

DYNAMICS OF 3c-2e BONDED ARYL GROUPS IN ARYLCOPPER, -SILVER
AND -GOLD CLUSTER DERIVATIVES

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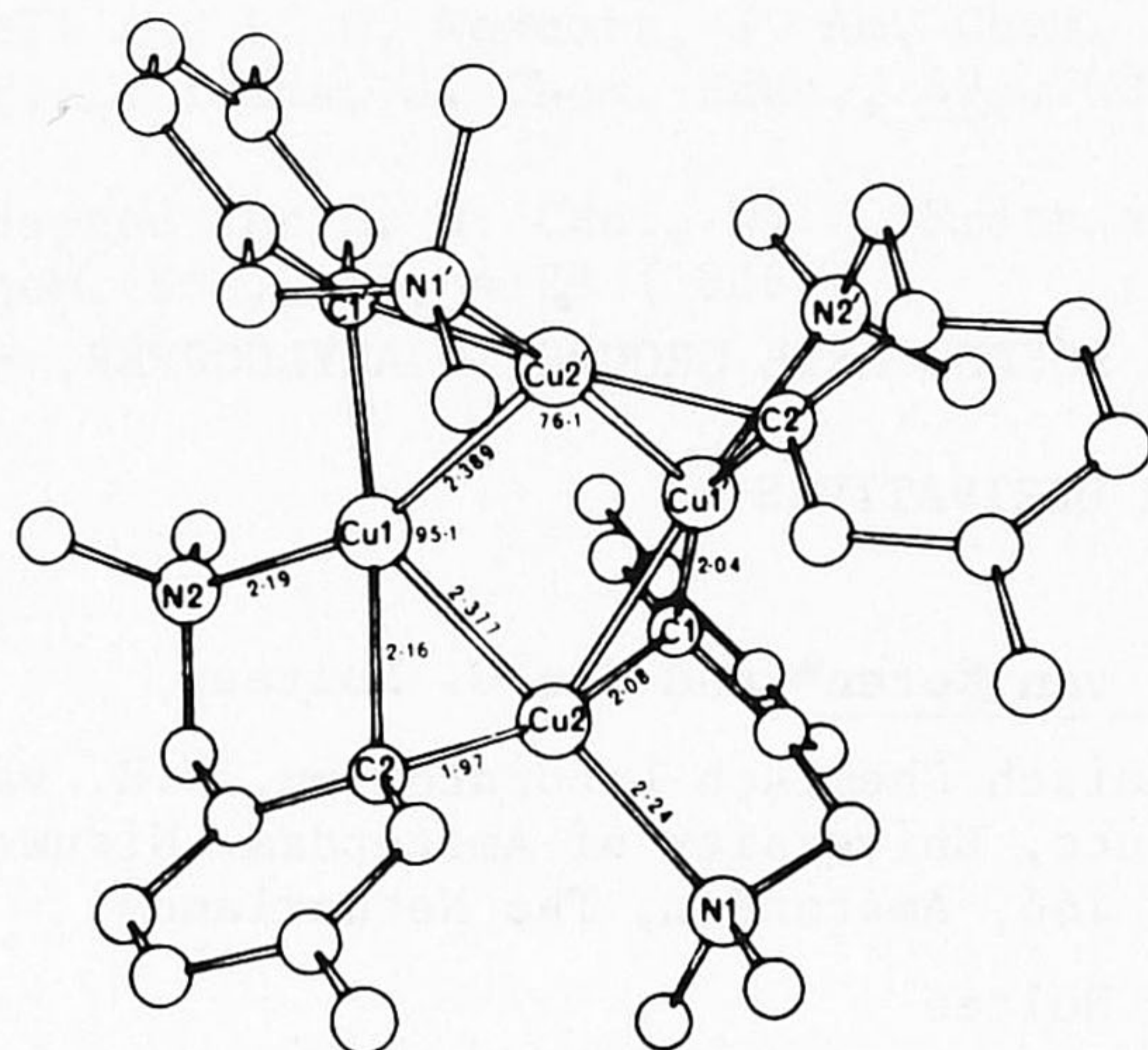
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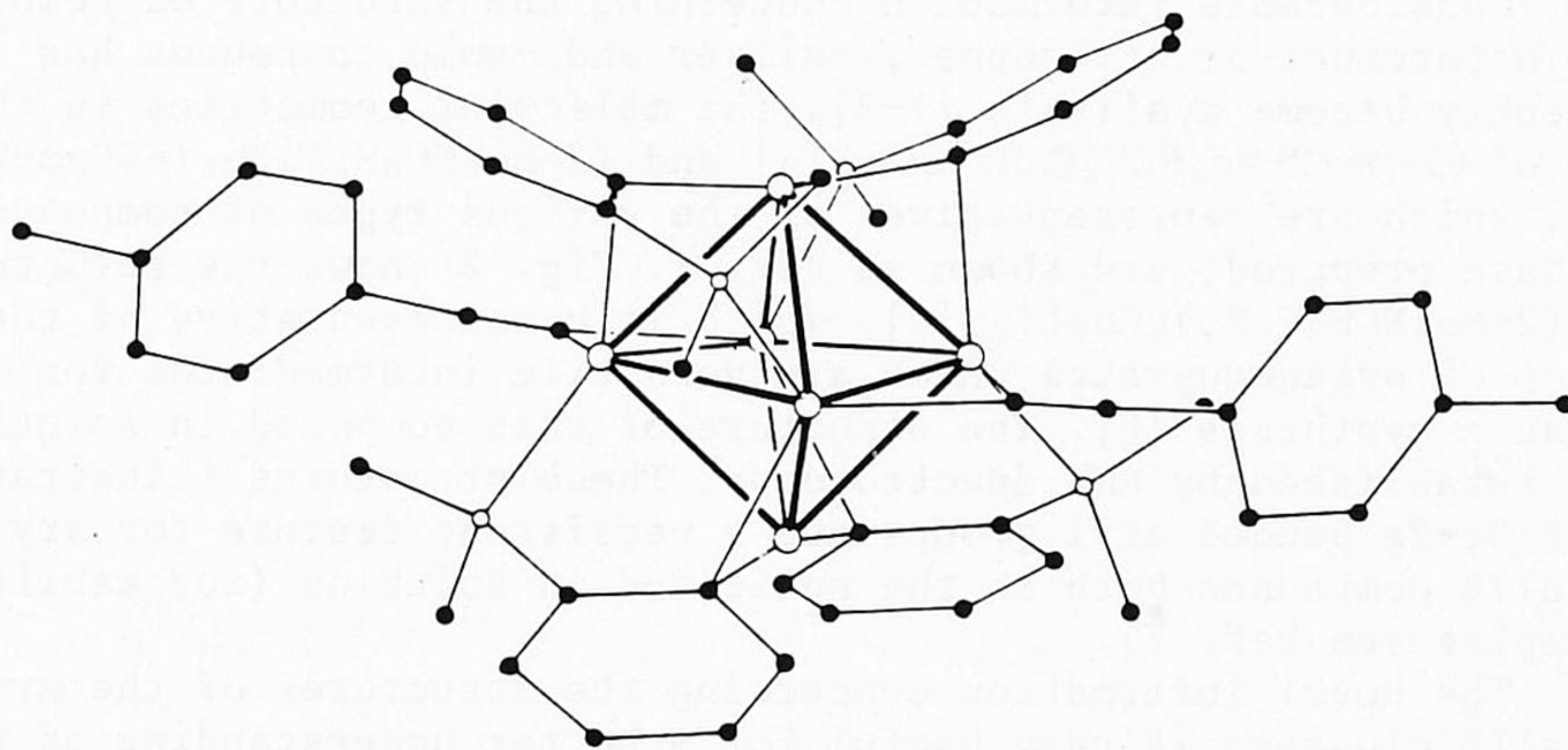
I. INTRODUCTION.

Considerable information concerning the structure of homo- and heteronuclear arylcopper, -silver and -gold compounds has recently become available [1-3]. The molecular geometries in the solid of $(5\text{-Me-2-Me}_2\text{NCH}_2\text{C}_6\text{H}_3)_4\text{Cu}_4$ [4] and $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6(\text{C}\equiv\text{C-p-Tol})_2$ [2], which are representatives of the various types of compounds we have prepared, are shown in Fig. 1. Fig. 2 shows the structure of $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_2\text{Li}_2$ [5], which is a representative of the class of organocuprates which are versatile intermediates for organic synthesis [6]. The structure of this compound in solution was established by NMR spectroscopy. These structures illustrate that 3c-2e bonded aryl groups are a persistent feature for aryl-metalIB compounds both in the solid and in solution (for earlier examples see ref. 7).

The novel information concerning the structures of the aryl-metalIB clusters is very useful for a better understanding of the products formed in organic reactions, in which organocopper compounds are used as synthetic intermediates. For example, various routes leading to cross-coupling in the reactions of arylcopper compounds with organic halides can now be discussed in terms of known reactions of well-defined arylcopper compounds [2]. The high selectivity of the C-C bond formation in the reaction of $(2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu})_n(\text{Ar}_n\text{Cu}_n)$ with $\text{CuC}\equiv\text{CR}$ (R=4-Me, 4-OMe, etc), affording exclusively $\text{ArC}\equiv\text{CR}$, follows from the fact that the hexanuclear copper compound $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6(\text{C}\equiv\text{CR})_2$ shown in Fig. 1 is formed as an intermediate (see eqn. 1).



a



b

Fig. 1. Molecular structures of a. $(5\text{-Me-}2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_3)_4\text{Cu}_4$ and b. $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6(\text{C}\equiv\text{C-p-Tol})_2$.

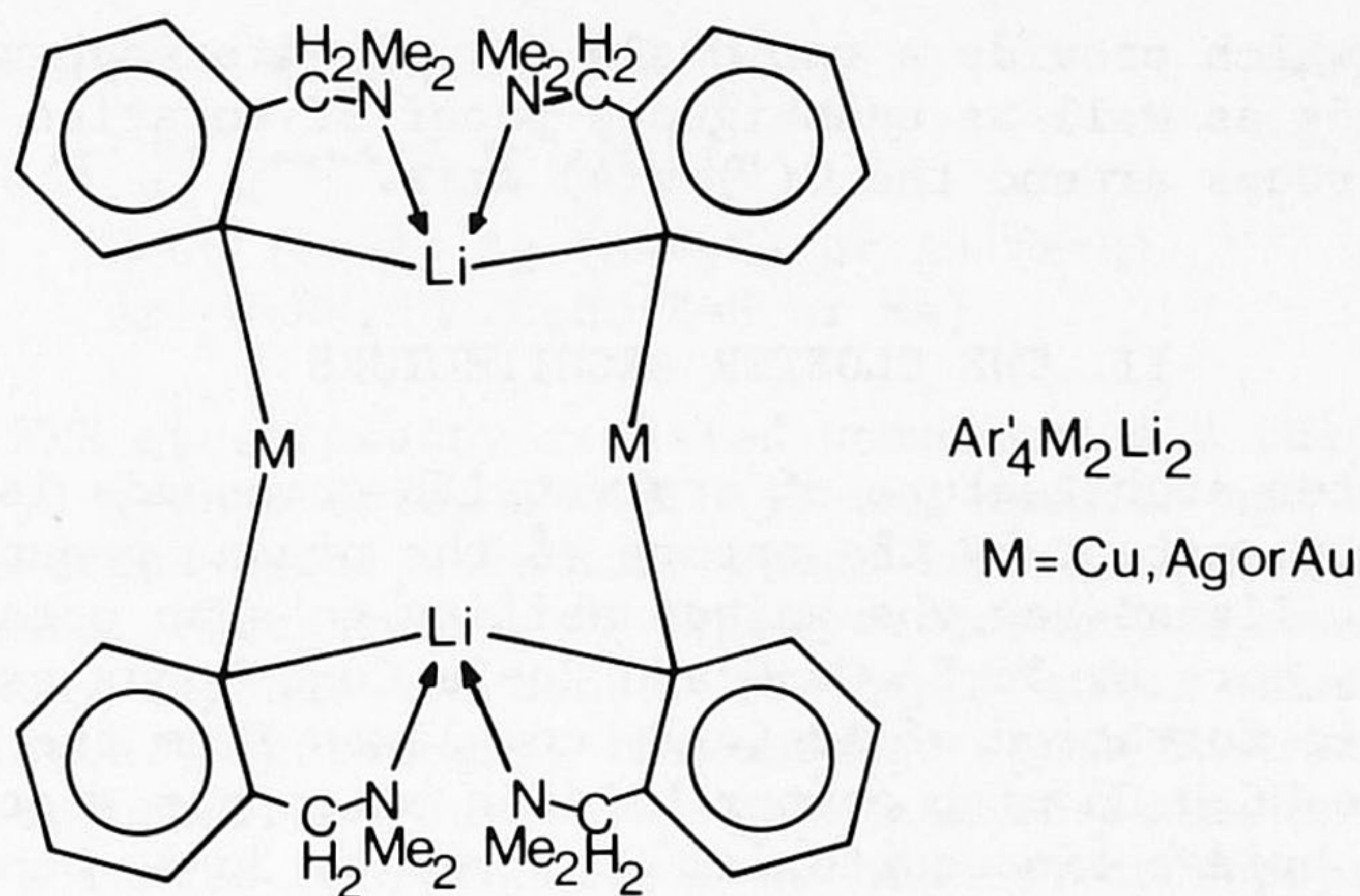
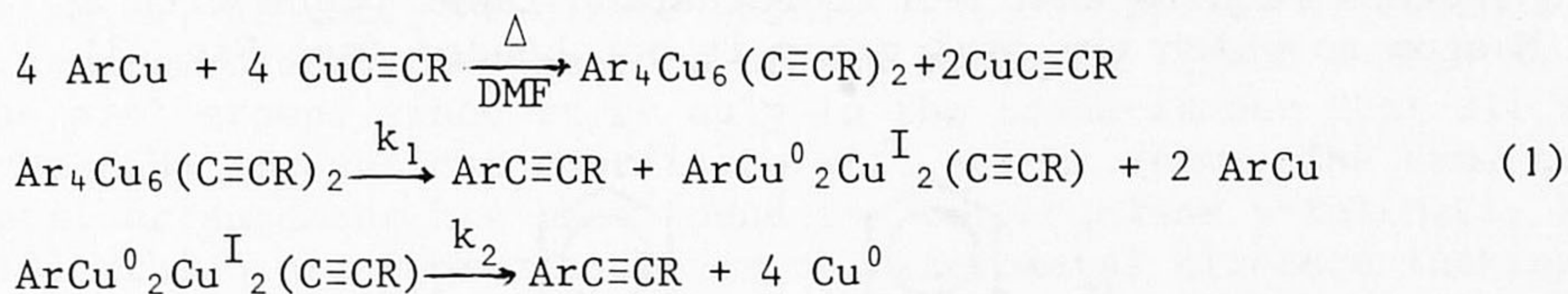


Fig. 2. Schematic structure of the $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{M}_2\text{Li}_2$ compounds.

This mixed-organocopper cluster contains exclusively triangular copper faces occupied by one Ar and one $\text{C}\equiv\text{CR}$ ligand, whereas Cu_3Ar_2 or $\text{Cu}_3(\text{C}\equiv\text{CR})_2$ faces are absent. We have tentatively proposed that this specific arrangement is responsible for the selective formation of asymmetric $\text{Ar}(\text{C}\equiv\text{CR})\text{Cu}^{\text{II}}$ centers by an intraaggregate valence disproportionation process [1] from which $\text{ArC}\equiv\text{CR}$ is formed by reductive elimination. These arguments must apply to the selective thermal decomposition of both $\text{Ar}_4\text{Cu}_6(\text{C}\equiv\text{CR})_2$ and the $\text{ArCu}^0_2\text{Cu}^{\text{I}}_2(\text{C}\equiv\text{CR})$ intermediate (see eqn. 1) [8]:



The results of these and other studies gave credence to the view point that both the nature of the central copper core and the way in which the Cu_n faces of the core are occupied by the organo groups play a decisive role in the product-forming step. A better understanding of these coupling processes which thus take place on Cu_n cluster surfaces requires elucidation of various points, i.e.: *i*, the factors which determine the cluster architecture, *ii*, the bonding of the aryl groups to the Cu_n surfaces and *iii*, the dynamics of the aryl groups on the Cu_n cluster surfaces. The latter aspect includes inter- and intraaggregate exchange processes as well as processes involving rotation of the aryl nucleus around the C(1)-C(4) axis.

In this paper synthetic and spectroscopic data for the heterometallic compounds of the type $\text{Ar}'_4\text{M}_2\text{Li}_2$ and $\text{Ar}_4\text{M}'_2\text{M}_4\text{X}_2$ clusters will

be presented which provide a rationale for the stereochemistry of these compounds as well as unambiguous proof of rotation of 3c-2e bonded aryl groups around the C(1)-C(4) axis.

II. THE CLUSTER ARCHITECTURE

The cluster architecture of arylmetalIB compounds is determined to a large extent by the nature of the organo group [9]. The 2-Me₂NC₆H₄ ligand has the unique ability to span octahedral faces of a Cu₆ core by 3c-2e Cu-C and 2c-2e Cu-N bonds as witnessed by the specific formation of Ar₄Cu₆X₂ complexes from the interaction of 2-Me₂NC₆H₄Cu with copper halides or copper acetylides. The X ligands bridge two equatorial Cu atoms by 3c-4e bonds (X=halide or OTf) or by 3c-2e bonds (X=C≡CR). The halogen atoms in Ar₄Cu₆X₂ can be substituted with retention of the Ar₄Cu₆ skeleton. It is noteworthy that the heterometal clusters Ar₄M'₂M₄X₂ in which M'=Au and M=Cu or Ag, are discrete cluster species [3]. In these clusters the Au^I atoms, which have a strong preference for linear two-fold coordination, reside at the apical sites. This is because only these sites in Ar₄M₆X₂ clusters have digonal coordination geometry.

Figures 1 and 2 show that the 2-Me₂NCH₂C₆H₄ group acts as a bidentate ligand in both (5-Me-2-Me₂NCH₂C₆H₃)₄Cu₄ and (2-Me₂NCH₂-C₆H₄)₄Cu₂Li₂. However, the cluster architecture is different. This can be explained by the fact that the 2-Me₂NCH₂ group can coordinate to one of the bridged metal atoms leading to a five-membered chelate ring. In contrast, for the 2-Me₂N substituted phenylcopper compounds steric factors require that N-M coordination takes place with a third M atom to which the aryl group is not bonded (see Fig. 3).

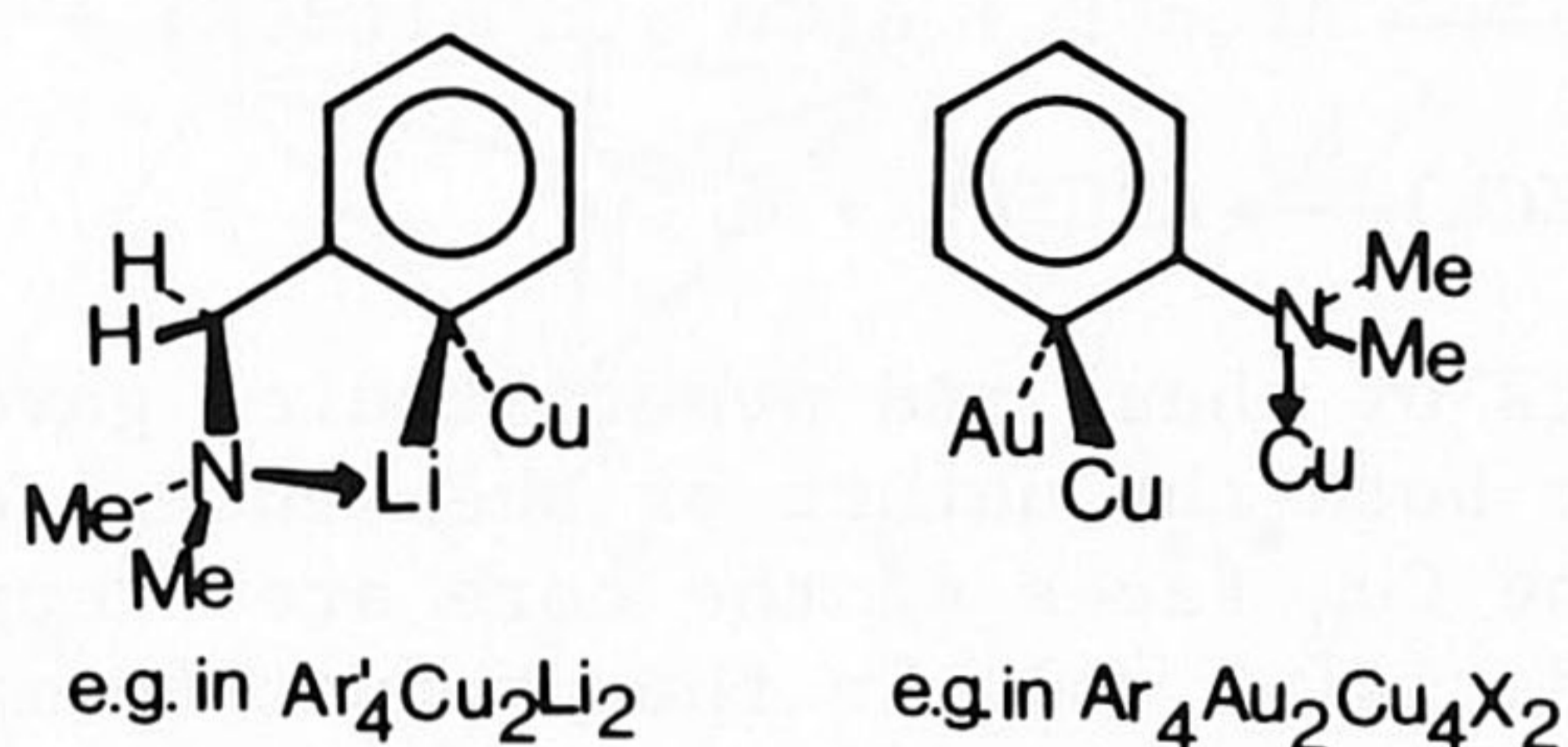
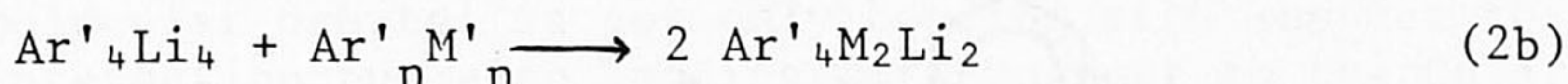
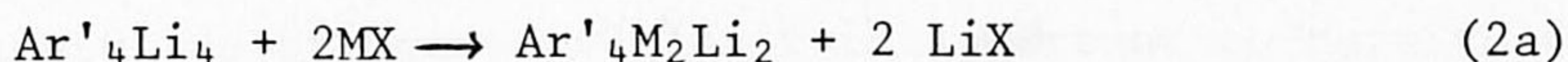


Fig. 3. Structures of (2-Me₂NCH₂C₆H₄)M₂ and (2-Me₂NC₆H₄)M₃ units in which the bridging carbon atom [C(1)] is chiral center.

The influence of the organo group on the cluster architecture is also reflected by the specific formation of the heterometalIB clusters Ar₄M₂Li₂ (M=Cu, Ag or Au) via the reactions shown in eqn.2.



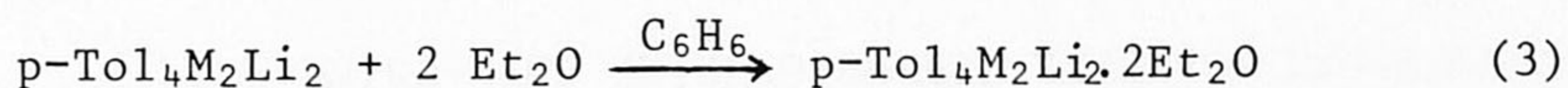
M=Cu (n=4), Ag (n=4,6) or Au (n=2)

Ar'=2-Me₂NCHZC₆H₄ (Z=H or Me)

¹³C and ¹H NMR spectroscopy revealed unambiguously that each of the four aryl groups bridges via C(1) one metalIB and one Li atom [5,10]. The trans-metal structure shown in Fig. 2 fully accounts for these data. Furthermore, ¹H NMR spectroscopy showed that the four 2-Me₂NCH₂ ligands are bonded to the Li atoms which thus are four-coordinate. Accordingly, the metalIB atoms in these compounds are two-coordinate. The fact that the metalIB atoms in the Ar₄M₂Li₂ clusters are indeed coordinatively saturated was supported by the following observations: *i*, molecular weight determinations of (2-Me₂NCH₂C₆H₄)₄Cu₂Li₂ in the presence of increasing amounts of PPh₃ revealed that complex formation with PPh₃ did not occur and *ii*, PPh₃ formed in the reaction of Ar'₄Li₄ with BrAuPPh₃ did not interfere with the isolation of pure Ar'₄Au₂Li₂.

The proposed symmetry at the metalIB atoms shown in Fig. 2 is based on the consideration that linear hybridization of orbitals at the metalIB atoms (M) requires the C(1)-M-C(1) angles to be smaller than 180°. C(1)-Cu-C(1) angles of 164° in Ar₄Cu₆X₂ (see Fig. 1 X=C≡CR [2] and X=Br [9]) and in (Me₃SiCH₂)₄Cu₄ [11] have been established by X-ray diffraction.

The exclusive formation of the Ar'₄M₂Li₂ aggregates having the M and the Li atoms arranged in a trans fashion points out that these aggregates are more stable than the other possible aggregates Ar'₄M₃Li, Ar'₄M₂Li₃ or cis-Ar'₄M₂Li₂. This stability difference is a consequence of the presence of the built-in ligand 2-Me₂NCH₂ in the aryl group, since it is only in the trans-isomer that all four 2-Me₂NCH₂ ligands can coordinate with the Li atoms. The same trans-metal arrangement has been found for tetranuclear p-Tol₄M₂Li₂.20Et₂ [12], which are representatives of heterometal clusters lacking built-in ligands. In these cases it is the coordination of the lithium atoms with an ether molecule which stabilizes the trans-metal arrangement.



M=Cu; δ(CH₂O) 2.72 q, δ(CH₃O) 0.64 (t) ppm.

Finally, the available structural data point out that the presence of built-in ligands also determines the stereochemistry of the metal core. In the simple arylcopper compounds, e.g. p-Tol₄Cu₄ [1], the aryl groups bridge the Cu₂ edges of an arrangement of four Cu atoms which as a result of linear hybridization at Cu (cf. Me₃SiCH₂Cu tetramer) has a planar configuration (see Fig. 4). Fig. 1 shows that in the presence of built-in ligands the Cu₄ core has a butterfly-type configuration which is a consequence of the

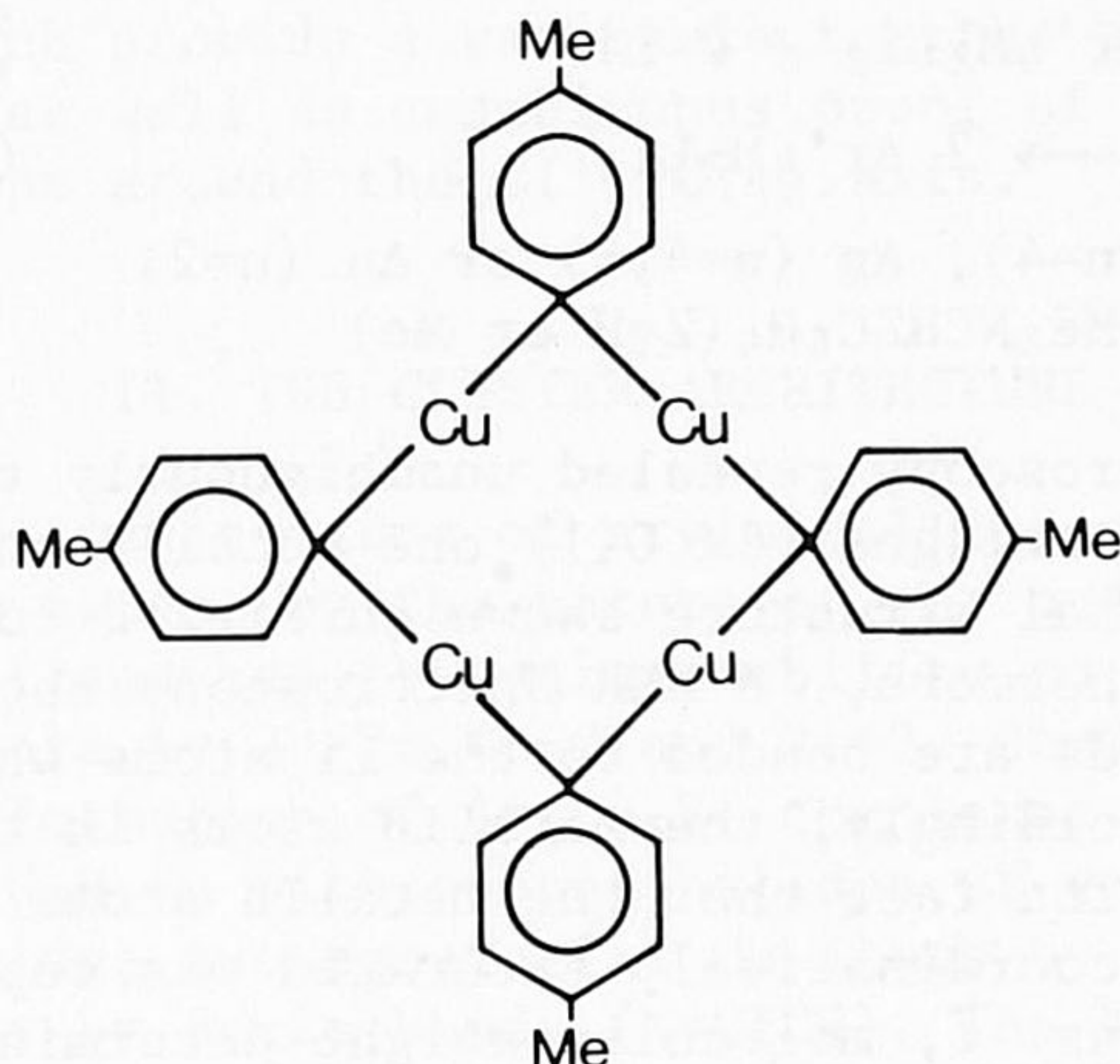


Fig. 4. Schematic structure of $(p\text{-tolyl})_4\text{Cu}_4$.

almost planar trigonal coordination geometry of each of the Cu atoms.

III. BONDING OF THE ARYL GROUPS IN $\text{Ar}'_4\text{M}_4$ AND $\text{Ar}'_4\text{M}_2\text{Li}_2$.

In contrast to the well-founded 2c-2e metal-carbon bond, only limited information is available about 3c-2e aryl-to-metal bonding. Bonding in the arylmetalIB clusters can be described with the molecular orbitals shown in Fig. 5. The molecular orbital, which is lowest in energy results from overlap of hybrids of s and p orbitals on copper (depending on the coordination symmetry sp or sp^2) and a carbon sp^2 orbital. The second molecular orbital involves overlap of a carbon p_z orbital with an antisymmetric combination of Cu orbitals. In view of the short Cu-Cu distances observed in the structures of $(5\text{-Me-2-Me}_2\text{NCH}_2\text{C}_6\text{H}_3)_4\text{Cu}_4$ (2.37 Å), $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{X}_2$ (X=Br, $\text{Cu}_{\text{ap}}\text{-Cu}_{\text{eq}}$ aryl bridged 2.52 Å, $\text{Cu}_{\text{eq}}\text{-Cu}_{\text{eq}}$ bromine bridged 2.69 Å; X=C≡C-p-Tol, $\text{Cu}_{\text{ap}}\text{-Cu}_{\text{eq}}$ aryl bridged 2.52 Å, $\text{Cu}_{\text{eq}}\text{-Cu}_{\text{eq}}$

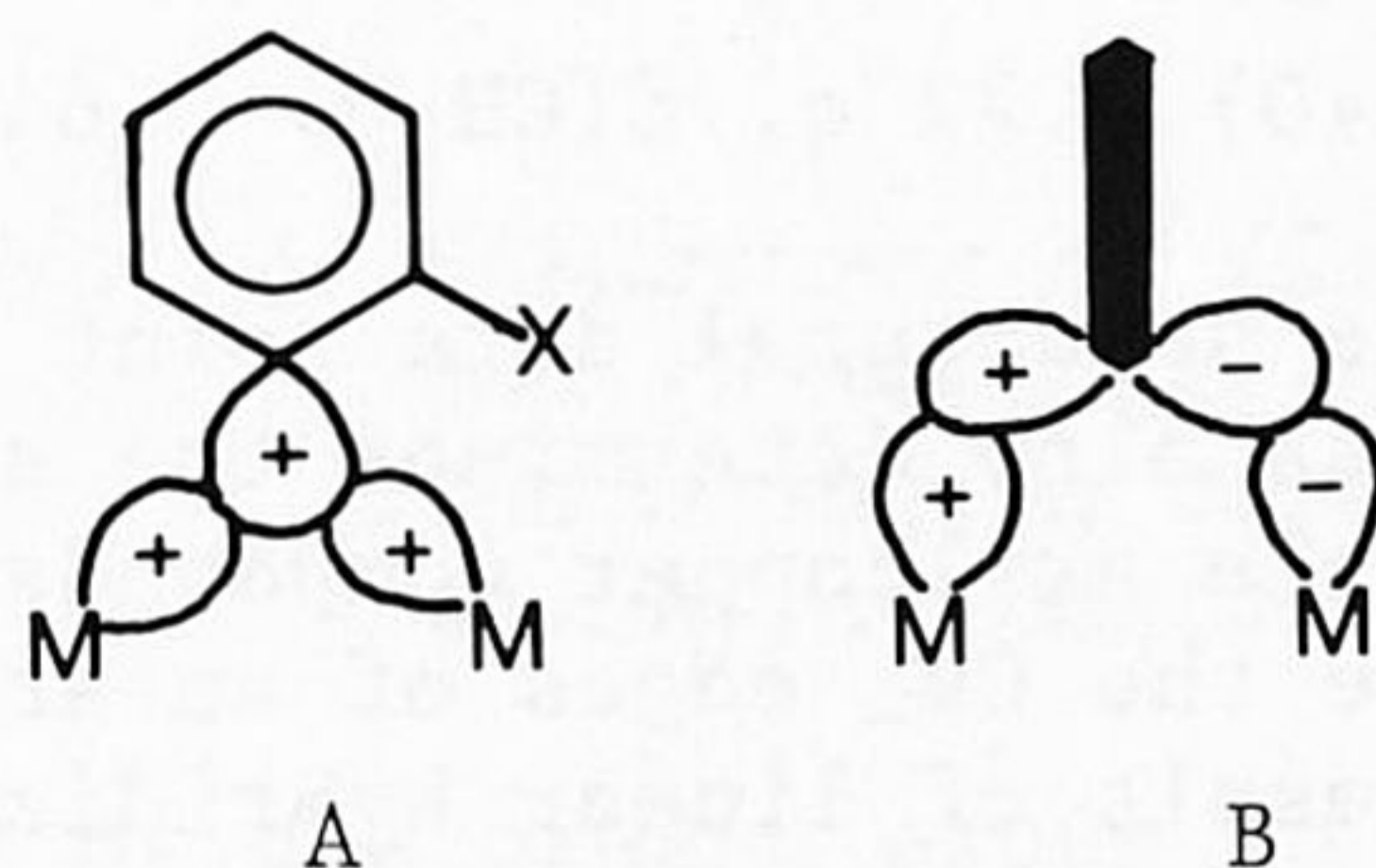


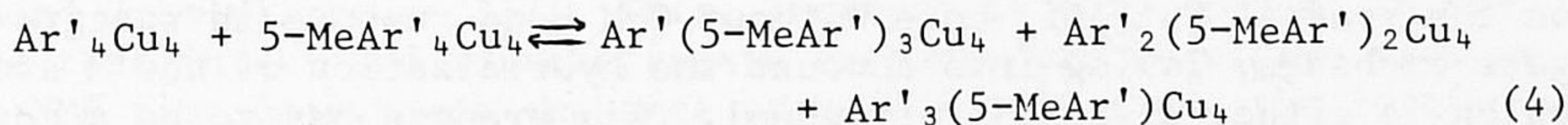
Fig. 5. Molecular orbitals involved in the 3c-2e ArM_2 bonding.

acetylide bridged 2.47 Å) it is important to note that the first molecular orbital is not only bonding with respect to the Ar-to-Cu interaction but also bonding with respect to the Cu atoms. The term "assisted Cu-Cu" bonding has been introduced for this type of bonding. The occurrence of direct Cu-Cu bonding in the organo-copper clusters was excluded 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 (IR, ^{63}Cu , ^{65}Cu NQR and Raman) for such an interaction. This 3c molecular orbital bond description also provides a qualitative explanation for the difference in $\text{Cu}_{\text{eq}}-\text{Cu}_{\text{eq}}$ distances in, for example, the $\text{Ar}_4\text{Cu}_6\text{X}_2$ structures. Whereas in $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6(\text{C}\equiv\text{C-p-Tol})_2$ the acetylide ligand is bonded via a 3c-2e bond of type A, the Br atoms in the bromide derivative are bonded via a 4e-3c interaction by a combination of A and B type bonding. Contribution of the type B bonding, which comprises an antibonding combination of Cu orbitals, accounts for the greater $\text{Cu}_{\text{eq}}-\text{Cu}_{\text{eq}}$ distance in $\text{Ar}_4\text{Cu}_6\text{Br}_2$.

In the solid the aryl nucleus occupies a position perpendicular to the Cu-Cu vector. Taking into account the bonding scheme shown in Fig. 5 *rotation of the aryl nucleus* around the C(1)-C(4) axis [C_{bridge} is sometimes used to refer to C(1)] must be expected to occur *in solution*. In each of the possible rotamers overlap in the type A molecular orbital will be equal. However, the presence of ortho-substituents will influence the rotamer population. When the ortho-substituent is very bulky (e.g., CH_2NMe_2 or CHMeNMe_2 , see sections V and VI) rotamers having an angle between the plane of the aryl ring and the M-M axis close or equal to zero will be less favourable whereas rotamers having their plane oriented approximately perpendicular will become more stable. Accordingly, the barrier to rotation of the aryl group will depend on the steric demand of the ortho substituent. Furthermore, coordination of the ortho-substituent with the bridged metals fixes the aryl ring in an almost perpendicular position. Rotation of the aryl ring in these compounds is only possible if the metal-built-in ligand bond is dissociated.

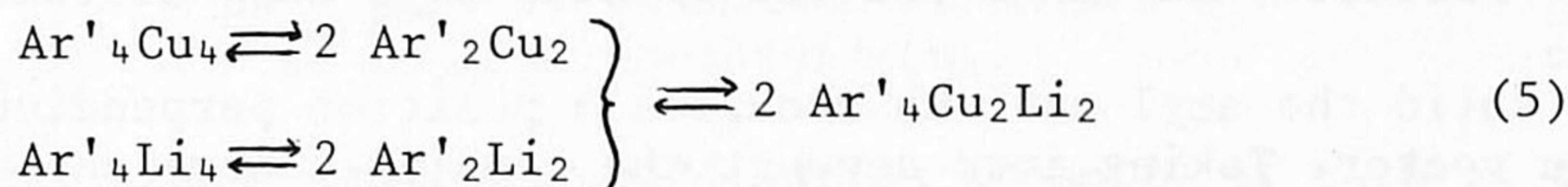
IV. INTRA- AND INTERAGGREGATE EXCHANGE PROCESSES.

Limited information is available concerning interaggregate exchange between polynuclear organocopper species. We have presented mass spectroscopic evidence for the occurrence of interaggregate exchange between the tetranuclear compounds $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_4(\text{Ar}'_4\text{Cu}_4)$ and its 5-methyl substituted analog $(5\text{-MeAr}'_4\text{Cu}_4)$ [4]:

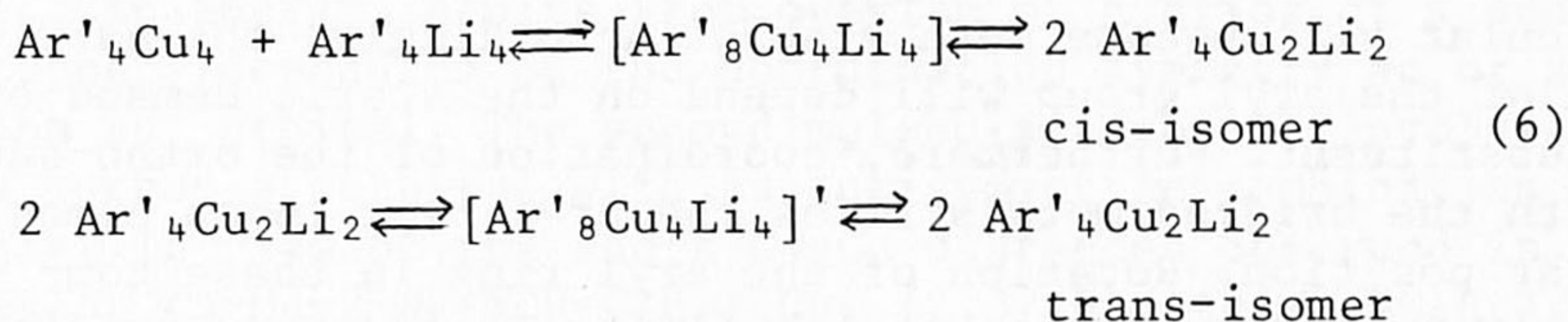


A similar equilibrium has been reported for the exchange between $(C_6F_5)_4Cu_4$ and $(2-F_3CC_6H_4)_4Cu_4$ [13]. The tetranuclear species present in these equilibria have comparable stabilities. Isolation of the individual species from the product mixture is therefore impossible. However, in section II it was shown that in certain cases a single species can have an unique stability as a result of favourable built-in ligand M interaction ($Ar'_4M_2Li_2$ or $Ar_4M_6X_2$) or because of preference of the metal atoms for one of the well-defined coordination geometries of the various sites in the metal core ($Ar_4Au_2M_4X_2$).

Brown et al. have elegantly shown that exchange reactions between polynuclear organolithium compounds involved associative or dissociative pathways of the species $Alkyl_nLi_n$ rather than exchange via alkyl anions [14]. Exchange between the tetranuclear arylcopper and aryllithium species (eqn. 2b) may likewise proceed via pathways involving dissociation or association, e.g. eqn. 5.



However, such processes necessarily involve rupture of the rather stable aryl-bridge bond. Alternatively the pathway shown in eqn. 6, which involves formation of an octanuclear intermediate $Ar'_8Cu_{8-n}Li_n$ or $Ar'_{8-n}(5-MeAr')_nCu_8$ by association of two tetranuclear species, makes complete aryl-metal bond rupture unnecessary and, therefore, provides an attractive explanation for the interaggregate exchange reactions (see eqn. 6).



Several observations in organocopper chemistry support this hypothesis. For example, Cairncross and Sheppard isolated the stable octanuclear arylcopper compound $(3-F_3CC_6H_4)_8Cu_8$ [13]. ^{19}F NMR spectroscopy revealed that in this octamer the $3-F_3CC_6H_4$ groups are mobile. The tetranuclear structure of $(2-Me_2NCH_2C_6H_4)_4Cu_4$ does not break down in the presence of monodentate ligands [15] which makes a dissociative pathway for the interaggregate exchange unlikely.

In Fig. 6 some of the interaggregate exchange steps each involving octanuclear intermediates are shown. In this intermediate the 3c-2e bonded aryl groups are mobile. The symmetry of the electron deficient bond allows the aryl groups to change edge positions on the central $Cu_{8-n}Li_n$ core without C-M bond rupture (intraaggregate exchange). Taking into account the hybridization of the M atoms, which is either digonal or trigonal, this process has to be a concerted edge-corner-edge migration involving all eight aryl groups.

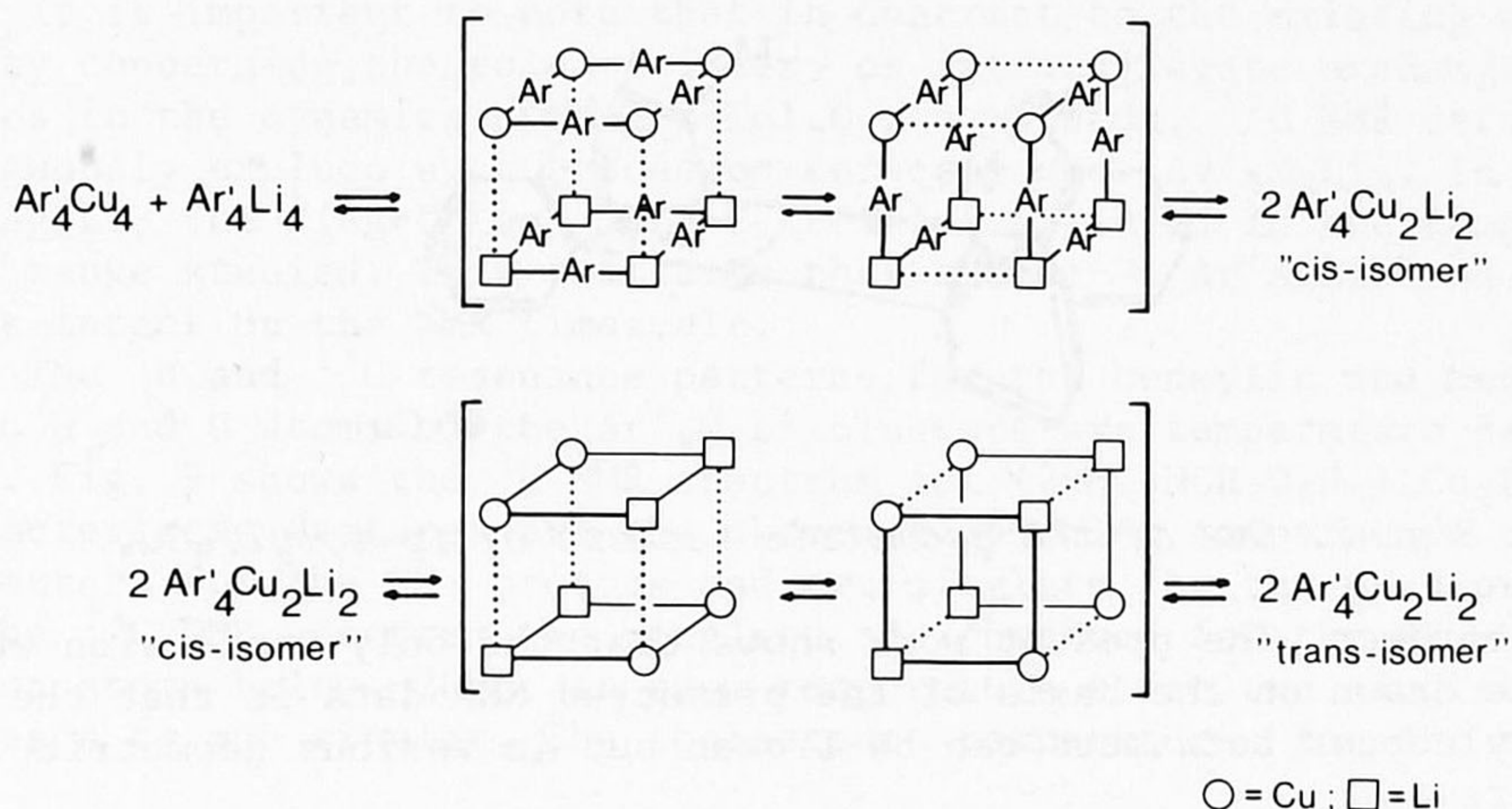


Fig. 6. Interaggregate exchange between tetranuclear $Ar'_4M_{4-n}M'_n$ species via an octanuclear intermediate.

The latter prerequisite points to a considerable energy barrier to interaggregate exchange which seems in agreement with the observation that this exchange is in the slow exchange limit on the NMR timescale.

The migration of the aryl groups in the octanuclear intermediate most probably involves a reversible change of the 3c-2e ArM_2 into a 2c-2e ArM bonding situation. A second possibility represents a process in which association of the two tetranuclear species having 3c-2e ArM_2 bonds results in formation of an octanuclear intermediate (transition state) with eight 2c-2e corner M-Ar interactions. Dissociation of the octanuclear intermediate into the tetranuclear species reestablishes the 3c-2e ArM_2 bonding situation.

V. ROTATION OF 3c-2e BONDED Ar' GROUPS AROUND THE C(1)-C(4) AXIS IN Ar'_4M_4 AND $Ar'_4M_2Li_2$.

Geometric isomerism in Ar'_4M_4 clusters. In principle Ar_4M_4 and $Ar_4M_2Li_2$ compounds containing dissymmetrically substituted aryl groups can exist as four unique geometric isomers (see Fig. 7). These are detectable by NMR spectroscopy because they will have different chemical shifts. Indeed, for the 2-tolylcopper tetramer multiplet resonance patterns are detected at low temperature [16] which were ascribed to the presence of such isomers [17]. The observation that these multiplets coalesce at higher temperatures was presented as evidence for the occurrence of rotation of the 3c-2e bonded 2-tolyl groups [17]. This, however, is only correct in the case that inter- and intraaggregate exchange processes are slow on the NMR timescale. Such exchange processes will cause the 2-tolyl groups to lose their identity with respect to their arrangement in

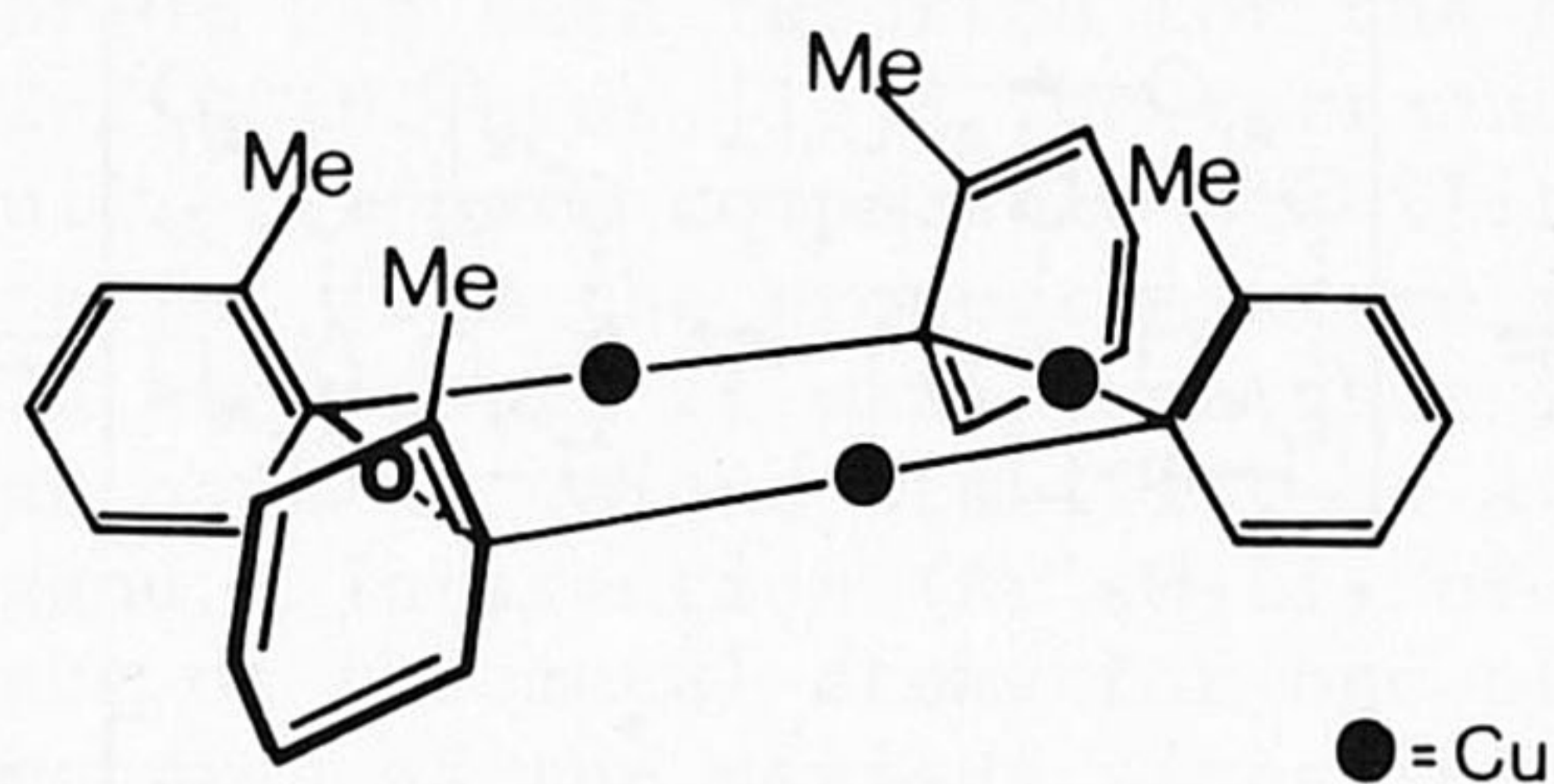


Fig. 7. One of the geometric isomers of $(p\text{-tolyl})_4\text{Cu}_4$.

the tetramer. The present work shows that the only conclusion which can be drawn on the basis of the presented NMR data is that the 2-tolylcopper tetramers can be frozen out in various geometric isomers.

Local environment concept in $\text{Ar}_4\text{M}_2\text{Li}_2$ clusters. The $\text{Ar}'\text{MLi}$ unit. If a 3c-2e bonded aryl group, which is dissymmetrically substituted, bridges two unlike metal centers, C_{bridge} [is C(1)] represents a chiral center. Two cases may be distinguished: *i*, the two metal atoms are different as in Fig. 3 and *ii*, the two metal atoms are similar but differ with respect to their coordination geometry (cf. Cu_{ap} and Cu_{eq} in $\text{Ar}_4\text{Cu}_6\text{X}_2$). Rotation of the 3c-2e bonded aryl group (see section III) around the C(1)-C(4) axis will cause a continuous inversion of configuration at C_{bridge} . For this process at C_{bridge} , which does not involve rearrangement of bonds by stereoisomerizations or bond dissociation/association (e.g. $\text{S}_{\text{N}2}$ or $\text{S}_{\text{N}1}$) processes, we propose the term fluxional chirality. Fig. 8 shows the enantiomeric pair $(S)_{C_{\text{b}}}$ and $(R)_{C_{\text{b}}}$ for one rotamer conformation in the limiting situation in $\text{Ar}'_4\text{Cu}_2\text{Li}_2$. When considering the local environment of the $\text{Ar}'\text{CuLi}$ unit instead of the total geometry of the $\text{Ar}'_4\text{Cu}_2\text{Li}_2$ cluster, inversion of configuration at C_{bridge} becomes detectable by NMR spectroscopy because the 2- Me_2NCH_2 group contains a prochiral center which can reflect the dissymmetry at C_{bridge} .

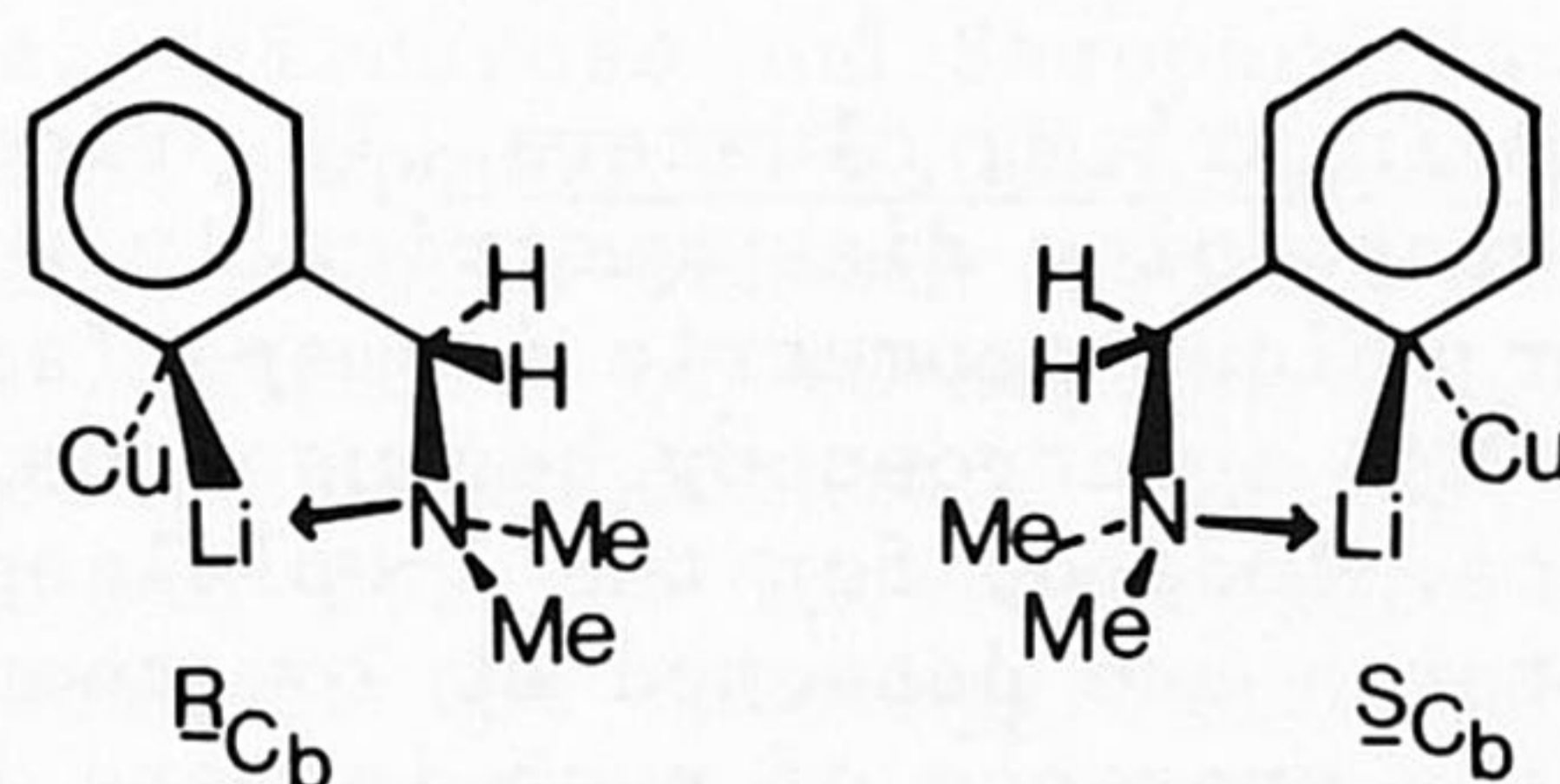


Fig. 8. Enantiomeric pair of one rotamer conformation of the $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CuLi}$ unit.

It is important to note that in contrast to the existing uncertainty concerning the role of inter- or intraaggregate exchange processes in the dynamics of the $2\text{-Tol}_4\text{Cu}_4$ compounds, ^{13}C NMR data unambiguously exclude such processes for compounds $\text{Ar}'_4\text{M}_2\text{Li}_2$. In $\text{Ar}'_4\text{Ag}_2\text{Li}_2$ the $J(\text{Ag}-\text{C}_\text{ip})$ and $J(\text{Li}-\text{C}_\text{ip})$ remain unaltered in the temperature range studied. This indicates that the 3c-2e $\text{Ar}'\text{AgLi}$ bond remains intact on the NMR timescale.

The ^1H and ^{13}C resonance patterns for the benzylic and methylamino H and C atoms of the $\text{Ar}'_4\text{M}_2\text{Li}_2$ clusters are temperature dependent. Fig. 9 shows the ^1H NMR spectrum for $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_2\text{Li}_2$. Characteristic features are the observation at low temperature of an AB pattern for the CH_2 protons and two singlets for the CH_3N protons. In the ^{13}C NMR spectrum two singlets are observed for the $\text{CH}_3\text{-N}$ carbon atoms below -20°C . At room temperature these two singlets coalesce to one singlet. The coalescence temperatures for the two

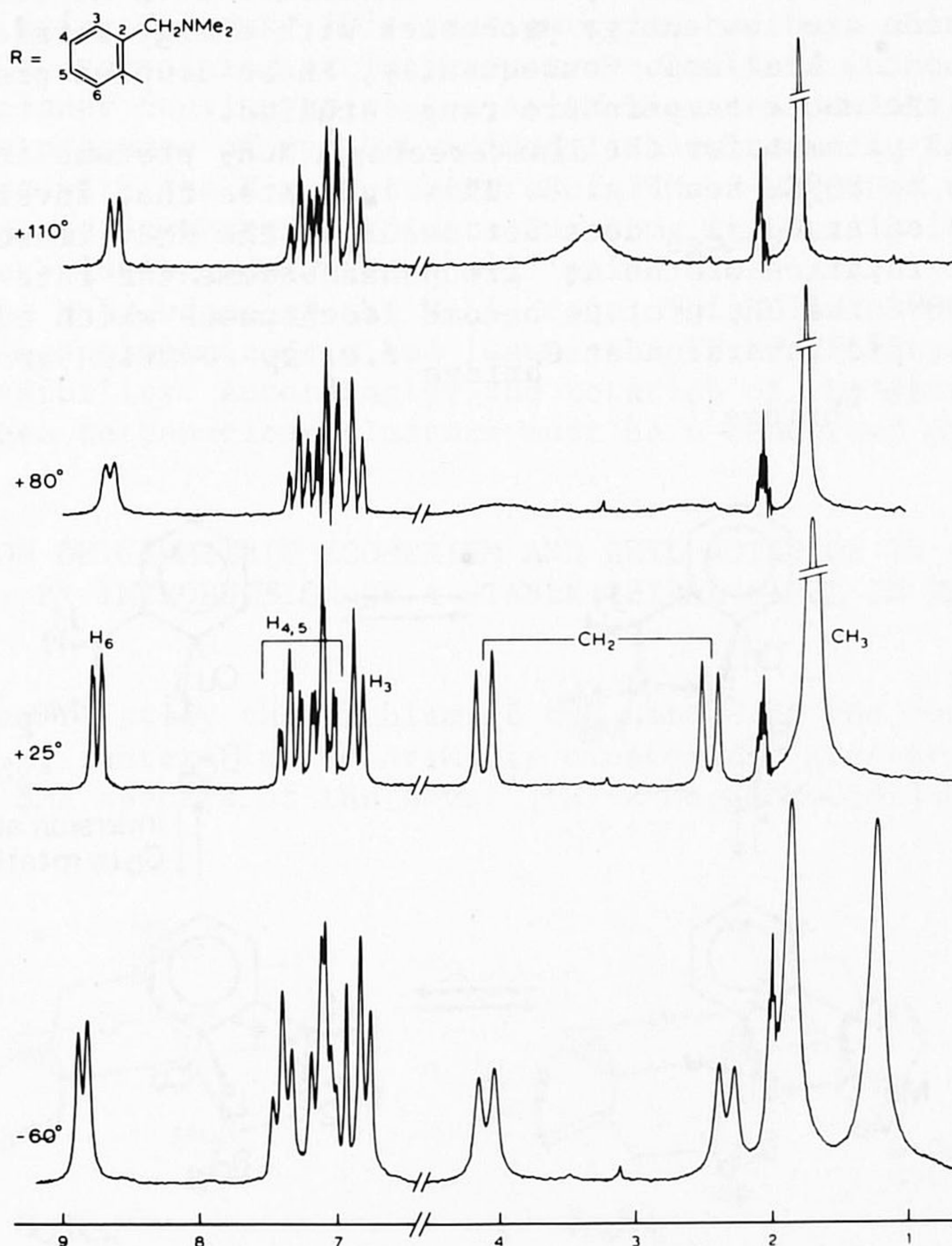


Fig. 9. ^1H NMR spectra (δ ppm) of $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_2\text{Li}_2$ in toluene- d_8 at different temperatures.

patterns in the ^1H NMR spectra in conjunction with the $\Delta\delta$ values (100 MHz; CH_2 , $T_c \approx 90^\circ$, $\Delta\delta$ 1.6–1.9 ppm and CH_3 , $T_c \approx 5^\circ\text{C}$, $\Delta\delta$ 0.7 ppm) point out that two different processes are responsible for the dynamic behaviour of the CH_2NMe_2 protons and C atoms. The scheme shown in Fig. 10 which involves; *i*, Li-N dissociation and *ii*, rotation of the Ar' group around C(1)-C(4), accounts for the observed spectra (compare these results with those obtained for the chiral triorganotin halides [18]).

In the coordinated situation both the CH_2 protons and the NMe_2 groups are diastereotopic. The NMe_2 groups are diastereotopic because Li-N coordination renders the N atom a stable prochiral assembly. This offers a second probe for the detection of dissymmetry at C_{bridge} . At higher temperatures the two NMe resonances become isochronous. This is explained by a process involving N-Li bond dissociation inversion at N and concomitant C-N bond rotation followed by coordination. Pyramidal inversion at N as well as C-N bond rotation are low energy processes with energy barriers amounting to about 9 kcal/mol. Consequently, these coupled processes are fast over the whole temperature range studied.

The AB pattern for the diastereotopic NCH_2 protons is still present up to 80°C , see Fig. 8. This indicates that inversion of configuration at C_{bridge} does not occur on the NMR timescale which shows that rotation of the Ar' group has become the rate determining step. At 90°C the CH_2 protons become isochronous which can only be caused by rapid inversion at C_{bridge} *i.e.* by rotation around C(1)-C(4) [C(1) is C_{bridge}].

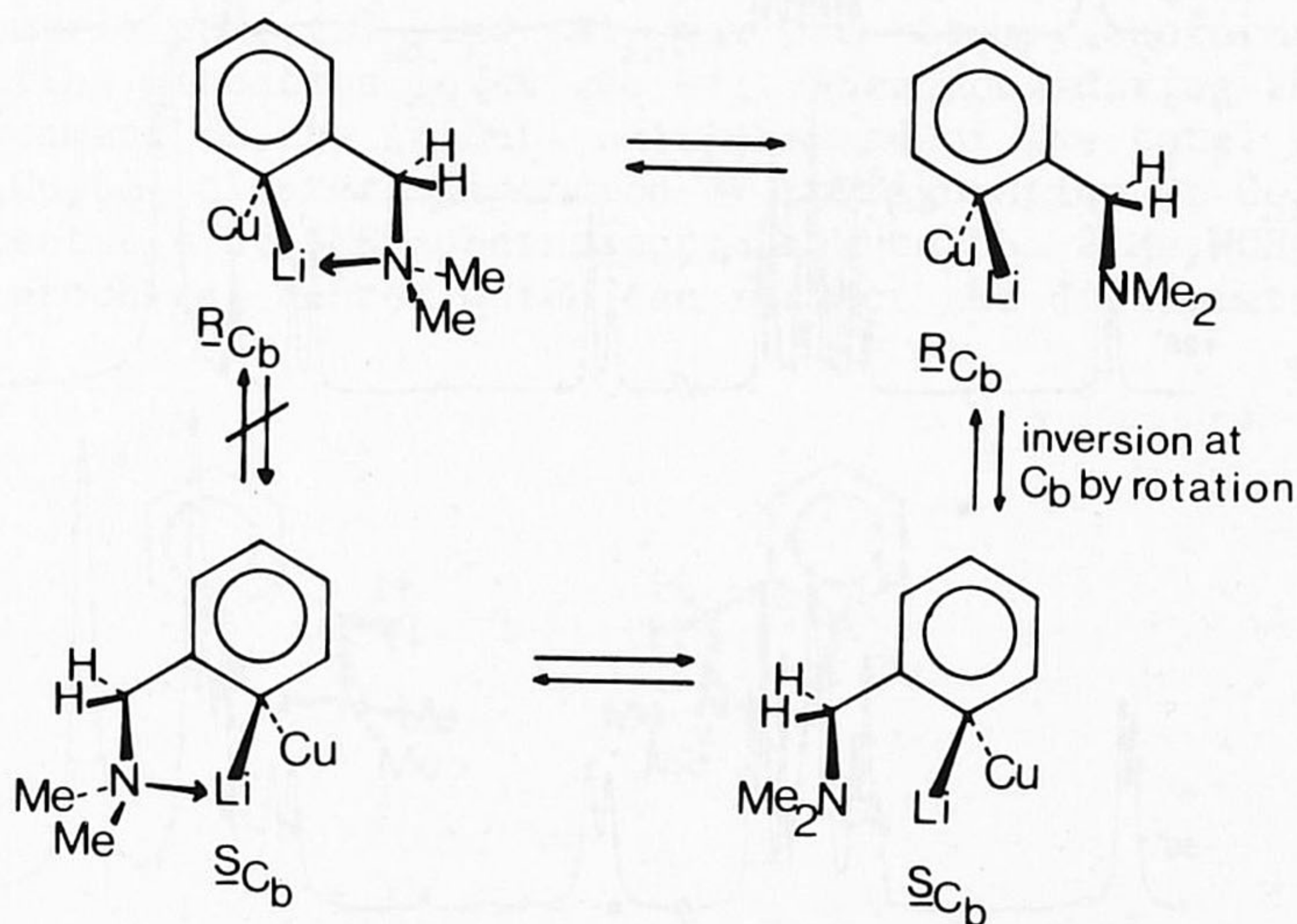


Fig. 10. Scheme showing the Li-N dissociation/aryl rotation process accounting for the spectra in Fig. 9.

The $\text{Ar}'_4\text{M}_2\text{Li}_2$ cluster. So far we have considered the chiroptical properties of the $\text{Ar}'\text{MLi}$ unit only. Combining the four units into an $\text{Ar}'_4\text{M}_2\text{Li}_2$ aggregate in principle can result in a number of unique geometric isomers having different spectra. However, only one ^1H and ^{13}C resonance pattern is observed at low temperature, i.e. at the situation of inert Li-N coordination. This can be rationalized as follows.

The trans-metal arrangement as well as the exclusive occurrence of N-Li coordination restricts the number of possible geometric isomers. The configuration at the C_{bridge} atoms of the two aryl groups bonded to the same Li atom are either *S* or *R*, see Fig. 11. Looking at the four metal atoms in $\text{Ar}'_4\text{M}_2\text{Li}_2$ the possible combinations reduce to two enantiomeric pairs $RR.SS/SS.RR$ and $SS.SS/RR.RR$. These will have different spectra also in achiral solvents. Inspection of a model shows that the $SS.RR/RR.SS$ enantiomeric pair can exist only if the four metal atoms are in one plane together with the bridging C atoms. This configuration has been observed in $(\text{Me}_3\text{SiCH}_2)_4\text{Cu}_4$ containing exclusively two-coordinate Cu atoms. However, a planar configuration for $\text{Ar}'_4\text{M}_2\text{Li}_2$ seems unlikely because of the presence of sp^3 hybridized lithium atoms in the M_2Li_2 core (compare with the X-ray structure of 5-Me-2-Me₂NCH₂C₆H₃Cu tetramer containing three-coordinate Cu atoms in Fig. 1). Consequently, the bridging aryl groups will point alternatively below and above the M-Li edges of the M_2Li_2 core. This eliminates the $SS.RR/RR.SS$ enantiomeric pair and leaves the $SS.SS/RR.RR$ pair as the only possibility. Accordingly, the rotation of the four aryl rings in these tetranuclear clusters must be a concerted process.

VI. DETECTION OF GEOMETRIC ISOMERISM AND ARYL ROTATION IN $\text{Ar}'_4\text{M}_4$ AND $\text{Ar}'_4\text{M}_2\text{Li}_2$ BY INTRODUCTION OF A STABLE CHIRAL LABEL IN THE Ar' GROUP.

In order to study the problem of the nature of the configuration at the C_{bridge} centers in the $\text{Ar}'_4\text{M}_2\text{Li}_2$ clusters in greater detail, the dynamic NMR spectra of the novel $[(S)\text{-}2\text{-Me}_2\text{NCHMeC}_6\text{H}_4]_4\text{M}_2\text{Li}_2$

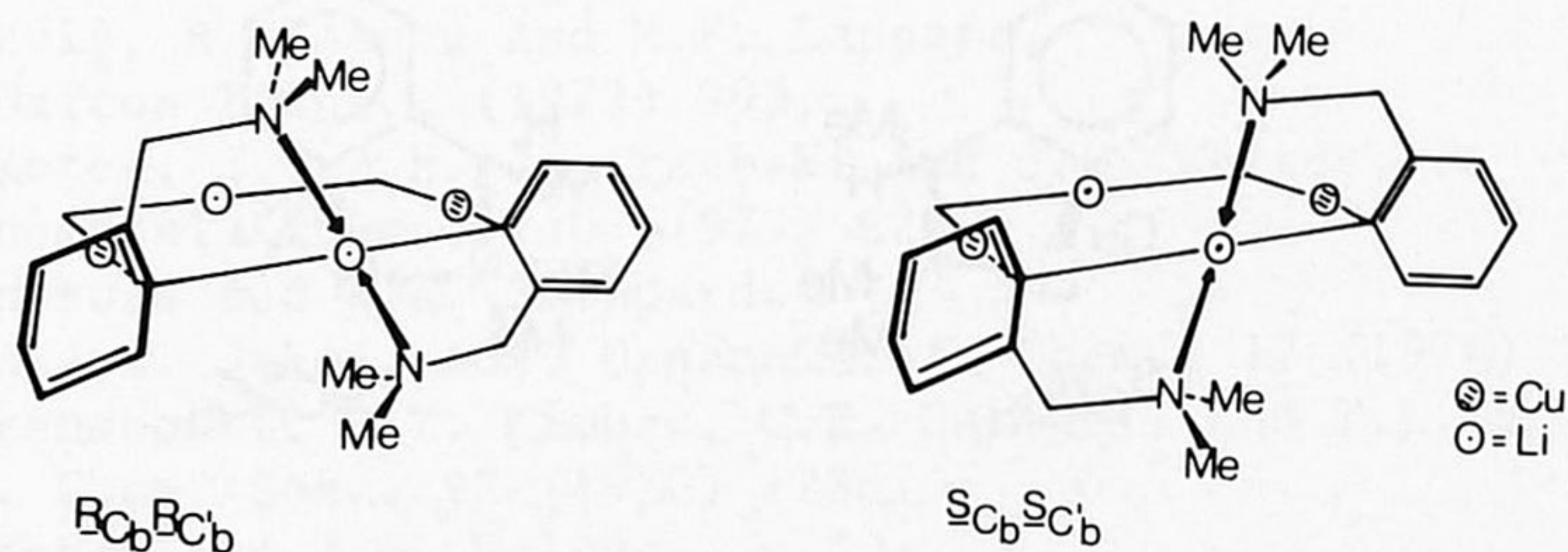


Fig. 11. The configuration at C_{bridge} of two aryl groups bonded to the same Li atom in $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Cu}_2\text{Li}_2$

clusters were investigated.

Introduction of a second center of chirality [CH(Me)NMe₂] of which the configuration cannot invert results in two diastereomeric forms $(S)_{C_b}(S)_C$ and $(R)_{C_b}(S)_C$ of the (S) -Ar'MLi units, see Fig. 12. This allows the detection of the stereochemistry of the (S) -Ar'₄M₂Li₂ aggregates because these diastereomeric units will have different resonance patterns.

The use of the chiral 2-Me₂NCH(Me) rather than the prochiral 2-Me₂NCH₂ group as a built-in ligand provided valuable information concerning the occurrence of Cu-N coordination as well as the stereochemistry of the Cu₄ aggregate in (S) -Ar'₄Cu₄. This information could not be obtained from the dynamic NMR spectra of the Ar'₄Cu₄ cluster [4]. The C_{bridge} atoms in the Cu₄ aggregate are prochiral because they bridge two Cu atoms, which have the same trigonal coordination geometry. Accordingly, the (S) -2-Me₂NCHMeC₆H₄Cu₂ units in (S) -Ar'₄Cu₄, unlike the (S) -Ar'MLi units in (S) -Ar'₄M₂Li₂, are not diastereomeric. However, in the case of the (S) -Ar'₄Cu₄ cluster, the formation of Cu-N coordination bonds in the geometric isomer having the butterfly Cu₄ core (see Fig. 1) can be effected in two ways, i.e. clockwise or counter clockwise. The resulting helicity in combination with the distinct chirality at the benzylic C-atoms then gives rise to two stereoisomers denoted $4(S)_{C^\alpha}Cu_4$ and $4(S)_{C^\beta}Cu_4$ which will have different spectra.

An extensive presentation of the NMR spectra supporting these conclusions will be presented elsewhere.

VII. CONCLUDING REMARKS.

In the foregoing discussion we have seen that the bulkiness of the ortho-substituent in the aryl group present in arylmetalIB clusters has great influence on the barrier to rotation of 3c-2e bonded Ar groups. The presence of a hetero atom in the ortho substituent, which can form a coordination bond to the bridged metal,

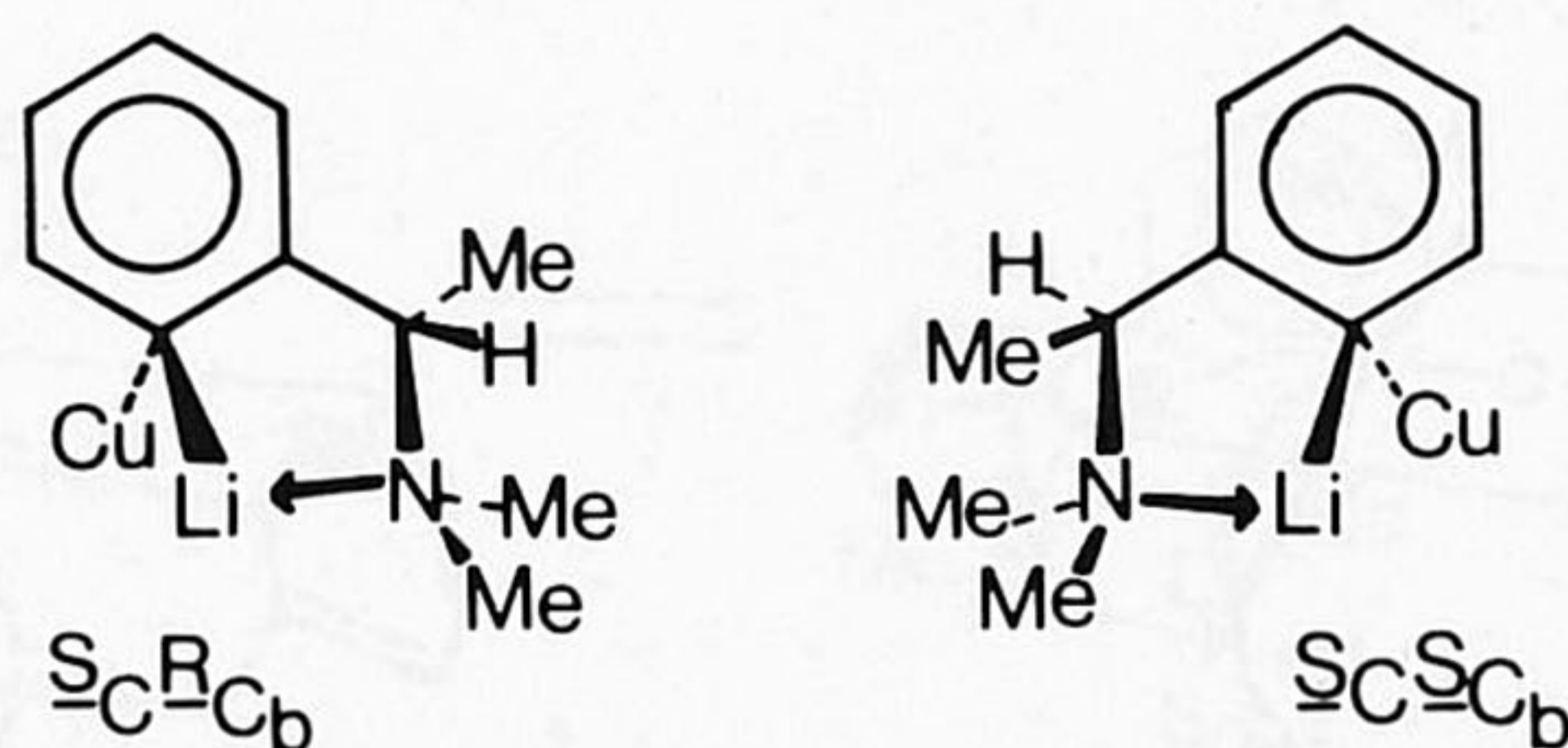


Fig. 12. The two diastereomeric forms of the (S) -2-Me₂NCHMeC₆H₄CuLi unit.

see Fig. 3, further contributes to this barrier depending on the strength of this M-hetero atom bond. Rotation depends in this case on M-hetero atom bond dissociation.

These considerations at the same time provide a rationale for the high kinetic stability of these ortho substituted arylmetalIB clusters of which the observed stability order is: 2-Me₂NHZCH₂ (Z=H or Me) \approx 2-Me₂CHCH₂C₆H₄ \approx 2-Me₂N \approx 2,6-(MeO)₂ \approx 2,6-Me₂>2-Me>4-Me \approx unsubstituted phenylcopper [1]. High population of rotamers having the aryl ring in about or in perpendicular position either as a result of the presence of bulky ortho groups or of coordinating ortho substituents will result in high electron density in the M₂C_{bridge} region. In these rotamers both MO's for the M₂C bonding (see section III) as well as backbonding from the metals to the aryl ring are effective.

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