Chemistry of Organocopper Clusters

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Chemistry of organocopper clusters

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Thermally stable ($T_{\text{dec}} > 150$ °C), hydrocarbon-soluble organocopper compounds have been isolated and structurally characterized. The examples discussed include mixed cluster compounds containing different organic ligands (e.g. $Cu_4(aryl)_2(alkenyl)_2$, $Cu_6(aryl)_4(alkynyl)_2$) or cluster compounds in which part of the Cu atoms have been replaced by other monovalent metals M such as Li or Au (e.g. $Cu_2M_2Ar_4$, $Cu_4M_2Ar_4X_2$).

Organocopper compounds have polynuclear structures consisting of a metal core to which organo ligands are bound via C(1) to two metal atoms by a two-electron three-centre bond. As shown by X-ray crystallography the geometry of the $Cu_2C(1)$ moiety in organocopper clusters varies little with the nature of the bridging organo ligand (alkyl, alkenyl, alkynyl or aryl).

The C(1) atom of asymmetrically substituted aryl groups that bridge unlike metal atoms is a centre of chirality. Rotation of the aryl group around the C(1) . . . C(4) axis causes a continuous inversion of configuration at C(1). Dynamic ^1H and ^{13}C n.m.r. studies have confirmed that such rotation actually occurs in solution for $2\text{-}Me_2NCH_2C_6H_4$–metal compounds $Ar_4M_2Li_2$ (M = Cu, Ag or Au). The prochiral methylene group offers a probe for monitoring the configuration at C(1).

The products formed in the reactions of organocopper clusters are determined to a large extent by the nature of the central copper core and by the way in which the faces of the core are occupied by the ligands. This is illustrated by the fully selective formation of the cross-coupling product observed upon thermolysis of an equimolar mixture of arylcopper and alkynylcopper compounds. This reaction proceeds via a mixed aryl–alkynyl Cu_6 cluster. Specific biaryl formation upon reaction of arylcopper compounds with a catalytic amount of copper triflate (CuOTf) likewise occurs intramolecularly in mixed aryl–triflate Cu_n clusters.

1. Introduction

In recent years organocopper compounds have gained an important role in organic synthesis as intermediates in carbon–carbon bond-forming reactions. The extreme versatility of organocopper reagents, which often show advantages over the more traditional Grignard or organolithium reagents, has strongly stimulated interest in organocopper chemistry. The organocopper reagents applied in synthetic studies have generally been reacted with the substrate molecule without prior isolation. Studies dealing with the nature and structure of organocopper compounds have received relatively less attention. The susceptibility of the copper–carbon bond to oxidation and hydrolysis as well as the lack of solubility of most organocopper compounds in hydrocarbon solvents have thwarted many attempts at isolating pure compounds.

It is only during the past decade that a limited number of organocopper compounds have been isolated in an analytically pure form and subjected to detailed structural studies in the solid state and in solution. As a result our understanding of the nature of organocopper compounds and the pathways by which they react is now beginning to develop (for a recent review see van Koten & Noltes 1982).

In this paper attention will be given to the synthesis and structural characterization of polynuclear organocopper compounds containing aryl, alkenyl and alkynyl ligands. The examples discussed, which represent thermally stable, hydrocarbon-soluble compounds, are taken from research at the Institute of Applied Chemistry, Utrecht. Furthermore, the dynamic behaviour of the organo ligand in arylcopper clusters, which involves a novel type of chirality, will be discussed. Examples of extremely specific carbon–carbon bond formation reactions occurring at the surface of organocopper clusters will also be given.

2. SYNTHESIS, STRUCTURE AND BONDING IN ORGANOCOPPER CLUSTERS

Simple alkylcopper compounds have low thermal stability, e.g. MeCu and EtCu decompose well below room temperature. Simple arylcopper compounds are somewhat more thermally stable, but PhCu, for example, is virtually insoluble in non-coordinating solvents. Alkenylcopper compounds like vinylcopper and *cis*- and *trans*-propenylcopper also decompose well below 0 °C.

In our work on arylcopper and alkenylcopper compounds we have followed an approach that earlier had allowed the isolation of stable aryl derivatives of transition metals. Rather than add an external ligand we have stabilized the Cu–C bond by introducing a potentially coordinating ligand in the aryl or alkenyl group bound to copper via a Cu–C bond in a position suitable for intramolecular coordination to occur. As internal or built-in ligands the Me_2N or Me_2NCH_2 groups have been used.

Organocopper compounds of this type are readily obtained by the reaction of the corresponding organolithium reagent with cuprous bromide in an ether solvent, e.g.

$$CuBr + LiC_6H_4CH_2NMe_2\text{-}2 \xrightarrow{Et_2O} CuC_6H_4CH_2NMe_2\text{-}2 + LiBr. \qquad (1)$$

The arylcopper compound shown in (1) is hydrocarbon-soluble and thermally stable up to 180 °C. In benzene solution the compound occurs as a tetramer $[Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4]$. An X-ray structural determination has revealed that in the solid this compound is also a tetramer (figure 1). The most remarkable feature is the presence of aryl groups bridging the edges of a butterfly-shaped Cu_4 frame with extremely short Cu–Cu distances (2.38 Å†). As a result of aryl to Cu_2 bridging and the occurrence of Cu–N intramolecular coordination the Cu atoms are tri-coordinate (van Koten & Noltes 1975*a*). It is possible to replace some of the copper atoms in this type of cluster by other monovalent metal atoms such as lithium (van Koten & Noltes 1979*a*) or gold (I) (van Koten & Noltes 1980) with retention of the cluster, e.g.:

$$[Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4] + [Li_4(C_6H_4CH_2NMe_2\text{-}2)_4] \longrightarrow 2[Cu_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]; \qquad (2)$$

$$[Au_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4] + 2CuI \longrightarrow [Cu_2Au_2(C_6H_4CH_2NMe_2\text{-}2)_4] + 2LiI. \qquad (3)$$

These compounds are thermally stable up to 170 °C and exist in benzene as discrete tetranuclear species. The formation of the Cu_2Li_2 cluster shown in (2) exemplifies cluster-exchange between tetranuclear clusters containing different metals. By using similar reactions the corresponding $Ar_4Ag_2Li_2$ and $Ar_4Au_2Li_2$ clusters have been obtained. ^{13}C and ^{1}H n.m.r. spectroscopy has revealed unambiguously (cf. observation of $J(^{107,109}Ag\text{–}^{13}C_1)$ and $J(^{7}Li\text{–}^{13}C_1)$

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† $1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$.

that each of the four aryl groups bridges one of the Group IB metals and one lithium atom giving rise to an M_2Li_2 core with the two M and the two Li atoms in the *trans*-positions (figure 2). Furthermore, ^1H n.m.r. spectroscopy showed that the four 2-Me_2NCH_2 ligands are bonded to the Li atoms. Thus the Li atoms in these compounds are four-coordinate and the Group IB metals two-coordinate (van Koten & Noltes 1979).

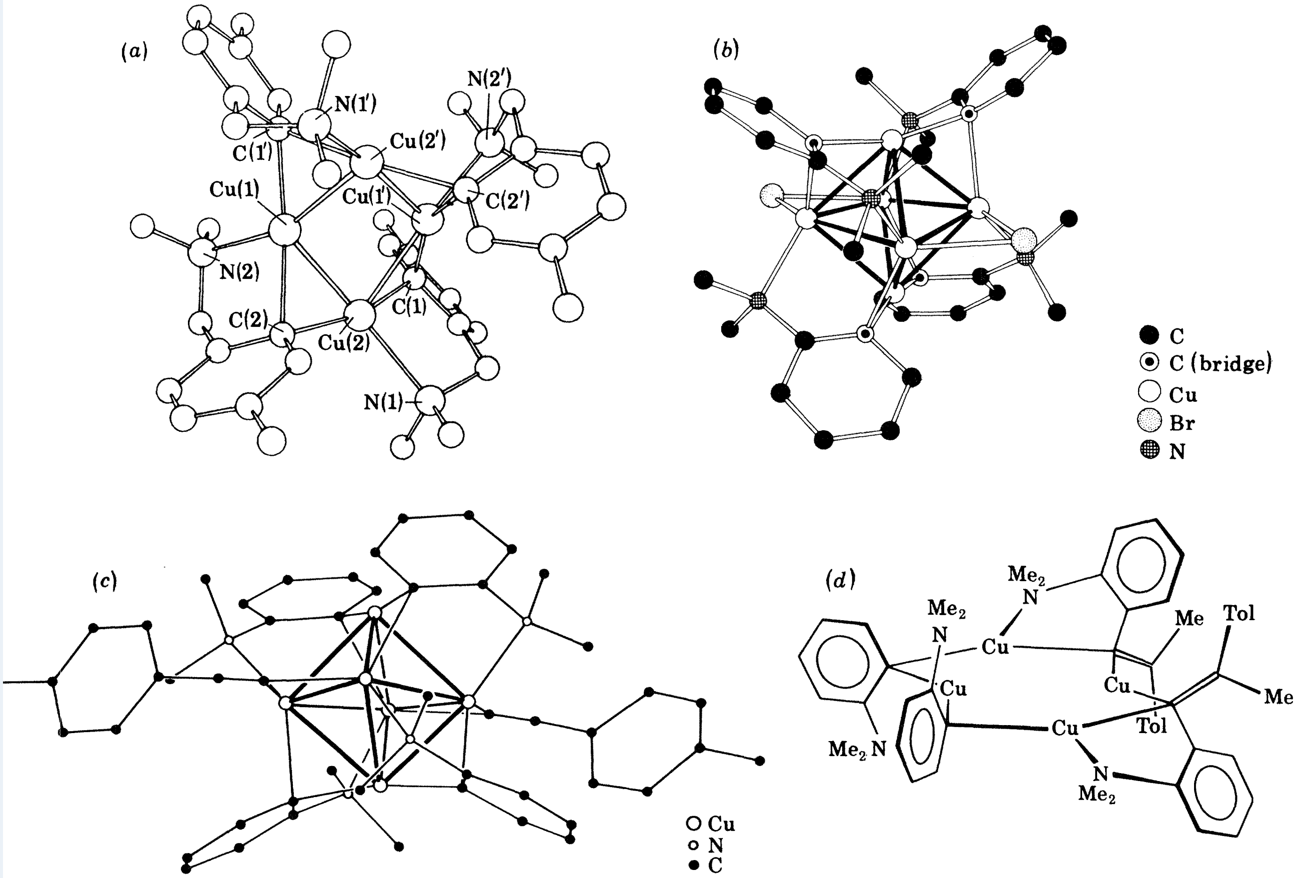

FIGURE 1. Structure of (*a*) [$Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4$], (*b*) [$Cu_6(C_6H_4NMe_2\text{-}2)_4Br_2$], (*c*) [$Cu_6(C_6H_4NMe_2\text{-}2)_4(C{\equiv}CC_6H_4Me\text{-}4)_2$] and (*d*) [$Cu_4\{(4\text{-}MeC_6H_4)MeC{=}C(C_6H_4NMe_2\text{-}2)\}_2(C_6H_4NMe_2\text{-}2)_2$].

The presence of built-in ligands is not a prerequisite for stability in these mixed-metal clusters, e.g. tetranuclear *p*-tolyl Group IB metal–lithium compounds have been isolated. Here, the lithium atoms are three-coordinate as a result of the coordination of one molecule of diethylether (figure 2).

Simple arylcopper compounds like *o*-tolylcopper and *p*-tolylcopper are also tetranuclear in benzene solution. In this case the Cu_4 core of the molecule will be planar as a result of digonal coordination of the four Cu atoms. By using X-ray crystallographic methods the Cu_4 core of the alkylcopper compound [$Cu_4(CH_2SiMe_3)_4$] has been shown also to have a square planar configuration (Jarvis *et al.* 1977).

In principle Ar_4M_4 and $Ar_4M_2Li_2$ compounds containing asymmetrically substituted aryl groups can exist as four unique geometric isomers depending on whether the substituents are above or below the Cu_4 or M_2Li_2 core. Figure 3 shows one of the geometric isomers of

$[Cu_4(C_6H_4Me\text{-}2)_4]$. The observation of multiplet resonances for the methyl groups, if the ^1H n.m.r. spectrum is recorded at −60 °C (Hofstee *et al.* 1978), shows that the *o*-tolylcopper tetramer can indeed be frozen out in various geometric isomers.

The structure of arylcopper compounds containing a 2-dimethylamino built-in ligand differs from that of those containing a 2-Me_2NCH_2 substituent. In the Me_2NCH_2-substituted compounds the Me_2N group can coordinate to one of the Cu atoms bridged by the aryl group, thereby forming a five-membered chelate ring. The same type of coordination for the Me_2N-substituted compounds leads to a four-membered chelate ring, which is sterically unfavourable. For the latter compounds a structure in which the Me_2N group coordinates to a third Cu atom is preferred.

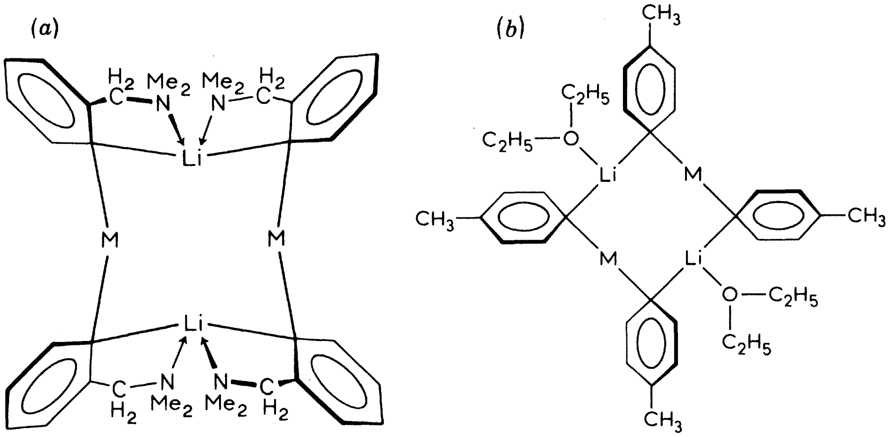

FIGURE 2. Schematic structure of (*a*) $[M_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$ and (*b*) $[M_2Li_2(C_6H_4Me\text{-}4)_4(Et_2O)_2]$ (M = Cu, Ag or Au).

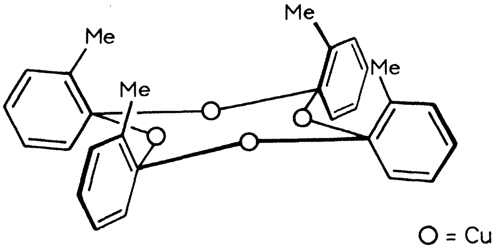

FIGURE 3. One of the geometric isomers of $[Cu_4(C_6H_4Me\text{-}2)_4]$.

The reaction of $CuC_6H_4NMe_2$-2 with cuprous halides in benzene, if performed in a 2 : 1 molar ratio, yields bright-red, mixed aryl–halide copper clusters:

$$(4/n)\ [Cu_n(C_6H_4NMe_2\text{-}2)_n] + (2/m)[Cu_mX_m] \xrightarrow[20\ ^\circ C]{\text{benzene}} [Cu_6(C_6H_4NMe_2\text{-}2)_4X_2]. \qquad (4)$$

These compounds, which are benzene-soluble, are hexanuclear in solution. The schematic structure of the Cu_6 cluster, where X = Br, is shown in figure 1 (van Koten & Noltes 1975*b*). The four aryl groups bridge equatorial and apical Cu atoms of a distorted Cu_6 octahedron. The Me_2N group is coordinated to a third equatorial Ca atom. Thus each anilino ligand bridges a triangular Cu_3 face. The two Br atoms bridge *trans*-equatorial edges of the Cu_6 octahedron.

The mixed aryl–bromide Cu_6 clusters can undergo substitution of halogen with retention of the hexanuclear cluster structure. Of particular interest is the replacement of halogen by organic ligands, which gives rise to mixed organocopper cluster compounds. This type of reaction, among others, has been applied to the synthesis of mixed aryl–alkynyl Cu_6 clusters:

$$[Cu_6(C_6H_4NMe_2\text{-}2)_4Br_2] + 2LiC{\equiv}CC_6H_4Me\text{-}4 \longrightarrow [Cu_6(C_6H_4NMe_2\text{-}2)_4(C{\equiv}CC_6H_4Me\text{-}4)_2] + 2LiBr. \quad (5)$$

The same compounds can be obtained by the 2:1 reaction of arylcopper and alkynylcopper compounds by cluster exchange:

$$(4/n)\ [Cu_n(C_6H_4NMe_2\text{-}2)_n] + (2/m)[Cu_m(C{\equiv}CC_6H_4Me\text{-}4)_m] \longrightarrow [Cu_6(C_6H_4NMe_2\text{-}2)_4(C{\equiv}CC_6H_4Me\text{-}4)_2]. \quad (6)$$

X-ray structural determination has confirmed that the octahedral structure is retained upon ligand substitution (ten Hoedt *et al.* 1979*a*) (figure 1). The arylacetylide ligands bridge the *trans*-edges of the equatorial plane symmetrically. The acetylenic carbon atoms, which show extremely short C≡C distances of 1.175 Å, are colinear in the equatorial plane.

The ability of the $2\text{-}Me_2NC_6H_4$ group (Ar) to act as a tridentate ligand by spanning three metal atoms confers considerable stability on the Ar_4M_6 skeleton. A variety of hexanuclear Group IB metal compounds have been prepared in which Cu atoms in $Ar_4Cu_6X_2$ have been replaced by Ag or Au atoms (van Koten *et al.* 1977*c*):

$$(4/n)\ [Cu_nAr_n] + 2\ AgOTf \longrightarrow Ar_4Cu_4Ag_2(OTf)_2; \quad (7)$$

$$(4/n)\ [Au_nAr_n] + 4\ CuOTf \longrightarrow Ar_4Cu_4Au_2(OTf)_2 + 2\ AuOTf; \quad (8)$$

$$[Au_2Li_2Ar_4] + 4\ AgOTf \longrightarrow Ar_4Ag_4Au_2(OTf)_2 + 2\ LiOTf. \quad (9)$$

As shown in figure 1, the apical metal atoms in $Ar_4Cu_6X_2$ compounds are two-coordinate and the equatorial metal atoms three-coordinate. For monovalent Group IB metals the tendency for linear twofold coordination increases in the series $Cu^I < Ag^I < Au^I$. Indeed, in these mixed clusters the Au atoms show a distinct site preference, with the Au atoms occupying the apical positions of the $M_4M'_2$ octahedron. This structure has been confirmed by Au–Mössbauer experiments.

In contrast to the thermally quite labile *cis*- and *trans*-propenylcopper compounds, perfectly stable ($T_{dec} > 150$ °C) alkenylcopper compounds may be obtained if the alkenyl ligand is sterically crowded and contains a potentially coordinating ligand suitable for intramolecular coordination (ten Hoedt *et al.* 1979*b*):

$$2\ Li(alkenyl) + 2\ CuBr \longrightarrow [Cu_4(alkenyl)_2Br_2] \quad (10)$$

(alkenyl = $(4\text{-}MeC_6H_4)MeC{=}C(C_6H_4NMe_2\text{-}2)$).

Upon the attempted preparation of alkenylcopper compounds $[Cu_n(alkenyl)_n]$, mixed alkenyl–bromo Cu_4 clusters form spontaneously. Like the $Ar_4Cu_6Br_2$ clusters, the alkenyl–bromo Cu_4 compounds undergo ligand-substitution reactions with retention of the tetranuclear structure. In this way mixed alkenyl-alkynyl and mixed alkenyl–aryl clusters have been isolated (ten Hoedt *et al.* 1979*b*):

$$[Cu_4(alkenyl)_2Br_2] + 2\ ArLi \longrightarrow [Cu_4(alkenyl)_2(Ar)_2] + 2\ LiBr \quad (11)$$

(Ar = $C_6H_4NMe_2\text{-}2$).

The schematic structure of an $(\text{alkenyl})_2(\text{aryl})_2\text{Cu}_4$ cluster which has been solved by X-ray analysis (Noltes *et al.* 1982) is shown in figure 1. The two alkenyl and aryl ligands, which are in a *cis*-position, are again each bridging two Cu atoms. Only the Me_2N groups attached to the alkenyl ligand are coordinated, giving rise to the presence of two two-coordinate and two three-coordinate copper atoms which are in mutually *trans*-positions. As a result of the different co-ordination geometries the four Cu atoms are arranged in a rhombus pattern and not in a square as in $[Cu_4(CH_2SiMe_3)_4]$.

The structure of the aryl–alkenylcopper cluster confirms that multicentre bonding is the preferred bonding mode of organic groups in organocopper compounds. This is true not only for alkyl, alkenyl, alkynyl and aryl groups, but also for more exotic organic ligands, e.g. (2-dimethylaminomethyl)ferrocenylcopper is tetranuclear in the solid as a result of the cyclopentadienyl C_1 carbon atoms bridging the edges of a Cu_4 square (Nesmeyanov *et al.* 1977).

FIGURE 4. Molecular orbitals involved in two-electron–three-centre ArM_2 bonding.

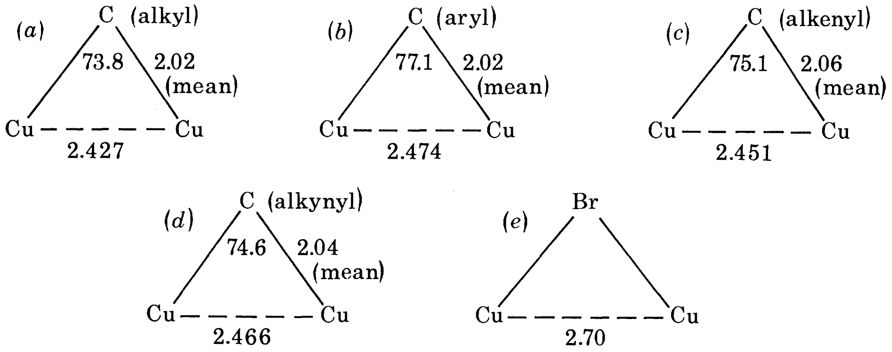

FIGURE 5. Geometry of the Cu_2C_{bridge} moiety in some organocopper clusters: (*a*) $(Me_3SiCH_2)_4Cu_4$; (*b*) $Ar_2Cu_4(\text{alkenyl})_2$; (*c*) $Ar_2Cu_4(\text{alkenyl})_2$; (*d*) $Ar_4Cu_6(\text{alkynyl})_2$; (*e*) $Ar_4Cu_6Br_2$. Bond lengths in ångströms, angles in degrees.

The bonding of the organic ligands in organocopper compounds can be described in terms of a simple two-electron–three-centre bonding model (figure 4). The molecular orbital that is lowest in energy results from overlap of hybrids of s and p orbitals on copper (sp or sp^2 depending on the coordination geometry) and an sp^2 orbital of the bridging aryl carbon. This molecular orbital is also bonding with respect to the two Cu atoms, and thus we speak of 'assisted' Cu–Cu bonding, as distinct from direct Cu–Cu bonding, taking place. Direct Cu–Cu bonding in organocopper clusters is considered to be unimportant on the basis of the high energy requirements for the necessary promotion of d electrons to s or p levels. This conclusion is supported by the absence of any spectroscopic evidence (i.r., Raman or $^{63,65}Cu$ n.q.r.) for such an interaction. The second molecular orbital involves overlap of a carbon p_z orbital with an antibonding combination of Cu orbitals. Bonding will be optimizal when the direction of the p_z orbital is parallel to the Cu–Cu vector. Back-donation from copper to ligand likewise requires an antibonding combination of Cu orbitals. The shortest Cu–Cu distance is, of course, expected, if only the first-type molecular orbital is occupied.

The results of the various X-ray structure determinations have revealed that the geometry of the Cu_2C(bridge) moiety in multicentre bonded organocopper compounds varies little with the nature of the organo ligand (figure 5). Replacement of, for example, an alkynyl group by a bromide atom results in considerable lengthening (from 2.47 to 2.70 Å) of the bridged Cu–Cu distance. Because the bromine atom acts as a three-electron donor (four-electron–three-centre bonding), an antibonding combination of Cu orbitals is involved (figure 4), which accounts for the longer Cu_{eq}–Cu_{eq} distance in $Ar_4Cu_6Br_2$ (ten Hoedt *et al.* 1979*a*).

3. Dynamic behaviour of aryl groups in arylcopper clusters

As shown in figure 4 the two-electron–three-centre bond has axial symmetry for the lowest energy molecular orbital. Orbital overlap is independent of the position of the aryl nucleus with respect to the Cu–Cu vector. Rotation of the aryl group around the C(1)–C(4) axis does not affect the A-type bridge bond and therefore might well occur in solution. It turns out that the aryl-bridged mixed metal clusters discussed in § 2 are exactly suitable for obtaining information concerning the question whether rotation of two-electron–three-centre bonded aryl groups actually takes place in solution.

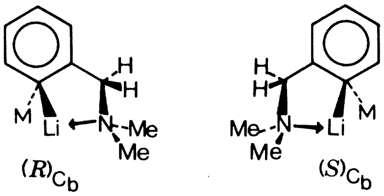

FIGURE 6. Enantiomeric pair of one rotamer conformation of the (2-$Me_2NCH_2C_6H_4$)CuLi unit.

The bridging aromatic carbon atom in compounds $[M_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$ (M = Cu, Ag or Au) (see figure 2) represents a centre of chirality: (i) the aryl group bridges unlike metal atoms; (ii) the aryl group is asymmetrically substituted. The enantiomeric pair of one rotamer conformation of the 2-$Me_2NCH_2C_6H_4CuLi$ unit is shown in figure 6. It should be noted that rotation of the two-electron–three-centre bonded aryl group around the C(1)–C(4) axis will cause a continuous inversion of configuration at C_{bridge}. This process at C_{bridge} does not involve bond dissociation–association processes (e.g. S_N1 or S_N2). The term fluxional chirality has been used in this connection (van Koten & Noltes 1979*b*).

The 2-$Me_2NCH_2C_6H_4MLi$ unit contains two prochiral centres. Therefore ^1H and ^{13}C n.m.r. spectroscopy allow the detection of whether C_{bridge} is a stable or fluxional chiral centre.

The ^1H n.m.r. resonance patterns for the methylene and methylamino protons in $[Cu_2Li_2(C_6H_4CH_2NMe\text{-}2)_4]$ are temperature dependent. At −60 °C an AB pattern is observed for the CH_2N protons and two singlets are observed for the NCH_3 protons. At room temperature the latter two singlets coalesce to one singlet. The AB pattern for the CH_2N protons is present up to 80 °C. The coalescence temperatures for the two patterns in conjunction with the $\Delta\delta$ values (100 MHz; CH_2, $T_c \approx 90$ °C, $\Delta\delta = 1.6\text{–}1.9 \times 10^{-6}$. CH_3, $T_c \approx 5$ °C, $\Delta\delta = 0.7 \times 10^{-6}$) indicate that two different processes are responsible for the dynamic behaviour of the NCH_3 and CH_2N protons. The scheme shown in figure 7, which involves (i) Li–N dissociation and (ii) rotation of the aryl group around the C(1)–C(4) axis, accounts for the observed spectra. The aryl group is anchored in a fixed position if the Me_2N group is coordinated to the Li atom. Rotation of the aryl group is not possible and C_{bridge} is a stable chiral centre. Li–N coordination renders the N atom a stable prochiral centre because inversion at N is blocked. Both the CH_2 protons and the NMe_2 groups are therefore diastereotopic, as is indeed observed at −60 °C. Coalescence of the NMe_2 singlets is explained by a process involving Li–N bond dissociation, inversion at N and concomitant CH_2–N bond rotation followed by coordination. The coupled inversion and C–N bond rotation processes are fast over the whole temperature range studied. Both are low-energy processes with barriers amounting to 25 kJ mol^{-1}. The observation of an AB pattern for

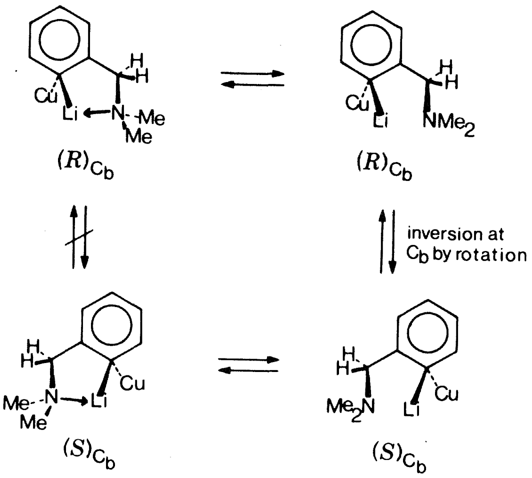

FIGURE 7. Li–N dissociation – aryl rotation process accounting for the dynamic n.m.r. spectra of $[M_2Li_2(C_6H_4CH_2NMe\text{-}2)_4]$.

the NCH_2 protons up to 80 °C indicates that inversion of configuration at C_{bridge} does not occur on the n.m.r. timescale. It is only at 90 °C that the CH_2 protons become isochronous and this can only be explained by rapid inversion of configuration at C_{bridge}, i.e. by rotation of the aryl group around the C(1)–C(4) axis (van Koten & Noltes 1979*b*).

According to one of the longstanding axioms of organic chemistry, racemization of chiral carbon compounds does not occur without the breaking of a bond at the chiral carbon atom (Hückel 1931). This axiom does not necessarily hold for multicentre bonded organometallic clusters, as shown by the results presented here. That indeed no bonds are broken in the $M_2Li_2Ar_4$ clusters is confirmed by the observation that, e.g., $J(^{107,109}Ag\text{–}^{13}C_{br})$ and $J(^{7}Li\text{–}^{13}C_{br})$ remain unaltered over the temperature range −60 °C to +90 °C.

Introduction in the aryl group of a second centre of chirality of which the configuration cannot invert results in two diastereomeric forms of the Ar_2CuLi unit. Figure 8 shows the two diastereomeric forms of the Ar_2CuLi unit obtained on replacing the Me_2NCH_2 groups in $[Cu_2Li_2(C_6H_4\text{-}CH_2NMe_2)_4]$ by S-2-Me_2NC^*HMe (Ar′) groups. In principle, this technique of chiral labelling allows the detection of the stereochemistry of the C_{bridge} atoms in (*S*)-$Ar'_4M_2Li_2$ clusters, because the diastereomeric units will display different n.m.r. chemical shifts, e.g. the observation at 27 °C of only one resonance pattern for the various protons in the ^1H n.m.r. spectrum of (*S*)-$Ar'_4Au_2Li_2$ simply allows the conclusion that all four C_{bridge} atoms have the same configuration. At this temperature aryl group rotation is blocked and hence C_{bridge} is a stable chiral centre. Therefore, two patterns for each signal would have been present if C_{bridge} atoms with both *S* and *R* configuration had been present. The presence of the additional Me group in the built-in ligand apparently results in the fully stereoselective formation of only one (*S*)-$Ar'_4Au_2Li_2$ stereoisomer in which all four C_{bridge} atoms have the same configuration, either *S* or *R* (van Koten & Noltes 1979*b*).

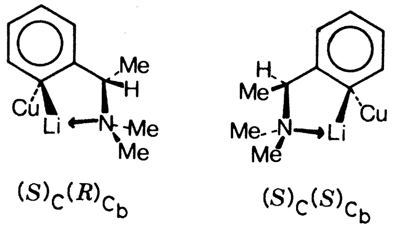

FIGURE 8. Diastereomeric pair of one rotamer conformation of the (*S*-2-$Me_2NCHMeC_6H_4$)CuLi unit.

4. SELECTIVE C–C BOND FORMATION AT THE SURFACE OF COPPER CLUSTERS

Organocopper compounds both in the solid and in solution possess well-defined polynuclear structures. It is to be expected that product formation in reactions of organocopper compounds will be determined to a large extent by the nature of the central copper core and by the way in which the faces of the copper core are occupied by the ligands.

The selective cross-coupling observed upon thermolysis of an equimolar mixture of $CuC_6H_4NMe_2$-2 (CuAr) and a copper arylacetylide ($CuC{\equiv}CAr'$) is a case in point. In principle, symmetric (formation of ArAr and $Ar'C{\equiv}C{-}C{\equiv}CAr'$) as well as asymmetric (formation of $ArC{\equiv}CAr'$) coupling might be expected to take place. If free radicals are involved, the formation of arene (ArH) and alkyne ($Ar'C{\equiv}CH$) must be expected. In practice, only one product, the cross-coupling product $Ar{\equiv}CAr'$, is observed. This result can be rationalized on the basis of the molecular architecture of mixed arylcopper–alkynylcopper clusters occurring as intermediates in these reactions (van Koten *et al.* 1977*b*; ten Hoedt *et al.* 1979*a*).

The thermolysis of an equimolar mixture of CuAr and $CuC{\equiv}CAr'$ (equation (16)) proceeds in several discrete steps (equations (12)–(15)):

$$4CuAr + 2CuC{\equiv}CAr' \longrightarrow [Cu_6Ar_4(C{\equiv}CAr')_2]; \tag{12}$$

$$[Cu_6Ar_4(C{\equiv}CAr')_2] \longrightarrow ArC{\equiv}CAr' + [Cu^{I}_4Cu^{0}_2Ar_3(C{\equiv}CAr')]; \tag{13}$$

$$[Cu^{I}_4Cu^{0}_2Ar_3(C{\equiv}CAr')] \longrightarrow 2CuAr + [Cu^{I}_2Cu^{0}_2Ar(C{\equiv}CAr')]; \tag{14}$$

$$[Cu^{I}_2Cu^{0}_2Ar(C{\equiv}CAr')] \longrightarrow 4Cu^{0} + ArC{\equiv}CAr'; \tag{15}$$

$$2CuAr + 2CuC{\equiv}Car' \longrightarrow 4Cu^{0} + 2ArC{\equiv}CAr'. \tag{16}$$

The first and crucial step is the formation of the mixed aryl–alkynyl Cu_6 cluster from the two organocopper compounds (equation (12)). The structure of an example of a $[Cu_6Ar_4(C{\equiv}CAr')_2]$ cluster that has been solved by X-ray analysis is shown in figure 1. In this structure only triangular faces occupied by one aryl and one alkynyl ligand are present. Cu_3 faces occupied by two aryl or two alkynyl ligands are absent. This specific arrangement is responsible for the formation of asymmetric $Ar(C{\equiv}CR)Cu^{\text{II}}$ centres by an intra-aggregate valence disproportionation from which ArC≡CAr′ is formed by reductive elimination (equation (13)). The Cu_3 faces act as a template. The resulting copper species undergoes cluster reorganization (equation (14)) with the CuAr generated being recycled in step 1 (equation (12)). The resulting cluster again undergoes reductive coupling (equation (15)). Summation of (12)–(15) shows the actually observed stoichiometry of the thermolysis (equation (16)).

A second example of highly selective C–C coupling on a Cu_n cluster surface concerns the formation of biaryls through the interaction of arylcopper clusters with copper triflate (CuOTf). These reactions illustrate the strong influence of the nature of the counteranion on the behaviour of organocopper clusters (van Koten *et al.* 1977*b*).

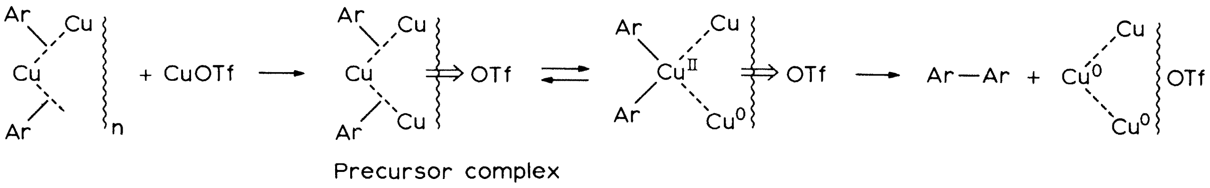

FIGURE 9. Mechanism for CuOTf-catalysed pairwise release of aryl groups from arylcopper clusters.

The reaction of $[Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4]$ with a stoichiometric quantity of CuOTf leads to quantitative formation of $(2\text{-}Me_2NCH_2C_6H_4\text{–})_2$. Similarly, $[Cu_6(C_6H_4NMe_2\text{-}2)_4Br_2]$ quantitatively yields $(2\text{-}Me_2NC_6H_4\text{–})_2$. This Cu_6 cluster is perfectly stable in the presence of excess of CuBr. Both reactions require stoichiometric amounts of CuOTf, because the biaryls formed each coordinate to two CuOTf molecules, which are thereby blocked for further reaction. Indeed, the absence of internal ligand in the arylcopper cluster renders the reaction catalytic in CuOTf, e.g. the reaction of $[Cu_4(C_6H_4Me\text{-}4)_4]$ with a catalytic amount of CuOTf in benzene at 20 °C yields *p*,*p*′-bitolyl in 100 % yield.

In these reactions, products arising from H abstraction are not formed. This observation excludes pathways involving free radicals. The clean, quantitative decomposition points to an intramolecular pathway leading to pairwise release of aryl groups. It is proposed that these reactions proceed via an arylcopper–CuOTf precursor complex formed by extension of the copper core of the parent arylcopper cluster with one or more copper atoms of copper triflate. A representative example of this type of cluster with OTf counteranions that is sufficiently stable to be isolated and characterized is formed in this reaction:

$$(4/n)\ [Cu_n(C_6H_4NMe_2\text{-}2)_n] + 2CuOTf \longrightarrow [Cu_6(C_6H_4NMe_2\text{-}2)_4OTf_2]. \qquad (17)$$

The driving force for the coupling reaction is charge transfer in the precursor complex $[Cu_{n+m}\,Ar_n\,OTf_m]$ from the $Ar_n\,Cu_{n+m}$ skeleton to the strongly electron-attracting OTf ligands. The electron density in the $Cu_2\text{–}C_{br}$ regions of the cluster and thus the kinetic stability of the $Cu_2\text{–}C_{br}$ bonds is thereby reduced. The bond-weakening effect of electron transfer away from the arylcopper cluster framework has several precedents. The formation of ArAr and ArX in the reaction of $[Cu_4Ar_4]$ with Cu^{II} halides is one example (van Koten & Noltes 1975*c*). Such reactions proceed via an inner-sphere encounter complex with electron transfer taking place via a $Cu^I\text{–}X\text{–}Cu^{II}$ bridge. A second example is provided by the mass spectral fragmentation pattern of $[Cu_4Ar_4]$ clusters. The parent ion $[Cu_4Ar_4]^{+\cdot}$ undergoes fragmentation exclusively by loss of a radical $Ar^{\cdot}$ indicating that an electron has been removed from the Cu_2C_{br} molecular orbital resulting in bond weakening rather than from the Cu_4 core of the molecule (van Koten & Noltes 1975*c*).

A mechanism for the pairwise release of aryl groups from arylcopper clusters catalysed by CuOTf is shown in figure 9. A mechanism involving intracluster valence disproportionation followed by reductive coupling best accounts for the large influence of the counteranion on the occurrence of coupling (OTf against Br). The strong electron-acceptor properties of the hard OTf ligand will favour the Cu^{II} oxidation state, whereas the softer electron-donating halide ions will favour the Cu^{I} state.

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