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GROUP IB ORGANOMETALLIC CHEMISTRY

XXXI *. SYNTHESIS AND CHARACTERIZATION OF TETRANUCLEAR Me_2N- AND Me_2NCH_2-SUBSTITUTED DIARYLPROPENYLCOPPER—COPPER ANION COMPOUNDS ($Vi_2Cu_4X_2$) CONTAINING BRIDGING PROPENYL LIGANDS. ISOLATION OF A THERMALLY STABLE MIXED DIARYLPROPENYL/ARYLCOPPER COMPOUND ($Vi_2Cu_4Ar_2$)

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Summary

Thermally stable 1,2-diarylpropenylcopper compounds $(ViCu_2X)_n$ (Vi = $(2\text{-}Me_2NC_6H_4)C{=}C(Me)(C_6H_4Me\text{-}4)$, X = Br ($n$ = 2) or OTf ‡ and Vi = $(2\text{-}Me_2NCH_2C_6H_4)C{=}C(Me)(C_6H_4Me\text{-}4)$, X = Br ($n$ = 2)) have been prepared by reaction of configurationally pure *E*-ViLi compounds with copper(I) salts. Via ligand substitution reactions of $Vi_2Cu_4Br_2$ (Vi = $(2\text{-}Me_2NC_6H_4)$ C=C(Me)-$(C_6H_4Me\text{-}4)$) with RLi (R = $4\text{-}MeC_6H_4C{\equiv}C$ or $4\text{-}MeOC_6H_4C{\equiv}C$) mixed alkenyl/alkynylcopper compounds $(ViCu_2R)_n$ were obtained. Reaction of $Vi_2Cu_4Br_2$ with 2-dimethylaminophenyllithium (ArLi) yielded $Vi_2Cu_4Ar_2$, the first representative of the class of mixed alkenyl/arylcopper compounds. This compound was also prepared via reaction of $Ar_4Cu_6Br_2$ with ViLi. Based on molecular weight data and dynamic NMR spectral evidence a tetranuclear structure with $2e$—$3c$ bonded diarylpropenyl and $4e$—$3c$ bonded bromine ($Vi_2Cu_4Br_2$) or $2e$—$3c$ bonded aryl ($Vi_2Cu_4Ar_2$) ligands positioned on opposite edges of a Cu_4 rectangle is proposed.

Introduction

Vinylcopper compounds and vinylcopperlithium compounds (vinylcuprates) have recently found wide application as reagents for the stereo- and regio-selec-

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[*] Part XXX, see ref. 30. For a preliminary account of this work see ref. 14.

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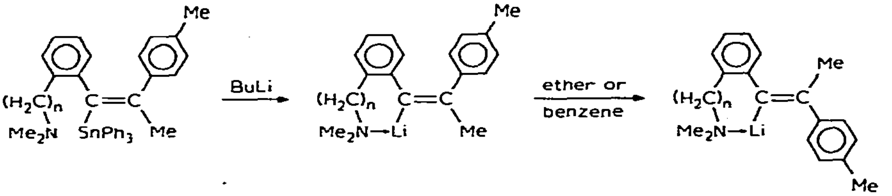
[‡] OTf = trifluoromethanesulphonate = triflate.

tive introduction of vinyl groups in organic substrates [1—4]. In spite of their extensive use little is known about the structure of vinylcopper compounds. This is perhaps not surprising, because vinylcopper compounds in general have low thermal stability (e.g. propenylcopper rapidly decomposes at 25°C, even in the presence of PBu_3 [5]), which hampers their isolation and characterization.

Recent studies have shown that the stability of arylcopper compounds can be considerably enhanced by the introduction into the aryl group of potentially coordinating and/or sterically demanding substituents near the Cu—C bond [6—13]. We have used the concept of intramolecular coordination and/or steric crowding as a possible means for obtaining alkenylcopper compounds sufficiently stable to allow their isolation and characterization *. For this purpose alkenyllithium reagents containing both bulky groups and a potentially coordinating substituent in a position suitable for intramolecular coordination were prepared. The synthesis by the transmetallation route (1) of the configurationally pure *E*-1,2-diaryl-1-propenyllithium compounds V and VI starting



(1)

(I,II) (III,IV) (V,VI)

(I,III,V : n = 0 ; II,IV,VI : n = 1)

from the configurationally pure *E*-(1,2-diaryl-1-propenyl)triphenyltin compounds I and II has recently been reported [15]. Reaction of V (ViLi) with cuprous bromide led to the isolation of a remarkably thermally stable (dec. temp. 155°C) propenylcopper—copper bromide compound of composition $Vi_2Cu_4Br_2$ [14].

Earlier research has shown that compounds $Ar_4Cu_6Br_2$ (Ar = $2\text{-}Me_2NC_6H_4$) are capable of undergoing replacement of Br by organic ligands with retention of the hexanuclear cluster structure [11]. The structure of the mixed aryl/alkynylcopper compound $(2\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CC_6H_4Me\text{-}4)_2$ was recently elucidated by X-ray analysis [16]. The observed cluster structure provides insight into the extremely specific formation of ArR which takes place upon thermolysis of a 1/1 mixture of ArCu (Ar = $2\text{-}Me_2NC_6H_4$) and copper arylacetylides RCu, a reaction which proceeds via a $Ar_4Cu_6R_2$ intermediate [17].

The isolation of propenylcopper compounds of the type $Vi_2Cu_4Br_2$ is of obvious interest, not only because it provides for the first time an opportunity to study alkenylcopper compounds in greater detail, but in particular because in principle it opens up the possibility of obtaining mixed propenyl/organocopper compounds of the type $Vi_2Cu_4R_2$. The availability of such compounds may lead to a better understanding of C—C coupling reactions in organic synthesis using alkenylcopper or alkenylcuprate reagents.

We describe here: (i) the synthesis of some 1,2-diarylpropenylcopper-copper

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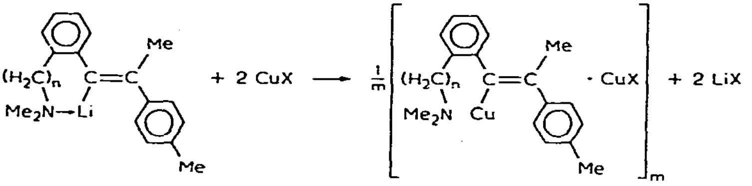
* For a preliminary account of this work see ref. 14.

anion compounds of the type $Vi_2Cu_4X_2$; (ii) the synthesis of a novel mixed propenyl/arylcopper cluster of the type $Vi_2Cu_4Ar_2$; (iii) a proposal for the structure of these new compounds based on the results of molecular weight measurements and ^{1}H NMR spectra.

Synthesis of compounds $Vi_2Cu_4X_2$ and $Vi_2Cu_4Ar_2$

Reaction of *E*-ViLi [*E*-1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyllithium (V) and *E*-1-(2-*N*,*N*-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propenyllithium (VI)] with CuBr in diethyl ether afforded high yields (75—85%) of yellow crystalline products, which according to the elemental analysis are 1/1 complexes of ViCu and CuBr (eq. 2):



(2)

(V,VI)

(VII, VIII, IX)

(V,VII : n = 0 ; X = Br, m = 2.
VI, VIII : n = 1 ; X = Br, m = 2.
IX : n = 0 ; X = OSO_2CF_3 , m unknown)

Molecular weight measurements in benzene revealed a dimeric molecular weight, and thus a $Vi_2Cu_4Br_2$ stoichiometry for VII and VIII (cryosc., VII: found: 905; calcd.: 905; VIII: found: 887; calcd.: 942; conc. independent). VII and VIII decompose at 155°C and 194°C, respectively.

In a similar reaction, addition of 2 equivalents of CuOTf * to a diethyl ether solution of V ** gave a white 1/1 complex of ViCu and CuOTf according to elemental analysis. The insolubility of the product (IX, eq. 2) in common solvents (diethyl ether, benzene) prevented a molecular weight measurement. IX decomposes at 140°C.

Attempts to obtain pure 1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenylcopper (X, ViCu) free of cuprous bromide were unsuccessful. Attempted replacement of the bromide anion in $Vi_2Cu_4Br_2$ (VII) via reaction with ViLi (V) in a 1/2 molar ratio failed. Neither change of solvents (benzene instead of diethyl ether) nor prolonged reaction times resulted in the formation of X. Reverse addition, i.e. addition of CuBr to a solution of ViLi (V), which at least at the start of the reaction ensures large excess of V, likewise was unsuccessful (cf. ref. 18 for the important effect of order of addition of reagents in the preparation of pure arylcopper compounds ArCu).

In contrast, reaction of $Vi_2Cu_4Br_2$ (VII) with *para*-substituted arylethynyl-

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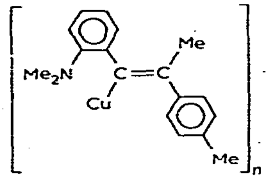
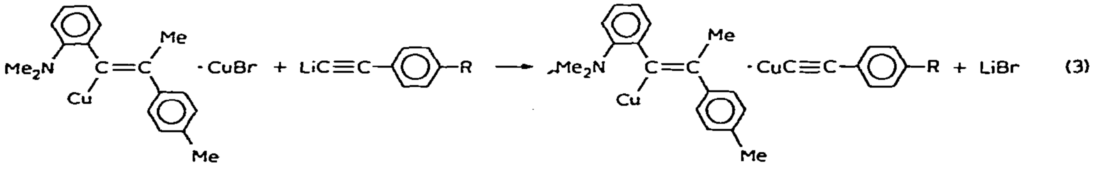
* OTf = trifluoromethanesulphonate = triflate.

** Reverse addition can be expected to result in decomposition [13].



(X)

lithium compounds gave quantitative replacement of bromine by the ethynyl ligand (eq. 3):

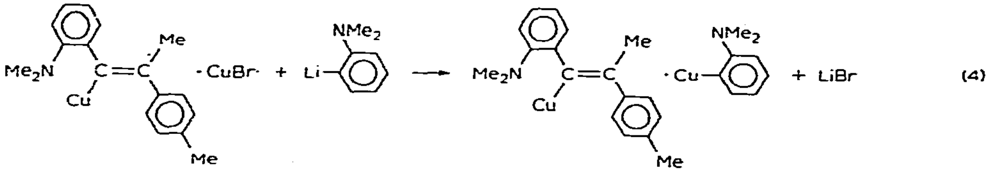


(VII) (XI, XII)

(XI : R = Me ; XII : R = OMe)

NMR spectroscopy (see Table 1) establishes the 1/1 ratio of the diarylpropenyl and the arylethynyl ligand in XI and XII. However, attempts at isolation and purification of both compounds were unsuccessful. XI, which was obtained as an oil, showed extreme solubility in organic solvents (even in pentane) which prevents the removal of organic impurities by solvent extraction. XII which was obtained as a solid, was contaminated with $CuC{\equiv}CC_6H_4OMe$-4 from which it could not be separated. This result contrasts with the $ViCu_2C{\equiv}CC_6H_4R$-4 stoichiometry observed in solution (NMR spectrum), and indicates that some cluster disproportionation has taken place upon isolation.

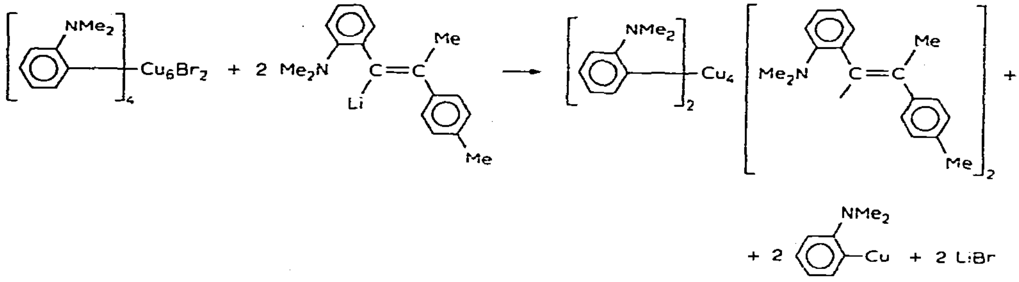
Addition of 2-*N*,*N*-dimethylaminophenyllithium (ArLi) to $Vi_2Cu_4Br_2$ (VII) in diethyl ether gave a yellow crystalline precipitate. According to elemental analysis and molecular weight measurements replacement of bromine has taken place with retention of the tetranuclear structure, leading to the formation of the novel mixed propenyl/arylcopper cluster compound XIII (eq. 4). (Mol.wt. cryosc., found: 925; calcd.: 996; conc. independent). XIII decomposes at 225°C.



(VII) (XIII)

Interestingly, XIII was also obtained from the reaction of the diarylpropenyllithium compound V with the hexanuclear cluster $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$

(eq. 5):



(5)

In contrast to the reaction of $Ar_4Cu_6Br_2$ with lithium arylacetylides (R'Li), from which the hexanuclear compounds $Ar_4Cu_6R'_2$ can be isolated [11], the above reaction is apparently accompanied by cluster disproportionation.

NMR spectral data for all compounds are summarized in Table 1.

Structure of $Vi_2Cu_4Br_2$ and $Vi_2Cu_4Ar_2$

Analytical and molecular weight determinations revealed $Vi_2Cu_4Br_2$ stoichiometry for compounds VII and VIII and $Vi_2Cu_4Ar_2$ stoichiometry for compound XIII.

The NMR spectra of VII, VIII and XIII show single resonance patterns for the Me_2N, C=CMe and the C_6H_4Me-4 methyl protons (see Table 1 and Fig. 1). This indicates that in solution only one compound is present. It also indicates a symmetrical arrangement on the NMR time scale of the organic ligands with respect to each other *.

X-ray structure determinations of organocopper compounds have revealed in every case a polynuclear structure in which the organic ligands each bridge two copper atoms. This is true for alkyl ($(Me_3SiCH_2)_4Cu_4$ [19]), alkynyl ($(2\text{-}Me_2NC_6H_4)_4Cu_6(C{\equiv}CC_6H_4Me\text{-}4)_2$ [16]) and aryl ($(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3Cu)_4$ [20], $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$ [21]) compounds. The fact that compounds which lack ligands suitable for intramolecular coordination are also polynuclear (e.g. $(2\text{-}MeC_6H_4Cu)_4$ [13,22], $(C_6F_5Cu)_4$ [23] and $(2\text{-}F_3CC_6H_4Cu)_4$ [23]) confirms that the presence of multi-centre bonded organic ligands is a common structural feature for organocopper compounds.

It would seem likely, therefore, that the propenyl ligands present in VII, VIII and XIII are also three-centre bonded. Recently, the first example of a terminally bridging alkenyl ligand has been established by X-ray analysis: the t-BuCH=CH groups in $(t\text{-}BuCH{=}CH)_2(i\text{-}Bu)_4Al_2$ symmetrically bridge two Al atoms [24]. The proposed description of the bonding in alkenylcopper compounds is formally similar to the 2*e*—3*c* bonding scheme for arylcopper compounds [8,16]. MO's result from overlap of the filled C_{Vi}-sp^2 orbital with a mutually bonding combination of copper orbitals (Fig. 2A) and of the alkenyl π-

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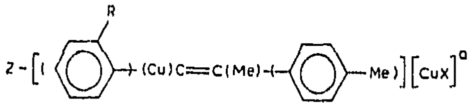
* Fast (NMR time scale) exchange of alkenyl ligands by an intermolecular exchange process of the type $Vi_2Cu_4Br_2 + Vi^*_2Cu_4Br_2 \rightarrow 2ViVi^*Cu_4Br_2$ would account for the observed single resonance pattern. This possibility is excluded for VIII on the basis of the observed DNMR spectra (see below).

TABLE 1

^1H NMR SPECTRAL DATA FOR THE COMPOUNDS



X	R	Comp.	Temp (°C)	$N(CH_3)_2$	NCH_2	$PhCH_3$	$C{=}CCH_3$	Others
Br	NMe_2	VII	+34	2.40 [b]	—	2.23 [c]	2.09 [c]	
			−10	2.46/2.15 [b]	—	2.24 [c]	2.09 [c]	
Br	CH_2NMe_2	VIII	+25	2.15 [d]	δ_1 3.52 δ_2 2.45 J 11.5 Hz [e]	1.79 or 2.05	1.79 or 2.05	
			−5	2.15/2.11 [d]	δ_1 3.42 δ_2 2.37 J 11.5 Hz [e]	1.74 or 2.06	1.79 or 2.06	
$2\text{-}Me_2NC_6H_4$	NMe_2	XIII	+45	2.04 [f]	—	2.30	2.04	2.76 [g]
			−25	2.26/1.68 [f]	—	2.34	2.00	2.74 [g]
$C{\equiv}CC_6H_4Me\text{-}4$	NMe_2	XI	ambient	2.57	—	2.13	2.10	2.00 [h]
$C{\equiv}CC_6H_4OMe\text{-}4$	NMe_2	XII	ambient	2.57	—	2.13	2.10	3.20 [i]

[a] δ(H) ($C_6D_5CD_3$ for VII, VIII and XIII, C_6D_6 for XI and XII, TMS internal, δ(ppm)). [b] Coalescence temp.: 20°C. [c] Assignment based on comparison with $Z\text{-}[2\text{-}RC_6H_4(Cu)C{=}C(Me)C_6H_5][CuBr]$ (impure sample). [d] Coalescence temp.: +10°C. [e] Coalescence temp.: + 95°C. [f] Coalescence temp.: +20°C. [g] $Me_2N(X)$. Assignment based on the observation that δ(NMe) >2.5 ppm in $(2\text{-}Me_2NC_6H_4)_nCu_{m+n}X_m$ compounds [10,11] and δ(NMe) <2.6 ppm in diarylalkenylcopper compounds (VII, XI and XII). [h] $4\text{-}MePhC{\equiv}C$. [i] $4\text{-}MeOPhC{\equiv}C$.

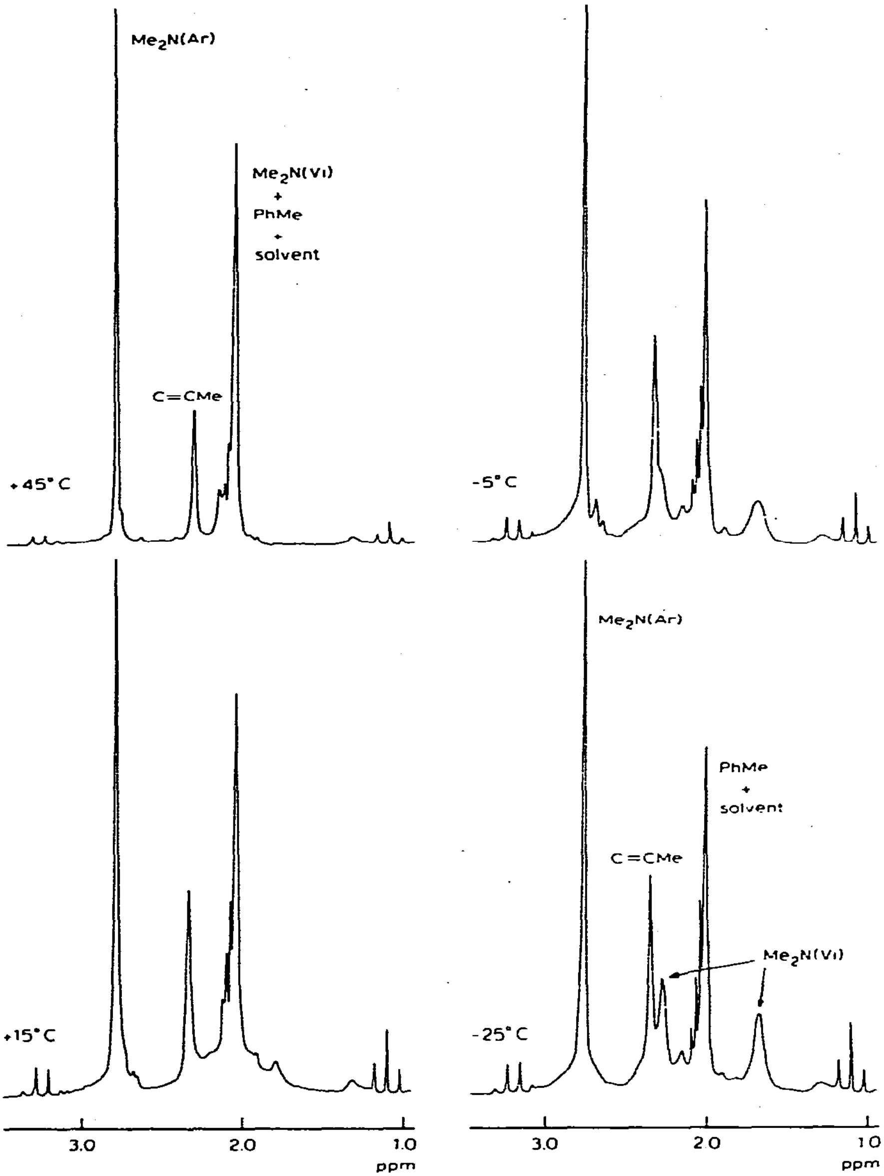


Fig. 1. ^{1}H NMR spectra (δ, ppm) of [Z-(2-Me$_2$NC$_6$H$_4$) C=C(Me) (C$_6$H$_4$Me-4)]$_2$-[2-Me$_2$NC$_6$H$_4$]$_2$Cu$_4$ (XIII) in C$_6$D$_5$CD$_3$ at different temperatures. Solvent resonance lines at about 2.0 ppm. Resonance lines at 3.28 (quartet) and 1.12 (triplet) result from trace amount of diethyl ether. For the assignment of the resonances of XIII, see Table 1.

systems with an antibonding combination of copper orbitals (Fig. 2B, π-donation; Fig. 2C, π *-acceptance).

The C-type bonding will be enhanced in case of N—Cu coordination [8]. Overlap in B and C type MO's will be optimal when the alkenyl ligand is oriented perpendicular to the Cu—Cu vector [8,16]. A perpendicular orientation of the alkenyl ligand has indeed been observed in the structure of the compound (t-BuCHCH)$_2$(i-Bu)$_4$Al$_2$ [24].

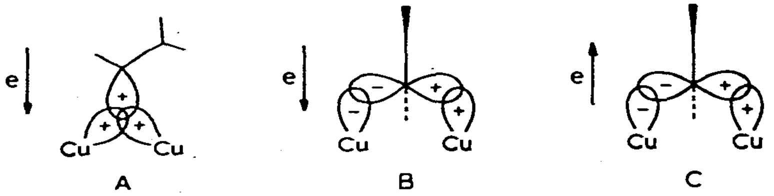


Fig. 2.

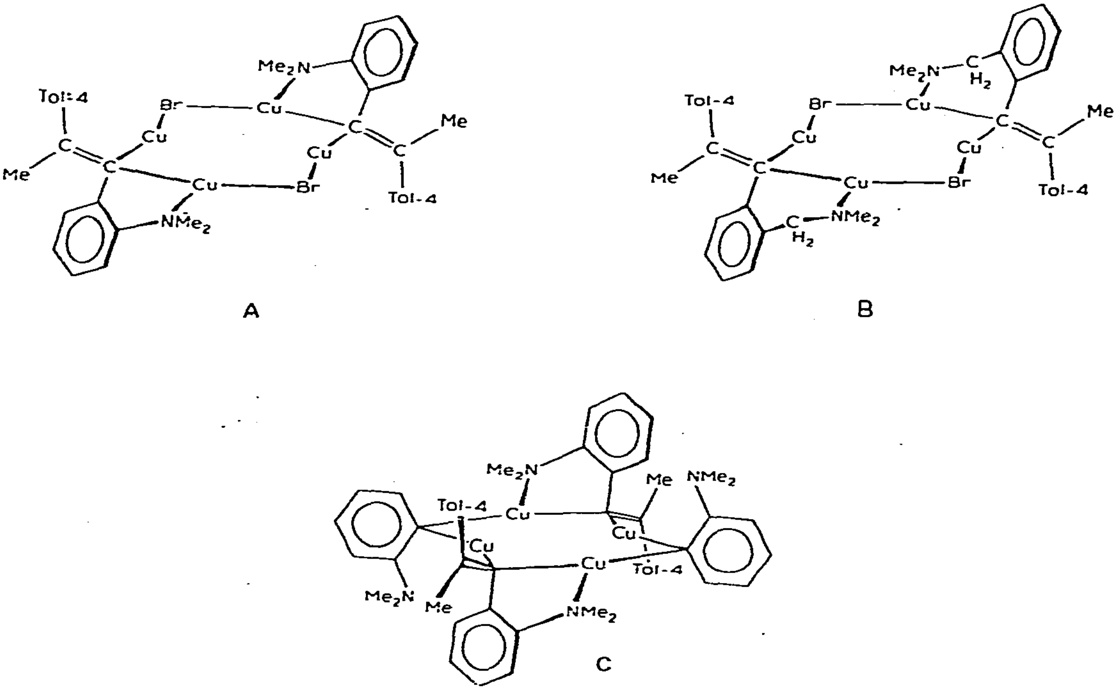


Fig. 3. Proposed structures of (A) $[(2\text{-Me}_2NC_6H_4)C{=}C(Me)(C_6H_4Me\text{-}4)]_2Cu_4Br_2$ (VII), (B) $[(2\text{-Me}_2NCH_2C_6H_4)C{=}C(Me)(C_6H_4Me\text{-}4]_2Cu_4Br_2$ (VIII) and (C) $[(2\text{-Me}_2NC_6H_4)C{=}C(Me)\text{-}(C_6H_4Me\text{-}4)]_2[2\text{-Me}_2NC_6H_4]_2Cu_4$ (XIII).

Based on the above considerations we propose for compounds VII, VIII and XIII the structures A, B and C in Fig. 3. The proposed *Z*-configuration of the diarylpropenyl ligand in VII, VIII and XIII is based on the observation that transmetallation reactions in general proceed with retention of configuration * [15,25,26]. The presence of bridging bromine atoms in a *trans*-arrangement for VII and VIII has a precedent in the structure of $Ar_4Cu_6Br_2$ (Ar = $2\text{-Me}_2NC_6H_4$). X-ray analysis has shown that the two bromine atoms bridge *trans*-equatorial edges of a copper octahedron [21]. Similarly, the acetylide ligands in $Ar_4Cu_6R_2$ (R = $C{\equiv}CC_6H_4Me\text{-}4$) are in a *trans*-arrangement [16]. A *cis*-structure for $Vi_2Cu_4Br_2$ and $Vi_2Cu_4Ar_2$ cannot be excluded on the basis of the NMR data, but is unlikely because of steric crowding observed in models. The proposed

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* The configurations of *E*-ViLi (V) and *Z*-ViCu · CuBr (VII, VIII) are the same, because the *E*- and *Z*-configurational rules are based on atomic weights [27].

arrangement of the Vi ligands in VII, VIII and XIII is based on the observation that in models steric crowding is considerably less if the NMe_2-substituents coordinate from opposite sides of the Cu_4-square. Steric hindrance is probably responsible for the failure of attempts to replace bromine in VII by reaction with 1,2-diarylpropenyllithium compounds. The aggregation number of organolithium compounds has been found to decrease with increasing bulkiness of the organic group [28]. The dimeric molecular weight observed for *E*-1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyllithium (V) [15] is in accordance with the considerable bulkiness of the organic group. Menthyllithium is the only other example of a dimeric organolithium compound reported in the literature [29]. Substitution by sterically less bulky ligands such as $C{\equiv}CC_6H_4Me$-4, $C{\equiv}CC_6H_4OMe$-4 and 2-$Me_2NC_6H_4$, can be achieved.

The dynamic NMR spectra of VII, VIII and XIII provide further structural information (cf. Table 1 and Fig. 1). At low temperature the ^1H NMR spectrum in each case displays anisochronous signals for the Me_2N(alkenyl) protons, indicating inequivalence of the *N*-methyl groups *. On raising the temperature coalescence of the two singlets is observed (cf. Table 1). The Me_2N(aryl) protons in XVI are observed as a singlet in the temperature range studied (—70 till +90° C).

The observation of two singlets for the Me_2N(alkenyl) protons at low temperature is explained in terms of rate-determining Cu—N coordination (cf. refs. 11, 13 and 30). When coordinated, the Me_2N(alkenyl)group in VII, VIII and XIII is a stable prochiral centre, because pyramidal inversion at nitrogen is blocked. The copper atoms bridged by the alkenyl ligand have different coordination symmetry in the case of Cu—N coordination as a result of which the bridging C_{Vi}-carbon atom is chiral and the methyl groups at nitrogen are diastereotopic. Coalescence at higher temperatures of the two NMe singlets is explained by a process involving dissociation of the Cu—N bond followed by inversion at nitrogen and rotation around C_{Ar}—N (VII and XIII) or CH_2—N (VIII). Observation of the NMe_2(aryl) protons in XIII as a singlet in the temperature range —70 till +90° C indicates the absence (on the NMR time scale) of Cu—N coordination for this Me_2N group.

The AB pattern for diastereotopic CH_2N protons in VIII remains unchanged up to 90° C indicating that dissymmetry is maintained in the absence of Cu—N coordination. A study of a model of VIII indicates that as a result of severe steric crowding not only the alkenyl ligand will be held in a preferred conformation with respect to the Cu_4 core, but also that rotation of the $Me_2NCH_2C_6H_4$ group around the C(aryl)—C(bridge) bond is strongly hindered. Any conformation of VIII in which the prochiral NCH_2 group lacks a molecular symmetry plane, must be expected to show anisochronous signals for the benzylic protons. Moreover, the observation of diastereotopic NCH_2 protons excludes the occurrence of intermolecular exchange because the latter process would result in a loss of identity of the two Vi groupings.

In the proposed structures of $Vi_2Cu_4Br_2$ and $Vi_2Cu_4Ar_2$ (see Fig. 3) the

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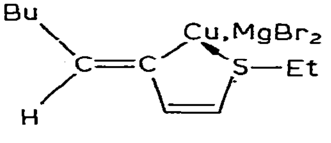
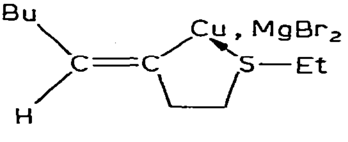
* The assignment to Me_2N(alkenyl) or Me_2N(aryl) of the Me_2N resonance lines for compound XIII has been based on a comparison with δ-values observed for $Ar_4Cu_6Br_2$ [10], $Ar_4Cu_6R_2$ [11], VII, XI and XII.

$Me_2N(Vi)$ group coordinates with one of the bridged Cu atoms thus forming a five- (A and C) or six-membered (B) chelate ring. The presence of two sp^2-hybridized carbon atoms in the chelate ring which contributes to its rigidity will be a further stabilizing factor.

Recently, Normant et al. [31—33] and Vermeer et al. [34—36] reported a variety of regioselective syntheses based on vinylcopper intermediates obtained by the addition of alkylcopper reagents to hetero-substituted alkynes. Intramolecular metal-heteroatom coordination must be responsible for the observed regioselectivity. In this connection the higher yields reported for the butadienyl reagent A as compared with the butenyl reagent B [31] is of interest.



A



B

Reagent A contains a stable constrained five-membered chelate ring with two sp^2-hybridized C atoms fully comparable to the situation in the stable alkenyl compounds VII and XIII.

The importance of intramolecular coordination in 1,2-diarylpropenylcopper compounds is illustrated by the failure of our attempts to isolate *Z*-1,2-diphenyl-1-propenylcopper-copper bromide from the reaction of *E*-1,2-diphenyl-1-propenyllithium with CuBr.

Experimental

General

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

The following compounds were prepared by literature methods: cuprous bromide [37], cupric chloride [38], cuprous triflate [39], 4-methylphenylacetylene [40], 4-methoxyphenylacetylene [40], 2-lithio-*N,N*-dimethylaniline [9], tetrakis(2-*N,N*-dimethylaminophenyl)hexacopper dibromide [10], *E*-1-(2-*N,N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyllithium [15] and *E*-1-(2-*N,N*-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propenyllithium [15]. n-Butyllithium in hexane was commercially available.

Melting points (dec.) were determined in capillaries under nitrogen. Mass spectra were obtained from a Finnigan 3100D Gas chromatography/Mass spectrometer by Mrs. G.G. Versluis-de Haan and Mrs. C.M. Bijlsma-Kreuger. IR spectra were recorded on a Perkin-Elmer Grating Infrared spectrometer Nr. 577 by Mrs. C.M. Bijlsma-Kreuger, who also carried out the molecular weight determinations. ^1H NMR spectra were recorded on a Varian Associates T-60 spectrometer, temperature dependent spectra by Mr. J.W. Marsman on a Bruker WH-90 spectrometer. Elemental analyses were carried out in our Institute under supervision of Mr. W.J. Buis.

Synthesis of the diarylpropenylcopper compounds

Z-bis-[1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]-tetrakiscopper dibromide (VII). A solution of *E*-1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyllithium [15] (8.3 mmol) in 100 ml of diethyl ether was added to solid cuprous bromide (16.7 mmol) during 10 min at room temperature. After 3 h with continuous stirring, the solvent was removed by vacuum evaporation. The slightly greenish-yellow residue was extracted with benzene (50 ml, 4 times). The combined extract was evaporated, washed with pentane (30 ml) and dried in high vacuo, giving VII as a yellow solid in 78% yield. M.p. 155°C (dec.). Anal.: Found: C, 46.76; H, 4.43; N, 3.15; Cu, 27.42; Br, 17.49%. $C_{36}H_{40}N_2Cu_4Br_2$ calcd.: C, 47.27; H, 4.41; N, 3.06; Cu, 27.78; Br, 17.47%. Mol.wt. (cryosc. in benzene): Found: 905; calcd.: 905. For NMR data see Table 1.

Z-bis-[1-(2-N,N-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propenyl]tetrakiscopper dibromide (VIII). This compound was prepared by the method given for compound VII. Yellow crystalline solid. Yield 80%. M.p. 194°C (dec.). Anal.: Found: C, 48.46; H, 4.89; N, 2.93; Cu, 26.37; Br, 16.58%. $C_{38}H_{44}N_2Cu_4Br_2$ calcd.: C, 48.41; H, 4.71; N, 2.97; Cu, 26.96; Br, 16.95%. Mol.wt. (cryosc. in benzene): Found: 887; calcd.: 942. For NMR data see Table I.

Z-[1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]biscopper trifluoromethanesulphonate (IX). Solid CuOTf · $\frac{1}{2}C_6H_6$ (2.7 g; 10.37 mmol) was added to a solution of *E*-1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyllithium (6.5 mmol) in diethyl ether (60 ml). During the addition the colour of the solution changed from yellow via red to yellow again. After stirring for 2 h the red supernatant liquid was decanted from the formed precipitate. This solid was washed with diethyl ether (20 ml, 3 times) and pentane (20 ml, 2 times) and dried in high vacuum, giving IX as a faintly greenish-white compound in 87% yield. M.p. 140°C (dec.). Anal.: Found: C, 42.74; H, 3.87; N, 2.60; Cu, 23.86; F, 10.41%. $C_{19}H_{20}NSO_3F_3Cu_2$ calcd.: C, 43.34; H, 3.83; N, 2.66; Cu, 24.14; F, 10.82%. IR frequencies for the OTf anion absorptions (Nujol mull, cm^{-1}): 1310 and 1204 (ν_1(E) SO_3, asym. stretch), 1020 ($\nu_1(A_1)$ SO_3, sym. stretch), 762 ($\nu_2(A_1)$ SX, stretch?), 632 ($\nu_5(E)$ SO_3, asym. deformation), 524 ($\nu_3(A_1)$ SO_3, sym. deformation). (For assignments see ref. 13).

Reaction of $Vi_2Cu_4Br_2$ (VII) with 4-methylphenylethynyllithium

A solution of 4-methylphenylacetylene (2.58 mmol) in diethyl ether (15 ml) was added to n-butyllithium in hexane (1.4 ml, 1.7 *N*, 2.38 mmol). The suspension was stirred for 45 min and then added to a suspension of VII (2.4 mmol) in benzene (75 ml). The colour changed from yellow to dark-brown. After 2 h the clear solution was evaporated. A very dark oil remained. After addition of benzene (30 ml) the obtained suspension was centrifuged (2000 rps, 20 min). The greenish-brown supernatant was decanted and a greenish-white solid remained. Evaporation of the extract again gave an oily residue. On addition of pentane or diethyl ether a clear solution was obtained. All attempts to solidify the product or to effect further purification were unsuccessful. An NMR spectrum of a benzene solution of the product revealed the formation of a 1/1 propenyl/ethynylcopper compound. NMR spectral data (C_6D_6, TMS internal. δ(ppm)): 2.57 (s, 6 H, NMe_2), 2.13 (s, 3 H, 4-Me (?)), 2.10 (s, 3 H, C=CMe (?)), 2.00 (s, 3 H, $C{\equiv}CC_6H_4Me$-4).

On addition of HCl to a pentane solution the dark colour disappeared and a clear solution was obtained. Neutralization with ammonia gave a dark blue water layer. The clear organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated. The residual oil contained 4-methylphenylacetylene (50%), *E*-1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propene (40%) and *Z*-1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propene (10%). NMR (C_6D_6, TMS internal, δ(ppm)): 4-methylphenylacetylene: 1.94 (s, 3 H, 4-Me), 2.75 (s, 1 H, C≡CH); "E-propene": 2.53 (s, 6 H, NMe_2), 2.15 (s, 3 H, 4-Me), 2.18 (d, *J* 1.3 Hz, 3 H, C=CMe); "*Z*-propene": 2.63 (s, 6 H, NMe_2), 2.07 (s, 3 H, 4-Me), 2.17 (d, *J* 1.4 Hz, 3 H, C=CMe).

Reaction of $Vi_2Cu_4Br_2$ (VII) with 4-methoxyphenylethynyllithium

n-Butyllithium in hexane (4.2 ml, 1.3 *N*, 5.46 mmol) was added to a solution of 4-methoxyphenylacetylene (5.45 mmol) in pentane (60 ml). After stirring for 1 h the suspension was centrifuged (2000 rps, 20 min). After decanting the supernatant, the resulting white precipitate was washed once with pentane (50 ml). After drying in high vacuum, the white solid *p*-methoxyphenylethynyllithium was suspended in diethyl ether (40 ml) and added to a suspension of VII (5.47 mmol) in diethyl ether (40 ml). During the addition the colour changed from yellow to green. After 2 h with continuous stirring the solvent was removed from the resulting suspension by vacuum evaporation. The residue was extracted with benzene (30 ml). Evaporation of the benzene extract gave an oily foam. Upon addition of pentane (50 ml) a green-yellow solid resulted, which was isolated, washed once with pentane (50 ml), dried and again washed with diethyl ether (40 ml). According to NMR analysis the species present in solution is a 1/1 complex of 4-methoxyphenylethynylcopper and 1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenylcopper ((C_6D_6, TMS internal, δ(ppm)): 2.58 (s, 6 H, NMe_2), 2.15 (s, 3 H, 4-Me(?)), 2.10 (s, 3 H, C=CMe(?)), 3.18 (s, 3 H, $C{\equiv}CC_6H_4OMe$-4)). However, elemental analysis revealed the presence in the isolated solid of an excess of $CuC{\equiv}CC_6H_4OMe$-4. Anal.: Found: C, 58.71; H, 4.18; N, 1.70; Cu, 25.24; O, 7.81%. $ViCu_2R \cdot 1.5CuR$ ($C_{40.5}H_{37.5}NCu_{3.5}O_{2.5}$) calcd.: C, 60.75; H, 4.73; N, 1.75; Cu, 27.77; O, 4.99%. Further purification was not undertaken because of the observed decrease of the propenyl/ethynyl ratio on washing. In a repeat experiment similar properties have been observed.

Z-Bis-[1-(2-N,N-dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]bis[2-N,N-dimethylaminophenyl]tetracopper (XIII)

a. Via reaction of VII with 2-N,N-dimethylaminophenyllithium. A solution of 2-*N*,*N*-dimethylaminophenyllithium [9] (2.84 mmol) in diethyl ether (30 ml) was added to a suspension of VII (2.84 mmol) in diethyl ether (40 ml). Immediately after addition a clear dark-red solution was formed. After 10 min a precipitate appeared. After 2 h the brown supernatant diethyl ether solution was decanted. The precipitate was washed twice with diethyl ether (10 ml) and with pentane (15 ml). After drying in high vacuum XIII was isolated as a yellow compound in 50% yield. M.p. 225°C (dec.). Anal.: Found: C, 61.74; H, 6.07; N, 5.63; Cu, 25.54%. $C_{52}H_{60}N_4Cu_4$ calcd.: C, 62.76; H, 6.08; N, 5.57; Cu, 25.45%. Mol.wt. (cryosc. in benzene): Found: 925; calcd.: 996. For NMR data see Table 1 and Fig. 1.

b. Via reaction of tetrakis(2-N,N-dimethylaminophenyl)hexacopper dibromide with ViLi (V). A solution of V (7.9 mmol) in diethyl ether (40 ml) was added to a suspension of tetrakis(2-*N*,*N*-dimethylaminophenyl)-hexacopper dibromide (3.96 mmol) in diethyl ether (20 ml). No reaction occurred. Therefore the diethyl ether was removed by vacuum evaporation and benzene (100 ml) was added. NMR analysis indicated the occurrence of a very slow reaction (increasing amount of $Vi_2Cu_4R_2$ (XIII) in respect to $R_4Cu_6Br_2$). After 8 days with continuous stirring the suspension was centrifuged (2200 rps, 20 min). The supernatant liquid was decanted, and the residue was washed once with benzene (50 ml) leaving a white solid.

This solid was thoroughly washed with diethyl ether and dried in high vacuum, giving 2-*N*,*N*-dimethylaminophenylcopper [9] (5.5 mmol) according to elemental analysis (Anal.: Found: C, 52.98; H, 5.78; N, 7.54; Cu, 33.70%. $C_8H_{10}NCu$ calcd.: C, 52.30; H, 5.49; N, 7.62; Cu, 34.59%) and the result of a hydrolysis experiment which gave exclusively N,N-dimethylaniline according to NMR analysis.

The combined benzene extracts were evaporated. The brown-yellow residue was washed with diethyl ether (30 ml) and twice with pentane (40 ml). After high vacuum drying 2.5 g of a yellow solid was isolated. According to NMR spectroscopy and elemental analysis this was a mixture of $R_4Cu_6Br_2$ and $Vi_2Cu_4R_2$. Anal.: Found: C, 55.17; H, 5.71; N, 5.47; Cu, 28.39; Br, 4.57%. For a 1/5 mixture of $R_4Cu_6Br_2$ and $Vi_2Cu_4Br_2$ calcd.: C, 55.43; H, 5.47; N, 5.59; Cu, 28.96; Br, 4.55%.

Reaction of $Vi_2Cu_4Br_2$ (VII) with CuOTf

Excess of cuprous triflate was added to a suspension of VII (0.7 mmol) in benzene (20 ml). The colour of the suspension changed from green to red-brown. After 20 h ammonia was added and the mixture was extracted with diethyl ether. The ether extract was washed with water, dried over $MgSO_4$ and evaporated, leaving a mixture of isomeric dimers (ViVi, 92%) and *E*-1-(2-*N*,*N*-dimethylaminophenyl)-2-(4-methylphenyl)-1-propene (*E*-ViH, 8%). NMR (C_6D_6, TMS internal, δ (ppm)): ViVi (non separable mixture of isomers): 2.47/2.52 (NMe_2), 1.70 (C=CMe), 2.27/2.24 (4-Me); *E*-ViH: 2.53 (NMe_2), 2.15 (4-Me), 2.18 (d, *J*, 1.3 Hz, C=CMe).

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