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## A view of organocopper compounds and cuprates

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### Abstract

Research on the chemistry and structural aspects of *ortho*-substituted-arylcopper and -cuprate compounds in which the *ortho*-substituents either interfere sterically with the C<sub>ipso</sub>-to-copper bonding or have a potentially coordinating heteroatom, is described. Concluded is that the simple arylcopper and *ortho*-ligand substituted arylcopper compounds have many similar structural features. However, the self-complexed copper compounds have an essential extra feature; i.e. the number of possible aggregates is much more restricted since only in a few aggregate structures can all *ortho*-ligands equally partake in the bonding to copper. At present, new achievements have been made in the rational design and synthesis of organo(arylthiolate)copper derivatives that contain a Lewis-acidic copper centre. The successful application of these mixed organo(arylthiolate)copper compounds in 1,4-addition reactions with  $\alpha,\beta$ -unsaturated ketones is ascribed to prior coordination of the unsaturated substrate to the Lewis-acidic copper centre.

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The first chemical account I wrote, which also marks the start of my research career in 1967, was about the state of the art in the field of the synthesis and structural aspects of organocopper compounds [1]. By necessity this account was very short: although the first organocopper compounds had been isolated as early as 1923 [2], in 1967 still only a few isolated examples of such compounds had been reported [3–12]. Since then, we have learned how the intrinsically labile copper-carbon bond can be stabilized so that relatively stable organocopper compounds can now be synthesized and isolated [13]. Over the years, I became more and more fascinated by the challenge that organocopper chemistry represents for the synthetic chemist, and by the versatility, the unusual bonding features, and in particular the beauty of the structures of the organocopper compounds. Here I will describe how organocopper chemistry evolved from the first tentative attempts to arrive at stable organocopper compounds to the rational design and synthesis of novel types of organocopper arylthiolate copper compounds with a Lewis acidic copper(I) center as reactive intermediates for organic synthesis.

### Simple and *ortho*-ligand-substituted arylcopper compounds

In retrospect it is surprising that our initial attempt to devise a route to a class of organocopper compounds with reasonable thermal and hydrolytic stability proved

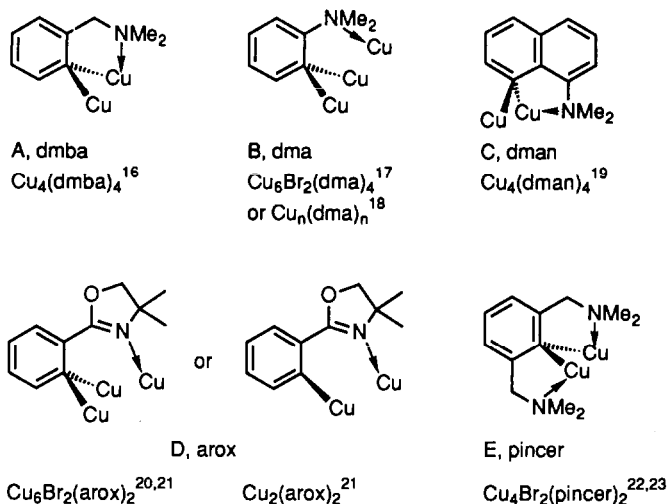


Fig. 1. Arylcopper compounds with various heteroatom containing substituents: i.e. the monoanionic groups dmdba, 2-[(dimethylamino)methyl]phenyl; dma, 2-(dimethylamino)phenyl; dman, 8-(dimethylamino)-1-naphthyl; arox, 2-oxazolinyphenyl; pincer, 2,6-bis[(dimethylamino)methyl]phenyl. The main bonding modes in their corresponding arylocopper derivatives of each of these anions via  $C_{ipso}$  and the donor atoms is given.

so successful. Rather than attempting to improve the stability of the Cu–C bond in alkyl- and aryl-copper compounds by the introduction of either fluorine- [14] or trialkylsilyl-substituents [15] our approach was to introduce functionalized heteroatom containing substituents in the *ortho*-position(s) of phenylcopper. We reasoned that a phosphorus-containing ligand would coordinate too strongly to copper(I) and therefore opted to use nitrogen-based substituents instead. Eventually our attempts were successful and led to the isolation and characterization of a fascinating series of arylocopper compounds. For a selection of these compounds, the type of *ortho*-ligand used as well as representative examples of the *ortho*-ligand substituted arylocopper unit, are shown in Fig. 1.

A common structural feature of these compounds is their central copper core to which the aryl groups are two-electron three-centre (2e–3c) bonded. This feature is also found in arylocopper compounds that lack heteroatoms in the *ortho*-substituents, as shown by the structures of  $\text{Cu}_5(\text{mesityl})_5$  [24],  $\text{Cu}_4(\text{C}_6\text{H}_2\text{Pr}_3^i-2,4,6)_4$  [25] and  $\text{Cu}_4(\text{C}_6\text{H}_4\text{Me}-2)_4(\text{DMS})_2$  [26] (DMS = dimethyl sulfide). The structures of the last two are shown in Fig. 2.

A possible answer to the question of why our initially naive approach was so successful is indicated by the  $C_{ipso}$ –Cu bonding-mode in arylocopper compounds. The electron deficient nature of the  $\text{C} \cdots \text{Cu}$  bonding, which can also account for the short Cu–Cu distances (2.37–2.45 Å) in these organocopper compounds, plays an important role in the stabilization of the  $C_{ipso}$ –Cu bond. On the basis of qualitative arguments we [16,27] and others [28] proposed a bonding scheme for this bridge-bonding of  $C_{ipso}$  in which the lowest occupied MO (molecular orbital) is a combination of the filled  $sp^2 C_{ipso}$  orbital with a bonding combination of empty orbitals on copper, while a second, higher energy MO comprises a combination of a  $\pi^* C_{ipso}$  orbital with a filled, anti-bonding combination of orbitals on copper (see

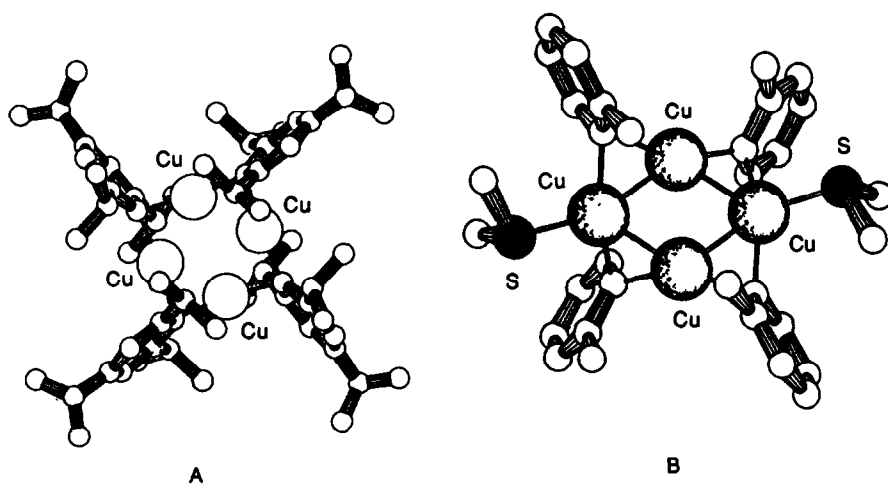


Fig. 2. (A) Structure of 2,4,6-tris(isopropyl)phenyl copper with unsymmetrical  $\sigma$ - $\pi$  bonded aryl ligands [25]. (B) Structure of *ortho*-tolylcopper-dimethyl sulphide adduct with linearly two-coordinate and trigonal three-coordinate copper atoms [26]. Note that in this conformer all *ortho*-methyl groups are on the same side of the Cu<sub>4</sub>-array.

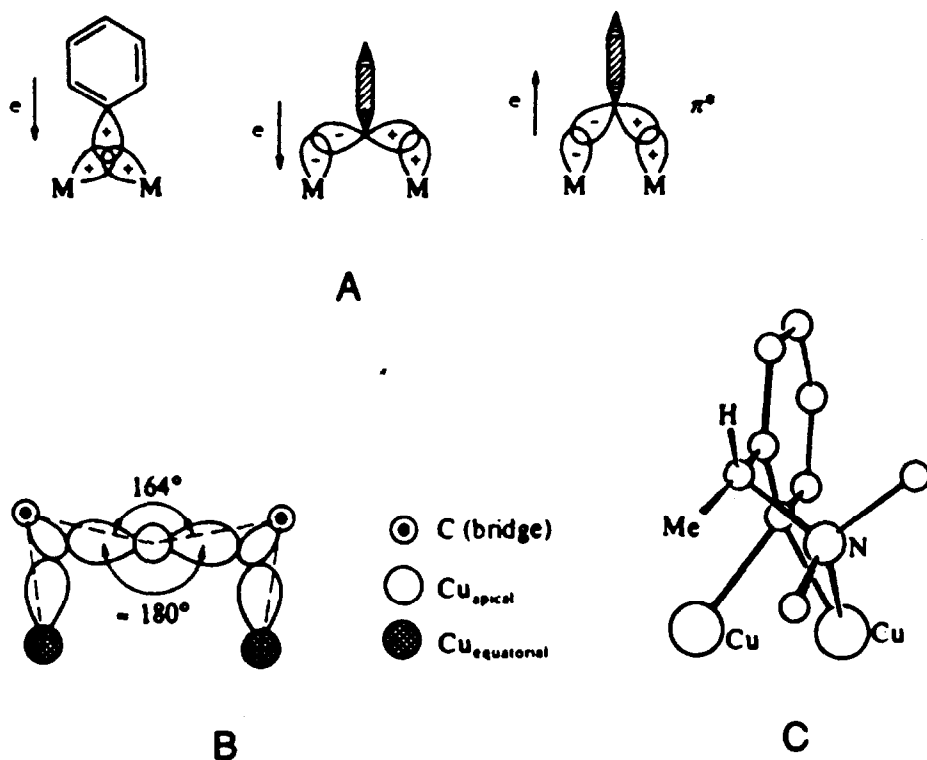


Fig. 3. (A) Molecular orbitals involved in the 2e-3c (aryl)C<sub>ippo</sub>-to-Cu<sub>2</sub> bonding. (B) Comparison of the angles in the 2e-3c bridged C<sub>ippo</sub>-Cu<sub>2</sub> unit [30]. (C) Puckering of the five-membered chelate ring in the [CuC<sub>6</sub>H<sub>4</sub>CH(Me)NMe<sub>2</sub>-2-(S)]<sub>4</sub> [31].

Fig. 3). Since the first MO also involves a bonding interaction between the copper atoms themselves the Cu–Cu distances can become as short, as has been observed. (Note that the Cu–Cu distance in metallic copper is 2.58 Å).

Contribution by the second MO to the Cu–C-bonding increases the electron density in the  $C_{ipso}$ –Cu<sub>2</sub>-region and thus the kinetic stability of this bond. Another stabilizing effect in arylcopper compounds is the preference of the aryl–Cu<sub>2</sub> rotamer (rotation around the C<sub>4</sub>–C<sub>ipso</sub> axis) to keep the plane of its aryl nucleus perpendicularly oriented to the Cu–Cu vector. In this rotamer situation there is a minimum interaction between the Cu-atoms and the *ortho*-substituents (H<sub>2</sub> and H<sub>6</sub> in the case of phenyl). Consequently, this rotamer will be particularly stabilized when the aryl group contains bulky *ortho*-substituents. These can either be alkyl groups (cf. Fig. 2 methyl or *i*-propyl) or heteroatom-containing substituents (vide infra cf. Fig. 7) when these are not coordinated to copper [29]. In my opinion, it is precisely this effect exerted by the *ortho*-substituents on the rotamer distribution (and so on the kinetic stability of the  $C_{ipso}$ –copper interaction) that make the essential contribution to the stabilization of the *ortho*-substituted arylcopper species.

In the arylcopper aggregate as a whole, the copper atoms can either have a linear or a trigonal bonding mode. The linear type of bonding becomes apparent when only the copper- and  $C_{ipso}$ -orbitals (that interact with each other) in a RCuR unit are considered and *not* the angles between the direct C–Cu vectors between  $C_{ipso}$  and copper in the solid-state structures (see Fig. 3b). For example, in Cu<sub>4</sub>(C<sub>6</sub>H<sub>4</sub>Me-2)<sub>4</sub>(DMS)<sub>2</sub>, for the two-coordinate Cu atoms the angle Cu–C<sub>ipso</sub>–Cu is 75° and the  $C_{ipso}$ –Cu–C<sub>ipso</sub> angle 149°, whereas the  $C_{ipso}$ –Cu–C<sub>ipso</sub> overlap of the MO's is nearly linear. It is noteworthy that in mononuclear [CuR<sub>2</sub>]<sup>–</sup> species, of which several examples are now known [32–34], the  $C_{ipso}$ –Cu–C<sub>ipso</sub> vector falls together with the linear bonding interaction. The same holds true for the few organocopper atoms with electron-precise  $C_{ipso}$ –Cu bonds, e.g. in PhCu(triphos) [35] (triphos 1,1,1-tris[(diphenylphosphino)methyl]ethane) CuMe(PPh<sub>3</sub>)<sub>3</sub> [36] and in Cu<sub>2</sub>(arox)<sub>2</sub> (see Fig. 1d for arox) [21].

The influence of *ortho*-substituents in arylcopper compounds either on the overall structure of the aggregate or on the nature of the  $C_{ipso}$ –Cu bonding can be pronounced; it can be of purely steric origin or arise from interaction of ligands either *via* inter- or intramolecular coordination. Steric effects exerted by *ortho*-substituents are clearly indicated by the changes of the structural features in a series of bis-*ortho*-substituted arylcopper compounds: i.e. 2,4,6-trimethyl- [24], 2,4,6-triisopropyl- [25], and 2,4,6-triphenyl-phenylcopper [37]. In these compounds, the increasing bulk of the *ortho*-substituents changes the nature of the  $C_{ipso}$ –Cu bonding from a symmetrical 2e–3c in the trimethyl-substituted compound via unsymmetrical bonding in the triisopropyl, to a purely 2e–2c  $C_{ipso}$ –Cu bonding in the 2,4,6-triphenyl-substituted arylcopper compound [38]. In particular, the unsymmetrical arylcopper unit observed in Cu<sub>4</sub>(C<sub>6</sub>H<sub>2</sub>Pr<sub>3</sub><sup>i</sup>-2,4,6)<sub>4</sub> is interesting. The bonding in this unit could also be interpreted as a 2e–2c  $C_{ipso}$ –Cu bonding which bridges the copper atom of another arylcopper via a π-type  $C_{ipso}$ –Cu' interaction. This kind of  $C_{ipso}$ –metal bonding is commonly encountered in cuprate structures (vide infra, Figs. 4 and 7).

At first glance, the interaction of weakly coordinating ligands (solvent molecules) seems to leave the overall composition of the initial aggregate unaffected. The basic structural features (the nature of the copper aggregate and the bonding) of

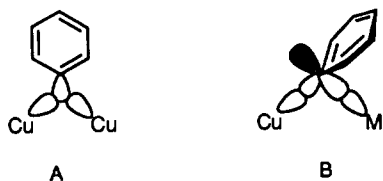


Fig. 4. Comparison of a symmetrical  $C_{ipso}$ - $Cu_2$  bridge bonding mode (copper atoms have similar coordination geometries) and an unsymmetrical one (M is either a copper atom with a higher coordination geometry than Cu or is for example a lithium cationic site).

$Cu_4(C_6H_4Me-2)_4(DMS)_2$  [26] and  $Cu_4(C_6H_5)_4(DMS)_2$  [39] seem to be similar to those of uncomplexed alkyl- and aryl-copper species for which the solid-state structure is known. For example,  $Cu_4(CH_2SiMe_3)_4$  is tetranuclear and consists of a planar  $Cu_4$  core [15]. The  $CH_2SiMe_3$  groups are bound to the edges of this plane via  $2e-3c$  C-Cu<sub>2</sub> bonds, as is also the case in  $Cu_4(aryl)_4(DMS)_2$ . However, as a result of DMS coordination, the copper centres in the latter compounds are not exclusively two-coordinate as in  $Cu_4(CH_2SiMe_3)_4$ , but are either two- and three-coordinate. Since the latter coordination is of the trigonal planar type, the planar  $Cu_4$ -arrangement changes into a butterfly-shaped  $Cu_4$ -arrangement. Moreover,  $Cu_4(aryl)_4(DMS)_2$  can be regarded as a species that is built up from two  $[Cu(C_6H_4Me-2)_2]^-$  anions bridged by  $[(DMS)Cu]^+$ -cations. Consequently, the  $2e-3c$  aryl-to-Cu<sub>2</sub> bridge will be unsymmetrical, since the bonding orbital combination on neighbouring Cu-centres can be expected to be unsymmetrical. This view of the bonding-mode in arylcopper-DMS species bridges the gap between the pure organocopper species and the cuprates (e.g.,  $Cu_2Li_2Ph_4 \cdot (OEt_2)_2$  vide infra) [40]: in these tetranuclear neutral cuprates each  $[(DMS)Cu]^+$ -cation is replaced by a  $[(solvent)_nLi]^+$ -cation.

Arylcopper compounds that contain heteroatom substituents are interesting because intramolecular coordination with these heteroatoms can and does occur. In comparison with the simple arylcopper compounds discussed earlier, these arylcopper compounds can be envisaged as self-complexed arylcopper compounds; i.e., the heteroatom containing groups can be seen as intramolecularly positioned solvent molecules that are complexed to copper [38,41]. In the case of the 2-(dimethylamino)methyl substituent in the monoanionic aryl ligand *dmmba* (see Fig. 1a for *dmmba*) the N-lone pair is favourably positioned to give the tetranuclear aggregate structure  $Cu_4(dmmba)_4$  (cf. Fig. 5A for the structure of the 5-methyl substituted compounds).

The Cu-N coordination in the last compound leaves the arylcopper bridge-bonding unaffected because the "five-and-a-half" membered chelate ring has sufficient flexibility to become puckered (see Fig. 3C) while, the Cu-N coordination renders all the copper atoms equally three-coordinate. When this chelate ring is made more rigid, as is the case in  $Cu_4(dman)_4$  [19] (see Fig. 1c for *dman*) the charge distribution in the copper aggregate becomes markedly different from that in  $Cu_4(dmmba)_4$ . In  $Cu_4(dman)_4$  (see Fig. 5B) the N-donor atoms coordinate pair-wise to copper. As a result the aggregate contains two- and four-coordinate Cu-atoms, which leads to the interpretation of this aggregate as being built up of  $[(dman)_2Cu]^-$ -anions and  $[(Me_2N)_2Cu]^+$ -cations that bridge the anions. As a result, the charge distribution in this aggregate is similar to that of the neutral cuprates,

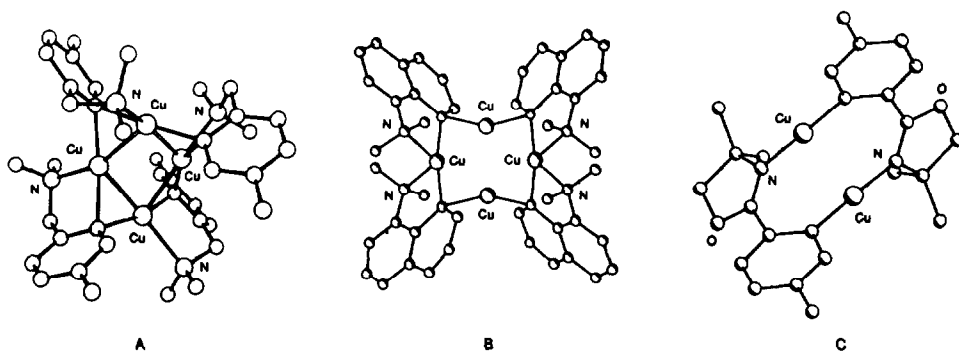


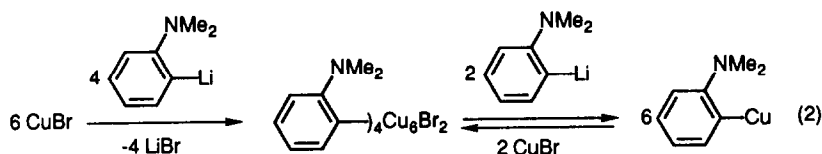
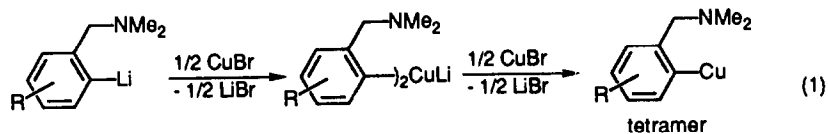
Fig. 5. Comparison of the structure of  $\text{Cu}_4(\text{C}_6\text{H}_3\text{CH}_2\text{NMe}_2\text{-2-Me-5})_4$  (A) [16],  $\text{Cu}_4(1\text{-C}_{10}\text{H}_6\text{NMe}_2\text{-8})_4$  [19] (B) and  $\text{Cu}_2(\text{aroX})_2$  (C) showing the effect of different chelate ring flexibility on the structural features.

$\text{Cu}_2\text{Li}_2(\text{aryl})_4$  (*vide infra*), which is confirmed by the fact that  $\text{Cu}_4(\text{dman})_4$  shows high reactivity in reactions that, up till now, were considered to be restricted to cuprate species [19]. A final example, which illustrates the influence that self-complexation has on the nature of the copper aggregate thus produced, is the formation of the dinuclear aggregate compound  $\text{Cu}_2(\text{aroX})_2$ . The dinuclear nature of this compound with  $2e-2c$  Cu-C bonds has been ascribed to the nearly parallel positioning of the lone pairs on  $C_{ipso}$  and the oxazolyl-N atom (see Fig. 1d). This arrangement of the lone pairs lowers the stability of bidentate  $C,N$ -bonding encountered in  $\text{Cu}_4(\text{dmba})_4$  with respect to the linear  $C_{ipso}\text{-Cu-N}$  bonding observed in the  $\text{Cu}_2(\text{aroX})_2$  dimer (see Fig. 5C) [20,21].

In conclusion, the simple arylcopper and self-complexed copper aggregates have many similar structural features. However, the self-complexed copper aggregates have one additional essential feature. Owing to their capacity to coordinate intramolecularly, the number of possible aggregates is much more restricted than for the simple arylcopper compounds since it is only in a few aggregate structures that all *ortho*-ligands of the aryl groups can take part equally in the bonding to copper. This selective formation of aggregates contrasts with the observation that the structure of simple arylcopper aggregates can range from  $[\text{CuPh}_2]^-$ -anions to an assembly of very complex multiples of  $[\text{CuPh}_2]^-$ ,  $\text{CuPh}$  and  $\text{LiPh}$  which, moreover, seem to be solvent-dependent. For example,  $[\text{CuPh}_2]^-$  is formed when the Cu-cation is stabilized by strong complexation (e.g., as  $[\text{DPPE}_2\text{Cu}]^+$ ; DPPE 1,2-bis[(diphenylphosphino)ethane]) [24] while higher aggregates are found in the presence of a weakly complexing ligand such as DMS [39].

### Heterocopper and cuprate compounds

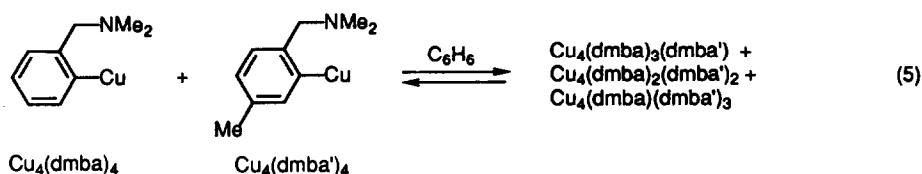
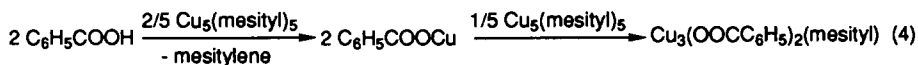
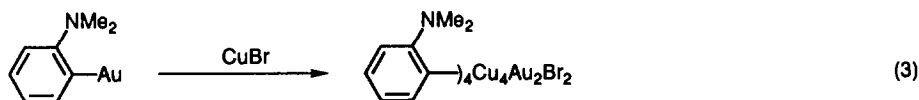
At the outset of our studies in 1967, it was common knowledge that the isolation of pure organocopper compounds was an extremely difficult and tricky undertaking. In particular the separation of organocopper species from metal halides was laborious and seemed in the beginning almost impossible [42]. As our aim was the synthesis of pure organocopper compounds rather than mixtures, we concentrated on the details of the organocopper synthesis. Soon we discovered [43] that two cases could be distinguished, as illustrated by the routes shown in Eqs. 1 and 2.



The synthesis of *dmba* must proceed via its cuprate (i.e., slow addition of CuBr to a suspension of Li(*dmba*)) because the reverse addition leads to intractable and thermally unstable mixtures of Cu(*dmba*) and CuBr [43]. In contrast,  $\text{Cu}_n(\text{dma})_n$  can only be obtained via the well-defined hexanuclear arylcopper-copper bromide aggregate  $\text{Cu}_6\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2\text{-}2)_4$ , Eq. 2 [17]. In retrospect, it can be seen that it was again the presence of an ortho-chelating substituent, either  $\text{CH}_2\text{NMe}_2$  or  $\text{NMe}_2$ , that opened only one reaction channel in these reactions, thus leading to the formation of single products via well-defined intermediates; a cuprate,  $\text{Cu}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)_4$ , in the case of the *dmba* ligand and a mixed arylcopper-copper halide aggregate  $\text{Cu}_6\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2\text{-}2)_4$  for *dma*. It must be noted that at the time of their isolation both species were unique: they were the first examples of a neutral arylcuprate [44] and of a mixed (hetero)copper aggregate [17], respectively.

The structural features of  $\text{Cu}_6\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2\text{-}2)_4$  (see Fig. 6a) are unique. This aggregate can be thought to be built up from a  $[\text{Cu}_4\text{Br}_2]^{2+}$ -dicationic unit that forms the equatorial plane of an octahedron and two linear  $[\text{R}_2\text{Cu}]^-$ -units which then occupy the apical sites. When we realized this in 1975 we expected that mixed AuCu species with  $\text{Au}_2\text{Cu}_2$ -stoichiometry would be very stable, since  $\text{Au}^{\text{I}}$  has the stronger preference for two-coordination [45]. This view was confirmed by the selective formation and isolation of  $\text{Au}_2\text{Cu}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)_4$  [46].

Applying the same concept to the *dma* ligand, we were able to synthesize quantitatively  $\text{Au}_2\text{Cu}_4\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2\text{-}2)_4$  (see Eq. 3) and  $^{197}\text{Au}$  Mössbauer studies



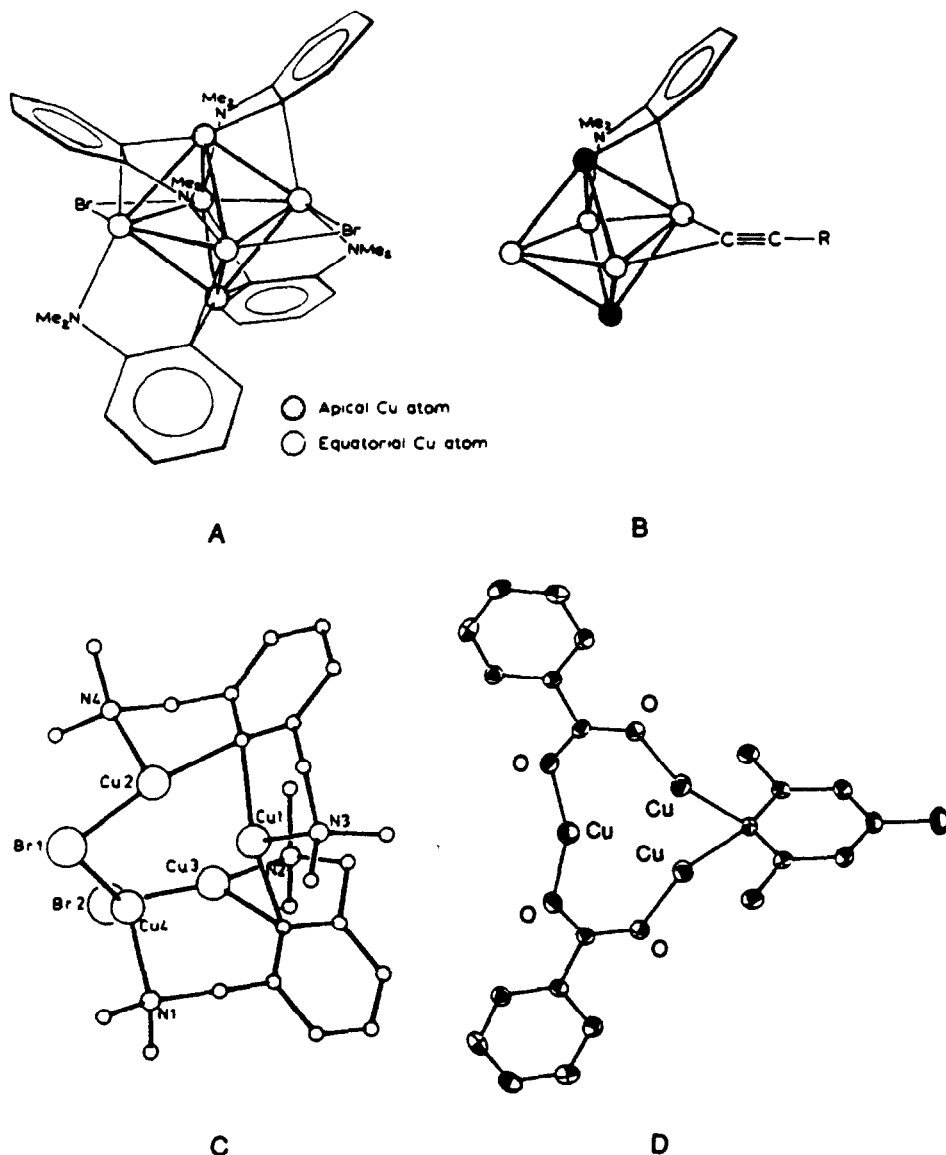


Fig. 6. Some structures of heteroorganocopper compounds with the dman and pincer ligands and mesityl: A,  $\text{Cu}_6\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2-2)_4$ ; B,  $\text{Cu}_6(\text{C}_6\text{H}_4\text{NMe}_2-2)_4(\text{C}\equiv\text{C}-p\text{-Tol})_2$  only one trinuclear face is shown; C,  $\text{Cu}_4\text{Br}_2(\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6)_2$ ; D,  $\text{Cu}_3(\text{O}_2\text{CC}_6\text{H}_5)_2(\text{mesityl})$ .

on this hexanuclear aggregate confirmed that the apical positions were occupied by  $\text{Au}^{\text{I}}$  [46,47]. The explanation we put forward for the different reactivities of  $\text{Cu}(\text{dmba})$  and  $\text{Cu}(\text{dma})$  towards  $\text{CuBr}$  is based on the specific chelating properties of  $\text{dmba}$  and  $\text{dma}$  anions [17]. In  $\text{dmba}$  the  $C_{\text{ipso}}$  and amine N lone pairs are directed towards each other whereas in  $\text{dma}$  they are positioned almost parallel. This feature makes the  $\text{dma}$ -grouping extremely suitable for bridging a  $\text{Cu}_3$ -face, as can be seen from Fig. 1B. Hence, it is this influence that the *ortho*-heteroatom



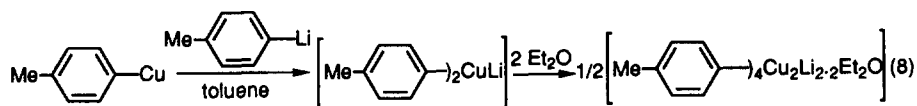
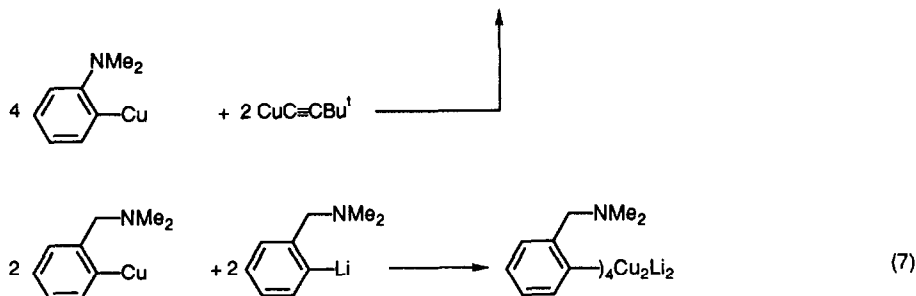
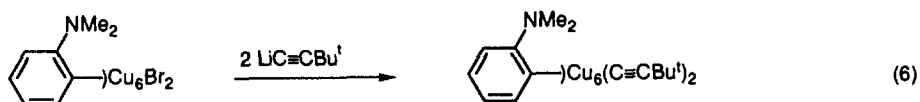
containing substituents exerts on the stability of the arylcopper aggregate which is absent in the simple parent phenylcopper compounds and its derivatives. In the case of the dma-anion, the aggregate is actually stabilized only when copper(I) halide units are included in the structure, thus leading to  $\text{Cu}_6\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2)_4$ . Further substitution of the Br anions in this aggregate is only possible under special solvent conditions (cf. Eq. 2, i.e., in benzene  $\text{Cu}_n(\text{dma})_n$  can be formed) or with special organyl groups (cf. Eq. 6, i.e., the substitution with alkynyl anions occurs with retention of the hexanuclear aggregate structure, *vide infra*).

A fascinating example of the incorporation of copper(I) halide entities apparently required to arrive at a stable aggregate structure was observed when we used our pincer monoanionic ligand (Fig. 1e for pincer) [22,23]. In this case, pure  $\text{Cu}_n(\text{pincer})_n$  could not be obtained. Instead, CuBr is incorporated in the aggregate, and this leads to a structure in which all *ortho*-substituents can coordinate equally to copper (see Fig. 6C). In this tetranuclear aggregate the 2e-3c bonded aryl ligands (Cu-Cu 2.407(2) and 2.411(2) Å), as well as the 4e-3c bonded Br anions (Cu-Cu 2.736(2) Å) are *cis*-positioned. Consequently, all the copper atoms have attained three-coordination in this aggregate structure. However, this type of incorporation of anions in organocopper aggregates is not restricted to self-complexing organocopper compounds. For example, Power et al. observed  $[(\text{Me}_3\text{Si})_2\text{CHCuBr}]^-$  in association with a  $[\text{12-crown-4}]_2\text{Li}^+$ -cation [34], and when we studied the synthesis of copper(I) carboxylates via the reaction of mesityl- or para-tolyl-copper with carboxylic acids we isolated the first mixed neutral organo-organic copper compound [48,49]. In particular, for the mesitylcopper reaction we were able to isolate the aggregate  $\text{Cu}_3(\text{O}_2\text{CC}_6\text{H}_5)_2(\text{mesityl})$  when we used an excess of mesitylcopper (see Eq. 4). The structure of the resulting trinuclear aggregate is shown in Fig. 6d. It should be noticed that a 2e-3c bonded mesityl group (Cu-Cu 2.421(2) Å) and 4e-donating bridging benzoate groups (Cu-Cu 2.888(2) Å) are present.

At this point, the astute reader will have noted that the formation of these copper aggregates can be extremely selective. For example, in the reaction of copper(I) benzoate and mesitylcopper (Eq. 4) it is obvious that out of these species, which are themselves aggregates, the mixed trinuclear copper(I) aggregate  $\text{Cu}_3(\text{O}_2\text{CC}_6\text{H}_5)_2(\text{mesityl})$ , is exclusively formed. This high selectivity contrasts with the formation of a statistical ratio of tetranuclear aggregates when two corresponding compounds,  $\text{Cu}_4(\text{dmba})_4$  and  $\text{Cu}_4(\text{dmba}')_4$ , were mixed in benzene, see Eq. 5 (dmba' is dmba with a 5-Me group) [16]. The formation of  $\text{Cu}_3(\text{O}_2\text{CC}_5\text{H}_5)_2(\text{mesityl})$  seems to be an excellent example of self-assembly of a specific organometallic aggregate. At present, it is not clear what makes this mixed species thermodynamically more stable than the starting components  $\text{Cu}_5(\text{mesityl})_5$  [24] and  $\text{Cu}_4(\text{O}_2\text{CC}_6\text{H}_5)_4$  [50]. An important feature could very well be that all arrangements in this copper aggregate are set up to realize an ideal two-coordination around each copper atom.

The formation of mixed organocopper aggregates by inter-aggregate exchange reactions is a general phenomenon in organocopper chemistry and often mixed species with a specific composition are formed. Some pertinent examples are shown in Eqs. 6-8.

An example that deserves further comment is the synthesis of a mixed organo-copper aggregate  $\text{Cu}_6(\text{C}_6\text{H}_4\text{NMe}_2)_4(\text{C}\equiv\text{CR})_2$ . Initially this aggregate was synthesized via the direct substitution of Br in  $\text{Cu}_6(\text{C}_6\text{H}_4\text{NMe}_2)_4\text{Br}_2$  by use of  $\text{LiC}\equiv\text{CR}$ , see Eq. 6 [27]. The X-ray structure showed that for  $\text{Cu}_6(\text{C}_6\text{H}_4\text{NMe}_2)_4(\text{C}\equiv\text{CR})_2$



the  $\text{C}\equiv\text{CR}$  anions had taken the positions of the  $\text{Br}^-$ -anions in  $\text{Cu}_6\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2-2)_4$ . Moreover the expected decrease of the now  $2e-3c$   $\text{RC}\equiv\text{C}$  bridged  $\text{Cu}-\text{Cu}$  distances from 2.70 Å in the  $4e-3c$   $\text{Br}$  bridge distance to 2.474(4) Å, is indeed observed, (cf. Fig. 6a and 6b). An excellent route to this compound appeared to us to be, the interaggregate exchange reaction of pure  $\text{Cu}_n(\text{dma})_n$  with pure  $[\text{CuC}\equiv\text{CR}]'_n$  and this proved to be the case [51]. Since then, many further examples of this type of reaction have been found in my group and a particularly interesting one will be discussed below.

A very successful reaction was the synthesis (see Eq. 7) and characterization in solution by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [44] and in the solid state by X-ray crystallography [52], of the first example of a neutral arylcuprate via the inter-aggregate exchange reaction between  $\text{Li}_4(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$  [53] and  $\text{Cu}_4(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$ . The corresponding argentate and aurate species were made similarly [31,41,52,54]. Without going into detail here, it is now apparent that this (self-complexed) arylcuprate (see Fig. 7a) shows many of the general structural features which have recently been encountered for simple organocuprates by Power in  $[\text{Cu}_2\text{Li}_2(\text{CH}_2\text{SiMes})_4(\text{DMS})_2]_n$  [39] and by Weiss et al. in  $[\text{Cu}_2\text{Li}_2(\text{C}_6\text{H}_4)_4(\text{OEt}_2)_2]$  [40], i.e., (i) the tetranuclear  $\text{Cu}_2\text{Li}_2$  core has a *trans*-metal configuration; (ii) the  $\text{C}_{ipso}-\text{Cu}-\text{C}_{ipso}$  interaction is almost linear; and (iii) the lithium centres are either three- or four-coordinate by interaction with two neighbouring  $\text{C}_{ipso}$  centres and either one ( $\text{Et}_2\text{O}$  or  $\text{DMS}$ ) or two *ortho*- $\text{CH}_2\text{NMe}_2$  complexing interactions; and (iv) the  $\text{C}_{ipso}$  bonding is markedly unsymmetrical with a strong  $\sigma$ -component to copper and an additional weaker  $\pi$ -type  $\text{Li}-\text{C}_{ipso}$  interaction [52]. The latter conclusion is supported by X-ray as well as  $^{13}\text{C}$ ,  $^7\text{Li}$  and  $^{109}\text{Ag}$  NMR studies that were carried out on our  $\text{M}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$  aggregates ( $\text{M} = \text{Cu}, \text{Ag}$  or  $\text{Au}$ ).

In my opinion, an important difference between the two classes of organyl groups is that (i) in the cuprates with the simple alkyl or aryl groups, they can form

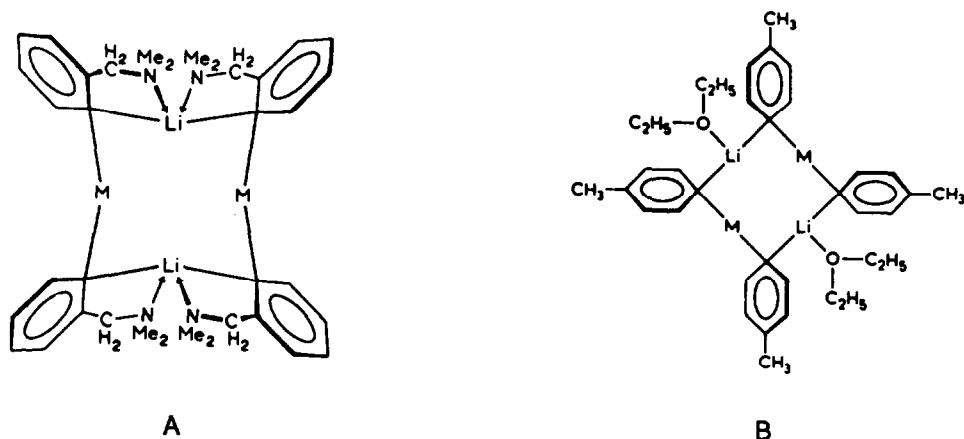


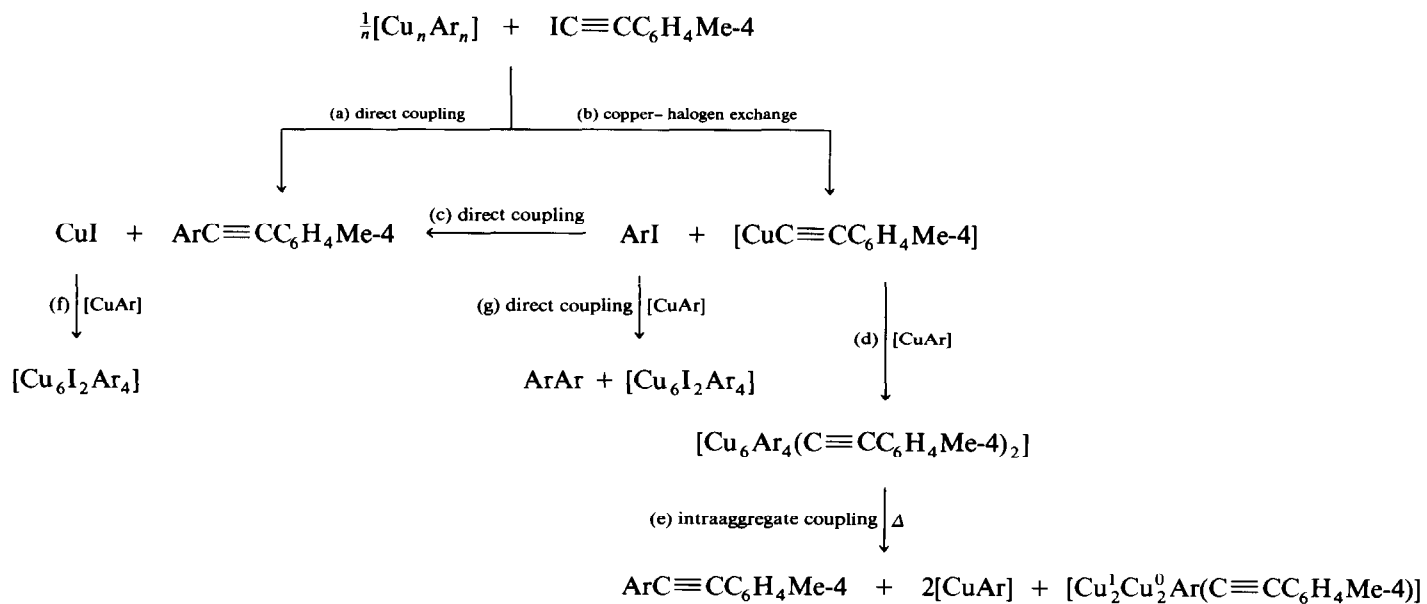
Fig. 7. Comparison of the schematic structure of a self-complexed and a simple arylcuprate; A,  $\text{Cu}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_4$ ; B,  $\text{Cu}_2\text{Li}_2(\text{C}_6\text{H}_4\text{Me}-4)_4(\text{OEt}_2)_2$  (proposed structure [56] which has now been confirmed by X-ray [40]).

a bewildering array of anionic and cationic aggregates (depending on solvents and ligands) [39,55], and (ii) in the case of the self-complexing cuprates, as a result of the specific coordination properties of the heteroatom-containing substituents, the formation of well-defined aggregates is more selective [38,41]. When account is taken of these points, even with simple aryl groups, neutral cuprates can be synthesized in quantitative yield. An example is the selective synthesis of *para*-tolylcuprate-etherate adducts shown in Eq. 8. The interaggregate exchange reaction of *para*-tolylcopper and *para*-tolyllithium in toluene affords insoluble *para*-tolylcuprates that can subsequently be solubilized by titration of the latter suspension with diethyl ether. This route then leads to the quantitative formation of the soluble *para*-tolylcuprate-diethyl ether adduct, for which we already proposed the tetranuclear structure in 1977 [56] (see Fig. 7b). The correctness of this proposal was recently confirmed by the structure of  $\text{Cu}_2\text{Li}_2(\text{phenyl})_4(\text{Et}_2\text{O})_2$  [40].

### Structure-reactivity relationships: arylcopper compounds in organic synthesis

Apart from the fundamental importance of the synthesis and characterization of organocopper compounds, these studies can provide substantial support and inspiration for the organic synthetic chemist who uses copper as a catalyst or as an in situ prepared reagent. A pertinent example is the interaction of organocopper reagents and organic halides; an important method for the formation of new carbon-carbon bonds (cross-coupling). Likewise, the biaryl formation in the Ullmann reactions has been shown to involve the coupling of an aryl halide with an organocopper intermediate (cross-coupling). Since there is an on-going debate about the intimate steps of these coupling reactions, we examined the novel organocopper species that emerged from our program for their relevance as intermediates in Ullmann type coupling reactions.

In the cross-coupling reactions of  $\text{Cu}_n(\text{dma})_n$  with  $\text{IC}\equiv\text{CC}_6\text{H}_4\text{Me}-4$  (see Scheme 1) we unambiguously established that in addition to direct cross-coupling extensive copper-iodine exchange also takes place [57]. The last reaction produces not only

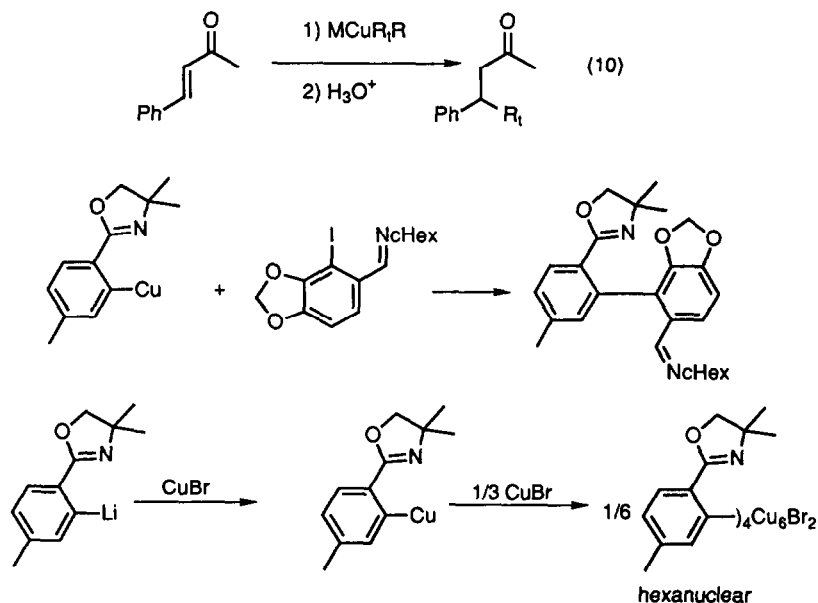
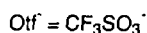
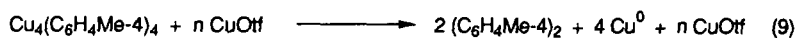


(Ar = C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)

Scheme 1. Reactions taking place in the cross-coupling reaction of Cu<sub>n</sub>(C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>n</sub> with IC≡CC<sub>6</sub>H<sub>4</sub>Me-4 [57].

$\text{IC}_6\text{H}_4\text{NMe}_2\text{-2}$  but also  $\text{Cu}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})$ , which reacts selectively with  $\text{Cu}_n(\text{dma})_n$  to give the hexanuclear mixed-organocopper aggregate  $\text{Cu}_6(\text{C}_6\text{H}_4\text{NMe}_2\text{-2})_4(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})_2$  (vide supra Eq. 6) [27,51]. In separate reactions we showed that when heated this mixed-organocopper aggregate in DMF (*N,N*-dimethylformamide) produces exclusively the cross-coupling product, via an intra-aggregate C–C coupling reaction. An obvious reason for this selectivity can be deduced from the structure of  $\text{Cu}_6(\text{C}_6\text{H}_4\text{NMe}_2\text{-2})_4(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})_2$  in the solid state; each  $\text{Cu}_3$ -face of the octahedron in this structure is occupied by one alkynyl and one aryl bridging group (see Fig. 6b) [27]. The most remarkable result of this study was that, on the basis of the fact that the organocopper intermediates are aggregated species, an explanation could be given for the formation of the various side products commonly encountered in the Ullmann coupling reaction (originating from oxidation, condensation, or homo-coupling reactions) [51,57,58].

Homo-coupling of arylcopper compounds can be induced either thermally or by oxidation with one electron oxidants such as  $\text{O}_2$  or copper(II) salt [43]. A very interesting way of inducing biaryl formation was found when we studied the reaction of tetranuclear arylcopper aggregates with catalytic amounts of copper(I) triflate (see Eq. 9) [29]. In this reaction an arylcopper-copper triflate aggregate is formed that is activated towards intra-aggregate coupling of two aryl groups by the presence of the electron attracting triflate anion in the aggregate. It is thought that this electron release lowers the activation-barrier for a valence disproportionation reaction within the aggregate leading to  $\text{Cu}^0$  and  $\text{aryl}_2\text{Cu}^{\text{II}}$  and the latter undergoes a reductive elimination reaction of biaryl.



Scheme 2. Cross-coupling reaction with in situ prepared  $\text{Cu}(\text{arox})$  [59] and the synthetic route for the preparation of pure, well-defined  $\text{Cu}_2(\text{arox})_2$  (see Fig. 5C for its structure) and the  $\text{CuBr}$  adduct  $\text{Cu}_6\text{Br}_2(\text{arox})_4$  (see ref. 21 for its X-ray structure).

At this point, I would like to recall that the interest of the organic chemist in the nature and reactivity of organocopper compounds will go beyond those of simple alkyl- and aryl-copper compounds. This is obvious from the biaryl coupling reaction used by Ziegler et al. as the key step (see Scheme 2) in the synthesis of  $\pm$ -steganocin [59]. In this example, it is particularly the *ortho*-oxazoline substituent in the arylcopper derivative [20,21] (see Fig. 5c) that governs the reactivity of the copper-carbon bond and directs the reaction towards the highly selective formation of the C-C cross-coupled product [21].

### Design and synthesis of (organo)(aryliothiolate)copper derivatives as reagents in organic synthesis

In the last few years, our research in the field of organocopper chemistry has been concentrated on the synthesis of hetero-copper and -cuprate compounds. Fascinated by the selective formation of  $\text{Cu}_3(\text{O}_2\text{CC}_6\text{H}_5)_2(\text{mesityl})$  we posed the question of whether hetero-copper compounds with the ability to function as copper reagents in Michael-type addition reactions with  $\alpha,\beta$ -unsaturated ketones and esters could be made (see Eq. 10). Our aim was to synthesize cuprate compounds of the type  $\text{MCuR}_1(\text{SR})$  [60], in which the organo group  $\text{R}_1$  represents a transferable- and the thiolate anion  $\text{SR}$  a non-transferable group. To this end, we selected and synthesized a simple arylthiolate group  $[\text{SC}_6\text{H}_4\text{CH}(\text{R})\text{NMe}_2\text{-2}]^-$  since: (i) it contains an *ortho*-substituent which can potentially coordinate with one of the metal centres of the cuprate reagent and thus can stabilize vacant coordination sites and (ii) the introduction of a stereogenic centre at the benzylic carbon atom is seemingly

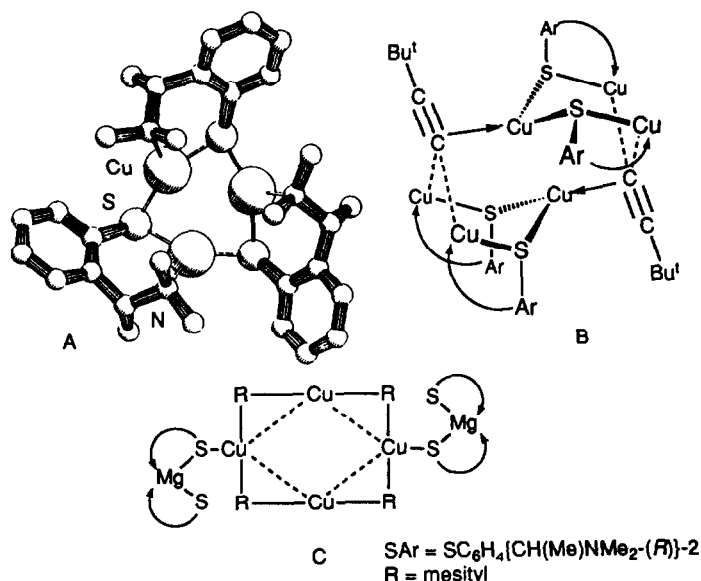
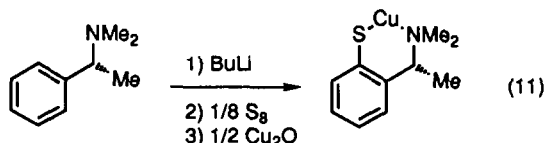


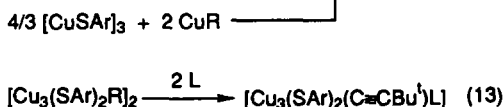
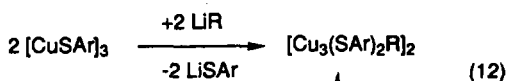
Fig. 8. Structure of the 42 electron copper(I) arylthiolate  $(\text{CuSAr})_3$  (A); the schematic structure of the hexanuclear aggregate  $[\text{Cu}_3(\text{SAr})_2(\text{C}\equiv\text{CBu}')_2]_2$  (B) and the schematic structure of  $\text{Cu}_4(\text{mesityl})_4(\mu_2\text{-SAr})_2(\text{MgSAr})_2$  (C):  $\text{SAr}$  is  $\text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-}(R)\text{-2}$ .

easy. It soon became apparent that the thiolate anion  $[\text{SC}_6\text{H}_4\text{CH}_2\text{NMe}_2-2]$  with copper(I) forms a novel type of copper(I)thiolate compounds (see Eq. 11), which rather than being ionic species (cf.  $\text{CuSPh}$ ) have well-defined neutral trinuclear structures (see Fig. 8) [61].

These trinuclear aggregates have as a common structural feature a bridging thiolate S atom and intramolecular Cu–N coordination. The introduction of alkyl substituents (R) at the  $\alpha$ -benzylic carbon atom is feasible and, moreover, leads to the formation of trinuclear copper thiolates as distinct diastereoisomers. The structure of  $[\text{CuSC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-2-(R)]_3$  contains very acute Cu–S–Cu angles of  $79.6^\circ$ . This is remarkable, since to date, the thiolate–copper bridged bonding has been described in terms of an  $sp^3$  hybridized thiolate S atom that acts as a 4e donor and leads to Cu–S–Cu angle close to the tetrahedral value of  $109^\circ$ . In contrast, we describe the acute angle in our copper thiolate complexes as a  $sp^2$  hybridized thiolate S atom that binds to the copper pair via a (electron deficient)  $2e-3c$   $\text{SCu}_2$  bonding mode [62] (cf. the  $\text{CCu}_2$  bridge bonding discussed above and shown schematically in Fig. 3). Consequently, in this bonding scheme each  $\text{SC}_6\text{H}_4\text{CH}(\text{R})\text{NMe}_2-2$  anionic ligand contributes 4 electrons (two via the S- and two via the N-donor) to the bonding in this 42 electron trinuclear aggregate (14 valence electrons/copper centre).



Most relevant is our finding that reaction of these copper thiolates does not involve the formation of mixed cuprate species. So far we have found two distinctly different reaction patterns: (i) partial thiolate group substitution that leads to a mixed organo arylthiolate copper aggregate, and (ii) complete substitution of the thiolate group with formation of an organocopper aggregate. The first reaction pattern is exemplified by the reaction of  $[\text{CuSC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-(R)-2]_3$  with  $\text{LiC}\equiv\text{CBu}^t$  (see Eq. 12). This reaction results in the quantitative formation of  $[\text{Cu}_3(\text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-(R)-2)_2(\text{C}\equiv\text{CBu}^t)]_2$  via an arylthiolate/ $\text{C}\equiv\text{CBu}^t$  exchange; i.e. in this reaction rather than a lithium cuprate a new copper aggregate



$\text{SAr} = \text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-(R)-2$ ;  $\text{R} = \text{C}\equiv\text{CBu}^t$ ;  
 $\text{L} = \text{PPh}_3$  or  $\text{P}(\text{OMe})_3$

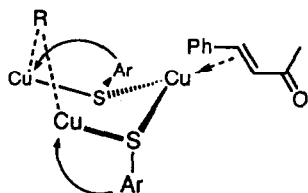
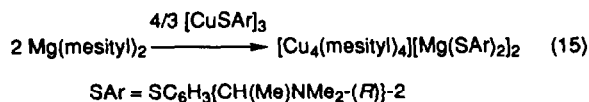
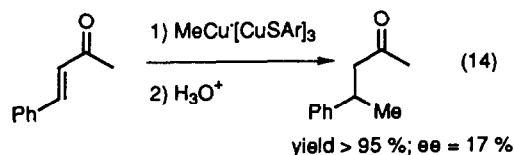


Fig. 9. Proposed bonding of the  $\alpha,\beta$ -unsaturated ketone to the Lewis-acidic copper centre in organo-copper-copper thiolate key intermediates leading to a 1,4-addition reaction of the organo-group (see Eq. 13).

species is formed that contains both thiolate and organo anionic groups. Interestingly, this heterocopper species is also accessible via the inter-aggregate exchange reaction of the copper arylthiolate and copper alkynyl compounds (see Eq. 12). The structure of this new heterocopper aggregate consists of two identical 40 electron trinuclear units, each of which contains two coordinatively saturated copper atoms and one unsaturated (i.e., Lewis acidic) copper atom (see Fig. 8b) [63]. Obviously, the unsaturation of the trinuclear unit is a consequence of the substitution of a 4e donating arylthiolate ligand by a 2e donating alkynyl group. The hexanuclear aggregate is formed by a new alkynyl-to-copper bonding mode that links the two trinuclear units together. This bonding description is supported by the observed cleavage of the hexanuclear  $[\text{Cu}_3(\text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-(R)-2)_2(\text{C}\equiv\text{CBu}^t)]_2$  into two trinuclear aggregates,  $[\text{Cu}_3(\text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-(R)-2)_2(\text{C}\equiv\text{CBu}^t)(L)]$ , on reaction with two equivalents of an electron donating ligand L (is either  $\text{PPh}_3$  or  $\text{P}(\text{OMe})_3$ , see Eq. 13).

We now use the trinuclear  $\text{Cu}_3(\text{SAr})_2(\text{C}\equiv\text{CBu}^t)$  aggregate as a general model for a new type of heterocopper reagent  $[\text{Cu}_{m+n}(\text{SAr})_m\text{R}'_n]$ . It is noteworthy that an almost quantitative methyl transfer to the  $\beta$ -position of benzylideneacetone was observed when pure (normally unreactive) methylcopper is mixed with pure  $[\text{CuSC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-(R)-2]_3$  (see Eq. 14) [63]. This 1,4-transfer reaction is common for cuprate reagents but not for copper compounds. Currently, we are investigating whether the first step in the 1,4-transfer reaction with our trinuclear aggregate is indeed the complexation of the  $\alpha,\beta$ -unsaturated ketone (via the olefinic or ketonic function) to the Lewis acidic copper centre (see Fig. 9; cf. the complexation with phosphines, Eq. 13).



The second reaction pattern we found when  $[\text{CuSC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2-(R)-2]_3$  was treated with dimesitylmagnesium (see Eq. 15). This reaction resulted in a complete arylthiolate/mesityl exchange, thus forming quantitatively the mesityl-



copper-magnesium thiolate compound  $[(\text{Cu}_4(\text{mesityl})_4)(\mu_2\text{-SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-}(R)\text{-}2)_2(\text{MgSC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-}(R)\text{-}2)_2]$  (see Fig. 8c) [64]. The overall structure of the central mesitylcopper unit is comparable, for example, to that of  $\text{Cu}_4(\text{C}_6\text{H}_4\text{Me-}2)_4(\text{DMS})_2$  (see Fig. 2b); i.e., the  $\text{Mg}(\text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-}(R)\text{-}2)_2$  unit is bonded to the  $\text{Cu}_4(\text{mesityl})_4$  unit through thiolate  $\text{S} \rightarrow \text{Cu}$  donative coordination (cf., the coordination of DMS). However, another feasible bonding description is based on an ionic structure with a  $[\text{Cu}_4(\text{mesityl})_4(\text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-}(R)\text{-}2)_2]^{2-}$  anion and two  $[\text{Mg}(\text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-}(R)\text{-}2)]^+$  cations, wherein each is bonded to a thiolate sulfur atom of the heterocuprate species by a  $\text{S} \rightarrow \text{Mg}$  bond. Further studies are currently being carried out in order to elucidate which bonding description will be the most applicable, in particular with regards to the reactivity of these reagents in 1,4-conjugate addition reactions to  $\alpha,\beta$ -unsaturated ketones [62].

This new direction of our research may fill the void that exists concerning the structural information on the kinetically active species in solutions of the so-called heterocuprates  $[\text{MCu}_r\text{R}_r\text{R}_1]$  ( $\text{M} = \text{Li}^+, \text{MgX}^+$ ). The observation that, in contrast to what was expected, organocopper aggregates of  $\text{Cu}_3(\text{thiolate})_2(\text{organo})$  stoichiometry with a Lewis-acidic copper(I) centre are accessible and can, moreover, be highly active reagents in reactions that up till now were restricted to cuprate type reagents, can be taken as an indication that we are just beginning to understand the structure/reactivity relationships of organocopper and cuprate reagents in organic synthesis.

### Acknowledgement

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