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XIX *. SYNTHESIS AND CHARACTERIZATION OF MIXED-ORGANOCOPPER CLUSTER COMPOUNDS $R_4R'_2Cu_6$ CONTAINING ARYL AND ACETYLIDE LIGANDS

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Summary

Mixed-organocopper cluster compounds $Ar_4Cu_6(C{\equiv}CR)_2$ ($Ar = 2\text{-}Me_2NC_6H_4$, R = phenyl, 4-tolyl, 2,4-xylyl or mesityl) have been prepared in high yield by the ligand-substitution reaction of $Ar_4Cu_6Br_2$ with two equivalents of $LiC{\equiv}CR$. $Ar_4Cu_6(C{\equiv}CC_6H_4CH_3\text{-}4)_2$ has also been prepared via the aryl—arylacetylide exchange reaction of Ar_nCu_n with $HC{\equiv}CC_6H_4CH_3\text{-}4$ as well as via the reaction of Ar_nCu_n with polymeric $CuC{\equiv}CC_6H_4CH_3\text{-}4$.

IR and NMR spectroscopy reveal that $Ar_4Cu_6(C{\equiv}CR)_2$ and $Ar_4Cu_6Br_2$ have the Ar_4Cu_6 skeleton as a common structural feature. Dynamic NMR spectroscopy provides information about the occurrence of intra-cluster Cu—N coordination. The position of the $\nu(C{\equiv}C)$ band ($\approx 2040\ cm^{-1}$) and considerations concerning the number of cluster electrons in $Ar_4Cu_6X_2$ clusters (84*e*) suggest that the $C{\equiv}CR$ ligand acts as a three electron ligand bridging two equatorial Cu atoms of the Cu_6 core. In solution the $Cu_2C{\equiv}CR$ interaction is probably fluxional ($\sigma,\pi \longleftrightarrow \sigma(2e\text{—}3c) \longleftrightarrow \pi,\sigma$).

Introduction

In previous reports [1—4] we described the synthesis and characterization of arylcopper compounds R_nCu_n containing equal aryl groups R which are bound to a central copper core or to a polymeric Cu_n structure by 2*e*—3*c* Cu—C bonds. Organocopper cluster compounds containing unlike ligands reported so far are of the type $Ar_4Cu_6X_2$ having four aryl groups [Ar = 2-(dimethylamino)phenyl]

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* Part XVIII see ref. 8.

** Present address: Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam (The Netherlands) and two anionic groups (X = Cl, Br, I [5—7] or CF_3SO_3 [8]) bound to a hexanuclear copper core. The existence of organocopper cluster species $R_nR'_mCu_{n+m}$ containing two unlike organic ligands has been inferred from spectroscopic data of mixtures of two organocopper compounds "RCu" and "R'Cu". For example, the presence of mixed species $R_3R'Cu_4$, $R_2R'_2Cu_4$ and RR'_3Cu_4 in a 1/1 mixture of R_4Cu_4 and R'_4Cu_4 (R = 2-$Me_2NCH_2C_6H_4$; R' = 5-Me-2-$Me_2NCH_2C_6H_3$) has been established by mass spectrometry [4].

Recently, we have found that mixed-organocopper cluster compounds of the type $Ar_4Cu_6(C{\equiv}CR)_2$ can be isolated almost quantitatively from reaction of a 2/1 mixture of $LiC{\equiv}CR$ and $Ar_4Cu_6Br_2$ [9]. These compounds appear to be key-intermediates in cross-coupling reactions of Ar_nCu_n with $CuC{\equiv}CR$ [10]:

$$4\ ArCu \xrightarrow{2\ CuC\equiv CR} Ar_4Cu_6(C{\equiv}CR)_2 \xrightarrow{2\ CuC\equiv CR} 4\ ArC{\equiv}CR + 4\ Cu^0 \qquad (1)$$

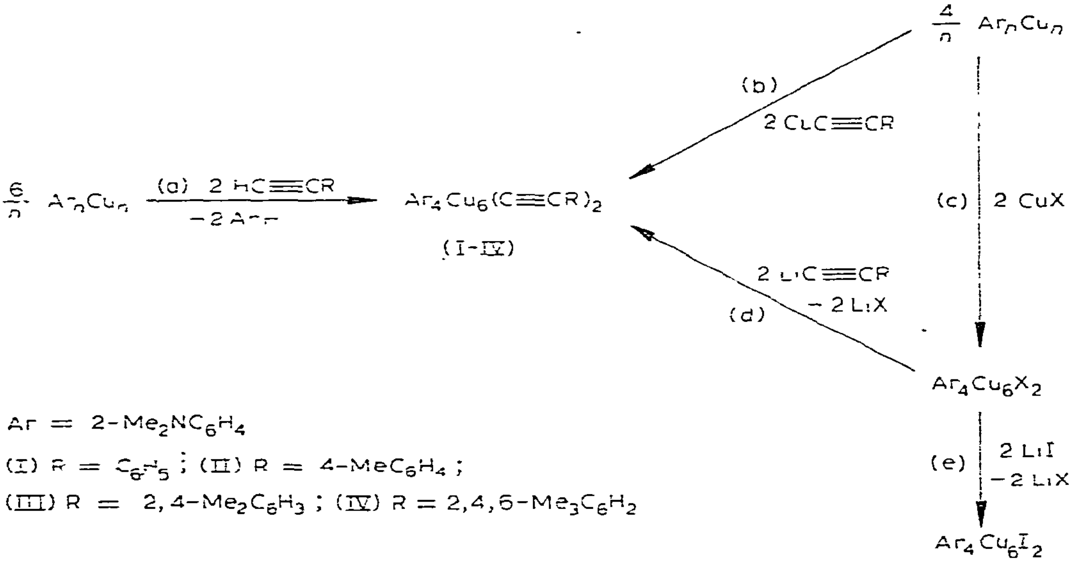
(89—95% yield)

The observed selectivity of the cross-coupling has been rationalized on the basis of the arrangement of the two unlike organo groups on the hexanuclear copper core [10]. In the present paper, a more detailed description of the synthesis and characterization of these mixed aryl/acetylide copper clusters is presented.

Results and discussion

Several routes are available for the synthesis of the dimethylaminophenyl/acetylide copper cluster compounds I—IV (see Scheme 1).

SCHEME 1. Routes for the synthesis of $(2\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CR)_2$.



The aryl—arylacetylide exchange reaction a between polymeric 2-(dimethylamino)phenylcopper (V) and (4-methylphenyl)acetylene affords the mixed aryl/acetylide species II in 58% yield. Similar metallations have been reported

TABLE 1

TETRAKIS[2-(DIMETHYLAMINO)PHENYL]BIS(ARYLETHYNYL)HEXACOPPER (I—IV)

	Compounds	Yield (%)	M.p. (°C, dec.)	Mol. wt. [a] found (calcd.)
I	$Ar_4Cu_6(C{\equiv}CC_6H_5)_2$	92	128	1072 (1063)
II	$Ar_4Cu_6(C{\equiv}CC_6H_4Me\text{-}4)_2$	87	138	1073 (1092)
III	$Ar_4Cu_6(C{\equiv}CC_6H_3Me_2\text{-}2,4)_2$	68	165	1086 (1120)
IV	$Ar_4Cu_6(C{\equiv}CC_6H_2Me_3\text{-}2,4,6)_2$	89	189	

[a] Cryometric in benzene.

for the synthesis of $CuC{\equiv}CC_6H_5$ from the reaction of Cu—O—t-Bu with phenylacetylene [11], while $(C_6F_5)_2CuLi$ has been prepared by the reaction of $LiCuMe_2$ with C_6F_5H [12].

A second route involves the interaction of the two pure organocopper compounds, Ar_nCu_n and $CuC{\equiv}CR$, in DMF at temperatures below 80°C (route b) [10]. This route is analogous to the formation of the mixed aryl/anion clusters via the interaction of the pure organocopper with copper salts (route c). A representative example of route b is the reaction of 2-(dimethylamino)phenylcopper with cuprous (4-methylphenyl)acetylide in a 1/1 molar ratio in DMF which affords the mixed-organocopper cluster compound II in 31% yield. However, the best preparative method is the halogen—arylacetylide exchange route d. This reaction is based on the earlier observation that ligand substitution reactions of type e occur with retention of the hexanuclear Ar_4Cu_6 skeleton [7]. Indeed, reaction of $Ar_4Cu_6Br_2$ (VI) with various substituted-phenylethynyllithium derivatives in a benzene/ether mixture affords, in addition to the expected amount of LiBr, the compounds I to IV in 70 to 95% yield (see Table 1). Elemental analysis of these compounds which are all yellow solids confirms the presence of $2\text{-}Me_2NC_6H_4$ and $RC{\equiv}C$ groups in 2/1 molar ratio.

The thermal stability of compounds I to IV increases with increasing number of methyl groups in the phenyl nucleus of the arylethynyl group. The solubility in aromatic solvents decreases in the same direction. The mesityl derivative is insoluble in benzene or toluene, but dissolves in coordinating solvents such as pyridine. All compounds are stable in air for prolonged periods.

Cryometric molecular weight determinations showed that I, II and III exist in benzene as dimeric units and thus have $Ar_4Cu_6(C{\equiv}CR)_2$ stoichiometry. This points out that the net result of reaction d is a ligand substitution reaction which takes place with retention of the Ar_4Cu_6 cluster structure [7,8]. The results of an IR and NMR spectroscopic investigation of these compounds support this view.

The structure of $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$ (VI) in the solid, which is known from an X-ray structure determination [6,7], consists of four $2\text{-}Me_2NC_6H_4$ groups each spanning a triangular face of an octahedral copper cluster (cf. Fig. 1) with the bromine atoms spanning two equatorial copper atoms. Comparison of the IR spectra of $Ar_4Cu_6X_2$ and $Ar_4Cu_6(C{\equiv}CR)_2$ in the 2100—200 cm^{-1} region reveals the similarity of the absorption patterns due to the $2\text{-}Me_2NC_6H_4$ group. In the 550—400 cm^{-1} region, where vibrations involving ligand—copper

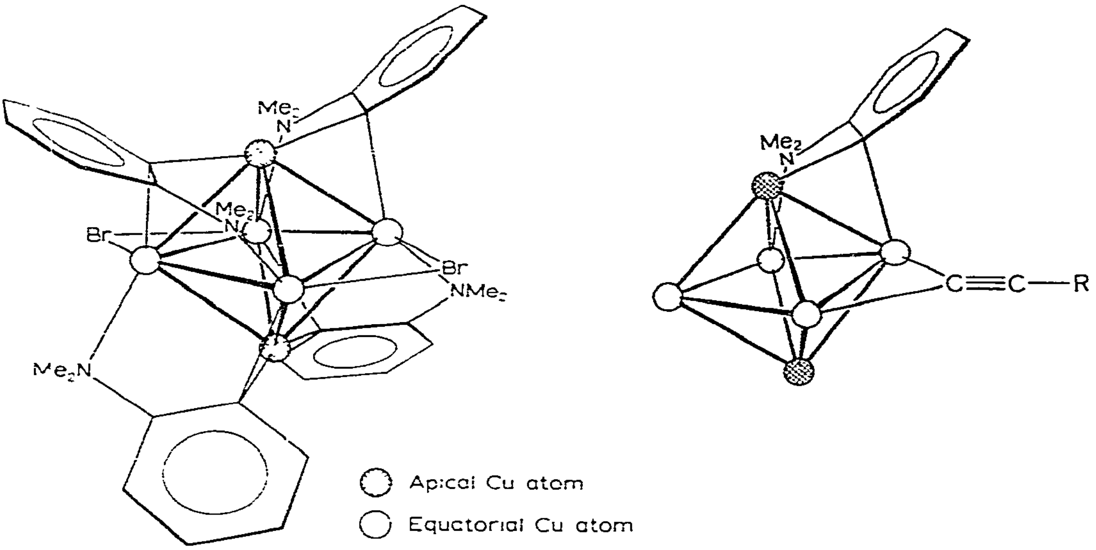


Fig. 1. Structure of $Ar_4Cu_6Br_2$ and proposed bonding in $Ar_4Cu_6(C{\equiv}CR)_2$.

bonds occur only minor changes are observed going from $Ar_4Cu_6Br_2$ to $Ar_4Cu_6(C{\equiv}CR)_2$. This supports the view that $Ar_4Cu_6Br_2$ and the $Ar_4Cu_6(C{\equiv}CR)_2$ compounds have the Ar_4Cu_6 skeleton as a common structural feature (see Fig. 1). Indeed, the infrared spectrum of $2\text{-}Me_2NC_6H_4Cu$ (V), which has a polymeric structure [2], is totally different in this region with absorption bands at 555w, 495s and 462 cm^{-1}, whereas bands in the region from 718vs to 555w cm^{-1} observed in the spectra of $Ar_4Cu_6X_2$ and $Ar_4Cu_6(C{\equiv}CR)_2$ are absent *.

For each of the arylethynyl-dimethylaminophenylcopper clusters one medium intensity $\nu(C{\equiv}C)$ band is observed. The unchanged position of this band upon dissolution of the compounds in benzene suggests similar bonding of the arylethynyl group in the solid and in solution. The fact that this band is observed at ca. 100 cm^{-1} higher wavenumber than in the corresponding copper arylacetylides indicates that in the $Ar_4Cu_6(C{\equiv}CR)_2$ clusters less extensive electron donation of π-electron density into vacant Cu orbitals takes place.

Two extreme possibilities (Fig. 2. A, B) for the bridging of the equatorial copper atoms by the arylethynyl group, can be envisaged. A precedent for the symmetric electron deficient bridging (Fig. 2A) is provided by the crystal structure of methyl(1-propynyl)beryllium trimethylamine reported by Morosin and Howatson [13]. In this structure the propynyl group is almost perpendicular to the Be—Be axis, and acts as a one-electron ligand. A recent X-ray study [14] of diphenyl(phenylethynyl)aluminium dimer [15] reveals that the phenylethynyl group bridges two Al atoms via one Al—C σ-bond and one Al—C π-interaction. Accordingly, in this case the acetylenic group acts as a three-electron ligand. This type of bonding is also found in recently reported $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$

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* Recently we arrived at the same conclusion for $R_4M_6X_2$ (M = Group IB metal, Cu, Ag and/or Au) derivatives in which X represents a weak electron-donating bidentate ligand such as trifluoromethanesulphonato (triflate anion, CF_3SO_3) [8].

A: one-electron ligand B: three-electron ligand

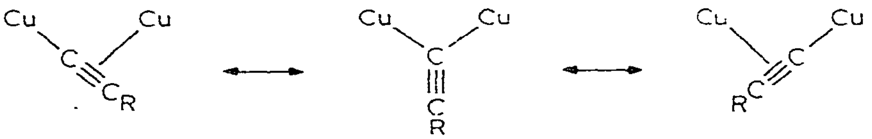
Fig. 2.

which contains Ir—C σ-bonds and unsymmetric copper-acetylene π-interactions [16]. Interestingly, the ν(C≡C) values of about 2040 cm^{-1} in the compounds I to IV are similar to that reported for the copper—iridium cluster. Therefore, bonding scheme B for the interaction of the acetylide ligand with the equatorial copper atoms cannot be excluded (cf. ref. 9) *.

Scheme B is consistent with the fact that the ligand substitution reaction d occurs with retention of the Ar_4Cu_6 skeleton. Substitution of bromine by arylacetylide which are both three electron donors leaves the total number of 84 cluster electrons unaffected **. The possibility that in solution a fluxional situation occurs as depicted in Fig. 3 seems, however, likely.

Further information about the structure of the mixed-organocopper cluster compounds emerges from their dynamic NMR spectra [7]. The chemical shift values for the $2\text{-}Me_2NC_6H_4$ protons in the compounds I to IV and of $Ar_4Cu_6Br_2$ (VI) are nearly identical as would be expected if these two types of compounds have the Ar_4Cu_6 skeleton in common (see Table 2).

Furthermore, the NMR spectra provide information on the occurrence of Cu—N coordination. The spectrum recorded at low temperature reveals two singlets for the NMe_2 protons. This observation (see Table 2) indicates that at this temperature Cu—N bond dissociation is slow on the NMR timescale. In the



σ-π σ_{bridge} π-σ

Fig. 3. Fluxional behaviour of the arylacetylide ligand bridging two equatorial Cu atoms in $(2\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CR)_2$.

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[*] An X-ray structure determination of $Ar_4Cu_6(C{\equiv}CC_6H_4CH_3\text{-}4)_2$ (II) has been planned. ^{63,65}Cu NQR data obtained for II, which indicate asymmetry in the equatorial plane, will be published separately [17].

[**] Electron counting in which the $2\text{-}Me_2NC_6H_4$ ligand as well as the Br or C≡CR ligands are considered to act as three-electron ligands affords 84 cluster electrons for these compounds. A recent precedent for this type of Group IB metal clusters is $Cu_6H_6(PPh_3)_6$ [18], which likewise has a total number of 84 electrons, while $Au_6(PPh_3)_6(BF_4)_2$ [19] can be considered to consist of a 76-electron dication $Au_6(PPh_3)_6{}^{2+}$ and BF_4 anions.

TABLE 2

TEMPERATURE DEPENDENT NMe RESONANCES IN $(2\text{-Me}_2NC_6H_4)_4Cu_6X_2$ CLUSTERS (X = Br or C≡CR) [a]

Compound	Low temp.	Room temp.	High temp.
$Ar_4Cu_6Br_2$		1.84, 2.94(br) [b]	2.42s [b,c]
$Ar_4Cu_6(C\equiv CC_6H_5)_2$	1.73, 2.98s [b,d]	1.6—3.3(br)	2.47s [e]
$Ar_4Cu_6(C\equiv CC_6H_4CH_3\text{-}4)_2$	1.74, 3.02s [b,f]	1.5—3.5(br)	2.46s [e]
$Ar_4Cu_6(C\equiv CC_6H_3(CH_3)_2\text{-}2,4)_2$	1.79, 2.98s [g]	1.7—3.0(br)	2.44s [e]

[a] In C_6D_6 unless stated otherwise. TMS internal standard. δ in ppm. s, singlet; (br), broad. [b] $CD_3C_6D_5$. [c] 90°C. [d] −20°C. [e] 80°C. [f] −10°C. [g] +5°C.

coordinated situation, pyramidal inversion at nitrogen * is blocked, which renders the nitrogen atom a stable prochiral center. The anisochronism of the NMe signals reflects the dissymmetry at the bridging arylcarbon atom [7,20]. This dissymmetry is a consequence of the different coordination symmetry of the apical (digonal) and equatorial (trigonal) copper atoms, respectively [7]. At higher temperatures the two NMe singlets coalesce into one singlet by a process involving dissociation of the Cu—N bond (k_d) followed by inversion at nitrogen (k_i) and rotation around C_{Ph}—N **.

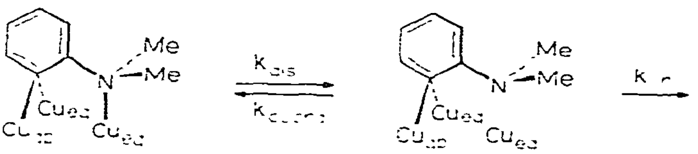

Fig. 4. Process accounting for the dynamic NMR pattern observed for the NMe protons in $(2\text{-Me}_2NC_6H_4)_4Cu_6(C\equiv CR)_2$ (rate constants k_{dis} for Cu_{eq}—N dissociation; $k_{coord.}$ for Cu_{eq}—N coordination; $k_{i,r}$ for inversion at N and concommitant rotation around C—N).

The observed dynamic NMR patterns for the NMe_2 protons reveal that either interaggregate exchange between Cu_6 clusters or intra-aggregate exchange of groups within a Cu_6 cluster is absent or extremely slow. Both processes would change the dissymmetry at C_{bridge}, thereby influencing the anisochronism of the NMe protons.

Experimental

General

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

The acetylenes were prepared by established methods [21].

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[*] Inversion at nitrogen has an estimated barrier of <6 kcal/mol; cf. ref. 8.

[**] A second process involves Cu—N bond dissociation followed by rapid rotation of the phenyl nucleus around the axis through C(1) and C(4) which inverts the configuration of C(1). However, the energy barrier for rotation of electron-deficient bonded aryl groups is estimated to be higher than the barrier for pyramidal inversion at nitrogen [20].

The organocopper compounds 2-(dimethylamino)phenylcopper and tetrakis-[2-(dimethylamino)phenyl]hexacopper dibromide were obtained as described in ref. 7, while the cuprous (4-methylphenyl)acetylide was synthesized as reported by Castro et al. [22].

Melting points (dec.) were determined in capillaries under nitrogen. PMR spectra were recorded on a Varian Associates HA-100 spectrometer and IR spectra on a Perkin—Elmer Grating Infrared spectrophotometer nr. 577.

Elemental analysis were carried out in this Institute under supervision of mr W.J. Buis.

Synthesis of tetrakis[2-(dimethylamino)phenyl]bis(arylethynyl)hexacopper (I—IV)

Via reaction of [2-$Me_2NC_6H_4$]$_4Cu_6Br_2$ (VI) with arylethynyllithium

Tetrakis[2-(dimethylamino)phenyl]bis[(4-methylphenyl)ethynyl]hexacopper (II). The synthesis of II is described as a typical example. 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 ($2-Me_2NC_6H_4)_4Cu_6Br_2$ (3.97 mmol) in 120 ml of benzene. The resulting mixture was stirred for 3 h. The solvent was removed by evaporation and the residue was extracted with benzene (3 × 50 ml). The benzene extract was evaporated to dryness, whereafter the solid residue was washed with ether (40 ml; removal of LiBr), pentane (4 × 40 ml) and dried in vacuo affording II as a yellow solid (3.8.g; 87% yield). M.p. 138°C (dec.). (Found: C, 54.10; H, 4.89; N, 5.19; Cu, 34.43. $C_{50}H_{54}N_4Cu_6$ calcd.: C, 54.98; H, 4.98; N, 5.13; Cu, 34.90%). Mol. wt. (cryometric in C_6H_6): mean 1073, $\bar{n}$ 1.0 (concentration independent); IR spectrum (C_6H_6, cm^{-1}): $\nu(C{\equiv}C)$ 2042. NMR spectrum (C_6D_6, TMS internal, δ (ppm) room temp.): 2.09 (s, 4-CH_3), 1.5—3.5 (very broad, NCH_3). (For temperature dependent values see Table 2).

Tetrakis[2-(dimethylamino)phenyl]bis(phenylethynyl)hexacopper (I). Brown solid. M.p. 128°C (dec.). (Found: C, 54.2; H, 4.9; N, 5.1; Cu, 35.2. $C_{48}H_{50}N_4Cu_6$ calcd.: C, 54.18; H, 4.74; N, 5.27; Cu, 35.82%). Mol. wt. (cryometric in C_6H_6): mean 1072, $\bar{n}$ 1.0 (concentration independent). IR spectrum (C_6H_6, cm^{-1}): $\nu(C{\equiv}C)$ 2040. NMR spectrum (C_6D_6, TMS internal, δ (ppm), room temp.): 1.6—3.3 (very broad, NCH_3), (For temperature dependent values see Table 2).

Tetrakis[2-dimethylamino)phenyl]bis[(2,4-dimethyl)phenylethynyl]hexacopper (III). Yellow solid. M.p. 165°C (dec.). (Found: C, 56.52; H, 5.39; N, 5.01; Cu, 33.41. $C_{52}H_{58}N_4Cu_6$ calcd.: C, 55.74; H, 5.23; N, 5.00; Cu, 34.03%). Mol. wt. (cryometric in C_6H_6): mean 1086, $\bar{n}$ 1.0 (concentration independent). IR spectrum (C_6H_6, cm^{-1}): $\nu(C{\equiv}C)$ 2033. NMR spectrum (C_6D_6, TMS internal δ (ppm), room temp.): 1.7—3.0 (very broad, NCH_3), 2.14 (s, 6H, 4-CH_3), 2.70 (s, 6H, 2-CH_3), (For temperature dependent values see Table 2).

Tetrakis[2-(dimethylamino)phenyl]bis[(2,4,6-trimethyl)phenylethynyl]hexacopper (IV). Yellow solid. M.p. 189°C (dec.). (Found: C, 56.2; H, 5,5; N, 4.9; Cu, 32.5. $C_{54}H_{62}N_4Cu_6$ calcd.: C, 56.48; H, 5.44; N, 4.88; Cu, 33.20%). Mol. wt. not measured because IV is insoluble in the common organic solvents. IR spectrum (Nujol, cm^{-1}): $\nu(C{\equiv}C)$ 2036. NMR spectrum (C_5D_5N, TMS internal, δ (ppm), room temp.): 2.16 (s, 6H, 4-CH_3), 2.53 (s, 12H, 2,6-CH_3), 2.98 (s, 24H, NCH_3).

Via reaction of 2-(dimethylamino)phenylcopper and (4-methylphenyl)acetylene

A mixture of (4-methylphenyl)acetylene (3.44 mmol) and 2-(dimethylamino)phenylcopper (10.29 mmol) in 70 ml of benzene, was stirred for two days. The brown precipitate was filtered off and extracted with benzene (2 × 50 ml). The combined benzene extracts were concentrated, yielding yellow II (58%), which was finally washed with pentane (3 × 50 ml). (Found: C, 53.80; H, 4.98; N, 4.79; Cu, 32.86. $C_{50}H_{54}N_4Cu_6$ calcd.: C, 54.98; H, 4.98; N, 5.13; Cu, 34.90%). NMR spectrum (C_6D_6, TMS internal, δ (ppm), room temp.): 2.0—2.3 (very broad, NCH_3), 2.10 (s, 4-CH_3).

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 II (31% yield). (Found: C, 55.27; H, 5.07; N, 5.12; Cu, 34.61. $C_{50}H_{54}N_4Cu_6$ calcd.: C, 54.98; H, 4.98; N, 5.13; Cu, 34.90%). NMR spectrum (C_6D_6, TMS internal, δ (ppm), room temp.): 2.0—3.0 (very broad, NCH_3), 2.10 (s, 4-CH_3).

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