

GROUP IB ORGANOMETALLIC CHEMISTRY

XIV*. INTRAMOLECULAR RING-CLOSURE REACTIONS OF NOVEL ARYL COPPER COMPOUNDS RCuI_2 . SYNTHESIS OF 7,8-DIHYDRODIBENZO-[*f,b*] [1,4]DIOXECIN AND 7,8-DIHYDRODIBENZO-6,9-DIMETHYL[*f,b*]-[1,4] DIAZECIN

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Summary

The reaction of 1,2-bis{*N*-[2-(bromomagnesio)benzyl]-*N*-methylamino}ethane (III) with CuCl_2 results in the formation of 1,2-bis[*N*-(2-cupriobenzyl)-*N*-methylamino]ethane (I, $2,2'\text{-Cu}_2\text{R}_N$) and of the product of intramolecular ring-closure 7,8-dihydrodibenzo-6,9-dimethyl[*f,h*] [1,4] diazecin (VII). The formation of $2,2'\text{-R}_N$ (VII) is explained in terms of a concerted electron-transfer/C—C coupling reaction within a complex of the monomagnesium species $2,2'\text{-MgR}_N$ (VIII) with CuCl_2 . Molecular weight determinations and NMR spectroscopic data for I point to a tetranuclear structure $(2,2'\text{-Cu}_2\text{R}_N)_2$ in which $(2,2'\text{-Cu}_2\text{R}_N)_2$ in which the two multicenter-bonded aryl groups in each of the R_N ligands are arranged in a *trans*-manner. This structure accounts for the exclusive formation of $2,2'\text{-R}_N$ (VII) upon thermal decomposition of I. The inter-action of 1,2-bis[2-(bromomagnesio)benzyloxy]ethane (X) with CuCl_2 affords the ring-closed product 7,8-dihydrodibenzo[*f,h*] [1,4] dioxecin (IX) in addition to the organodicopper XII. Thermal decomposition of XII yields $2,2'\text{-R}_O$ (IX) quantitatively.

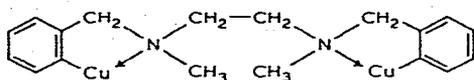
Introduction

Recent studies have shown that the thermolysis of organocopper compounds RCu may proceed by concerted, radical or metal hydride-elimination pathways depending on the type of R [2-4]. We have found that thermolysis of $(2\text{-Me}_2\text{-NC}_6\text{H}_4)_4(4\text{-MeC}_6\text{H}_4\text{C}\equiv\text{C})_2\text{Cu}_6$ ($\text{Ar}_4\text{R}_2\text{Cu}_6$) results in exclusive formation of the mixed coupling product $2\text{-Me}_2\text{NC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4}$. The specificity of this reaction has been explained in terms of a template effect exerted by the octahedral

* For Part XIII, see ref. 1.

copper cluster: four triangular faces each containing one Ar and one R bridging ligand are present, but Ar_2Cu_3 and R_2Cu_3 faces leading to ArAr and RR , respectively, are absent [4]. In principle the thermolysis of organodicopper compounds Cu_2R containing two favourably positioned $\text{Cu}-\text{C}$ bonds might then provide an attractive method of achieving intramolecular ring-closure.

In a recent review [5] the synthesis of the organodicopper compound 1,2-bis[*N*-(2-cupriobenzyl)-*N*-methylamino]ethane (I) was mentioned, and structure II was proposed*. However, in view of our finding [7] that arylcopper compounds generally have a polynuclear structure, with bridging $2e-3c$ bonded aryl groups, we considered this structure unlikely.



(II)

I, $(2,2'-\text{Cu}_2\text{R}_N)^{**}$, had been synthesized via the 1/1 reaction of the corresponding diGrignard 1,2-bis[*N*-[2-(bromomagnesium)benzyl]-*N*-methylamino]ethane (III) with cupric chloride. We have recently found that the type of products ($\text{R}-\text{R}$, $\text{R}-\text{H}$ or $\text{R}-\text{Hal}$) formed upon interaction of organo-copper or -lithium compounds with cupric halides depends on the structure of $(\text{RCu})_n$ or $(\text{RLi})_n$ [1]. Thus information about the nature of the organic products formed in the electron-transfer step of the reaction would be of interest.

This paper deals with (i) the synthesis and structural characterization of I, (ii) the nature of the products formed in the reaction of the Grignard III with CuCl_2 and (iii) the synthesis of novel dioxecin and diazecin derivatives via thermolysis of appropriate organodicopper compounds.

Results and discussion

Preparation of the organocopper compound I

On the basis of our earlier work [1,8] concerned with the synthesis of 2-(dimethylamino)methyl-substituted phenylcopper compounds, the reaction of the hitherto unreported dilithium compound 1,2-bis[*N*-(2-lithiobenzyl)-*N*-methylamino]ethane (IV) with cuprous or cupric halides was selected for the preparation of I.

As shown by NMR spectroscopy the metal-halogen exchange reaction of 1,2-bis[*N*-(2-bromobenzyl)-*N*-methylamino]ethane (V) with butyllithium afforded, in addition to $2,2'-\text{Li}_2\text{R}_N$ (IV) in 60% yield some other, unidentified organolithium compounds. Attempts to obtain pure $2,2'-\text{Li}_2\text{R}_N$ via metal-hydrogen exchange reaction of $2,2'-\text{H}_2\text{R}_N$ (VI) were likewise unsuccessful. NMR and IR spectroscopy of the deuterolyzed reaction mixtures showed that metal-hydrogen exchange had taken place for about 95% (calculated for the exchange

* We kindly thank Dr. P. Burba for making available a copy of the Diplom-Arbeit of Dr. W. Weidemüller [6].

** The 2,2'-disubstituted organic group R is abbreviated as $2,2'-\text{X}_2\text{R}_N$ in which X represents $\text{Br}-$, $\text{BrMg}-$, $\text{Cu}-$, $\text{H}-$, or $\text{D}-$ and R_N [$-\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{Me})\text{CH}_2$] $_2$.

of two protons), viz. 65% exchange of the *ortho*-hydrogen atoms and 30% exchange of the benzylic hydrogen atoms (α -lithiation)*.

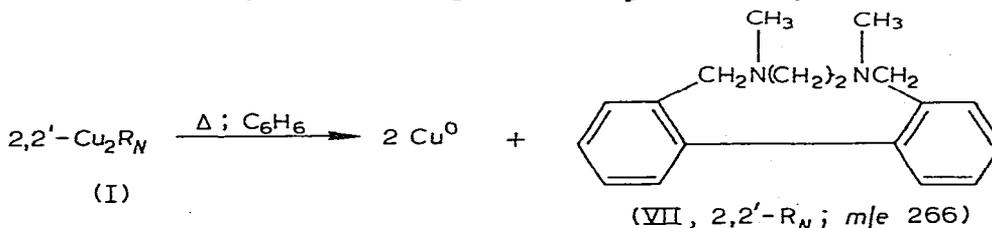
The formation of unwanted metalated products does not occur when 2,2'-Br₂R_N is converted into the corresponding diGrignard reagent 2,2'-(BrMg)₂R_N (III) by reaction with magnesium in THF [10]. Although Grignard reagents are often inferior starting materials for the preparation of pure arylcopper compounds [11], I has been successfully synthesized starting from 2,2'-(BrMg)₂R_N.

Addition of cupric chloride to a solution of an equivalent amount of 2,2'-(BrMg)₂R_N in THF at -20°C afforded a yellow precipitate and a "brown solution" (see following section). The elemental analysis of the precipitate suggested it to be the dicopper compound 2,2'-Cu₂R_N slightly contaminated with magnesium halides. The latter impurity was removed by recrystallization from a dioxane/benzene mixture. The yield of pure I was about 25% (calculated on the amount of CuCl₂ used).

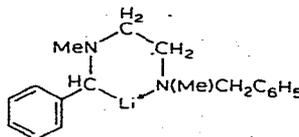
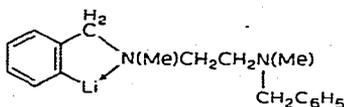
The identity of I was established by elemental analysis, IR spectroscopy (1,2-substitution pattern for the aryl nucleus) [12] and NMR spectroscopy (see below). I is rather stable in air and shows a high stability towards hydrolysis. When heated in a capillary tube under nitrogen I decomposes slowly at 125-130°C and fast at 133°C.

NMR spectroscopy at different temperatures provided information about the thermal stability of I in solution. Upon heating a benzene solution to 80°C, a black solid precipitated and the solution which had turned from yellow to colourless showed a totally different NMR spectrum (see Fig. 1). The complete disappearance of the doublet of doublets at δ 8.61 ppm, belonging to the proton *ortho* with respect to the copper-carbon bond [13], pointed to a total decomposition of I (see Fig. 1).

The study of the decomposition reaction on a preparative scale revealed that the intramolecular ring-closure product 7,8-dihydrodibenzo-6,9-dimethyl-[*f,h*] [1,4] diazecin (VII, 2,2'-R_N)**, [characterized by means of IR, NMR and mass spectrometry (see Table 1)] is formed quantitatively.



* The higher stability of (*ortho*-lithiated benzyl)dimethylamine as compared with the α -lithiated product has been ascribed [9] to stabilization of the former isomer by intramolecular Li-N coordination. The lithiation reaction of 2,2'-H₂R_N with BuLi can be expected to occur both at the *ortho*- and at the α -site because the two lithio derivatives can both be stabilized by intramolecular Li-N coordination:



** Thanks are due to Dr. L.C. Willemsens for providing the nomenclature of compounds VII and IX.

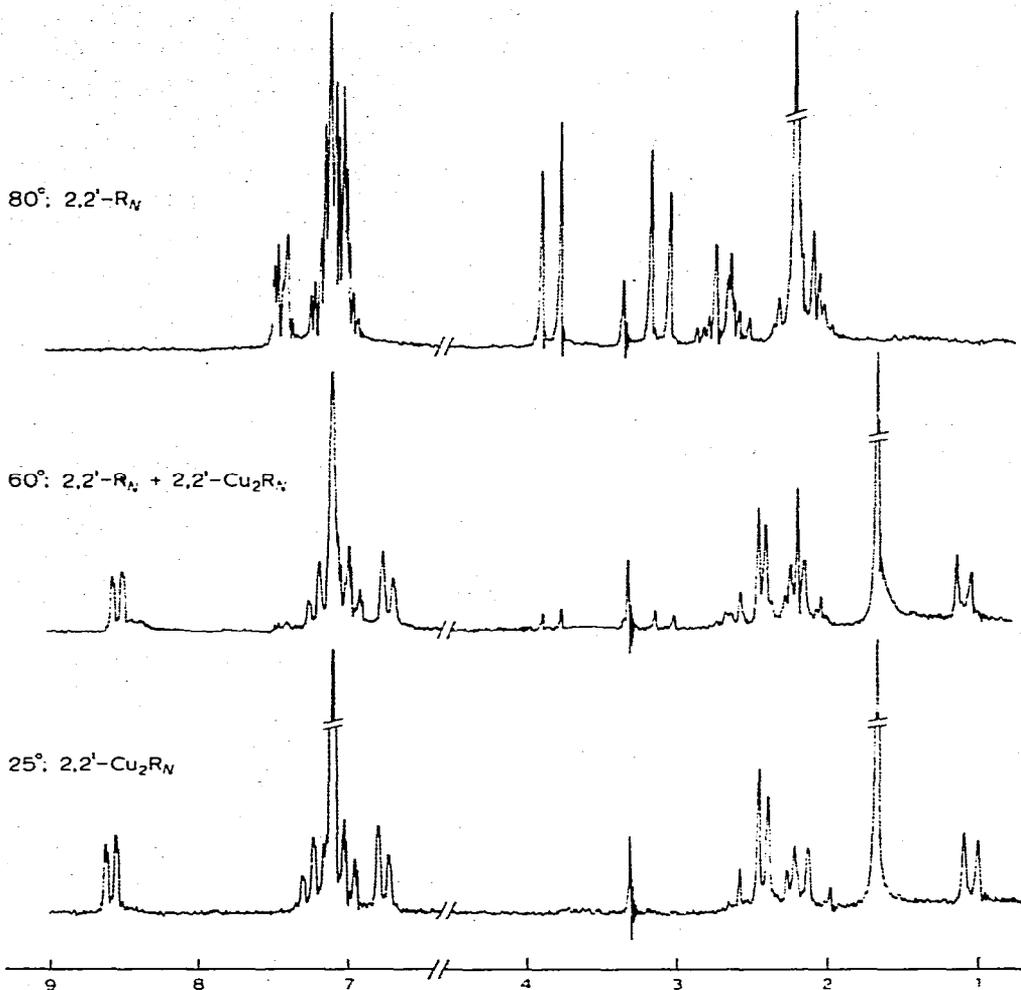
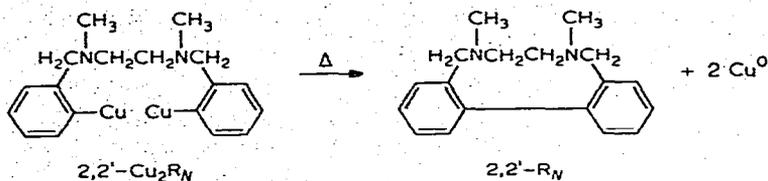


Fig. 1. NMR spectra (δ ppm; benzene- d_6) showing the thermal decomposition of a solution of 2,2'- Cu_2R_N (I) to 2,2'- R_N (VII).

Structural characterization of 2,2'- Cu_2R_N

The structure of 2,2'- Cu_2R_N in the solid is not known. However, on the basis of both the NMR spectra at different temperatures and the data obtained from molecular weight determinations a plausible structure for 2,2'- Cu_2R_N can be proposed.

The results of cryometric molecular weight measurements shows this compound to exist in benzene as discrete dimeric units (2,2'- Cu_2R_N)₂ which

TABLE 1
NMR AND MASS SPECTROSCOPIC DATA FOR 2,2'-R_N AND 2,2'-R_O

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

^a TMS internal standard; room temperature. ^b Some very abundant ions are mentioned. The asterisk indicates the base peak in the spectrum. ^c See ref. 15.

thus contain four copper atoms. The NMR spectrum of I in benzene-d₆ at 25°C is shown in Fig. 1 (see also Table 2). The assignment of the resonances in the aromatic region parallels those for the 2-(dimethylamino)methyl-substituted aryl-copper compounds [13]. The arrangement of the two bifunctional R_N ligands around the four copper atoms can be deduced from the observed proton resonance patterns of the prochiral benzyl-CH₂(N) and ethylenic-CH₂(N) groups. Both the benzyl-CH₂ and ethylenic-CH₂ protons appear as singlets in the spectra

TABLE 2
NMR SPECTRA FOR 2,2'-X₂R_Y COMPOUNDS

Compound	δ (ppm) ^a in benzene-d ₆ (CCl ₄)			
	NCH ₃	YCH ₂ CH ₂ Y	PhCH ₂ Y	Aromatic-H
R _N = $\begin{array}{c} \text{—C}_6\text{H}_4\text{CH}_2\text{N(Me)CH}_2 \\ \\ \text{—C}_6\text{H}_4\text{CH}_2\text{N(Me)CH}_2 \end{array}$				
VI, 2,2'-H ₂ R _N	2.10(2.13) (s, 6)	2.50(2.49) (s, 4)	3.36(3.44) (s, 4)	7.0-7.4(7.0-7.4) (m, 10)
V, 2,2'-Br ₂ R _N	2.08 (s, 6)	2.47 (s, 4)	3.54 (s, 4)	6.6-7.6 (m, 8)
I, 2,2'-Cu ₂ R _N	1.69 (s, 6)	1.07 and 2.19 (2d, 4) ^c	2.36 and 2.54 (2d, 4H, <i>J</i> _{gem} 12.5 Hz)	H ₃ 8.61 (<i>J</i> _{3,4} 7, <i>J</i> _{3,5} 1.5 Hz) H ₆ 6.78 (<i>J</i> _{5,6} 7, <i>J</i> _{4,6} 1 Hz) H _{4,5} 6.7-7.4 (m) ^b
R _O = $\begin{array}{c} \text{—C}_6\text{H}_4\text{CH}_2\text{OCH}_2 \\ \\ \text{—C}_6\text{H}_4\text{CH}_2\text{OCH}_2 \end{array}$				
XIV, 2,2'-H ₂ R _O		3.46(3.50) (s, 4)	4.36(4.42) (s, 4)	(7.0-7.5) (m, 10)
XV, 2,2'-Br ₂ R _O		3.43(3.72) (s, 4)	4.49(4.55) (s, 4)	6.6-7.7(6.9-7.6) (m, 8)

^a TMS internal standard; room temperature. ^b Masked by C₆D_xH_{6-x}. ^c Separation 9 Hz, see text.

of 2,2'-H₂R_N and 2,2'-Br₂R_N (see Table 2), whereas in the tetranuclear copper compound these protons give rise to two multiplet patterns; ethylenic-CH₂ (AA'XX')*, centered at δ 1.07 and at 2.19 and benzylic-CH₂ (AB) δ 2.36 d and 2.54 d ppm. In 2,2'-H₂R_N and 2,2'-Br₂R_N compounds the CH₂ protons do not become diastereotopic because rapid nitrogen inversion and N—C bond rotation occur at the temperatures considered. However, in the case of the tetranuclear copper compound the multiplet patterns point to nitrogen inversion which is slow on the NMR time scale, or even blocked as a result of the stereochemistry of R_N in the (2,2'-Cu₂R_N)₂ structure. Additional information emerges from the observation that the spectrum is temperature independent; i.e. up to the temperature at which decomposition occurs as well as upon cooling the resonance pattern remains unchanged. No broadening of the AB pattern or a change in the separation of the peaks in the AA'XX' pattern is observed, which means that nitrogen inversion is an energetically unfavourable process and conformational changes of the NCH₂CH₂N bridge are restricted** [17].

The tetranuclear structures schematically shown in Fig. 2a account for these observations. The two R_N ligands, which can be placed in a *cis*- or a *trans*-geometry, reside on different sides of the copper core. The two phenyl groups of each R_N ligand are assumed to bridge the copper atoms via electron-deficient bonds (in analogy with the solid state structure of (5-Me-2-Me₂NCH₂C₆H₃)₄Cu₄ [7a] and with the structure in solution of (2-Me₂NCH₂C₆H₄)₄Cu₂Li₂ [7]). The *trans*-structure is preferred on the basis of the following arguments (Fig. 2b shows one of the many possible conformations of the R_N ligand; the N atoms are pointing to the Cu core, but Cu—N coordination [7a] is not necessarily involved). The observation of only one pattern for the methyl protons, for the protons *ortho* to the Cu—C bond and the bridge-CH₂ protons indicate that both halves [—C₆H₄—CH₂N(Me)CH₂—] of the bifunctional R_N group reside in the same magnetic environment***. Moreover, inspection of a model of the tetranuclear copper compound reveals that the large $\Delta\delta$ (1.12 ppm) for the ethylenic protons H_A and H_B can be explained on the basis of their different positions with respect to the

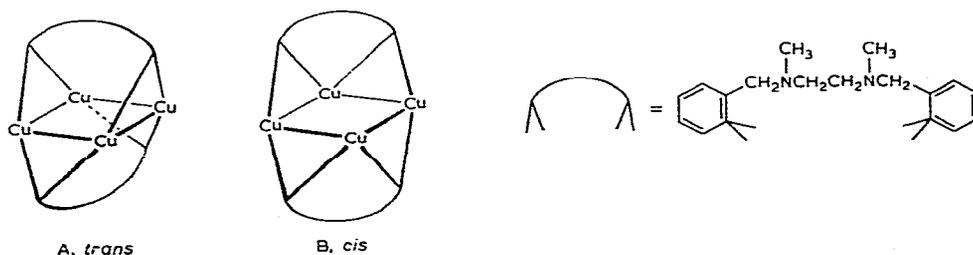


Fig. 2a. Arrangement of the bifunctional group R_N in (2,2'-Cu₂R_N)₂ in a *trans* (A) and in a *cis* (B) manner.

* Because of the limited solubility of I, only the two strong absorptions (separated by $J_{AX} + J_{AX'}$ and centered at δ_A and δ_X) [16] of the AA'XX' multiplet can be observed, which makes full analysis of this pattern impossible.

** Of the two coupling constants J_{AX} and $J_{AX'}$ the vicinal constant $J_{AX'}$ is dihedral-angle dependent.

*** In view of the fact that the spectra were invariant in the temperature range 0-80°C it seems unlikely that the observed symmetry is due to rapid intramolecular rearrangements (e.g. "*cis*" \rightleftharpoons "*trans*") or to interaggregate exchange processes.

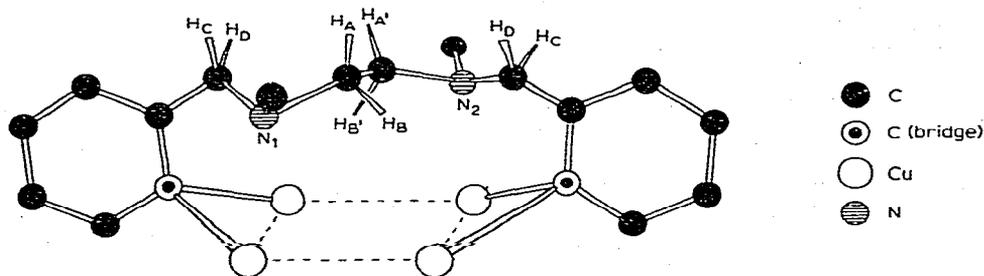


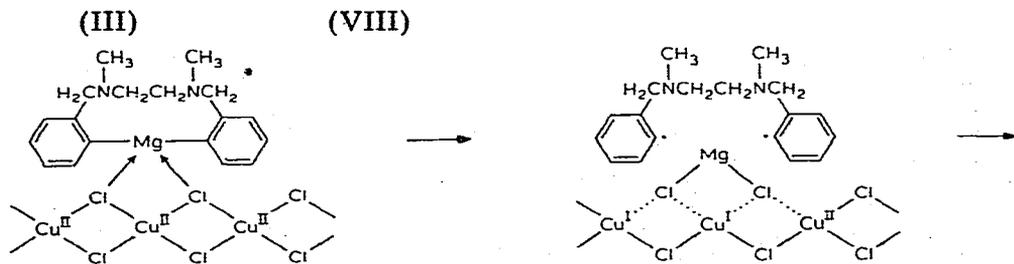
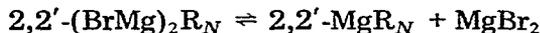
Fig. 2b. Proposed structure for $(2,2'\text{-Cu}_2\text{R}_N)_2$. Only the R_N group above the Cu_4 plane is shown.

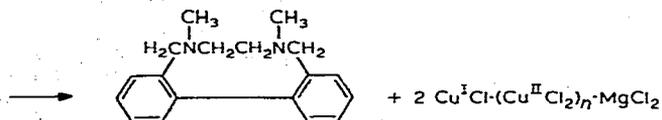
copper core. In the *trans*-structure H_B points towards and H_A points away from the copper core, whereas in the *cis*-structure both protons reside in an almost identical environment so that for this structure a large $\Delta\delta$ is not to be expected.

Furthermore, the proposed structure accounts for the specific thermal decomposition of $(2,2'\text{-Cu}_2\text{R}_N)_2$ to the cyclic product $2,2'\text{-R}_N$ (VII). The R_N ligands are positioned in such a way that *concerted* homolytic $\text{Cu}\text{-C}$ bond cleavage and intramolecular $\text{C}\text{-C}$ bond formation occurs to the exclusion of other possible reactions. In contrast, for the structure proposed by Weidemüller [6] the formation of oligomeric or polymeric species $\text{-(R}_N\text{)}_n$ as well as H-abstraction products would be expected. We propose that a template effect exerted by the Cu_4 square in $(2,2'\text{-Cu}_2\text{R}_N)_2$ (fully analogous to the template effect exerted by the Cu_3 triangular faces in $\text{Ar}_4\text{Cu}_6\text{R}_2$) is responsible for the specificity of the ring-closure.

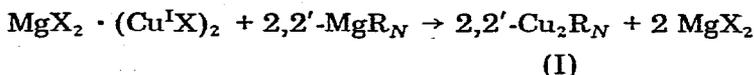
The course of the reaction of $2,2'\text{-(BrMg)}_2\text{R}_N$ with CuCl_2

The formation of $2,2'\text{-Cu}_2\text{R}_N$ containing monovalent copper indicates that during the reaction of $2,2'\text{-(BrMg)}_2\text{R}_N$ with $\text{Cu}^{\text{II}}\text{Cl}_2$ an electron-transfer process takes place. An NMR and mass spectrometric study of the brown solution (vide supra) revealed that the only product formed in addition to $2,2'\text{-Cu}_2\text{R}_N$ is the product of intramolecular ring-closure $2,2'\text{-R}_N$ (VII, m/e 266, see Table 1). Oligomeric or polymeric products could not be detected in the reaction mixture. The exclusive formation of VII suggests that within one organic group R_N two phenyl radicals are generated synchronously and at close proximity, to the effect that intramolecular coupling rather than hydrogen abstraction, ligand-transfer reduction with CuCl_2 or oligomer formation takes place (cf. ref. 1). For this reason we assume that the monomagnesium species $2,2'\text{-MgR}_N$ (VIII) rather than the dimagnesium species $2,2'\text{-(BrMg)}_2\text{R}_N$ (III) interacts with CuCl_2 :





In a heterogeneous reaction the $2,2'$ - MgR_N species attacks the surface of the CuCl_2 -coordination polymer with the formation of an inner-sphere complex in which synchronous one-electron oxidation of the $\text{Mg}-\text{C}$ bond* and ring-closure take place. In a separate reaction the cuprous chloride formed reacts with the Grignard reagent to form the corresponding organodicopper compound I:



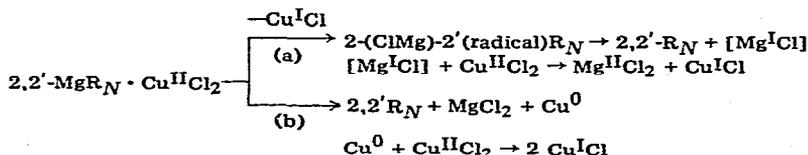
Synthesis of 7,8-dihydrodibenzo[f,h][1,4]dioxecin (IX)

The easy availability of the novel biaryl $2,2'$ - R_N via the electron-transfer reaction of $2,2'$ - $(\text{BrMg})_2\text{R}_N$ with $\text{Cu}^{\text{II}}\text{Cl}_2$ as well as via thermolysis of $2,2'$ - Cu_2R_N 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 7,8-dihydrodibenzo[f,h][1,4]dioxecin (IX, $2,2'$ - R_O)** has been investigated.

The 1/1 reaction of the diGrignard $2,2'$ - $(\text{BrMg})_2\text{R}_O$ (X) [10] with cupric chloride in THF afforded a white precipitate (XI) which was removed by filtration. From the filtrate $2,2'$ - R_O (IX) was isolated in 51% yield. Its identity was established by elemental analysis, by IR and NMR spectroscopy*** as well as by mass spectrometry (see Table 1). According to the elemental analysis the white precipitate (XI) consists of the organocopper $2,2'$ - Cu_2R_O (XII) contaminated with magnesium halides. This view was confirmed by formation of $2,2'$ - D_2R_O (XIII) upon deuterolysis of a sample of XI. Thermolysis for 24 h of a suspension of XI in boiling benzene afforded a colourless solution containing a black solid. The NMR spectrum of the solution was identical to that of a pure sample of IX.

These results indicate that preparation of the intramolecular ring-closed product IX does not require the isolation of pure $2,2'$ - Cu_2R_O , and that a virtually

* It is assumed that $\text{Cu}^{\text{I}}\text{Cl}$ (two equivalents) and MgCl_2 are formed in one step. Alternatives are:



Route a which is analogous to the biaryl formation mechanism put forward by Russell [14], suggests that a $\text{Mg}-\text{C}$ bond is a better radical trap than $\text{Cu}^{\text{II}}\text{Cl}_2$. This is, however, not very likely (see ref. 1). The second route b does not differ essentially from the one given in the equation but offers alternative interpretation of what happens in the $\text{Cu}^{\text{II}}\text{Cl}_2$ coordination polymer.

** R_O stands for $[-\text{C}_6\text{H}_4\text{CH}_2\text{OCH}_2]_2$.

*** Molecular models of the ring-closed products $2,2'$ - R_N (VII) and $2,2'$ - R_O (IX) 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 [15].

room temperature to a solution of 2 mmol of 1,2-bis[*N*-(2-bromobenzyl)-*N*-methylamino]ethane (2,2'-Br₂R_N) 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 C₆D₆. An NMR spectrum of this solution showed broadened resonances at (δ ppm): 8.32 (d, H₃ of 2-lithiated-R_N), 7.5-6.7 (aromatic-H), 4.2 and 2.88 (2d, $J \approx 11$ Hz, assigned to benzylic-H of 2-lithiated-R_N), 2.6-0.6 (butyl-H). The main solution was hydrolyzed with H₂O (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 Na₂SO₄, filtered and concentrated, affording 0.35 g of a yellow oil. NMR spectrum (C₆D₆, TMS internal, δ ppm): 2,2'-H₂R_N, 2.08 (s, 6, NCH₃), 2.47 (s, 4, NCH₂CH₂N), 3.35 (s, 4, PhCH₂N); other broadened multiplets are found at 0.9, 1.3, 2.1, 2.5 and 3.4. Estimated yield of 2,2'-H₂R_N about 60%. No starting product 2,2'-Br₂R_N could be detected.

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'-H₂R_N was stirred at room temperature during 48 h. The resulting dark-red solution was added to a mixture of D₂O and benzene (10/50 *v/v*). The benzene/ether layer was dried over MgSO₄, filtered and concentrated to give a yellow oil (75% yield). This oil was distilled, to give pure (GC) D₂R_N. B.p. 140°C/0.3 mm. NMR spectrum (CCl₄, TMS internal, δ ppm): 2.13 (s, 6, NCH₃), 2.50 (s, 4, NCH₂CH₂N), 3.44 (s, 3.4, PhCH₂N), 7.22 (m, 8.7, aromatic H). IR (neat, cm⁻¹): ν (C-D) 2250(br) (*ortho*-D substituted R_N)* and 2053(br) (α -D substituted R_N).

Synthesis of 2,2'-Cu₂R_N

A solution of the diGrignard 2,2'-(BrMg)₂R_N (obtained from the reaction of 150 mg-atom Mg with 42 mmol of 2,2'-Br₂R_N in 180 ml of THF) was added at -20°C to a suspension of 36 mmol of anhydrous CuCl₂ in THF (60 ml). After 2 h stirring at -20°C 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 × 20 ml) and dried in vacuo (3.55 g). The yellow solid did not dissolve upon addition of dioxane. 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 × 40 ml). From the combined benzene extracts orange crystalline 2,2'-Cu₂R_N was isolated (2.05 g; 25% yield). (Found: C, 54.5; H, 5.7; N, 7.0; Cu, 30.8; Br, 0.9. C₁₈H₂₂N₂Cu₂ calcd.: C, 54.95; H, 5.63; N, 7.12; Cu, 32.34; Br, 0.0%). The presence of dioxane (≈ 5.6 mol%) was confirmed by NMR (resonance at δ 3.33 ppm, see Fig. 1). Mol. wt. (cryometric in C₆H₆): mean 790, \bar{n} 2.0 (concentration independent). IR spectrum (nujol, cm⁻¹): 1575m; 1351vw; 1302m; 1253w; 1222w; 1186w; 1156vw; 1136w; 1130w(sh); 1098w(sh); 1088m; 1060w; 1040vw; 1020m; 1009(sh); 1003s; 973m; 960s; 942m; 926w; 868w; 821(sh); 806vs; 779(sh); 714s; 675vw; 638vw; 625vw; 614vw; 578m; 515s; 496w.

* IR (2-deuteriobenzyl)dimethylamine (neat, cm⁻¹): ν (C-D) 2252 cm⁻¹ [8].

Thermolysis of 2,2'-Cu₂R_N; isolation of 2,2'-R_N

A solution of 2,2'-Cu₂R_N (2.24 mmol) in benzene (10 ml; partly dissolved) was refluxed for 2 h. Immediate decomposition occurred, with formation of a 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 (VII), see Fig. 1. The precipitate was filtered off. Work-up of the filtrate (acid-base procedure) afforded pure 2,2'-R_N (according to GLC: one peak) as a colourless oil in 85% yield. For spectroscopic data, see Table 1.

Direct synthesis of 2,2'-R_N

The mixture obtained from the reaction of 21 mmol of 2,2'-(BrMg)₂R_N with 18 mmol of CuCl₂ in THF was concentrated. A dioxane/benzene (10 ml/100 ml) mixture was added* and the resulting mixture stirred at 80°C for 6 h. NMR spectroscopy revealed the presence of 2,2'-R_N while no organocopper of 2,2'-H₂R_N species could be detected. Hydrolysis of the reaction mixture with 4 N HCl and a subsequent work-up (acid-base procedure) gave a yellow oil. NMR spectrum, see Tables 1 and 2: 92% 2,2'-R_N and 8% 2,2'-H₂R_N; MS (70 eV): *m/e* 268 (2,2'-H₂R_N)⁺ and *m/e* 266 (2,2'-R_N)⁺.

Reaction of 2,2'-(BrMg)₂R_O with cupric chloride

A solution of the diGrignard 2,2'-(BrMg)₂R_O [from 88.3 mg-atom of Mg and 30 mmol of 2,2'-Br₂R_O in THF (80 ml)] was added at -20°C to a suspension of cupric chloride (25.7 mmol) in THF (40 ml). The reaction mixture was stirred at -20°C for 2 h and then at room temperature. THF was removed at low pressure. The resulting white residue was extracted with dioxane (60 ml), followed by extraction with benzene (60 ml). From the benzene/dioxane extracts a colourless oil was isolated. NMR spectroscopy in C₆D₆ (see Tables 1 and 2) revealed the product to be a mixture of 2,2'-R_O (IX) and 2,2'-H₂R_O (XIV) in a 5/1 molar ratio (i.e. 24% yield of IX and 4.7% of XIV).

The dioxane/benzene insoluble residue XI was deuterolyzed with D₂O (see *i*) and heated in benzene (see *ii*).

i. A suspension of XI in Et₂O/D₂O (20/1) was stirred for 24 h. The ether layer was separated, extracted with H₂O and then dried over Na₂SO₄. The Na₂SO₄ was filtered off and the filtrate concentrated, which afforded an oily residue. NMR (see Tables 1 and 2): 2,2'-R_O/2,2'-D₂R_O 1/4.5 molar ratio (calcd. from the peak area ratio of the AB pattern due to PhCH₂O of 2,2'-R_O and the singlet resonance due to PhCH₂O of 2,2'-D₂R_O); the amount of D in 2,2'-D₂R_O from the peak area ratio of O(CH₂)₂O/PhCH₂O/aromatic-H ≈ 4/4/8.2. IR (neat): ν(C-D) 2254 cm⁻¹; weak absorption at 699 cm⁻¹ points to the presence of monosubstituted aryl groups (2,2'-H₂R_O).

ii. A suspension of XI in benzene (20 ml) was refluxed for 24 h. The NMR spectrum (see Table 1) indicated quantitative formation of 2,2'-R_O (IX). Concentration of the solution gave white crystalline IX. M.p. 99-100°C. (Found: C, 79.7; H, 6.6; O, 13.2. C₁₆H₁₆O₂ calcd.: C, 79.97; H, 6.71; O, 13.32%).

* See footnote on p. 135.

Direct synthesis of 2,2'-R_O

The reaction mixture obtained from the 2,2'-(BrMg)₂R_O (30 mmol)/CuCl₂ (25.7 mmol) reaction in THF was concentrated. Addition* of benzene/dioxane (100/15) to the resulting mixture and subsequent heating of the mixture at 80°C for 10 h gave 2,2'-R_O in 85% yield, in addition to some unidentified products.

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* See footnote on p. 135.