Journal of Organometallic Chemistry, 84 (1975) 419—429

THE REACTIONS OF 2-[(DIMETHYLAMINO)METHYL]PHENYLCOPPER AND -LITHIUM TETRAMER WITH CUPROUS AND CUPRIC HALIDES*

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(Received August 9th, 1974)

Summary

2-[(Dimethylamino)methyl]phenylcopper tetramer (R_4Cu_4) forms a red 1/1 complex $(RCu \cdot CuBr)_n$ with cuprous bromide. The 1/1 interaction of 2-[(dimethylamino)methyl]phenylcopper with cupric halides results in the formation of the dimer R—R, the 2-halo-substituted benzylamine R—Halide and minor amounts of *N,N*-dimethylbenzylamine RH. 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 $R_4Cu_3Cu - - - X - - - Cu^{II}X(Cu^{II}X_2)_{n-1}$. The course of the metathesis reaction of 2-[(dimethylamino)methyl]phenyllithium with cuprous bromide depends on the order of addition of the reactants. Reversed addition (RLi to CuBr) results in the formation of an inseparable mixture of complexes of the type $(RCu)_x(CuBr)_y$. Upon addition of CuBr to RLi the uncomplexed organocopper compound R_4Cu_4 is formed.

Introduction

Of the reported arylcopper compounds only relatively few have been isolated pure [1-5]. This has been ascribed to their general low solubility, which hampers their purification, as well as to the tendency to form complexes with the metal salts as by-products in the preparations (e.g. MgX_2 or LiX) [6, 7]. Recently, we have observed that arylcopper compounds can form complexes with copper(I) halides [8] and that this type of complex formation often interferes seriously with attempts to isolate pure, well-defined species**.

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* Part XII of the series of papers dealing with Group IB organometallic chemistry. For Part XII see ref. 1.

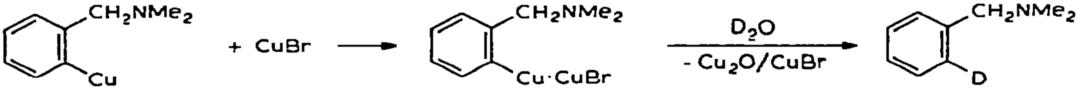
** See, for example, the synthesis of dimethylamino-substituted phenylcopper compounds [1].

To gain a better insight into 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.



(I) R_4Cu_4, yellow

(III) RCu • CuBr, red

(IV)

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 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 $RCu{\cdot}CuBr/C_6H_6$ molar ratio of 1/0.2. The IR spectra of IIIa and IIIb (Fig. 1) were identical in the 2000-400 cm^{-1} region which suggests that in both cases a mixture of a discrete complex with cuprous bromide (probably the 1/1 complex RCu · CuBr) had been formed*. Compared with the parent organocopper (I) (dec. at 175-185°), the 1/1 complex has a considerably decreased thermal stability (e.g. IIIa, dec. at 96-98°).

The deuterolysis of both IIIa and IIIb, which required prolonged reaction times (96 h with D_2O; 24 h with DOAc), gave (2-deuteriobenzyl)dimethylamine

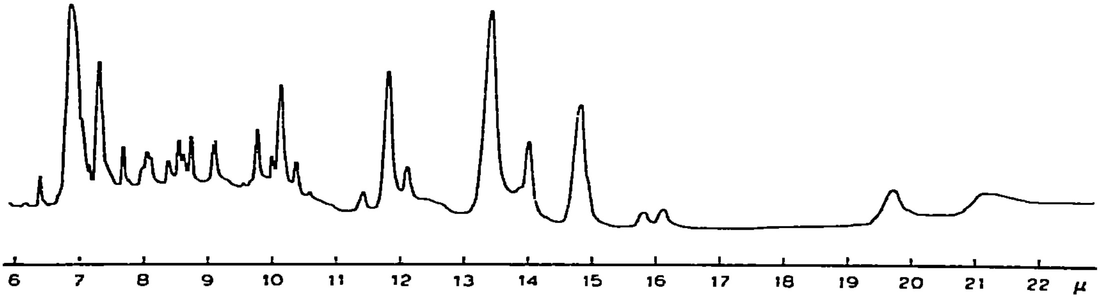


Fig. 1. IR spectrum (Nujol) of 2-[(dimethylamino)methyl]phenylcopper-cuprous bromide (III).

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[*] Probably the reaction, which is sluggish, had not yet gone to completion.

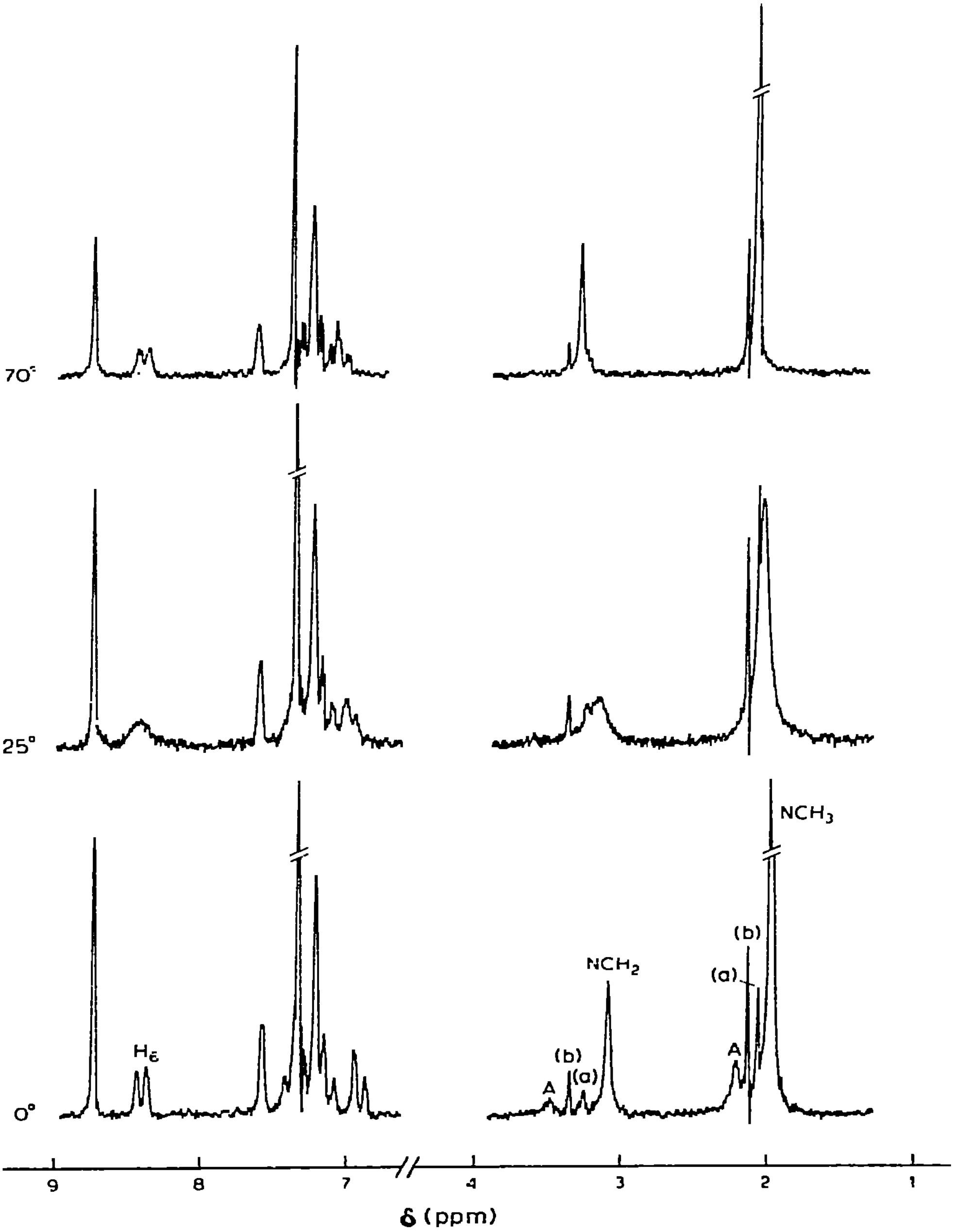

Fig. 2. ^{1}H NMR spectrum (δ ppm) of III in pyridine-d_5 at different temperatures. RR (V) [resonances marked with (a)] and RH (VI) [resonances marked with (b)] are present as impurities.

[RD, (IV)] in about 70 and 90% yield, respectively. No trace of the dimer 2,2'-bis[(dimethylamino)methyl]biphenyl [RR, (V)] could be detected in the reaction mixtures*.

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* Reaction of the 1/1 complex 2-[(dimethylamino)methyl]phenylsilver-silver bromide (RAg · AgBr) [9] with DOAc afforded RD (IV) in quantitative yield. However, deuterolysis with D_2O resulted in the formation of the biaryl RR (V) (100% yield).

The 1/1 complex RCu · CuBr is insoluble in hydrocarbon solvents and ethers, but slightly soluble in pyridine*. Its ^{1}H NMR spectrum has been recorded at various temperatures in pyridine-d_5, (Fig. 2). The resonances of the various protons have the same chemical shift values as those observed for 2-[(dimethylamino)methyl]phenylcopper (I) [10]. 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 δ 2.27 (NCH_3) and at 3.54 ppm (NCH_2) 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 ($CuBr_2$-reaction) or metallic brown ($CuCl_2$-reaction) upon stirring the reaction mixture at room temperature for five days. For the 2/1 reaction ($RCu/CuBr_2$) 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

TABLE 1

REACTION OF RCu (I) WITH CUPRIC HALIDES

$RCu/xCuBr_2$ or $RCu/yCuCl_2$ (mol. ratio)	Products (mol. % calcd. on RCu)[a]				Total R (%)[b]
	RH	RBr	RCl	RR total (solution; precipitate)	
$x = 1$ (1/1)	7	18		37 (9; 28)	99
$x = ½$ (2/1)	2.5	8		28 (12; 16)	66.5[c]
$y = 1$ (1/1)	9		34	28 (28; —)	99

[a] (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). [b] Calculated on the starting amount of R in the organocopper RCu. [c] 37% of R is present in the precipitate as RCu, see Table 2.

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[*] The insolubility in non-complexing solvents suggests a polymeric structure $(RCu{\cdot}CuBr)_n$ rather than a discrete cluster structure such as has been established by X-ray analysis for the 2/1 complex of 2-(dimethylamino)phenylcopper with cuprous bromide [8].

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

of I with cupric halides 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 $CuBr_2$ the amount of R_{found} (R_{found}/RCu ≈ 0.66) exceeds the amount expected on the basis of a simple single electron redox mechanism ($R_{to\ be\ found}$/RCu = 0.50).

The following reaction course, which can account for these results, is proposed. The arylcopper compound I exists in solution as a tetramer [10]. The key step in the interaction of the organocopper compound (I) with the benzene-insoluble cupric halides involves complex formation at the crystal surface. This results in the formation of an innersphere activated complex XII*, in which internal electron-transfer reduction of Cu^{II} to Cu^{I} takes place with concomitant production of an R radical. In this process an organocopper—cuprous bromide complex is formed**:

$$\mathrm{R_4Cu_4} + (\mathrm{CuX_2})_n \longrightarrow \underset{(\mathrm{XII})}{\left[\mathrm{R_4Cu_3^{I}Cu^{I} \quad X \quad Cu^{II}X(Cu^{II}X_2)_{n-1}}\right]} \longrightarrow \underset{(\mathrm{XIII})}{\left[\mathrm{R^{\bullet}\ R_3Cu_3^{I}Cu^{I}X\ Cu^{I}X(Cu^{II}X_2)_{n-1}}\right]}$$

For the R radical two possibilities for further reaction can be envisaged:

(*i*) escape of R˙ from the solvent cage followed by hydrogen abstraction from the solvent (formation of RH) or dimerization (formation of R—R):

$$(\mathrm{XIII}) \longrightarrow \mathrm{R_3Cu_3^{I}Cu^{I}X \cdot Cu^{I}X(Cu^{II}X_2)_{n-1}} + \mathrm{R^{\bullet}}$$

$$\mathrm{R^{\bullet}} \begin{cases} \xrightarrow{\mathrm{solv.H}} \mathrm{RH} \\ \xrightarrow{+\,\mathrm{R^{\bullet}}} \mathrm{RR} \end{cases}$$

(*ii*) intramolecular reaction of R˙ with a Cu^{I}—R or with a Cu^{II}—X bond:

$$(\mathrm{XIII}) \longrightarrow \mathrm{R{-}R} + \mathrm{R_2Cu_2^{I}Cu^{0}Cu^{I}X \cdot Cu^{I}X(Cu^{II}X_2)_{n-1}}$$

$$(\mathrm{XIII}) \longrightarrow \mathrm{R{-}X} + \mathrm{R_3Cu_3^{I}Cu^{I}X \cdot 2Cu^{I}X(Cu^{II}X_2)_{n-1}}$$

In view of the low yield of RH (Table 1) possibility (*i*) seems to represent the less probable reaction path. Obviously, intramolecular trapping of the R radical by the Cu^{I}—R bond (to give Cu^{0} and RR) or by the Cu^{II}—X bond*** (to give Cu^{I} + RX) is preferred. The latter two reactions are competitive, the RR/RX ratio depending on the type of cupric halide used (Table 1). These reactions also provide an explanation for the R_{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 I with cupric bromide. The "concentration" of Cu^{I}—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.

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[*] A similar complex has been proposed as a possible intermediate in the reaction of trialkylboranes and copper(II) halides [11].

[**] The precipitate formed in the early stage of the reaction is red [cf. red colour of RCu · CuX].

[***] Recently Snider [12] reported the oxidative coupling of *trans*-$CF_3CF{=}C(CF_3)Ag$(R'Ag) with $CuBr_2$ 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).

The reactions of 2-[(dimethylamino)methyl]phenyllithium (II) with curpous 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 $(\mathrm{RCu})_x \cdot (\mathrm{CuBr})_y$ were obtained.

$$\mathrm{CuBr} \xrightarrow[\mathrm{Et_2O}]{+\,\mathrm{RLi\,(II)}} \underset{\text{Insoluble}}{(\mathrm{RCu})_x\cdot\mathrm{CuBr}_y}$$

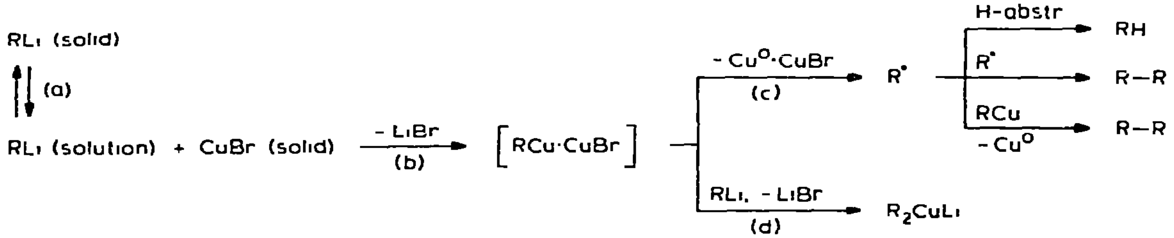
It appeared that only the addition of cuprous bromide to the organolithium solution allows the isolation of pure RCu (I).

$$\mathrm{RLi} \xrightarrow[\mathrm{Et_2O}]{+\,\mathrm{CuBr}} \underset{\text{(I) Insoluble}}{\mathrm{RCu}} + \text{"Black solid"} + \mathrm{RR} + \mathrm{RH}$$

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 $\mathrm{RLi/CuBr_2}$ 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. $\mathrm{CuBr/RLi} \leqslant \frac{1}{2}$



ii. $\frac{1}{2} < \mathrm{CuBr/RLi} \leqslant 1$

$$\mathrm{R_2CuLi} + \mathrm{CuBr\ (solid)} \xrightarrow[\mathrm{(e)}]{-\,\mathrm{LiBr}} 2\,\mathrm{RCu}$$

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[*] See Experimental, synthesis of (I), work-up of the filtrate.

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 $(RCu)_x \cdot (CuBr)_y$ (step b). Several of these complexes are thermally unstable and decompose via homolytic cleavage of the Cu—C bond to give $Cu^0 \cdot (CuBr)_y$ (the so-called "black solid") and products originating from $R^{\cdot}$ (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_2CuLi) 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) [13]. When the CuBr/LiR ratio exceeds 1/2, reaction (e) occurs 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 insoluble CuR · CuBr complexes formed 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 (CuBr/RLi $\leq \frac{1}{2}$).

The course of the reaction of RLi (II) with $CuBr_2$ is much more complicated. In principle this reaction may give rise to the formation of diorganocopper(II) compounds. However, examples of stable organocopper(II) compounds are restricted to the rather exotic biscarboranecopper(II) compound $(Et_4N)_2Cu^{II}[(B_{10}C_2H_{10})_2]_2$ [14]. It has been assumed that during the interaction of RLi (or RMgX) with cupric salts $RCu^{II}X$ 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 [15]. Evidence has been presented that the group R is not generated as a free radical but that intramolecular reaction pathways are involved [16].

Taking into account that also organolithium compounds are highly associated species we propose a course for the reaction of $(RLi)_n$* with CuX_2 salts similar to that described for the reaction of $(RCu)_4$ with CuX_2; i.e.,

$$\underset{\text{(II)}}{R_nLi_n} + CuBr_2 \rightarrow \underset{\text{Innersphere activated complex}}{[R_nLi_{n-1}Li \text{ - - - } Br \text{ - - - - } Cu^{II}Br(Cu^{II}Br_2)_{n-1}]} \rightarrow$$

$$\rightarrow [R^{\cdot}\, R_{n-1}Li_{n-1}LiBr \cdot Cu^{I}Br(Cu^{II}Br_2)_{n-1}] \rightarrow \text{etc.}$$

$$RLi + [LiBr \cdot CuBr] \rightarrow \underset{\text{(I)}}{RCu} + LiBr$$

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[*] E.g., 5-methyl-2-[(dimethylamino)methyl]phenyllithium [13] exists in benzene as a tetramer. For this species a structure (Li_4 core with 2e—3c bonded aryl groups) is proposed similar to that established for the corresponding organocopper compound [10].

In the innersphere activated complex, the groups R are in 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—Li or $Cu^{II}X$ bonds are possible.

Experimental (with Mr. C.A. Schaap)

General

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

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

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° to a freshly prepared suspension of 60 mmol of 2-[(dimethylamino)methyl]phenyllithium (II) [5] in ether (160 ml). The mixture was stirred at −20° for 1 h, warmed 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 for bromide ion (from LiBr) in the filtrate (vide infra) was negative. From the residue pure (I) was isolated [4, 5].

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 to yield an oil containing *N,N*-dimethylbenzylamine (VI) and 2,2′-bis[(dimethylamino)methyl]-biphenyl (V). NMR (C_6D_6, TMS internal, δ ppm): (VI), 2.12 (s, 6H, NCH_3), 3.32 (s, 2H, NCH_2); (V), 2.02 (s, 12H, NCH_3), 3.01 and 3.06 (2 × d, 2H, $J_{gem} \approx 13$ Hz).

Addition of RLi (II) to CuBr: "reversed addition". A solution of 30 mmol of (II) was added at −20° to a well-stirred suspension of CuBr in ether. As distinct from the result in reaction described above, a black-brown solid precipitated from the reaction mixture, the colour of which turned slowly to red-brown upon continued stirring at −20° for 1 h. The mixture was filtered. Both the precipitate and the benzene-soluble brown solid obtained from the filtrate gave a positive test for bromide ion. 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° 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 × 20 ml) and with pentane (2 × 20 ml) and was dried in vacuo (3 h, 20°/0.2 mm). According to elemental analysis the red solid (IIIa) [70% yield based 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. $C_9H_{12}NCu \cdot 1.4CuBr \cdot 0.2C_6H_6$ calcd.: C, 29.57; H, 3.21; Br, 27.02; Cu, 36.81; N, 3.38%.)Decomposition at 96-98°. 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 based on (I)] which decomposed at 100-101°. (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 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. $C_9H_{12}NCu_{3.1}Br_{3.1} \cdot 0.3\ C_6H_6$ (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 mat Cu. NMR spectrum (C_6H_6; TMS internal, δ ppm): RH, 2.13 (s, 6 H, NCH_3), 3.36 (s, 2 H, NCH_2); RBr, 2.10 (s, 6 H, NCH_3), 3.46 (s, 2 H, NCH_2); RR, 2.05 (s, 12 H, NCH_3), 3.05 (d, 2 H) and 3.35 (d, 2 H, $J_{gem} \approx 13$ Hz).

Deuterolysis of (VII). (VII) (0.5 g) was suspended in a mixture of benzene (10 ml) and $DOAc/D_2O$ (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)

TABLE 2

STOICHIOMETRY OF THE PRECIPITATES (VII)-(IX)

Precipitate	Colour	NMR data of the deuterolyzed reaction mixture			Stoichiometry[b]
		RR	RD	RD/RR[a]	
(VII) (From RCu/$CuBr_2$ 1/1)	Light-brown	+	—	—	$C_9H_{12}NCu_{3.1}Br_{3.1} \cdot 0.3\ C_6H_6$ (Composition: 0.5 RR, 3.1 CuBr, 0.3 C_6H_6)
(VIII) (From RCu/$CuBr_2$ 2/1)	Red	+	+	2.37/1	$C_9H_{12}NCu_{2.0}Br_{1.3} \cdot 0.03\ C_6H_6$ (Composition: 0 23 RR, 0.54 RCu, 1.3 CuBr, 0.16 Cu^0, 0.03 C_6H_6)
(IX) (From RCu/$CuCl_2$ 1/1)	Metallic brown				

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

(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 · 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 mat Cu. NMR spectrum (C_6H_6; TMS internal, δ 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 deuterolyzed 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).

Acknowledgement

Financial support by International Copper Research Association, Inc., New York is acknowledged.

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