

Group 1B Organometallic Chemistry. Part 25.¹ Crystal and Molecular Structure of 1,2,3:1,4,5;2,3,6;4,5,6-Tetrakis- μ_3 -2-dimethylaminophenyl-2,5;3,4-bis- μ_2 -4-tolylethynyl-octahedro-hexacopper(I)

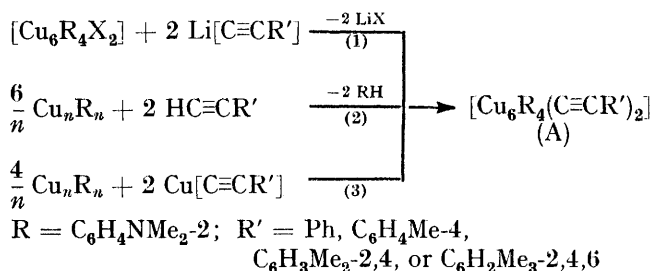
By Richard W. M. ten Hoedt and Jan G. Noltes,* Institute for Organic Chemistry TNO, P.O. Box 5009, 3502 JA Utrecht, The Netherlands

Gerard van Koten, Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, The Netherlands

Anthony L. Spek, Department of Structural Chemistry, University of Utrecht, Utrecht, The Netherlands

The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray diffraction data by Patterson and Fourier methods. Refinement by a block-diagonal least-squares procedure based on 3 643 observed reflections has converged at R 0.044 and R' 0.057. Crystals are triclinic, space group $P\bar{1}$, with $a = 11.596(2)$, $b = 18.184(3)$, $c = 11.719(2)$ Å, $\alpha = 110.18(1)$, $\beta = 95.35(1)$, $\gamma = 91.49(1)^\circ$, and $Z = 2$. The molecule consists of a central, slightly distorted, octahedral arrangement of copper atoms. The dimethylamino-phenyl groups span triangular faces by bridging *via* carbon a $\text{Cu}_{\text{ap}}-\text{Cu}_{\text{eq}}$ edge and bonding to a third Cu_{eq} atom by nitrogen co-ordination. Two opposite edges of the equatorial Cu_4 plane are symmetrically bridged by 4-tolylethynyl ligands which act as one-electron donors. The bonding is discussed in terms of structural information available for other organocopper compounds. The architecture of the molecule accounts for the exclusive formation of the asymmetric coupling product 2- $\text{Me}_2\text{NC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{Me}$ -4 upon thermolysis of the title compound.

In the course of our research concerning the synthesis and characterization of polynuclear arylcopper compounds^{2,3} we found that mixed compounds of type (A) are accessible by ligand substitution [equation (1)], by aryl-arylacetylide exchange [equation (2)], and by interaction of a pure arylcopper compound with copper(I) acetylide [equation (3)].⁴ The importance of this novel



type of organocopper compound lies in the fact that two different organic groups are bound to one metal core. Details concerning the synthesis of these compounds have recently been reported.⁴ Based on spectroscopic and molecular-weight data, a hexanuclear structure was tentatively proposed⁵ in which four Cu_3 faces of a Cu_6 octahedron are occupied by one μ_2 -C-bonded acetylide ligand and one μ_2 -C, σ -N-bonded $\text{C}_6\text{H}_4\text{NMe}_2$ ligand.

The compounds $[\text{Cu}_6\text{R}_4(\text{C}\equiv\text{CR}')_2]$ display very specific decomposition behaviour: on heating, selective and quantitative formation of the asymmetric coupling product $\text{RC}\equiv\text{CR}'$ is observed. This finding, which was recently reported in detail,⁶ represents one of the few examples^{7,8} in organometallic chemistry where it has

been unambiguously demonstrated that a metal-cluster surface exerts a matrix effect in the formation of an organic molecule starting from smaller entities.

The general importance of selective C-C bond-forming processes and the lack of structural information concerning polynuclear organometallic compounds containing different organic ligands prompted us to establish the molecular structure of a representative of type (A) by X-ray analysis. In this paper the results of this investigation are presented together with a discussion of aryl- and ethynyl-to-copper core bonding in this type of compound. Furthermore, the C-C bond-forming process is discussed in the light of the structural information which has become available.

EXPERIMENTAL

The preparation of the compound is described in ref. 4. Crystals were obtained by slow distillation of pentane into a solution of the compound in toluene.

Crystal Data.— $\text{C}_{50}\text{H}_{54}\text{Cu}_6\text{N}_4$, $M = 1\ 092.3$, Triclinic, $a = 11.596(2)$, $b = 18.184(3)$, $c = 11.719(2)$ Å, $\alpha = 110.18(1)$, $\beta = 95.35(1)$, $\gamma = 91.49(1)^\circ$, $U = 2\ 304.8$ Å³, $Z = 2$, $F(000) = 1\ 112$, $\lambda(\text{Mo-K}\alpha) = 0.710\ 69$ Å, space group $P\bar{1}$, $D_c = 1.574$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 28.6$ cm⁻¹.

Intensity Data Collection.—A suitable specimen of the orange crystals was mounted in a Lindemann capillary under nitrogen. Intensity data up to 2θ 47.2° were collected on an Enraf-Nonius CAD 4 diffractometer using $\text{Mo-K}\alpha$ radiation. The applied ω -scan angle was $\Delta\omega = 0.40 + 0.40 \tan \theta$. The horizontal aperture was set to $0.75 + 2.58 \tan \theta$. The intensities of two reflections were monitored and used to correct for very short- and long-range fluctuations in the intensity. There was no indication of decay

¹ Part 24, G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *J. Organometallic Chem.*, 1977, **140**, C23—C27.

² G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *Inorg. Chem.*, 1977, **16**, 1782.

³ J. G. Noltes, *J. Organometallic Chem.*, 1975, **100**, 177 and refs. therein.

⁴ R. W. M. ten Hoedt, G. van Koten, and J. G. Noltes, *J. Organometallic Chem.*, 1977, **133**, 113.

⁵ G. van Koten and J. G. Noltes, *J.C.S. Chem. Comm.*, 1974, 575.

⁶ G. van Koten, R. W. M. ten Hoedt, and J. G. Noltes, *J. Org. Chem.*, 1977, **42**, 2705.

⁷ W. H. Mandeville and G. M. Whitesides, *J. Org. Chem.*, 1974, **39**, 400.

⁸ G. van Koten and J. G. Noltes, *J. Organometallic Chem.*, 1976, **104**, 127.

during the data collection. With the application of the rejection criterion $I > 2.5\sigma(I)$ and averaging of equivalents, 3 643 reflections were considered to be observed. The intensities were corrected for Lorentz and polarization effects.

Structure Determination and Refinement.—The positions of the six independent Cu atoms were located from a three-dimensional Patterson synthesis (R 0.28). The non-hydrogen atoms were found by the application of standard

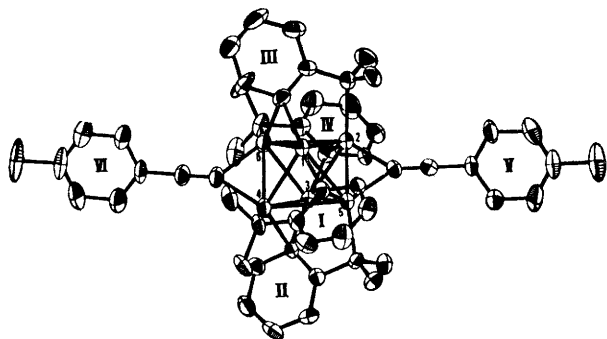


FIGURE 1 An ORTEP drawing (40% probability) of the molecule showing the thermal motions of the atoms

Fourier methods. The structure was refined, assuming anisotropic thermal motion for all the non-hydrogen atoms, by a block-diagonal least-squares procedure. Unit weights were applied. The refinement converged to $R = 0.062$ and $R' = [\sum w(|F_c| - |F_o|)^2 / \sum |F_o|^2]^{1/2} = 0.097$. At this point a difference-Fourier was calculated, from which 48 hydrogen atoms were located. The remaining six hydrogen-atom positions were calculated assuming standard bond

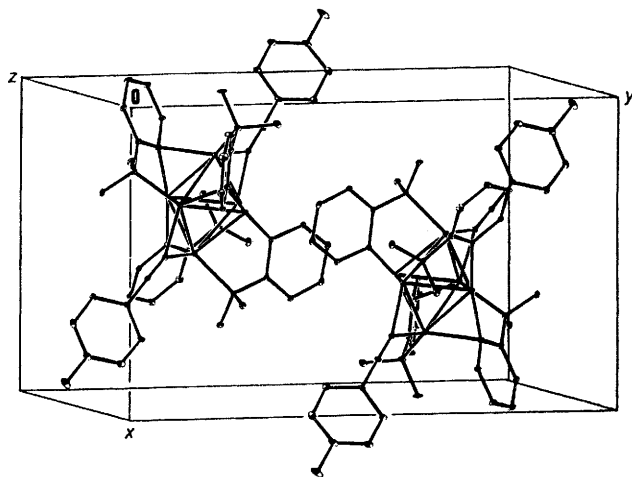


FIGURE 2 Molecular packing in the unit cell

lengths and angles. The isotropic thermal parameter for the hydrogen atoms was set to $B = 2.5 \text{ \AA}^{-2}$. Four low-order reflections were left out of the final stages of the refinement because they apparently suffered from extinction effects. When refinement was stopped with all the parameter shifts within half their standard deviation, $R = 0.044$ and $R' = 0.057$. A subsequent difference-Fourier synthesis was featureless with no densities higher than 0.45 e\AA^{-3} .

⁹ P. A. Toyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

¹⁰ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

Neutral-atom scattering factors were employed for the non-hydrogen atoms.⁹ Scattering factors for hydrogen were

TABLE I

Final refined co-ordinates ($\times 10^4$) for the non-hydrogen atoms with estimated standard deviations in parentheses

| Atom | x | y | z |
|-------|------------|-----------|-----------|
| Cu(1) | 3 235(1) | 1 524(1) | 3 403(1) |
| Cu(2) | 3 760(1) | 2 302(1) | 5 764(1) |
| Cu(3) | 3 983(1) | 3 513(1) | 5 198(1) |
| Cu(4) | 3 476(1) | 2 830(1) | 2 921(1) |
| Cu(5) | 5 159(1) | 2 258(1) | 4 285(1) |
| Cu(6) | 2 022(1) | 2 682(1) | 4 257(1) |
| N(11) | 3 971(9) | 2 051(6) | 1 244(8) |
| C(11) | 4 455(13) | 2 536(8) | 583(12) |
| C(12) | 2 908(13) | 1 603(8) | 529(12) |
| C(13) | 4 798(11) | 1 502(7) | 1 489(10) |
| C(14) | 4 675(10) | 1 332(7) | 2 586(10) |
| C(15) | 5 435(10) | 796(7) | 2 791(11) |
| C(16) | 6 256(12) | 457(8) | 2 000(13) |
| C(17) | 6 340(12) | 652(9) | 992(13) |
| C(18) | 5 604(13) | 1 164(8) | 702(13) |
| N(21) | 6 464(7) | 3 068(5) | 4 244(9) |
| C(21) | 6 973(11) | 3 534(7) | 5 524(11) |
| C(22) | 7 386(10) | 2 647(8) | 3 574(12) |
| C(23) | 5 906(10) | 3 617(6) | 3 703(10) |
| C(24) | 4 730(9) | 3 751(6) | 3 909(10) |
| C(25) | 4 239(10) | 4 269(7) | 3 426(11) |
| C(26) | 4 840(12) | 4 659(8) | 2 767(12) |
| C(27) | 5 979(12) | 4 488(8) | 2 592(12) |
| C(28) | 6 533(10) | 3 975(7) | 3 070(12) |
| N(31) | 2 668(8) | 1 391(6) | 5 926(9) |
| C(31) | 3 284(12) | 664(7) | 5 573(13) |
| C(32) | 2 474(14) | 1 619(9) | 7 213(13) |
| C(33) | 1 615(10) | 1 291(7) | 5 097(12) |
| C(34) | 1 711(10) | 1 464(7) | 4 007(12) |
| C(35) | 699(10) | 1 349(8) | 3 189(12) |
| C(36) | -364(12) | 1 083(9) | 3 414(14) |
| C(37) | -429(11) | 939(9) | 4 493(16) |
| C(38) | 549(12) | 1 027(8) | 5 303(14) |
| N(41) | 1 331(8) | 3 478(6) | 5 757(9) |
| C(41) | 1 219(13) | 4 245(9) | 5 601(14) |
| C(42) | 155(11) | 3 167(10) | 5 833(16) |
| C(43) | 2 145(11) | 3 577(7) | 6 845(11) |
| C(44) | 3 323(10) | 3 473(7) | 6 698(10) |
| C(45) | 4 099(10) | 3 613(7) | 7 744(11) |
| C(46) | 3 721(12) | 3 852(8) | 8 912(11) |
| C(47) | 2 583(14) | 3 931(10) | 9 041(13) |
| C(48) | 1 780(12) | 3 803(9) | 8 013(14) |
| C(51) | 5 431(10) | 2 008(7) | 5 831(10) |
| C(52) | 6 141(10) | 1 790(7) | 6 409(11) |
| C(53) | 7 042(10) | 1 513(7) | 7 073(11) |
| C(54) | 6 814(12) | 910(8) | 7 475(12) |
| C(55) | 7 705(15) | 666(9) | 8 147(14) |
| C(56) | 8 790(13) | 1 010(9) | 8 399(13) |
| C(57) | 9 014(13) | 1 607(10) | 8 005(14) |
| C(58) | 8 177(11) | 1 868(9) | 7 344(13) |
| C(59) | 9 715(18) | 740(11) | 9 143(18) |
| C(61) | 1 763(10) | 3 020(7) | 2 756(12) |
| C(62) | 980(10) | 3 179(8) | 2 200(12) |
| C(63) | -0(10) | 3 346(8) | 1 485(12) |
| C(64) | 10(13) | 4 003(10) | 1 177(17) |
| C(65) | -963(15) | 4 128(11) | 453(17) |
| C(66) | -1 884(13) | 3 605(10) | 91(14) |
| C(67) | -1 924(12) | 2 966(9) | 430(14) |
| C(68) | -992(11) | 2 826(9) | 1 114(12) |
| C(69) | -2 908(17) | 3 755(13) | -737(18) |

taken from ref. 10. Anomalous dispersion for copper was taken into account with $f' = 0.36$. Most of the crystallographic calculations were carried out with the X-Ray system.¹¹ The final positional parameters for the non-hydrogen atoms are listed in Table I.

¹¹ The X-Ray system, Technical Report TR-192, the Computer Science Center, University of Maryland, as implemented and extended by the Dutch X-Ray System Group, 1973.

Observed and calculated structure factors as well as the final anisotropic thermal parameters, hydrogen-atom coordinates, bond distances, and bond angles are listed in Supplementary Publication No. SUP 22345 (50 pp.).*

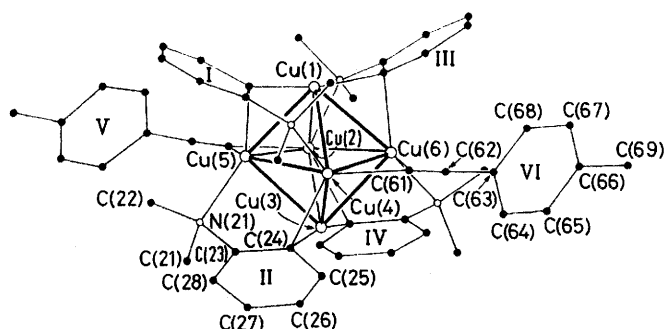


FIGURE 3 Numbering scheme (inverted projection with respect to Figure 1)

DISCUSSION

The Molecular Geometry.—The crystal structure of the title compound consists of discrete molecular units $[\text{Cu}_6(\text{C}_6\text{H}_4\text{NMe}_2)_4(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me}-4)_2]$ separated by normal van der Waals distances. Figure 1 gives an ORTEP drawing of the molecule, which has approximate D_2 symmetry, Figure 2 the molecular packing of the unit cell, Figure 3 the numbering scheme (the projection of the molecule shown is similar to that of $[\text{Cu}_6\text{R}_4\text{Br}_2]$ in Figure 1 of ref. 12), and Figures 4 and 5 the relevant bond distances and angles.

The centre of the molecule consists of a somewhat distorted octahedral arrangement of copper atoms. Four triangular faces are spanned by dimethylaminophenyl groups, while two *trans*-equatorial copper-copper

respective values are 2.69 (bromide bridged), 2.52 (aryl bridged), and 2.58 and 2.63 Å (both unbridged).¹²

The apical copper atoms are almost linearly coordinated to two bridging aryl carbon atoms, the $\text{C}_{\text{aryl}}(\text{bridge})-\text{Cu}_{\text{ap}}-\text{C}_{\text{aryl}}(\text{bridge})$ angle being 168.3° (mean). A comparable value (164°) was found in $[\text{Cu}_6\text{R}_4\text{Br}_2]$.¹² The equatorial copper atoms are three-co-ordinate as a result of bonding to one aryl C, one ethynyl C, and one N atom. The total of the angles around these Cu atoms amounts to 345° (mean), while for $[\text{Cu}_6\text{R}_4\text{Br}_2]$ this value is 343° . Thus, the geometry around the Cu_{eq}

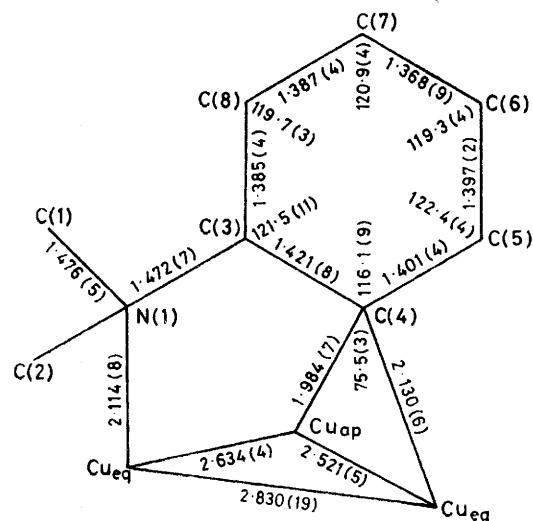


FIGURE 4 Mean distances (Å) and angles ($^\circ$) within the Cu_3 face bridged by the dimethylaminophenyl unit

atoms, which is approximately planar, is similar in both compounds.

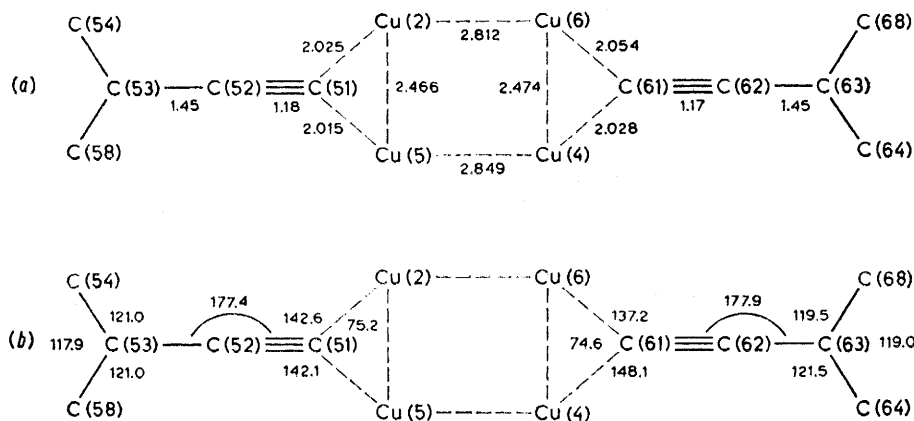


FIGURE 5 Bond distances (Å) (a) and angles ($^\circ$) (b) within the equatorial plane

edges are bridged by the 4-tolyethynyl groups. Within the central copper core four different peripheral Cu-Cu distances are observed, *i.e.* $\text{Cu}_{\text{eq}}-\text{Cu}_{\text{eq}}$ (ethynyl bridged) 2.47, $\text{Cu}_{\text{ap}}-\text{Cu}_{\text{eq}}$ (aryl bridged) 2.52, and $\text{Cu}_{\text{ap}}-\text{Cu}_{\text{eq}}$ and $\text{Cu}_{\text{eq}}-\text{Cu}_{\text{eq}}$ (both unbridged) 2.63 and 2.70 Å respectively. For the corresponding $[\text{Cu}_6\text{R}_4\text{Br}_2]$ compound the

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

Bond distances and bond angles of the aniline ligand are given in Figure 4 (mean values for the four groups present). The phenyl rings of the aniline ligands are entirely flat, the carbon atoms being <0.01 Å out of the least-squares plane.

¹² J. M. Guss, R. Mason, K. M. Thomas, G. van Koten, and J. G. Noltes, *J. Organometallic Chem.*, 1972, **40**, C.79; G. van Koten and J. G. Noltes, *ibid.*, 1975, **102**, 551.

The most interesting feature in the structure is the presence of ethynyl ligands which symmetrically bridge two *trans*-equatorial copper-copper edges. The acetylenic triple bond is perpendicular to the internuclear Cu-Cu vector. The co-ordination geometry in the equatorial plane showing this structural feature is given in Figure 5. The triple bond C(51)-C(52) is collinear with a central line through the midpoints of the edges Cu(2)-Cu(5) and Cu(4)-Cu(6), while C(61)-C(62) deviates only by 5°.

The 4-tolylethynyl ligands are not significantly distorted from linearity, as indicated by the angles C(61)-C(62)-C(63) (177.9°) and C(51)-C(52)-C(53) (177.4°). The carbon-carbon triple-bond length (1.175 Å, mean) is equal within the experimental error to the value (1.17 Å) found in [$\text{BeMe}(\text{C}\equiv\text{CMe})\cdot\text{NMe}_3$]₂,¹³ but is smaller than in unco-ordinated acetylene [1.204(2) Å].¹⁴

The ethynyl phenyl rings V [C(53)-C(58)] and VI [C(63)-C(68)] make angles of 44 and 55° with the least-squares plane through the equatorial copper atoms, the angle between the rings being 11°.

Bonding in the Molecule.—The set of rules combined in the Polyhedral Skeletal Electron Pair Theory^{15,16} is of limited applicability for the interpretation of the structural features of polynuclear Group IB metal compounds. Mingos¹⁷ has pointed out that the fact that gold valence orbitals do not generate a set of strongly bonding molecular orbitals which are tangential to the polyhedral surface represents the most relevant difference between transition-metal clusters and polynuclear gold(I) compounds. This is largely due to the large 6s→6p promotion energy* of the free Au atom and the large Au-Au distance which reduces the 6p_π-6p_π overlaps considerably. The lack of structural information based on X-ray analysis and the more complex nature of the ligands bound to the Group IB metal core (e.g. C₆H₄CH₂NMe₂-2 and C₆H₄NMe₂-2) so far seems to have hampered a more detailed discussion of the bonding in polynuclear organometal IB compounds. Combination of the structural features of the present structure and those of the previously reported [Cu₆R₄Br₂]¹² makes such a discussion possible. In analogy with the qualitative symmetry-based theory for the stereochemistry of polynuclear complexes as proposed by Mason and Mingos,¹⁹ it is possible to describe the Cu-Cu interaction as well as the bonding of the organic group to the metal core in terms of localized three-centre bonding.

The organic ligands fall into three groups: (i) alkyl ligands which act as one-electron donors by overlap of a

* We have excluded unassisted Cu-Cu bonding in [Cu₄{C₆H₃(CH₂NMe₂-2)(Me-5)}₄] on the basis of the high energy required for the necessary promotion of *d* electrons to *s* or *p* levels. This conclusion was supported by the absence of any spectroscopic evidence (i.r., Raman, n.q.r.).¹⁸ To avoid ambiguity we refer to 'assisted Cu-Cu bonding' as in aryl-bridged systems and 'unassisted Cu-Cu bonding' for 'direct' (unbridged) Cu-Cu bonds (K. Wade, personal communication).

† This synergic process, which depends on the donation by the ligand and the effective nuclear charge on copper, increases the electron density in, and the kinetic stability of, the Cu-C bond.^{2,18}

¹³ B. Morosin and J. Howatson, *J. Organometallic Chem.*, 1971, **29**, 7.

filled *sp*³ orbital; (ii) aryl and vinyl ligands which can act either as one- or three-electron ligands (in addition to the donation *via* a *sp*² molecular orbital, *p*_π orbitals can be used for bonding); and (iii) ethynyl ligands which can participate in a maximum number of three molecular orbitals (one *sp* and two *p*_π overlaps) thus acting as one-, three-, or five-electron donors. These organic ligands may be co-ordinated to one or more metal atoms. Examples of the types of carbon-to-metal interaction reported so far in the literature are included in Table 2. The aryl-to-Cu_n and ethynyl-to-Cu_n bonding in the present structure will be discussed in greater detail.

The molecular orbitals (m.o.s) describing the aryl-to-Cu₂ bonding are depicted in Figure 6. Donation of electron density from the aryl ligand to copper takes place by combination of the *sp*² m.o. of the bridging carbon atom with a mutually bonding combination of Cu orbitals [(a), assisted Cu-Cu bond]. Additional donation of electron density requires overlap of suitable *p*_z or *p*_π ligand m.o.s with an antibonding combination of Cu orbitals (b). Bond type (b) is optimal when the direction of the *p*_z orbital is parallel to the copper-copper vector. Back donation from copper to ligand likewise requires an antibonding combination of Cu orbitals (c). It is obvious that the shortest copper-copper distance is expected when only the m.o. of type (a) is occupied. Any participation of the (b) and (c) m.o.s will lengthen

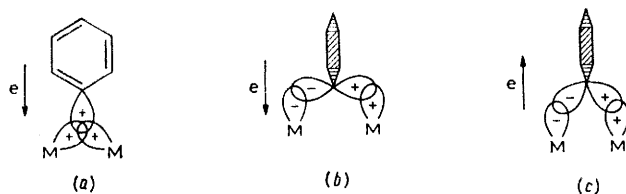


FIGURE 6 Aryl-to-Cu₂ bonding

the Cu-Cu distance.† This correlation has been established by Mason and Mingos¹⁹ for a series of transition-metal compounds.

In the previously reported [Cu₄{C₆H₃(CH₂NMe₂-2)(Me-5)}₄] the bonding in the localized Cu₂(aryl) unit was described in terms of a contribution of (a) and (b) m.o.s while back donation (c) was assisted by additional electron donation of the built-in ligand NMe₂ to Cu.¹⁸ The bonding in octahedral [Cu₆R₄Br₂] was described in similar terms¹² and this description also applies to the bonding of the aniline ligand to the Cu₆ core of the present

¹⁴ 'Molecular Structures and Dimensions,' eds. O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pettersen, and W. G. Town, N. V. A. Oosthoek, Utrecht, 1972, vol. A1, p. S2.

¹⁵ K. Wade, *Chem. Comm.*, 1971, 792; *Chem. in Britain*, 1975, 177.

¹⁶ D. M. P. Mingos, *Nature Phys. Sci.*, 1972, **236**, 99; K. M. Thomas, R. Mason, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, 1973, **95**, 3802.

¹⁷ D. M. P. Mingos, *J.C.S. Dalton*, 1976, 1163.

¹⁸ G. van Koten and J. G. Noltes, *J. Organometallic Chem.*, 1975, **84**, 129.

¹⁹ R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.

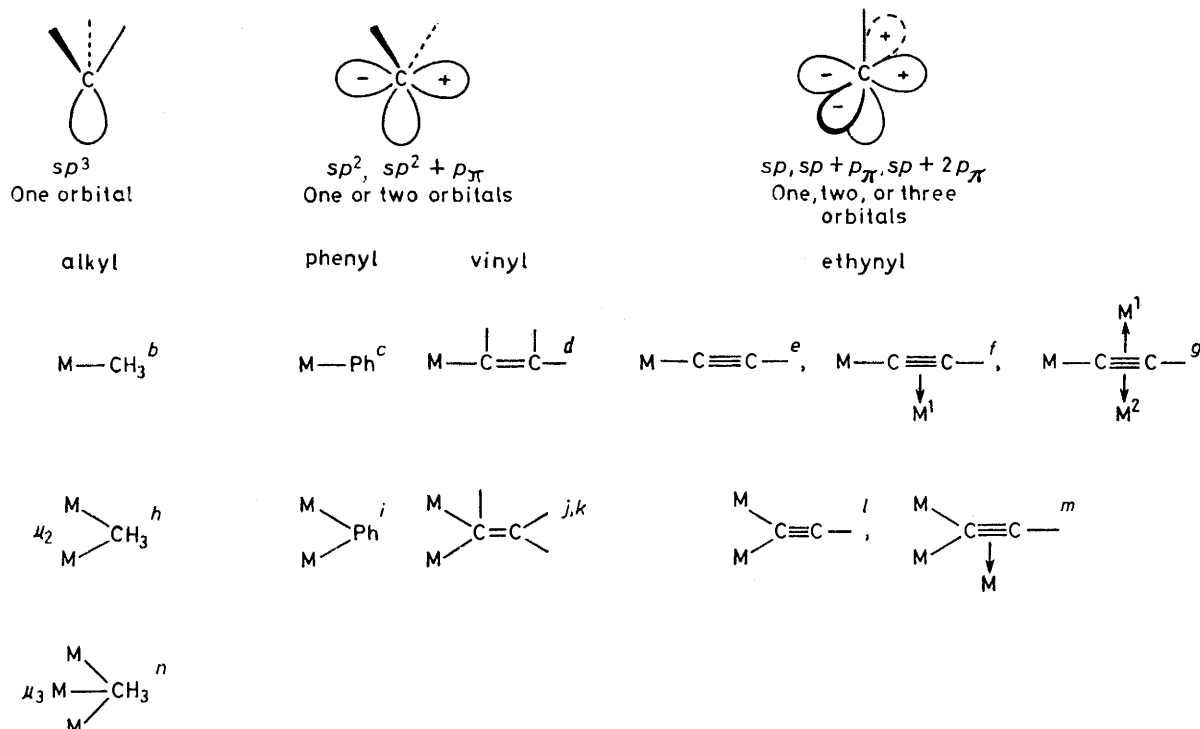
structure. Interpretation of the influence of the built-in ligand on the bonding is difficult because in the aniline ligand electronic effects arising from the aryl nucleus and the nitrogen ligand cannot be separated.

The most interesting feature in the structure is the symmetrical bonding of each of the ethynyl ligands to the Cu_6 core. To our knowledge the only precedent for this type of bonding is found in $[\{\text{BeMe}(\text{C}\equiv\text{CMe})\cdot\text{NMe}_3\}_2]$.¹³

the ethynyl ligands act as one-electron donors and that additional electron donation (*b*) or backbonding (*c*) does not take place. Any π -type overlap (*b*) will increase the $\text{C}\equiv\text{C}$ bond length as illustrated by $\text{C}\equiv\text{C}$ bond lengths for σ, η -co-ordinated ethynyl ligands (see Table 2).

The C-C distance (1.45 Å) for C(52)-C(53) and C(62)-C(63) which is in the range of a single C-C bond excludes interaction between the tolyl and acetylenic π systems.

TABLE 2
Bonding of alkyl, aryl, vinyl, and ethynyl ligands to one or more metal atoms^a



^a If available, examples are given for Group 1B organometallic compounds. ^b $[\text{CuMe}(\text{PPh}_3)]$ (A. Miyashita and A. Yamamoto, *Bull. Chem. Soc. Japan*, 1977, **50**, 1102, 1109). ^c $[\text{Cu}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ (G. van Koten and J. G. Noltes, *J. C. S. Chem. Comm.*, 1972, 452). ^d Numerous examples in main-group and transition-metal chemistry. ^e For example, $[\text{Ni}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)_2]$ (G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. (A)*, 1967, 1750; A. W. Spofford III, P. D. Carfagna, and E. L. Amma, *Inorg. Chem.*, 1967, **6**, 2677). ^f For example, $[(\text{Ph}_3\text{P})_2(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{C}\equiv\text{CPh})\text{CuCl}]$ (N. V. Raghavan and R. E. Davis, *J. Cryst. Mol. Structure*, 1976, **6**, 73), $[\{\text{Cu}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_3\}_4]$ (P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, 1966, **21**, 957), $[\{\text{Ag}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_3\}_n]$ (P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, 1966, **20**, 502), $[\text{RhAg}_2(\text{C}\equiv\text{C}_6\text{F}_5)_2(\text{PPh}_3)_3]$ (M. R. Churchill and B. G. de Boer, *Inorg. Chem.*, 1975, **14**, 2630), and $[\text{Cu}_4\text{Ir}_2(\text{C}\equiv\text{CPh})_8(\text{PPh}_3)_2]$ (M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 1974, **13**, 1418). ^g $[\text{Fe}_3(\text{C}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)(\text{CO})_7]$ (K. Yasufuku, K. Aoki, and H. Yamazaki, *Bull. Chem. Soc. Japan*, 1975, **48**, 1616) and $[\{\text{Cu}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_3\}_4]$ as in footnote *f*. ^h $[\{\text{Cu}(\text{CH}_2\text{SiMe}_3)_4\}_4]$.²⁰ ⁱ $[\text{Cu}_4(\text{C}_6\text{H}_4\text{NMe}_2-2)_4\text{Br}_2]$.¹² $[\text{Cu}_4(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4]$.¹⁸ ^j $[\text{Al}_2\text{Bu}_4(\text{CH}=\text{CHBu}^t)_2]$ (M. J. Albright, W. M. Butler, T. J. Anderson, M. D. Glick, and J. P. Oliver, *J. Amer. Chem. Soc.*, 1976, **98**, 3995). ^k Recently we isolated the first example of a stable polynuclear copper compound with the composition Cu_4 (substituted vinyl)₂Br₂. An X-ray analysis is in progress. ^l $[\{\text{BeMe}(\text{C}\equiv\text{CMe})\cdot\text{NMe}_3\}_2]$.¹³ ^m Not reported. ⁿ $(\text{LiEt})_4$ (H. Dietrich, *Acta Cryst.*, 1963, **16**, 681) and $(\text{LiMe})_4$ (E. Weiss and G. Hencken, *J. Organometallic Chem.*, 1970, **21**, 265).

The $\text{C}\equiv\text{C}$ bond length (1.17 Å) in the beryllium compound and the perpendicular position of the $\text{C}\equiv\text{C}$ system with respect to the Be-Be vector indicate that the propynyl ligand acts as a one-electron donor because any contribution of type (*b*) bonding would result in a lengthening of the $\text{C}\equiv\text{C}$ bond. Beryllium as a first-row element cannot participate in back bonding. Therefore, the value of 1.17 Å provides an excellent reference point for the $\text{C}\equiv\text{C}$ bond length of an ethynyl ligand acting as a one-electron donor. The $\text{C}\equiv\text{C}$ length observed in the present structure confirms that also in $[\text{Cu}_6\text{R}_4(\text{C}\equiv\text{CR}')_2]$

This is also supported by the normal bond lengths (1.375 Å) and bond angles (120.0°) in the tolyl rings. Furthermore, the single-bond character of the C-tolyl bond implies that the direction of the tolyl rings V [C(53)-C(58)] and VI [C(63)-C(68)] is determined by steric and crystal-packing effects rather than by bonding requirements.

That the $\text{C}\equiv\text{CC}_6\text{H}_4\text{Me}-4$ ligand acts as a one-electron donor is also reflected in the Cu-Cu distance which is shorter than the aryl-bridged Cu-Cu distance, *i.e.* 2.47 vs. 2.52 Å. Inverting this line of argument we can also

say that, in the case of the aryl-to-copper bonding, m.o.s (*b*) and/or (*c*) participate to some extent, resulting in the use of m.o.s which are antibonding with respect to the Cu-Cu interaction thus resulting in Cu-Cu bond lengthening. As compared with bridged copper edges, the unbridged copper edges have longer internuclear distances (Cu_{ap}-Cu_{eq} 2.63, Cu_{eq}-Cu_{eq} 2.70 Å). When the ethynyl ligand is replaced by bromide {going from [Cu₆R₄(C≡CC₆H₄Me-4)₂] to [Cu₆R₄Br₂]¹²} the bridged Cu_{eq}-Cu_{eq} distance increases from 2.47 to 2.70 Å. The bromine atom donates two additional electrons *via* overlap of a filled bromine *p* orbital with empty copper orbitals introducing a (*b*)-type molecular bond. This bond now makes a full contribution which explains the greater Cu_{eq}-Cu_{eq} distance in the bromide-bridged compound. This three-centre molecular bond description also provides a qualitative explanation for the difference in copper-copper distance in the compounds [Cu(CH₂SiMe₃)₄] (2.417 Å),²⁰ [Cu[N(SiMe₃)₂]₄] (2.685 Å),* and [Cu(OBu^t)₄] (2.709 Å),²¹ which all have square planar structures. Whereas the CH₂SiMe₃ ligand is bonded *via* a two-electron-three-centre bond of type (*a*), the N(SiMe₃)₂ and OBu^t ligands act as three-electron donors and like the Br atom in [Cu₆R₄Br₂] are bonded *via* a four-electron-three-centre bond by a combination of (*a*) and (*b*) type bonding (*cf.* Figure 6). The full contribution of type (*b*) bonding accounts for the greater Cu-Cu distance.

The influence of the number of methyl substituents in the ethynyl phenyl ring is indicated by an increase in decomposition temperature {[Cu₆R₄(C≡CR')₂] R' = Ph, 128; 4-tolyl, 138; 2,4-xylyl, 165; 2,4,6-mesityl, 189 °C (ref. 4)}. The inductive electron-donating properties of the methyl groups will lower the electron demand of the copper core and simultaneously strengthen the metal-carbon bond.

Electron counting within the hexanuclear bromide [Cu₆R₄Br₂] yields a total number of 84 cluster electrons. The same number of cluster electrons is found for the related compounds [Cu₄Ag₂R₄X₂] and [Cu₄Au₂R₄X₂],² and for [Cu₆H₆(PPh₃)₆].²² In contrast [Cu₆R₄(C≡CC₆H₄Me-4)₂] is an 80-electron species. The reason for σ-bridge co-ordination of the acetylenic unit rather than σ,η-bonding, which would result in a total number of 84 cluster electrons, remains unclear. In the solid, crystal-packing effects may play an important role (see below); in solution σ,η interaction may occur.⁴

C-C Coupling Process.—The molecular geometry of [Cu₆R₄(C≡CR')₂] in the solid state confirms the unique arrangement of the aniline and ethynyl groups on four of the triangular faces of the hexanuclear copper core. The geometry of one triangular face, of which one edge is occupied by an aryl and a second edge by an ethynyl ligand, is shown in Figure 7. The geometry in the solid is in line with the earlier proposed structure of [Cu₆R₄(C≡CR')₂] in solution and thus is further support for

the proposed matrix effect of the cluster on the selective asymmetric C-C coupling process on heating these compounds. Symmetric C-C coupling to give R₂ and R'C≡C-C≡CR' was not observed. Moreover, a free-radical mechanism can be excluded because hydrogen-abstraction products RH and R'C≡CH are absent. The fact that the coupling reaction is independent of the polarity of the solvent supports the proposed intramolecular nature of the coupling (see ref. 6).

Although any detailed proposal for the mechanism of this C-C coupling process would be highly speculative, several remarks can be made when the present results are placed in the perspective of earlier findings concerning coupling processes taking place on polynuclear copper assemblies. The coupling process can be divided into two steps which occur with different rates.⁶ In view of

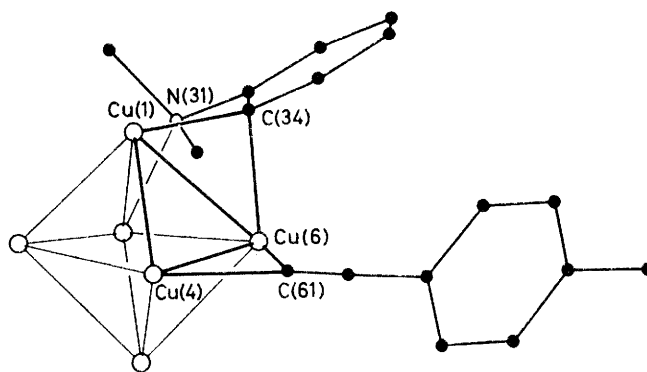
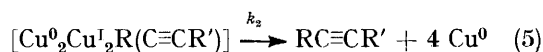
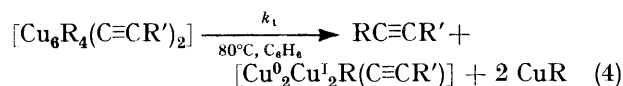


FIGURE 7 Occupation of a Cu₃R(C≡CR') triangular face

the unknown nature of the mixed-valence cluster [Cu₀₂Cu₁₂R(C≡CR')] the discussion will be focused on the



process responsible for the coupling taking place in the first step.

The hexanuclear structure of [Cu₆R₄(C≡CR')₂] in solution is retained when its solutions are heated. This can be concluded from the unchanged molecular weight at 80 °C. Indications for the arrangement of the organic groups at the respective faces of the copper polyhedron can be obtained from dynamic n.m.r. spectroscopy which at room temperature indicates low mobility, if any, of these groups. Copper-nitrogen co-ordination is inert on the n.m.r. time scale indicating also that the spanning of the aniline groups over the Cu₃ triangular faces is inert (see Figure 7). At ca. 25 °C, rate-determining Cu-N dissociation starts to occur which means that at least the aniline group obtains a higher degree of freedom. At sufficiently high temperatures even rotation of the group R around the C(4)-

* D. C. Bradley, unpublished work; personal communication.

²⁰ J. A. J. Jarvis, R. Pearce, and M. F. Lappert, *J.C.S. Dalton*, 1977, 999.

²¹ T. Greiser and E. Weiss, *Chem. Ber.*, 1976, **109**, 3142.

²² M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, 1972, **11**, 1818.

C(7) axis must be taken into account.^{2,23} An important consequence of Cu-N dissociation is that electrons are withdrawn from the cluster thereby increasing its electron deficiency. However, as a result of the ambidentate character of the equatorial ethynyl ligand the electron withdrawal can be compensated for by rearrangement from a pure σ (one-electron donor) to a σ, η interaction (three-electron donor) with the bridged Cu atoms (*cf.* ref. 4).

In Figure 8 various paths describing the first step are depicted. Route (i) involves a concerted Cu-C bond cleavage and C-C bond-forming process* taking place on the triangular Cu surface. Routes (ii) and (iii) have

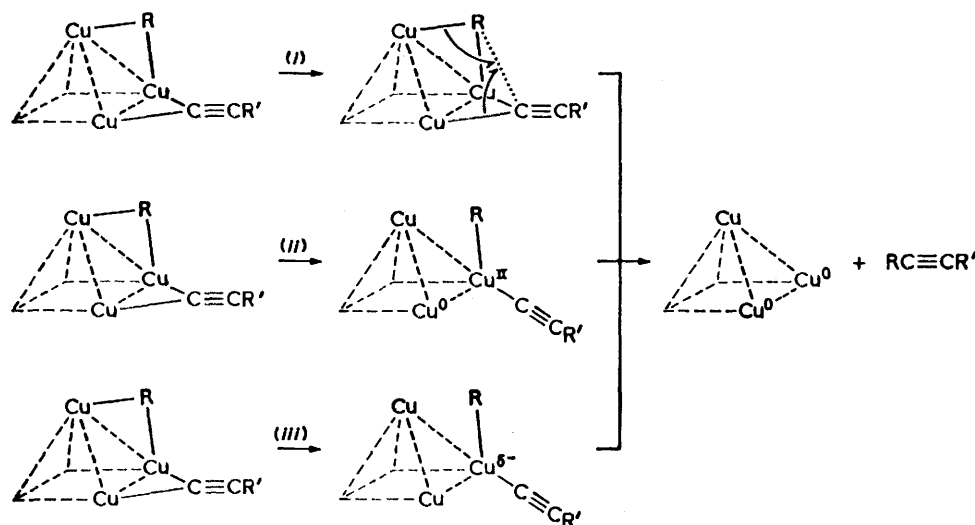


FIGURE 8 Possible decomposition paths for the elimination of the asymmetric coupling product $RC\equiv CR'$

the σ to σ, η rearrangement of the Cu_2 (ethynyl) bonding interaction in common. Consecutive valence disproportionation takes place in route (ii), whereas in (iii) a two-electron-three centre bonded aryl group becomes two-electron-two centre bonded (for a similar shift see ref. 2). The result is that both organic groups become bonded to one Cu centre from which the asymmetric product is then formed by elimination. The fact that in route (iii) elimination takes place from a copper centre with high electron density makes this route unlikely. The most likely process therefore seems to be (ii) which involves C-C bond formation by reductive elimination of $RC\equiv CR'$ from a copper(II) centre formed as a result of an intra-aggregate valence-disproportion-

* A stepwise process involving the formation of an aryl radical R which then is trapped in the aggregate by a Cu-C bond would also produce R_2 .

²³ G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *J.C.S. Chem. Comm.*, 1977, 203.

ation process. Recently, we have put forward arguments for the occurrence of such a process in the selective formation of biaryls from polynuclear arylcopper-copper trifluoromethanesulphonate intermediates²⁴ (see also the explanation given for the selective C-C coupling process of dialkylcuprates with alkyl halides reported by Pearson and Gregory²⁵). The hypothesis that valence disproportionation is an important process for the activation of Cu-C bonds is in line with our general interpretation of the bonding of organic groups to the polynuclear copper core in terms of localized two-electron-three-centre Cu_2-C bonds. It is only in such a system that localized activated centres at which coupling

takes place can be formed. In the case of the present $[Cu_6R_4(C\equiv CR')_2]$ compound the matrix effect is to be interpreted in terms of the unique arrangement of the organic groups on the Cu_3 faces. This specific arrangement is responsible for the selective formation of asymmetric $Cu^{II}R(C\equiv CR')$ centres and thus for the selectivity of the C-C coupling process. Similar arguments must apply to the selective thermal decomposition of $[Cu_2-Cu^I_2R(C\equiv CR')]$ into Cu^0 and $RC\equiv CR'$.⁴

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²⁴ G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *J. Org. Chem.*, 1977, **42**, 2047.

²⁵ R. G. Pearson and C. D. Gregory, *J. Amer. Chem. Soc.*, 1976, **98**, 4098.