The Role of Mixed Organocopper Cluster Compounds $R_nR'_mCu_{n+m}$ in Selective C–C Coupling Reactions of 2- and 4-(Dimethylamino)phenylcopper with Copper Arylacetylides[1]

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The 1/1 interaction of Ar_nCu_n (Ar = 2-$Me_2NC_6H_4$) with CuC≡CR (R = phenyl, 4-tolyl, 2,4-xylyl, mesityl, 4-chlorophenyl, 4-methoxyphenyl, and 4-nitrophenyl) in DMF at 125 °C affords the asymmetric cross-coupling products ArC≡CR in almost quantitative yield. It is shown that these reactions involve the intermediate formation of well-defined mixed organocopper cluster species $Ar_4Cu_6(C{\equiv}CR)_2$ which have been isolated and characterized [decomposition between 128 °C (R = phenyl) and 189 °C (R = mesityl)]. The high selectivity of the C–C bond-forming process follows from the fact that the hexanuclear copper intermediate contains exclusively triangular copper faces occupied by one Ar and one C≡CR ligand, whereas Cu_3Ar_2 or $Cu_3(C{\equiv}CR)_2$ faces are absent. A separate study of the decomposition pattern of $Ar_4Cu_6(C{\equiv}CR)_2$ reveals that release of an ArC≡CR molecule is followed by cluster rearrangement of a transient $Ar_3Cu^0{}_2Cu^I{}_4C{\equiv}CR$ intermediate to give Ar_nCu_n (2 equiv) and the mixed valence species $ArCu^0{}_2Cu^I{}_2C{\equiv}CR$. The latter species finally decomposes to give ArC≡CR and Cu^0. These findings are compared with the products formed in the reactions of ArI with CuC≡CR (ArC≡CR, ArI, HC≡CR) and ArCu with IC≡CR (ArC≡CR, ArAr, ArH, and 1-methyl-2-(4-methylphenyl)-3-iodoindole). Various routes leading to cross-coupling and to side products have been discussed in terms of known reactions of a well-defined arylcopper compound.

There is much current interest in asymmetric C–C coupling brought about by reactions involving organocopper intermediates.[2] A recent example is the synthesis of arylacetylenes.[3]

$$RI + CuC{\equiv}CR' \rightarrow RC{\equiv}CR' + CuI \qquad (1)$$

$$RCu + IC{\equiv}CR' \rightarrow RC{\equiv}CR' + CuI \qquad (2)$$

The route starting from copper arylacetylides and aryl iodides (the so-called Castro coupling reaction[4]) has been extensively studied. The interaction of arylcopper compounds with iodoacetylenes has recently been reported by Oliver and Walton.[5] The formation of an asymmetric product in addition to biaryls, biacetylenes, and arenes, which are frequently encountered as side products, is explained in terms of reactions taking place in the ligand sphere of mononuclear copper complexes.[3–5] Recently, we have found that diarylacetylenes are selectively formed upon thermal decomposition of hexanuclear mixed organocopper clusters $(2\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CR)_2$.[6] Based on this observation we anticipated that, also in the asymmetric coupling reactions cited above, polynuclear copper species, in which unlike organo groups are bound to a copper core, are intermediates.

We now report a novel route for the synthesis of 2- and 4-(dimethylamino)-substituted biarylacetylenes via the interaction of 2- or 4-(dimethylamino)-substituted arylcopper compounds with various copper arylacetylides. Mixed organocopper cluster derivatives which appear to be key intermediates have been isolated and characterized. A mechanism for the coupling reaction is presented and placed in the perspective of the discussion concerning the mechanism of asymmetric C–C coupling reactions involving organocopper intermediates.

Results

Coupling Reactions. *N,N*-Dimethyl-2-(arylethynyl)-benzenamines are formed in high yield when pure 2-(dimethylamino)phenylcopper[7] (**1**) is allowed to react with cuprous arylacetylides in a 1/1 molar ratio.

In order to make possible a comparison of our results with those reported earlier for the organocopper/organic halide reactions[3–5] and for the thermal decomposition of pure **1** in dimethylformamide (DMF),[8] standard conditions (125 °C, DMF) have been used throughout this study. The coupling reactions proceed with high specificity (see Table I). Only very small amounts (<1%) of one of the possible symmetric coupling products, i.e., 2,2′-bis(dimethylamino)biphenyl (**2**), could be detected in the reaction mixtures. Biacetylenes appear to be essentially absent. Table I suggests that progressive substitution of the phenyl nucleus of the copper arylacetylide with methyl groups results in an increase of the amount of the reduction product *N,N*-dimethylaniline (**3**) formed (entries 1–4a of Table I). However, a closer study revealed that **3** is not formed via thermal decomposition of **1**. Heating of pure **1** in DMF at 130 °C affords not only **3** (60% yield), but also the dimer **2** (40% yield). The absence of **2** in the ArCu/CuC≡CR reaction mixtures (entries 1–4a), in spite of a 2.5-h reaction period at 125 °C, strongly suggests that after that time organocopper species containing copper–dimethylaminophenyl bonds are still present and that the arene **3** is formed during the hydrolytic work-up procedure.

When the 1/1 reaction of **1** with cuprous (4-methylphenyl)acetylide (**5**) was conducted at 60 °C in addition to unreacted **5**, a large amount of a benzene-soluble yellow solid was isolated. The asymmetric coupling product was isolated in only 4% yield. Identification by elemental analysis and NMR and IR spectroscopy showed the solid to be identical with the hexanuclear cluster compound $(2\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CC_6H_4CH_3\text{-}4)_2$. The synthesis and characterization of this type of cluster compounds, which contain the aryl and the acetylide group in a 2/1 ratio, have been described in a separate paper.[9]

These above experiments establish that formation of the mixed organocopper clusters takes place at temperatures below the point at which thermal decomposition of the parent arylcopper compound starts.

$$4ArCu + 4CuC{\equiv}CR \rightarrow Ar_4Cu_6(C{\equiv}CR)_2 + 2CuC{\equiv}CR \qquad (3)$$

$$Ar = 2\text{-}Me_2NC_6H_4$$

Furthermore, the stoichiometry of the reaction (3) explains why the arylcopper compound **1** is not present in the reaction mixture. It must be noted that thermal decomposition of the cuprous arylacetylides requires temperatures far above 125 °C.[4]

Table I. Product Distribution[a] in the Coupling Reaction of 2-(Dimethylamino)phenylcopper [ArCu] (1) with Copper Arylacetylides [CuC≡CR] (4–10)

R	ArC≡CR	ArAr	ArH
1. $-C_6H_5$ (**4**)	0.90	<0.005	0.06
2. $-C_6H_4(CH_3)$-4 (**5**)	0.90	<0.005	0.07
3. $-C_6H_3(CH_3)_2$-2,4 (**6**)	0.79		0.17
4a. $-C_6H_2(CH_3)_3$-2,4,6 (**7**)	0.29	0.012	0.65
4b. $-C_6H_2(CH_2)_3$-2,4,6 (**7**)[b]	0.84		0.16
5. $-C_6H_4OCH_3$-4 (**8**)	0.89	0.005	0.04
6. $-C_6H_4NO_2$-4 (**9**)	0.76	0.100	0.12
7. $-C_6H_4Cl$-4 (**10**)	0.92		0.05

[a] The mole ratio as determined by GLC analysis. The products were identified by GC/MS analysis. Other products ($\ll$0.05) were detected in trace amounts only. [b] Reaction carried out at 95 °C for 4 h followed by 1 h at 150 °C.

Table II. Product Distribution in Different Types of Coupling Reactions

	Products		
Reaction	ArC≡CR	ArAr	ArH
$4\text{-}H_3CC_6H_4C{\equiv}CCu$ + $2\text{-}Me_2NC_6H_4Cu$ (pure)	0.90	<0.005	0.06
$4\text{-}H_3CC_6H_4C{\equiv}CCu$ + $2\text{-}Me_2NC_6H_4Cu$ (in situ)	0.21		0.55
$4\text{-}H_3CC_6H_4C{\equiv}CCu$ + $2\text{-}Me_2NC_6H_4I$	0.22		*a*
$4\text{-}H_4CC_6H_4C{\equiv}CI$ + $2\text{-}Me_2NC_6H_4Cu$	0.76	0.18	0.022[a]

[a] See Experimental Section.

Table III. Product Distribution in the Coupling Reaction of 4-(Dimethylamino)phenylcopper (26) [ArCu] with Copper Arylacetylides [CuC≡CR] (5, 8–10)[a]

R	ArC≡CR	ArAr	ArH
1. $-C_6H_4CH_3$-4 (**5**)	0.48	0.26	0.11
2. $-C_6H_4OCH_3$-4 (**8**)	0.83		0.12
3. $-C_6H_4NO_2$-4 (**9**)[b]	0.17	0.42	0.20
4. $-C_6H_4Cl$-4 (**10**)	0.81		0.12

[a] 4-(Dimethylamino)phenylcopper was obtained via the reaction of metallic lithium with 4-bromo-*N*,*N*-dimethylaniline [ArBr]. Unreacted ArBr has been detected in reaction 1, 0.06; 3, 0.02; and 4, 0.02. [b] RC≡CH, 0.07.

A separate study of one of these clusters $Ar_4Cu_6(C{\equiv}CC_6H_4CH_3\text{-}4)_2$ (**12**) provided information about the products formed upon hydrolysis and thermal decomposition. Hydrolysis of **12** with ammonia resulted in the formation of the arene **3** in almost quantitative yield. Thermal decomposition of **12** involves several steps.[6] Heating of a benzene solution of **12** at 80 °C for 7 h affords the asymmetric coupling product *N*,*N*-dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine (**16**) together with only a very small amount of the arene (**3**). The symmetric coupling product (**2**) is not detected in the reaction mixture. The precipitate which is formed during the reaction consists of almost pure 2-(dimethylamino)phenylcopper (**1**). Furthermore, a benzene-soluble dark colored product, which appeared to be highly sensitive toward oxygen and water, was isolated. This product (**22**) contains both the aryl and the acetylide ligand as appeared from NMR spectroscopy. The overall reaction course can be represented by the following equation:

$$Ar_4Cu_6(C{\equiv}CC_6H_4CH_3\text{-}4)_2 \xrightarrow[80\ °C,\ C_6H_6]{k_1} \underset{(\mathbf{22})}{[ArCu^0{}_2Cu^I{}_2(C{\equiv}CC_6H_4CH_3\text{-}4)]} + ArC{\equiv}CC_6H_4CH_3\text{-}4 + 2ArCu \quad (4)$$

Upon continued heating at 80 °C in benzene, again the asymmetric product was formed but at a far slower rate.

$$\underset{(\mathbf{22})}{[ArCu^0{}_2Cu^I{}_2(C{\equiv}CC_6H_4CH_3\text{-}4)]} \xrightarrow{k_2} ArC{\equiv}CC_6H_4CH_3\text{-}4 + 4Cu^0 \quad (5)$$

It must be expected that the mixed organocopper clusters formed in the 1/1 reaction mixtures of the organocopper (**1**) and copper arylacetylides decompose along the same route.

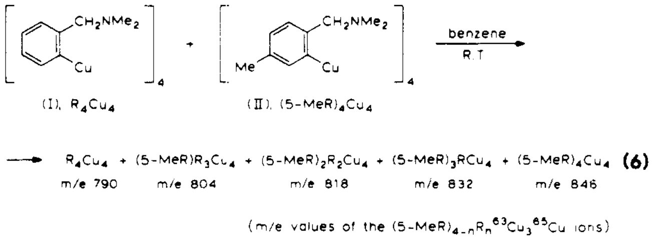
2-(Dimethylamino)phenylcopper formed during the decomposition reaction is recycled into a mixed organocopper cluster by reaction with copper arylacetylide (which is present in excess during the entire reaction period, cf. eq 4 and 3). Accordingly, the decomposition temperature relative to the reaction temperature determines the yield of the coupling product. The compound containing the mesitylethynyl group is thermally the most stable in the series mixed organocopper clusters $Ar_4Cu_6(C{\equiv}CR)_2$; R = phenyl (**11**, dec temp 128 °C) < 4-tolyl (**12**, 138 °C) < 2,4-xylyl (**13**, 165 °C) < mesityl (**14**, 189 °C). This explains the low yield of the cross-coupling product **18** in the reaction of 2-(dimethylamino)phenylcopper (**1**) with cuprous (2,4,6-trimethylphenyl)acetylide (**7**) at 125 °C. Indeed, heating of the 1/1 mixture of **1** and **7** to 95 °C for 4 h followed by heating to 150 °C for 1 h resulted in almost quantitative formation of the asymmetric coupling product **18** (cf. entry 4b in Table I).

The synthesis of *N*,*N*-dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine (**16**) by the two possible organocopper/organic halide routes gives rise to the formation of considerable amounts of by-products (see Table II). The 1/1 reaction of cuprous (4-methylphenyl)acetylide (**5**) with 2-iodo-*N*,*N*-dimethylaniline (**23**) at 125 °C in DMF affords **16** in only 22% yield. Castro et al.[4] observed for similar reactions in DMF at 120 °C (reaction time 22 h) the formation of indoles, whereas in pyridine at 110 °C asymmetric coupling products were obtained in 25–90% yield. The second route,[10] involving the 1/1 reaction of 2-iodo-1-(4-methylphenyl)acetylene (**24**) with **1** at 125 °C in DMF, gives rise to the formation of asymmetric product **16** (76%), dimer **2** (18%), *N*,*N*-dimethylaniline (**3**, 2.2%), and novel 1-methyl-2-(4-methylphenyl)-3-iodoindole[11] (**25**, 6%).

The influence of the position of the dimethylamino ligand on the course of the coupling reaction is illustrated by the results of 1/1 reactions of 4-(dimethylamino)phenylcopper[7] (**26**) with various copper arylacetylides (see Table III). The results fall into two categories. Selective coupling is observed in the reaction of **26** with the 4-methoxy- and the 4-chloro-substituted phenylacetylides, whereas asymmetric coupling and the formation of the biaryl 4,4′-bis(dimethylamino)biphenyl (**27**) takes place with the 4-methyl- and the 4-nitro-substituted derivatives. Most probably the relatively large amount of the dimer **27** in the case of the 4-nitrophenylacetylide (cf. entry 3, Table III) is due to oxidative coupling caused by the presence of nitro-substituted compounds in the reaction mixture (see also entry 6 in Table I).[12] The amount of arene **3** present in the reaction mixtures arises from some hydrolysis taking place during the preparation and handling of the organocopper reagent.

Discussion

The C–C Coupling Process. To our knowledge, the compounds of the type $Ar_4Cu_6(C{\equiv}CR)_2$ (cf. ref 6 and 9) are the first examples of isolated organocopper species which have structures containing different organic ligands bound via carbon to one central copper core. In recent reports the existence of mixed organocopper species $R_nR'_mCu_{n+m}$ in mixtures of two organocopper compounds R_nCu_n and R'_mCu_m has been inferred from NMR and IR spectroscopic data.[6,13,14] However, isolation and characterization of discrete mixed organocopper clusters appeared to be impossible, because the clusters studied so far were all subject to interaggregate exchange processes. For example, van Koten and Noltes[13] established intercluster exchange of organo groups to take place in a 1/1 mixture of $2\text{-}Me_2NCH_2C_6H_4Cu$ (**28**) and its 5-methyl derivative (**29**). This exchange has been proposed to proceed via an associative pathway involving octameric species $R_n(5\text{-MeR})_{8-n}Cu_8$. The various tetranuclear species in eq 6 can be assumed to be of comparable stability, because each of the R and 5-MeR groups bridges two copper atoms in essentially the same way, while the built-in ligand coordinates to one of these copper atoms via a five-membered chelate ring (cf. x-ray structure determination of $(5\text{-MeR})_4Cu_4$).[13] In contrast, copper–nitrogen interaction of the built-in ligand in anilinocopper derivatives involves a third copper atom.[15] It is this unique property of the anilino ligand which renders the $Ar_4Cu_6^{2+}$ skeleton a stable entity and allows the isolation of a variety of $Ar_4Cu_6X_2$ (X = halogen[7,15] (cf. x-ray,[16] Otf,[17] C≡CR[9]) cluster species.



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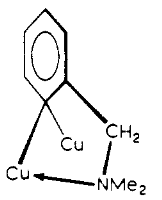

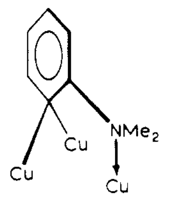

When discussing the thermal decomposition of organocopper clusters it is important to realize that, as a result of their polynuclear structure, reacting groups are in close proximity to the effect that concerted or consecutive intraaggregate metal–carbon bond-breaking and C–C bond-forming processes are possible which would not easily occur otherwise. This is illustrated by the recent report on the thermal decomposition of $[2\text{-}CuC_6H_4CH_2N(CH_3)CH_2]_2$ dimer (**30**) which produces exclusively the intramolecular ring-closed product

$$\overline{CH_2(CH_3)NCH_2C_6H_4C_6H_4CH_2N(CH_3)CH_2}$$

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without a trace of H-abstraction or oligomeric products.[18] It was proposed that a template effect exerted by the Cu_4 square in **30** was responsible for the specificity of the ring closure. Another example is the thermolysis of $(m\text{-}CF_3C_6H_4)_8Cu_8$, which proceeds via pairwise elimination of $m\text{-}CF_3C_6H_4$ groups and likewise is a nonfree radical reaction.[19]

In principle, symmetric as well as asymmetric dimer formation may be expected to occur upon thermal degradation of mixed organocopper clusters. The fact that in $Ar_4Cu_6(C{\equiv}CR)_2$ clusters exclusively asymmetric coupling occurs and symmetric coupling or H-abstraction products are not observed indicates that these reactions proceed via a nonfree radical pathway. More importantly, in spite of an Ar/C≡CR ratio of 2/1 in the cluster, exclusive asymmetric coupling takes place. This observation gives relevance to the viewpoint that both *the nature of the central copper core and the way in which the Cu_n faces are occupied by organo groups play a decisive role in the product-forming step.*

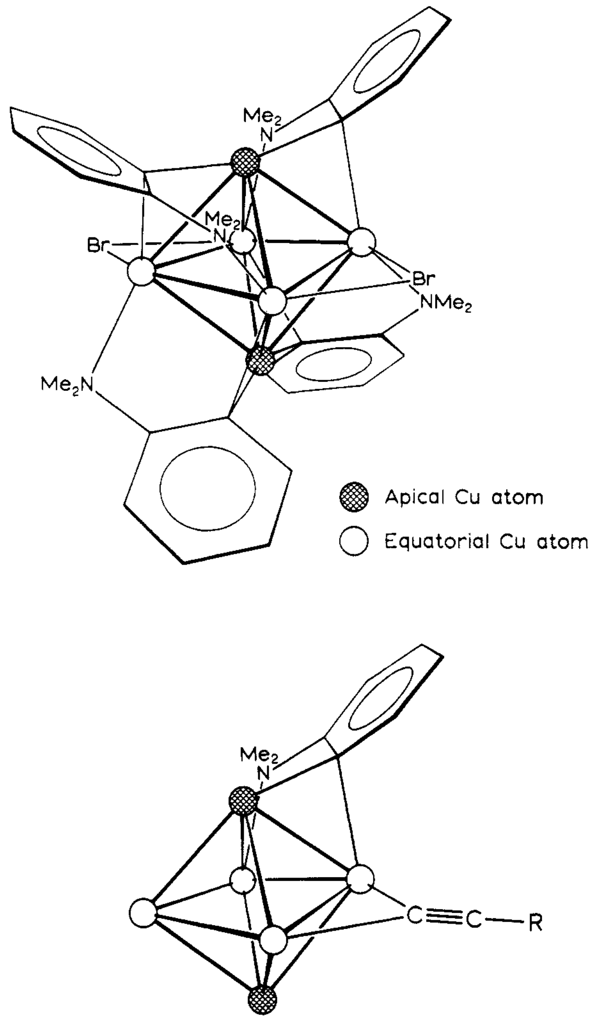


Figure 1. Structure of $Ar_4Cu_6Br_2$ (top, ref 15) and proposed bonding in $Ar_4Cu_6(C{\equiv}CR)_2$ (bottom, ref 9).

The occurrence of specific coupling in $Ar_4Cu_6(C{\equiv}CR)_2$ can be inferred from its structural features[9] (see Figure 1). Four triangular faces are present, each occupied by one Ar and one C≡CR bridging group, whereas Cu_3Ar_2 or $Cu_3(C{\equiv}CR)_2$ faces are absent.

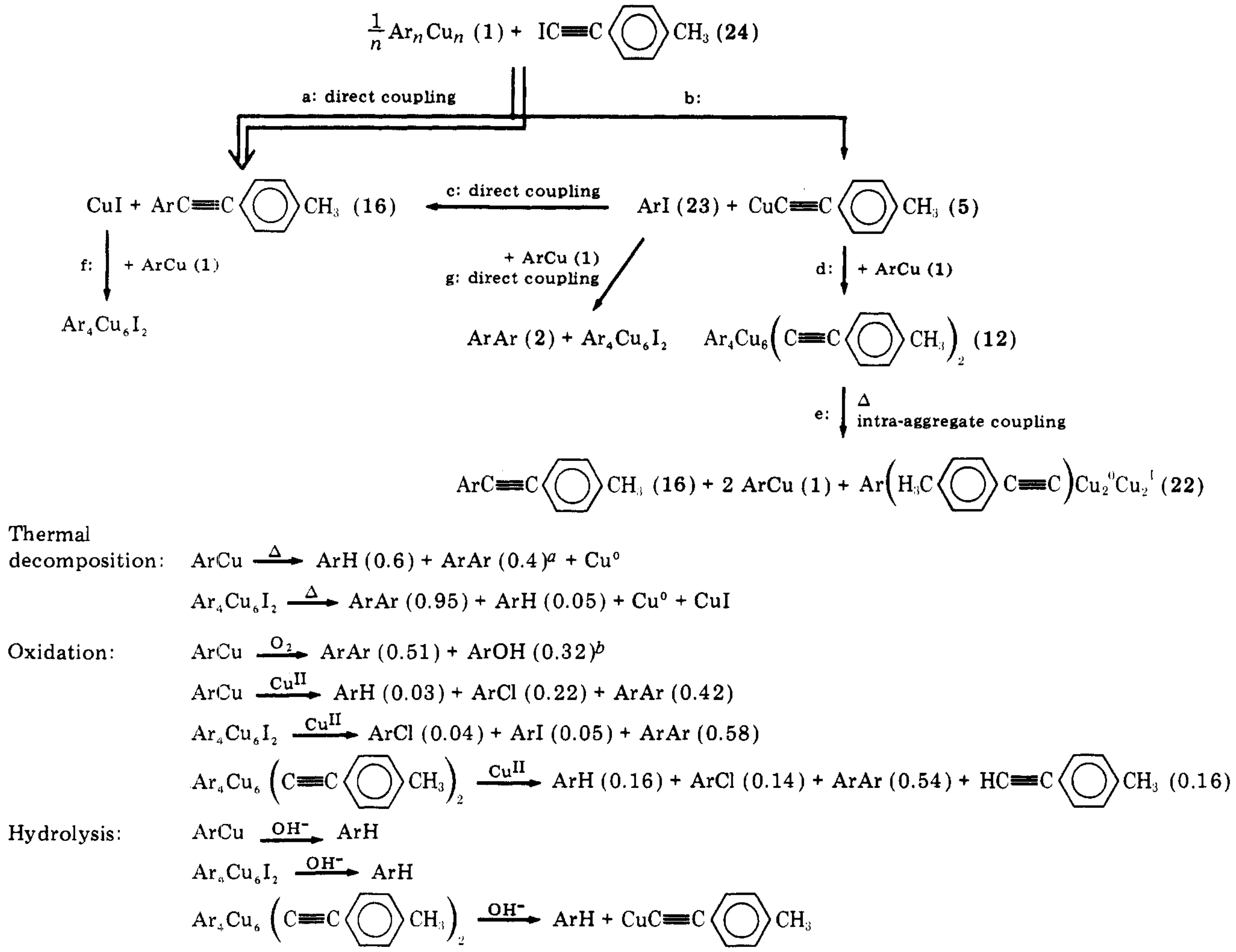
The observation that thermolysis proceeds in two stages and that in the first stage only 1 equiv of ArC≡CR together with 2 equiv of ArCu are formed can be explained by the following reaction course. The first stage

$$Ar_4Cu_6(C{\equiv}CR)_2 \rightarrow ArC{\equiv}CR + Ar_3Cu^I_4Cu^0_2(C{\equiv}CR) \quad (7)$$

$$Ar_3Cu^I_4Cu^0_2(C{\equiv}CR) \rightarrow 2ArCu + [ArCu^I_2Cu^0_2(C{\equiv}CR)] \quad (8)$$

involves elimination of 1 equiv of ArC≡CR and transient formation of a hexanuclear $Ar_3Cu^I_4Cu^0_2(C{\equiv}CR)$ species which undergoes cluster rearrangement leading to polymeric ArCu and a new Cu^ICu^0 cluster. The nature of the latter mixed-valence copper cluster which is still under investigation has a precedent in recently reinvestigated[20] $(m\text{-}CF_3C_6H_4)_6\text{-}Cu^I_6Cu^0_2$ reported by Cairncross and Sheppard.[19] In the second stage (eq 5), metallic copper and a second equivalent of ArC≡CR are formed.

Scheme I [Ar = 2-*N*,*N*-dimethylaminophenyl]



[a] mol % Ar. [b] Ar = 5-methyl-2-[(dimethylamino)methyl]phenyl.

Summation of eq 3, 7, 8, and 5 gives rise to the observed overall stoichiometry in the 1/1 reaction of ArCu with CuC≡CR:

$$2\text{ArCu} + 2\text{Cu}{\equiv}\text{CR} \rightarrow 2\text{ArC}{\equiv}\text{CR} + 4\text{Cu}^0 \qquad (9)$$

On the basis of these considerations, it is interesting to note that also the reactions of 4-$Me_2NC_6H_4Cu$ with CuC≡CR (R = 4-$MeOC_6H_4$ or 4-ClC_6H_4) results in nonstatistical distributions of coupling products (see Table III). This can be explained by the formation of a well-defined mixed organocopper intermediate which in analogy with the proposed polymeric structure of 4-$Me_2NC_6H_4Cu$[7] might consist of alternating 4-$Me_2NC_6H_4$ and C≡CR groups each bridging copper atoms of a copper chain. Collapse of organic groups in these polymers then results in specific asymmetric coupling.

Relationship to Cross-Coupling Reactions of Organocopper Compounds with Organic Halides. Reactions of organocopper reagents with organic halides have been extensively studied as a route for the formation of new C–C bonds.[2,21]

$$\text{RCu} + \text{R}'\text{Hal} \rightarrow \text{RR}' + \text{CuHal} \qquad (10)$$

However, the applicability of these reactions suffers from the formation of side products.[2] The influence of the solvent and the presence of copper salts or of metallic copper on the product distribution in these reactions have been explained in terms of detailed mechanisms involving either nucleophilic displacement of halogen by the organo group R[2-4] or the formation by oxidative addition of transient Cu^{III} intermediates, RR′CuHal, followed by collapse into the ultimate products.[2,22,23] A reconsideration of the mode of product formation in these reactions would seem to be timely in view of the increasing number of reports describing the structure and reactivity of well-defined organocopper compounds.[6-8,15,17]

In Scheme I, we present a variety of well-established reactions of the organocopper compound **1**, which, pieced together, provide an overall picture of what can happen in a cross-coupling reaction of an organocopper compound with an organic iodide in DMF.[24]

It is obvious from Scheme I that the formation of cross-coupling product $ArC{\equiv}CC_6H_4CH_3$-4 (**16**) can occur via different routes: (i) via direct coupling (a); (ii) via copper–halogen exchange (b) followed by direct coupling of the exchanged products (c), and (iii) via copper–halogen exchange (b) and formation of mixed organocopper clusters (d) which, subsequently, can release a cross-coupling product by intraaggregate coupling (e). However, each of these reactions generate side products which can induce secondary reactions, which in turn are responsible for a decrease of the cross-coupling product **16**: i, cuprous iodide interacts with the organocopper (**1**) to yield the stable hexanuclear cluster compound $Ar_4Cu_6I_2$ (f: cf. ref 14); ii, 2-iodo-*N*,*N*-dimethylaniline (**23**) which is formed in the copper–halogen exchange reaction (b) can interact with unreacted **1** to give the symmetric coupling product ArAr (**2**) and $Ar_4Cu_6I_2$ (g: cf. ref 7). The only "side" reaction which gives rise to the formation of asymmetric coupling product (**16**) is the thermal decomposition e of the mixed organocopper cluster (**12**) generated via b, d.

Each of these reaction sequences has its own set of rate constants. Accordingly, the solvent and the reaction temperature will play an important role in the product distribution. The role of the solvent is demonstrated by the fact that the reaction of ArI (**23**) with **1** in benzene stops at the stage of $Ar_4Cu_6I_2$.[8] Only a 30% yield of ArAr (**2**) is formed, whereas the same reaction in DMF (g) affords **2** quantitatively.[8] The reaction temperature is not only important with respect to the rates of the various reaction sequences. The mixed organocopper or organohalide–copper clusters formed as intermediates have different decomposition temperatures. For example, the organocopper **1** is stable in DMF up to 90 °C, but rapidly degrades at 125 °C into ArAr (**2**), ArH (**3**), and Cu^0.[8] In contrast, $Ar_4Cu_6I_2$ is stable up to 120 °C for a few hours, but above this temperature clean decomposition into ArAr, CuI, and Cu^0 takes place.[25] furthermore, the present paper shows that the formation of the mixed organocopper cluster $Ar_4Cu_6(C\equiv CR)_2$ occurs at temperatures below the decomposition temperature of the parent organocopper compound ArCu. In conclusion, if the temperature applied for the cross-coupling reaction is too high, thermal degradation processes become competitive with respect to the formation of the direct coupling product.

The influence of oxygen on the reaction course is illustrated by the observation that in the presence of oxygen ArCu (**1**) is oxidized to ArAr (**2**) in benzene,[26] whereas, e.g., 2-[(dimethylamino)methyl]-5-methylphenylcopper tetramer gives dimer and the phenol $2\text{-}Me_2NCH_2\text{-}5\text{-}MeC_6H_3OH$ both in benzene and in ether.[27] Moreover, the presence of oxygen in the reaction mixture causes oxidation of cuprous salts generated in the reaction. Accordingly, oxidation of organocopper cluster species Ar_nCu_n, $Ar_nCu_{n+m}X_m$ (X = halogen or $C\equiv CR$), present in the reaction mixture, by Cu^{II} species can be anticipated, and examples of such reactions are included in Scheme I.[8,28]

Protic reagents (of course) will react with the organocopper compounds present, although it should be realized that these reactions take place at different rates, i.e., ArCu (**1**) > $Ar_4Cu_6I_2 \approx Ar_4Cu_6(C\equiv CC_6H_4CH_3\text{-}4)_2$.[26]

Finally, two other side reactions can occur. Addition of ArCu across the triple bond of the acetylenic moiety has been observed for in situ prepared ArCu reagents which contain magnesium or lithium salts.[29] Cyclization of the cross-coupling products to indoles is known to be promoted by copper salts.[4] Both reactions are well-precedented and, moreover, are solvent dependent.

The results of the organocopper/organic halide reactions presented in Table II confirm the importance of the proper choice of reactants (either ArCu/$IC\equiv CC_6H_4CH_3$-4 or ArI/$CuC\equiv CC_6H_4CH_3$-4). In this particular case the ArCu/$CuC\equiv CC_6H_4CH_3$-4 couple affords superior results.

Experimental Section

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

Phenylacetylene was obtained from Fluka AG and used without further purification. 4-Bromo-*N*,*N*-dimethylaniline was obtained from Schuchardt München. Methylation of 2-bromoaniline (Fluka AG) with Me_2SO_4 afforded 2-bromo-*N*,*N*-dimethylaniline.[30] 4-Methyl-, 2,4-dimethyl-, 2,4,6-trimethyl-, and 4-chlorophenylacetylene were obtained via routes involving halogenation of the respective substituted acetophenones with fosfor pentachloride followed by dehydrohalogenation of the α,α'-dichloroarylethanes with an alcoholic–potassium hydroxide solution.[31] 4-Nitro- and 4-methoxyphenylacetylene were synthesized according to published procedures.[31,32]

2-(Dimethylamino)phenylcopper and tetrakis[2-(dimethylamino)phenyl]hexakiscopper dibromide were obtained as described in ref 15, while the cuprous acetylides were synthesized as described by Castro et al.[4]

Iodination of cuprous (4-methylphenyl)acetylide afforded 1-iodo-2-(4-methylphenyl)acetylene.[33]

Melting points were determined on a Reichert melting point microscope and are uncorrected. ^1H NMR spectra were recorded on a Varian Associates HA-100 spectrometer, IR spectra on a Perkin-Elmer grating infrared spectrophotometer nr. 577. GLC analyses were run on a F & M chromatograph Model 810 (column, 6′ ss, 3% Me-PhSil-Fluid), while GC/MS measurements were carried out on a Finnigan 3100 D gas chromatography/mass spectrometer.

Elemental analyses were carried out in this Institute under the supervision of W. J. Buis.

Synthesis of *N*,*N*-Dimethyl-2-(arylethynyl)benzenamines. Via Reaction of 2-(Dimethylamino)phenylcopper (1) with Copper Arylacetylides. The synthesis of ***N*,*N*-dimethyl-2-[(4-methoxyphenyl)ethynyl]benzenamine (19)** is described as an example. A suspension of cuprous (4-methoxyphenyl)acetylide (5.65 mmol) and 2-(dimethylamino)phenylcopper (5.40 mmol) in 40 mL of dimethylformamide (DMF) was stirred at 125 °C for 2.5 h. The dark-colored reaction mixture was cooled to room temperature after which ammonia (50 mL; 6 N) was added. Stirring was continued for another 30 min, followed by the addition of an ether/water mixture. Metallic copper was filtered off. The ether layer was separated, thoroughly washed with water, and dried over $MgSO_4$. Filtration and concentration afforded 1.38 g of a dark brown oil which according to GLC and GC/MS analysis consisted of *N*,*N*-dimethyl-2-[(4-methoxyphenyl)ethynyl]benzenamine (89%, *m/e* 250 (M^+), 235, 220, 207), 2,2′-bis(dimethylamino)biphenyl (0.5%, *m/e* 238 (M^+), 221, 207, 291), and *N*,*N*-dimethylaniline (4%, *m/e* 120 (M^+), 105, 91, 77).

N,*N*-Dimethylaniline and 2,2′-bis(dimethylamino)biphenyl were almost completely removed by washing of an ether solution of the crude product with diluted hydrochloric acid (20 mL; 0.2 N). The ether solution was dried over $MgSO_4$ and concentrated. The resulting residue was crystallized from petroleum ether (60–80 °C), affording light-brown crystals of the pure asymmetric coupling product (85% yield), mp 63–65 °C.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.25; H, 6.84; N, 5.66.

***N*,*N*-Dimethyl-2-(phenylethynyl)benzenamine (15):** recrystallized from MeOH/H_2O; mp 45–48 °C; *m/e* 220 (M^+), 204, 190, 178. ***N*,*N*-dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine (16):** oil, bp 158 °C (0.15 mm), *m/e* 234 (M^+), 218, 204, 189. ***N*,*N*-Dimethyl-2-[(2,4-dimethylphenyl)ethynyl]benzenamine (17):** oil; purified by column chromatography (SiO_2 Woelm, 0.063–0.1 mm, column length 40 cm, using a 1/1 mixture of $CHCl_3$/hexane as an eluent); *m/e* 248 (M^+), 232, 217, 202. ***N*,*N*-Dimethyl-2-[(4-nitrophenyl)ethynyl]benzenamine (20):** recrystallized from petroleum ether (60–80 °C); mp 76–78 °C; *m/e* 265 (M^+), 250, 235, 219. ***N*,*N*-Dimethyl-2-[(4-chlorophenyl)ethynyl]benzamine (21):** oil; purified by column chromatography, see **17**; *m/e* 254 (M^+), 238, 224, 218. For NMR and IR data, see Table IV.

The synthesis of ***N*,*N*-Dimethyl-2-[(2,4,6-trimethylphenyl) ethynyl]benzenamine (18)** required heating the mixture of 2-(dimethylamino)phenylcopper and cuprous (2,4,6-trimethylphenyl)acetylide at 95 °C for 4 h and for another 1 h at 150 °C. Recrystallization of the crude product from a MeOH/H_2O mixture yielded white crystalline **18**, mp 48–51 °C.

Synthesis according to the procedure described above for **19** gives rise to the formation of a mixture of *N*,*N*-dimethyl-2-[(2,4,6-trimethylphenyl)ethynyl]benzenamine (29%) and *N*,*N*-dimethylaniline (65%). The use of pyridine instead of DMF as a solvent, without any further change of the reaction conditions and the work-up procedure, afforded (according to NMR spectroscopy) a mixture of *N*,*N*-dimethylaniline (70%), 2,2′-bis(dimethylamino)biphenyl (3.7%), and *N*,*N*-dimethyl-2-[(2,4,6-trimethylphenyl)ethynyl]benzenamine (26%). NMR (CCl_4): *N*,*N*-dimethylaniline δ 2.88 (NCH_3); 2,2′-bis(dimethylamino)biphenyl δ 2.50 (NCH_3); *N*,*N*-dimethyl-2-[(2,4,6-trimethylphenyl)ethynyl)]benzenamine δ 2.90 (NCH_3), 2.24 (4-CH_3), 2.44 (2,6-CH_3).

Via Reaction of in Situ Prepared 2-(Dimethylamino)phenylcopper with Cuprous Phenylacetylide. A solution of 2-(dimethylamino)phenyllithium [obtained from the reaction of 2-bromo-*N*,*N*-dimethylaniline (29.7 mmol) with lithium (69.5 mmol)[6]] in 60 mL of ether was added to a suspension of cuprous bromide (29.3 mmol) in the same solvent kept at −20 °C. The mixture was stirred for 1 h and then concentrated. Benzene (60 mL) was added and stirring continued for 16 h. Benzene was removed by evaporation. Subsequently, cuprous phenylacetylide (30.4 mmol) and 200 mL of dimethylformamide were added. This mixture was heated at 125 °C for

Table IV. Spectral Data for *N,N*-Dimethyl-2- and 4-[Arylethynyl]benzenamines

Aryl	IR, $\nu_{C\equiv C}$ (cm^{-1})[a]	NCH_3	NMR, δ (ppm)[b] aryl ring substituents				
	2-[Arylethynyl] Derivatives						
1. Phenyl (**15**)	2211	2.73					
2. 4-Methylphenyl (**16**)	2208	2.75	2.00 (4-CH_3)				
3. 2,4-Dimethylphenyl (**17**)	2203	2.74	2.06 (4-CH_3), 2.48 (2-Me)				
4. 2,4,6-Trimethylphenyl (**18**)	2196	2.73	2.10 (4-CH_3), 2.62 (2-Me), 6.76 (3,5 H)				
5. 4-Methoxyphenyl (**19**)	2211	2.78	3.18 (4-OCH_3)				
6. 4-Nitrophenyl (**20**)	2202	2.70					
7. 4-Chlorophenyl (**21**)	2213	2.72					
			4-X[c]	$H_{3,5}$[d]	$H_{2,6}$[d]	$H_{2,6}$[e]	$H_{3,5}$[e]
	4-[Arylethynyl] Derivatives						
8. 4-Methylphenyl (**32**)	2210	2.37	2.00	7.52	6.37	7.58	6.84
9. 4-Methoxyphenyl (**33**)	2210	2.37	3.18	7.52	6.39	7.60	6.62
10. 4-Nitrophenyl (**34**)	2209	2.36		7.55	6.36	7.71	*f*
11. 4-Chlorophenyl (**35**)	2213	2.36		7.54	6.36	7.24	6.93

[a] Dissolved in C_6H_6. Frequency region 2200 to 2000 cm^{-1} was calibrated with DCl gas. [b] C_6D_6 solution, Me_4Si internal standard. [c] Para substituent in the aryl ring. [d] Protons (J = 8 Hz) in the aromatic ring containing the dimethylamino group. [e] Protons (J = 8 Hz) of the aryl ring. [f] Resonances masked by the solvent.

2.5 h. Working-up of the resulting reaction mixture, as described above, gave rise to the isolation of a dark-colored oil which according to NMR spectroscopy contained *N,N*-dimethylaniline (55%) and *N,N*-dimethyl-2-(phenylethynyl)benzenamine (21%). NMR (C_6D_6): *N,N*-dimethylaniline δ 2.50 (s, 6, NCH_3); *N,N*-dimethyl-2-[phenylethynyl]benzenamine δ 2.73 (s, 6, NCH_3).

Via Reaction of 2-Iodo-*N,N*-dimethylaniline and Cuprous (4-Methylphenyl)acetylide. A mixture of 2-iodo-*N,N*-dimethylaniline (5.26 mmol) and cuprous 4-methylphenylacetylide (5.37 mmol) in 50 mL of DMF was heated at 125 °C for 3 h. After cooling, 100 mL of ammonia (6 N) and 100 mL of ether were added. The precipitate was filtered off after stirring for an additional 30 min. The filtrate was extracted with ether. The ether extract was thoroughly washed with water and dried over $MgSO_4$. Filtration and evaporation of the solvent afforded a slightly red-colored oil (1.3 g), which according to NMR spectroscopy consisted of 2-iodo-*N,N*-dimethylaniline (50%), (4-methylphenyl)acetylene (28%), and *N,N*-dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine (22%). NMR (C_6D_6): 2-iodo-*N,N*-dimethylaniline δ 2.43 (s, 3 H, NCH_3); (4-methylphenyl)acetylene δ 2.75 (s, 1 H) 1.94 (s, 3 H, 4-CH_3); *N,N*-dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine δ 2.75 (s, 6 H, NCH_3), 2.00 (s, 3 H, 4-CH_3).

Via Reaction of 2-(Dimethylamino)phenylcopper and 1-Iodo-2-(4-methylphenyl)acetylene. 1-Iodo-2-(4-methylphenyl) acetylene (7.23 mmol) was added to a suspension of 2-(dimethylamino)phenylcopper in 50 mL of DMF. This mixture was stirred at 125 °C for 3 h. After cooling to room temperature, 50 mL of ammonia (6 N), 100 mL of water, and 100 mL of ether were added. The resulting mixture was stirred for 30 min and the yellow precipitate (cuprous(4-methylphenyl)acetylide according to elemental analysis and IR) was filtered off. The filtrate was extracted with ether. The ether extract was thoroughly washed with water and dried over $MgSO_4$. After concentration, an oil remained (1.43 g), which according to GLC and GC/MS consisted of 2-iodo-*N,N*-dimethylaniline (9%; *m/e* 247 (M^+), 119, 104, 91), *N,N*-dimethylaniline (2.2%; *m/e* 120 (M^+), 105, 92, 77), 2,2′-bis(dimethylamino)biphenyl (18%, *m/e* 240 (M^+), 209, 194, 180), 1-methyl-2-*p*-tolyl-3-iodoindole (6%; *m/e* 347 (M^+), 219, 204, 190), *N,N*-dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine (76%; *m/e* 234 (M^+), 218, 204, 189). NMR (CCl_4): 1-Methyl-2-*p*-tolyl-3-iodoindole δ 2.38 (s, 3 H, *p*-CH_3), 3.54 (s, 3 H, NCH_3).[11]

Synthesis of *N,N*-Dimethyl-4-(arylethynyl)benzenamines. In a typical experiment, a solution of 4-(dimethylamino)phenyllithium [obtained from the reaction of 4-bromo-*N,N*-dimethylaniline (10.5 mmol) with lithium (29.0 mmol)[7]] in 50 mL of ether was added at 0 °C to a suspension of cuprous bromide (10.1 mmol) in 20 mL of ether. The resulting blue-colored mixture was stirred for 1 h followed by removal of the solvent by evaporation. Subsequently, cuprous (4-methylphenyl)acetylide (10.1 mmol) and 50 mL of DMF was added. The resulting suspension was stirred at 120 °C for 2.5 h. After cooling to room temperature, 50 mL of ammonia was added and stirring continued for 30 min. After filtration, the mixture was extracted with ether. The ether extract was thoroughly washed with water and dried over $MgSO_4$. Filtration followed by evaporation of the solvent afforded a dark-brown oil (1.35 g) consisting of 4-bromo-*N,N*-dimethylaniline (6%; *m/e* 201 (M^+), 185, 157, 118), *N,N*-dimethylaniline (11%; *m/e* 121 (M^+), 105, 91, 77), 4,4′-bis(dimethylamino)biphenyl (26%, *m/e* 240 (M^+), 225, 209, 196), and ***N,N*-dimethyl-4-[(4-methylphenyl)ethynyl]benzenamine (32)** (48%; *m/e* 235 (M^+), 219, 189, 176) (GLC and GC/MS analysis). The benzenamine could be obtained almost pure by washing a solution of the oil in ether (50 mL) with hydrochloric acid (25 mL; 0.08 N) and water (3 × 20 mL). Sublimation of the crude product yielded pure ***N,N*-dimethyl-4-[(4-methylphenyl)ethynyl]benzenamine (32)** as yellow crystals, mp 160–162 °C. Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.01; H, 7.40; N, 5.68. ***N,N*-Dimethyl-4-[(4-methoxyphenyl)ethynyl]benzenamine (33):** recrystallized from petroleum ether (60–80 °C); mp 135–136 °C, *m/e* 251 (M^+), 236, 221, 208. ***N,N*-Dimethyl-4-[(4-nitrophenyl)ethynyl]benzenamine (34):** mp 214–217 °C (after sublimation); *m/e* 266 (M^+), 250, 236, 220. ***N,N*-Dimethyl-4-[(4-chlorophenyl)ethynyl]benzenamine (35):** mp 147–148 °C (after sublimation); *m/e* 255 (M^+), 239, 221, 212. For NMR and IR data, see Table IV.

Synthesis of Tetrakis[2-(dimethylamino)phenyl]bis[4-methylphenylethynyl]hexakiscopper (12). Via Reaction of 2-(Dimethylamino)phenylcopper and Cuprous (4-Methylphenyl)acetylide. A suspension of 2-(dimethylamino)phenylcopper (10.8 mmol) and cuprous (4-methylphenyl)acetylide (5.6 mmol) in 40 mL of DMF was stirred at 65 °C for 2 h. Addition of a pentane/ether mixture (100 mL/60 mL) afforded a yellow precipitate. The solvent was decanted and the yellow residue was extracted with benzene. The benzene extract was concentrated to dryness and the remaining yellow solid was washed with pentane and dried in vacuo. Elemental analysis and NMR spectroscopy revealed this solid to be pure **12** (31% yield). Anal. Calcd for $C_{50}H_{54}N_4Cu_6$: C, 54.98; H, 4.98; N, 5.13; Cu, 34.90. Found: C, 55.27; H, 5.07; N, 5.12; Cu, 34.61. NMR (C_6D_6, 20 °C): δ 2.10 (s, 6 H, 4-Me), 2.0–2.3 (v br, NCH_3).

Via Reaction of $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$ with (4-Methylphenyl)ethynyllithium. A solution of 1-lithio-2-(4-methylphenyl)-acetylene [obtained by reaction of (4-methylphenyl)acetylene (7.95 mmol) with *n*-butyllithium (5.56 mL; 1.43 N)] in 20 mL of ether was added to a suspension of $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$ (3.97 mmol) in 120 mL of benzene. The resulting mixture was stirred for 3 h. The solvent was removed by evaporation and the resulting residue was extracted with benzene (3 × 50 mL). The benzene extract was concentrated to dryness, whereafter the solid residue was washed with ether (40 mL; removal LiBr) and pentane (4 × 40 mL), and dried in vacuo affording **12** as a yellow solid (3.8 g; 87% yield), mp 138 °C dec. Anal. Calcd for $C_{50}H_{54}N_4Cu_6$: C, 54.98; H, 4.98; N, 5.13; Cu, 34.90. Found: C, 54.10; H, 4.89; N, 5.19; Cu, 34.43. Mol wt Calcd for $C_{50}H_{54}N_4Cu_6$: 1092; found: 1073 (cryometric in benzene, concentration independent). Infrared spectrum (C_6H_6): C≡C at 2040 cm^{-1}. NMR (C_6D_6): δ_{NCH_3}, temperature dependent, 80 °C, 2.46 (s, 24 H); −10 °C ($C_6D_5CD_3$) 3.02 (s, 12 H), 1.74 (s, 12 H); $\delta_{4\text{-}CH_3}$ 20 °C, 2.09 (s, 6 H).

Thermal Decomposition of $(2\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CC_6\text{-}$

H_4Me-4)$_2$ (12) in Benzene at 80 °C. A solution of **12** (2.5 mmol) in benzene (60 mL) was refluxed. After 4 h, NMR spectroscopy of the dark reaction mixture revealed that undecomposed product was still present (cf. $\delta_{p\text{-}CH_3}$ 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. An IR spectrum (Nujol) of this solid was identical to that recorded for a pure sample of 2-(dimethylamino)phenylcopper (**1**) (yield 4.8 mmol).

The clear, dark red-brown benzene filtrate was concentrated. The black residue was extracted with pentane (3 × 20 mL) yielding a black pentane-insoluble, highly oxygen-sensitive 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 °C. Continued heating of a sample at 80 °C resulted in the slow formation of asymmetric coupling product **16** and Cu^0.

The pentane extract was concentrated. The NMR spectrum of the residue in C_6D_6 showed *N,N*-dimethylaniline (**3**, δ_{NCH_3} 2.50 ppm) and asymmetric coupling product (**16**, δ_{NCH_3} 2.75 ppm) to be present in a 0.07/1 mol ratio (**3**/**16**). The symmetric dimer **2** 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 °C for 1 h. Subsequently, the benzene layer was extracted with 8 mL of 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 *N,N*-dimethyl-2-[(4-methylphenyl)-ethynyl]benzenamine (**16**) as a light-red-colored oil in 51.2% yield (2.56 mmol). (For IR and NMR data see Table IV.)

Reactions of (2-$Me_2NC_6H_4$)$_4$(4-$MeC_6H_4C{\equiv}C$–)$_2Cu_6$ (12) with NH_3/H_2O and $CuCl_2$. With NH_3/H_2O. Ammonia (3.5 mL, 6 N) was added to a suspension of **12** (0.51 mmol) in DMF (25 mL) and then stirred for 2 h. Work-up of the reaction mixture (see above) afforded a colorless oil, which according to NMR spectroscopy consisted of *N,N*-dimethylaniline (88%), (4-methylphenyl)acetylene (7%), and *N,N*-dimethylbenzenediamine (5%). NMR (CCl_4): *N,N*-dimethylaniline δ 2.87 (s, NCH_3); (4-methylphenyl)acetylene δ 2.30 (s, 3 H, 4-CH_3), 2.83 (s, 1 H, $C{\equiv}CH$); *N,N*-dimethylbenzenediamine δ, 2.74 (s, NCH_3).

In a separate experiment, cuprous acetylide was stirred with ammonia. NMR spectroscopy (using 1,4-di-*tert*-butylbenzene as an internal standard) revealed that after 1-h hydrolysis had occurred for 40%. NMR (CCl_4); see above.

With $CuCl_2$. Solid **12** (0.366 mmol) was added to a solution of $CuCl_2$ (1.49 mmol) in 20 mL of DMF and stirred for *x* hours. Ammonia (30 mL, 6 N) was added and the resulting mixture was worked-up as described above. The composition of the resulting reddish oil was determined by NMR spectroscopy (using 1,4-di-*tert*-butylbenzene as an internal standard) after 2.5, 20, and 72 h reaction time. After 2.5 h, the oil consisted of *N,N*-dimethylaniline (43%), 2,2′-bis(dimethylamino)biphenyl (39%), 2-chloro-*N,N*-dimethylaniline (12%), and (4-methylphenyl)acetylene (7%). After 20 h, the oil consisted of *N,N*-dimethylaniline (16%), 2,2′-bis(dimethylamino)biphenyl (54%), 2-chloro-*N,N*-dimethylaniline (14%), and (4-methylphenyl)acetylene (16%). After 72 h the result was the same as after 20 h. NMR (CCl_4): *N,N*-dimethylaniline δ 2.90 (NCH_3); 2,2′-bis(dimethylamino)biphenyl δ 2.62 (NCH_3); 2-chloro-*N,N*-dimethylaniline δ 2.76 (NCH_3); (4-methylphenyl)acetylene δ 2.35 (4-CH_3).

With NH_3/H_2O Followed by $CuCl_2$. Ammonia (30 mL, 6 N) was added to a suspension of **12** (1.10 mmol) in 40 mL of DMF. This was immediately followed by the addition of solid cupric chloride (6.77 mmol). This mixture was stirred for 2 h. Subsequently, a water/ether mixture (200 mL/200 mL) was added. The precipitate was filtered off. The separated ether layer was washed with water and dried over $MgSO_4$. Concentration yielded 0.4 g of an oil, consisting of *N,N*-dimethylaniline (80%) and 2-*N,N*-dimethylbenzenediamine (20%), according to NMR spectroscopy (using 1,4-di-*tert*-butylbenzene as an internal standard). NMR spectrum (CCl_4): *N,N*-dimethylaniline δ 2.87 (s, NCH_3); 2-*N,N*-dimethylbenzenediamine δ 2.68 (s, NCH_3). A GLC and GC/MS analysis showed a mixture of *N,N*-dimethylaniline (71%; *m/e* 120 (M^+), 105, 91, 77) and 2-*N,N*-dimethylbenzenediamine (29%; *m/e* 136 (M^+), 121, 106, 94).

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(24) Table II presents results for these reactions (ArI/$CuC{\equiv}CR$, ArCu/$IC{\equiv}CR$).
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(27) The yield of 2-Me_2NCH_2-5-MeC_6H_3OH (**36**) is 8 and 15% in benzene and ether, respectively, whereas the yield of dimer (2-Me_2NCH_2-5-MeC_6H_4)$_2$ is 34 and 48%. NMR (C_6D_6) for **36**: δ 1.78 (s, 6 H, NMe), 2.14 (s, 3 H, 5-Me), 3.17 (s, 2 H, 2-NCH_2), 6.68 (q, J = 7 Hz, 2 H, $H_{3,4}$), 6.97 (s, 1 H, H_3), 10.4 (v br, 1 H, OH).
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