2,2'-\text{D}_2\text{R}_0$  from the peak area ratio of  $\text{OCH}_2\text{CH}_2\text{O}/\text{PhCH}_2\text{O}/\text{aromatic-H} \approx 4/4/8.2$ . IR (neat):  $\nu(\text{C-D})$   $2254\text{ cm}^{-1}$ ; weak absorption at  $699\text{ cm}^{-1}$  points to the presence of a small amount of monosubstituted aryl groups ( $2,2'-\text{H}_2\text{R}_0$ ).

*ii.* A suspension of (VI) (4.8 g) in benzene (20 ml) was refluxed for 24 h. For the results, see text. NMR spectrum of  $2,2'-\text{R}_0$  see Table 1.

### REFERENCES

- 1 G. BÄHR and P. BURBA, in HOUBEN-WEYL (Eds.), *Organo-Kupfer Verbindungen, Methoden der Organischen Chemie*, Vol. 13/1, 1970, p. 747.
- 2 W. WEIDEMÜLLER, *Diplom-Arbeit*, Technische Hochschule, Darmstadt, 1968.
- 3 E.g., W. H. PUTERBAUGH and C. R. HAUSER, *J. Amer. Chem. Soc.*, 85 (1963) 2467.
- 4 This thesis, Chapter II.



- 5 G.A.RUSSELL, R.KONAKA, E.T.STROM, W.C.DANEN, K.Y.CHANG and G. KAUPP, J.Amer.Chem.Soc., 90 (1968) 4646.
- 6 J.W.MARSMAN and G.VAN KOTEN, to be published.
- 7 G.BÄHR and F.W.KÜPPER, Chem.Ber., 100 (1967) 3992.



## CHAPTER VI

### SYNTHESIS AND CHARACTERIZATION OF ARYLCOPPER COMPOUNDS CONTAINING THE METHOXY OR DIMETHYLAMINO GROUP AS A BUILT-IN LIGAND

#### INTRODUCTION

In Chapters II-V some arylcopper compounds containing the  $\text{Me}_2\text{NCH}_2$  group as a built-in ligand have been described. The present Chapter deals with arylcopper compounds containing a built-in ligand the heteroatom of which is directly bound to the aryl nucleus. It should be expected that the influence of such ligands on the Cu-C bond is more complex than that of a  $\text{Me}_2\text{NCH}_2$  group. In addition to coordinative effects also electronic effects (mesomeric and inductive) exerted by the heteroatom through the ring system on the Cu-C bond will be of importance. The influence of electronic effects on the stability as well as on the aggregation state of arylcopper compounds is illustrated by a comparison of the *ortho*- and *meta*-trifluoromethyl-substituted phenylcopper compounds; i.e. *o*- $\text{CF}_3\text{C}_6\text{H}_4\text{Cu}$  tetramer [1], m.p.  $200-205^\circ$  (dec.) and *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{Cu}$  octamer [1], m.p.  $158^\circ$  (dec.).

In this Chapter the synthesis of some methoxy- and dimethylamino-substituted phenylcopper compounds\* are described.

#### RESULTS

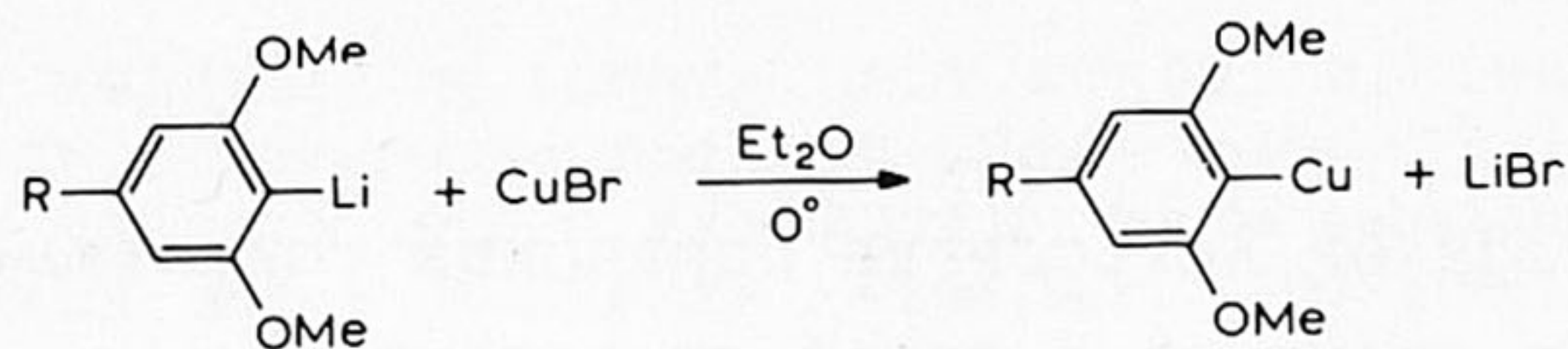
##### *Methoxy-substituted phenylcopper compounds*

Reaction of 2,6-dimethoxyphenyllithium (I) with an equimolar amount of cuprous bromide in ether at  $0^\circ$  resulted in the formation of an ether- and benzene-insoluble grey to grey-black solid which was isolated in 75 to 93% yield. Elemental analysis (C, H, Cu and Br) of the solids isolated from a series of preparations revealed a composition  $\text{CuC}_8\text{H}_9\text{O}_2 \cdot x\text{CuBr} \cdot y\text{C}_6\text{H}_6$  [ $0 \leq x(\text{or } y) < 0.3$ ]. Owing to the extreme insolubility of the organocopper compound (III) in ether and hydrocarbon solvents purification was not possible. Cuprous bromide is most probably present as a contaminant and not in a complexed form.

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\*For a preliminary account of the work described in this Chapter see ref. 2.





(I), R = H

(II), R = OMe

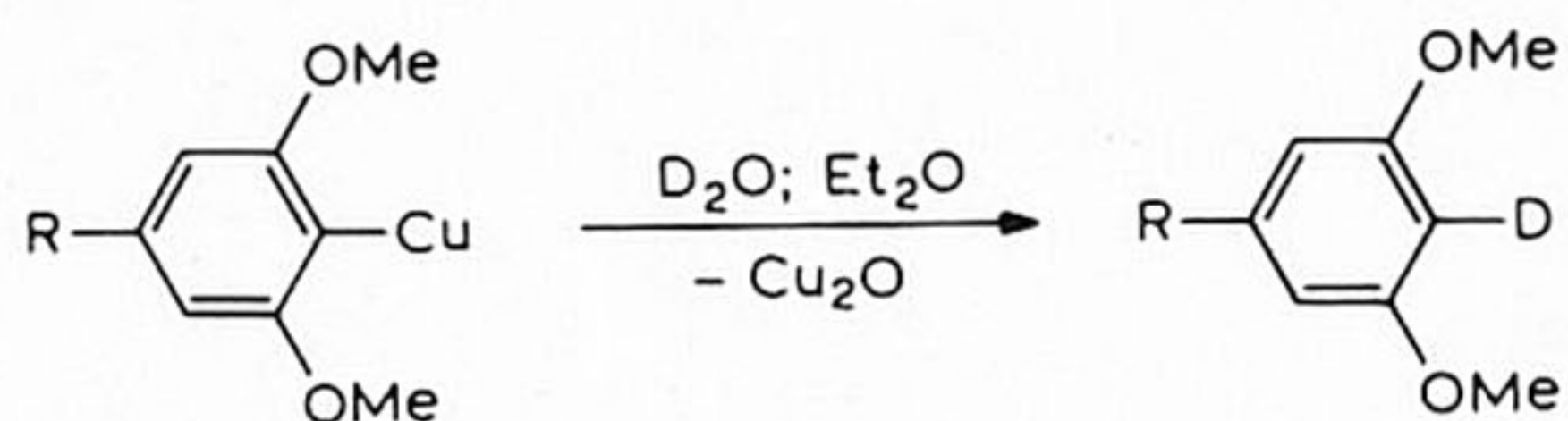
(III), R = H

(IV), R = OMe

Via the same route 2,4,6-trimethoxyphenylcopper (IV) (60-70% yield, cream coloured) was prepared. In contrast with the insolubility of the dimethoxy compound (III), the trimethoxy derivative (IV) appeared to be soluble in benzene and thus could be purified by recrystallization.

Proof for the identity of (III) and (IV) was obtained from their  $^1\text{H}$  NMR spectra using pyridine- $d_5$  [for (III)] or benzene- $d_6$  [for (IV)] as a solvent (see Table 1). The proton resonances belonging to the *ortho*-OCH<sub>3</sub> groups are shifted downfield (0.4-0.5 ppm) with respect to those of the parent arenes. This observation contrasts with the highfield shift of the *ortho*-OCH<sub>3</sub> resonance found in the  $^1\text{H}$  NMR spectrum of 2-methoxyphenylcopper [3]. The resonances due to the 4-OCH<sub>3</sub> group in (IV) and in the parent arene are found at almost the same position. This indicates that in solution the 4-methoxy group is not involved in coordination with the copper atom.

Both (III) and (IV) afforded the expected 2-deuterio derivatives upon reaction with D<sub>2</sub>O.



(III), R = H

(IV), R = OMe

(V), R = H (at least 144 h; 75% yield)

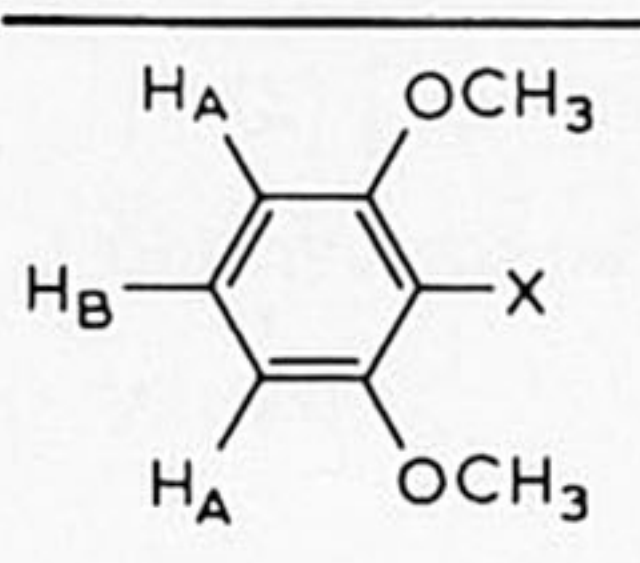
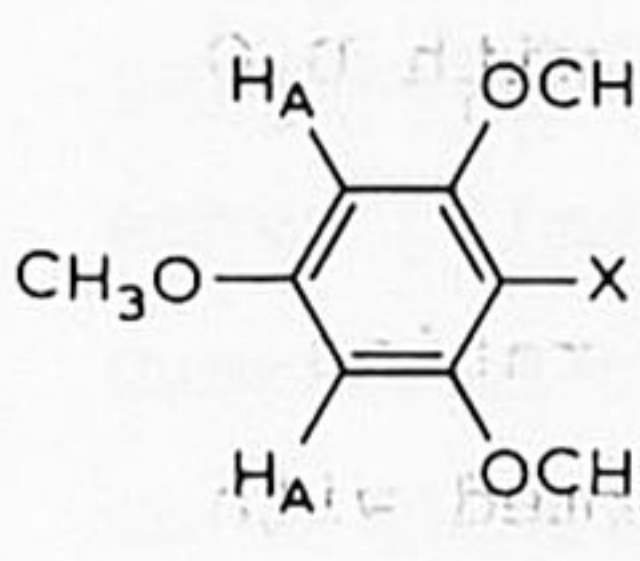
(VI), R = OMe (24 h; 80% yield)

The strikingly different properties of both organocopper compounds, viz.: *i*, (III) being insoluble and (IV) very soluble in ether and hydrocarbon solvents; *ii*, different deuterolysis rates (see eqn.); *iii*, (III) being rather stable in air vs. a rapid decomposition in air of (IV), illustrate the pronounced influence of the introduction of a methoxy group at the 4-position in 2,6-dimethoxyphenylcopper (III).

It is interesting to note that contrary to the Me<sub>2</sub>NCH<sub>2</sub> substituted phenylcopper compounds (Chapter IV) 2,4,6-trimethoxyphenylcopper (IV) does not form a



TABLE I (VI) NMR DATA OF THE METHOXY-SUBSTITUTED PHENYL COPPER COMPOUNDS AND THEIR PARENT ARENES

| Compound  | $\delta$ (ppm) <sup>a</sup> |                    |                 | Solvent                       |
|---|-----------------------------|--------------------|-----------------|-------------------------------|
|   | 2,6-OCH <sub>3</sub>        | 4-OCH <sub>3</sub> | H <sub>A</sub>  |                               |
|    |                             |                    |                 |                               |
| X = H   | 3.64<br>(s, 6H)             |                    | 6.58<br>(m, 2H) | 6.63<br>(s, br, 1H)           |
| (III), X = Cu <sup>b</sup>  | 4.03<br>(s, 6H)             |                    | 6.60<br>(d, 2H) | 7.14<br>(2xd, 1H)             |
|   |                             |                    |                 | $J_{A,B} \approx 8$ Hz        |
|  |                             |                    |                 |                               |
| X = H   | 3.36<br>(s, 9H)             |                    | 6.22<br>(s, 3H) | C <sub>6</sub> D <sub>6</sub> |
| (IV), X = Cu  | 3.85<br>(s, 6H)             | 3.32<br>(s, 3H)    | 6.04<br>(s, 2H) | C <sub>6</sub> D <sub>6</sub> |

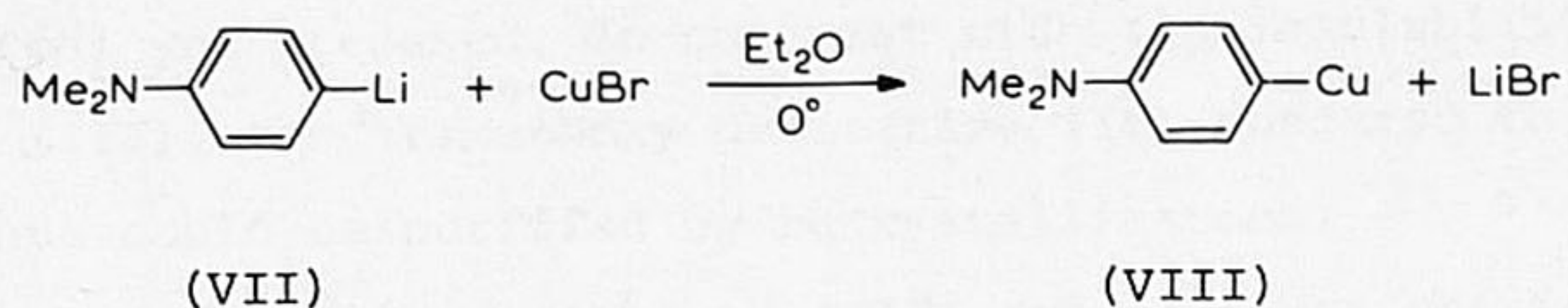
<sup>a</sup>Down-field from TMS internal; s, singlet; d, doublet. <sup>b</sup>Singlet at  $\delta$  7.35 ppm (C<sub>6</sub>H<sub>6</sub>): mol. ratio C<sub>6</sub>H<sub>6</sub>/RCu  $\approx$  0.16/1.



complex with cuprous bromide\*; from an equimolar mixture of CuBr and (IV) in benzene, which was stirred at room temperature during 40 h, the organocopper (IV) as well as CuBr were recovered unchanged.

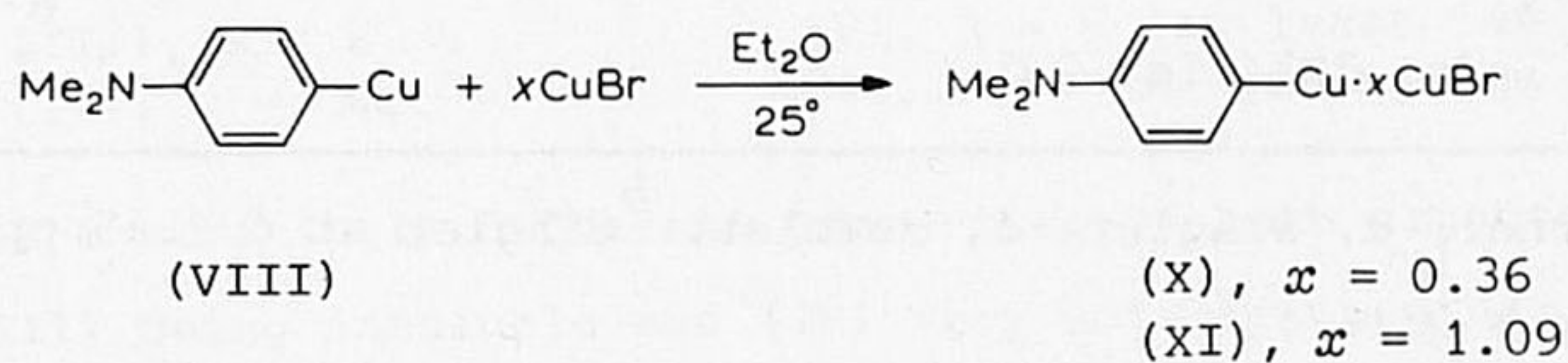
*Dimethylamino-substituted phenylcopper compounds*

a. *4-(Dimethylamino)phenylcopper*. 4-(Dimethylamino)phenylcopper (VIII) was synthesized as follows:



The addition of the first quantity of the organolithium solution to the cuprous bromide suspension, caused a colour change from white to purple. After completion of the addition of (VII) (1/1 molar ratio) a cream-coloured precipitate was present which was isolated by filtration (88% yield). This product, which appeared to be extremely sensitive towards oxidation and hydrolysis, consisted of almost pure 4-(dimethylamino)phenylcopper (VIII). The isolation of 4-deuterio-*N,N*-dimethylaniline (IX) (72% yield) from the reaction of (VIII) with D<sub>2</sub>O confirmed this picture.

The observed colour change of the CuBr suspension at (VII)/CuBr ratios lower than 1 is ascribed to complex formation of the organocopper formed with the excess of cuprous bromide present. This view is supported by the isolation of purple solids (in about 90% yield) from the reaction of (VII) with a slight excess of CuBr as well as from the 1/1 reaction of (VIII) with CuBr.



This complex formation increases the stability of the copper-carbon bond in (VIII) towards hydrolysis and oxidation. Moreover, the thermal stability depends

\*Recently, Camus and Marsich [4] have reported the isolation of 2-methoxyphenylcopper which is benzene-soluble and rather thermostable (dec. at 150°). It was stated that the yield was about 20%, but very dependent on the experimental conditions. We have observed that 2-methoxyphenylcopper forms readily complexes with cuprous bromide and that this complex formation interferes severely with attempts to isolate the organocopper in the pure state.





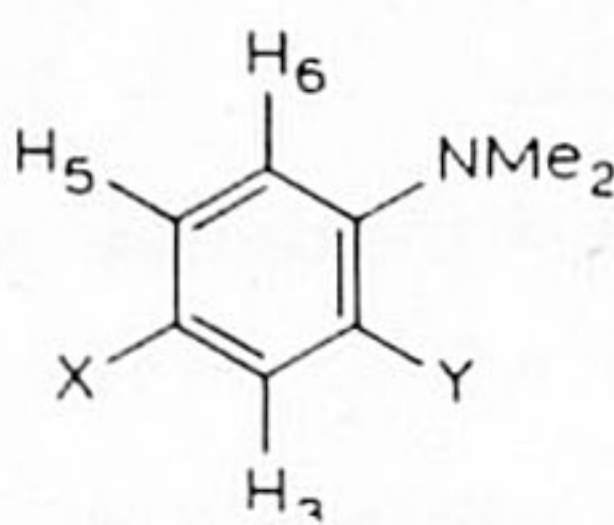


slowly into green. The reaction with  $D_2O$  proceeded very slowly; total decomposition required 7 days [86% yield of 2-deuterio-*N,N*-dimethylaniline (XIV)]. TGA analysis of (XIII) revealed that slow decomposition starts at  $109^\circ$  (heating rate  $3^\circ/\text{min}$ ; at  $194^\circ$  about 5% loss of weight); fast decomposition occurs at  $207-215^\circ$ .

*c. NMR spectra of (VIII) and (XIII).* NMR data of the 2- and 4-dimethylamino-substituted phenylcopper compounds (VIII) and (XIII), dissolved in pyridine- $d_5$ , are compiled in Table 2.

TABLE 2

NMR DATA<sup>a</sup> OF DIMETHYLAMINO-SUBSTITUTED PHENYLCOPPER COMPOUNDS

| Compound  | $\delta$ (ppm)   |                              |                              |                                  |   |                   |
|---|------------------|------------------------------|------------------------------|----------------------------------|---|-------------------|
|   | NCH <sub>3</sub> | H <sub>2</sub>               | H <sub>6</sub>               | H <sub>3</sub>                   | H <sub>5</sub>                                  | H <sub>4</sub>    |
|  |                  |                              |                              |                                  |   |                   |
| Y = H <sub>2</sub> ; X = H <sub>4</sub>   | 2.68<br>(s, 6H)  | 6.70<br>(m, 2H)              |                              | 7.24<br>(m, 2H)                  |   | ≈ 6.75<br>(m, 1H) |
| (VIII),<br>Y = H <sub>2</sub> ; X = Cu  | 2.70<br>(s, 6H)  | 6.71<br>(d, 2H) <sup>b</sup> |                              | 8.22<br>(d, 2H)                  |   |                   |
| (XIII),<br>Y = Cu; X = H <sub>4</sub>   | 2.92<br>(s, 6H)  |                              | 6.54<br>(d, 1H) <sup>c</sup> | 8.91<br>(d, br, 1H) <sup>d</sup> | 7.01<br>(tr of d, 1H)<br>and ≈ 7.2 <sup>e</sup> |                   |

<sup>a</sup>TMS internal; ambient temperature; in pyridine- $d_5$ . <sup>b</sup> $J_{2,3} \approx J_{5,6} \approx 8$  Hz. <sup>c</sup> $J_{5,6} \approx 8$  Hz. <sup>d</sup> $J_{3,4} \approx 7$  Hz. <sup>e</sup>Multiplet (H<sub>4</sub> or H<sub>5</sub>) partly masked by  $C_5D_{5-x}H_xN$  resonances.

The following observations are made:

*i. For (VIII) (Y = H<sub>2</sub> and X = Cu).* Both the protons H<sub>2</sub> and H<sub>6</sub> (*meta* to the Cu-C bond) and the NCH<sub>3</sub> protons are found at almost the same chemical shift values as in the spectrum of the parent arene, *N,N*-dimethylaniline. Apparently, only the protons H<sub>3</sub> and H<sub>5</sub> (*ortho* to the Cu-C bond), which appear about 1 ppm downfield (as compared with the arene), experience the anisotropy of the metal-carbon bond.



*ii.* For (XIII) ( $Y = Cu$  and  $X = H_4$ ). Again the protons which reside at the *ortho* positions with respect to the Cu-C bond are shifted downfield; i.e.  $H_3$  about 1.7 ppm and the  $NCH_3$  protons about 0.2 ppm. This additional downfield shift of  $H_3$  ( $\approx 0.7$  ppm) as compared with  $H_3$  in (VIII) can be explained on the basis of copper being in close proximity with the  $Me_2N$  group. Consequently the  $d$  electron cloud around copper which experiences the rather strong electric field from nitrogen will be distorted. This results in a change of the anisotropy of the metal-carbon bond [3].

## DISCUSSION

In contrast with the general *solubility* of the 2- $Me_2NCH_2$  substituted phenylcopper compounds, which facilitated the elucidation of their structures (see Chapter III), most of the compounds described in the present Chapter are *insoluble* in non- or weakly-coordinating solvents. Exceptions are the benzene-soluble 2/1 complex of 2-(dimethylamino)phenylcopper with cuprous bromide  $(2RCu \cdot CuBr)^*$  and 2,4,6-trimethoxyphenylcopper (IV). The structure of the latter compound is unclear at this moment; no conclusive molecular weight data could be obtained (values for  $n$  between 5 and 7 were measured).

Data collection which can offer information about the structure of the other compounds is hampered by their high insolubility. The insolubility of phenylcopper has been used by several authors as an argument for a polymeric structure, based upon the interaction of filled copper  $d$ -orbitals with anti-bonding  $\pi$ -orbitals of the phenyl nucleus. However, this proposal was made at a time when X-ray structural information concerning arylcopper compounds was not yet available. In view of the structural investigations presented in this thesis (cf. Chapters III, V, VII and IX) as well as in references 1 and 5 a plausible alternative for this proposal seems a polymeric structure in which each phenyl group bridges two copper atoms by two electron-three centre bonds (cf. Chapter III), as pictured in Fig. 1. In this proposed structure the copper atoms are assumed to be two-coordinate with an almost linear arrangement of the  $C_{Ph}-Cu-C_{Ph}$  bonds. This stereochemistry around copper has precedents in the structures of  $(2-Me_2NC_6H_4)_4Cu_6Br_2$  (Chapter VII), of  $(2-Me_2NCH_2C_6H_4)_4Cu_2Li_2$  (Chapter IX) and of  $(Me_3SiCH_2Cu)_4$  (ref. 5).

\*For a detailed discussion of the structure of this complex see Chapter VII.



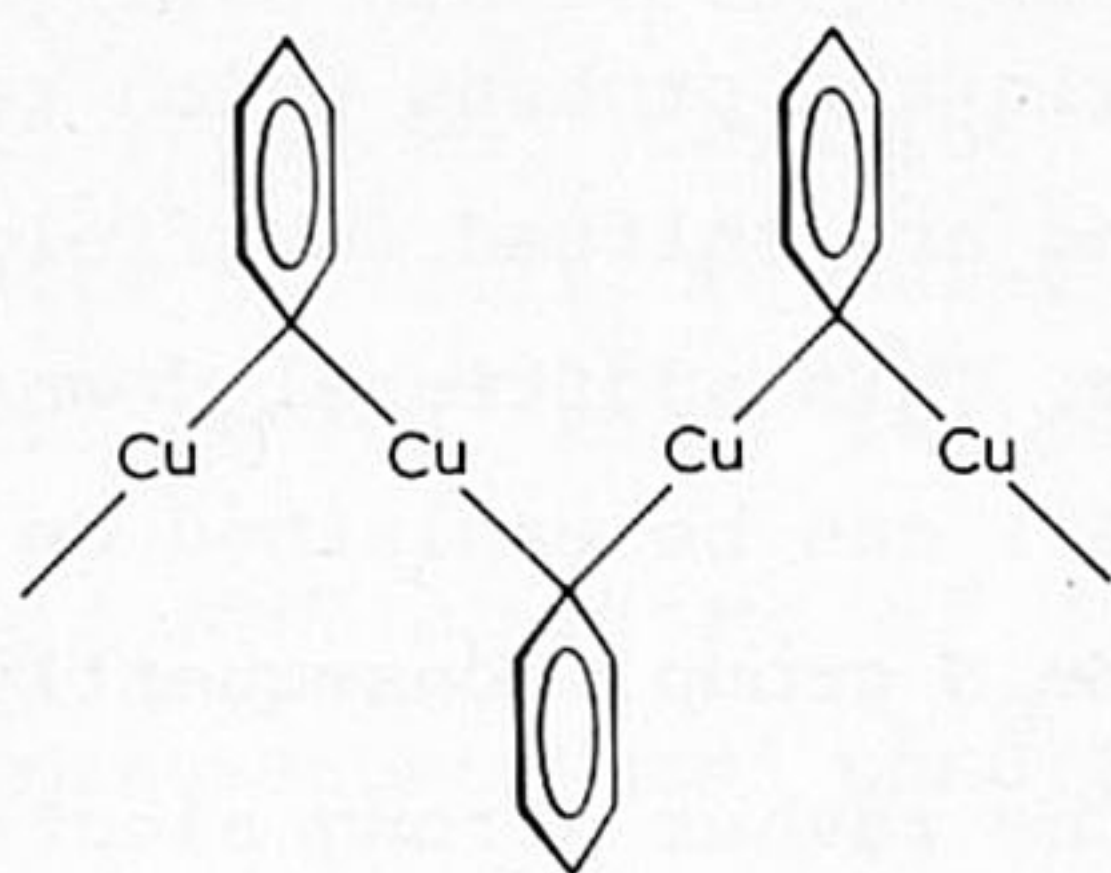


Fig. 1. Proposed structure for phenylcopper coordination polymer.

This proposal may serve as a basis for the structure of the insoluble and presumably polymeric methoxy- and dimethylamino-substituted phenylcopper derivatives. For  $2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu}$  (XIII) and  $2,6\text{-(MeO)}_2\text{C}_6\text{H}_3\text{Cu}$  (III) additional "inter-chain" Cu-N (or Cu-O) coordination is assumed which results in a network-structure as visualized in Fig. 2.

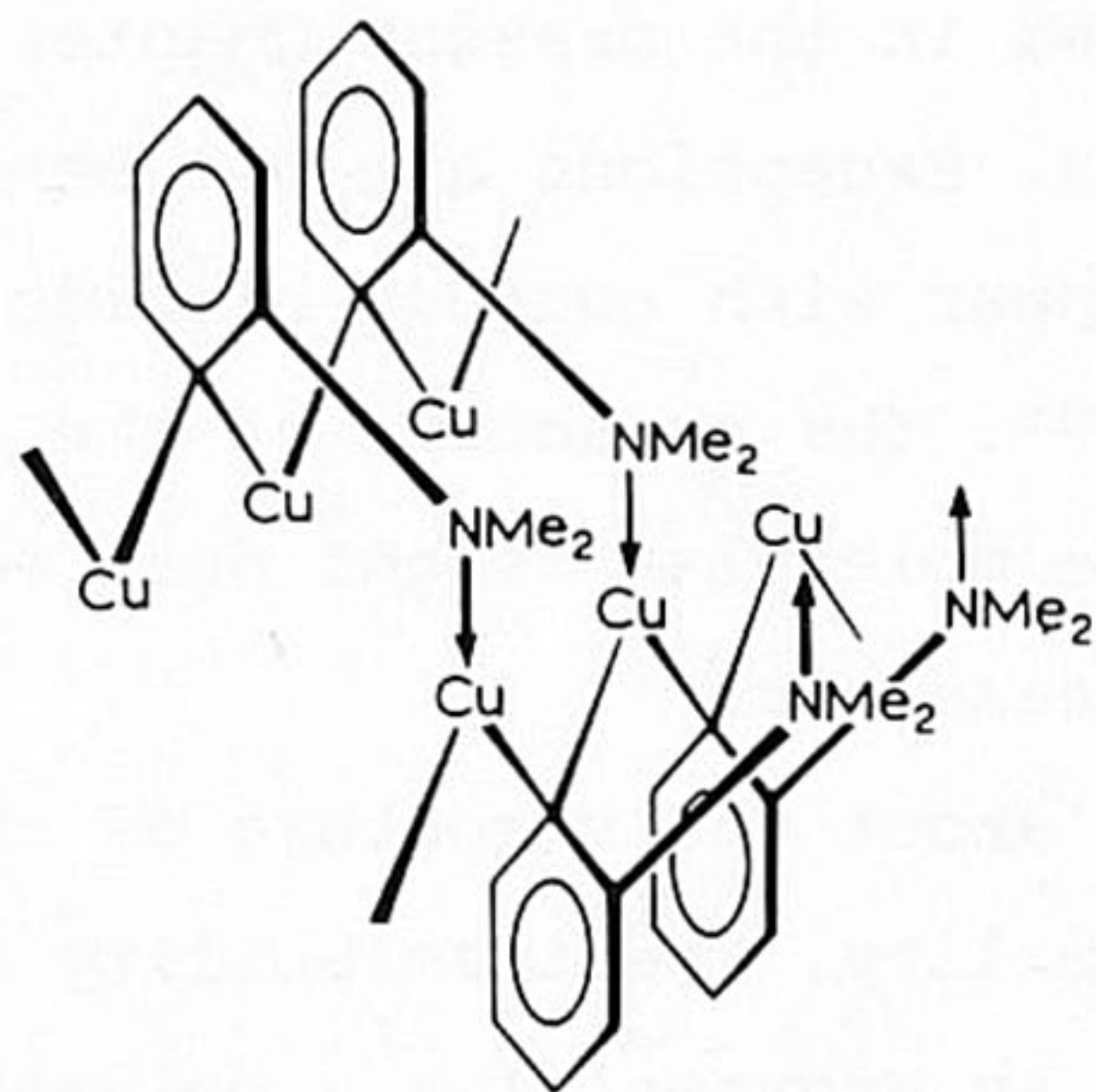


Fig. 2. Proposed structure for 2-(dimethylamino)phenylcopper coordination polymer.

In this type of structure the copper atoms are three-coordinate. Three-coordination of copper involving two Cu-C-electron-deficient bonds and one Cu-N-coordination bond has precedents in the structures of  $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Br}_2$  (equatorial copper atoms, Chapter VII) and of  $(5\text{-Me-2-Me}_2\text{NCH}_2\text{C}_6\text{H}_3)_4\text{Cu}_4$  (Chapter III).

A similar network-structure is proposed for 4-(dimethylamino)phenylcopper (VIII), Fig. 3.

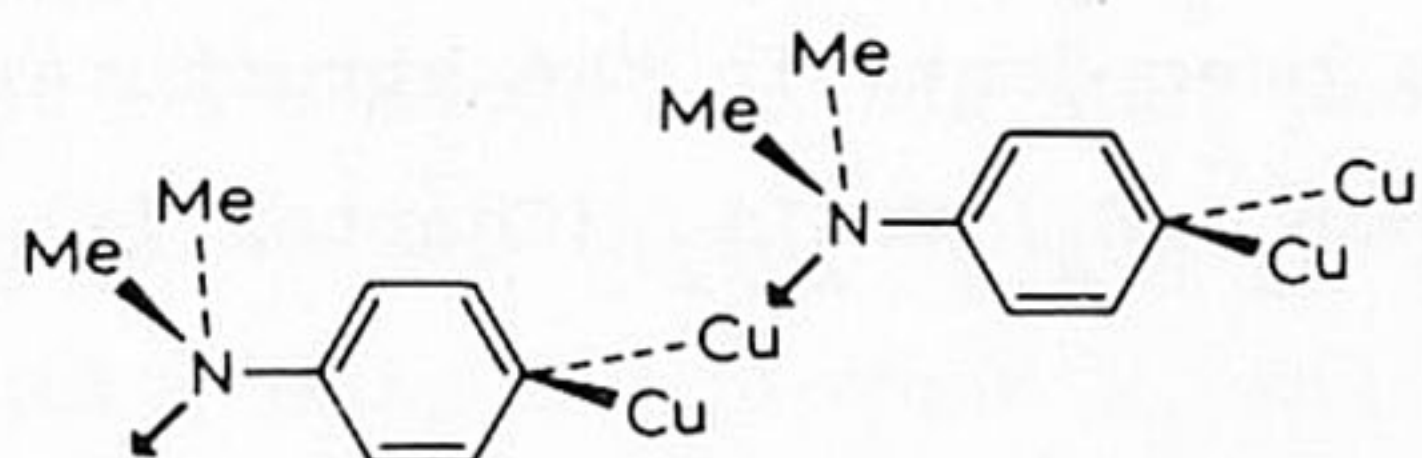
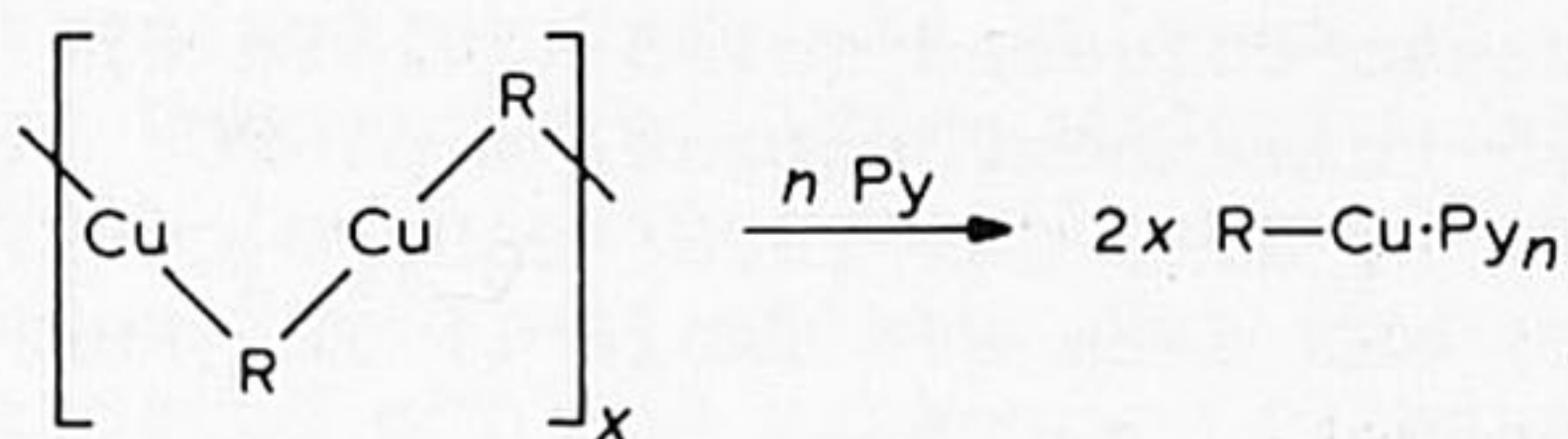


Fig. 3. proposed structure for 4-(dimethylamino)phenylcopper coordination polymer.



The presence of the dimethylamino-ligand in the 4-position will give rise to a less compact network, resulting in a smaller steric shielding of the Cu-C bond. This might explain the difference in oxidative and hydrolytic stability between the 2- and 4-substituted derivatives (VIII) and (XIII) [solid  $(4\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu})_n$  is much less stable than  $(2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu})_n$ ].

It is noteworthy that phenylcopper and the polymeric organocopper compounds discussed in this Chapter dissolve in strongly coordinating solvents such as pyridine. This may be explained by a break-down of their polymeric structures; i.e. the aryl groups change from a state of electron-deficient bonding into a state of electron-precise bonding [7].



## EXPERIMENTAL\*

### *Methoxyphenyllithium compounds (I) and (II)*

A solution of 1,3-dimethoxy- or 1,3,5-trimethoxybenzene (10 mmol) in diethyl ether (15 ml) was added to a solution of butyllithium (10 mmol) in ether (28 ml)/hexane (7 ml). The resulting mixture was stirred at room temperature for 70 h. These reaction mixtures, containing 2,6-dimethoxy- (I) or 2,4,6-trimethoxyphenyllithium (II), were used as such for the reactions with cuprous bromide.

*Reactions with  $D_2O$ .* The solution containing (I) or (II), respectively, was added to an ether (20 ml)/ $D_2O$  (2 ml) mixture. This mixture was stirred for 3 h, filtered and then dried over  $MgSO_4$ . Concentration of the ether filtrate afforded a yellow oil in the case of (I) and an almost white solid in that of (II). NMR spectroscopy (see ref. 6 for the  $\delta$  values) revealed that the respective 2-deuterio compounds (V) and (VI) were formed exclusively. IR (neat) of (V); characteristic absorptions at 785 s and 733 s  $cm^{-1}$ .

### *2,6-Dimethoxyphenylcopper (III)*

Cuprous bromide (100 mmol) was added at  $0^\circ$  to a solution of 2,6-dimethoxyphenyllithium (I) in ether (350 ml)/hexane (54 ml). After stirring for 3 h at  $0^\circ$  and for 1 h at room temperature the black suspension was filtered. The solid was extracted with ether (4 x 40 ml; removal of LiBr) and with benzene (4 x 15 ml) yielding a greyish-black ether and hydrocarbon insoluble solid (IIIa) (yield 92.5%; dec. temp. 185-189 $^\circ$ ). (Found: C, 41.0; H, 4.1; Br, 6.8; Cu, 29.8.

\*General directions dealing with solvents, apparatus and reaction conditions are presented in Chapter IX,



$C_8H_9O_2Cu \cdot 0.23CuBr \cdot 0.16C_6H_6$  calcd.: C, 43.71; H, 4.08; Br, 7.46; Cu, 31.75%.) NMR spectrum of (IIIa) in pyridine- $d_5$ : mol. ratio 2,6-(MeO) $_2C_6H_3Cu/C_6H_6$  1/0.16.

In another preparation extraction with benzene was omitted. A greyish-black solid (IIIb) was isolated. (Found: C, 46.3; H, 4.7; Br, 0.0; Cu, 32.5.  $C_8H_9Cu \cdot 0.06Cu$  calcd.: C, 46.98; H, 4.44; Cu, 32.93%.) The NMR spectrum identical with that of (IIIa) (see Table 1).

*Reaction with  $D_2O$ .* (IIIa) (3.5 mmol) in  $Et_2O$  (40 ml)/ $D_2O$  (2 ml), 144 h, room temperature; 75% of (V) and 80% of  $C_6H_6$  (GLC). NMR data see ref. 6.

#### 2,4,6-Trimethoxyphenylcopper (IV)

Cuprous bromide (19.5 mmol) was added at  $-20^\circ$  to a solution of 2,4,6-trimethoxyphenyllithium (II) (19.5 mmol) in ether (85 ml)/hexane (15 ml). During the reaction a cream-coloured solid precipitated from the reaction mixture. This solid was filtered off, extracted with ether (3 x 20 ml) and dried in vacuo. Recrystallization from benzene afforded a cream-coloured solid (IV) in 65% yield. Dec. temp.  $195-200^\circ$  [white crystals of 1,3,5-trimethoxybenzene, m.p.  $56^\circ$  (litt. [7] m.p.  $55^\circ$ ) were formed]. (Found: C, 48.4; H, 5.1; Cu, 25.6.  $C_9H_{11}O_3Cu \cdot 0.16C_6H_6$  calcd.: C, 49.19; H, 4.96; Cu, 26.13%.) NMR data see Table 1. IR (KBr)  $cm^{-1}$ : 943 w, 933 w, 911 vw, 818 (vbr), 677 w (benzene).

*Reaction with  $D_2O$ .* (IV) (1.90 mmol) in ether (10 ml)/ $D_2O$  (2 ml), 24 h, room temperature: 81% of (VI) and 73% of  $C_6H_6$  (GLC). NMR data see ref. 6.

*Interaction with  $CuBr$ .* (IV) (2.10 mmol)/ $CuBr$  (2.10 mmol) in benzene (30 ml), 40 h, room temperature. The cream-coloured precipitate was filtered off and extracted with benzene. Quantitative recovery of  $CuBr$ . (Found: Cu, 43.0.  $CuBr$  calcd.: Cu, 44.3%.) From the benzene extract pure (IV) (according to IR) was isolated quantitatively.

#### 4-(Dimethylamino)phenylcopper (VIII)

A solution of 4-bromo-*N,N*-dimethylaniline (30 mmol) in ether (45 ml) was added to chips of lithium (64.5 mat) in ether (30 ml). After addition ( $\frac{1}{2}$  h) of the bromo derivative the solution was stirred for another 2 h. The reaction mixture was filtered. A 2 ml sample of the filtrate was hydrolyzed with water (2 ml) and the amount of *N,N*-dimethylaniline determined by GLC [see synthesis of (XIII)]. Calculated yield of (VII) 80%.

The remaining solution of (VII) was added at  $0^\circ$  to a suspension of  $CuBr$  (24 mmol) in ether (40 ml). After stirring for 2 h at  $0^\circ$  and for  $1\frac{1}{2}$  h at room temperature the cream-coloured solid was filtered off. This solid was extracted with ether (3 x 20 ml) and then dried. (VIII) remained in 88% yield. (Found: C, 50.0; H, 5.4; N, 7.3; Br, 1.2; Cu, 33.2.  $C_8H_{10}NCu \cdot 0.03CuBr \cdot 0.05Et_2O$  calcd.: C, 51.37; H, 5.52; N, 7.31; Br, 1.25; Cu, 34.13%.) NMR spectrum of (VIII) in benzene- $d_6$ : mol. ratio 2,4,6-(MeO) $_3C_6H_2Cu/Et_2O \approx 1/0.045$ . NMR data see Table 2. IR (nujol)  $cm^{-1}$ : 1608 s (sh), 1590 vs, 1449 s, 1266 w, 1235 m, 1208 m, 1176 m, 1130 w, 1068 w, 1040 m, 1000 w, 950 m, 806 m (sh), 800 s, 750 m, 720 w, 690 w, 530 w (br), 520 w (vbr).

*Reaction with  $CuBr$ .* Solid (VIII) (10 mmol) was added at room temperature to a suspension of  $CuBr$  (10 mmol) in ether (30 ml). The resulting reaction mixture containing a purple-red solid was stirred for 24 h. Filtration followed by extraction of the precipitate with benzene afforded a purple-red solid (XI) (89% yield). (Found: C, 27.6; H, 3.1; N, 4.0; Br, 24.9; Cu, 37.6.  $RCu \cdot 1.09CuBr$  calcd.: C, 28.25; H, 2.96; N, 4.12; Br, 25.61; Cu, 39.05%.) IR (KBr)  $cm^{-1}$ : 1600 s (sh), 1582 s, 1504 s, 1445 s, 1264 w, 1235 m, 1205 s, 1175 m, 1130 w, 1064 w, 1033 m, 1012 m, 990 m, 943 m, 806 s (sh), 800 s, 796 (sh), 752 m, 693 m, 536 m (vbr).



*Reaction of (XI) with D<sub>2</sub>O.* (XI) (3.74 mmol) in benzene (10 ml)/D<sub>2</sub>O (1 ml), room temperature, 48 h: 72% of (IX). IR (IX) (neat) cm<sup>-1</sup>:  $\nu$ (C-D) 2286 (2294 and 2283 sh). NMR (CCl<sub>4</sub>)  $\delta$  ppm. 2.82 (s, 6H, NCH<sub>3</sub>), 6.58 (m, 2H, H<sub>2,6</sub>), 7.10 (m, 2H, H<sub>3,5</sub>).

### *2-(Dimethylamino)phenylcopper (XIII)*

A solution of 2-bromo-*N,N*-dimethylaniline (60 mmol) in ether (60 ml) was added in 1½ h to 128 mat of metallic lithium in ether (75 ml) containing 1.8534 g of *n*-decane as internal standard. The resulting mixture was refluxed for ¾ h and was subsequently filtered. The amount of organolithium in the filtrate was determined by GLC analysis (decane/*N,N*-dimethylaniline ratio) of a hydrolyzed sample of this solution.

The solution of 2-(dimethylamino)phenyllithium [(XII): 51 mmol] was added at -20° to a suspension of cuprous bromide (51 mmol) in ether (120 ml). The resulting red mixture was stirred at -20° for ¾ h and for an additional hour at room temperature. After addition of benzene (200 ml) the mixture was concentrated at low pressure until about 80% of the ether had been removed. The remaining mixture was stirred for 16 h at room temperature. The orange precipitate was filtered off and subsequently extracted with benzene (3 x 20 ml) and with ether (4 x 20 ml, removal of LiBr) after which it was dried in vacuo. The resulting orange-white solid was further purified by repeated extraction with benzene and pentane in a special apparatus. Solid, cream-coloured (XIII) was obtained in 72% yield. (Found: C, 52.0; H, 5.4; N, 7.6; Cu, 33.6. C<sub>8</sub>H<sub>10</sub>NCu calcd.: C, 52.30; H, 5.49; N, 7.62; Cu, 34.59%.) NMR data see Table 2. IR (nujol)\* cm<sup>-1</sup>: 1572 m, 1560 (sh), 1540 w, 1479 m, 1429 w, 1412 w, 1400 w, 1368 w, 1345 w, 1299 w, 1253 (sh), 1242 w, 1225 w, 1210 w, 1165 (sh), 1160 m, 1115 w, 1095 w, 1052 m, 1043 m, 1000 m, 945 m, 932 w, 835 w, 760 (sh), 752 s, 728 (sh), 718 s, 558 w, 536 w, 500 s, 462 m, 315 w.

*Reaction of (XIII) with D<sub>2</sub>O.* (XIII) (3.38 mmol) in benzene (10 ml)/D<sub>2</sub>O (1 ml), room temperature, 7 days, 86% yield of (XIV). IR (neat):  $\nu$ (C-D) 2283 cm<sup>-1</sup> and in the 900-600 cm<sup>-1</sup> region: 867 w, 844 w, 781-718 vs (br), 625 s.

### REFERENCES

- 1 A. CAIRNCROSS and W. A. SHEPPARD, *J. Amer. Chem. Soc.*, 93 (1971) 247, 248.
- 2 G. VAN KOTEN, A. J. LEUSINK and J. G. NOLTES, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 227.
- 3 A. BAICI, A. CAMUS and G. PELLIZER, *J. Organometal. Chem.*, 26 (1971) 431.
- 4 A. CAMUS and N. MARSICH, *J. Organometal. Chem.*, 14 (1968) 441.
- 5 J. A. J. JARVIS, B. T. KILBOURN and R. PEARCE, *J. Chem. Soc., Chem. Commun.*, (1973) 475.
- 6 A. J. LEUSINK, G. VAN KOTEN and J. G. NOLTES, *J. Organometal. Chem.*, 56 (1973) 379.
- 7 G. VAN KOTEN and J. G. NOLTES, unpublished results.

\*Recorded on a Perkin-Elmer 577 Grating Infrared Spectrophotometer.



Reaction of (XII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (12). The yield of (XIII) was 0.5 g (5%).

Reaction of (XIII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (13). The yield of (XIV) was 0.5 g (5%).

Reaction of (XIV) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (14). The yield of (XV) was 0.5 g (5%).

Reaction of (XV) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (15). The yield of (XVI) was 0.5 g (5%).

Reaction of (XVI) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (16). The yield of (XVII) was 0.5 g (5%).

Reaction of (XVII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (17). The yield of (XVIII) was 0.5 g (5%).

Reaction of (XVIII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (18). The yield of (XIX) was 0.5 g (5%).

Reaction of (XIX) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (19). The yield of (XX) was 0.5 g (5%).

Reaction of (XX) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (20). The yield of (XXI) was 0.5 g (5%).

Reaction of (XXI) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (21). The yield of (XXII) was 0.5 g (5%).

Reaction of (XXII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (22). The yield of (XXIII) was 0.5 g (5%).

Reaction of (XXIII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (23). The yield of (XXIV) was 0.5 g (5%).

Reaction of (XXIV) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (24). The yield of (XXV) was 0.5 g (5%).

Reaction of (XXV) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (25). The yield of (XXVI) was 0.5 g (5%).

Reaction of (XXVI) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (26). The yield of (XXVII) was 0.5 g (5%).

Reaction of (XXVII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (27). The yield of (XXVIII) was 0.5 g (5%).

Reaction of (XXVIII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (28). The yield of (XXIX) was 0.5 g (5%).

Reaction of (XXIX) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (29). The yield of (XXX) was 0.5 g (5%).

Reaction of (XXX) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (30). The yield of (XXXI) was 0.5 g (5%).

Reaction of (XXXI) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (31). The yield of (XXXII) was 0.5 g (5%).

Reaction of (XXXII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (32). The yield of (XXXIII) was 0.5 g (5%).

Reaction of (XXXIII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (33). The yield of (XXXIV) was 0.5 g (5%).

Reaction of (XXXIV) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (34). The yield of (XXXV) was 0.5 g (5%).

Reaction of (XXXV) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (35). The yield of (XXXVI) was 0.5 g (5%).

Reaction of (XXXVI) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (36). The yield of (XXXVII) was 0.5 g (5%).

Reaction of (XXXVII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (37). The yield of (XXXVIII) was 0.5 g (5%).

Reaction of (XXXVIII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (38). The yield of (XXXIX) was 0.5 g (5%).

Reaction of (XXXIX) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (39). The yield of (XXXX) was 0.5 g (5%).

Reaction of (XXXX) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (40). The yield of (XXXXI) was 0.5 g (5%).

Reaction of (XXXXI) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (41). The yield of (XXXXII) was 0.5 g (5%).

Reaction of (XXXXII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (42). The yield of (XXXXIII) was 0.5 g (5%).

Reaction of (XXXXIII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (43). The yield of (XXXXIV) was 0.5 g (5%).

Reaction of (XXXXIV) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (44). The yield of (XXXXV) was 0.5 g (5%).

Reaction of (XXXXV) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (45). The yield of (XXXXVI) was 0.5 g (5%).

Reaction of (XXXXVI) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (46). The yield of (XXXXVII) was 0.5 g (5%).

Reaction of (XXXXVII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (47). The yield of (XXXXVIII) was 0.5 g (5%).

Reaction of (XXXXVIII) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (48). The yield of (XXXXIX) was 0.5 g (5%).

Reaction of (XXXXIX) with  $\text{P}_2\text{O}_5$  (1.5 g, 0.01 mol) in benzene (10 ml) at room temperature, 45 min (49). The yield of (XXXXX) was 0.5 g (5%).

REFERENCES

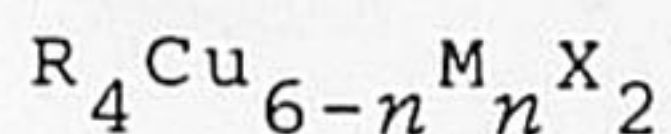
1. A. CAIRNS and W. A. SHEPARD, *J. Amer. Chem. Soc.*, **55** (1933) 347, 355.
2. G. VAN ROTEM, A. J. LEESTER and J. G. HOUTER, *Rec. Trav. Chim. Pays-Bas*, **7** (1931) 327.
3. A. BAICI, A. GAMUS and S. PELLISER, *J. Organometal. Chem.*, **26** (1957) 431.
4. A. GAMUS and W. MARKEIC, *J. Organometal. Chem.*, **14** (1958) 441.
5. J. A. GARVIS, S. T. KILBORN and R. REICHERT, *J. Chem. Soc., Chem. Commun.*, **1957** 475.
6. A. J. LEESTER, G. VAN ROTEM and J. G. HOUTER, *J. Organometal. Chem.*, **56** (1957) 375.
7. G. VAN ROTEM and J. G. HOUTER, unpublished results.

\*Recorded on a Perkin-Elmer 521 Grating Infrared Spectrophotometer.



## CHAPTER VII

### SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF HEXANUCLEAR BIS[2-(DIMETHYLAMINO)PHENYLCOPPER]METAL-IB HALIDE COMPOUNDS



#### INTRODUCTION

In the preceding Chapters several examples of complex formation of aryl-copper compounds with cuprous halides have been presented, e.g.  $[2\text{-Me}_2\text{NCH}_2\text{-C}_6\text{H}_4\text{Cu}\cdot\text{CuBr}]_n$  (Chapter IV);  $[4\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu}\cdot x\text{CuBr}]$  (Chapter VI). In general these complexes are insoluble in the common organic solvents.

Complex formation of organocopper compounds with metal halides ( $\text{LiX}$  [1,2],  $\text{MgX}_2$  [1-3],  $\text{CuX}_n$ , etc.) plays an important rôle in their synthesis and isolation. In addition, it is well-known that the chemical reactivity of organocopper compounds is strongly influenced by metal halides [4]. This has been ascribed to the presence in solution of organocopper-metal halide complexes (the so-called heterocuprates; e.g.  $\text{Li}^+\text{CuBrPh}^-$ ) [4]. However nothing is known with certainty about the nature of these complexes.

In the course of a closer study of the synthesis of 2-(dimethylamino)-phenylcopper it was found that this compound forms a benzene-soluble 2/1 complex with cuprous bromide (see Chapter VI). With the availability of this well-defined organocopper-cuprous bromide complex, which possesses favourable physical properties (good solubility, high thermal stability), the study of the nature of this kind of complex formation has become possible for the first time.

The results of this study, which also includes complex formation reactions of 2-(dimethylamino)phenylcopper with silver bromide, are reported in this Chapter.

#### RESULTS AND DISCUSSION

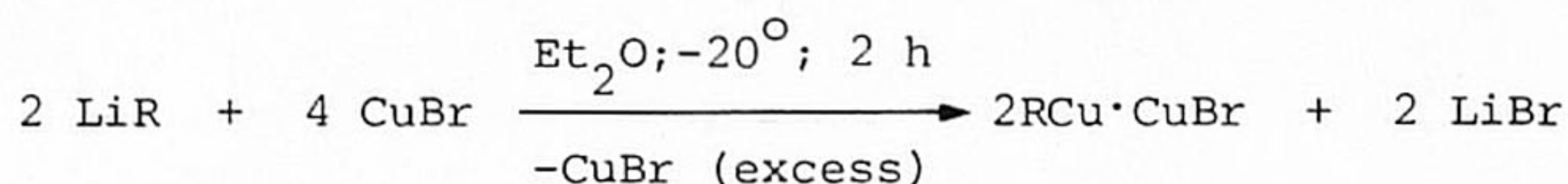
##### *Synthesis of bis[2-(dimethylamino)phenylcopper]metal-IB halide complexes*

*The  $2\text{RCu}\cdot\text{CuX}$  complexes.* The formation of the 2/1 complex of 2-(dimethylamino)phenylcopper (I) with cuprous bromide,  $2\text{RCu}\cdot\text{CuBr}$  (II), is the first



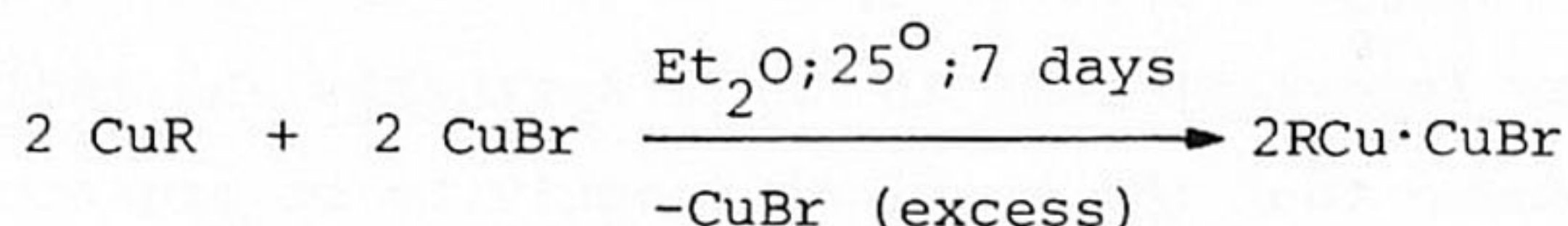
step in the 1/1 reaction of 2-(dimethylamino)phenyllithium (III) with cuprous bromide (addition of RLi to the CuBr suspension). A closer examination of this reaction revealed that (II) can be synthesized in two ways:

(i). Starting from 2-(dimethylamino)phenyllithium [LiR; (III)];



When a solution of (III) in ether was slowly added at  $-20^\circ$  to a suspension of CuBr in ether [(III)/CuBr molar ratio 1/2] the 2/1 complex (II) could be isolated from the reaction mixture in 90% yield based on the amount of (III) (after recrystallization from benzene). Elemental analysis was in accordance with the proposed 2/1 stoichiometry (see Table 1).

(ii) Starting from 2-(dimethylamino)phenylcopper [RCu; (I)];



The reaction of (I) with an equimolar amount of cuprous bromide in ether, which proceeded very slowly, afforded the 2/1 complex  $2\text{RCu}\cdot\text{CuBr}$  which was isolated in 71% yield (after recrystallization from benzene).

Bis[2-(dimethylamino)phenylcopper]cuprous bromide (II) decomposes at  $198-202^\circ$ . Upon exposure to the atmosphere the bright-red colour of the complex remained unchanged for seven days.

Reaction of a *solution* of  $2\text{RCu}\cdot\text{CuBr}$  in benzene with  $\text{D}_2\text{O}$  proceeded very slowly. After 13 days 2-deuterio-*N,N*-dimethylaniline (IV) had been formed in only 55% yield. This indicates that complex (II) is very stable against hydrolysis [compare e.g., the parent organocopper (I): 86% (IV) after 7 days and phenylcopper [1] or fluorinated phenylcopper [5] compounds: rapid hydrolysis with  $\text{H}_2\text{O}$ ].

The synthesis of the corresponding iodo complex  $2\text{RCu}\cdot\text{CuI}$  (V) was achieved similarly as described for the bromo derivative, i.e.

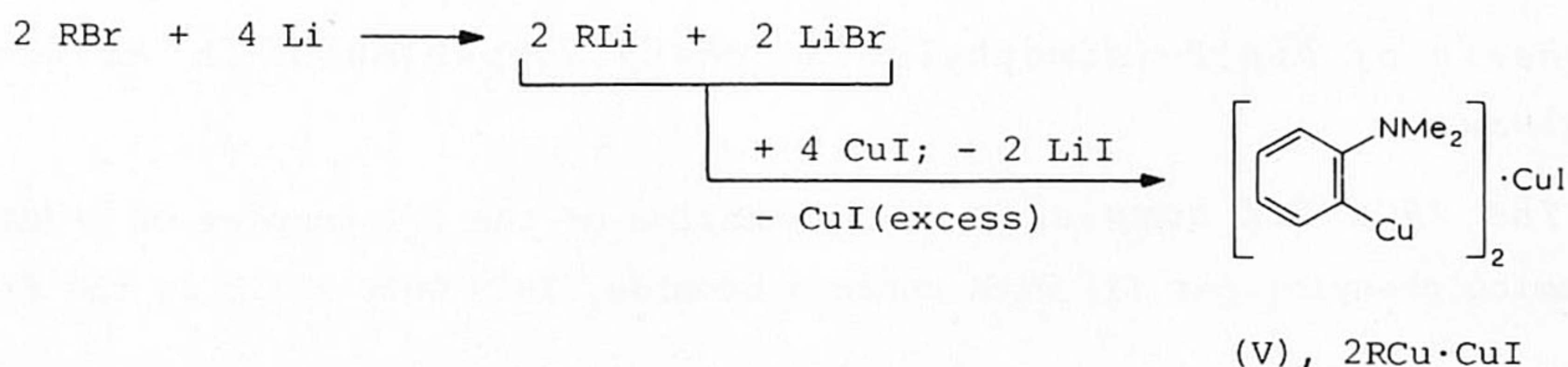




TABLE 1

ANALYTICAL AND PHYSICAL DATA OF BIS[2-(DIMETHYLAMINO)PHENYL-COPPER]METAL-IB HALIDE COMPLEXES

| Compound  | Analysis found (calcd.) % |        |        |          | Cu      | Mol.wt. <sup>a</sup> |              |
|---|---------------------------|--------|--------|----------|---------|----------------------|--------------|
|   | C                         | H      | N      | X        |         | Found<br>(Calcd.)    | $\bar{n}$    |
| (II)  | 37.5                      | 4.0    | 5.4    | Br, 15.6 | 37.2    | 984                  | 1.92 A       |
| C <sub>16</sub> H <sub>20</sub> N <sub>2</sub> Cu <sub>3</sub> Br                                       | (37.62)                   | (3.95) | (5.48) | (15.64)  | (37.31) | 1027<br>(510.5)      | 2.01 B       |
| (V)   | 37.7                      | 3.8    | 4.7    | I, 19.7  | 31.7    | 1150                 | 2.06 B       |
| C <sub>16</sub> H <sub>20</sub> N <sub>2</sub> Cu <sub>3</sub> I·<br>·0.45C <sub>6</sub> H <sub>6</sub> | (37.87)                   | (3.89) | (4.72) | (21.40)  | (32.14) | (557.5)              |              |
| (VI)/(V) mix-<br>ture calcd. for<br>8.41/1 ratio <sup>b</sup>   | 36.9                      | 4.0    | 5.4    | Br, 15.4 | 36.3    |                      |              |
|   | (37.97)                   | (3.98) | (5.54) | (14.11)  | (37.66) |                      |              |
|   |                           |        |        | Cl, 0.8  |         |                      |              |
|   |                           |        |        | (0.74)   |         |                      |              |
| (VI)  | 40.4                      | 4.5    | 5.7    | Cl, 7.9  | 39.4    | 469, 618,            | 1.01 B       |
| C <sub>16</sub> H <sub>20</sub> N <sub>2</sub> Cu <sub>3</sub> Cl·<br>·0.07CuCl                         | (40.59)                   | (4.26) | (5.92) | (8.01)   | (41.21) | 761 (466)            | 1.33<br>1.63 |
| (VII)   | 34.8                      | 3.8    | 4.9    |          | 23.1    |                      |              |
| C <sub>16</sub> H <sub>20</sub> N <sub>2</sub> Cu <sub>2</sub> AgBr                                     | (34.61)                   | (3.63) | (5.05) |          | (22.89) |                      |              |

<sup>a</sup>Concentration independent unless stated otherwise. A via cryometry and B via ebulliometry in benzene. <sup>b</sup>See text.

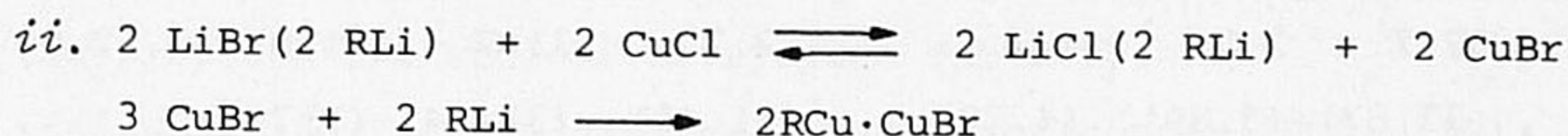
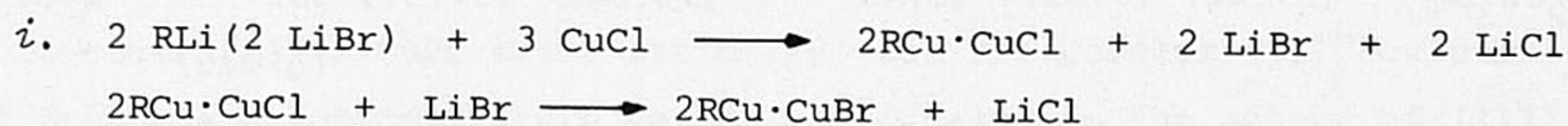
Orange, crystalline (V) was isolated in 64% yield (after two crystallizations from benzene). Elemental analysis pointed to a stoichiometry 2RCu·CuI·0.45C<sub>6</sub>H<sub>6</sub> for the isolated product, see Table 1. IR spectroscopy confirmed the presence of benzene in the complex (absorption band at 685 cm<sup>-1</sup>). The compound decomposes between 195 and 197°.

Surprisingly, the synthesis of the chloro derivative 2RCu·CuCl (VI), following the same reaction sequence, failed. During the addition of the in situ prepared organolithium (III) solution (which thus contained an equivalent amount of LiBr) to the CuCl suspension, a large amount of a black solid was

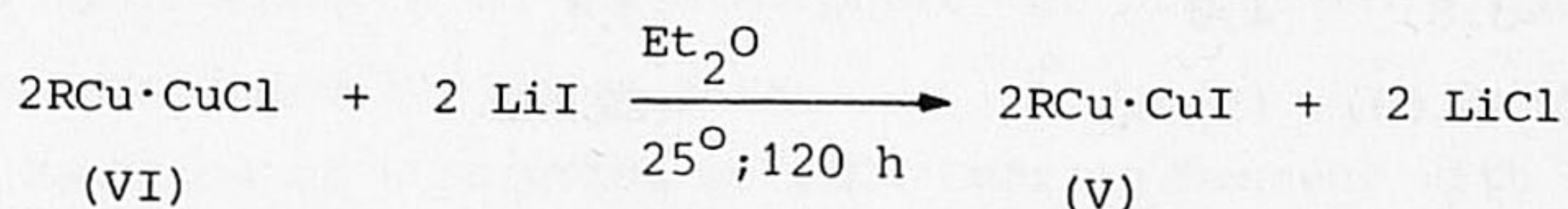


formed. Extraction of this solid with benzene afforded an orange product. Elemental analysis (see Table 1) as well as IR spectroscopy\* showed this solid to consist of the bromo complex (II) contaminated with a small amount of the chloro derivative (VI) (at. ratio Br/Cl  $\approx$  8.41). The overall yield of this product was rather low (30%).

Possible explanations for the isolation of (II) with a small amount of (VI) instead of the chloro derivative (VI) are given in the following reaction sequences:



Sequence *i* involves the primary formation of a  $2\text{RCu}\cdot\text{CuCl}$  complex which in a second step undergoes halogen exchange with the LiBr present in solution, affording the obviously more stable organocopper-cuprous bromide complex. In sequence *ii* halogen exchange between CuCl and LiBr occurs prior to the arylating reaction. This reaction sequence implies in fact that CuCl does not react, or at best very slowly, with the arylating lithium compound to give the organocopper. The first explanation is supported by the observation that the reaction of  $2\text{RCu}\cdot\text{CuCl}$  (see below) with LiI affords quantitatively the  $2\text{RCu}\cdot\text{CuI}$  complex (V).



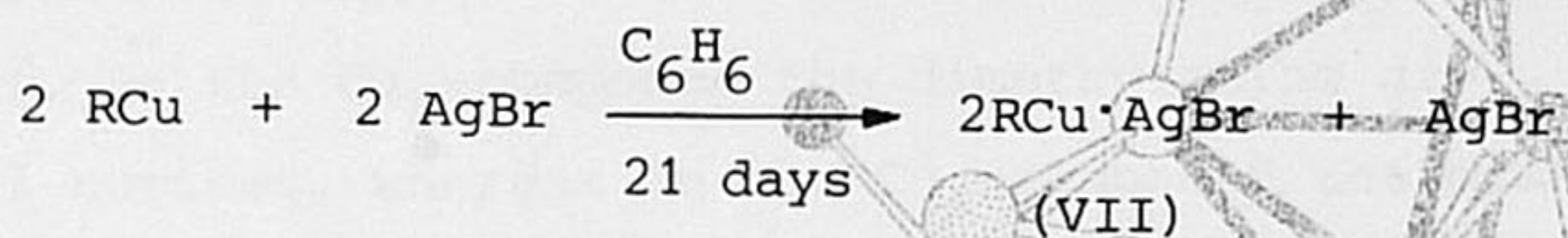
A second approach towards the synthesis of (VI) was more successful. Pure 2-(dimethylamino)phenylcopper (I) was stirred for 14 days with an excess of CuCl (1/1 RCu/CuCl molar ratio) in benzene. The orange solid obtained from this reaction (80% yield) consisted of (VI) ( $2\text{RCu}\cdot\text{CuCl}$ ) contaminated with a small amount of CuCl (see Table 1). The compound decomposes at 181-183 $^\circ$ .

*The  $2\text{RCu}\cdot\text{AgBr}$  complex.* The reaction of 2-(dimethylamino)phenylcopper (I) with AgBr in benzene was carried out several times. The reaction mixtures were stirred at room temperature for periods ranging from 14 to 21 days. During

\*The IR spectrum of this solid was identical to that of the bromo complex (II). The pure chloro complex shows in the 770-715  $\text{cm}^{-1}$  region a somewhat more complex absorption pattern.



this time the cream colour of the suspension turned into brown. The isolation of the resulting complexes, which are soluble in benzene, was complicated by the fact that both starting compounds — the organocopper as well as AgBr — were present in the reaction mixture as very finely divided solids. From one of these reactions, in which the organocopper and AgBr were used in an exact 1/1 molar ratio, a benzene-soluble compound with stoichiometry  $2\text{RCu}\cdot\text{AgBr}$  (see Table 1) was isolated in about 70% yield:



This complex (VII) decomposed between  $182$  and  $185^\circ$ .

### Structural investigation of bis[2-(dimethylamino)phenylcopper]-metal-IB halide compounds

Molecular weight determinations of bis[2-(dimethylamino)phenylcopper]metal-IB halide compounds in benzene revealed their dimeric aggregation state ( $\text{R}_4\text{Cu}_6\text{X}_2$  stoichiometry) in solution (see Table 1). The IR and NMR spectra of these compounds appeared to be of restricted value for the elucidation of their structures (cf.  $\text{R}_4\text{Cu}_4$  compounds, Chapters II and III). Fortunately, attempts to grow single crystals were successful in the case of the CuBr complex (II). The structure of (II) in the solid state has been solved by the group of Prof. Mason at the University of Sussex, England.

*Solid state structure of  $\text{R}_4\text{Cu}_6\text{Br}_2$  (II)\*.* The complex crystallizes from benzene as  $(2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu})_4 \cdot (\text{CuBr})_2 \cdot 1.5\text{C}_6\text{H}_6$ \*\*. The crystals are triclinic with the Delaunay reduced cell:  $a$  10.29,  $b$  13.27,  $c$  17.50 Å,  $\alpha$   $95.5^\circ$ ,  $\beta$   $115.5^\circ$ ,  $\gamma$   $98.3^\circ$ ; space group  $P\bar{1}$ ;  $Z$  2,  $d_m$  1.79,  $d_c$  1.78 g/cm<sup>3</sup>; Mo- $K_\alpha$  radiation;  $R$  0.066. The stereochemistry is shown in Fig. 1.

The following conclusions can be drawn:

1. The six copper atoms are positioned in an octahedral arrangement\*\*\*.
2. The bromine atoms bridge *trans*-equatorial edges of the octahedron. The

most interesting feature is that each aryl ligand bridges two copper atoms. Each

\*For a preliminary account, see ref. 6.

\*\*Recrystallization of (II) from benzene affords  $\text{R}_4\text{Cu}_6\text{Br}_2 \cdot 1.5\text{C}_6\text{H}_6$ . When these crystals are suspended in pentane  $\text{R}_4\text{Cu}_6\text{Br}_2$  as such can be isolated (see Experimental).

\*\*\*A somewhat similar arrangement of the copper atoms has been found in  $\text{Cu}_6\text{H}_6(\text{PPh}_3)_6 \cdot \text{DMF}$  (mean Cu-Cu distances of 2.54 and 2.65 Å) [7].



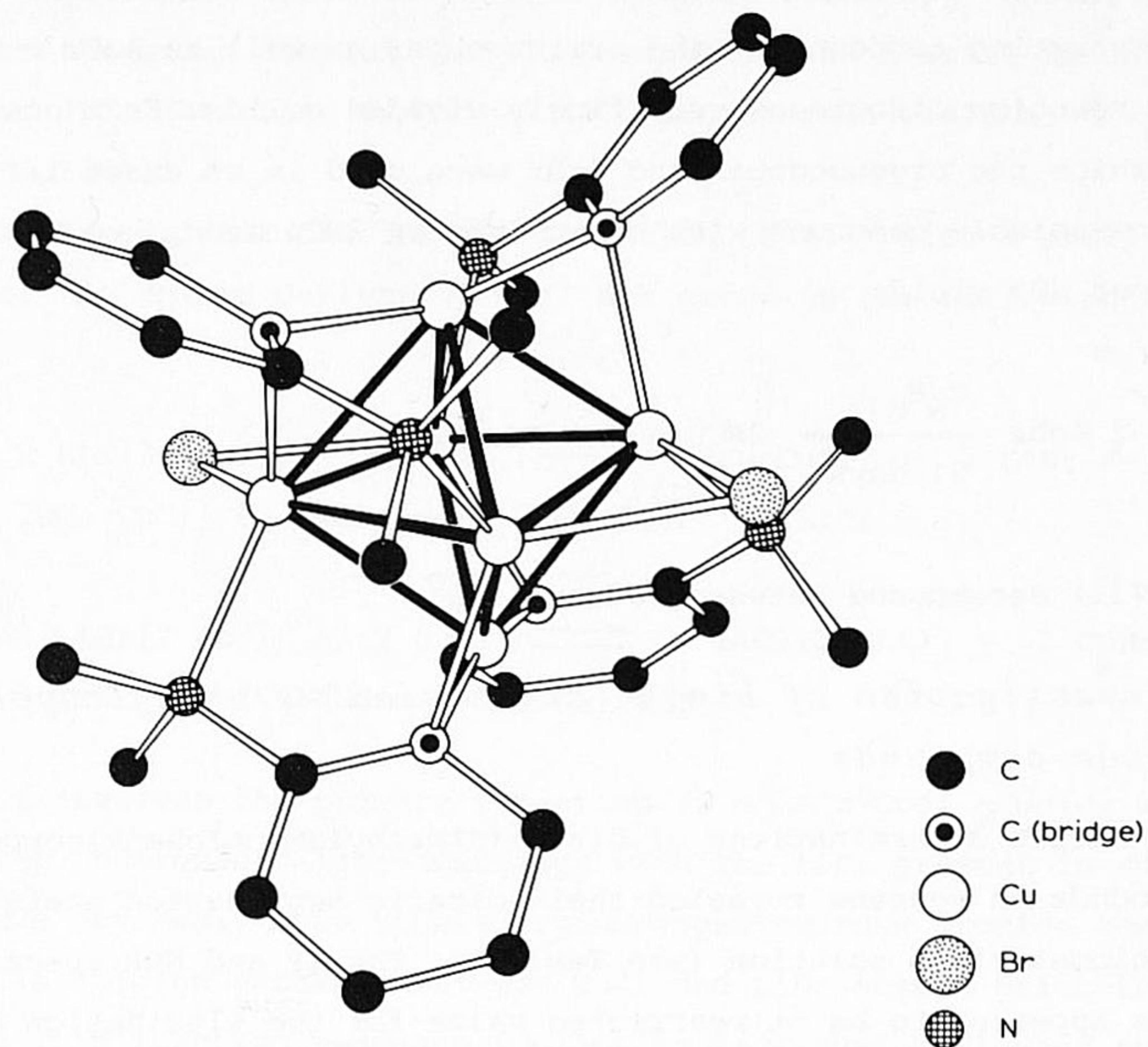


Fig. 1. Structure of hexanuclear bis[2-(dimethylamino)phenylcopper]cuprous bromide.

dimethylamino-nitrogen atom is coordinated to a third copper atom, such that each anilino ligand "bridges" a triangular face of the copper octahedron.

3. The Cu-Cu distances depend on the nature of the bridging ligands. The apical and equatorial copper atoms bridged by the aryl ligands have a mean separation of 2.48 Å and thus are appreciably shorter than the 2.56 Å distance in copper metal. The bromine-bridged 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, 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 approximately linear\* (C-Cu-C  $164^\circ$ ).

5. The difference between the mean Cu-N distances in the  $R_4Cu_6Br_2$  compound (2.11 Å) and in the tetrameric  $R_4Cu_4$  compound (2.21 Å; see Chapter III) may be related to the increased electronegativity of the bromine-bridged copper atoms.

A direct comparison between the bonding in the  $R_4Cu_4$ -cluster compound 5-methyl-2-[(dimethylamino)methyl]phenylcopper and that in the  $Cu_6$ -complex under discussion is difficult for the following reasons:

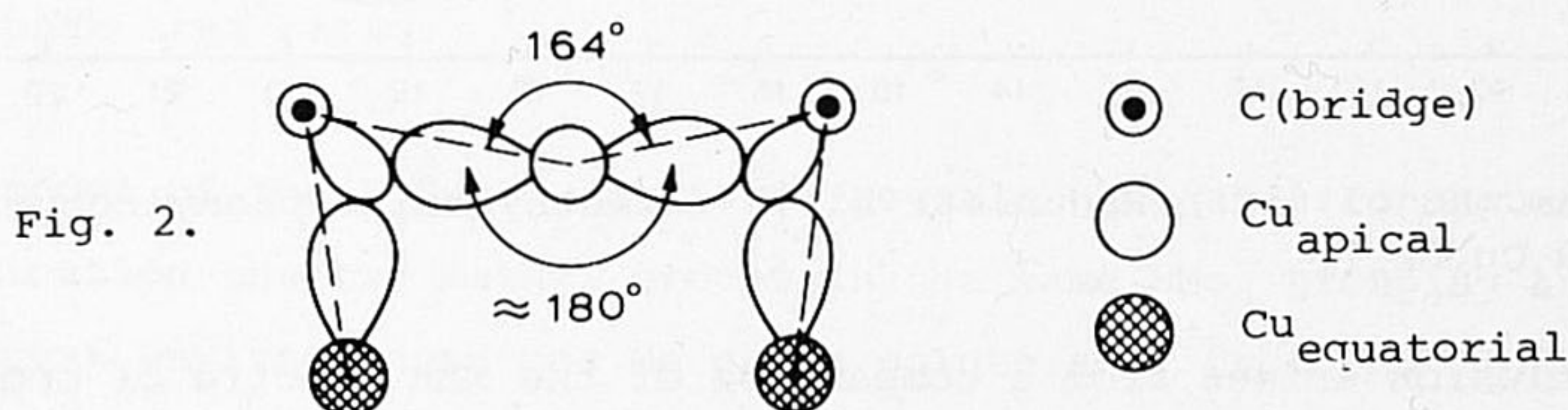
*i.* In the  $Cu_6$ -compound the dimethylamino group is directly attached to the phenyl nucleus, whereas in the  $Cu_4$ -compound the dimethylamino group is separated from this nucleus by a  $CH_2$  group. Thus, in the anilino compound the dimethylamino group contributes electron density to the copper cluster (via  $Cu_2C$ ) both by a mesomeric effect and by direct coordination to copper (via Cu-N). These two effects are coupled in the  $R_4Cu_6Br_2$  compound.

*ii.* The equal C-C distances in the aryl nucleus indicate that the aryl ligand is bonded to the  $Cu_6$ -cluster via two electron-three centre bonds. However, in the  $R_4Cu_6Br_2$  compound the carbon  $sp^2$ -hybrid orbital overlaps with two unlike copper hybrid orbitals.

Linear hybridization\*\* occurs at the apical copper atom\*\*\* whereas at the equatorial copper atom trigonal hybridization is operative.

\*It is worthy of note that in  $(Me_3SiCH_2)_4Cu_4$  exactly the same C-Cu-C angle of  $164^\circ$  has been found for the two-coordinate copper atoms [8].

\*\*As illustrated in Fig. 2 linear hybridization at the apical copper atom implies an angle between the internuclear Cu-C axes which is smaller than  $180^\circ$ .



\*\*\*In *organic*-Group IB metal chemistry a variety of linear complexes is known. In each of these complexes the metal ions have the  $d^{10}$  electronic configuration. Examples are  $CuCl_2^-$  and  $Ag(CN)_2^-$ . Orgel [9] and Jorgensen and Pouradier [10] have pointed out that a small difference between the excited  $d^9s$  and the  $d^{10}$  ground state (see Chapter III p. 20) is the essential condition for the formation of such linear complexes. However, NQR investigations by Bowmaker et al. [11] did not provide conclusive data about the state of hybridization,  $ds$  or alternatively  $sp$ , at the copper ions in linear  $CuX_2^-$  complexes. Investigations concerning the structures of *organo*-Group IB metal compounds revealed that also for compounds with a metal-carbon bond linear arrangement of the ligands is a common structural feature, viz.  $R_4Cu_6Br_2$  (at  $Cu_{ap}$ , this Chapter),  $R_4Cu_2Li_2$  and  $R_4Ag_2Li_2$  (Chapter IX),  $(Me_3SiCH_2Cu)_4$  [8] and  $RAu \cdot L$  [12].



Structures of bis[2-(dimethylamino)phenylcopper]copper chloride (VI) and iodide (V). The structures of the chloro and iodo derivatives (VI) and (V), respectively, follow from a comparison of molecular weight determinations and of the IR and NMR spectra of these compounds with corresponding data of the  $R_4Cu_6Br_2$  derivative.

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. It appears that both the  $Br-$  and the  $I-$ derivative exist in benzene solution as stable hexanuclear species with the stoichiometry  $R_4Cu_6X_2$ . On the contrary, the hexanuclear structure of the chloro derivative is less stable as appears from its concentration-dependent molecular weight ( $n$  increases from 1.01 to 1.63 with increasing concentration).

The IR spectra of  $R_4Cu_6Br_2$  and  $R_4Cu_6I_2$  are superimposable in the  $1600-200\text{ cm}^{-1}$  region, whereas the spectrum of  $R_4Cu_6Cl_2$  contains some additional bands in the C-H bending region. This indicates that the observed vibrations are insensitive to the bridging halogen atoms  $X$  and thus seem to be specific for  $R$  in the  $R_4Cu_6$ -skeleton (Fig. 3 shows the IR spectrum of  $R_4Cu_6Br_2$ ).

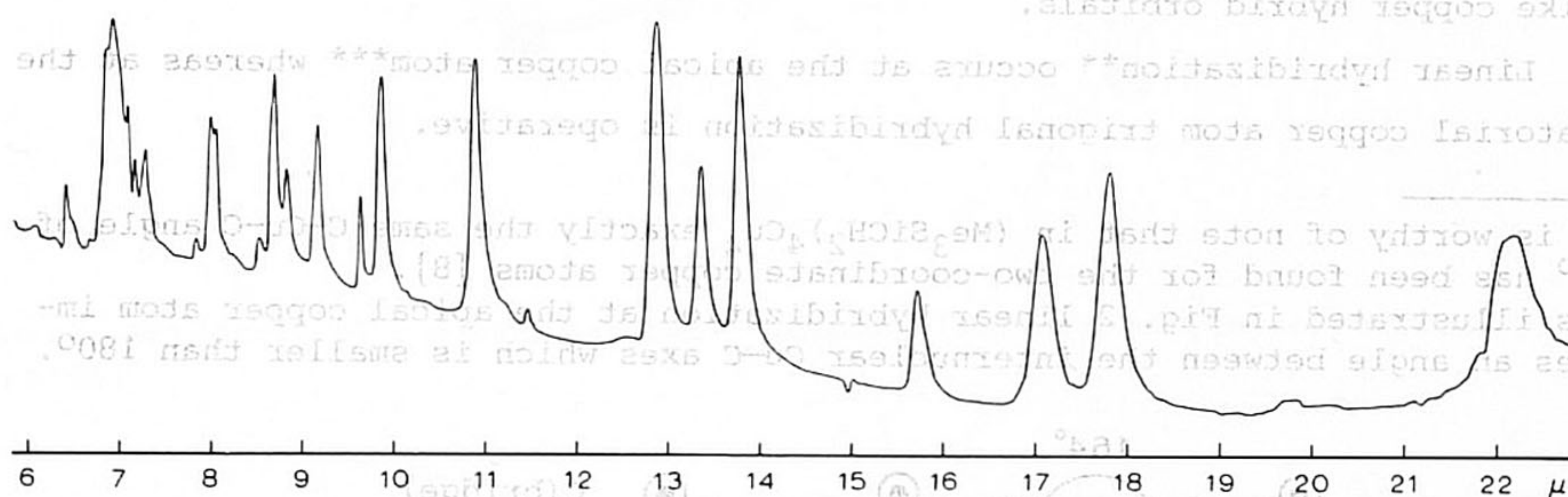


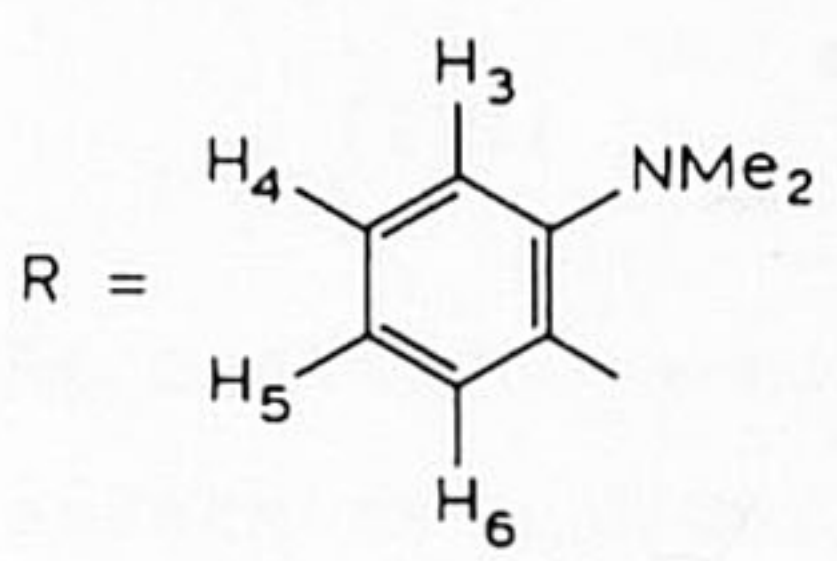
Fig. 3. IR spectrum (nujol) of hexanuclear bis[2-(dimethylamino)phenylcopper]cuprous bromide ( $R_4Cu_6Br_2$ ).

The same conclusion arises from a comparison of the NMR spectra of compounds  $R_4Cu_6X_2$  recorded at  $25^\circ$  (see Table 2). In Fig. 4 the NMR spectrum is shown of the bromo derivative recorded at different temperatures. At room temperature the respective proton resonances of each of the three compounds (II), (V) and (VI) appear at almost the same chemical shift positions, which indicates an identical magnetic environment for each of the  $R$  groups in the several  $R_4Cu_6X_2$  compounds. 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



TABLE 2

NMR DATA OF THE HEXANUCLEAR COPPER COMPOUNDS  $R_4Cu_6X_2$ 

| Compound  | Temp.<br>(°C)              | $\delta$ (ppm) <sup>a</sup>     |                                 |                |
|---|----------------------------|---------------------------------|---------------------------------|----------------|
|   |                            | NCH <sub>3</sub>                | H <sub>3</sub>                  | H <sub>6</sub> |
| <i>N,N</i> -dimethylaniline <sup>b</sup><br>(RH)  | 25                         | 2.50 (s)                        | 6.59 (m)                        | 7.20 (m)       |
| <br>R = | 25                         | 1.84 and 2.92 (br) <sup>d</sup> | 6.64 (m)                        | 8.3 (m)        |
|   | $R_4Cu_6Cl_2$ <sup>c</sup> | 110                             | 2.42 s, sharp and<br>2.35 broad |                |
| (II)<br>$R_4Cu_6Br_2$ <sup>c</sup>  | 25                         | 1.84 and 2.94 (br) <sup>d</sup> | 6.64 (m)                        | 8.48 (m)       |
|   | 90                         | 2.42 s, sharp                   |                                 |                |
| (V)<br>$R_4Cu_6I_2$ <sup>c</sup>  | 25                         | 1.78 and 2.87 (br) <sup>d</sup> | 6.62 (m)                        | 8.46 (m)       |
|   | 110                        | 2.42 s, sharp                   | 6.74 (m)                        | 8.42 (m)       |

<sup>a</sup>Downfield from TMS; s, singlet; m, multiplet; br, broad. <sup>b</sup>In C<sub>6</sub>D<sub>6</sub>. <sup>c</sup>In CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>.  
<sup>d</sup>1/1 peak area ratio.

of a model 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<sub>2</sub> grouping indeed reside in different environments; one Me group points away from the cluster whereas the other resides near a triangular face of this cluster. At higher temperatures the equilibrium between non-coordinated and coordinated NMe<sub>2</sub> groups shifts to the non-coordinated situation. That the cluster structure remains intact at higher temperatures appears from the molecular weight data for the bromo and iodo derivative at 80° (see Table 1). In the non-coordinated situation the methyl groups become equivalent by rotation around the C<sub>Ph</sub>-N bond, which explains the coalescence of the doublet to one singlet (at 2.42 ppm) at about 90°.

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). This observation sug-



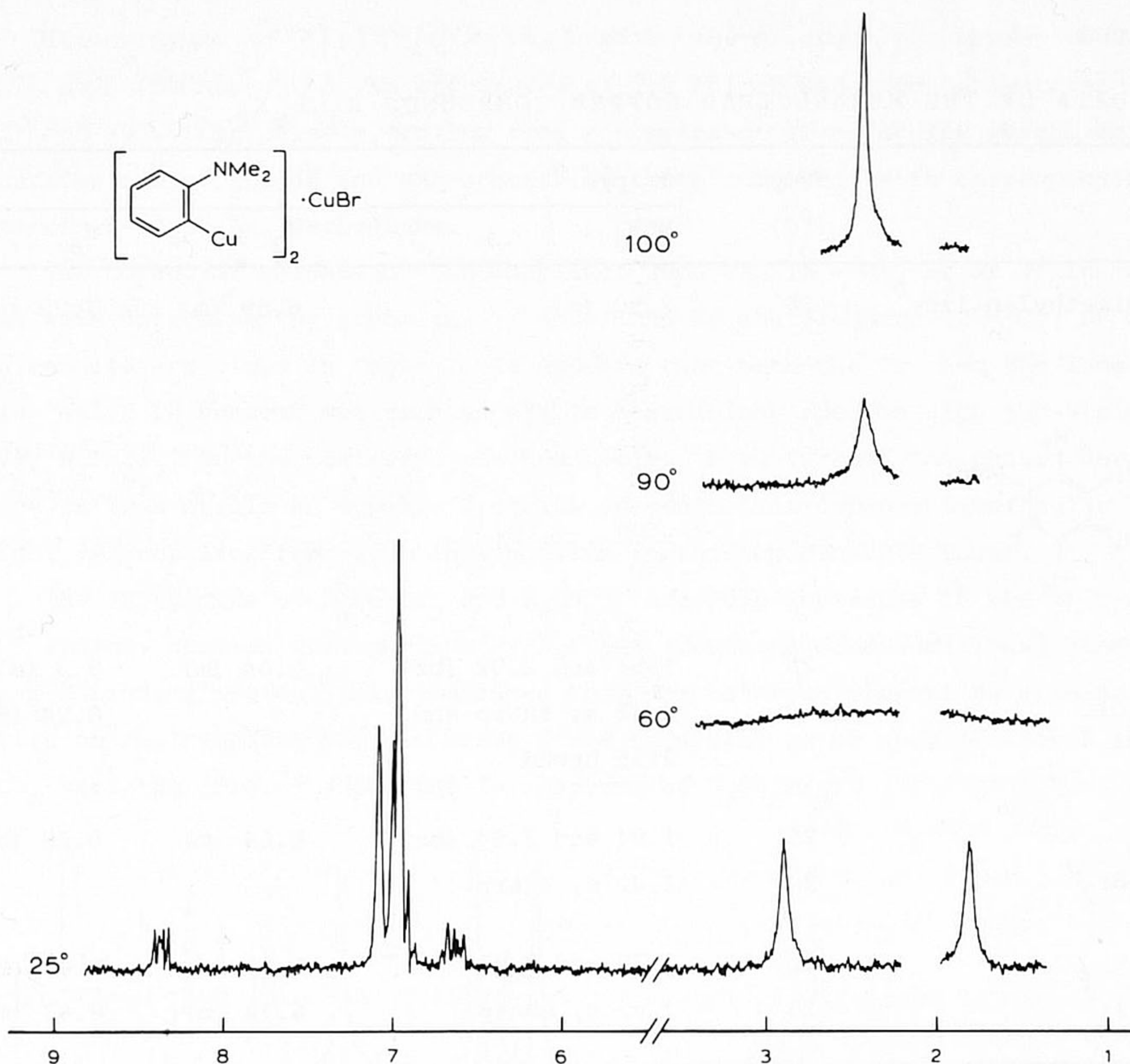


Fig. 4. NMR spectrum ( $\delta$  ppm) of  $\text{R}_4\text{Cu}_6\text{Br}_2$  (II) in toluene- $d_8$  ( $\text{CH}_x\text{D}_{3-x}$  resonances are not shown), see also Table 2.

gests that the dimer is in equilibrium with another aggregate, most probably the monomer (cf. the concentration dependence of the molecular weight at  $80^\circ$ , Table 1). The dimerization of two monomers  $\text{R}_2\text{ClCu}_3$  can be explained by a change from intra- into inter-molecular coordination of the chloro atom as depicted in Fig. 5.

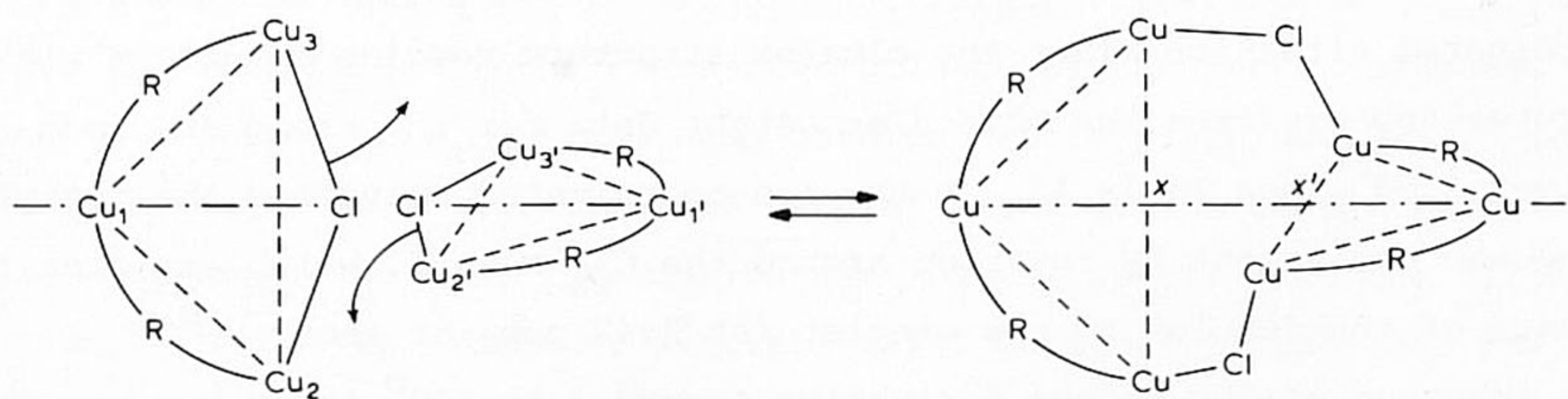
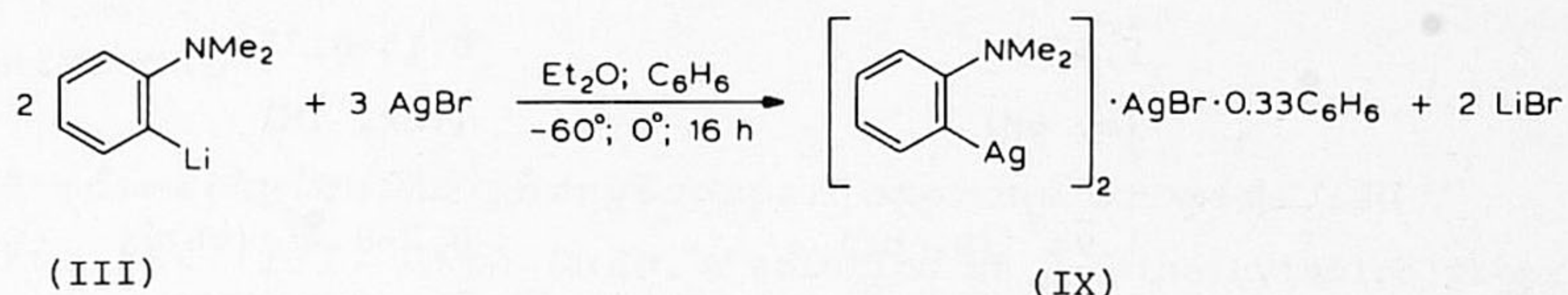


Fig. 5. Dimerization of two monomers  $\text{R}_2\text{ClCu}_3$  to hexanuclear  $\text{R}_4\text{Cu}_6\text{Cl}_2$  ( $x = x'$ ).

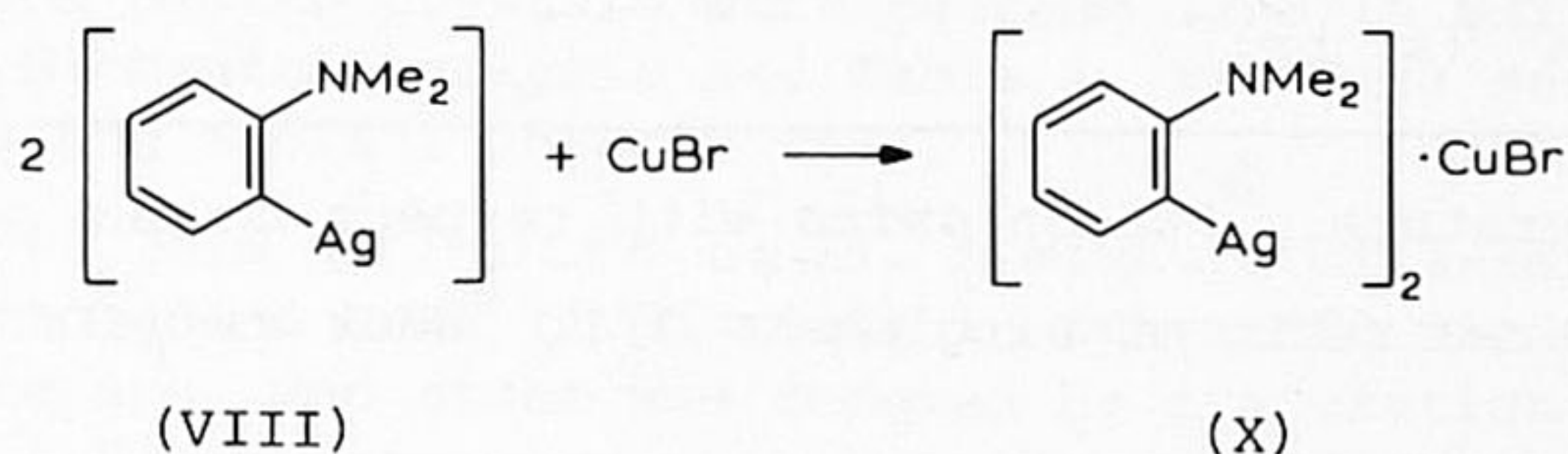


Structures of the bis[2-(dimethylamino)phenylcopper]silver bromide complexes  $R_4Ag_{6-n}Cu_nBr_2$  ( $n = 0, 2, 4$ ). The 2/1 complex of 2-(dimethylamino)phenylsilver (VIII) with silver bromide has been isolated as a yellow, benzene-soluble solid from the 2/3 reaction of 2-(dimethylamino)-phenyllithium (III) with silver bromide [13].



According to a molecular weight determination in benzene this complex (IX) exists as a dimer and thus has  $R_4Ag_6Br_2$  stoichiometry.

A mixed copper-silver complex was obtained from the 1/1 reaction of (in situ prepared) 2-(dimethylamino)phenylsilver (VIII) with cuprous bromide [13].



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 [13] 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. According to analysis (VII) can be formulated as  $R_4Ag_2Cu_4Br_2$ .

For all these complexes a structure similar to that of  $R_4Cu_6Br_2$  (cf. Fig. 1) in which copper atoms have been 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 compiled 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, an equilibrium mixture of hexanuclear species of the type  $R_4Cu_mAg_nBr_2$  [ $m + n = 6$ ], being present. This equilibrium between hexanuclear species  $R_4Cu_mAg_nBr_2$  can be interpreted in terms of



TABLE 3

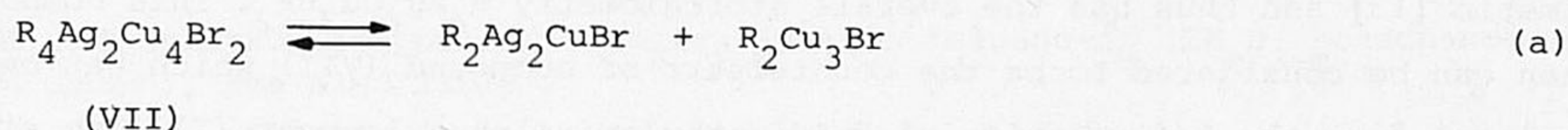
NMR DATA OF THE  $R_4Cu_{6-n}Ag_nBr_2$  COMPLEXES (VII), (IX) AND (X)

| Compound                              | Chemical shift $\delta$ (ppm) <sup>a</sup>   |   |
|---------------------------------------|--|---|
|                                       | NMe  | H <sub>6</sub> <sup>b</sup>               |
| (IX)<br>$R_4Ag_6Br_2$ <sup>c</sup>    | 2.42<br>(s, 6H)  | 8.15-8.35<br>(vbr, 1H)                    |
| (X)<br>$R_4Ag_4Cu_2Br_2$ <sup>c</sup> | 1.94 <sup>d</sup> (s, br)<br>2.1-2.8 (vbr)<br>2.42 <sup>e</sup> (s)<br>2.94 <sup>d</sup> (s, br) | 8.2-8.4 <sup>e</sup> (vbr)<br>8.4-8.6 (m) |
| (VII)<br>$R_4Ag_2Cu_4Br_2$            | 1.83 <sup>d</sup> (s, br)<br>2.1-2.7 (vbr)<br>2.94 <sup>d</sup> (s, br)                          | 8.4-8.55 (m)                              |

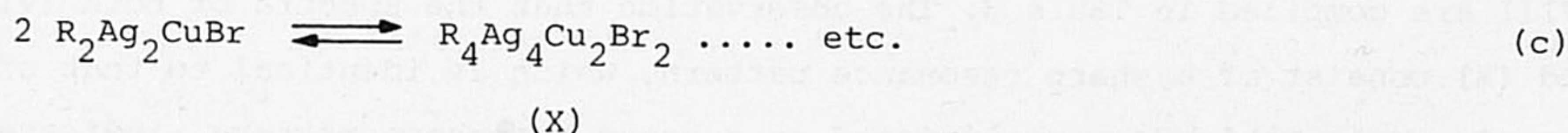
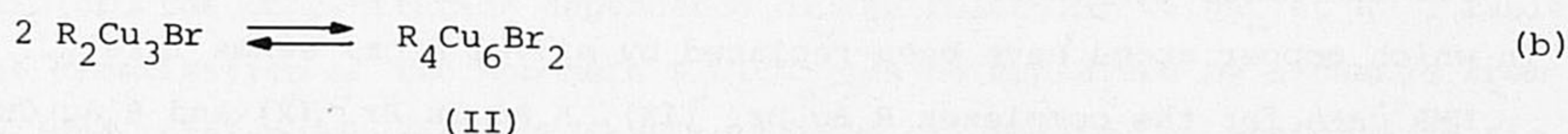
<sup>a</sup>TMS internal; C<sub>6</sub>D<sub>6</sub>; room temperature. <sup>b</sup>Proton *ortho* with respect to the M-C bond. <sup>c</sup>See ref. 13. <sup>d</sup>Peak area ratio of singlets  $\approx 1/1$ . <sup>e</sup>Weak signals.

interaggregate exchange reactions\*; viz.:

*i. Dissociation;*



*ii. Association*



For the dissociation step (*i*) M-N and M-Br coordination bonds must be broken. In the case of  $R_4Cu_6Br_2$  this process will be rate-determining and very slow on the

\*That in the dissociation step monomeric species RCu or RAg are involved seems unlikely in view of their tendency to form coordination polymers which are highly insoluble (see Chapter VI).



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. (c)] then account for the additional broad resonance pattern.

#### EXPERIMENTAL\*

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

*Via RLi (III) with CuBr.* A solution of 2-(dimethylamino)phenyllithium\*\* [(III); 19.8 mmol] was added at  $-20^\circ$  to a suspension of cuprous bromide (39.6 mmol) in ether (40 ml). This mixture was stirred for  $\frac{1}{2}$  h at  $-20^\circ$  and for  $2\frac{1}{2}$  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 ( $60^\circ$ ) benzene. The crystals contained crystal-benzene when isolated directly from the benzene solution. (Found: Cu, 34.1; Br, 13.9.  $2RCu \cdot CuBr \cdot 0.75 C_6H_6$  calcd.: Cu, 33.50; Br, 14.04%.)

When the benzene solution was decanted from the crystals, followed by extraction of the crystals with pentane (2 x 15 ml) complex (II) was isolated as such. Elemental analysis see Table 1. NMR data see Table 2. IR spectrum see Fig. 3 and Table 2 Chapter VIII.

*Via RCu (I) with CuBr.* A mixture of 2-(dimethylamino)phenylcopper [(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 affording a grey-coloured residue (unreacted CuBr) and a red benzene extract. From this benzene extract a red, crystalline solid was obtained which according to IR spectroscopy and copper analysis (found: Cu, 36.6.  $2RCu \cdot CuBr$  calcd.: Cu, 37.31%) appeared 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 with red precipitate; the solution contains 55% of (IV). After standing for 4 days in the atmosphere the content of (IV) raised to 70%. Subsequent work-up of the still yellow-coloured solution with a 4 N HCl solution, followed by neutralization of the acidic layer and extraction of this layer with ether afforded a yellow oil. IR spectroscopy of this oil revealed that a mixture of 2-deuterio-*N,N*-dimethylaniline (see above) and *N,N*-dimethylaniline (absorption at  $692\text{ cm}^{-1}$ ) was isolated.

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

The synthesis of complex (V) was carried out in essentially the same way as has been described for the CuBr complex (II).

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

*Via RLi (III) with CuCl.* A solution of 2-(dimethylamino)phenyllithium

\*General directions dealing with solvents, apparatus and reaction conditions are presented in Chapter IX.

\*\*See synthesis of compound (XIII) Chapter VI.



(III) (18.5 mmol) in ether was added at  $-20^{\circ}$  to a suspension of CuCl (37 mmol) in ether (50 ml). The resulting black-coloured mixture was stirred for 2 h at  $-20^{\circ}$  and for 6 h at room temperature. The precipitate was filtered off, washed with ether (3 x 20 ml; removal of LiBr) and dried in vacuo affording a red-brown solid. This solid was extracted with benzene (2 x 100 ml). Concentration of the benzene filtrate afforded an orange solid which was washed with pentane (2 x 15 ml) and dried in vacuo (yield 30%). Elemental analysis pointed to the isolation of a mixture of the CuBr and the CuCl complex (molar ratio 8.4/1  $2\text{RCu}\cdot\text{CuBr}/2\text{RCu}\cdot\text{CuCl}$ ), see Table 1. Decomposition starts at  $191-193^{\circ}$ ; total dec. at  $204^{\circ}$ .

*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) afforded in 80% yield (VI) as an orange crystalline solid. Reaction time 14 days. Elemental analysis see Table 1. NMR data see Table 2.

#### *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 x 60 ml). The benzene extract was concentrated to about 10 ml; addition of pentane (10 ml) afforded light-brown (VII) in 70% yield. Elemental analysis see Table 1. NMR data see Table 3.

#### *Exchange reaction of $2\text{RCu}\cdot\text{CuCl}$ (VI) with LiI*

Solid lithium iodide [14] (0.815 mmol) was added to a suspension of  $2\text{RCu}\cdot\text{CuCl}$  (VI) (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 affording orange, crystalline  $2\text{RCu}\cdot\text{CuI}$  (V) in quantitative yield. (Found: C, 35.2; H, 3.7; N, 5.1; I, 22.1.  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Cu}_3\text{I}$  calcd.: C, 34.45; H, 3.61; N, 5.02; I, 22.75%.)

#### REFERENCES

- 1 E.g., G.COSTA, A.CAMUS, L.GATTI and N.MARSICH, *J.Organometal.Chem.*, 5 (1966) 568.
- 2 A.CAMUS and N.MARSICH, *J.Organometal.Chem.*, 14 (1968) 441.
- 3 G.BÄHR and P.BURBA, see ref. 12, Chapter I.
- 4 J.F.NORMANT, *Synthesis*, (1972) 63.
- 5 A.CAIRNCROSS, H.OMURA and W.A.SHEPPARD, *J.Amer.Chem.Soc.*, 93(1971)248.
- 6 J.M.GUSS, R.MASON, K.M.THOMAS, G.VAN KOTEN and J.G.NOLTES, *J.Organometal.Chem.*, 40 (1972) C 79.
- 7 M.R.CHURCHILL, S.A.BEZMAN, J.A.OSBORN and J.WORMALD, *Inorg.Chem.*, 11 (1972) 1818.
- 8 J.A.J.JARVIS, B.T.KILBOURN and R.PEARCE, *J.Chem.Soc., Chem.Comm.*, (1973) 475.
- 9 L.E.ORGEL, *An Introduction to Transition Metal Chemistry*, 2nd. ed., Methuen, London, 1966, p. 69.
- 10 C.K.JORGENSEN and J.POURADIER, *J.Chim.Phys.*, 67 (1970) 124.
- 11 G.A.BOWMAKER, L.D.BROCKLISS and R.WHITING, *Aust.J.Chem.*, 26 (1973) 29.
- 12 B.AMER and H.SCHMIDBAUER, *Angew.Chem.*, 82(1970)120, and ref. cited therein.
- 13 A.J.LEUSINK, G.VAN KOTEN and J.G.NOLTES, *J.Organometal.Chem.*, 56(1973)379.
- 14 M.D.TAYLOR and L.R.GRANT, *J.Amer.Chem.Soc.*, 77 (1955) 1507.

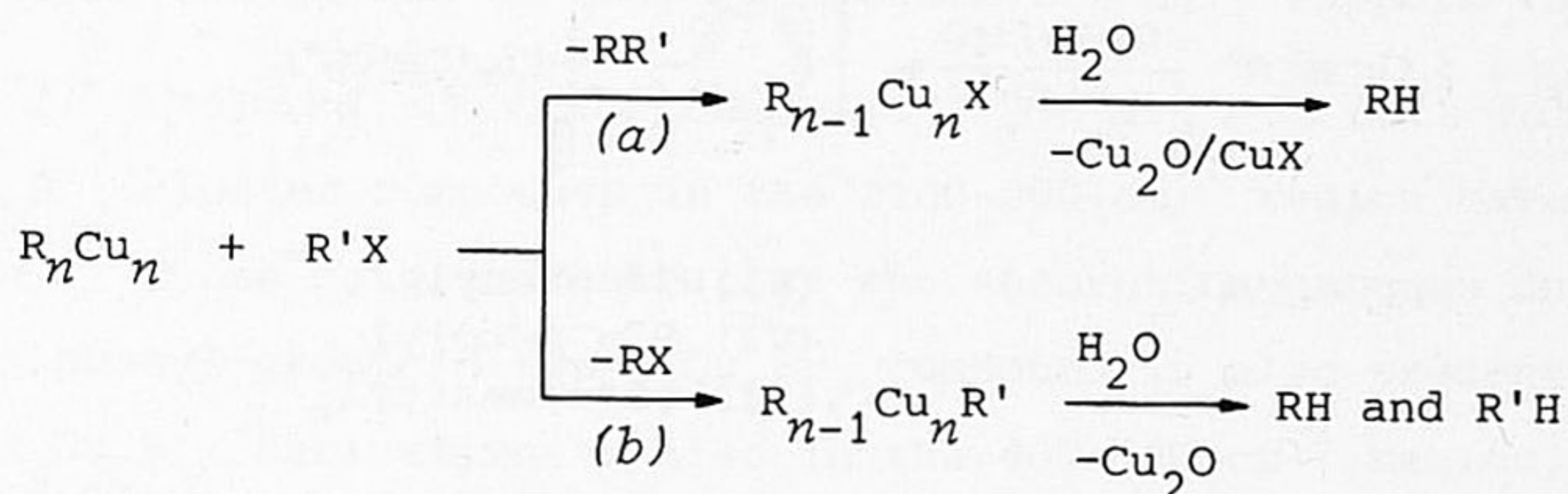


## CHAPTER VIII

### SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOME ORGANO-COPPER COMPOUNDS OF THE TYPE $R_n R'_m Cu_{n+m}$

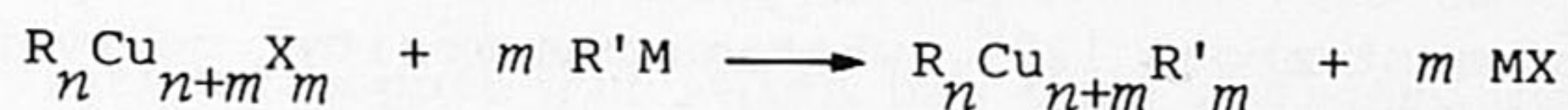
#### INTRODUCTION

In Chapter VII the isolation and characterization of organocopper cluster compounds  $R_n Cu_m X_2$  containing both organic and halogeno ligands have been discussed. So far, no organocopper compounds containing unequal *organic* ligands (i.e.  $R_n R'_m Cu_{n+m}$ ) had been isolated. Such species are of interest because they may serve as model compounds for the intermediates which may occur in cross-coupling reactions of organocopper compounds with organic halides ( $R_n Cu_n + R'_X$ ). In addition to  $RR'$  (a) such reactions afford  $R'H$  formed as a consequence of metal-halogen exchange (b):



Evidence for the existence of mixed organocopper compounds  $R_n R'_m Cu_{n+m}$  has been presented in Chapter III. The mass spectrum of a 1/1 mixture of  $R_4 Cu_4$  and  $R'_4 Cu_4$  ( $R = 2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4$ ;  $R' = 5\text{-Me-2-Me}_2\text{NCH}_2\text{C}_6\text{H}_3$ ) showed the presence of the mixed species  $R_3 R'_1 Cu_4$ ,  $R_2 R'_2 Cu_4$  and  $RR'_3 Cu_4$ . This ligand exchange was supposed to proceed via a mechanism involving formation of an octameric intermediate followed by dissociation into two tetramers.

In principle ligand-substitution reactions of the type:



should present a second route towards mixed organocopper cluster compounds. That ligand-substitution reactions can indeed occur with retention of the metal cluster  $Cu_{n+m}$  is illustrated by the quantitative formation of  $R_4 Cu_6 I_2$  ( $R = 2\text{-Me}_2\text{NC}_6\text{H}_4$ ) from the 1/2 reaction of  $R_4 Cu_6 Cl_2$  with LiI (see Chapter VII):



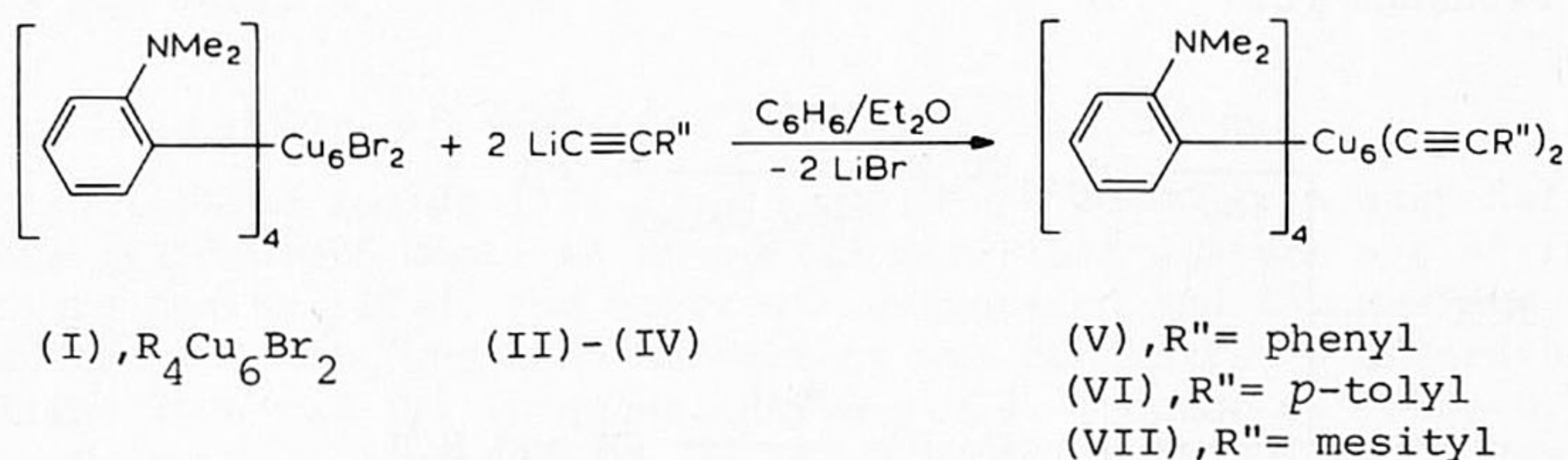


The present Chapter deals with the synthesis of some mixed organocopper compounds  $R_4R'_2Cu_6$  by ligand-substitution reactions using appropriate organolithium reagents.

## RESULTS AND DISCUSSION

### *Synthesis and characterization of $R_4R'_2Cu_6$ compounds*

*Reaction of  $R_4Cu_6Br_2$  with phenyl-, *p*-tolyl- and mesitylethynyllithium.* Reaction of  $R_4Cu_6Br_2$  (I) with phenylethynyllithium (II) in a benzene/ether mixture afforded a clear, dark-coloured solution. From this solution, in addition to the expected amount of lithium bromide, a dark-green solid was isolated in 92% yield. Elemental analysis of the green solid pointed to the composition  $(PhC\equiv C)(2-Me_2NC_6H_4)_2Cu_3$  (V).



This type of reaction has been extended to the *p*-tolyl- and mesitylethynyl derivatives. Also for these compounds [brown (VI) and bright-yellow (VII)] elemental analysis confirmed the presence of 2-(dimethylamino)phenyl (R) and arylethynyl (R') groups in a 2/1 ratio (see Table 1).

A striking difference between the physical properties of these organocopper compounds was found: (i), whereas the phenyl- and *p*-tolylethynyl derivatives are very soluble in aromatic solvents (benzene, toluene) and moderately soluble in ethers, the mesityl derivative appeared to be very insoluble in these solvents; it only dissolves in  $\sigma$ -base type solvents like pyridine; (ii), the two compounds (V) and (VI) decompose at about  $120^\circ$ , whereas the mesityl derivative (VII) decomposes at  $186\text{--}193^\circ$ .

Cryometric molecular weight determinations showed that (V) and (VI) exist in benzene as dimeric units which thus have the stoichiometry  $R_4R'_2Cu_6$ . This result points out that a ligand-substitution reaction has taken place with retention of the  $R_4Cu_6^I$  cluster structure. The results of an IR and NMR spectro-



TABLE 1

SOME DATA REGARDING MIXED ORGANOCOPPER COMPOUNDS  $R_4R'_2Cu_6$  (V) - (VII)

| $R'^a$                    | Colour            | Analysis found (calcd.) (%) |               |               |                              | M.p.<br>(°C)   |
|---------------------------|-------------------|-----------------------------|---------------|---------------|------------------------------|----------------|
|                           |                   | C                           | H             | N             | Cu                           |                |
| (V)<br>PhC≡C-             | Dark-green        | 54.2<br>(54.18)             | 4.9<br>(4.74) | 5.1<br>(5.27) | 35.2<br>(35.82)              | 127-129 (dec.) |
| (VI)<br><i>p</i> -TolC≡C- | Brown             | 54.7<br>(54.98)             | 5.1<br>(4.98) | 5.0<br>(5.13) | 34.1<br>(34.90)              | 115-120 (dec.) |
| (VII)<br>MesitylC≡C-      | Bright-<br>yellow | 56.2<br>(56.48)             | 5.5<br>(5.44) | 4.9<br>(4.88) | 32.5 <sup>b</sup><br>(33.20) | 186-193 (dec.) |

<sup>a</sup> $R = 2\text{-Me}_2\text{NC}_6\text{H}_4$ . <sup>b</sup>Using a more efficient destruction method: Cu, 32.9 and 33.0% was found.

scopic investigation of these compounds strongly support this view.

*IR spectra of  $R_4Cu_6Br_2$  and  $R_4Cu_6R'_2$ .* IR data for the  $R_4Cu_6Br_2$  and  $R_4Cu_6R'_2$  cluster compounds in the 2100-200  $\text{cm}^{-1}$  region have been compiled in Table 2. These data indicate that the absorption pattern due to the 2-(dimethylamino)phenyl group in the  $R_4Cu_6Br_2$  compound is also present in the spectra of the  $R_4Cu_6R'_2$  derivatives\*. Also in the 400-550  $\text{cm}^{-1}$  region, where vibrations involving ligand-copper bond participation occur, only minor changes are observed going from  $R_4Cu_6Br_2$  to  $R_4Cu_6R'_2$ . In contrast, the IR spectrum of 2-(dimethylamino)phenylcopper (VIII), which has a polymeric structure, is totally different in this region with absorption bands at 555 w, 536 w, 495 s and 462 m  $\text{cm}^{-1}$  (no bands are present in the region from 718 vs to 555 w  $\text{cm}^{-1}$ ). This supports the view that  $R_4Cu_6Br_2$  and the  $R_4Cu_6R'_2$  compounds have the  $R_4Cu_6$ -skeleton as a common structural feature.

The absorption band at 530  $\text{cm}^{-1}$  in the IR spectrum of  $R_4Cu_6(C\equiv CPh)_2$  (V) corresponds with the strong absorption at 525  $\text{cm}^{-1}$  in the spectrum of polymeric phenylethynylcopper [1] which has been assigned to  $\nu_{22} \Phi(C-C)$ . Furthermore, the strong absorption at 685  $\text{cm}^{-1}$  (diagnostic for mono-substituted phenyl) in the spectrum of phenylethynylcopper is also found in the spectrum of the hexa-

\*The absorption patterns arising from the ethynyl groups are weak in the 1880-800  $\text{cm}^{-1}$  region, cf. IR spectrum of PhC≡CCu [1].



TABLE 2

 IR SPECTRAL DATA<sup>a</sup> OF R<sub>4</sub>Cu<sub>6</sub>R'<sub>2</sub> (V) - (VII)<sup>b</sup>, R<sub>4</sub>Cu<sub>6</sub>Br<sub>2</sub> (I) AND  
 (RCu)<sub>n</sub> (VIII)

| PhC≡C—<br>(V)       | p-TolC≡C—<br>(VI)   | MesC≡C—<br>(VII)    | R <sub>4</sub> Cu <sub>6</sub> Br <sub>2</sub><br>(I) | (RCu) <sub>n</sub><br>(VIII) |
|---------------------|---------------------|---------------------|---|------------------------------|
| 2051 (sh)           |                     |                     |   |                              |
| 2041 m <sup>c</sup> | 2046 m <sup>c</sup> | 2036 m <sup>c</sup> |   |                              |
| 2037 (sh)           | 2031 (sh)           | 2031 m              |   |                              |
| 1592 m              |                     | 1575 w              |   |                              |
| 1567 w              |                     | 1563 m              | 1563 w  | 1570 s                       |
| 1555 m              | 1550 w              | 1558 w              |   | 1558 (sh)                    |
|                     | 1504 m              |                     | 1538 vw   | 1538 m                       |
|                     |                     |                     |   | 1342 s                       |
|                     |                     |                     |   | 1299 (sh)                    |
| 1256 m              | 1261 m              | 1263 m              | 1279 vw   |                              |
| 1247 m              | 1248 m              | 1253 m              | 1250 m  | 1250 (sh)                    |
|                     |                     |                     | 1247 m (sh)   | 1242 m                       |
|                     | 1217 vw             | 1217 m              |   | 1225 m                       |
| 1202 m              | 1202 m              | 1202 vw             |   | 1209 m                       |
| 1174 w              | 1176 w              | 1182 w              | 1174 vw   | 1163 (sh)                    |
| 1156 m              | 1163 m              | 1163 m              | 1155 s  | 1160 m                       |
| 1136 q              | 1139 m              | 1139 m              | 1150 s (sh)   |                              |
|                     | 1109 vw             | 1109 w              | 1134 m  | 1114 w                       |
|                     | 1101 vw             | 1101 w              |   |                              |
| 1098 w              | 1096 m              | 1098 w              | 1096 (sh)   | 1093 vw                      |
| 1089 m              |                     |                     | 1090 m  |                              |
| 1066 w              |                     |                     |   | 1062 m                       |
| 1042 m              | 1042 m              | 1048 m              | 1040 m  | 1044 m                       |
| 1020 m              | 1022 m              | 1022 m              | 1016 s  |                              |
| 1012 (sh)           | 1016 (sh)           |                     |   |                              |
| 1000 vw             |                     |                     |   | 1000 m                       |
|                     |                     | 948 (sh)            |   | 943 m                        |
| 921 s               | 924 s               | 928 s               | 919 s   | 933 w                        |
| 909 (sh)            |                     |                     |   |                              |
|                     | 865 vw              | 850 m <sup>d</sup>  | 872 vw  |                              |
| 837 vw              | 833 vw <sup>d</sup> |                     |   | 837 w                        |
|                     | 818 vs <sup>d</sup> |                     |   |                              |
| 770 vs              | 774 vs              | 777 vs              | 778 vs  |                              |
|                     | 769 s (sh)          | 772 s (sh)          |   |                              |
| 759 vs <sup>d</sup> |                     |                     |   | 760 (sh)                     |
| 753 vs              | 753 w               | 758 m <sup>d</sup>  | 748 m   | 752 vs                       |
| 728 (sh)            | 725 (sh)            | 732 m <sup>d</sup>  | 729 vs  | 728 (sh)                     |
| 719 vs              | 721 s               | 723 vs              | 725 (sh)  |                              |
|                     |                     | 719 vs              | 718 (sh)  | 718 vs                       |
|                     |                     | 716 (sh)            |   |                              |
| 692 vs <sup>d</sup> |                     |                     |   |                              |
|                     | 677 w               | 677 vw              |   |                              |
|                     | 646 vw              |                     |   |                              |
| 632 vw              | 635 w               | 636 vw              | 638 w   |                              |
|                     |                     | 600 vw              |   |                              |



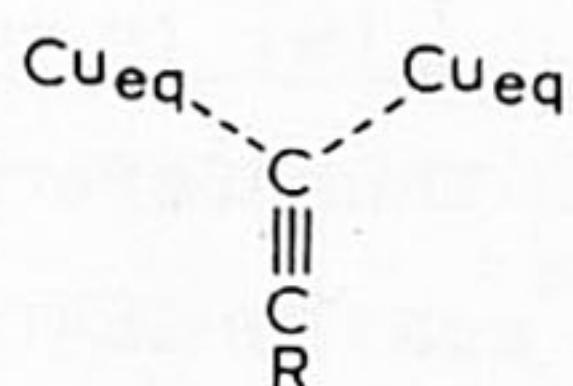
TABLE 2 (Continued)

| PhC≡C-<br>(V)                            | <i>p</i> -TolC≡C-<br>(VI)                | MeSC≡C-<br>(VII)                         | R <sub>4</sub> Cu <sub>6</sub> Br <sub>2</sub><br>(I) | (RCu) <sub>n</sub><br>(VIII) |
|--|--|--|---|------------------------------|
| 585 m                                    | 584 m                                    | 588 m <sup>d</sup><br>575 m <sup>d</sup> | 588 m   |                              |
| 562 m <sup>d</sup><br>530 m <sup>d</sup> | 559 m <sup>d</sup><br>527 m <sup>d</sup> | 565 m                                    | 562 m   | 555 w<br>536 w               |
| 505 vw<br>447 m                          | 508 vw<br>449 m<br>408 vw                | 510 m<br>448 m                           | 510 vw<br>452 m                                       | 495 s<br>462 m               |
| 380 w<br>348 vw                          | 382 w<br>349 vw                          | 382 w<br>350 w                           | 382 m<br>345 vw<br>322 m                              |                              |
|  | 311 vw<br>302 (sh)                       | 310 m                                    | 310 w<br>305 w  |                              |
| 270 w                                    | 275 w                                    | 270 m                                    |   |                              |
|  |  |  | 240 m   |                              |
| 215 m                                    | 215 m                                    | 210 m                                    |   |                              |

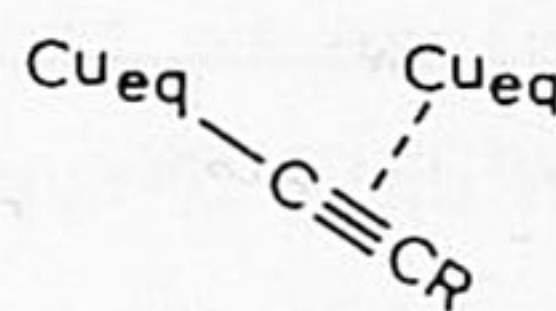
<sup>a</sup>Spectra (nujol mulls) were recorded on a Grubb-Parsons Spectromaster (2600-650 cm<sup>-1</sup>; accuracy ± 5 cm<sup>-1</sup>) and on a Perkin-Elmer 577 Grating Infrared Spectrophotometer (650-200 cm<sup>-1</sup>; accuracy ± 3 cm<sup>-1</sup>). <sup>b</sup>R = 2-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; R' = PhC≡C-, *p*-TolC≡C- or MeSC≡C-. <sup>c</sup> $\nu(\text{C}\equiv\text{C})$ . <sup>d</sup>Bands arising from the substitution pattern of the aryl group in R'.

nuclear compound (V) (at 692 vs cm<sup>-1</sup>).

A question which remains to be answered is the way in which the ethynyl groups are bound to the R<sub>4</sub>Cu<sub>6</sub> skeleton. Two possibilities can be envisaged, viz.:



(IXa), two electron-three centre bond (2e-3c)



(IXb), one  $\sigma$ - and one  $\pi$ -ethynyl-copper bond

Electron-deficient bonded (2e-3c) ethynyl groups (IXa) have been postulated by Jeffery, Mole and Saunders in dimeric PhC≡CAIR<sub>2</sub> (R = Me, Ph) [2]. Structure (IXb), in which the ethynyl groups have one  $\sigma$ - and one  $\pi$ -bonding interaction with the Cu<sub>6</sub>-skeleton, has a precedent in the structure of Cu<sub>4</sub>Ir<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(C≡CPh)<sub>8</sub> [3]. A border-line case is found in the structure of polymeric phenylethynyl-copper where according to Coates [4] each phenylethynyl group seems to be  $\sigma$ -bonded to one copper atom, symmetrically  $\pi$ -bonded to a second one and unsymmetrically  $\pi$ -bonded to a third copper atom (see Fig. 1a). However, the bonding



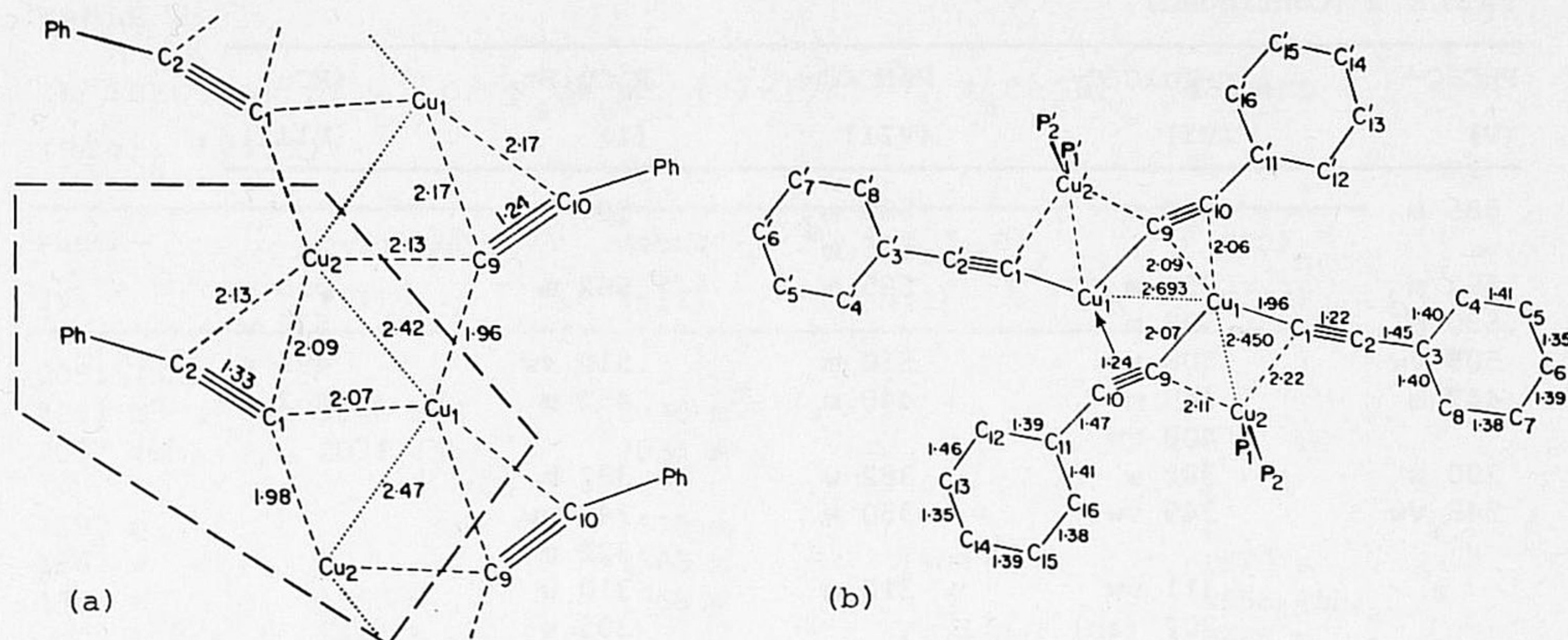


Fig. 1. (a), structure of phenylethynylcopper  $(\text{CuC}\equiv\text{CPh})_2$ ; (b), structure of the tetrameric complex  $(\text{PhC}\equiv\text{CCuPMe}_3)_4$  (according to ref. 4).

in phenylethynylcopper may be explained as well in terms of one  $2e-3c$  bond with  $\text{Cu}_1$  and  $\text{Cu}_2$  and one  $\pi$ -interaction with  $\text{Cu}_3$  (see encircled part in Fig. 1a). The structure in the solid of the 1/1 complex of phenylethynylcopper with  $\text{PMe}_3$  [5], which is shown in Fig. 1b, can be interpreted in terms of (a) phenylethynyl groups which are only  $2e-3c$ -bonded and of (b) phenylethynyl groups which are  $2e-3c$ - and  $\pi$ -bonded.

$\nu(\text{C}\equiv\text{C})$ -frequency data for these compounds have been compiled in Table 3. From this Table it appears that the values for  $\nu(\text{C}\equiv\text{C})$  of the  $\text{R}_4\text{Cu}_6\text{R}'_2$  compounds (V)-(VII) are rather close to those found for the  $\text{Cu}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_n$  [6] ( $n = 2$  or 3) complexes, in which only  $\sigma$ -type interactions will be present. Therefore it seems plausible to conclude that the ethynyl groups in  $\text{R}_4\text{R}'_2\text{Cu}_6$  are  $2e-3c$ -type bonded (see IXa) to the  $\text{R}_4\text{Cu}_6$ -skeleton and that  $\pi$ -interaction (see IXb) with copper is not important. The fact that the IR spectra of benzene- $d_6$  solutions of (V) and (VI) are equal to those of the nujol mulls of these compounds points to the same type of bonding in solution (see also NMR).

*NMR spectroscopy.* As shown in Table 4, the chemical shift values for the (dimethylamino)phenyl protons in the NMR spectra of the  $\text{R}_4\text{Cu}_6\text{R}'_2$  compounds (V) and (VI) and of  $\text{R}_4\text{Cu}_6\text{Br}_2$  (I) are nearly identical, as would be expected if these two types of compounds have the  $\text{R}_4\text{Cu}_6$ -skeleton in common.

The methyl protons of the  $\text{N}(\text{CH}_3)_2$ -group in (V) and (VI) appear as two singlets at  $-20^\circ$ , indicating the occurrence of Cu-N-coordination. These two singlets coalesce at room temperature into one singlet (see Table 4). The higher



TABLE 3

 $\nu(\text{C}\equiv\text{C})$  DATA FOR SEVERAL ETHYNYL-METAL COMPOUNDS

| Compound  | Type of Cu...C $\equiv$ C interaction <sup>a</sup> | $\nu(\text{C}\equiv\text{C})$ (cm <sup>-1</sup> ) | Ref.         |
|---|--|---|--------------|
| (CuC $\equiv$ CPh) <sub>n</sub>   | 2e-3c + $\pi$                                      | 1933  | 4            |
| Cu <sub>4</sub> (C $\equiv$ CPh) <sub>4</sub> (PMe <sub>3</sub> ) <sub>4</sub>  | 2e-3c and<br>2e-3c + $\pi$                         | 2045 and 2019 <sup>b</sup>                        | 5            |
| Cu(C $\equiv$ CPh)(PMe <sub>3</sub> ) <sub>n</sub><br>n = 2   | 2e-3c or<br>2e-2c                                  | 2035 and 2048 <sup>b</sup>                        | 6            |
| n = 3   | 2e-3c or<br>2e-2c                                  | 2034 and 2051 <sup>b</sup>                        | 6            |
| (V)<br>Cu <sub>6</sub> (C $\equiv$ CPh) <sub>2</sub> (2-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>4</sub>     |  | 2037 (sh), 2041 m<br>and 2051 (sh) <sup>d</sup>   | <sup>c</sup> |
| (VI)<br>Cu <sub>6</sub> (C $\equiv$ CTol-p) <sub>2</sub> (2-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>4</sub> |  | 2046 m and 2031 (sh) <sup>d</sup>                 | <sup>c</sup> |
| (VII)<br>Cu <sub>6</sub> (C $\equiv$ CMe) <sub>2</sub> (2-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>4</sub>   |  | 2036 m and 2031 m <sup>d</sup>                    | <sup>c</sup> |

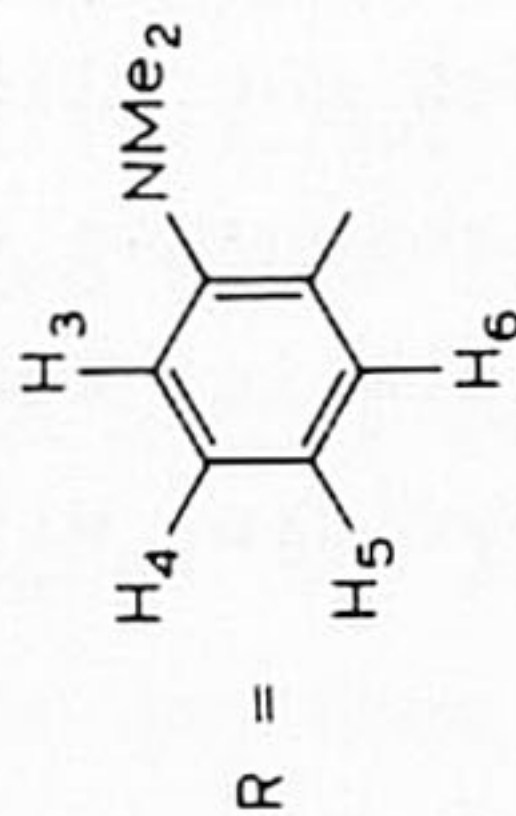
<sup>a</sup>2e-3c, two electron-three centre bond; 2e-2c, two electron-two centre bond.<sup>b</sup>In KBr disc. <sup>c</sup>This thesis. <sup>d</sup>In nujol.

coalescence temperature for the NMe-signals in the spectrum of R<sub>4</sub>Cu<sub>6</sub>Br<sub>2</sub> (I) points to a weaker Cu-N-coordination in the R<sub>4</sub>Cu<sub>6</sub>R'<sub>2</sub> compounds than in R<sub>4</sub>Cu<sub>6</sub>Br<sub>2</sub>. This reflects the different electron-attracting properties of the ethynyl groups R' as compared with Br.

The NMR spectrum of the mesitylethynyl derivative (VII) has been recorded in pyridine-d<sub>5</sub>. The low solubility of (VII) in this solvent does not allow a complete assignment of its resonance pattern. The NCH<sub>3</sub> proton resonance appears as a singlet which most probably is due to a shift of the equilibrium N(coord)  $\rightleftharpoons$  N(free) to the right as a result of coordination of the pyridine with copper.



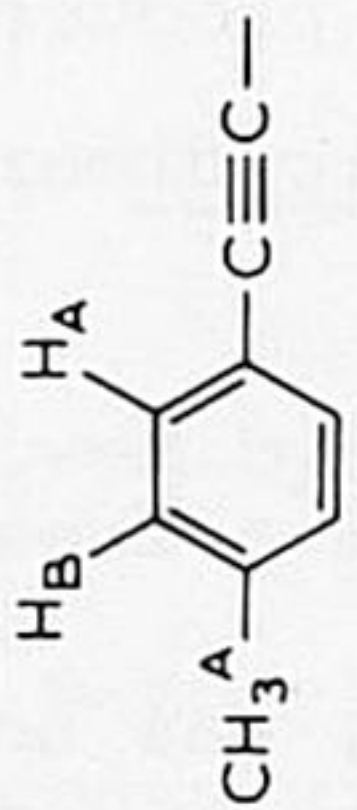
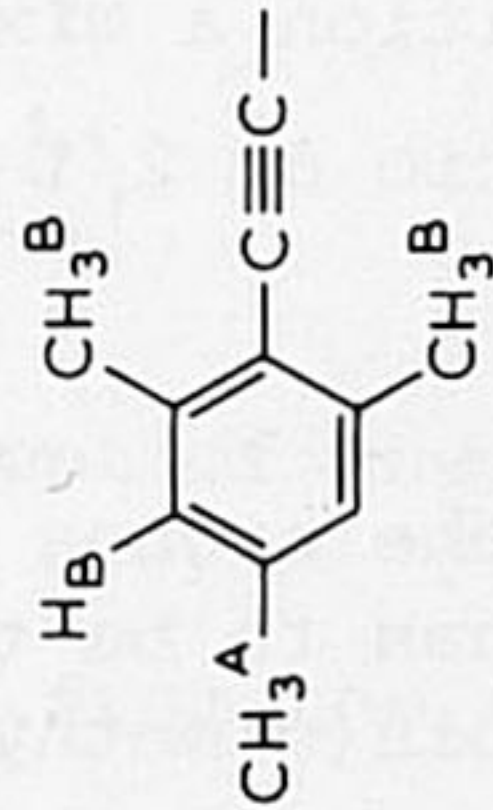
TABLE 4

NMR DATA OF THE  $R_4R'_2Cu_6$  COMPOUNDS (V) - (VII) AND OF  $R_4Cu_6Br_2$  (I)

| R'      | Temp.<br>(°C) | Solvent                                       | $\delta$ (ppm) <sup>a</sup>           |  |  |                                       |  |  |
|---------|---------------|---|---------------------------------------|--|--|---------------------------------------|--|--|
|         |               |   | H <sub>6</sub>                        | H <sub>3</sub> , H <sub>B</sub> <sup>b</sup> | H <sub>4,5</sub> , H <sub>C</sub> <sup>b</sup> | H <sub>A</sub>                        | NCH <sub>3</sub>   | CH <sub>3</sub> <sup>A</sup><br>CH <sub>3</sub> <sup>B</sup> |
| <br>(V) | Ambient       | C <sub>6</sub> D <sub>6</sub>                 | 8.60<br>(m, 4H)                       | 6.68<br>(m, 8H)                              | 7.1<br>(m, 10H)                                | 7.66<br>(d of d,<br>4H)               | 1.6-3.3<br>(s, br, 24H)                                  |  |
|         | 80            | C <sub>6</sub> D <sub>6</sub>                 | 8.64<br>(d of d <sup>c</sup> ,<br>4H) | 6.67<br>(m, 8H)                              | 7.05<br>(m, 10H)                               | 7.65<br>(d of d <sup>d</sup> ,<br>4H) | 2.47<br>(s, 24H)   |  |
|         | -20           | C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub> | 8.54<br>(m, 4H)                       | 6.58<br>(m, 8H)                              | 7.1<br>(m, 10H)                                | 7.62<br>(d of d,<br>4H)               | 2.98 <sup>e</sup><br>(s, 12H)<br>and<br>1.73<br>(s, 12H) |  |



TABLE 4 (Continued)

| R'   | Temp.<br>(°C) | Solvent                                       | $\delta$ (ppm) <sup>a</sup> |  |  |                              |                                      |                              |                              |
|--|---------------|---|-----------------------------|--|--|------------------------------|--------------------------------------|------------------------------|------------------------------|
|  |               |   | H <sub>6</sub>              | H <sub>3</sub> , H <sub>B</sub> <sup>b</sup> | H <sub>4,5</sub> , H <sub>C</sub> <sup>b</sup> | H <sub>A</sub>               | NCH <sub>3</sub>                     | CH <sub>3</sub> <sup>A</sup> | CH <sub>3</sub> <sup>B</sup> |
| <br>(VI)    | Ambient       | C <sub>6</sub> D <sub>6</sub>                 | 8.60<br>(m, 4H)             | 6.66<br>(m, 8H)                              | 7.0<br>(m, 8H)                                 | 7.60<br>(d, 4H) <sup>f</sup> | 1.5-3.4 <sup>g</sup><br>(s, br, 24H) | 2.09<br>(s, 6H)              |                              |
|  | 80            |   |                             |  |  |                              | 2.46<br>(s, 24H)                     | 2.12<br>(s, 6H)              |                              |
|  | -10           | C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub> |                             |  |  |                              | 3.02 <sup>e</sup><br>(s, 12H)        |                              |                              |
| <br>(VII) | Ambient       | C <sub>5</sub> D <sub>5</sub> N               | 8.6<br>(br, 4H)             | <i>h</i>                                     | <i>h</i>                                       | <i>h</i>                     | 2.98<br>(s, 24H)                     | 2.16<br>(s, 6H)              | 2.53<br>(s, 12H)             |
|  | 80            |   |                             | 8.58<br>(m, 4H)                              | 7.4-6.5<br>(m, 16H)                            |                              |                                      |                              |                              |
| R <sub>4</sub> Cu <sub>6</sub> Br <sub>2</sub>   | Ambient       | C <sub>6</sub> D <sub>5</sub> CD <sub>3</sub> | 8.48<br>(m, 4H)             | 6.64<br>(m, 4H)                              |  |                              | 2.94<br>(s, br, 12H)                 |                              |                              |
|  | 90            |   |                             |  |  |                              | and 1.84<br>(s, br, 12H)             |                              |                              |
|  |               |   |                             |  |  |                              | 2.42<br>(s, sharp, 24H)              |                              |                              |

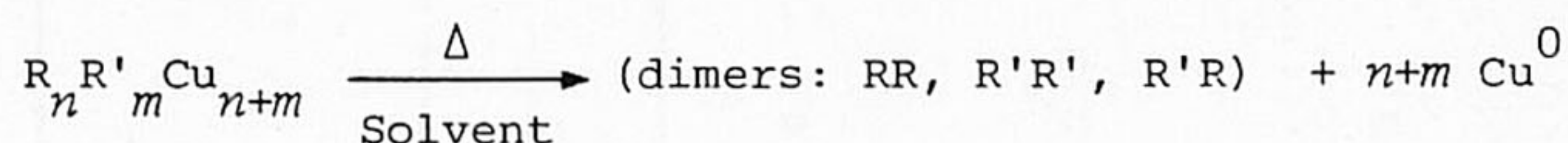
<sup>a</sup>TMS internal. <sup>b</sup>H<sub>B</sub> and H<sub>C</sub> tentatively assigned. <sup>c</sup>J<sub>56</sub> 5.5 and J<sub>46</sub> 3.5 Hz. <sup>d</sup>J<sub>AB</sub> 8 and J<sub>AC</sub> 2 Hz. <sup>e</sup>Two singlets collapse at about 20 ° (see spectrum at ambient temperature). <sup>f</sup>J<sub>AB</sub> 8 Hz. <sup>g</sup>Very small broadened singlets at 2.98 and 1.84 ppm are present in this region. <sup>h</sup>Due to the low solubility of the compound these resonances are hardly observable.



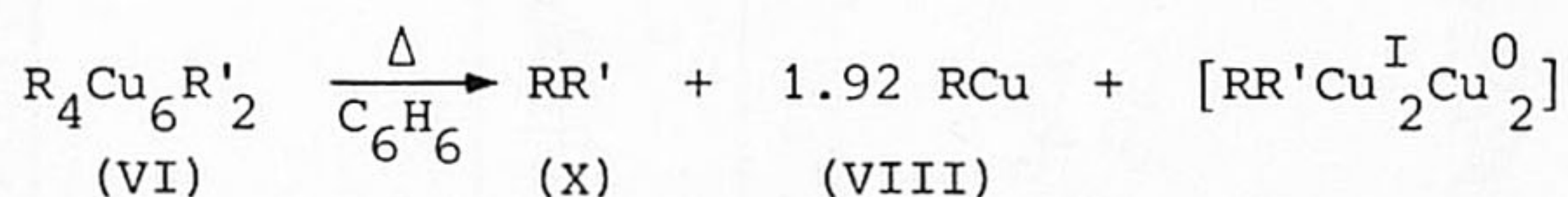
### Thermal degradation of $R_4Cu_6R'_2$ compounds

In connection with our interest in the course of cross-coupling reactions between organic halides and organocopper compounds (cf. also the Ullmann reactions and the copper-catalyzed decarboxylative coupling reactions [7-9]) a start has been made with a study of the thermal degradation of mixed organocopper cluster compounds  $R_4Cu_6R'_2$ .

In principle, symmetric (RR and R'R') as well as asymmetric (RR') dimer formation may be expected to occur upon thermal degradation of a mixed organocopper compound  $R_nR'_mCu_{n+m}$ \*.



Surprisingly, heating of a benzene/ether solution of  $(2-Me_2NC_6H_4)_4^-(p-MeC_6H_4C\equiv C)_2Cu_6$  (VI) for 7 h afforded as the major product the asymmetric dimer 2-(*p*-tolylethynyl)-*N,N*-dimethylaniline (X) (isolated and characterized; see Experimental), together with only a very small amount of the arene, *N,N*-dimethylaniline (according to NMR spectroscopy)\*\*. The precipitate which had formed during the reaction consisted of 2-(dimethylamino)phenylcopper (VIII) (according to IR spectroscopy). Furthermore, a benzene-soluble dark-coloured product was isolated (Cu-content: 44%) which appeared to be highly sensitive towards oxygen and water. The NMR spectrum of this product showed broad resonances both in the aromatic and aliphatic region. Upon heating to 80° again the asymmetric dimer was formed in a very slow reaction. The overall reaction course can be represented by the following equation:



These preliminary results show that:

- (i), the thermal decomposition of the mixed organocopper cluster compound (VI) does not proceed via a free-radical mechanism (cf. ref. 10);
- (ii), upon thermal decomposition a mixed  $Cu^I Cu^0$ -species is produced;
- (iii), in spite of a R/R' ratio of 2/1 exclusively asymmetric dimer formation takes place.

\*Moreover, the formation of the arenes RH or R'H, either via a free radical path or via direct H-abstraction has to be taken into account.

\*\*The symmetric dimer, 2,2'-bis(dimethylamino)biphenyl (RR), was not detected [ $\delta(NCH_3)$  in  $C_6D_6$ , 2.40 ppm].



Whitesides et al. [10], when studying the mechanism of thermal decomposition reactions of alkyl- and alkenylcopper compounds, observed that such reactions generally do not proceed via a free radical mechanism. In contrast Hashimoto et al. [11] have proposed a free radical mechanism for the thermal decomposition of in situ prepared substituted phenylcopper\* compounds.

Our results concerning the thermal decomposition of  $R_4Cu_4$  [12] and  $R_2Cu_4^I$  compounds (see Chapter V) indicate that these reactions do not proceed via free radicals but involve a concerted homolytic Cu-C-bond cleavage/C-C-bond formation. In polynuclear arylcopper compounds dimer formation will proceed via a lengthening of two electron-deficient  $Cu_2$ -C-bonds and a synchronous formation of a new C-C-bond, with the faces of the central copper cluster acting as a template.

On the basis of this view-point the formation of the asymmetric dimer and the absence of symmetric dimers follows from the proposed structure for the  $R_4Cu_6R'_2$  compounds. Four triangular faces are present in this hexanuclear structure, each containing one R and one R' as bridging groups, whereas  $Cu_3R_2$  or  $Cu_3R'_2$  faces are absent (see Fig. 2).

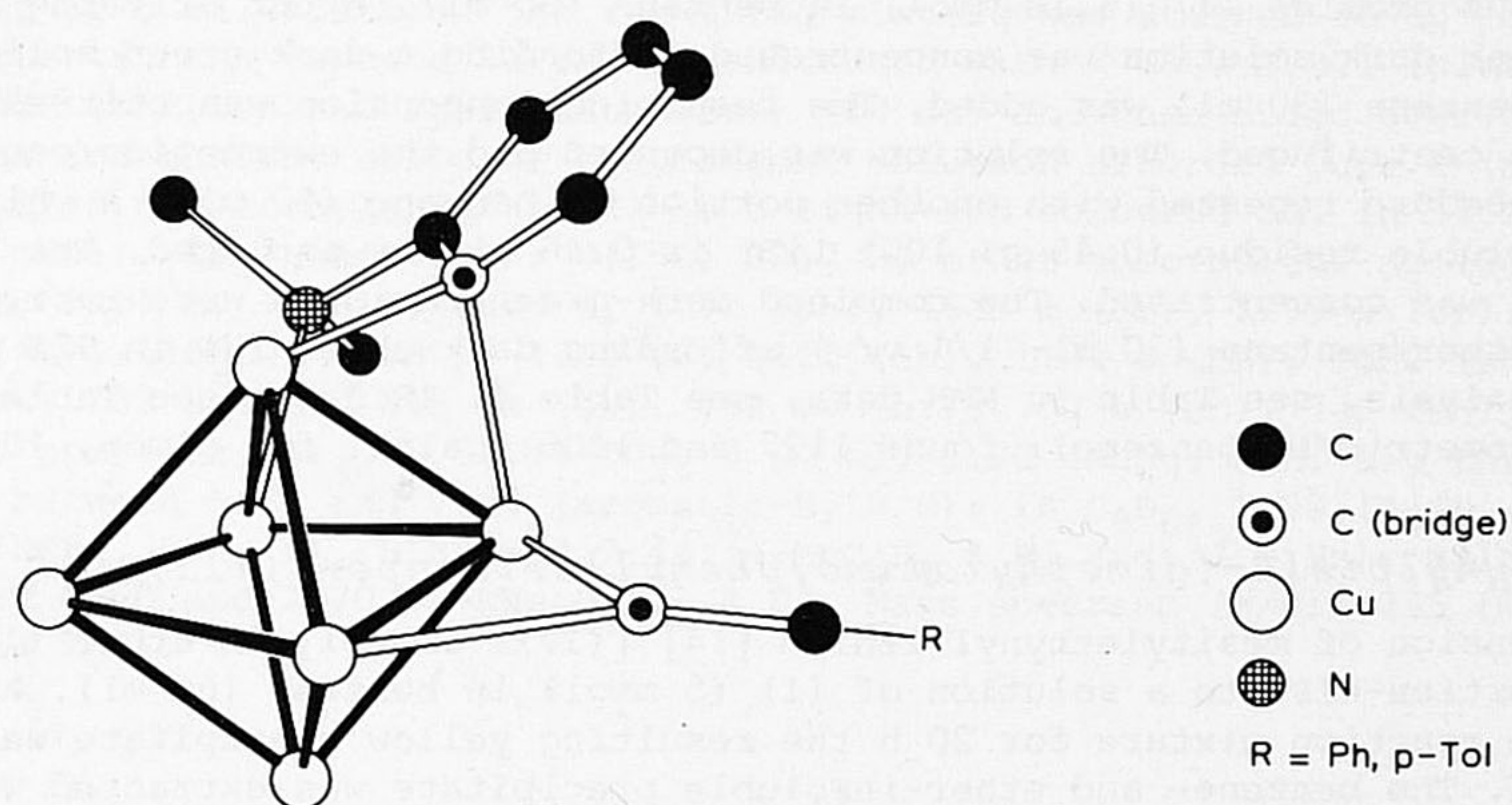
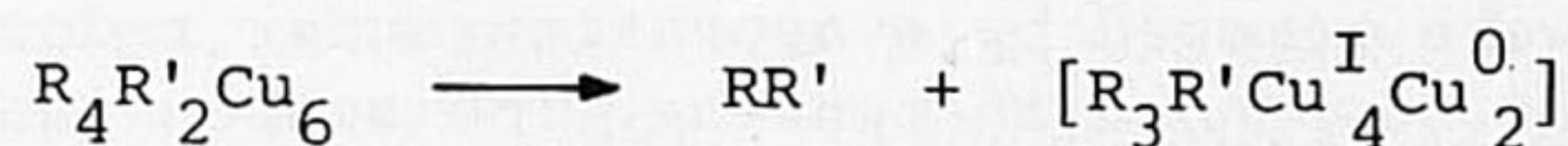


Fig. 2. Part of the proposed structure for  $(2-Me_2NC_6H_4)_4(RC\equiv C)_2Cu_6$ .

Consequently, the first step in the decomposition reaction could be:

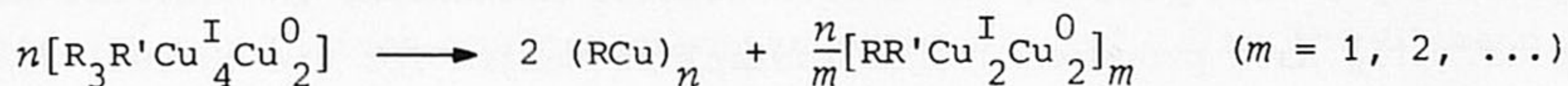


This is followed by a cluster-rearrangement of the obviously unstable inter-

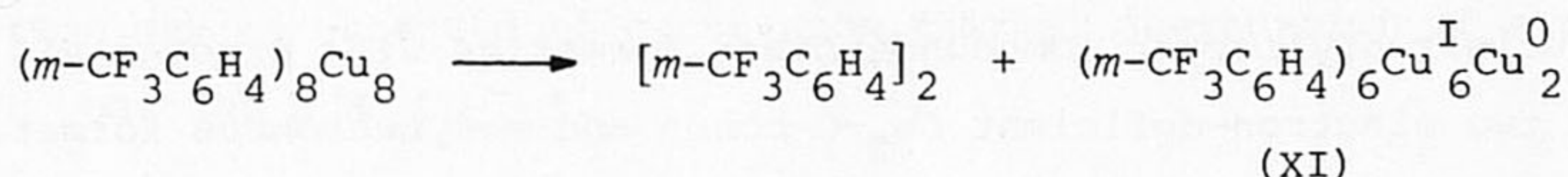
\*Phenyl- and *p*-tolylcopper were prepared from the reactions of the respective Grignard reagents with cuprous iodide.



mediate hexanuclear  $R_3R'Cu^I_4Cu^0_2$  species to polymeric  $RCu$  (VIII) and a new  $Cu^ICu^0_2$  cluster compound:



The nature of the latter mixed-valency copper cluster is still under investigation. An example of an octameric  $Cu^ICu^0_2$  cluster (XI) has recently been isolated by Cairncross and Sheppard [13]:



#### EXPERIMENTAL\*

##### *Phenylethynylbis[2-(dimethylamino)phenyl]tricopper (V)*

A solution of phenylethynyllithium [14] (II) (5.18 mmol) in ether (24 ml) was added at room temperature to a solution of bis-[2-(dimethylamino)phenyl-copper]cuprous bromide (I) (5.18 mmol) in benzene (60 ml). After stirring for 2½ h the clear dark solution was concentrated, affording a dark-green solid. To this solid benzene (30 ml) was added. The resulting suspension was stirred for ¾ h and then centrifuged. The solution was decanted and the extraction/centrifugation procedure repeated with another portion of benzene (20 ml). A white benzene-insoluble residue (0.45 g; 100% LiBr is 0.46 g) was isolated. The benzene extract was concentrated. The combined dark-green residues were recrystallized from ether/pentane (30 ml; 1/1 v/v) affording dark-green (V) in 92% yield. Elemental analysis, see Table 1. NMR data, see Table 4. IR data, see Table 2. Mol.wt. (cryometric in benzene): found 1127 and 1006; calcd. for dimer, 1063.

##### *Mesitylethynylbis[2-(dimethylamino)phenyl]tricopper (VII)*

A suspension of mesitylethynyllithium [14] [(IV); 5 mmol] in ether (10 ml) was added portion-wise to a solution of (I) (5 mmol) in benzene (60 ml). After stirring the reaction mixture for 20 h the resulting yellow precipitate was filtered off. The benzene- and ether-insoluble precipitate was extracted with ether (3 x 15 ml) and with benzene (2 x 15 ml). Yield of (VII) 89%. Elemental analysis, see Table 1. NMR data, see Table 4. IR data, see Table 2.

##### *p-Tolyethynylbis[2-(dimethylamino)phenyl]tricopper (VI)*

A solution of *p*-tolyethynyllithium [14] [(III), 5 mmol] in ether (10 ml) was added at room temperature to a solution of (I) (5 mmol) in benzene (60 ml). After stirring for 3 h the solvents were removed by evaporation under reduced pressure. The yellow-green residue was suspended in benzene. The suspension was centrifuged and the solution decanted. This procedure was repeated twice affording a white insoluble residue (0.47 g; 100% LiBr is 0.44 g). The benzene

\*General directions dealing with solvents, apparatus and reaction conditions are presented in Chapter IX.



extracts were concentrated to about 5 ml. Slow addition of pentane (+ 30 ml) resulted in the precipitation of a brown solid which was filtered off. Extraction with pentane (3 x 10 ml) afforded a brown solid (VI) in 93% yield. Elemental analysis, see Table 1. NMR data, see Table 4. IR data, see Table 2. Mol.wt. (cryometric in benzene): found, 933; calcd. for dimer, 1091.

#### Thermal degradation of (VI)

A solution of (VI) (2.5 mmol  $R_4R'_2Cu_6$ ) in benzene (60 ml) was refluxed. After 4 h NMR spectroscopy of the dark reaction mixture revealed that still undecomposed product was present [cf.  $\delta(p-CH_3)$  2.13 ppm]. After 7 h no starting product was detectable by NMR. The dark solution, containing a dark precipitate, was centrifuged. The solution was decanted and the precipitate again extracted with benzene (10 ml). The precipitate was dried affording a grey solid. IR (nujol): identical to a pure sample of 2-(dimethylamino)phenylcopper (VIII) (4.8 mmol).

The clear dark, red-brown benzene filtrate was concentrated. The black residue was extracted with pentane (1 x 40 and 2 x 20 ml; centrifugation procedure) yielding a black pentane-insoluble residue (found: Cu, 44.4%). NMR spectroscopy of a solution of this residue in  $C_6D_6$  showed very broad absorptions between 1.6-3.5 and 6.0-7.9 ppm both at room temperature and at 80°.

The pentane extract was concentrated. The NMR spectrum of the residue in  $C_6D_6$  showed *N,N*-dimethylaniline (RH) [ $\delta(NCH_3)$  2.50 ppm singlet] and the mixed dimer (X) to be present in a 1/0.07 mol ratio [(X)/RH]. The symmetric dimer RR could not be detected. The residue was taken up in benzene (12 ml)/KCN solution (600 mg in 5 ml) mixture. The resulting mixture was stirred at 60° during 1 h. Subsequently the benzene layer was extracted with 8 ml 2 *N* HCl solution, with 4 *N* NaOH solution and again with water (10 ml) and then dried over  $Na_2SO_4$ . Filtration and concentration of the benzene solution afforded pure 2-(*p*-tolylethynyl)-*N,N*-dimethylaniline (X) as a light-red coloured oil in 51.2% yield (2.56 mmol). IR (neat)  $cm^{-1}$ :  $\nu(C\equiv C)$  2217 w, other absorptions at 1600 m, 1567 w, 1517 m, 1497 m, 1453 m, 1434 m, 1412 (sh), 1333 m (br), 1279 w (br), 1203 m, 1189 (sh), 1166 w, 1139 w, 1124 vw, 1111 (sh), 1101 w (br), 1062 (sh), 1052 m, 1022 vw, 952 s (br), 818 vs (br), 792 vw (br), 757 s (br), 746 (sh), 710 vw. NMR ( $\delta$  ppm): in  $CCl_4$ , 2.32 (4- $CH_3$ , 3 H, s), 2.90 ( $NCH_3$ , 6 H, s), three multiplets between 6.66 and 7.44 (aromatic-H, 8 H); in  $C_6D_6$ , 1.99 (4- $CH_3$ , 3 H, s), 2.73 ( $NCH_3$ , 6 H, s), 6.84 and 7.44 (4-Me $C_6H_4$  4 H, 2xd, *J* 8 Hz), multiplets between 6.60 and 7.70 (2-NMe $_2C_6H_4$ , 4 H). Mass spectrum (*m/e*): 235 (*M*) (calcd. mol.wt: 235).

#### REFERENCES

- 1 I. A. GARBUSOVA, V. T. ALEXANJAN, L. A. LEITES, I. R. GOLDING and A. M. SLADKOV, *J. Organometal. Chem.*, 54 (1973) 341.
- 2 E. A. JEFFERY, T. MOLE and J. K. SAUNDERS, *Aust. J. Chem.*, 21 (1968) 137.
- 3 O. M. ABU SALAH and M. I. BRUCE, *J. Chem. Soc., Chem. Commun.*, (1972) 858.
- 4 P. W. R. CORFIELD and H. M. M. SHEARER, cited in G. E. COATES, M. L. H. GREEN and K. WADE (Eds.), *Organometallic Compounds, Vol. 2, Transition Elements*, Methuen, London, 1968, p. 274.
- 5 See ref. 4, p. 278.
- 6 G. E. COATES and C. PARKIN, *Advan. Chem. Coord. Compounds*, MacMillan, New York, 1961, p. 173.
- 7 E.g., M. NILSSON and C. ULLENIUS, *Acta Chem. Scand.*, 24 (1970) 2379 and



references cited therein.

- 8 E.g., J.CHODOWSKA-PALICKA and M.NILSSON, Acta Chem.Scand. 25 (1971) 3451 and references cited therein.
- 9 E.g., T.COHEN and T.POETH, J.Amer.Chem.Soc., 94 (1972) 4363 and references cited therein.
- 10 E.g., G.M.WHITESIDES, E.R.STREDRONSKY, C.P.CASEY and J.SAN FILLIPO Jr., J.Amer.Chem.Soc., 92 (1970) 1426; G.M.WHITESIDES, C.P.CASEY and J.K.KRIEGER, *ibid.*, 93 (1971) 1379.
- 11 H.HASHIMOTO and T.NAKANO, J.Org.Chem., 31 (1966) 891.
- 12 G.VAN KOTEN and J.G.NOLTES, to be published.
- 13 A.CAIRNCROSS and W.A.SHEPPARD, J.Amer.Chem.Soc., 93 (1971) 247.
- 14 L.BRANDSMA, Preparative Acetylenic Chemistry, Elsevier, Amsterdam, 1971.



## CHAPTER IX

### SYNTHESIS AND CHARACTERIZATION OF BIS(ORGANO)COPPERLITHIUM COMPOUNDS OF THE TYPE $R_4Cu_2Li_2^*$

#### INTRODUCTION

In recent years among the organometallic compounds used in organic synthesis the so-called organocuprates\*\* have rapidly gained a very important position. Such compounds have been used for the synthesis of a wide variety of otherwise difficultly accessible organic molecules. The literature on synthetic applications of organocuprates\*\*\* has recently been reviewed by Normant [1] and by Posner [2].

Conclusive studies concerning the mechanism by which these compounds react have not been presented in the literature. So far, mechanistic discussions were largely speculative because the information concerning the nature of the organocopperlithium species was lacking.

From the literature it appears that to date the number of "cuprate" compounds, which have been isolated or for which the structure has been studied by physico-chemical techniques is very limited (see Table 1). Such studies are hampered by the extreme sensitivity of these compounds towards oxygen and moisture, whereas the low thermal stability of the bis(alkyl)copperlithium compounds is a further limiting factor.

Earlier work on the synthesis of 2-[(dimethylamino)methyl]phenylcopper by reaction of the corresponding organolithium compound with cuprous bromide\*\*\*\* had provided indications for the formation of an organocopperlithium species

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\*For a preliminary account of this work see ref. 3. Full details of the synthesis and characterization of analogous bis{2-[(dimethylamino)methyl]phenyl}silverlithium have been reported [4].

\*\*"Organocuprates" are not limited to combinations of organocopper and organolithium compounds ( $R_2CuLi$ ), but comprise combinations of organocopper compounds with other organometallics ( $R_{n+m}Cu_m^I M^n$ ).

\*\*\*Although these compounds in general are discussed in terms of being ionic species  $R_2Cu^-Li^+$  or  $RXCu^-Li^+$ , no evidence has been presented to support this formulation. The compounds discussed in this Chapter are certainly not ate-complexes [5] and therefore we prefer the name organocopperlithium compounds instead of organocuprates.

\*\*\*\*See Chapter IV.



TABLE 1

## SOME "ORGANOCUPRATE" COMPOUNDS REPORTED IN THE LITERATURE

| Compound <sup>a, b</sup>  | Remarks  | Ref. |
|---|--|------|
| Me <sub>2</sub> Cu <sup>-</sup> Li <sup>+</sup>   | Prepared in situ;  | 6    |
| [(EtO) <sub>3</sub> P] <sub>2</sub> Cu <sup>-</sup> $\begin{matrix} \text{CN} \\ \text{Li}^+ \\ \text{Me} \end{matrix}$ | <sup>1</sup> H NMR investigation;<br>stable at 0° for some hours |      |
| PhCu·PhLi·nEt <sub>2</sub> O  | Isolated; stable at room   | 7    |
| (PhCu) <sub>4</sub> ·PhLi·3.5Et <sub>2</sub> O  | temperature  |      |
| (PhCu) <sub>2</sub> ·Ph <sub>2</sub> Mg·nTHF  |  |      |
| m-TolCu·m-TolLi   | Isolated; stable at room   | 8    |
|   | temperature  |      |
| Cu <sub>4</sub> MgPh <sub>6</sub> ·Et <sub>2</sub> O  | Isolated: <sup>1</sup> H NMR investi-                            | 9    |
| Cu <sub>4</sub> MgTol <sub>6</sub> ·Solv <sup>c</sup>   | gation; dec. > 130°  |      |

<sup>a</sup>Represented as formulated by the respective authors. <sup>b</sup>Me methyl; Et ethyl; Ph phenyl; Tol tolyl. <sup>c</sup>Solv, Et<sub>2</sub>O or THF.

with unusual thermal stability. The isolation and structural characterization of this organocopperlithium species, bis{2-[(dimethylamino)methyl]phenyl}copperlithium, described in this Chapter, for the first time provided information about the true nature of this class of compounds in solution.

## RESULTS AND DISCUSSION

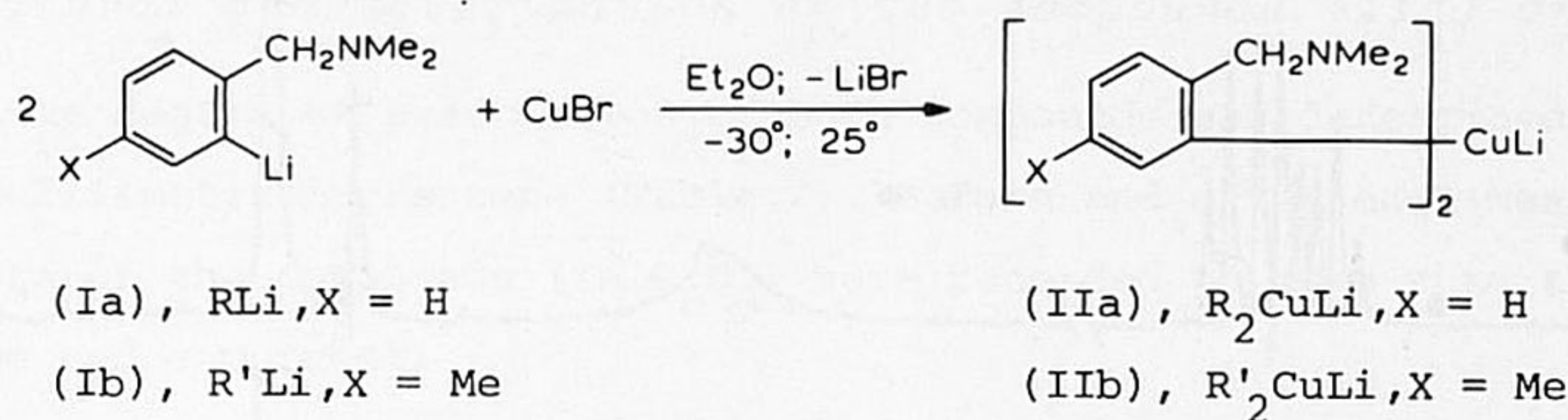
*Synthesis of bis{2-[(dimethylamino)methyl]phenyl}copperlithium and its 5-methyl analogue*

The 2/1 reaction\* of 2-[(dimethylamino)methyl]phenyllithium (Ia) at -30° with cuprous bromide, using ether as a solvent, afforded white crystalline bis{2-[(dimethylamino)methyl]phenyl}copperlithium (IIa; X = H) in about 50% yield. The copper analysis of the isolated product (found: Cu, 18.8; calcd.:

\*CuBr was slowly added to the respective organolithium solutions. For a discussion, see Chapters II and IV.

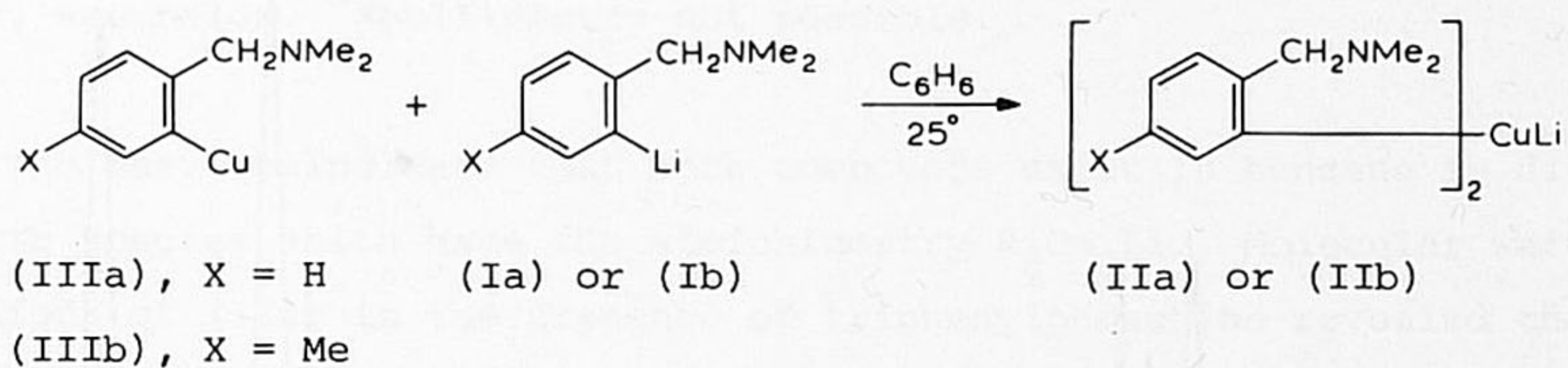


Cu, 18.68%) as well as  $^1\text{H}$  NMR (vide infra) and IR spectroscopy (*ortho*-disubstitution pattern for the aryl nucleus) pointed to the isolation of (IIa) in the pure state.



The attempted synthesis of the 5-methyl-substituted derivative (IIb) along the same route afforded a product which according to the copper analysis (found: Cu, 20.1. R'<sub>2</sub>CuLi calcd.: Cu, 17.32; 2R'<sub>2</sub>CuLi·R'Cu calcd.: Cu, 20.08%) as well as to NMR spectroscopy [peak area ratio NCH<sub>2</sub>(R'<sub>2</sub>CuLi)/NCH<sub>2</sub>(R'Cu) ≈ 1.8/1 (calculated from Cu analysis 2/1)] had the composition R'<sub>5</sub>Cu<sub>3</sub>Li<sub>2</sub>. Addition of one equivalent of R'Li (Ib) to a solution of this product (R'<sub>5</sub>Cu<sub>3</sub>Li<sub>2</sub>) in benzene afforded a white solid which according to NMR spectroscopy [absence of the starting product R'Li (Ib) as well as of the organocopper (IIIb)] was pure R'<sub>2</sub>CuLi (IIb).

The organocopperlithium compounds (IIa) and (IIb) were also prepared via the 1/1 reactions of the respective organocopper compounds (IIIa) and (IIIb) with the corresponding organolithium compounds using benzene as a solvent\*.



NMR spectroscopy (see Fig. 1) revealed that the organocopperlithium compounds had been formed quantitatively. However, the yield of isolated products was lower, e.g. (IIb) was obtained from this solution in 50% yield.

The organocopperlithium compounds (IIa) and (IIb) appeared to be highly reactive towards oxygen and water. Upon exposure to the atmosphere rapid decomposition occurred. The solid compounds upon heating in a capillary tube (under N<sub>2</sub>) decompose between 178 and 182° (IIa) and between 187 and 192° (IIb) which implies a surprisingly high thermostability for this type of compounds. Solu-

\*For a detailed discussion of this 1/1 reaction, see p. 112.



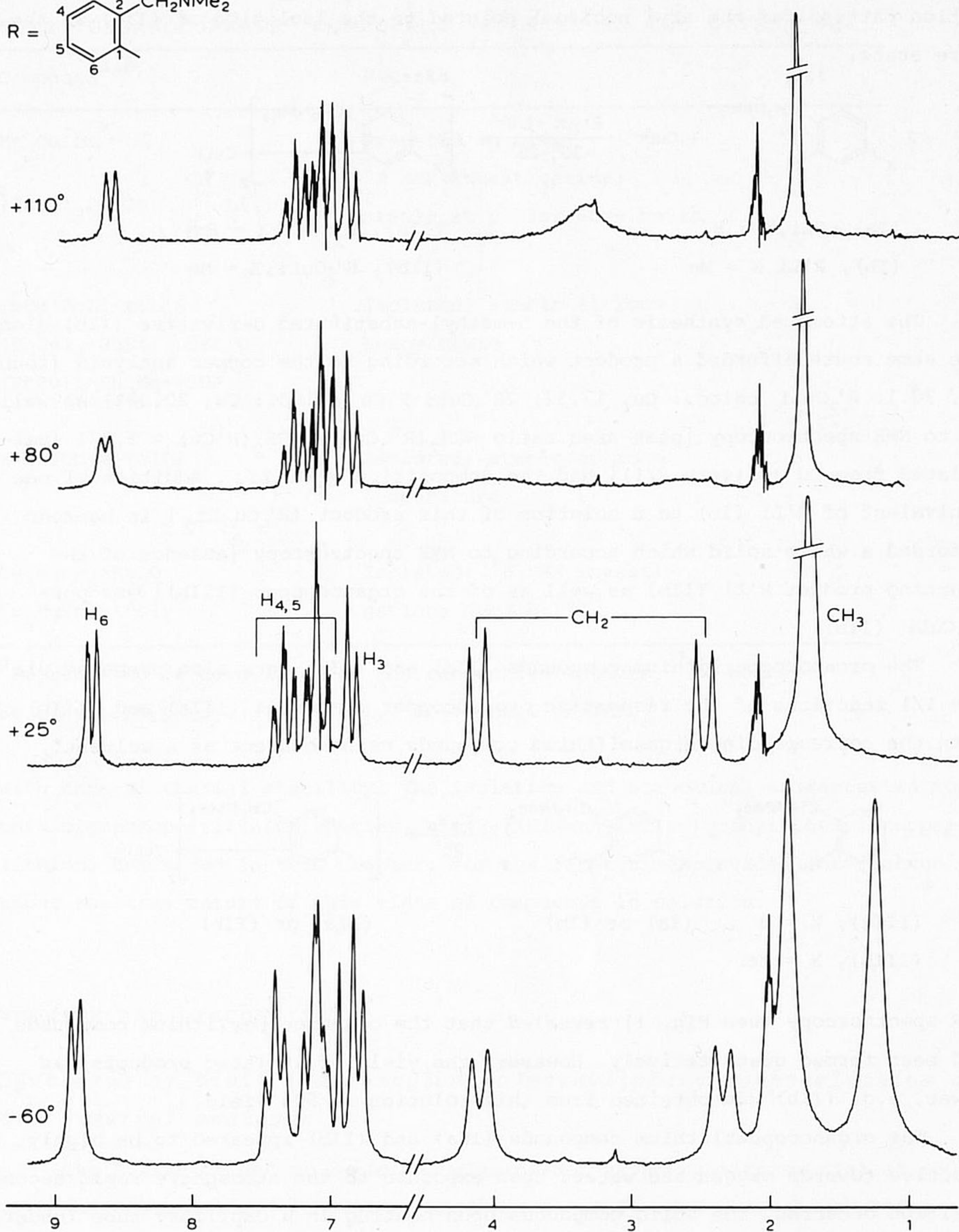
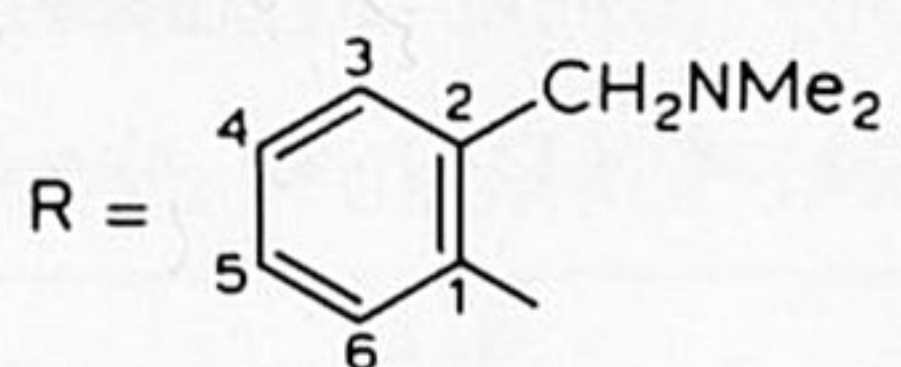


Fig. 1.  $^1\text{H}$  NMR spectrum ( $\delta$  ppm) of tetranuclear bis{2-[(dimethylamino)methyl]phenyl}copperlithium  $\text{R}_4\text{Cu}_2\text{Li}_2$  (IIa) in  $\text{toluene-}d_8$  (see also Table 4).



tions of the organocopperlithium compounds in benzene or toluene can be heated at 80° for several hours without any observable decomposition.

*Structural characterization of the compounds (IIa) and (IIb)*

The degree of association of both compounds was determined by cryometry and by ebulliometry in benzene (Table 2). Before and after each measurement the NMR spectra of the compounds (in C<sub>6</sub>D<sub>6</sub>) were recorded to make sure that no decomposition had occurred\*.

TABLE 2

MOLECULAR WEIGHTS OF COMPOUNDS (IIa) AND (IIb)

| Compound                                | Mol.wt.             |                    | Degree of association $\bar{n}$ | Method                 |
|---|---------------------|--------------------|---------------------------------|------------------------|
|   | Calcd. <sup>a</sup> | Found <sup>b</sup> |                                 |                        |
| (IIa), R <sub>2</sub> CuLi <sup>c</sup> | 338.5               | 711                | 2.10                            | Cryometry              |
|   |                     | 635                | 1.88                            | Ebulliometry           |
| (IIb), R' <sub>2</sub> CuLi             | 366.5               | 722                | 1.97                            | Cryometry <sup>d</sup> |

<sup>a</sup>Calculated for the monomer. <sup>b</sup>Mean values are given (concentration range 1 x 10<sup>-2</sup>-5 x 10<sup>-2</sup> M). <sup>c</sup>Mol.wt. data for mixtures of (IIa) with triphenylphosphine, see below. <sup>d</sup>Ebulliometry not possible.

The results indicate that both compounds exist in benzene as discrete dimeric species which have the stoichiometry R<sub>4</sub>Cu<sub>2</sub>Li<sub>2</sub>. Molecular weight determinations of (IIa) in the presence of triphenylphosphine revealed that complex formation between R<sub>4</sub>Cu<sub>2</sub>Li<sub>2</sub> and PPh<sub>3</sub> does not occur (see Experimental).

The structure of the R<sub>4</sub>Cu<sub>2</sub>Li<sub>2</sub> compounds in benzene solution was deduced from their <sup>1</sup>H and <sup>13</sup>C NMR spectra. The observed <sup>13</sup>C chemical shift data and assignments for (IIa) and (IIb) have been compiled in Table 3. For comparison also the <sup>13</sup>C NMR data for two other compounds with a R<sub>4</sub>M<sub>4</sub> stoichiometry, viz. the organocopper compound R<sub>4</sub>Cu<sub>4</sub> (IIIa) and the organolithium compound R'<sub>4</sub>Li<sub>4</sub> (Ib) (vide infra), have been given.

\*Hydrolysis by traces of water would give rise to the formation of the organocopper compound (RCu) and the arene (RH), which are both detectable by NMR spectroscopy:

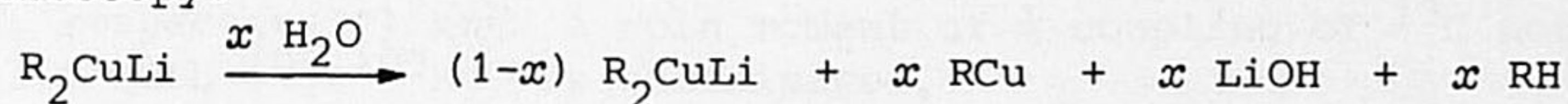
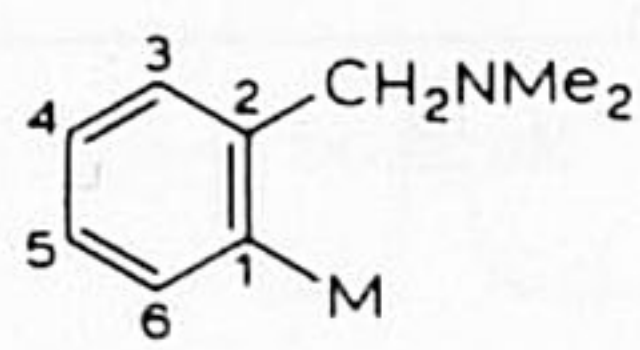




TABLE 3

NATURAL ABUNDANCE  $^{13}\text{C}$  NMR SPECTRA<sup>a</sup> OF  $\text{R}_4\text{Cu}_2\text{Li}_2$  (IIa) AND (IIb),  
 $\text{R}_4\text{Cu}_4$  (IIIa) AND  $\text{R}_4\text{Li}_4$  (Ib)

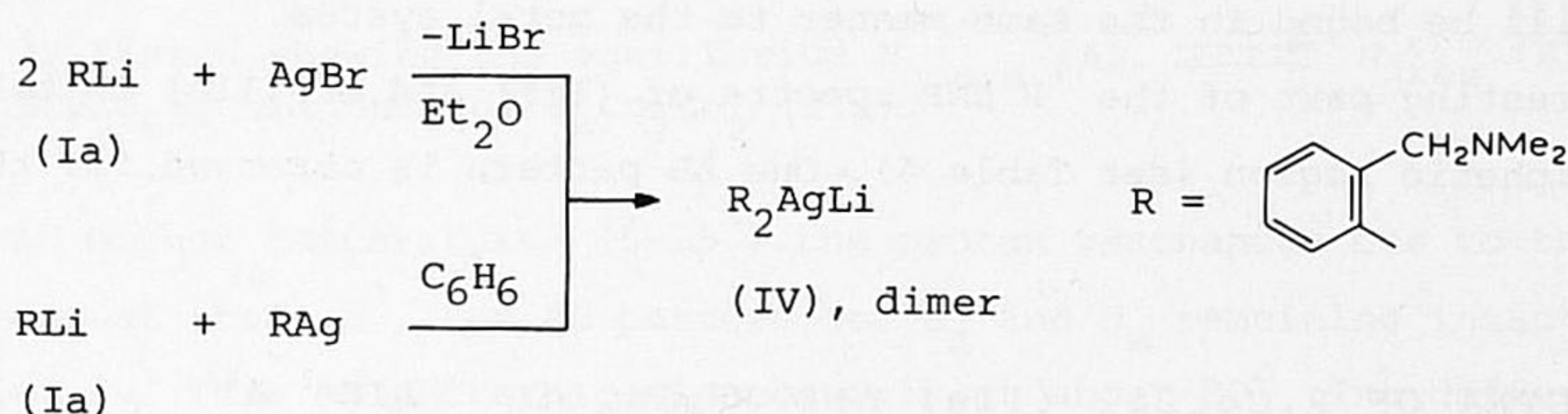
| Peak assignment  | $\delta$ (ppm)     |                     |                     |                     |
|--|--------------------|---------------------|---------------------|---------------------|
|  | (IIa) <sup>b</sup> | (IIb)               | (IIIa) <sup>e</sup> | (Ib) <sup>f</sup>   |
| Methyl(amino)-C  | 46.63              | 46.62               | 49.23 ( 45.63)      | 18.65               |
| 5-Methyl-C   |                    | 21.72               |                     | 15.88               |
| Benzylic-C   | 72.42              | 71.99               | 75.25 ( 71.41)      | 42.23               |
| <i>Aromatic-C</i>  |                    |                     |                     |                     |
|  | 125.32             | 125.87              | 128.52 (124.99)     | 105.86 <sup>g</sup> |
|  | 125.85             | 127.54 <sup>c</sup> | 129.03 (125.43)     | 112.94 <sup>g</sup> |
|  | 127.71             | 133.92              | 129.84 (126.15)     | 122.10 <sup>g</sup> |
|  | 143.73             | 144.94              | 147.30 (143.60)     |                     |
|  | 147.94             | 145.13              | 156.82 (153.21)     |                     |
|  | 167.68             |                     |                     |                     |
| $\text{C}_1$   | 167.98             | N.O. <sup>d</sup>   | 157.11 (153.32)     | 147.6               |
|  | 168.22             |                     |                     | (Broad)             |
|  | 168.52             |                     |                     |                     |
|  |                    |                     |                     |                     |

<sup>a</sup>With  $^1\text{H}$  decoupling. TMS internal standard. <sup>b</sup>0.7 g of (IIa) in benzene- $d_6$  (4 ml). <sup>c</sup>A resonance at 128.55 ppm is ascribed to an impurity. <sup>d</sup>Owing to the low solubility of (IIb) not observed (N.O.). <sup>e</sup>0.8 g of  $\text{RCu}$  in benzene- $d_6$  (4 ml). Values between brackets: 0.2 g of  $\text{RCu}$  in pyridine- $d_5$  (4 ml). <sup>f</sup> $\text{c-C}_6\text{H}_{12}$  internal standard:  $\delta(\text{c-C}_6\text{H}_{12}) - \delta(\text{TMS}) \pm 27$  ppm. <sup>g</sup> $\text{C}_{2-6}$ ; other resonances masked by  $\text{C}_6\text{D}_6$  resonances.



As appears from Table 3 the low-intensity resonance at lowest field has been assigned to the carbon atom  $C_1$  which is bound to the metal system, i.e. in the case of the organocopper compound (IIIa) to the bridging carbon atom\*. In the spectrum of the organocopperlithium compound (IIa) the resonance for  $C_1$  appears as a quartet ( $J \approx 7$  Hz). The observed multiplicity, which has been ascribed to  $^{13}\text{C}-^7\text{Li}$  coupling\*\*,\*\*\*, reveals that *each phenyl group is bonded to one lithium atom only*. In view of the fact that the copper atom is more electro-negative than the lithium atom it seems plausible to assume that each phenyl group bridges one copper and one lithium atom (see Fig. 2).

The presence of aryl groups bridging one lithium and one silver atom in the corresponding silverlithium compound, bis{2-[(dimethylamino)methyl]phenyl}-silverlithium (IV), has been unambiguously established by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [4]\*\*\*\*. This compound, which like the  $\text{R}_4\text{Cu}_2\text{Li}_2$  compound exists in benzene as a dimer ( $\text{R}_4\text{Ag}_2\text{Li}_2$ ), was synthesized in a similar way as (IIa), viz. via:



The  $^{13}\text{C}$  resonance of  $C_1$  in  $\text{R}_4\text{Ag}_2\text{Li}_2$  (IV) couples both with *one lithium atom* [ $J(^{13}\text{C}-^7\text{Li}) 7.2 \pm 0.2$  Hz] and with *one silver atom* [ $J(^{13}\text{C}-^{107}\text{Ag}) 118.3 \pm 0.8$  and  $J(^{13}\text{C}-^{109}\text{Ag}) 136.0 \pm 0.8$  Hz] (see Fig. 2).

The  $^1\text{H}$  NMR spectrum of (IIa) at room temperature shows only one resonance pattern for each hydrogen (see Fig. 1 and Table 4); e.g. the *ortho*-hydrogen atom

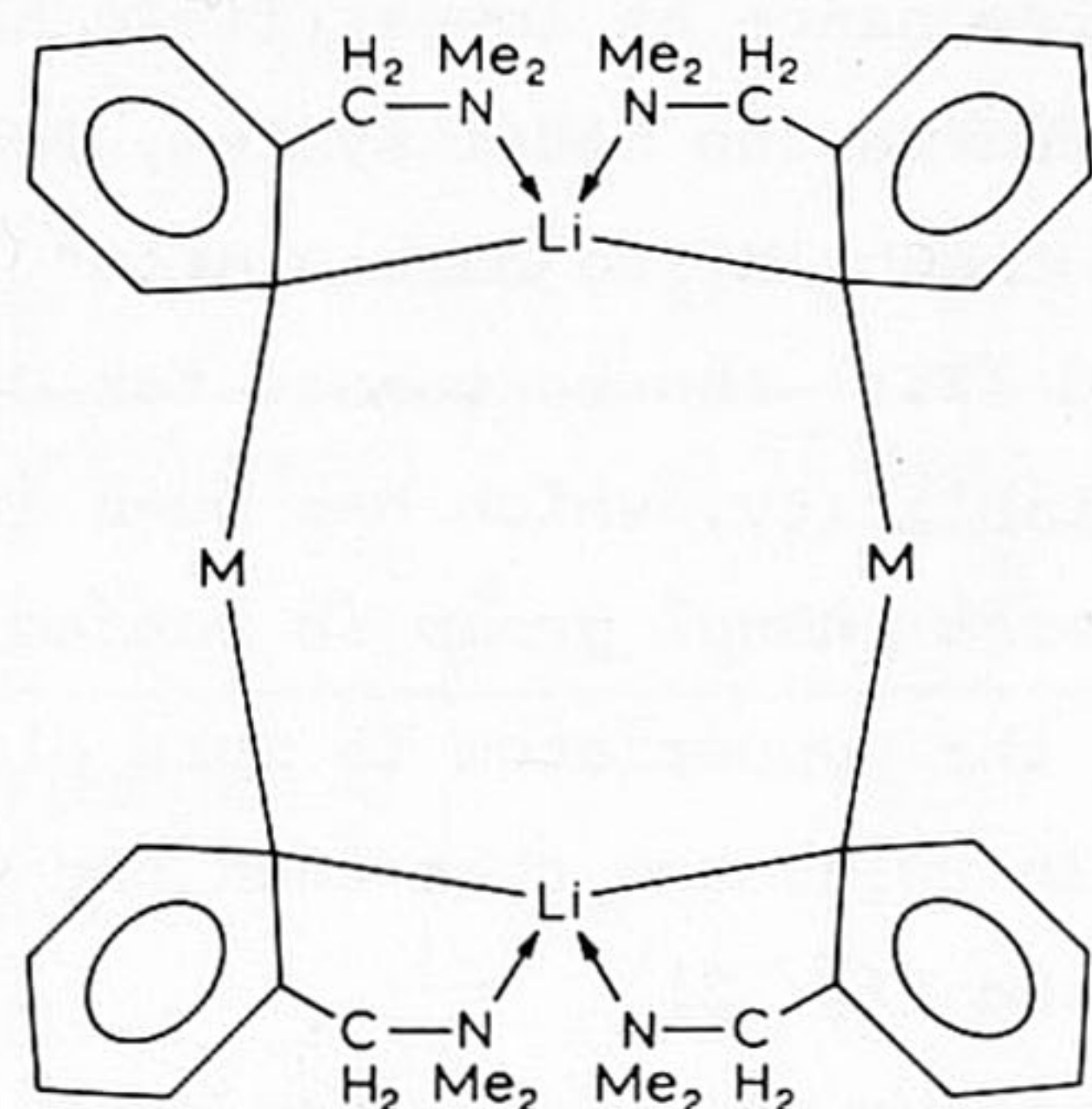
\*In spite of the fact that both copper isotopes  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  (total natural abundance 100%) have a spin moment of 3/2 no  $^{13}\text{C}-^{63,65}\text{Cu}$  couplings were observed. This may be due to the large quadrupole moment of the copper atom which interferes with the electric field gradient produced by the surrounding electric charges at the position of the copper nucleus.

\*\*Also the lithium atom possesses a quadrupole moment, the magnitude of which is comparable with that of the copper nucleus. However, the electron environment of the lithium atom (having only s electrons) is hardly susceptible towards distortions by surrounding electric charges.

\*\*\*In the  $^{13}\text{C}$  NMR spectrum of (IIb) this quartet was not observed which is most probably due to the limited solubility of (IIb) in  $\text{C}_6\text{D}_6$ .

\*\*\*\*Since both isotopes of silver ( $^{107}\text{Ag}$  and  $^{109}\text{Ag}$ , natural abundance 51.8 and 48.2%, respectively) have a spin moment of  $\frac{1}{2}$  coupling of  $^{13}\text{C}$  not only with  $^7\text{Li}$  but also with  $^{107,109}\text{Ag}$  was anticipated.





$R_4M_2Li_2$ ; M=Cu or Ag

Fig. 2. Schematic structure of the tetranuclear bis[2-[(dimethylamino)methyl]phenyl]copper(or silver)lithium compounds (IIa) and (IV), respectively.

$H_6$  appears as a sharp doublet of doublets ( $J_{5,6} \approx 7$ ;  $J_{4,6} \approx 1.5$  Hz). This indicates that all four aryl ligands are in the same magnetic environment and, therefore, will be bound in the same manner to the metal system.

An interesting part of the  $^1H$  NMR spectra of (IIa) and of (IIb) in toluene- $d_8$  is the aliphatic region (see Table 4). One AB pattern is observed for the

TABLE 4

$^1H$  NMR SPECTRA OF  $R_4Cu_2Li_2$  (IIa) AND  $R'_4Cu_2Li_2$  (IIb) AT AMBIENT TEMPERATURE

| Compound                                   | $\delta$ (ppm) <sup>a</sup> |  |   |
|--|-----------------------------|--|---|
|  | NCH <sub>3</sub>            | NCH <sub>2</sub>                                 | <i>ortho</i> -H   |
| (IIa)<br>(in toluene- $d_8$ )              | 1.74 (s, sharp)             | 4.12 (d) and 2.48 (d)<br>$J_{gem} \approx 12$ Hz | 8.74 (m, $J_{ortho} \approx 7$ ; $J_{meta} \approx 1.5$ Hz) |
| (IIb)<br>(in benzene- $d_6$ ) <sup>b</sup> | 1.82 (s, sharp)             | 4.20 (d) and 2.56 (d)<br>$J_{gem} \approx 12$ Hz | 8.69 (d)  |

<sup>a</sup>TMS internal. <sup>b</sup> $\delta(5-Me)$  2.53 ppm.

benzylic protons ( $H_A$  and  $H_B$ ) and also one resonance pattern for the NMe protons\*. This indicates that the 2-Me<sub>2</sub>NCH<sub>2</sub> ligands are coordinated to the same metal. In view of the HSAB principle it has been assumed that all four "hard" nitrogen

\*The same features were observed in the spectrum of  $R_4Ag_2Li_2$  (IV) [4].



ligands exclusively coordinate to the "hard" lithium atoms which then are four-coordinate\*, see Fig. 2. This coordination environment around lithium can account for the observed temperature dependence of the  $^1\text{H}$  NMR spectra of (IIa) and (IIb).

At low temperatures ( $-60^\circ$ ) the two methyl groups (two singlet resonances) as well as  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$  (doublet of doublets) in each  $2\text{-Me}_2\text{NCH}_2$  ligand are magnetically non-equivalent on the NMR time-scale. This is a result of (i) inertness of the Li-N bonds at this temperature and (ii) the arrangement of the ligands. Inspection of a model of the  $\text{R}_4\text{Cu}_2\text{Li}_2$  structure reveals that the situation around the nitrogen atom can be represented by conformation (A) (see Fig. 3).

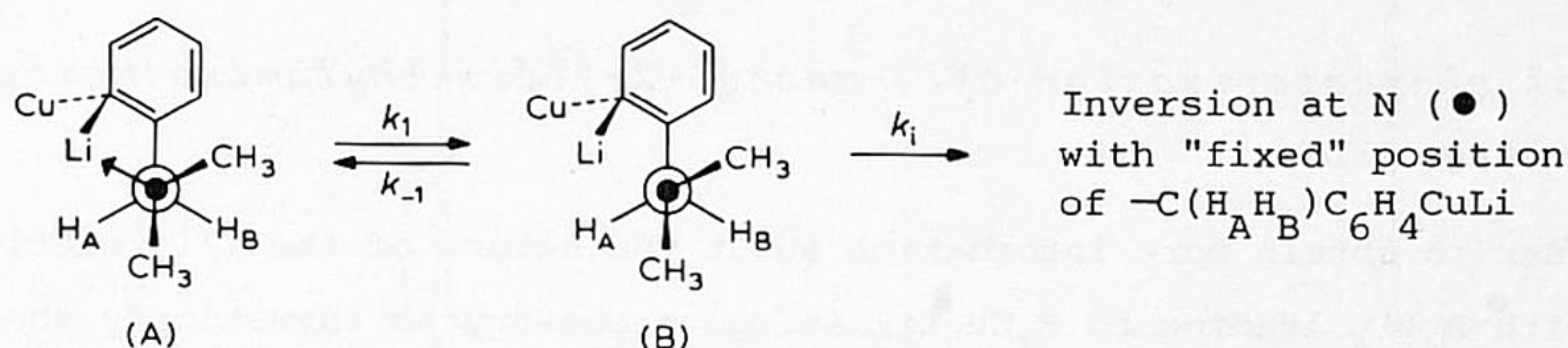


Fig. 3. Sketch showing the equilibrium  $\text{N}_{\text{coord.}}$  (A)  $\rightleftharpoons$   $\text{N}_{\text{free}}$  (B) in one  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CuLi}$  unit of  $\text{R}_4\text{Cu}_2\text{Li}_2$  (IIa).

At higher temperatures ( $5\text{-}25^\circ$ ) the proton resonances due to the NMe-protons coalesce at about  $5^\circ$ , the AB pattern for  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$  remaining intact with unchanged  $\Delta\nu$ . This AB pattern coalesces only at about  $80^\circ$ . The difference in coalescence temperatures indicates that the NMe- and benzylic-protons are non-equivalent at low temperature for different reasons.

For the  $\text{R}_4\text{Cu}_2\text{Li}_2$  compound an equilibrium  $\text{N}_{\text{coord.}}$  (situation A)/ $\text{N}_{\text{free}}$  (situation B) is assumed (see Fig. 3). In the  $\text{N}_{\text{coord.}}$  situation (A) the two methyl groups in  $\text{CH}_2\text{NMe}_2$  are in magnetically non-equivalent environments. In the  $\text{N}_{\text{free}}$  situation (B) inversion at N occurs. Only when the inversion process (rate constant  $k_i$ ) is rapid on the NMR time-scale and  $k_i \gg k_{-1}$  the methyl signals will coalesce.

In spite of the occurrence of inversion at N  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$  remain magnetically non-equivalent since the different positions of  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$  with respect to the metal cluster are retained. As appears from the occurrence of a sharp pattern for  $\text{H}_6$  (doublet of doublets) and of the sharp quartet splitting for  $\text{C}_1$  in the  $^{13}\text{C}$  NMR spectrum of (IIa) this is the case at ambient temperature.  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$  can become equivalent only when rotation around the  $\text{C}_{\text{benzylic}}\text{-C}_{\text{phenyl}}$  bond is

\*In this structure the copper atoms are two-coordinate, a situation which has also been found for bis[2-(dimethylamino)phenylcopper]cuprous bromide,  $\text{R}_4\text{Cu}_2\text{Br}_2$  (see Chapter VII).



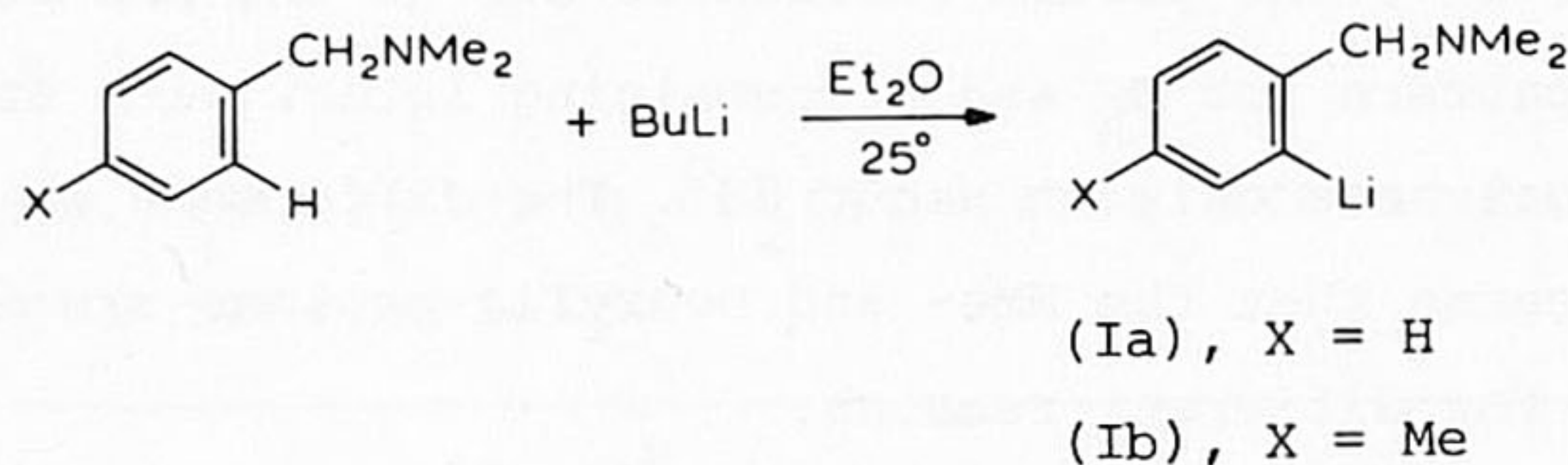
fast on the NMR time-scale and  $k_1 \gg k_{-1}$ . Apparently this situation is only reached at 80° (broadening of H<sub>6</sub>-multiplet; coalescence of the AB pattern), see Fig. 1.

This explanation for the observed difference in coalescence temperatures of the benzylic and of the NMe protons is supported further by the spectrum observed upon adding THF (6 equivalents) to a toluene-*d*<sub>8</sub> solution of R<sub>4</sub>Cu<sub>2</sub>Li<sub>2</sub>. Under these conditions it appears that already at room temperature the AB pattern has coalesced to one broadened singlet resonance, whereas the aryl pattern is broadened. This is as expected because now the THF-molecules compete with the Me<sub>2</sub>NCH<sub>2</sub> ligands for coordination with the lithium atoms.

*Structural characterization of 5-methyl-2-[(dimethylamino)methyl]-phenyllithium (Ib)*

In order to obtain more information about the nature of the 1/1 reaction of R<sub>4</sub>Cu<sub>4</sub> with R<sub>4</sub>Li<sub>4</sub> leading to R<sub>4</sub>Cu<sub>2</sub>Li<sub>2</sub> it was necessary to investigate the structure of the organolithium compounds more closely.

2-[(Dimethylamino)methyl]phenyllithium (Ia) as well as its 5-methyl derivative (Ib) have been prepared via lithium-hydrogen exchange reactions\*:



(Ia) is highly insoluble in ethers as well as in hydrocarbon solvents. However, its 5-methyl derivative (Ib) shows excellent solubility in both types of solvents. (Ib) is extremely sensitive towards oxidation and hydrolysis, but is thermally quite stable (dec. 170-175°). Molecular weight determinations of (Ib) at 5° using benzene as a solvent yielded an average value for *n* of 3.4<sup>\*\*\*</sup>, i.e. a degree of association in between a tetramer and a trimer. This low value for *n* is ascribed to impurities formed by hydrolysis during the determination. Most probably (Ib) exists in benzene as a tetramer for the following two reasons:

\*See also Chapter II.

\*\*By ebulliometry (benzene) a value of 624±100 (*n* 4.0±0.6) has been found. The solution turned yellow during the determination.

\*\*\*Recently Viswanathan and Wilkie [10] reported mol.wt. and <sup>1</sup>H NMR data for (Ia) dissolved in DMSO. The NMR data (especially the observation of only one resonance for all aromatic protons at the position of the parent arene) suggest that instead of the organolithium compound its protolysis product *N,N*-dimethylbenzylamine, originating from the reaction of (Ia) with DMSO, has been measured.



(i) no concentration dependence has been found, which is expected to occur in the case of an equilibrium mixture involving aggregates with different molecular weights, and (ii) the NMR spectrum showed only one resonance pattern for each hydrogen (vide infra).

$^1\text{H}$  NMR spectra recorded at various temperatures are shown in Fig. 4; the  $^{13}\text{C}$  NMR spectral data at ambient temperature have been presented in Table 3.

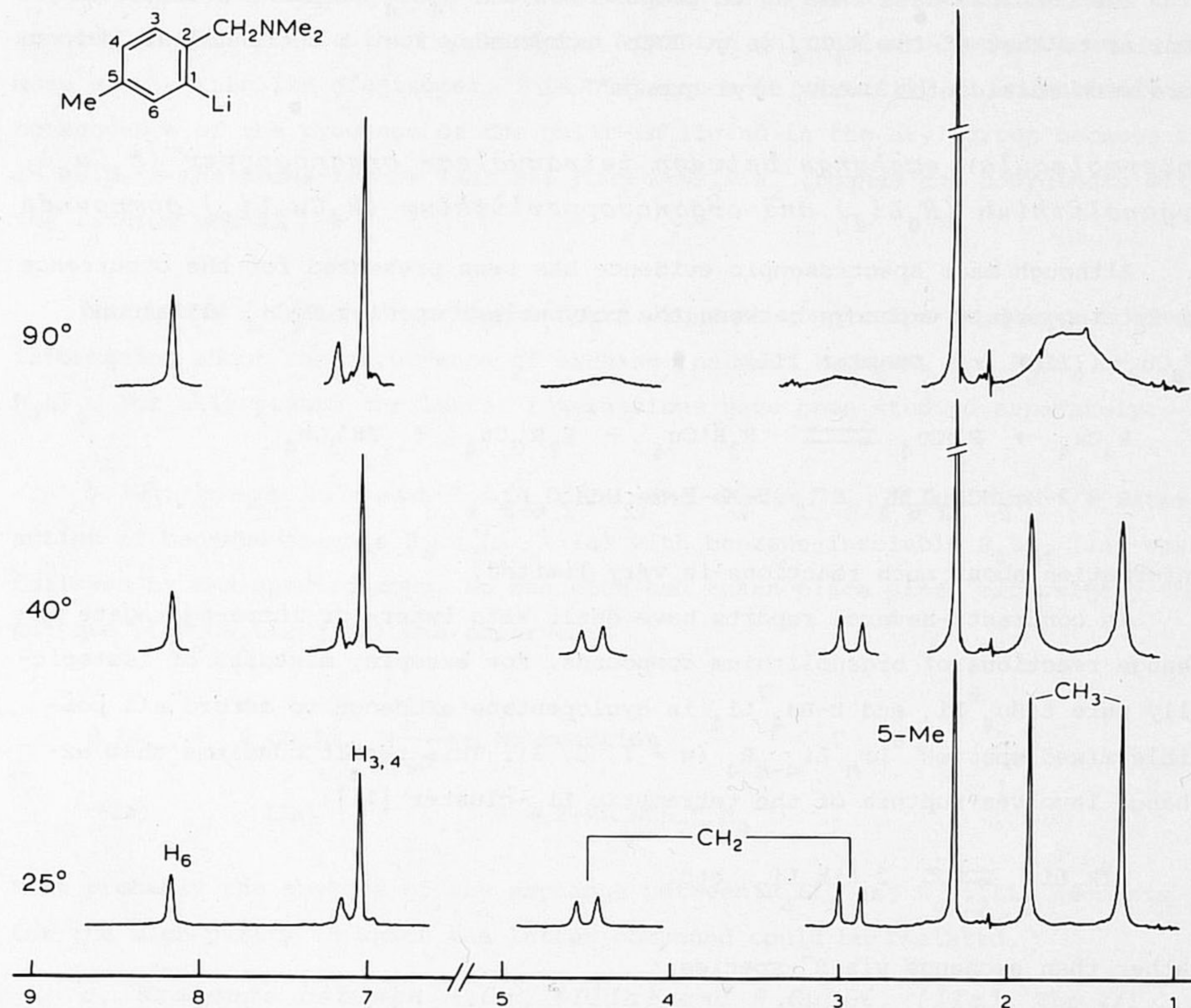


Fig. 4.  $^1\text{H}$  NMR spectra ( $\delta$  ppm) of tetranuclear 5-methyl-2-[(dimethylamino)-methyl]phenyllithium (Ib) in benzene- $d_6$  at different temperatures.

The unresolved, broad resonance for  $\text{C}_1$  does not allow a definite conclusion regarding the nature of the aryl-lithium bonding. The temperature-dependent  $^1\text{H}$  NMR spectrum gives rise to the following observations:

(i). Only one pattern is observed for all protons which indicates that all four  $5\text{-Me-2-Me}_2\text{NCH}_2\text{C}_6\text{H}_3$ -groups reside in magnetically equivalent environments.



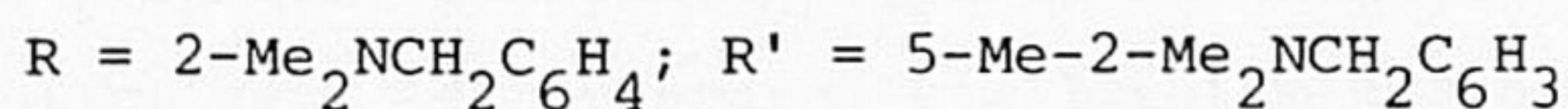
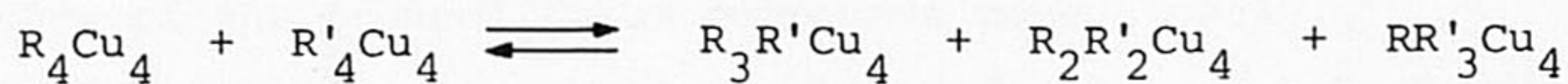
(ii). Just like the  $R_4Cu_2Li_2$  spectra the NMe-protons (two singlets) as well as the benzylic protons  $H_A$  and  $H_B$  are magnetically non-equivalent (AB pattern)\*.

(iii). From the observed coalescence temperatures for the NMe-resonances it can be concluded that the metal-N bond in  $R'_4Li_4$  (Ib) ( $T_c \approx 70^\circ$ ) is stronger than in one of the other tetranuclear species  $R_4Cu_4$  ( $T_c < -60^\circ$ ) and  $R_4Cu_2Li_2$  ( $T_c \approx 5^\circ$ ).

The combined data lead us to propose for the  $R_4Li_4$  compound a structure similar to that of the  $R_4Cu_4$  (e.g. IIIb) compounds, i.e. a tetranuclear lithium core with multicenter bonded aryl groups\*\*.

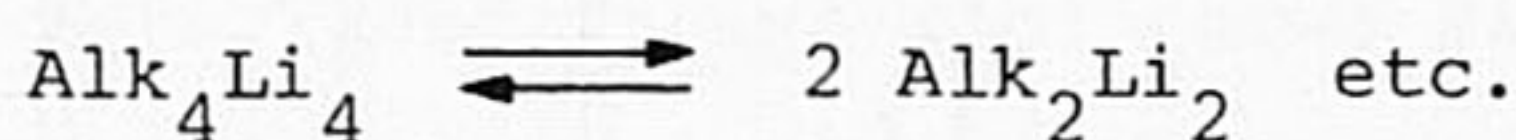
*Intermolecular exchange between tetranuclear organocopper ( $R_4Cu_4$ ), organolithium ( $R_4Li_4$ ) and organocopperlithium ( $R_4Cu_2Li_2$ ) compounds*

Although mass spectroscopic evidence has been presented for the occurrence of interaggregate exchange between the polynuclear species  $R_4Cu_4$  (IIIa) and  $R'_4Cu_4$  (IIIb) (cf. Chapter III):

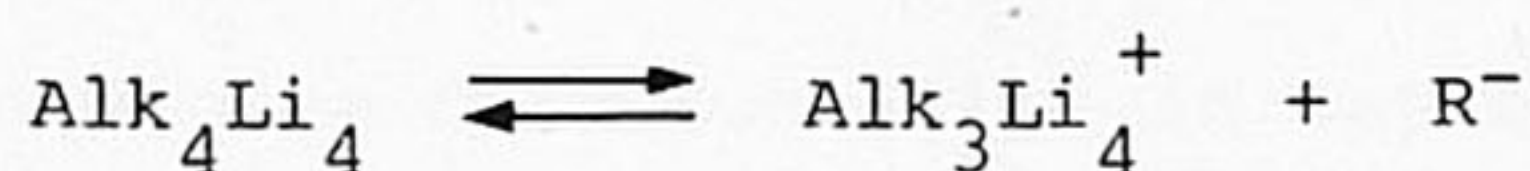


information about such reactions is very limited.

In contrast, several reports have dealt with inter- or intra-aggregate exchange reactions of organolithium compounds. For example, mixtures of isotopically pure  $t\text{-Bu}_4^6\text{Li}_4$  and  $t\text{-Bu}_4^7\text{Li}_4$  in cyclopentane exchange to afford all possible mixed species  $^6\text{Li}_n^7\text{Li}_{4-n}\text{R}_4$  ( $n = 1, 2, 3$ ). This result confirms that exchange involves rupture of the tetrameric  $\text{Li}_4$ -cluster [11]:



rather than exchange via  $R^-$ -species:

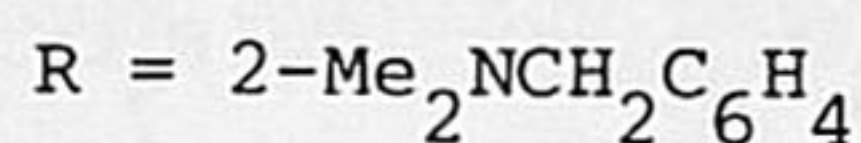
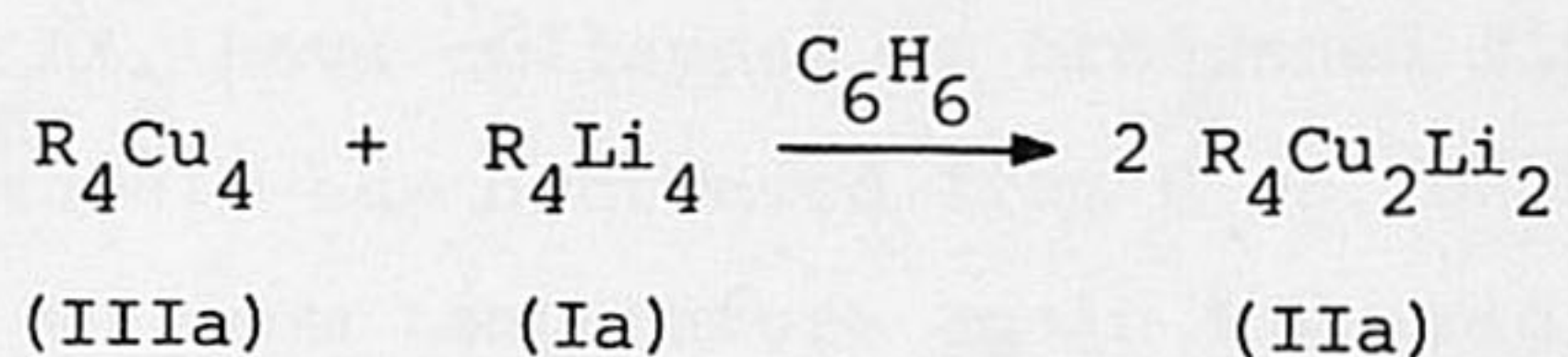


a. *Exchange between  $R_4Cu_4$  and  $R_4Li_4$ .* The formation of  $R_4Cu_2Li_2$  (IIa) from the 1/1 reaction of  $R_4Cu_4$  (IIIa) with  $R_4Li_4$  (Ia) provides another example of an exchange between two polynuclear organometallic species:

\*It is worth mentioning that the low-field doublet of the AB pattern is broadened whereas the high-field doublet has the same line-width as for example the methyl signals. Proton decoupling experiments failed to show the origin of this broadening. The occurrence of Li-H interaction cannot be excluded.

\*\*A detailed  $^{13}\text{C}$  NMR study is in progress.

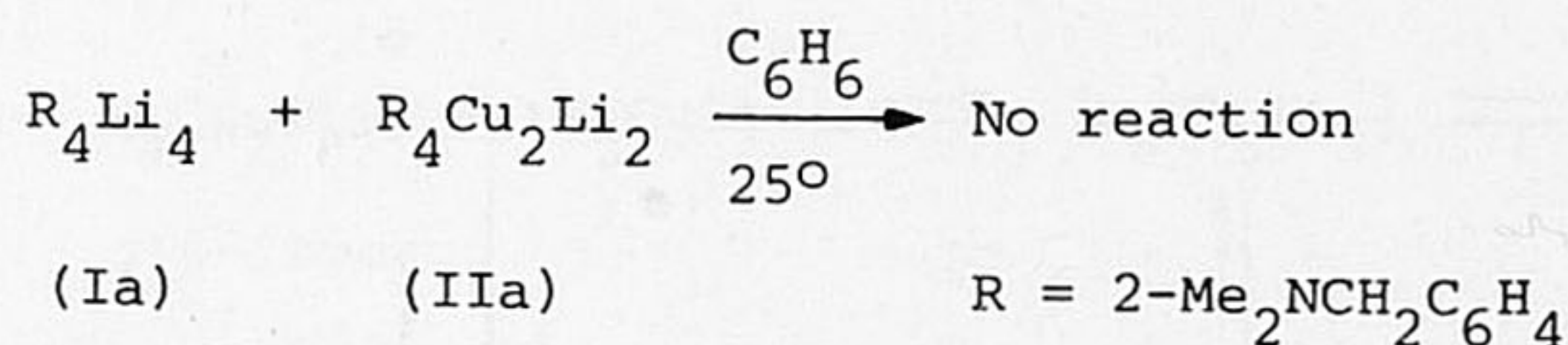




The exclusive formation of the mixed species (IIa), which has the copper and the lithium atoms arranged in a *trans*-fashion (see Fig. 2), indicates that this species is more stable than each of the starting polynuclear compounds and also more stable than its *cis*-isomer. This difference in stability is undoubtedly a consequence of the presence of the built-in ligand in the aryl group because it is *only in the trans-isomer that all four 2-Me<sub>2</sub>NCH<sub>2</sub> ligands can coordinate with the lithium atoms.*

Since the reaction described under *a.* runs to completion it does not give information about the occurrence of exchange between  $R_4Cu_2Li_2$  and  $R_4Cu_4$  or  $R_4Li_4$ . For this reason the latter interactions have been studied separately.

*b. Exchange between  $R_4Li_4$  (Ia) and  $R_4Cu_2Li_2$  (IIa).* The 1/1 interaction of benzene-soluble  $R_4Cu_2Li_2$  (IIa) with benzene-insoluble  $R_4Li_4$  (Ia) was followed by NMR spectroscopy. No reaction had taken place since exclusively the pattern of  $R_4Cu_2Li_2$  (IIa) was observed:

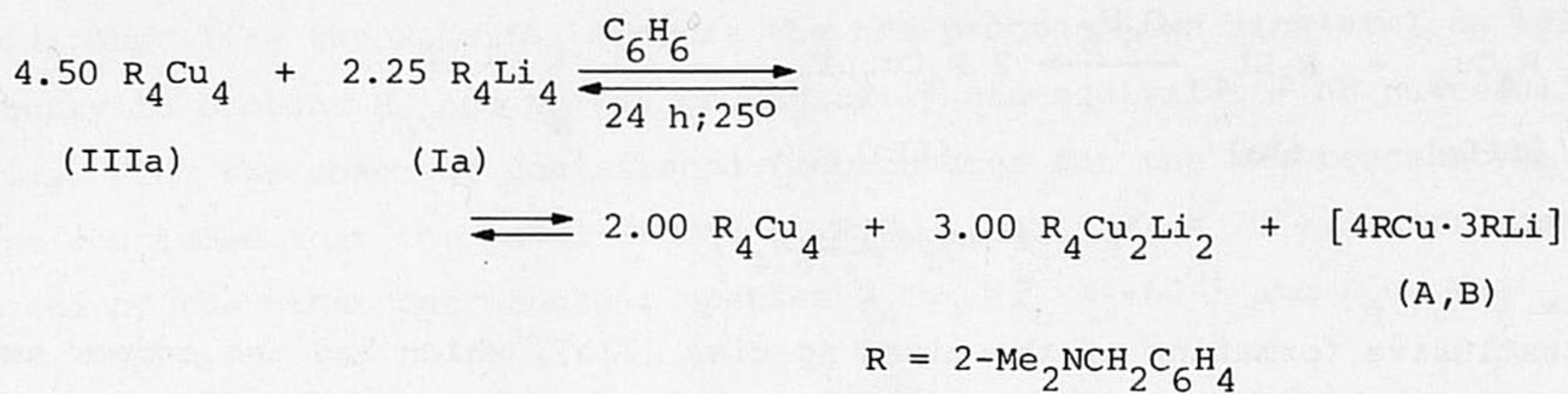


Most probably the absence of any exchange between  $R_4Li_4$  and  $R_4Cu_2Li_2$  accounts for the high purity in which the latter compound could be isolated.

*c. Exchange between  $R_4Cu_4$  (IIIa) and  $R_4Cu_2Li_2$  (IIa).* The 2/1 reaction of benzene-soluble  $R_4Cu_4$  (IIIa) with benzene-insoluble  $R_4Li_4$  (Ia) afforded a clear solution. According to NMR spectroscopy both  $R_4Cu_4$  and  $R_4Cu_2Li_2$  (IIa), together with two other unknown species A and B (see Fig. 5; resonances marked with A and B), were present in solution. The area ratios of the respective  $CH_2$ -resonance patterns pointed to the following equilibrium mixture\*:

\*A similar spectrum was obtained for the product  $R'_5Cu_3Li_2$  mentioned on p. 103. ( $R' = 5-Me-2-Me_2NCH_2C_6H_3$ ).





When the solution was heated to  $80^\circ$  the spectrum shown in Fig. 5 was obtained.  $\text{R}_4\text{Cu}_4$  is still present whereas the  $\text{CH}_3$  and  $\text{CH}_2$  patterns belonging to A, B and

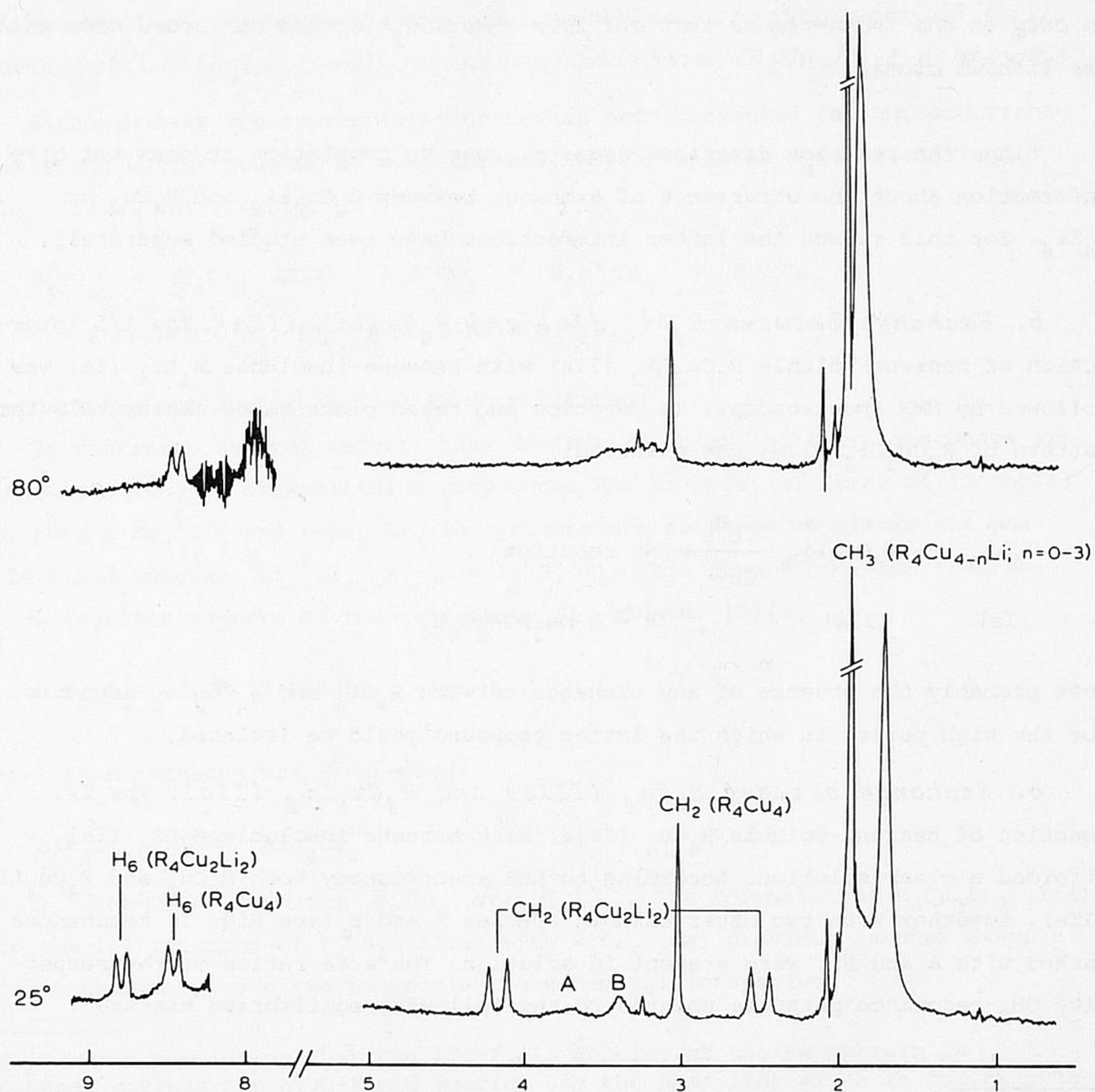


Fig. 5.  $^1\text{H}$  NMR spectra ( $\delta$  ppm) of the 1/1 mixture of  $\text{R}_4\text{Cu}_4$  (IIIa) and  $\text{R}_4\text{Cu}_2\text{Li}_2$  (IIa) in  $\text{C}_6\text{H}_6$ . See text.







Dissociation of a tetramer into two dimeric intermediates necessarily involves rupture of the rather stable phenyl-bridged bond. In pathway (i) two different dimers recombine to a new tetrameric species while in (ii) the dimeric intermediate recombines with a tetrameric species yielding a hexanuclear intermediate which undergoes subsequent bond rupture to give a dimer and a new tetrameric species.

In the associative pathway (iii) rupture of the electron-deficient  $\text{ArCu}_2$ - or  $\text{ArCuLi}$ -bond is not necessary because this pathway involves an octameric species  $\text{R}_8\text{Cu}_{8-n}\text{Li}_n$ . In this octamer the multicenter-bonded aryl groups are mobile; they can change edges of the central  $\text{Cu}_{8-n}\text{Li}_n$ -cube without a total bond rupture, see Fig. 6. In other words (iii) may provide a low-energy pathway for

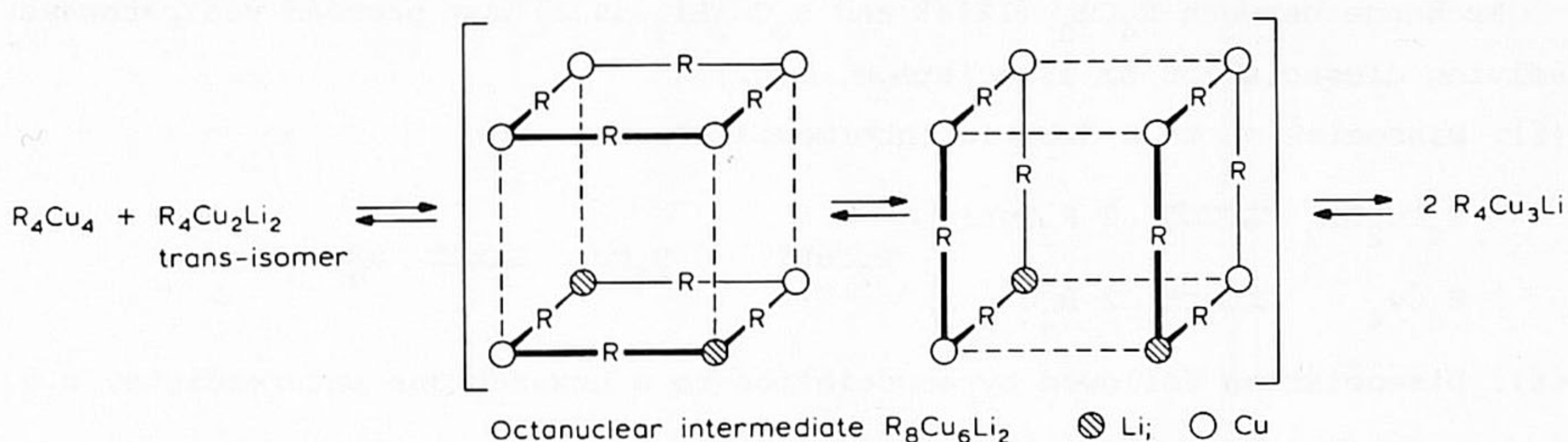


Fig. 6. Schematic representation of an interaggregate exchange between  $\text{R}_4\text{Cu}_4$  and  $\text{R}_4\text{Cu}_2\text{Li}_2$  (*trans*) via an associative pathway involving an octanuclear intermediate  $\text{R}_8\text{Cu}_6\text{Li}_2$ .

exchange. Moreover, the formation of both mixed species  $\text{R}_4\text{Cu}_3\text{Li}$  and  $\text{R}_4\text{CuLi}_3$  can be easily explained by this associative mechanism. In (i) and (ii) the formation of the latter species must occur via the less stable *cis*-isomer of  $\text{R}_4\text{Cu}_2\text{Li}_2$ .

Finally it must be emphasized that exchange between the various aggregates is strongly influenced by the presence of the built-in ligand. The tendency of the  $\text{Me}_2\text{NCH}_2$  ligand to form coordination-bonds with lithium rather than with copper strongly influences the product ratio in the equilibrium mixture at room temperature. At higher temperatures this coordinative interaction is less important, i.e. also the mixed species are more probable.

## EXPERIMENTAL

### Introduction

Valuable assistance in the experimental work was lent by Mr. C.A. Schaap.  $^1\text{H}$  NMR spectra, which were run by Mrs. L. van der Grift-Veldstra, Miss T. Volp and Mr. J.W. Marsman, were recorded on a Varian Associates HA-100 NMR



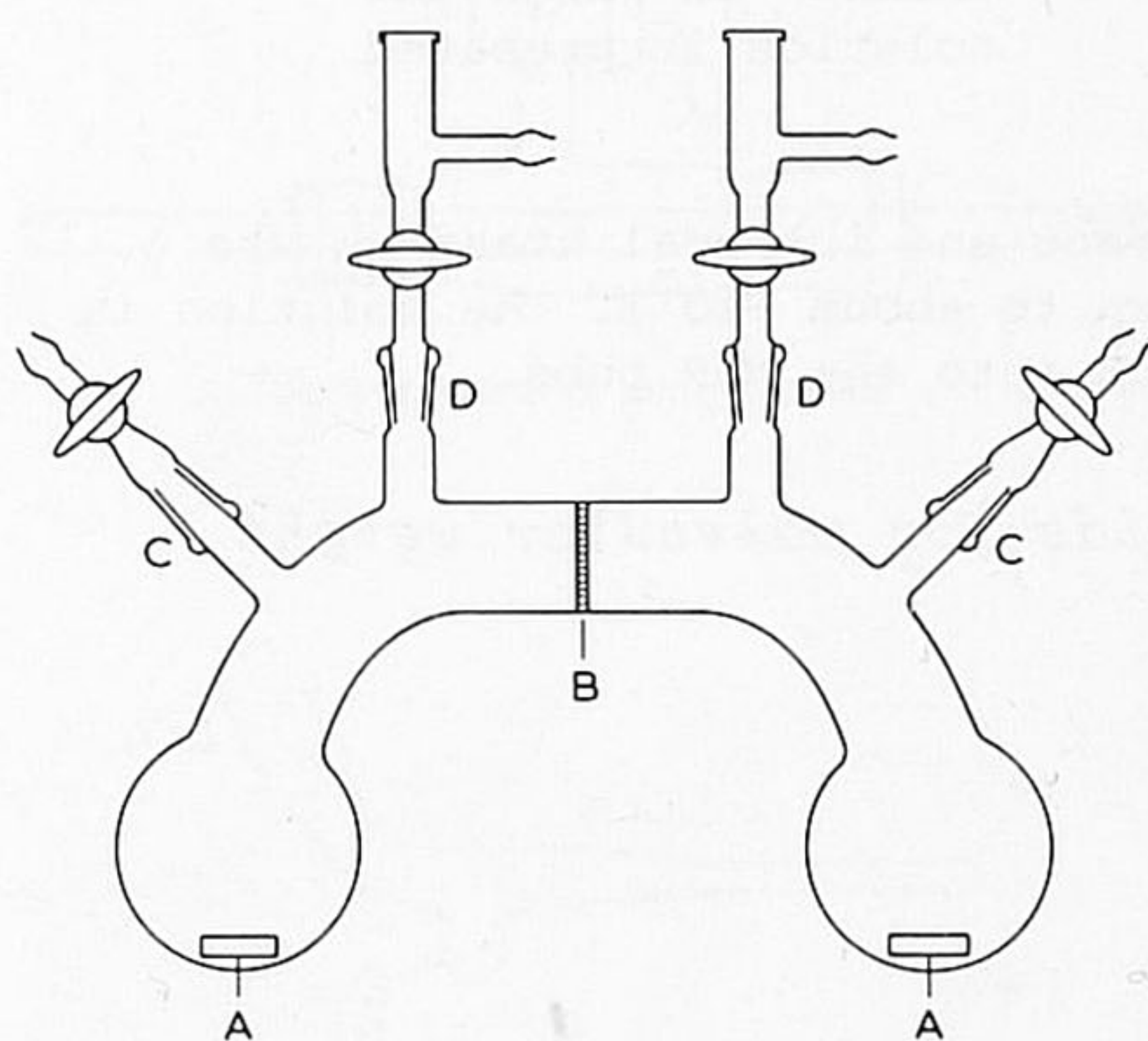
spectrometer.  $^{13}\text{C}$  NMR spectra were recorded by Mr. J.P.C.M. van Dongen and Dr. M.J.A. de Bie using a Varian XL-100/15 NMR spectrometer. IR spectra, which were run by Mrs. H. de Ridder-Alberda and Mrs. C.M. Bijlsma-Kreuger, were recorded on a Grubb-Parsons Spectromaster, unless stated otherwise. Molecular weight determinations were made by Miss E.Ch.Th. Gevers, Mrs. H. de Ridder-Alberda and Mrs. C.M. Bijlsma-Kreuger. Thermogravimetric analyses were kindly performed by Mr. A. Broersma at the Laboratory for Analytical Chemistry, State University, Utrecht, under supervision of Dr. A.H. Verdonk. Mass spectra were recorded on an AEI-MS 9 mass spectrometer by Mr. C. Versluis at the Laboratory for Analytical Chemistry, State University, Utrecht, under supervision of Dr. W. Heerma and by Mr. A. Kiewiet at the Laboratory for Organic Chemistry, State University, Groningen. Elemental analyses were carried out under supervision of Mr. W.J. Buis at the Analytical Department of the Institute for Organic Chemistry TNO, Utrecht.

### *General procedures, apparatus and reaction conditions*

All reactions were performed in an atmosphere of dry oxygen-free nitrogen. Solvents, which were handled by the syringe technique, were carefully purified, dried and distilled before use under nitrogen.

Manipulations were carried out using bench-top procedures. An inert gas atmosphere in the apparatus was maintained by connecting the apparatus fitted with inlets with a combined vacuum-inert gas system. Before each reaction the apparatus was filled with inert gas by three vacuum-inert gas cycles. Various examples of special glassware which proved to be useful during the synthetic work described in this thesis will be given below. They were assembled by Messrs. W.C. Helsdingen and W. van Neerbos.

### *Apparatus for extraction and for recrystallization of solids.*

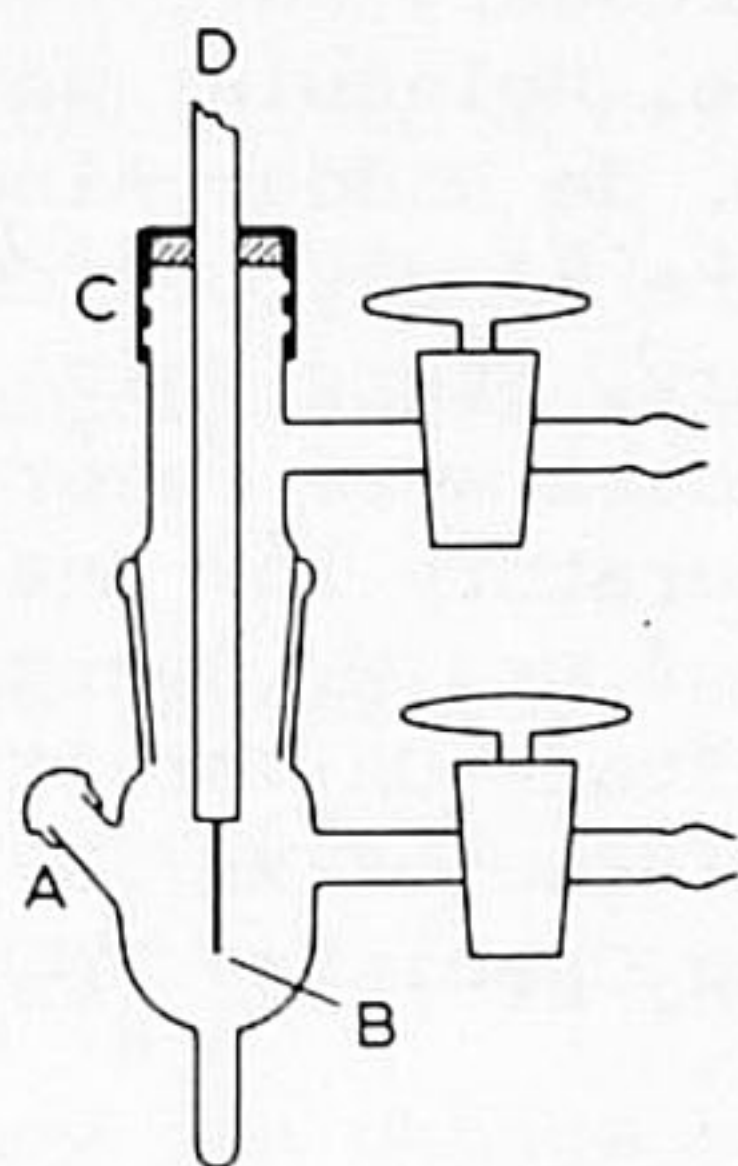


- A, magnetic stirring bars
- B, glass frit
- C, connection (B 14) for the introduction or removal of solids
- D, septum holders for the introduction or removal of solvent (via syringe)

Crude product and solvent are placed in the left bulb. By tilting the apparatus the (hot) solution is decanted over filter B into the right bulb. After the product has crystallized the mother liquor is transferred back into the left bulb. A second crystallization involves condensation at low pressure of an appropriate amount of solvent from the left into the right bulb.



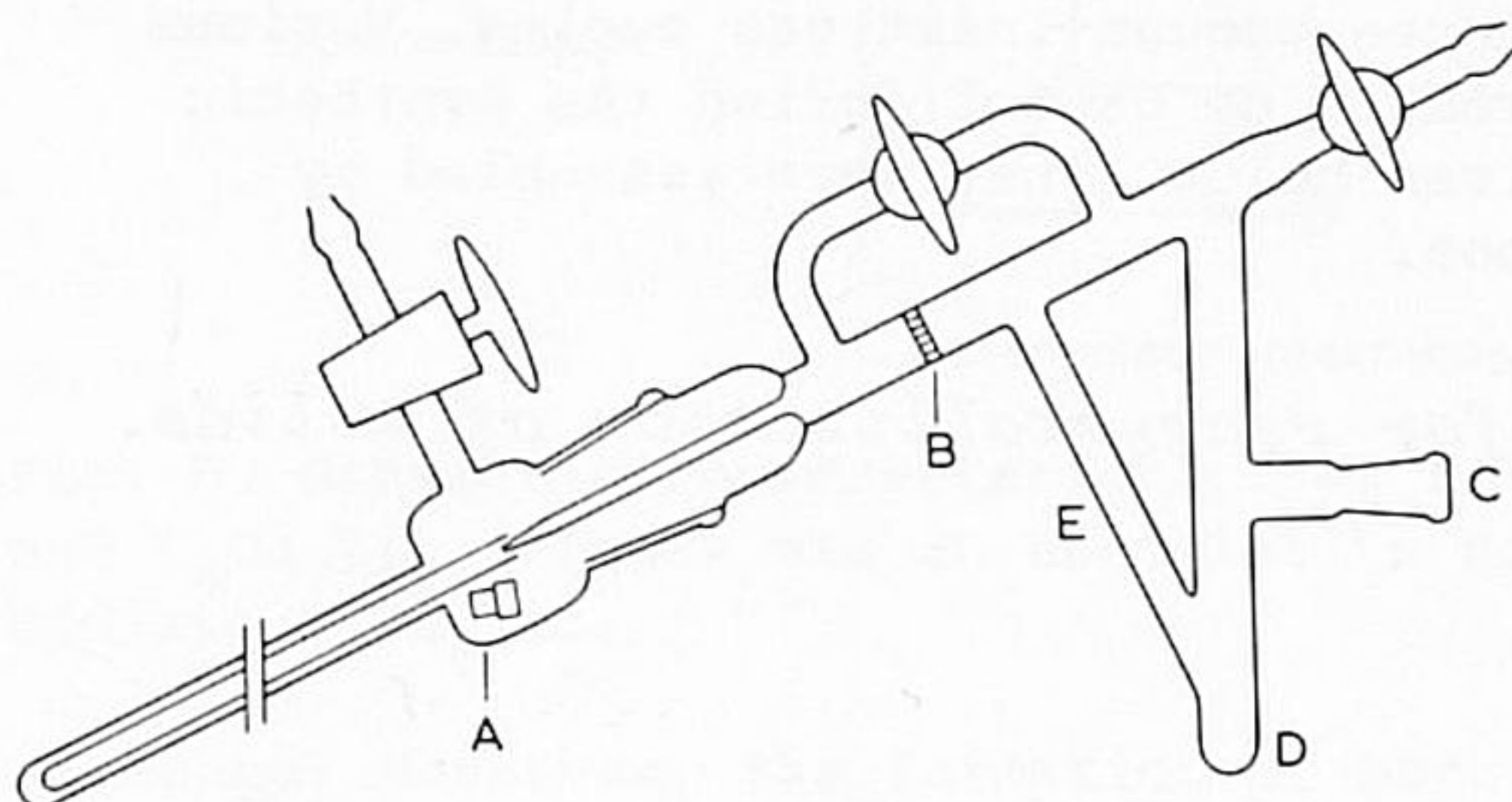
*Apparatus for sampling a MS-probe.*



- A, septum holder
- B, tip of the probe
- C, screw cap through which the probe holder is introduced
- D, MS-probe

Through the septum the tip of the probe can be sampled using a syringe. The solvent is removed by evacuating the apparatus.

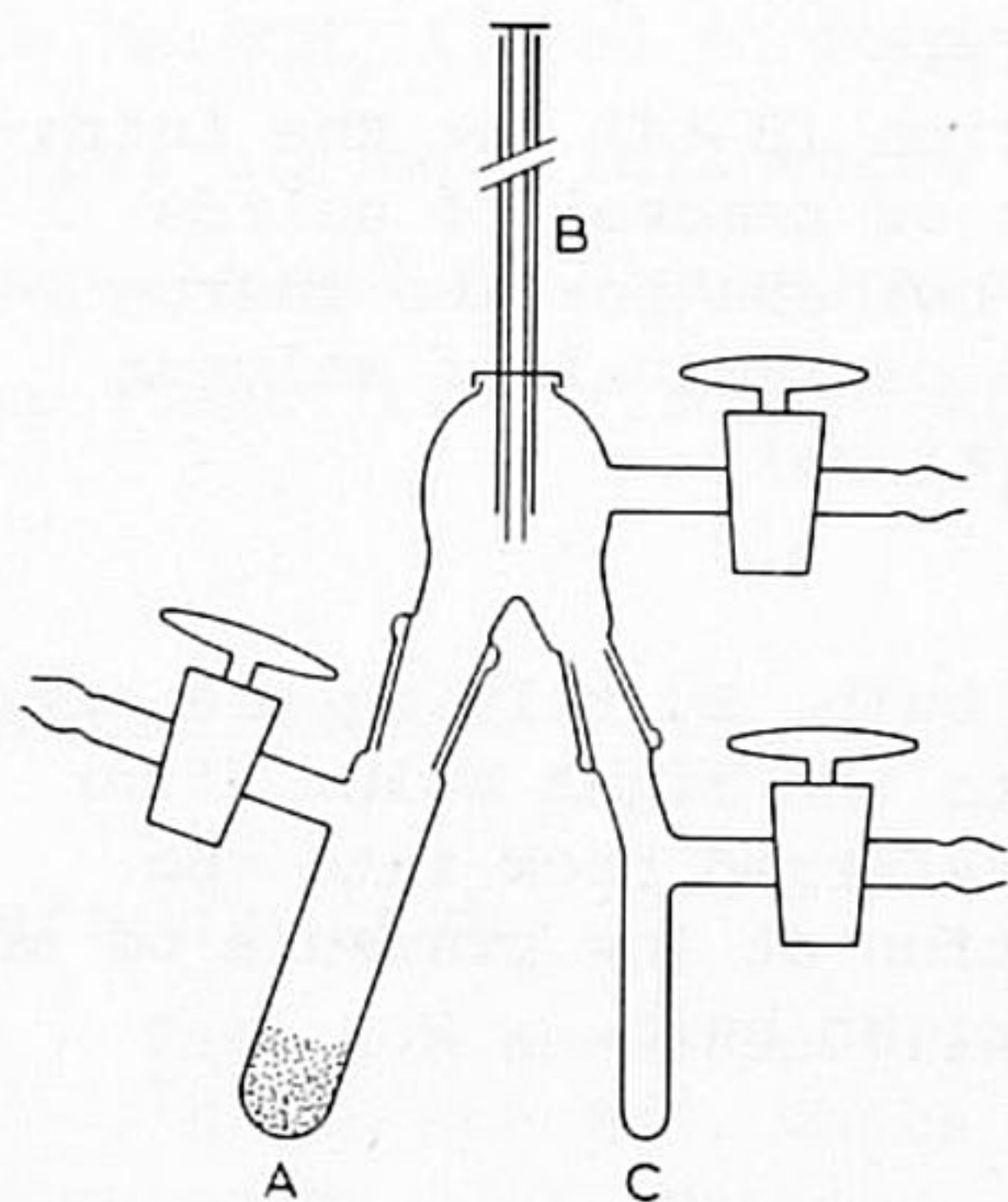
*Apparatus for the preparation of NMR solutions.*



- A, holder for the NMR tube
- B, glass frit
- C, connection through which the solid is introduced
- D, chamber in which the solution is prepared

Solid is introduced into D (via C). Solvent and internal standard are distilled directly (via C) into D (cooled-down to about  $-20^{\circ}$ ). The solution is transferred from D via tube E and glass frit B into the NMR tube.

*Apparatus for the sampling of solids for molecular weight determinations.*

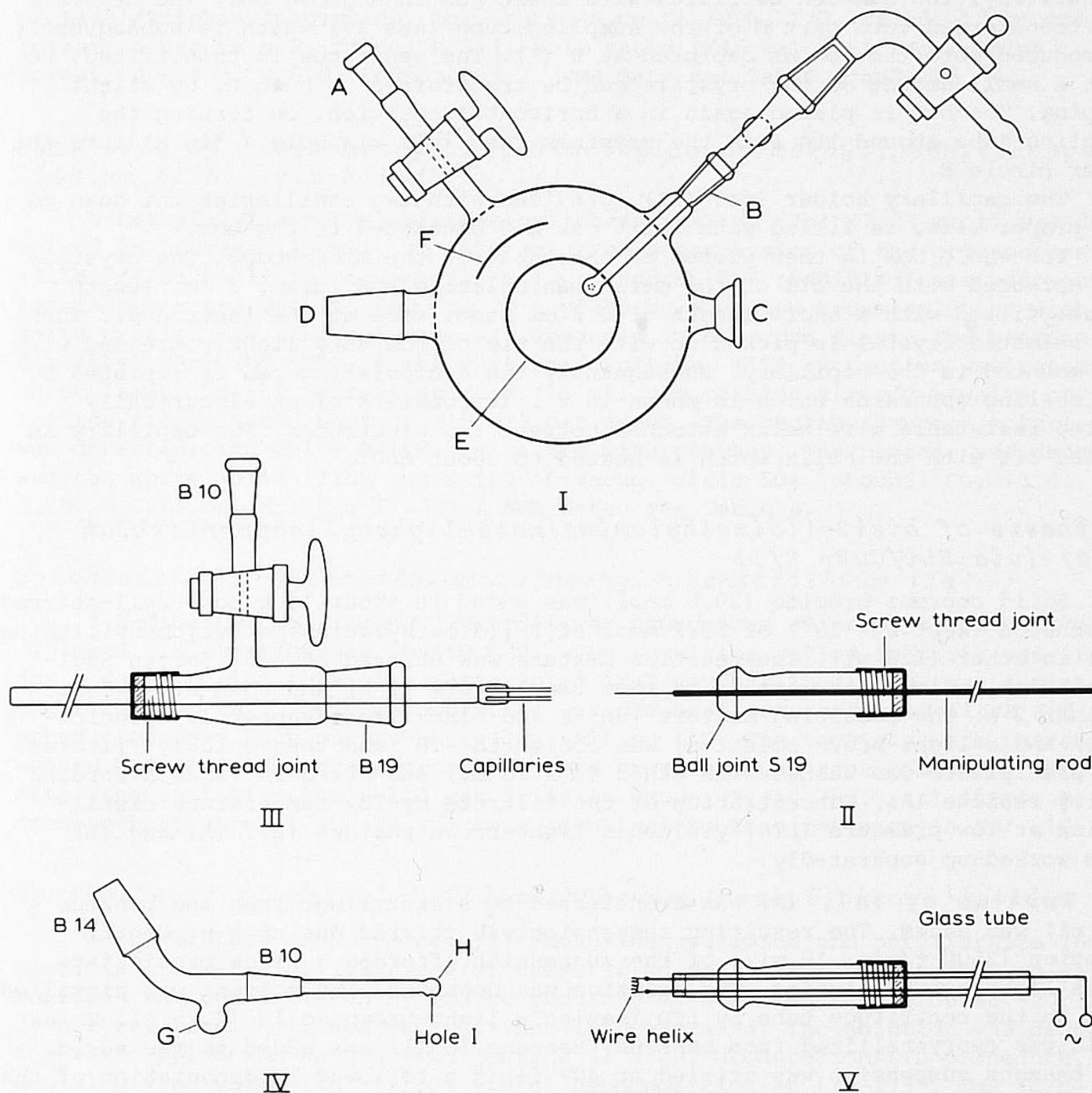


- A, container
- B, glass tube containing a glass plunger
- C, sample holder



Glass tube B is dipped into the solid in A. By pressing down the glass plunger a pill is formed. Then the glass tube is inserted in the sample holder C and the pill pressed out. The sample holder is closed with a rubber stopper and weighed. Subsequently the pill is transferred to the solution in which the molecular weight determination is carried out by connecting sample holder C with the molecular weight apparatus.

*Apparatus for sampling air and moisture sensitive single crystals for X-ray analysis (with Dr. J. Boersma).*



The main part of the apparatus (see I) [12], consists of a flat cylindrical box (internal diameter 8 cm, internal height 3 cm; parallel 2 mm glass end plates cemented with epoxy cement), which is placed on the table of a binocular polarising microscope with a recommended magnification of 6 to 25 times. Outlets are fitted on the vertical wall of the cylinder. These are A, connection to a



combined inert gas-vacuum system; B, B 10 outer joint through which a sampling tube (see IV) can be introduced; C, S 19 outer ball joint which connects to the manipulating rod (see II); D, B 19 inner joint connecting to the capillary holder (see III). Inside the box a cylindrical rim E (height 1 mm) is cemented on the centre of the bottom plate in order to keep the crystals within the reach of the manipulation rod and capillary holder. Screen F is placed before the inert gas inlet to prevent the crystals from being blown away when one of the other connections is opened.

The course of the sampling procedure is as follows. The box, without sampling tube and capillary holders, is flushed thoroughly with inert gas. Alternatively, the box can be filled with inert gas in a glove box. The crystals are transferred into part G of the sampling tube (see IV) which is subsequently introduced into the box as depicted at B (I). The apparatus is then tilted, so that a small amount of the crystals can be transferred to bulb H, by slight tapping. The box is placed again in a horizontal position. On turning the sampling tube around its axis the crystals then fall via hole I (in H) into the inner circle E.

The capillary holder (see III), provided with two capillaries cut down to the proper size, is filled with inert gas and connected to the box.

The whole box is then placed on the table of the microscope. The crystals are selected with the aid of the metal manipulating rod (diam. 3 mm, length 15 cm; fitted with a short length of 0.2 mm steel wire at the inner end). Then the selected crystal is picked up with the tip of the very lightly greased wire and mounted in the capillary. Subsequently the manipulating rod is replaced by the sealing apparatus which is shown in V. It consists of an electrically heated resistance wire helix attached between two electrodes. The capillary is sealed off with the helix which is heated to about 600°.

#### *Synthesis of bis{2-[(dimethylamino)methyl]phenyl}copperlithium (IIa) (via RLi/CuBr 2/1)*

Solid cuprous bromide (29.6 mmol) was added in about 1 $\frac{3}{4}$  h to a well-stirred suspension (kept at -20°) of 59.2 mmol of 2-[(dimethylamino)methyl]phenyllithium (Ia) in ether (120 ml). The reaction mixture was stirred at -20° for an additional 1 h, allowed to warm-up to room temperature (1 h) and then stirred for another 2 h. The resulting mixture [white and black (see Chapter IV) precipitates and a light-brown solution] was cooled to -78° and then quickly filtered. The precipitate was washed with ether (3 x 20 ml) and dried in vacuo affording a grey residue (A). Concentration of the filtrate by low temperature distillation at low pressure (LTD) yielded a light-brown residue (B). (A) and (B) were worked-up separately.

*Work-up of (A).* (A) was transferred to a centrifuge tube and benzene (60 ml) was added. The resulting suspension was stirred during  $\frac{1}{2}$  h. Centrifugation (2500 r/min; 10 min) of the suspension afforded a black precipitate and a light-brown solution. The solution was decanted. The solvent was distilled back in the centrifuge tube by LTD leaving a light-brown solid (4.25 g). This solid was recrystallized from benzene. Benzene (6 ml) was added to the solid. The benzene suspension was stirred at 40° for  $\frac{1}{2}$  h followed by decantation of the benzene solution in a second flask. The benzene was distilled back by LTD leaving an almost white residue (C). The whole procedure (stirring at 40°, decantation, back-distillation by LTD) was repeated 3 times. The white solid (C) was dissolved at 40° in benzene (about 14 ml). Pentane (about 20 ml) was added until cloudiness appeared. The resulting solution was slowly cooled to 4° affording white crystals of (IIa). The solution was decanted and the crystals washed with pentane affording white crystalline (IIa) in 11% yield. (Found: Cu, 18.9. C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>CuLi calcd.: Cu, 18.75%.)



From the benzene/pentane solution another portion of almost pure (IIa) (22% yield) was isolated.

*Work-up of (B).* Residue (B) was extracted with benzene (via the centrifugation procedure, see above) affording a white, benzene-insoluble residue (quantitative amount of LiBr). The benzene extract was concentrated by LTD affording a white sticky residue. Extraction of the residue with pentane yielded almost pure (IIa). Recrystallization afforded white crystalline (IIa) in 18% yield. (Found: Cu, 18.8.  $C_{18}H_{24}N_2CuLi$  calcd.: Cu, 18.75%.) Mol.wt.\* (cryometric in benzene): 702, 720 ( $\bar{n}$  2.10); calcd. for  $R_2CuLi$ : 338.5. Mol.wt. (ebulliometric in benzene): 623, 646 ( $\bar{n}$  1.88). Mol.wt. (cryometric in benzene) of (IIa)/triphenylphosphine: mol. ratio  $R_4Cu_2Li_2/PPh_3$  1/2, calcd. if no complex formation occurs  $n$  3; found:  $n$  3.1. Mol. ratio 1/4, calcd. if no complex formation occurs  $n$  5.0; found:  $n$  5.2. NMR data see Table 4 and Fig. 4.

*Synthesis of bis{5-methyl-2-[(dimethylamino)methyl]phenyl}copperlithium (IIb) (via  $R'Li/R'Cu$  1/1)*

5-Methyl-2-[(dimethylamino)methyl]phenyllithium (Ib) (7.33 mmol) was dissolved in benzene (15 ml). To this solution a suspension of the organocopper (IIb) (7.33 mmol) in benzene (15 ml) was added. The resulting heterogeneous reaction mixture was stirred for 24 h yielding a yellow-brown solution with a white precipitate. The solution was decanted in a second flask. The benzene was distilled back (by LTD) to the white precipitate. This extraction was repeated three times. To the benzene extract (15 ml), containing already a white crystalline precipitate, pentane (15 ml) was added. The pentane/benzene solution was decanted; the white solid was washed with pentane. The pentane was decanted and the white solid (IIb) was dried in vacuo. Yield 50%. (Found: Cu, 18.4.  $C_{20}H_{28}N_2CuLi$  calcd.: Cu, 17.32%.) NMR data, see Table 4.

*Synthesis of 2-[(dimethylamino)methyl]phenyllithium (Ia)*

*N,N*-dimethylbenzylamine (20 mmol) was added to a solution of butyllithium (20 mmol) in ether/hexane (65/10 v/v). The resulting yellow solution was stirred for 3 days. During this time white solid (Ia) crystallized which was isolated in the following way. The ether solution was decanted into a second flask and the ether condensed back on the white crystals by LTD. The crystals were thoroughly washed and the ether again decanted. This procedure was repeated three times. After the last time the solid was dried in vacuo. Yield 78%. (Ia) starts to decompose at about 129°. IR spectrum identical to that reported in ref. 10.

*Synthesis of {5-methyl-2-[(dimethylamino)methyl]phenyl}lithium (Ib)*

A 1/1 mixture of *N,N*-dimethyl(4-methylbenzyl)amine and butyllithium (60 mmol) in ether/hexane (125/32 v/v) was stirred for 3 days. The resulting yellow solution was concentrated by LTD to about 30 ml and then set aside at -20° for 24 h. Very finely divided crystalline (Ib) separated. The solution was decanted. The white solid was washed with pentane (3 x 20, decantation/LTD procedure, see above) giving white (Ib) in 80% yield. Decomposition at 170-175°. NMR ( $C_6D_6$ , TMS internal,  $\delta$  ppm); 1.31 and 1.86 (2 x s,  $NCH_3$ , 6H), 2.31 (s, 5- $CH_3$ , 3H), 2.93 and 4.49 (2 x d,  $J_{gem} \approx 13$  Hz,  $NCH_2$ , 2H), 7.01 (2 x d,  $J_{3,4} \approx 7$  Hz,  $J_{4,6} \approx 2$  Hz, 1 H), 7.05 (d,  $H_3$ , 1 H) and 8.17 (d, 1 H) (see also Fig. 4).

\*For experimental details see p. 118.



## REFERENCES

- 1 J.F.NORMANT, *Synthesis*, (1972) 63.
- 2 G.H.POSNER, *Org.Reactions*, 19 (1972) 1.
- 3 G.VAN KOTEN and J.G.NOLTES, *J.Chem.Soc., Chem.Comm.*, (1972) 940.
- 4 A.J.LEUSINK, G.VAN KOTEN, J.W.MARSMAN and J.G.NOLTES, *J.Organometal.Chem.*, 55 (1973) 419.
- 5 M.SCHLOSSER, *Struktur und Reaktivität polarer Organometalle*, Springer, Berlin, 1973, p. 11 and references cited therein.
- 6 H.O.HOUSE and W.F.FISHER, Jr., *J.Org.Chem.*, 33 (1968) 949.
- 7 G.COSTA, A.CAMUS, L.GATTI and N.MARSICH, *J.Organometal.Chem.*, 5 (1966) 568.
- 8 A.CAMUS and N.MARSICH, *J.Organometal.Chem.*, 14 (1968) 441.
- 9 L.M.SEITZ and R.MADL, *J.Organometal.Chem.*, 34 (1972) 415.
- 10 C.T.VISWANATHAN and C.A.WILKIE, *J.Organometal.Chem.*, 54 (1973) 1.
- 11 M.Y.DARENSBOURG, B.Y.KIMURA, G.E.HARTWELL and T.L.BROWN, *J.Amer.Chem.Soc.*, 92 (1970) 1236.
- 12 G.VAN KOTEN and J.BOERSMA, *Chem.Ind. (London)*, (1973) 1117.



## CHAPTER X

### SOME REMARKS CONCERNING THE SYNTHESIS OF ORGANOCOPPER COMPOUNDS AND THE STRUCTURE-REACTIVITY RELATIONSHIP FOR ORGANOCOPPER INTERMEDIATES IN ORGANIC SYNTHESIS

#### INTRODUCTION

Organocopper reagents used in organic synthesis [1] or postulated to occur as transient intermediates in several types of reactions [2] are generally represented by formulae such as  $\text{RCu}$ ,  $\text{R}_2\text{CuLi}$  or  $\text{RCu}\cdot\text{MX}$ . However, various studies [1, 3], in which attention had been given to the rôle of the organocopper reagents in organic synthesis, already contained indications that this representation is far removed from reality. Although the nature of the organocopper reagents had not been studied in depth, these investigations substantiated that the reactivity of organocopper compounds is strongly dependent on their method of preparation, the presence of metal salts, on the nature of the solvent and of the ligands used. Such results, however, can not be evaluated in the absence of basic knowledge concerning the organocopper compounds involved (e.g., aggregation state, reactivity towards metal halides and ligands, bonding relations).

In this Chapter an attempt has been made to place published data and the results presented in this thesis into a broader perspective.

#### THE SYNTHESIS OF ORGANOCOPPER COMPOUNDS

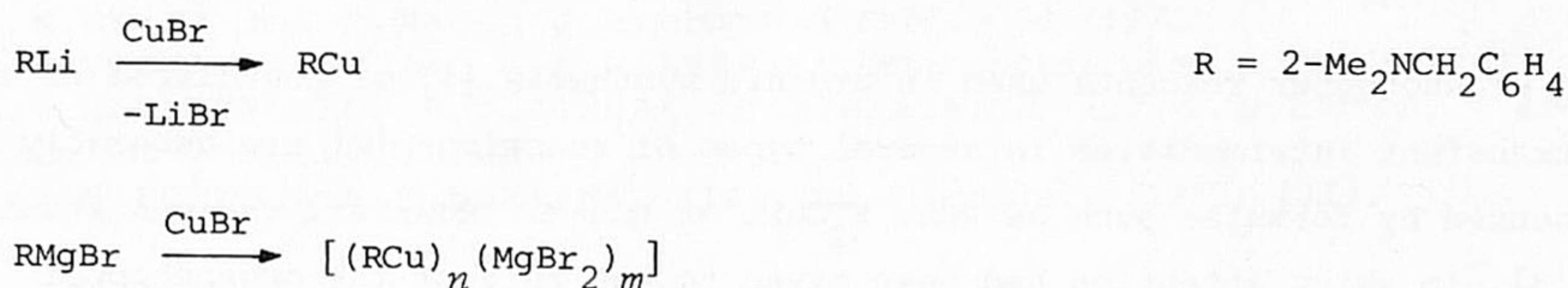
*The reaction of arylating reagents with copper(I) salts.* In the reactions of arylating reagents  $\text{RM}$  ( $\text{RLi}$ ,  $\text{R}_2\text{Zn}$ ,  $\text{RMgBr}$  and  $\text{R}_2\text{Mg}$ ) with cuprous halides transmetalation occurs:



No special difficulties arise when using organolithium reagents. Lithium halides formed are separable both from soluble and insoluble arylcopper compounds (cf. Ch. II and VI). However, when other arylating reagents are used complexation of the organocopper compound with metal halides formed is often a complicating factor. E.g., a complicated situation exists when using Grignard



reagents. Whereas a series of perfluoroarylcopper compounds have been isolated in the pure state [4], the synthesis of phenylcopper via the Grignard route failed. Costa et al. [5] found that the reaction of phenylmagnesium bromide with cuprous bromide afforded a complex formulated as  $5\text{CuBr}\cdot 2\text{MgPh}_2\cdot 7\text{THF}$  instead of phenylcopper. We have made similar observations. Whereas  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  was successfully isolated from the  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Li}/\text{CuBr}$  reaction (Ch. II), products with varying  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4/\text{Mg}/\text{Cu}/\text{Br}$  ratios were isolated when the Grignard route was followed [6]:



A second complicating factor, which so far has not been recognized in the literature, is the rôle of the copper halide during the formation of the organocopper compound. On several occasions it has been pointed out in this thesis that arylcopper compounds are capable of forming complexes with copper halides. This complex formation dictates the order of addition of the arylating reagents and the cuprous halide, viz.:

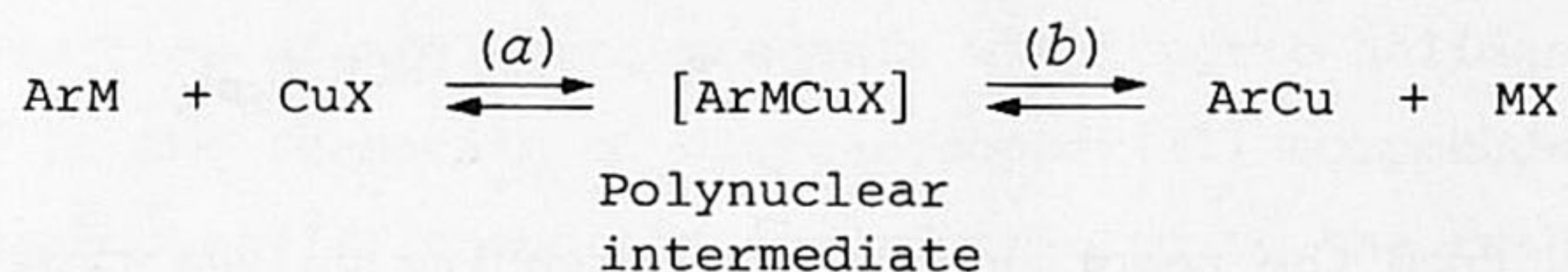
*i.*  $2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu}$  can only be isolated in the pure state when the organolithium reagent is added to the cuprous halide. As has been discussed in Ch. VI this reaction proceeds via the thermally stable, hydrocarbon soluble 2/1 complex of  $2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu}$  with copper halide (e.g.,  $\text{R}_4\text{Cu}_6\text{Br}_2$ ).

*ii.* In the synthesis of  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  cuprous bromide is inactivated for further reaction as a result of the formation of a highly insoluble 1/1 organocopper-cuprous bromide complex (Ch. IV). Therefore, cuprous bromide must be added to the organolithium reagent to allow the conversion of the organocopper-cuprous bromide complexes into the stable, ether-soluble bis(organocopper)-lithium compound  $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_2\text{Li}_2$  which then reacts further with cuprous bromide to  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  (see Ch. IV).

In our opinion the complex formation of organocopper compounds with metal halides and that with cuprous halides is basically similar in nature. This is based on the result of the structural investigation of  $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Br}_2$  (Ch. VII) which clearly shows that complex formation of polymeric  $2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu}$  with  $\text{CuBr}$  results in the formation of a new hexanuclear copper cluster compound. This interaction may illustrate what happens in transmetalation reactions



in which either organocopper compounds and metal halides (*b*) or copper(I) salts and arylating reagents (*a*) are involved, viz.:



In these reactions mixed copper-metal clusters are postulated as intermediates which either are stable and thus can be isolated or are of low stability and decompose into the transmetalation products.

In the reaction of cuprous halides with organolithium reagents the organocopper compound can be isolated when either RCu or LiX have low solubility in the reaction medium (equilibrium *b* shifts to the right). Organocopper compounds will enter into conjugate addition reactions with  $\alpha, \beta$ -unsaturated ketones only in the presence of lithium halides [1, 3]. Polynuclear mixed compounds [ArLiCuX] may be postulated to be the reactive species in these reactions\* (see next section).

De-Pasquale and Tamborski have shown that coordinating solvents have considerable influence on the reactivity of mixtures of pentafluorophenylcopper and magnesium halides towards a variety of substrates (alkyl and aryl halides, H<sub>2</sub>O, CO<sub>2</sub>, etc.) [7]. This observation can be explained on the basis of the existence in solution of polynuclear mixed Mg-Cu intermediates [C<sub>6</sub>F<sub>5</sub>CuMgX<sub>2</sub>] which are in equilibrium with their respective transmetalation products C<sub>6</sub>F<sub>5</sub>Cu/MgX<sub>2</sub> and C<sub>6</sub>F<sub>5</sub>MgX/CuX, respectively. Solvents like dioxane, which remove the magnesium halides from the solution in the form of insoluble complexes, shift the equilibria (*a*) and (*b*) to the right, thus causing a change in the concentration of the various reactive organometallic species present in solution. Only, if the MgX<sub>2</sub> salts are precipitated quantitatively and the organocopper compound is soluble RCu compounds can be isolated in the pure state [cf. the isolation of perfluorophenylcopper compounds [4] and of 2,2'-R<sub>2</sub>Cu<sub>n</sub> (Ch. V)].

The influence of the solvent on the type of polynuclear intermediate present is further illustrated by the results of the 1/1 reaction of 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cu with magnesium bromide [6].

\*Brown et al. [8] have shown that interaction of Me<sub>4</sub>Li<sub>4</sub> with LiBr resulted in the formation of an equilibrium mixture of the mixed species Me<sub>4-n</sub>Li<sub>4</sub>Br<sub>n</sub>.







are not stable\*.

*The reaction of arylating reagents with copper(II) salts.* The interaction of arylating reagents with cupric halides, in principle may give rise to the formation of diorganocopper(II) compounds. However, examples of organocopper(II) compounds are restricted to the rather exotic biscarborane-copper(II) compound  $(Et_4N)_2Cu^{II}[(B_{10}C_2H_{10})_2]_2$  [11]. It has been assumed that  $RCu^{II}X$  or  $R_2Cu^{II}$  species are formed as transient intermediates which decompose into copper(I) halides or organocopper(I) derivatives and products arising from R [12]. In the literature evidence has been presented that the group R is not generated as a free radical but that intramolecular reaction pathways are involved [13] (e.g.  $\beta$ -H abstraction when R is alkyl [13a]). However, it has not been sufficiently taken into account that organocopper and organolithium\*\* compounds are highly associated species.

We propose that in the reaction of arylating reagents with copper(II) halides innersphere activated complexes of the type  $R_nM_{n-1}M \cdots X \cdots Cu^{II}X(Cu^{II}X)_x$  (M = Cu or Li) are key intermediates (Ch. IV). In such intermediates the groups R are at close proximity so that concerted formation of an R radical by one electron-transfer reduction of  $Cu^{II}$  to  $Cu^I$  and intramolecular trapping of this radical by R-M or  $Cu^{II}-X$  bonds are possible. In this respect the formation of the intramolecular ring closure product 2,2'- $R_N$  by interaction of 2,2'-(BrMg) $_2R_N$  with  $CuCl_2$  is of interest (Ch. V).

Electron-transfer reactions of appropriate organometallic reagents with cupric halides would seem to offer useful synthetic routes to ring-closed products. A recent example is the intramolecular ring closure of  $x,x'$ -thienyl sulfides to thionothiophenes using a butyllithium- $CuCl_2$  system [14].

#### SOME ASPECTS OF THE STRUCTURE-REACTIVITY RELATIONSHIP FOR POLY-NUCLEAR ORGANOCOPPER COMPOUNDS

Although the first examples of alkyl- and arylcopper compounds were isolated already long ago, information about their structure has appeared in the

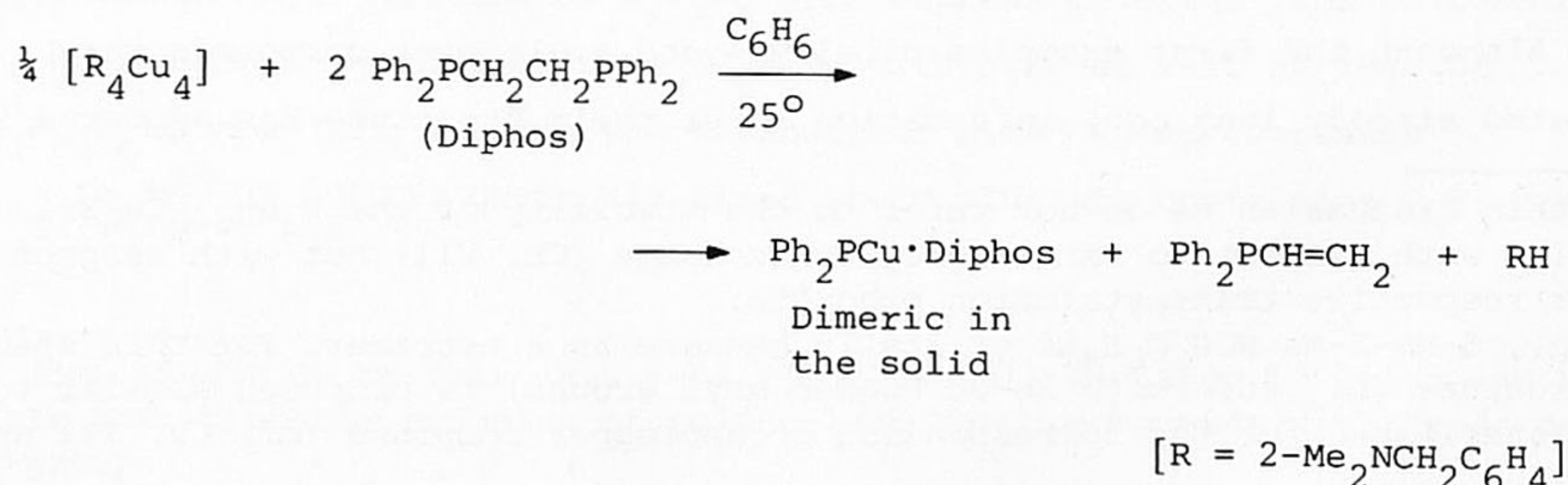
\*In this discussion we do not refer to the stability of the  $R_4Ag_{6-n}Cu_nBr_2$  species with respect to interaggregate exchange (Ch. VII) but with respect to their respective transmetalation products.

\*\*E.g., 5-Me-2-Me $_2$ NCH $_2$ C $_6$ H $_4$ Li exists in benzene as a tetramer. For this species a structure (Li $_4$  core with 2e-3c bonded aryl groups) is proposed similar to the one established for the corresponding organocopper compound (cf. Ch. III and IX).



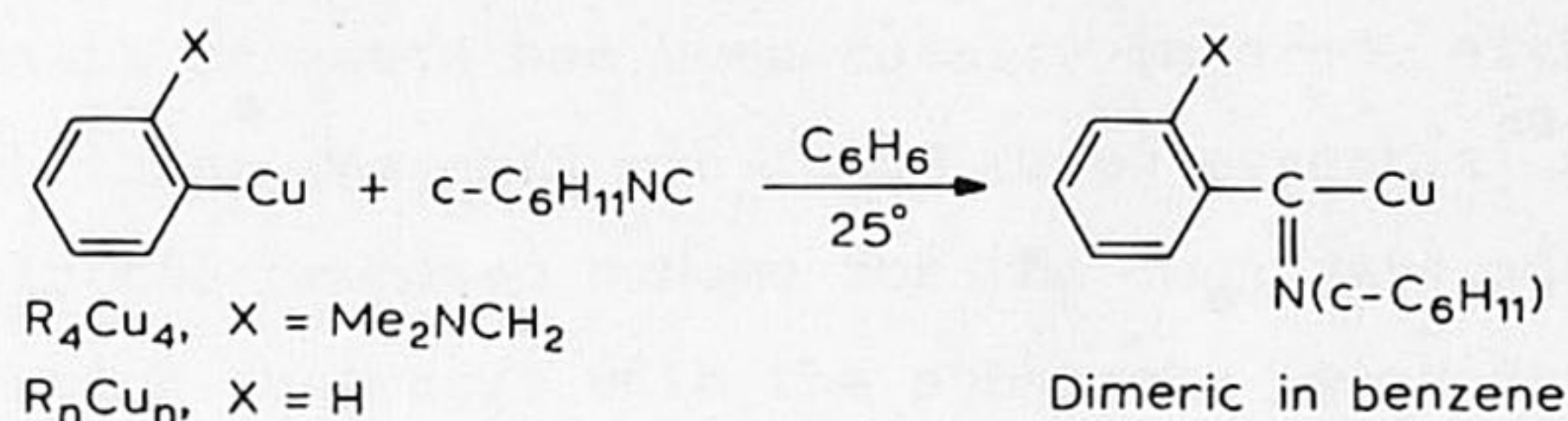
literature only during the past three years. The results obtained so far suggest that a polynuclear structure both in the solid [X-ray determinations of  $(5\text{-Me-2-Me}_2\text{NC}_6\text{H}_3)_4\text{Cu}_4$  (Ch. III),  $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Br}_2$  (Ch. VII) and of  $(\text{Me}_3\text{SiCH}_2\text{Cu})_4$  [15]] and in solution [ $(m\text{-CF}_3\text{C}_6\text{H}_4)_8\text{Cu}_8$ ,  $(o\text{-CF}_3\text{C}_6\text{H}_4)_4\text{Cu}_4$  and  $(\text{C}_6\text{F}_5)_4\text{Cu}_4$  [4],  $\text{R}_4\text{Cu}_4$  (Ch. III),  $(2,2'\text{-Cu}_2\text{R})_2$  (Ch. V),  $\text{R}_4\text{Cu}_{6-n}\text{Ag}_n\text{Br}_2$  (Ch. VIII),  $\text{R}_4\text{Cu}_2\text{Li}_2$  and  $\text{R}_4\text{Ag}_2\text{Li}_2$  (Ch. IX),  $\text{R}_4\text{R}'_2\text{Cu}_6$  (Ch. VIII) and  $(\text{Me}_3\text{SiCH}_2\text{Cu})_n$  ( $n = 4$  or  $6$ ) [16]] may be a general feature of organocopper compounds. Soluble organocopper compounds appear to have discrete polynuclear structures in which the organo groups are bonded to a closed  $\text{Cu}_n$  core ( $n = 2, 4, 6$  or  $8$ ) by  $2e-3c$  (electron deficient) bonds. Both linear and trigonal planar coordination environments around copper have been found. In this thesis the same structural features are proposed for the insoluble arylcopper compounds, which, however, have a linear (or cyclic)  $\text{Cu}_n$  chain structure (Ch. VI). The actual structure of the organocopper compounds will strongly depend on the substitution pattern of the bridging group.

Closed  $\text{Cu}_n$  structures may have considerable stability. Interaggregate exchange of groups R in  $\text{R}_4\text{Cu}_4$  (Ch. III) as well as ligand-substitution reactions of appropriate organometallics with  $\text{R}_4\text{Cu}_6\text{Br}_2$  (Ch. VII and VIII) occur with retention of the closed  $\text{Cu}_n$  structure. Moreover, even external ligands or strongly coordinating solvents may leave the copper cluster unaffected. E.g., molecular weight determinations and NMR spectroscopic data reveal that tetranuclear  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  does not form complexes with triphenylphosphine, acetonitrile or pyridine and does not break down to lower aggregates [17]. This was also found to be true for the interaction of triphenylphosphine with the bis-(organo)copperlithium compounds  $\text{R}_4\text{Cu}_2\text{Li}_2$  discussed in Chapter IX. However, the 1/1 interaction of tetranuclear  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}(\text{R}_4\text{Cu}_4)$  with 1,2-bis(diphenylphosphino)ethane (Diphos) results in a break-down of the initial  $\text{Cu}_4$  structure yielding a monomeric  $\text{RCu}\cdot\text{Diphos}$  complex, whereas addition of excess Diphos induces an unusual  $\text{C}_{\text{Alk}}-\text{P}$  bond cleavage reaction of the type shown in the following equation [17]:





In the presence of isocyanides arylcopper compounds undergo insertion reactions resulting in the formation of a novel type of organocopper compounds [18], viz.:



When discussing the reactivity of organocopper compounds it is important to keep in mind that as a result of the polynuclear structure reacting groups are in close proximity to the effect that concerted metal-carbon bond-breaking and C-C bond-formation processes are possible which would not easily occur otherwise. This applies in particular to thermal decomposition and oxidative coupling reactions. This is exemplified by the thermal decomposition of the compound  $(2,2'\text{-Cu}_2\text{R}_N)_2$  which produces exclusively the ring-closed product  $2,2'\text{-R}_N$  (Ch. V) and of the mixed-organocopper cluster compound  $\text{R}_4\text{R}'_2\text{Cu}_6$ , resulting in the exclusive formation of the mixed coupling product  $\text{RR}'$  (Ch. VIII). The specific course of such reactions can be explained on the basis of the arrangement of the ligands in the respective polynuclear compounds. Although both compounds are exceptional with regard to the rigidity of their structures their thermal decomposition patterns may provide insight into what is happening in more complex reaction mixtures where interaggregate exchange and cluster rearrangements can be expected to occur resulting in less specific thermal decomposition patterns.

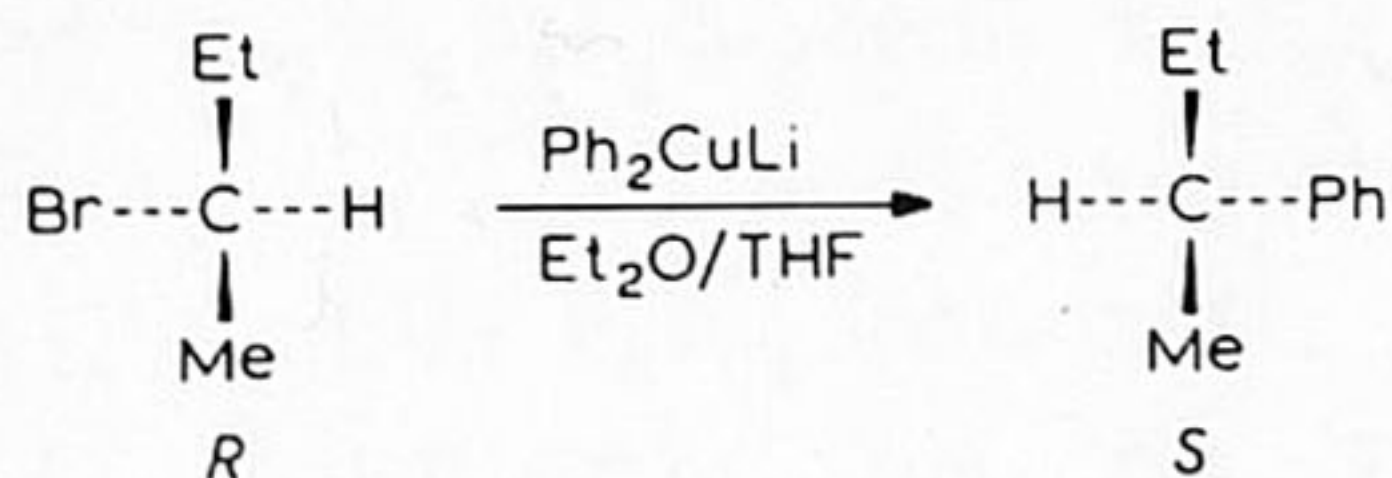
Similarly, when discussing the reactivity of bis(organo)copperlithium compounds the polynuclear character of these reagents should be taken into account. This discussion will be restricted to: *i*, the cross-coupling reaction with organic halides and *ii*, the conjugate addition reaction with  $\alpha,\beta$ -unsaturated ketones.

Organocopper compounds  $(\text{RCu})_n$  as such have limited synthetic utility in *(i)* and do not react in *(ii)* [1, 3]. However, the combination of an organocopper compound with a metal halide (e.g.,  $\text{LiX}$  or  $\text{MgX}_2$ ) or an appropriate organometallic compound (e.g.,  $\text{RLi}$  or  $\text{RMgX}$ ) leads to species readily entering into *(i)* or *(ii)* [1,3].

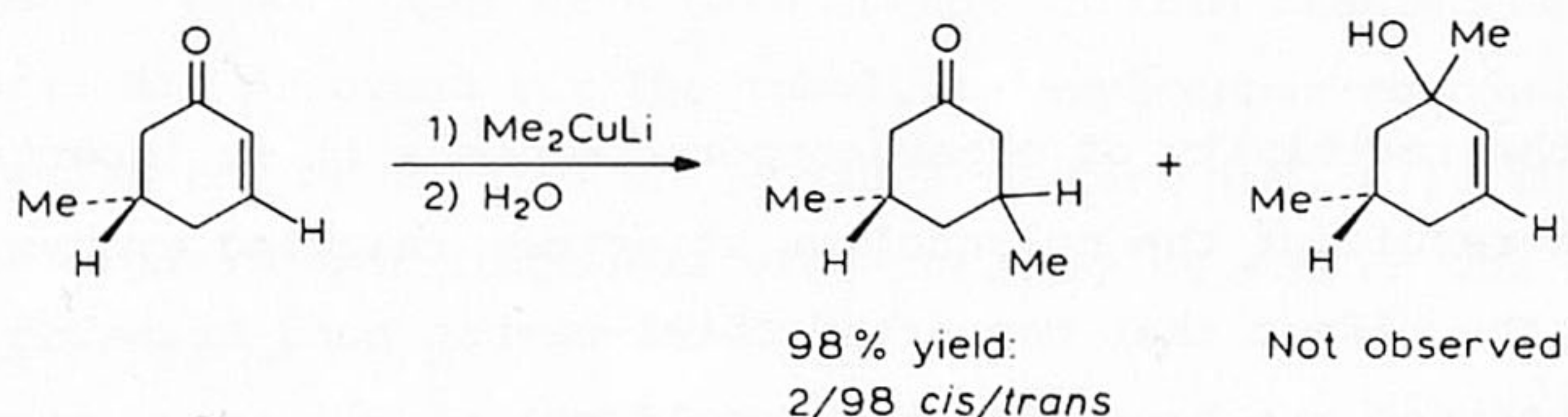
Substitution reactions of bis(organo)copperlithium compounds with alkyl



halides occur with inversion; e.g. [1c],

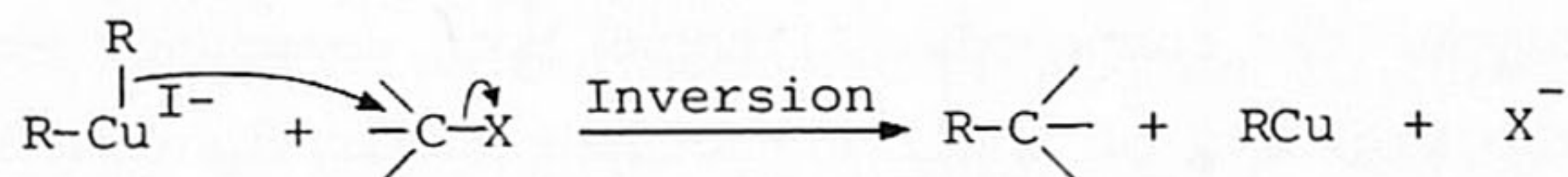


Conjugate addition reactions likewise proceed with a very high degree of stereospecificity; e.g. [1b],

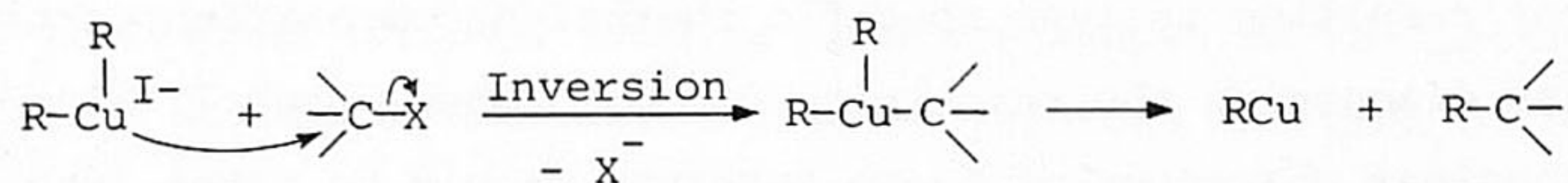


For cross-coupling reactions (i) the following mechanisms are frequently discussed [1c, 19]

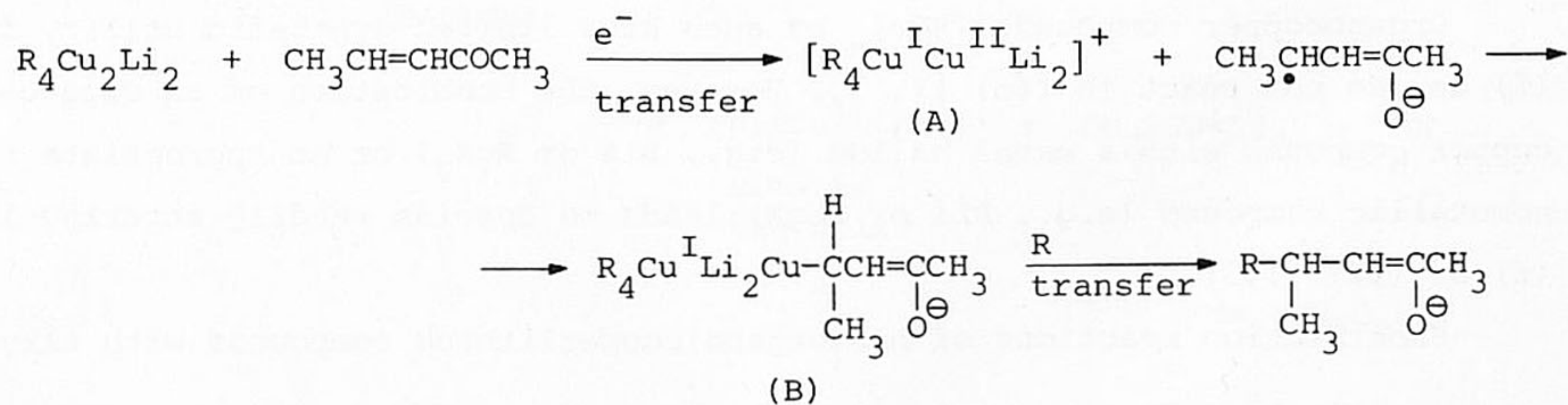
Nucleophilic attack by carbon:



Nucleophilic attack by copper:



For the conjugate addition reactions (ii) an electron-transfer mechanism has been proposed [1b]:





However, in these mechanistic discussions the fact that these compounds are polynuclear species containing electron-deficient bonded groups has not been taken into account. More surprisingly, the rôle of the lithium atom in  $R_2CuLi$  or  $RCuLiX$  reagents has been totally ignored, although the presence of  $RLi$  or  $LiX$  in these reagents was found to be essential for the reactions to occur.

In the proposed scheme for the conjugate addition (see above) the copper atom which interacts with the substrate is oxidized from  $Cu^I$  via  $Cu^{II}$  (intermediate A) to  $Cu^{III}$  (intermediate B). However, based on our results of the interaction of organocopper compounds with cupric halides (Ch. IV), one would expect that in species of the type (A) concerted intramolecular redox/C-C-coupling processes take place.

It must be assumed that the course of the reactions of bis(organo)copper-lithium compounds with organic molecules is greatly influenced by the metal-bridging capacity of the organic groups involved. In reactions of mixed-organo-copperlithium reagents  $R_tRCuLi$  in which the organic group R is an acetylide ligand [1b, 20] or a cyanide group [21] the group  $R_t$  (alkyl or aryl) is selectively transferred, whereas the  $C\equiv C-R$  or  $C\equiv N$  ligands do not participate in the reaction. The ability of these reagents to selectively transfer one ligand  $R_t$  can be easily rationalized. If, as we believe, the so-called cuprates are cluster compounds with bridging organic ligands then it is to be expected that their reactivity in cross-coupling\* and conjugate addition reactions will increase with decreasing bridging ability of the organic ligand. Thus, the tendency towards transfer will decrease in the sequence  $Alkyl > Aryl > C\equiv CR > C\equiv N$ .

As regards the rôle of the lithium or magnesium atom in conjugate addition reactions of  $R_{2n}Cu_nM_n$  or  $(RCuMX)_n$  reagents, it is postulated that the presence of these "hard" metals in the cluster is essential in that they allow coordination of the "hard" carbonyl group of the  $\alpha,\beta$ -unsaturated ketone as the first step of the reaction and that the arrangement of the ligands in the resulting complexes  $R_{2n}Cu_nM_n \cdot \text{substrate}$  or  $(RCuMX)_n \cdot \text{substrate}$  is favourable for specific C-C bond formation to take place.

House and Umen have reported [1b] that the reactivity of a series of  $\alpha,\beta$ -unsaturated ketones and esters towards  $Me_2CuLi$  correlates with the polarographic reduction potentials of these compounds. They suggest that this correlation is indicative for the electron-transfer process mentioned in the scheme above.

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\*In reactions of  $Alk_2CuLi$  compounds with aryl iodides metal-halogen exchange may constitute a serious problem [1c]. The latter reaction can be explained in terms of nucleophilic attack of the bridged  $Alk$  group on the I atom of  $ArI$ , affording  $AlkI$  and the more stable  $Aryl$  bridged  $CuLi$  cluster.



However, it would be reasonable to assume that these polarographic reduction potentials correlate with the affinity of the substrate for electrons, i.e. for the tendency to undergo nucleophilic addition at carbon. Moreover, the electrophilicity of the substrate will depend on the strength of the carbonyl-lithium coordination bond in the complex  $R_{2n}Cu_nLi_n \cdot \text{substrate}$  which we propose as an intermediate.

#### REFERENCES

- 1(a) Reviews: J.F.NORMANT, *Synthesis*, (1972) 63; G.H.POSNER, *Org.Reactions*, Vol. 19, Wiley, New York, 1972, p. 2; *ibid.*, 1974, to be published; G. BÄHR and P.BURBA, in HOUBEN-WEYL (Eds.), *Organo-Kupfer Verbindungen. Methoden der Organischen Chemie*, Vol. 13/1, 1970, p. 747.
- (b) H.O.HOUSE and W.F.FISHER Jr., *J.Org.Chem.*, 33 (1968) 949; H.O.HOUSE and M.J.UMEN, *J.Amer.Chem.Soc.*, 94 (1972) 5495; *ibid.*, 38 (1973) 38.
- (c) G.M.WHITESIDES, W.F.FISHER Jr., J.SAN FILLIPPO, R.W.BASHE and H.O.HOUSE, *J.Amer.Chem.Soc.*, 91 (1969) 4871.
- 2 E.g., T.COHEN and T.POETH, *J.Amer.Chem.Soc.*, 94 (1972) 4363
- 3 NGOC-TUYET, LUONG-THI and H.RIVIÈRE, *Tetrahedron Lett.*, (1970) 1579 and 1583; *ibid.*, (1971) 587.
- 4 A.CAIRNCROSS and W.A.SHEPPARD, *J.Amer.Chem.Soc.*, 90 (1968) 2186; *ibid.*, 93 (1971) 247; A.CAIRNCROSS, H.OMURA and W.A.SHEPPARD, *J.Amer.Chem.Soc.*, 93 (1971) 248.
- 5 G.COSTA, A.CAMUS, L.GATTI and N.MARSICH, *J.Organometal.Chem.*, 5 (1966) 568.
- 6 G.VAN KOTEN and J.G.NOLTES, unpublished results.
- 7 R.J.DE-PASQUALE and C.TAMBORSKI, *J.Org.Chem.*, 34 (1969) 1736.
- 8 D.P.NOVAK and T.L.BROWN, *J.Amer.Chem.Soc.*, 94 (1972) 3793.
- 9 L.M.SEITZ and R.MADL, *J.Organometal.Chem.*, 34 (1972) 415.
- 10 K.K.SUN and W.T.MILLER, *J.Amer.Chem.Soc.*, 92 (1970) 6985.
- 11 D.A.OWEN and M.F.HAWTHORNE, *J.Amer.Chem.Soc.*, 92 (1970) 3194.
- 12 E.g., K.WADA, M.TAMURA and J.K.KOCHI, *J.Amer.Chem.Soc.*, 92 (1970) 6656.
- 13(a) G.M.WHITESIDES, E.R.STEDRONSKY, C.P.CASEY and J.SAN FILLIPPO, *J.Amer.Chem.Soc.*, 92 (1970) 1426.
- (b) G.M.WHITESIDES, C.P.CASEY and J.K.KRIEGER, *ibid.*, 93 (1971) 1379.
- 14 F.DE JONG and M.J.JANSSSEN, *J.Org.Chem.*, 36 (1971) 1645.
- 15 J.A.JARVIS, B.T.KILBOURN, R.PEARCE and M.F.LAPPERT, *J.Chem.Soc., Chem.Comm.*, (1973) 475.
- 16 M.F.LAPPERT and R.PEARCE, *J.Chem.Soc., Chem.Comm.*, (1973) 24.
- 17 G.VAN KOTEN and J.G.NOLTES, *J.Chem.Soc., Chem.Comm.*, (1972) 941.
- 18 G.VAN KOTEN and J.G.NOLTES, *J.Chem.Soc., Chem.Comm.*, (1972) 59.
- 19 C.R.JOHNSON and G.A.DUTRA, *J.Amer.Chem.Soc.*, 95 (1973) 7783.
- 20 E.J.COREY and D.J.BEAMES, *J.Amer.Chem.Soc.*, 94 (1972) 7210.
- 21 J.-P.GORLIER, L.HAMON, J.LEVISALLES and J.WAGNON, *J.Chem.Soc., Chem.Comm.*, (1973) 88.



## SUMMARY\*

### CHAPTER I

A short review is given of the development of organocopper chemistry. The approach followed in the present study for the stabilization of the copper-carbon bond in organocopper compounds is discussed.

### CHAPTER II

The synthesis and isolation of 2-[(dimethylamino)methyl]phenylcopper and of its 5-methyl, 5-methoxy, 5-chloro and 3-chloro derivatives are described. These hydrocarbon-soluble arylcopper compounds are appreciably more thermostable than phenylcopper, e.g.  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  decomposes at  $175\text{-}185^\circ$ , whereas  $\text{C}_6\text{H}_5\text{Cu}$  slowly decomposes at  $25^\circ$ . Moreover, they display improved hydrolytic and oxidative stability.

Lithiation of 1-methoxy-4-[(dimethylamino)methyl]naphthalene with butyllithium was proven to occur at the 5-position. Metathesis of 1-methoxy-4-[(dimethylamino)methyl]-5-lithionaphthalene with cuprous bromide afforded the corresponding organocopper compound.

### CHAPTER III

$2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  and its 5-methyl and 5-methoxy derivatives are tetrameric in benzene solution.  $5\text{-Me-}2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_3\text{Cu}$  is tetrameric in the solid (X-ray structure determination). The bonding in this tetranuclear cluster (Cu-Cu 2.38 Å, multicenter bonded aryl groups) is discussed. NMR spectroscopy provided indications that Cu-N coordination observed in the solid is weak in solution. Mass spectra of  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  ( $\text{R}_4\text{Cu}_4$ ) and its 5-methyl analogue  $(5\text{-MeR})_4\text{Cu}_4$  revealed that the  $\text{Cu}_4$  cluster in both compounds has considerable stability. Although the  $\text{R}_4\text{Cu}_4^+$  ions in both spectra are very abundant, the  $\text{R}_3\text{Cu}_4^+$  ions (even electron species) forms the base peak in the  $\text{R}_n\text{Cu}_n$  part of the mass spectra. The occurrence in solution of an intercluster exchange between  $\text{R}_4\text{Cu}_4$  and  $(5\text{-MeR})_4\text{Cu}_4$  with formation of the three possible mixed species  $\text{R}(5\text{-MeR})_3\text{Cu}_4$ ,  $\text{R}_2(5\text{-MeR})_2\text{Cu}_4$  and  $\text{R}_3(5\text{-MeR})\text{Cu}_4$  was confirmed by mass spectrometry (five patterns

\*The experimental work has been described at the end of each Chapter.



in the parent peak region separated by 14 mass units).

#### CHAPTER IV

$2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  forms a 1/1 complex with cuprous bromide. The 1/1 interaction of  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$  ( $\text{R}_4\text{Cu}_4$ ) with cupric halides resulted in the formation of R-R, R-halide and minor amounts of R-H. The formation of these products can be explained on the basis of an intramolecular electron-transfer redox reaction taking place in innersphere activated complexes of the type  $\text{R}_4\text{Cu}_3\text{Cu}\dots\text{X}\dots$   
 $\dots\text{Cu}^{\text{II}}\text{X}(\text{Cu}^{\text{II}}\text{X}_2)_{n-1}$ . The course of the metathesis reaction of  $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Li}$  with CuBr depends on the order of addition. Reversed addition (RLi to CuBr) resulted in the formation of an inseparable mixture of complexes of the type  $(\text{RCu})_x(\text{CuBr})_y$ . Upon addition of CuBr to RLi the uncomplexed organocopper compound was formed.

#### CHAPTER V

The reaction of 1,2-bis[*N*-[2-(bromomagnesio)benzyl]-*N*-methylamino]ethane [ $2,2'\text{-(BrMg)}_2\text{R}_N$ ] with  $\text{CuCl}_2$  resulted in the quantitative formation of the product of the intramolecular ring closure  $2,2'\text{-R}_N$ , and of the dicopper compound  $2,2'\text{-Cu}_2\text{R}_N$ . The formation of  $2,2'\text{-R}_N$  is explained on the basis of a concerted electron-transfer/C-C coupling reaction taking place in a complex of the monomagnesium species  $2,2'\text{-MgR}_N$  with  $\text{CuCl}_2$ . Molecular weight determinations and NMR spectroscopic data provided indications for a tetranuclear complex  $(2,2'\text{-Cu}_2\text{R}_N)_2$  in which the two multicenter-bonded aryl groups in each of the  $\text{R}_N$  ligands are arranged in a *trans* manner. This arrangement may account for the exclusive formation of the intramolecular ring-closed product  $2,2'\text{-R}_N$  upon thermal decomposition of  $(2,2'\text{-Cu}_2\text{R}_N)_2$ . The interaction of 1,2-bis[2-(bromomagnesio)benzyloxy]ethane [ $2,2'\text{-(BrMg)}_2\text{R}_O$ ] with cupric chloride afforded the ring-closed product  $2,2'\text{-R}_O$  in addition to  $2,2'\text{-Cu}_2\text{R}_O$ . Thermal decomposition of  $2,2'\text{-Cu}_2\text{R}_O$  yielded  $2,2'\text{-R}_O$  quantitatively.

#### CHAPTER VI

The synthesis and isolation of 2,6-dimethoxy, 2,4,6-trimethoxy-, 2-(dimethylamino)- and 4-(dimethylamino)phenylcopper are described. The dimethylamino-substituted phenylcopper compounds form complexes with cuprous bromide.



For the insoluble compounds a polymeric structure in which each aryl group is multicenter-bonded to two copper atoms with additional interchain Cu-N (or Cu-O) coordination is proposed.

## CHAPTER VII

The synthesis and isolation of 2/1 complexes of 2-(dimethylamino)phenyl-copper with CuX (X = Cl, Br, I) and with AgBr as well as of 2-(dimethylamino)-phenylsilver with CuBr and AgBr are described. These complexes are dimeric in solution (molecular weight determinations) and thus have  $R_4M_6X_2$  (M = Cu or Ag) stoichiometry. The structure of  $R_4Cu_6Br_2$  in the solid has been established (X-ray determination: shortest Cu-Cu distance 2.48 Å; each anilino ligand bridges a triangular face of the  $Cu_6$  octahedron; the bromine atoms bridge *trans*-equatorial edges). Molecular weights, IR and NMR spectroscopic data revealed a similar structure for the other  $R_4M_6X_2$  compounds. In the 1/2 reaction of  $R_4Cu_6Cl_2$  with LiI quantitative halogen exchange with retention of the  $Cu_6$  cluster took place. NMR data for the complexes with  $R_4Ag_4Cu_2Br_2$  and  $R_4Ag_2Cu_4Br_2$  stoichiometry provided evidence that in solution an equilibrium mixture of hexanuclear species of the type  $R_4Cu_mAg_nBr_2$  ( $m+n = 6$ ) is present. These equilibria can be interpreted in terms of interaggregate exchange reactions involving dissociation into  $R_2Ag_{3-n}Cu_nX$ , followed by recombination to give  $R_4Ag_{6-n}Cu_nX_2$  ( $n = 1-5$ ) or  $R_4M_6X_2$  (M = Cu or Ag).

## CHAPTER VIII

Ligand-substitution reactions of  $R_4Cu_6Br_2$  (R being 2-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>) with aryl-ethynyllithium (R'Li in which aryl represents phenyl, *p*-tolyl or mesityl) afforded the products  $R_4R'_2Cu_6$  quantitatively. IR and NMR spectroscopic data of the ligand-substitution products confirmed the presence of the  $R_4Cu_6$  skeleton. The proposed structure, which contains exclusively triangular faces  $RR'Cu_3$  (one bridging R and one bridging R' group), accounts for the exclusive formation of the mixed dimer  $RR'$  upon thermal decomposition of  $R_4R'_2Cu_6$  (R' being -C≡C*tol-p*). Cluster rearrangement of the resulting  $R_3R'Cu^I_4Cu^0_2$  species afforded two equivalents of polymeric RCu and a soluble species with the stoichiometry  $RR'Cu^I_2Cu^0_2$ .



## CHAPTER IX

The 2/1 reaction of 2-[(dimethylamino)methyl]phenyllithium (RLi) with CuBr afforded bis{2-[(dimethylamino)methyl]phenyl}copperlithium ( $R_2CuLi$ ). Its 5-methyl derivative  $(5-MeR)_2CuLi$  as well as the corresponding silverlithium compound  $R_2AgLi$  were prepared in a similar way. Molecular weight determinations indicated that these compounds have  $R'_4M_2Li_2$  ( $M = Cu$  or  $Ag$ ;  $R' = R$  or  $5-MeR$ ) stoichiometry in benzene solution.  $^1H$  and  $^{13}C$  NMR spectroscopic investigations revealed the structure of  $R_4Cu_2Li_2$ ,  $R_4Ag_2Li_2$  and  $(5-MeR)_4Cu_2Li_2$  in solution: (i) each aryl ligand in  $R'_4M_2Li_2$  is multicenter-bonded to one copper (or silver) and to one lithium atom; (ii) the metals in the  $M_2Li_2$  core are arranged in a *trans* manner and (iii) all four  $Me_2NCH_2$  ligands coordinate to lithium. The different coalescence temperatures for the NMe and benzylic protons in the  $^1H$  NMR spectra of the  $R'_4M_2Li_2$  compounds have been explained on the basis of their structure. NMR investigations revealed that (i) interaggregate exchange of  $R_4Cu_4$  with  $R_4Li_4$  results in the exclusive formation of  $R_4Cu_2Li_2$ , (ii) no exchange occurs between  $R_4Cu_2Li_2$  and  $R_4Li_4$  and (iii) interaction of  $R_4Cu_4$  with  $R_4Cu_2Li_2$  results in an equilibrium mixture containing other tetranuclear Cu-Li species. For these interaggregate exchange reactions an associative pathway which proceeds via an octanuclear intermediate  $R_8Cu_{8-n}Li_n$  is discussed.

## CHAPTER X

On the basis of the results presented in the previous Chapters various aspects of organocopper synthesis and of the structure-reactivity relationships of organocopper intermediates in organic synthesis are discussed. It is pointed out and illustrated with examples that transmetalation reactions of arylcopper compounds  $ArCu$  with metal halides  $MX$ , as well as of copper(I) salts  $Cu^I X$  with arylating reagents  $ArM$ , may be strongly interrelated. For both reactions a common polynuclear intermediate  $[ArCuMX]$  consisting of a metal-copper core with multicenter-bonded aryl groups is postulated [cf. the isolation of  $R_4Ag_{6-n}Cu_nBr_2$  from the  $(RAg)_n/CuBr$  as well as from the  $AgBr/(RCu)_n$  reaction, Ch. VII]. An alternative course for the interaction of  $ArM$  with  $Cu^{II}X_2$  is discussed. This interaction may proceed via key intermediates of the type  $Ar_nM_{n-1}M...X...$   $...Cu^{II}X(Cu^{II}X_2)_x$  (cf. Ch. IV) rather than via the transient formation of  $R_2Cu^{II}$  or  $RCu^{II}X$  species.

The available structural data for organocopper compounds suggest that a polynuclear structure with multicenter-bonded organic groups, both in solution



(e.g.,  $R_4Cu_2Li_2$ ) and in the solid (e.g.,  $R_4Cu_6Br_2$ ), may be a common structural feature of these compounds. Tetranuclear  $2-Me_2NCH_2C_6H_4Cu$  and  $(2-Me_2NCH_2C_6H_4)_2CuLi$  are presented as examples of cluster compounds which upon interaction with  $PPh_3$  neither form complexes nor break down to lower aggregates. In contrast, the 1/1 reaction of tetranuclear  $2-Me_2NCH_2C_6H_4Cu$  with  $Ph_2PCH_2CH_2PPh_2$  (Diphos) afforded monomeric  $RCu \cdot Diphos$ . When excess Diphos is used a peculiar  $C_{Alk}-P$  bond cleavage reaction of Diphos occurs, yielding  $PPh_2CuDiphos$ ,  $Ph_2PCH=CH_2$  and  $RH$ . Isocyanides insert into the copper-carbon bonds of arylcopper compounds with formation of a novel type of organocopper derivative  $R'N=C(R)Cu$ .

The discussion of the structure-reactivity relationships of organocopper intermediates in organic synthesis has been concentrated on the thermal decomposition patterns of organocopper compounds, and on cross-coupling and conjugate addition reactions. It is pointed out that as a result of the polynuclear structure of organocopper compounds reacting groups are in close proximity, to the effect that concerted metal-carbon bond breaking and C-C bond formation processes occur (cf. selective thermal decomposition of  $R_4R'_2Cu_6$ , Ch. VIII); furthermore, that in cross-coupling but also in conjugate addition reactions the bridging capacity of the organic groups involved is of importance; finally, that the lithium atoms in bis(organo)copperlithium reagents play an important rôle as coordination centers in conjugate addition reactions of these compounds with  $\alpha, \beta$ -unsaturated ketones.