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XXXV *. CRYSTAL AND MOLECULAR STRUCTURE OF $[Cu_4\{(4\text{-}MeC_6H_4)\text{-}MeC{=}C(C_6H_4NMe_2\text{-}2)\}_2(C_6H_4NMe_2\text{-}2)_2]$, A TETRANUCLEAR ORGANOCOPPER COMPOUND CONTAINING BRIDGING ALKENYL AND ARYL GROUPS **

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Summary

The crystal and molecular structure of the title compound has been determined by a single crystal X-ray diffraction study using standard Patterson and Fourier methods. The structure was refined by a block-diagonal least-squares procedure to a final R value of 0.16 for 3454 reflections. Crystals are monoclinic, space group $P2_1/c$, with a 14.007(5), b 12.224(5), c 28.358(8) Å, β 99.60(1)°, and $Z = 4$.

The molecule consists of a central rhombus-type core of copper atoms to which the alkenyl and aryl groups are bound in a bridging fashion (two electron-three center bonding). The two alkenyl and the two aryl groups each occupy adjoining edges of the Cu_4 core. The dimethylamino groups of the alkenyl ligand coordinate to copper, whereas those of the bridging aryl ligand are free. As a result the copper core is made up of copper atoms which are alternatingly two- and three-coordinate.

The structure is discussed in terms of structural information now available for organocopper compounds. The geometry of the Cu_2C (bridge) moiety in

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[*] For Part XXXIV, see ref. 15.

[**] Dedicated to Professor Henry Gilman, "driving force" of so many organometallic reactions performed all over the world in the past decades.

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organocopper cluster compounds as expected varies little with the nature of the bridging one-electron organo ligand (alkyl, alkenyl, alkynyl or aryl).

Introduction

In the course of their classic study of the reactivity of organometallic compounds towards organic molecules containing functional groups Gilman et al. as early as 1936 have pointed out the synthetic potential of organocopper compounds [1]. However, it is only during the past two decades that organocopper compounds have found wide acceptance as particularly valuable tools of the synthetic organic chemist [2]. The extreme versatility of organocopperlithium compounds, first synthesized by Gilman et al. in 1952 [3], as reagents for C—C bond formation [4,5] has further stimulated interest in synthetic applications of organocopper compounds. Relatively few pure organocopper compounds have been isolated. As a result of the lack of availability of single crystals suitable for X-ray analysis structural aspects of organocopper compounds had remained largely unexplored. However, during the past decade considerable progress has been made and detailed structural information based on X-ray analysis is now available for representatives of alkyl- [6,7], alkynyl- [8,9] and aryl- [9—12] copper compounds (for a review including other methods of structure elucidation see ref. 13). In general these studies have shown that organocopper compounds have polynuclear structures consisting of a central copper core to which the organo groups are bonded by two electron—three centre (electron-deficient) carbon—metal bonds. The structure of a mixed aryl/alkynylcopper species of the type $[Cu_6Ar_4(C{\equiv}CAr')_2]$ [9] is particularly illuminating in this respect.

So far structural information concerning alkenylcopper compounds has been lacking. In our search for pure organocopper species suitable for X-ray structural investigation we have recently isolated tetranuclear alkenylcopper compounds of the type $[Cu_4Vi_2Br_2]$ in which Vi is a substituted 1,2-diarylpropenyl group [14]. Mixed alkenyl/alkynylcopper and alkenyl/arylcopper compounds were found to be accessible via ligand-substitution reactions of $[Cu_4Vi_2Br_2]$ with appropriate lithium arylacetylides or lithium aryls [14]. The results of elemental analysis and cryoscopic molecular weight determinations revealed that replacement of bromine in $[Cu_4Vi_2Br_2]$ by the 2-$Me_2NC_6H_4$ group takes place with retention of the tetranuclear structure [14]. Single crystals of $[Cu_4\{(4\text{-}MeC_6H_4)MeC{=}C(C_6H_4NMe_2\text{-}2)\}_2(C_6H_4NMe_2\text{-}2)_2]$ have successfully been grown. In the present paper we report the results of an X-ray crystallographic study of this mixed alkenyl/arylcopper compound. Results concerning the thermal behaviour and chemical reactivity of this type of alkenylcopper compounds has been recently reported [15].

Experimental

The preparation of the title compound is described in ref. 14. Single crystals were obtained by slow distillation of pentane into a solution of the compound in benzene.

TABLE 1

CRYSTAL DATA AND DETAILS OF THE DATA COLLECTION FOR $C_{52}H_{60}Cu_4N_4$

Crystal data

a	14.007(5) Å	β 99.60(1)°
b	12.224(5) Å	
c	28.358(8) Å	V 4787(3) $Å^3$
Spacegroup	$P2_1/c$	$Z = 4$
Formula	$C_{52}H_{60}Cu_4N_4$	
Mol. wt.	995.27	$F(000)$ 2064 electrons
D(calc)	1.381 g/cm^3	

Data collection

Diffractometer: CAD3	radiation: Mo-K_α (Zr-filtered)
θ_{max} 25°	λ 0.71069 Å
Scan mode: ω	scan angle: $\Delta\omega = 1.13 + 1.83\ tg(\theta)$

Total number of scanned reflexions: 9122.

Total number of observed ($I > 2\sigma(I)$) reflexions: 3454

Crystal data, structure determination and refinement

Table 1 gives the pertinent data on the structure determination of the title compound. Reflexion data were collected on a CAD3 diffractometer using zirconium filtered Mo-K_α-radiation. It turned out during the structure determination that the data-set at hand was not optimal, because of a combination of poor crystal quality and diffractometer malfunction. However, it was considered sufficiently accurate for the main topological purpose of this structure investigation.

The copper atoms were located from a Patterson map. All other non-hydrogen atoms were found by standard Fourier techniques. Hydrogen atoms were introduced in the subsequent blocked-full-matrix least-squares refinement on calculated positions and refined in the riding mode on the bonding non-hydrogen atom. All non-hydrogen atoms were refined with individual isotropic thermal parameters except for the copper atoms that were assigned anisotropic thermal motion parameters. Refinement was stopped at $R = 0.16$ for 3454 observed reflexions. A final difference Fourier synthesis showed no significant features. Table 2 lists the final values of the refined parameters.

The structure determination and refinement was carried out on an in-house ECLIPSE S/230 mini-computer with a locally adapted version of the SHELX76 package named ILIAS. All derived geometry calculations and structure illustration were done with the locally developed EUCLID package that includes a modified and extended version of PLUTO.

Results and discussion

The crystal structure of the title compound consists of four discrete molecular units per monoclinic unit cell. The shortest observed intermolecular contact is between two molecules related by a screw axis and is represented by the nonbonded distance C(11)—C(36) 3.36(5) Å. Figure 1 presents an overview of the molecule along with the adopted numbering scheme. A view along the line

TABLE 2. POSITIONAL AND THERMAL PARAMETERS AND THEIR esd IN PARENTHESES FOR $C_{52}H_{60}Cu_4N_4$ [a]

Atom	x/a	y/b	z/c	$U_{1,1}$ or U	$U_{2,2}$	$U_{3,3}$	$U_{2,3}$	$U_{1,3}$	$U_{1,2}$
Cu(1)	0.1403(3)	0.1993(4)	0.1447(1)	0.042(3)	0.052(3)	0.027(2)	−0.000(2)	0.009(2)	−0.010(3)
Cu(2)	0.1952(3)	0.2084(4)	0.0663(2)	0.043(3)	0.056(3)	0.043(3)	−0.007(3)	0.009(2)	−0.006(3)
Cu(3)	0.3591(3)	0.2895(4)	0.0831(1)	0.043(3)	0.048(3)	0.031(2)	−0.004(2)	0.010(2)	−0.002(2)
Cu(4)	0.3085(3)	0.2563(4)	0.1605(1)	0.040(3)	0.045(3)	0.022(2)	−0.001(2)	0.008(2)	−0.003(2)
N(1)	0.515(2)	0.333(3)	0.071(1)	0.06(1)					
N(2)	0.043(2)	0.258(3)	0.196(1)	0.049(9)					
N(3)	0.273(3)	0.324(4)	−0.036(2)	0.11(2)					
N(4)	0.002(3)	0.018(3)	0.069(1)	0.06(1)					
C(1)	0.522(3)	0.451(3)	0.066(1)	0.05(1)					
C(2)	0.539(3)	0.283(4)	0.027(2)	0.09(1)					
C(3)	0.564(3)	0.293(3)	0.119(1)	0.044(9)					
C(4)	0.653(3)	0.237(4)	0.119(2)	0.07(1)					
C(5)	0.695(3)	0.202(4)	0.165(1)	0.06(1)					
C(6)	0.656(3)	0.217(3)	0.200(1)	0.05(1)					
C(7)	0.568(3)	0.271(4)	0.202(2)	0.07(1)					
C(8)	0.518(2)	0.309(3)	0.159(1)	0.026(7)					
C(9)	0.416(2)	0.356(3)	0.145(1)	0.034(7)					
C(10)	0.396(2)	0.448(3)	0.167(1)	0.027(8)					
C(11)	0.461(3)	0.506(4)	0.214(1)	0.05(1)					
C(12)	0.292(2)	0.494(3)	0.159(1)	0.037(9)					
C(13)	0.254(2)	0.519(3)	0.116(1)	0.027(8)					
C(14)	0.166(3)	0.576(3)	0.103(2)	0.06(1)					
C(15)	0.114(3)	0.599(4)	0.137(2)	0.06(1)					
C(16)	0.012(4)	0.646(5)	0.124(2)	0.11(2)					
C(17)	0.153(3)	0.566(3)	0.187(1)	0.040(9)					
C(18)	0.247(2)	0.523(2)	0.199(1)	0.016(5)					
C(19)	−0.035(4)	0.330(4)	0.176(2)	0.09(2)					
C(20)	0.001(4)	0.146(4)	0.210(2)	0.09(2)					
C(21)	0.110(3)	0.294(4)	0.238(2)	0.07(1)					
C(22)	0.079(3)	0.368(4)	0.270(2)	0.07(1)					
C(23)	0.151(4)	0.403(5)	0.307(2)	0.09(2)					
C(24)	0.239(4)	0.376(4)	0.315(2)	0.08(1)					
C(25)	0.273(3)	0.305(4)	0.283(2)	0.07(1)					
C(26)	0.207(3)	0.260(4)	0.247(2)	0.07(1)					

Atom	x/a	y/b	z/c	U
C(27)	0.241(2)	0.179(3)	0.211(1)	0.023(8)
C(28)	0.264(2)	0.079(3)	0.223(1)	0.025(8)
C(29)	0.246(3)	0.029(3)	0.269(1)	0.05(1)
C(30)	0.308(2)	−0.005(2)	0.188(1)	0.015(7)
C(31)	0.275(2)	−0.106(2)	0.182(1)	0.016(7)
C(32)	0.324(4)	−0.177(4)	0.158(2)	0.08(1)
C(33)	0.405(3)	−0.153(4)	0.142(2)	0.07(1)
C(34)	0.450(4)	−0.235(5)	0.112(2)	0.10(2)
C(35)	0.438(3)	−0.047(3)	0.154(1)	0.040(9)
C(36)	0.393(2)	0.026(3)	0.180(1)	0.031(8)
C(37)	0.228(3)	0.396(3)	−0.010(1)	0.05(1)
C(38)	0.261(3)	0.347(4)	−0.085(1)	0.06(1)
C(39)	0.299(3)	0.217(3)	−0.020(1)	0.05(1)
C(40)	0.304(3)	0.186(3)	0.031(1)	0.04(1)
C(41)	0.335(3)	0.080(4)	0.037(2)	0.07(1)
C(42)	0.357(3)	0.006(4)	0.007(2)	0.07(1)
C(43)	0.354(3)	0.039(4)	−0.039(1)	0.06(1)
C(44)	0.325(3)	0.142(4)	−0.051(2)	0.06(1)
C(45)	0.095(3)	−0.022(4)	0.088(2)	0.08(1)
C(46)	−0.071(3)	−0.061(4)	0.059(2)	0.08(1)
C(47)	−0.017(3)	0.127(4)	0.062(2)	0.05(1)
C(48)	0.056(3)	0.205(4)	0.077(2)	0.07(1)
C(49)	0.028(4)	0.319(5)	0.067(2)	0.08(2)
C(50)	−0.060(3)	0.348(4)	0.037(2)	0.08(1)
C(51)	−0.123(4)	0.265(4)	0.026(2)	0.09(1)
C(52)	−0.106(4)	0.161(4)	0.037(2)	0.08(1)

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[a] The temperature factor has the form of exp(−T), where $T = 8\pi^2 U(\sin^2(\theta/\lambda))$ for isotropic atoms and $T = 2\pi^2 \Sigma_{i,j} (h_i \times h_j \times U_{i,j} \times a_i^* \times a_j^*)$ for anisotropic atoms, a_i^* are reciprocal axial lengths and h_i are Miller indices.

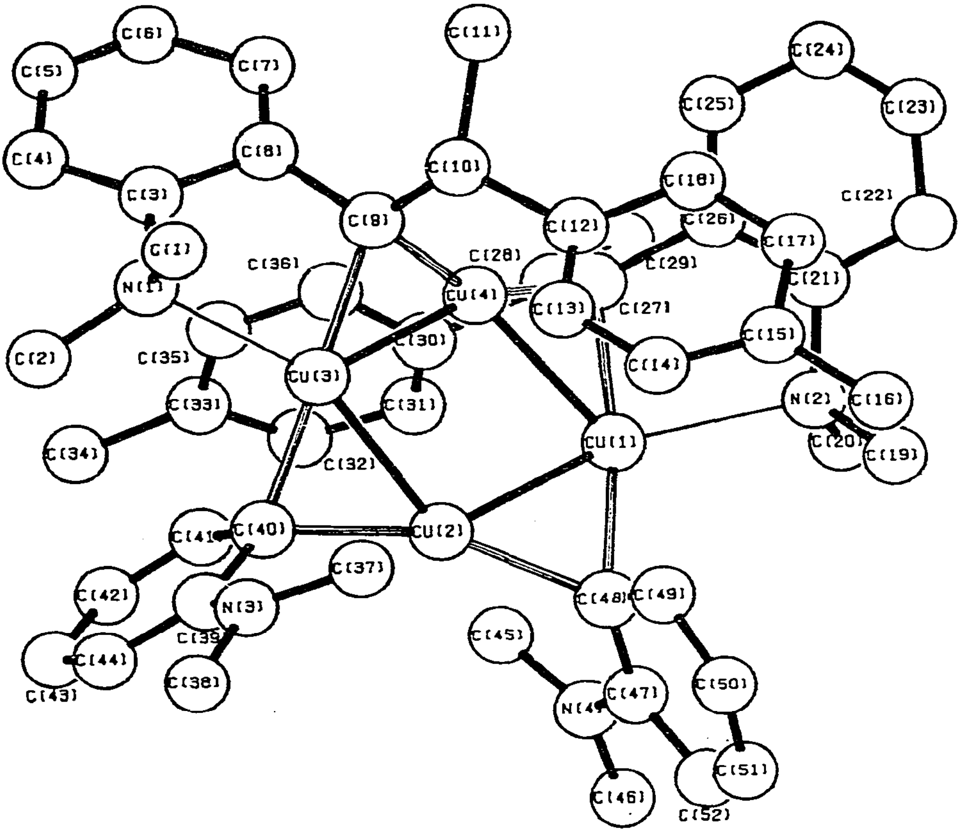

Fig. 1. Minimum overlap view with adopted numbering scheme.

Cu(4) → Cu(2) shown in Fig. 2 reveals that this line basically runs parallel to a pseudo-molecular twofold axis. Figure 3 depicts the copper core together with the bridging aryl and alkenyl carbon atoms and the atoms completing the chelate rings formed by the olefinic ligand. Relevant bond distances and angles are presented in Fig. 4 and Fig. 5.

Based on the structure of [$Ar_4Cu_6Br_2$] in which the two bromine atoms bridge *trans*-edges of a square Cu_4 arrangement [11] the bromine atoms in [$Vi_2Cu_4Br_2$] had been assumed to bridge *trans*-edges of the Cu_4 core and a mutual *trans*-arrangement of the two aryl and the two alkenyl ligands in the title compound had accordingly been proposed [14]. The X-ray study now reveals the *cis*-position of the two aryl (C(40) and C(48)) and alkenyl (C(9) and C(27)) carbon atoms (Fig. 3). The $Vi_2Cu_4Br_2$ compounds reported earlier [14] therefore will probably have the two alkenyl groups and the two bromine atoms in *cis*-position. The Me_2N(alkenyl) groups coordinate to copper resulting in the formation of CuC_3N chelate rings, but the Me_2N(aryl) groups are non-coordinating (Fig. 1). As a result the *trans*-positioned Cu(2), Cu(4) pair is two-coordinate, whereas Cu(1) and Cu(3) are three-coordinate. These coordination geometries are retained below room temperature upon dissolution in benzene

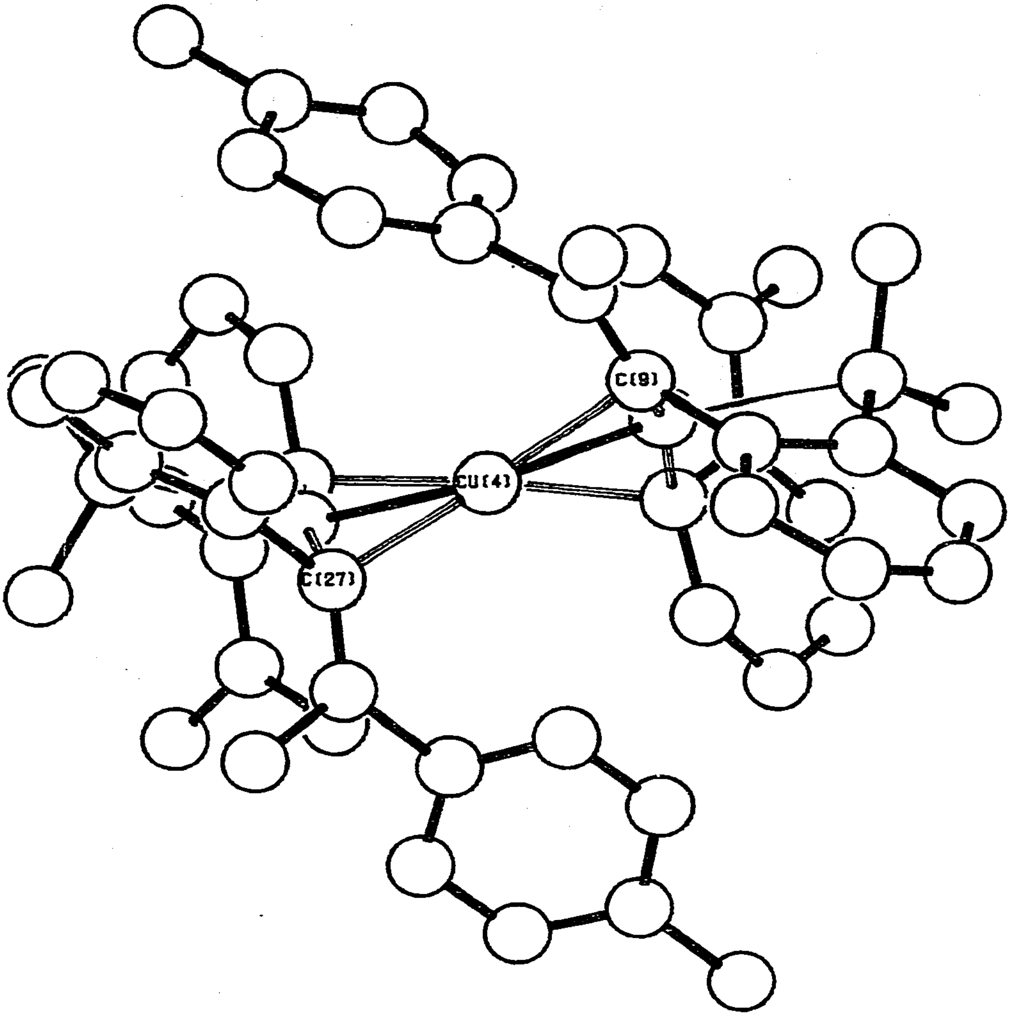

Fig. 2. View along Cu(4) → Cu(2) showing the pseudo twofold symmetry of the molecule.

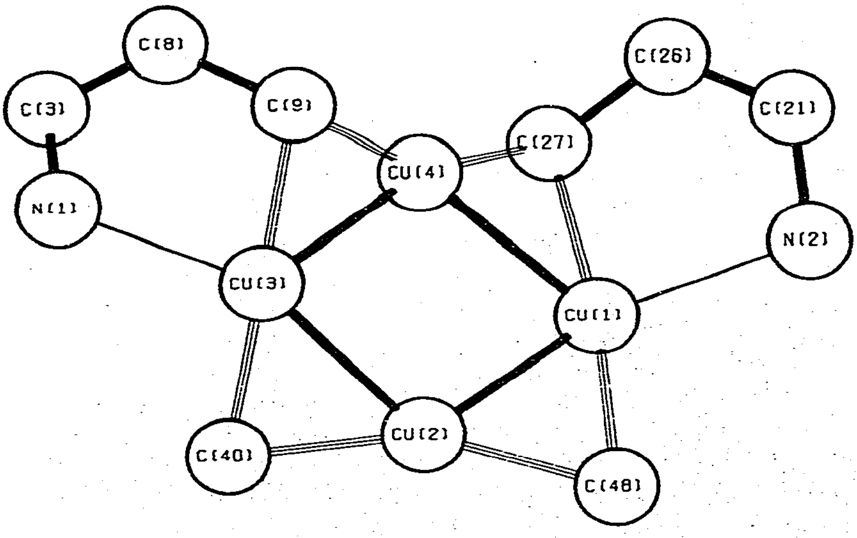

Fig. 3. The central core of the molecule.

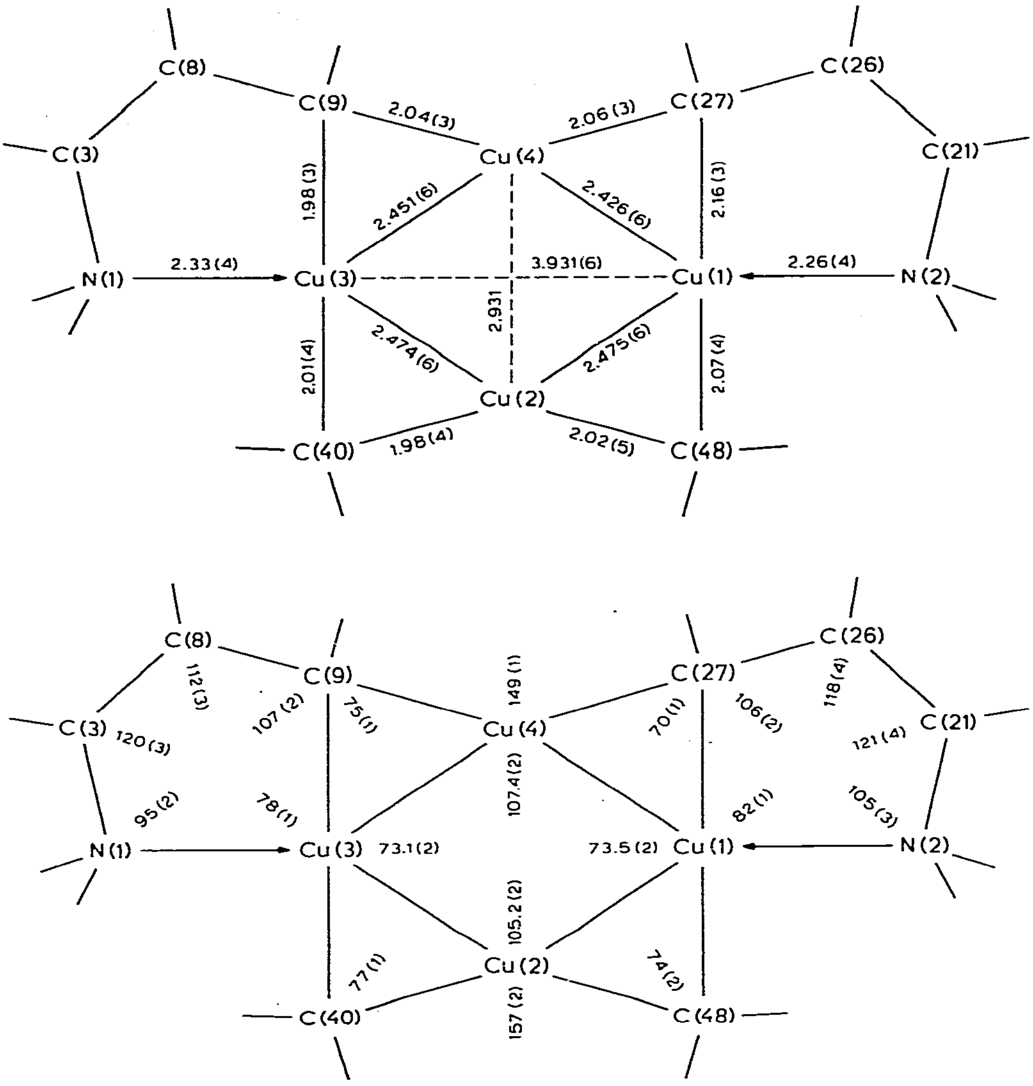

Fig. 4. Bond distances (Å) and angles (°) within the Cu_4C_4 framework.

as revealed by a dynamic ^1H NMR study of the Me_2N(alkenyl) and Me_2N(aryl) groups [14].

The observed structure confirms that both the alkenyl and the aryl groups are bound to the copper core via two electron—three center (electron-deficient) bonds. The molecular orbitals describing the aryl-to-Cu_2 [9,10,16] and alkenyl-to-Cu_2 [9,14] bonding have been discussed before.

The title compound has a total number of 52 cluster electrons and thus supplements the 48- ($[Cu_4(CH_2SiMe_3)_4]$ [6]) and 56- $[Cu_4(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}5)_4]$ [10] -electron tetranuclear organocopper clusters reported earlier.

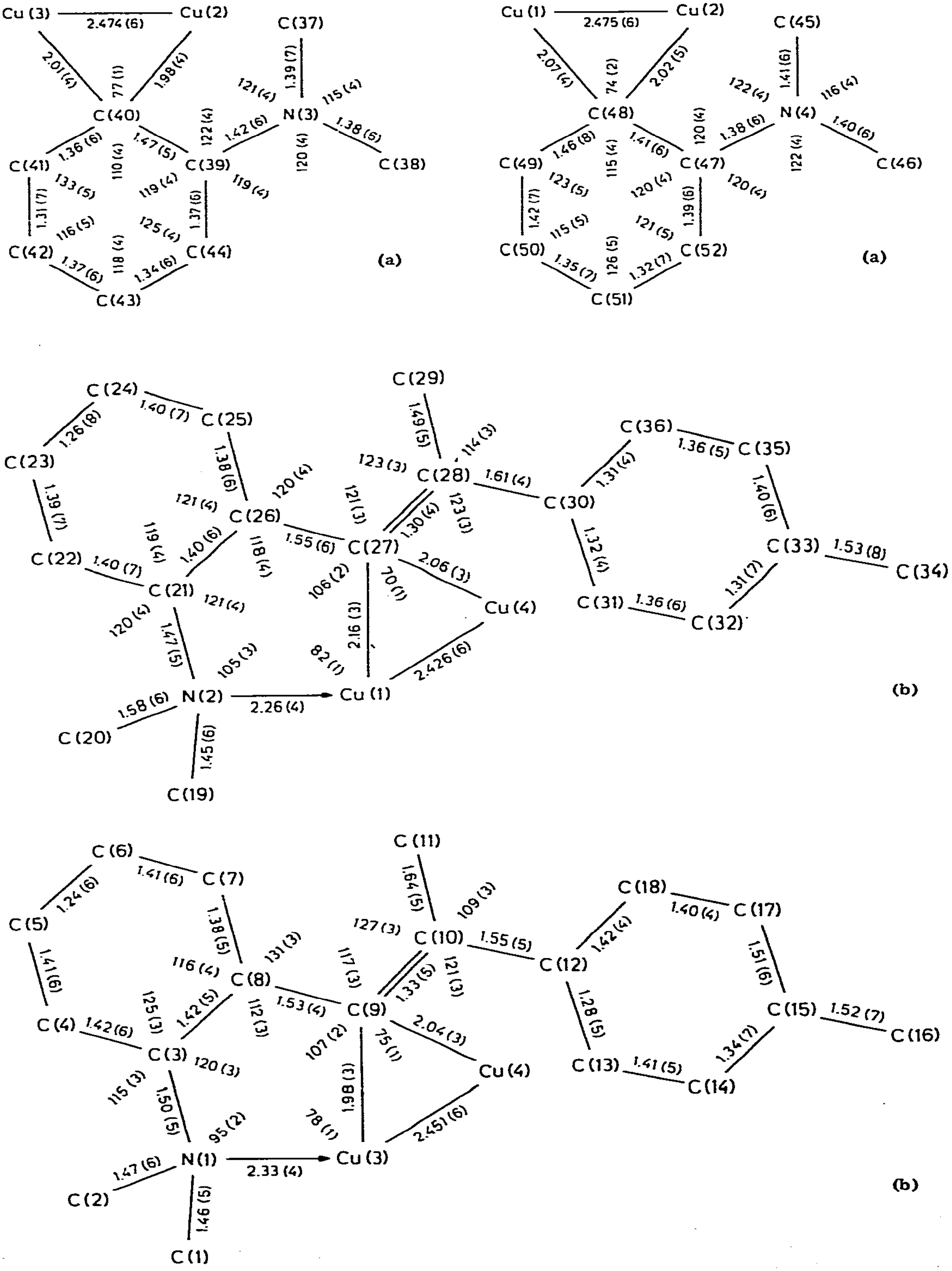

Fig. 5. Bond distances (Å) and angles (°) for (a) the aryl ligands and (b) the alkenyl ligands.

Geometry of the central Cu_4C_4 moiety (Fig. 4)

The four central copper atoms are arranged in an almost planar rhombus pattern. A least-squares plane through the four Cu atoms gives the following distances of the Cu_4C_4 atoms to this plane: Cu(1) + 0.08(2); Cu(2) — 0.07(1); Cu(3) + 0.07(2); Cu(4) — 0.08(2); C(9) + 0.55(4); C(27) — 0.64(4); C(40) — 0.84(4) and C(48) + 0.55(5) Å. The observation that in this 52-electron cluster the four bridging C atoms are alternatingly positioned above and below the Cu_4 core represents a striking difference with the planar Cu_4C_4 unit in the 48-electron $[Cu_4(CH_2SiMe_3)_4]$ cluster [6]. The aryl-bridged Cu—Cu distances (2.474(6) and 2.475(6) Å) are closely similar to the alkenyl-bridged distances of 2.451(6) and 2.426(6) Å. These values fit very well into the range of Cu—Cu distances bridged by one-electron organo ligands observed for a variety of polynuclear organocopper compounds (assisted Cu—Cu bonding, cf. ref. 9): 2.417 [6] for alkyl-, 2.521 [9], 2.377 [10], 2.48 [11] and 2.472 Å [12] for aryl- and 2.45 [8] and 2.474 Å [9] for alkynylcopper compounds. Unbridged Cu—Cu distances (2.69 [8], 2.84 [9], 2.63 [11] and 2.726 Å [12]) and three-electron halogen- (2.70 Å [9]) or alkoxy-bridged (2.709 Å [17]) Cu—Cu distances in polynuclear copper compounds are appreciably longer. We have earlier rationalized these findings [9]. The remaining two non-bridged Cu—Cu vectors which make up the diagonals of the rhombus are appreciably longer (Cu(2)—Cu(4) 2.931(6) and Cu(1)—Cu(3) 3.931(6) Å) and represent a non-bonding situation. That the four Cu atoms are arranged in a rhombus and are not accommodated in a square as in $[Cu_4(CH_2SiMe_3)_4]$ [6] arises from the different coordination geometries of the two *trans*-pairs of Cu atoms (Fig. 3). The two-coordinate Cu(2) and Cu(4) are forced into forming obtuse angles (105.2 and 107.4°) with the neighbouring Cu atoms, whereas the three-coordinate Cu(1) and Cu(3) form angles of 73.5 and 73.1°, respectively. The Cu(2) and Cu(4) atoms form CCuC interatomic bond angles of 149(1) and 157(2)° with bridging C(alkenyl) and C(aryl) atoms, respectively (cf. CCuC angles of 168° [9] and 164° [11] for copper atoms linearly coordinated to two bridging C(aryl) atoms; see molecular orbital picture outlined in ref. 18). The four Cu atoms in the 56-electron cluster $[Cu_4(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}5)_4]$ which are three-coordinate as a result of Cu—N coordination adopt a butterfly arrangement intermediate between square planar and tetrahedral [10].

The CuC(alkenyl)Cu (75(1)° and 70(1)°) and CuC(aryl)Cu (77(1)° and 74(2)°) angles do not appreciably differ from CuC(bridge)Cu angles observed in other organocopper compounds, e.g. CuC(alkyl)Cu 73.8° [6], CuC(alkynyl)Cu 74.6° [9] and CuC(aryl)Cu 75.3° [11] and 74.7° [12]. The Cu—C(alkenyl) (mean 2.06 Å) and Cu—C(aryl) (mean 2.02 Å) distances are in the range previously observed for Cu_2—C(alkyl) (2.02 Å [6]), Cu_2—C(aryl) (2.05 [9], 2.08 [10], 2.02 [11] and 2.04 Å [12]) and Cu_2—C(alkynyl) (2.02 [8] and 2.03 Å [9]) bonds. The X-ray results obtained thus far for various types of organocopper compounds clearly show that the geometry of the Cu_2C(bridge) moiety varies little with the nature of the bridging one-electron organo ligand (alkyl, alkenyl, alkynyl or aryl).

The non-bonding distance between the two bridging alkenyl carbon (C(9)—C(26)) and aryl carbon (C(40)—C(48)) atoms is 3.95 and 3.92 Å, respectively.

Geometry of the $C_6H_4NMe_2$-2 ligand (Fig. 5a)

Both ligands are observed to be essentially planar. The distances from the respective least-squares planes, as determined by the atoms of the phenyl rings, are within their standard deviations except for the atoms C(37) and C(45) which deviate by 0.25(10) and 0.33(10) Å. The distances of C(37) to Cu(2) and Cu(3) and of C(45) to Cu(1) and Cu(2) amount to 3.23(4), 3.22(4), 3.15(4) and 3.25(4) Å.

The observed planarity of the $C_6H_4NMe_2$ ligand which might suggest appreciable mesomeric electron-release of the Me_2N group towards the aryl ring is not uncommon. A screening of Me_2N-substituted aromatic compounds present in the Cambridge Crystallographic Data Base revealed a whole range of geometries varying from tetrahedral (sp^3) to planar (sp^2) for the nitrogen atom. The observed planarity here may be steric in origin.

The aryl ligand planes make angles of 80 and 84° with the Cu---Cu vectors, a perpendicular position enabling maximal orbital overlap for the Cu_2C(aryl) bond [9,10,16].

Geometry of the $(4\text{-}MeC_6H_4)MeC{=}C(C_6H_4NMe_2\text{-}2)$ ligand (Fig. 5b)

For the 1,2-diarylpropenyl ligand in the title compound the *Z*-configuration had been predicted [14] based on the synthesis method for the *E*-propenyllithium starting material [19] and on the reasonable assumption (cf. refs. 20 and 21) that the transmetallation step used for the preparation of the starting compound (*E*-ViLi → *Z*-$Vi_2Cu_4Br_2$) [14] proceeds with retention of configuration *. This stereochemistry is now confirmed by the X-ray study.

An analysis of both propenyl ligands in terms of torsion angles reveals essentially similar C—C bond conformations except for the fact that the signs of the torsion angles about the C(28)—C(30) bonds are opposite to those about the corresponding C(10)—C(12) bond. This is reflected in the inter phenyl plane angles of 50(2)° and 3(2)°, respectively.

The planarity of the alkenyl moieties may be assessed from the values of the relevant torsion angles: C(8)—C(9)—C(10)—C(11) −13(5)°, C(8)—C(9)—C(10)—C(12) −173(3)°; C(26)—C(27)—C(28)—C(29) 10(5)° and C(26)—C(27)—C(28)—C(30) −175(3)°. The phenyl rings are planar but not coplanar with the alkenyl planes.

The position of the alkenyl planes with respect to the bridged Cu---Cu vectors is essentially perpendicular as may be assessed from the Newman plots presented in Fig. 6 and the angles Cu(3)—C(9)—C(10) 132(2)°, Cu(4)—C(9)—C(10) 101(2)°, Cu(4)—C(27)—C(28) 120(2)° and Cu(1)—C(27)—C(28) 116(2)°. In the bonding picture presented for the Cu_2—C(alkenyl) interaction [14] orbital overlap is optimal, if the orientation of the alkenyl ligand is perpendicular. However, the observed carbon—carbon double bond distances of 1.33(5) and 1.30(4) Å are not appreciably different from that observed in e.g. *trans*-stilbene (1.338(2) Å [23]) suggesting that the alkenyl groups like alkynyl ligands [9] strictly act as one-electron donors and that π-contributions to the Cu_2—C (alkenyl) bonding [14] are not important. Likewise, in the only other structure

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* The configurations of *E*-ViLi and *Z*-$Vi_2Cu_4Br_2$ are the same, because the *E*- and *Z*-configurational rules are based on atomic weights [22].

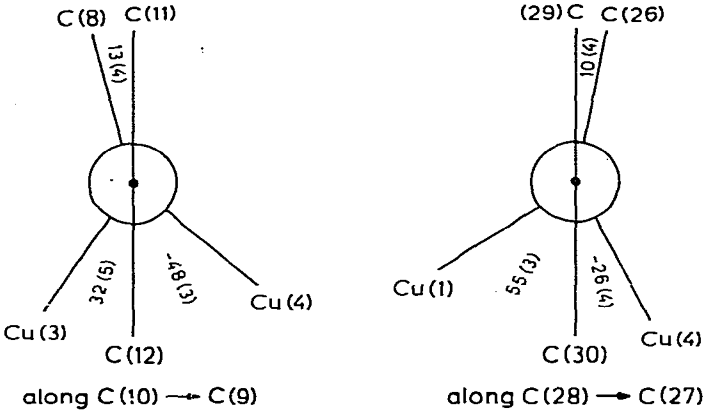

Fig. 6. Newman plots about the carbon—carbon double bond of the alkenyl ligands.

determination of an alkenyl-bridged system, i.e. $[Al_2(\mu\text{-CHCHBu-t})_2(\text{Bu-i})_4]$, the plane of the alkenyl group is perpendicular (89.3°) to that of the Al_2C_2 moiety [24].

The Cu—N bond lengths of 2.26(4) and 2.33(4) Å in the chelate rings formed by the alkenyl ligands differ little from those observed in $[Cu_4(C_6H_3CH_2NMe_2\text{-}2\text{-Me-}5)_4]$ (2.21 Å mean) [10,16]. The chelate rings are puckered, Cu(1) and Cu(3) being 0.9(1) and 1.4(1) Å out of the least-squares planes through the C_3N part of the chelate rings.

The results reported in this paper further confirm our earlier finding that multi-center bonding is the preferred bonding mode of organic groups in organometallic compounds of the Group IB elements copper and silver [13]. In this respect the organometallic chemistry of copper appears to be closely related to that of the Group IA metals where it has been known for some time that e.g. organolithium compounds are polynuclear with bridging organo ligands both in the solid and in solution [25].

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