

Some Synthetic and Structural Aspects of Neutral Organocuprate Reagents $\text{Cu}_n\text{Li}_m\text{R}_{n+m}$: The Asymmetric Bonding Configuration of the Bridging Organo Group

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Abstract

The number of synthetic applications of organocuprates is growing rapidly but the mechanistic understanding only slowly. Development of the latter aspect requires knowledge concerning the structural features (in the solid and solution) of these reagents which to date is still very limited. Recent studies in our laboratory have provided information concerning the structures in the solid of the unique series R_4Li_4 (**1a**), $\text{R}_4\text{Cu}_2\text{Li}_2$ (**2a**), and $\text{R}_4\text{Au}_2\text{Li}_2$ (**4a**) where R is $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2$.

These structures encompass for the first time: i, the change in the metal core going from an organolithium to a cuprate (or aurate) species and ii, the change of the aryl-metal bonding from a purely symmetrical two electron-four center (2e-4c) R-Li₃ bonding in the aryllithium **1a**, via an asymmetric 2e-3c R-CuLi bonding in the cuprate **2a** to a R-AuLi bonding with an almost pure 2e-2c R-Au bond in the aurate **4a**.

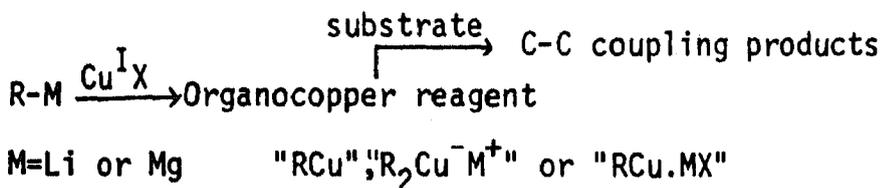
Information concerning the solution structure of **1a**, **2a** and **4a**, that is also pertinent to the interpretation of the reactivity of cuprates, comprises: i the ¹⁰⁹Ag and ⁷Li NMR spectra of analogous $\text{R}_4\text{Ag}_2\text{Li}_2$ that establish the retention of the neutral M_2Li_2 core in non-coordinating solvents and ii, the influence of the solvent on the structure, e.g. the R_4Li_4 structure of **1a** in Et_2O breaks down to a $\text{R}_2\text{Li}_2 \cdot 4\text{THF}$ structure in THF.

Based on this new information an analysis will be presented of the factors influencing the bonding of organo groups in organocuprate species.

Introduction

The number of synthetic applications of organocuprates is growing rapidly (**2a**) but the mechanistic understanding (**2b**) of organocuprate reactions only slowly. Devel-

oment of the latter aspect requires knowledge concerning the structural features of these reagents both in the solid and in solution. To date the available information is still limited (3). The main application of organocuprates is their use in C-C bond forming reactions as is outlined schematically in Scheme 1:



Reactivity of the organocopper reagent depends on:

1. Method of preparation
2. Presence of metal salts
3. Type of solvent used
4. Presence of additional ligands.

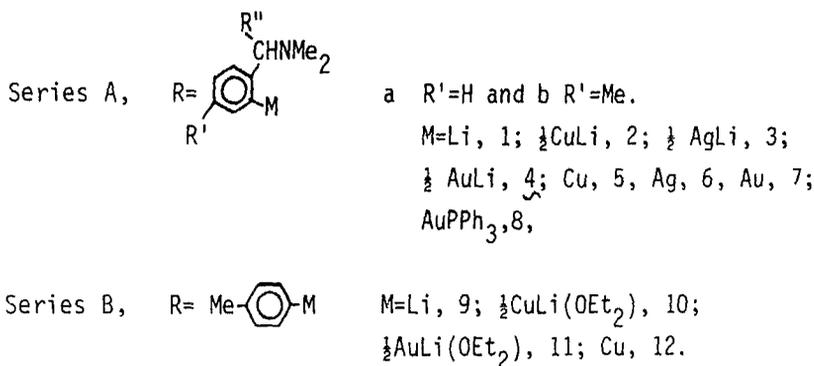
The organolithium or -magnesium reagent is made in situ and converted by addition of the appropriate equivalents of a copper(I) salt or compound (e.g. CuCN, $\text{CuC}\equiv\text{CR}$, etc.) into an organocopper (cuprate) reagent. Accordingly, the resulting mixture comprises a complex get-together of various metals (Li, Mg, Cu), anions (halides, CN , BF_4) and even in many cases of organo groups also (i.e., organo groups that form a stable bond to the copper lithium core, *vide infra*, and those that are transferrable to the substrate) (3). Furthermore, the reactivity as well as the reproducibility of these reagents have been found to be, sometimes critically, dependent on a series of factors (see Scheme 1: 1-4). It is obvious, therefore, that labelling these cuprate reagents as "RCu", "RR'CuM", "R₂Cu⁻" etc. is a serious oversimplification. This is misleading as to the nature of the organocuprate species present in solution and in particular hampers the mechanistic understanding of the cuprate reactions.

A more systematic study of the structural and bonding aspects of the cuprate reagents seems appropriate. However, so far almost all structural studies of organocuprates *in solution* using NMR spectroscopy have been carried out on mixtures of the type described above. For example, reports have appeared for alkyl-copperlithium and -coppermagnesium salt mixtures (4). In another case an elegant study was carried out on methylsilver lithium species by ¹H, ¹³C, ³¹P and ⁷Li NMR spectroscopy using the propitious magnetic properties of silver (*vide infra*) for detection of the connectivity of the various groups to silver and lithium (5). Even this study, however, lacked detailed structural information to warrant sensible

speculation as to both the nature of the species present in solution and the exchange reactions in which they are involved.

The general stability of cuprate species is low; they are extremely sensitive towards hydrolysis and oxidation while the thermal stability increases in the series alkyl < alkenyl ~ aryl < alkynyl (3). For the more stable aryl species some structural information is available (3,6,7). Actually, one of the compounds which is also a subject of this paper (2a, Figure 1) was the first and seems still to be the only pure cuprate reagent of which the structure *in solution* is known with certainty (6). This species has in solution and solid state (vide infra) a $\text{Cu}_2\text{Li}_2\text{R}_4$ stoichiometry and three center, two electron aryl-to-CuLi bonding.

In this paper we present a rather detailed picture of the structural and reactivity aspects of the interesting series of aryl-lithium, -copper and -copper lithium compounds as well as corresponding silver and gold species shown in Figure 1. The choice of these particular species for more detailed investigation is not accidental. It exemplifies the strategy we have been following in our study of the structure-reactivity relationship of cuprates, i.e. the chosen series fulfills a number of important criteria:



- i. the series comprises all stages encountered during preparation of the cuprate reagents.
- ii. The compounds are formed in high yields, i.e. they are not minor products such as are encountered in the reactions of, for example, RLi with CuBr to form " RCu " or " R_2CuLi ";
- iii. They can be isolated pure thus allowing careful structural characterizations (X-ray, NMR, mol. wt. determinations);
- iv. The compounds have sufficient thermal stability in solution to enable multinuclear NMR spectroscopic study over a sensible temperature range,

i.e. not only the structure but also the dynamic behaviour in solution of these compounds can be studied;

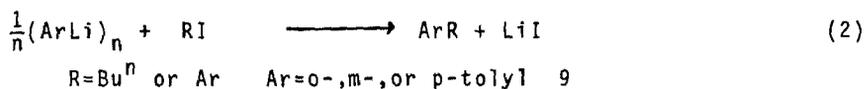
- v. The compounds have acceptable solubilities in different solvents, e.g. in Et₂O and C₆H₆, which allows study of the effects of the different preferences of Li and Cu towards ether coordination on the stability of the cuprate species.
- vi. Comparison of series A and B (Figure 1) may provide insight into the effect that a potentially coordinating substituent in the ortho-position of the C-M bond has on the structural and bonding features of cuprates. This information is relevant, because the cuprates used in organic synthesis often contain such coordinating substituents (8). In the following sections some recent results of our studies in this area will be discussed in the broader context of the understanding of the structure and reactivity of cuprates.

Synthetic Aspects

Since the isolation of *pure* aryllithium, -metal IB and -ate complexes thereof seems not to be a trivial affair (9) a short outline of the synthetic routes we are following will be given below.

A. Aryllithium Compounds (12)

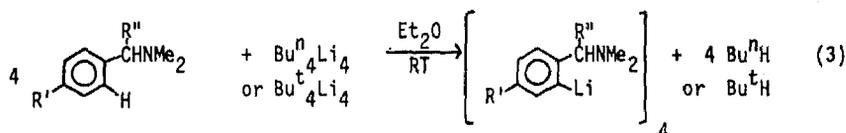
Pure, i.e. lithium salt-free (9), aryllithium compounds of the series B have been obtained by using the iodide-lithium exchange reaction 1 in apolar solvents (13).



The aryllithium compound crystallizes out from the reaction solution while secondary products (BuⁿI) remain dissolved. The cross-coupling reaction 2, which is a potential source of LiI, is blocked in hexane.

Reaction 1 is specific for aryl iodides. The corresponding aryl bromides only metallate in ether solvents but then reaction 2 also takes place and formation of LiBr interferes with the isolation of the pure, salt free, aryllithium compounds (*vide infra*).

The aryllithium compounds with the CH(Rⁿ)NMe₂ ortho-substituent (series A) are synthesized via the hydrogen-lithium exchange route 3 (11,12). This reaction, which in the case of Rⁿ=H takes about 19 h for completion when BuⁿLi is used, is extremely clean (only butane is formed).



R' = H(a) or Me(b)
R'' = H, Me, Et, Prⁱ or Bu^t

Reaction times:

For R'' = H: BuⁿLi 19 h
Bu^tLi 5 min.

When using arenes, RH, containing a benzylic substituent R'' of increasing size (see eqn. 3) we have recently found that the reaction slows down in the series R'' = H >> Me >> Et while no metallation is observed for R'' = Prⁱ or Bu^t (14).

Furthermore, in the case of R'' = Me we have found evidence that mixed (aryl)_{4-n}-(butyl)_nLi₄•RH_n intermediates are present in solution which leads to a mixture of inseparable aryllithium compounds. The latter problem can be solved by using the more basic tert.-butyllithium reagent. For R'' = H, Me or Et solutions of the pure aryllithium compounds were obtained in extremely short reaction times (5 minutes) (14).

B. Arylmetal IB Compounds (3)

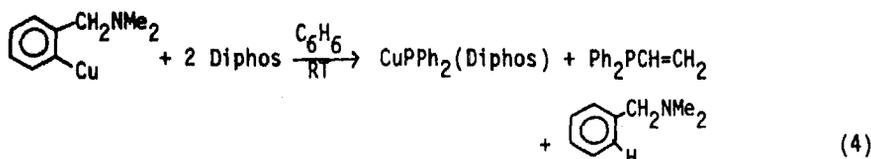
General requirements for the successful synthesis and isolation of pure, uncomplexed, arylmetal IB compounds of both series A and B are:

- i. the use of pure aryllithium compounds which may contain lithium halides but must be free from other metal halides or other ligands,
- ii. the correct order of addition of the metal IB halides or complexes and the aryllithium compounds and
- iii. the use of exact 1/1 molar ratios of the reagents as well as the appropriate reaction temperatures.

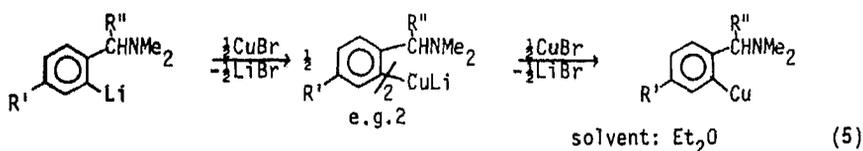
There is ample evidence that most of the arylmetal IB compounds can react with metal halide salts (3,15,16). The latter salts may be present as a result of the applied transmetallation reaction (when Grignard or organozinc reagents are used) or because excess of metal halide is applied.

These metal salts are often not present as separable contaminants but instead are integral parts of the polynuclear structures of these arylmetal IB compounds: e.g. in Cu₆Br₂(C₆H₄NMe₂-2)₄ (16) or in Cu₄Br₂{(Z)-(2-Me₂NC₆H₄)C=C(Me)-(C₆H₄Me-4)}₂ (17).

The presence of additional ligands (cf. i) may lead to ionic compounds: e.g. [(mesityl)₂Cu]⁻[CuDiphos₂]⁺ (18) or to secondary cleavage reactions, see eqn. 4 (19).

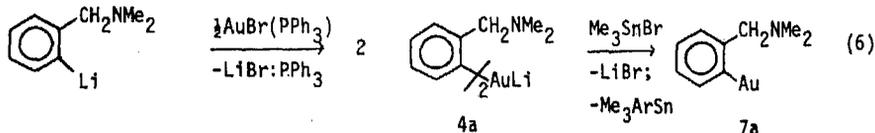


A synthesis in which the order of addition of the reagents is important is given in eqn. 5 (15):



For the synthesis of the arylcopper compounds of series A it is necessary to add the ether insoluble CuBr to the aryllithium solution or suspension. The reactions for R''=H or Me proceed via the ether soluble copper lithium complexes, e.g. 2, to give finally the less soluble arylcopper compounds when the Li/Cu ratio reaches unity. In contrast, reversed addition leads to direct formation of insoluble, stable arylcopper-copper bromide coordination polymers, e.g. Cu(C₆H₄CH₂NMe₂-2)·nCuBr (15), from which the pure arylcopper species can not be isolated.

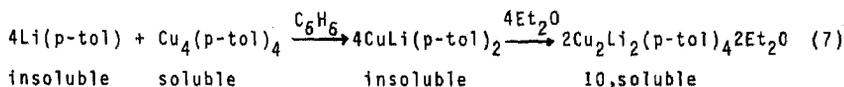
The synthesis of the arylgold(I) compounds 7 is interesting because here we take advantage of our knowledge that the arylgold lithium compounds of type 4 do not react with, for example, phosphines (20). Accordingly, to prepare pure 7a, 4a is isolated first and then reacted with Me₃SnBr to give the ligand free arylgold species 7a; see eqn. 6 (20):



Detailed experimental descriptions for the preparations of the other compounds can be found in the papers cited in reference 3.

C. Bis(aryl)metal IB lithium (-ate) Complexes

The ate complexes 2-4 (11,20,21), 10 (22) and 11 (22) can be formed directly from the 2/1 reaction of the aryllithium complexes and the appropriate metal IB salts (cf. eqns. 5 and 6). However, the preferred route leading directly to solutions of the pure ate complexes is the 1/1 reaction of the pure aryllithium and arylmetal IB complexes. For example, mixing p-tolylithium (vide infra) and -copper in a 1/1 molar ratio in benzene leads to the formation of the insoluble ate complex CuLi(p-tolyl)₂. On addition of exactly one equivalent of diethyl ether the latter complex dissolves completely in benzene forming 10 (22):



Similar observations were made during the synthesis of the corresponding gold(I) lithium species *11*.

The ate complexes *2-4* have likewise been prepared by the 1/1 reaction of the tetranuclear aryllithium and arylmetal IB compounds in benzene or toluene. These ate complexes are very soluble in both ether and aromatic solvents.

Structural Aspects

A. Aryllithium Compounds

Until recently little was known concerning the structures of aryllithium compounds (9b,23). For $\text{Li}(\text{C}_6\text{H}_3\text{CH}_2\text{NMe}_2-2-\text{Me}-5)$, *1b*, a tetranuclear structure in benzene was proposed based on cryoscopic molecular weight measurements (10,11). This proposal is now supported by the crystal structure (10) of *1a* shown schematically in Figure 2. The similarities of this structure with those of a subsequently reported unsubstituted phenyllithium-etherate, *13* (9b), are striking. (see Figure 2). In both compounds the aryl groups are four center, two electron bonded to a Li_3 face of the central Li_4 tetrahedron. Accordingly each Li atom takes part in three electron-deficient Li-C interactions using orbitals which are in a trigonal planar arrangement. Additional electron donation of a nitrogen lone pair of the well-positioned intramolecular ligand in *1a*, occurs to an empty Li orbital perpendicular to the

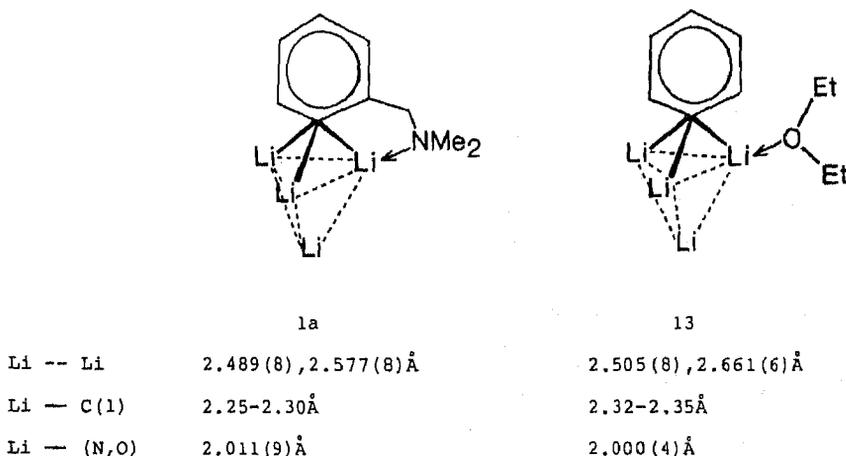
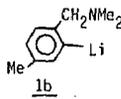
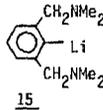
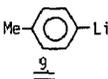


Figure 2. Schematic structures of *1a* (10) (involving intramolecular N donor coordination) and of the unsubstituted phenyllithium-etherate *13* (9b) (with O donor coordination of the diethyl ether molecule). Only the occupation of one triangular Li_3 face by the aryl ring is shown.

latter trigonal plane. In the unsubstituted phenyllithium structure the role of this N donor atom is taken over by an oxygen lone pair of the coordinated ether molecule. Power showed that LiBr can be incorporated into the polynuclear structure of phenyllithium. In $(\text{PhLi}\cdot\text{OEt}_2)_3\text{LiBr}$ one bridging phenyl group has been replaced by a four center bonded Br anion (9b).

Table I
Some Natural Abundance ^{13}C and ^6Li NMR Data of Some Aryllithium Compounds in Toluene- d_8 ^a

Compounds	Pure ^c	Et ₂ O		THF ^d		TMEDA
		1 eq.	excess	1 eq.	excess	
i. A series						
	176.0(12) ^e [3.58] Tetramer	N.C. ^f	N.C. ^g	189.2(20) ^{h,i} [2.74] Dimer		189.4(20) — Dimer
	189.3(20) ^h [2.41] Dimer	N.C.	N.C.	N.C.	N.C.	N.C.
ii. B series						
	Insol.	174.6(~11) ^e [1.93] Tetramer	174.7(~11) ^e [1.90]	175.9(~11) ^e [2.01] Tetramer	188.7(19.5) ^h [1.47] Dimer	186.8(19.5) ^h [1.47] Dimer
	Insol.	170.2(~11) ^e [1.80] Tetramer	170.9(~11) ^e [1.90]	171.3(11) ^e [2.17] Tetramer	178.7(20) ^h Dimer	182.8(20) ^h [1.89] Dimer
	Insol.	Insol.	182.8 [1.98]	185.5 [1.70]	188.1(20) ^h [1.38] Dimer	189.3(20) ^h [1.72] Dimer

^aChemical shift data: on first line $\delta^{13}\text{C}$ with $J(^{13}\text{C}(1), ^7\text{Li})^b$ between brackets, on second line $\delta^6\text{Li}$ (ppm relative to 70% LiCl in D_2O external) and on third line assignment of these data in terms of a structure. Spectra unless otherwise indicated recorded at 293 K.

^bExpected multiplicity for $^{13}\text{C}(1)$ in a two center, two electron bond, four equidistant lines (~40 Hz) of equal intensity; in a three center, two electron bond (*dimer*), seven lines (~20Hz) with 1:2:3:4:3:2:1 intensities and in a four center, two electron bond (*tetramer*), ten lines (11 Hz) with 1:3:6:10:12:12:10:6:3:1 intensities.

^cPure in toluene- d_8 .

^dAdded to the toluene- d_8 solutions as THF- d_6 . Excess is up to three equivalents.

^eLinewidth of 110 Hz which points to a $J(^{13}\text{C}(1), ^7\text{Li})$ of about 11 Hz, i.e. with four center, two electron bonding.

^fN.C. no change of the NMR data reported in the previous column: i.e. no change of the structural features.

^gAlso in pure Et₂O.

^hSeven line pattern, see footnote b.

ⁱOnly one half of **I** has been converted into the dinuclear species **14**, see eqn. (8). Data of the dimer **14** are given.

^j**I** has been completely converted into **14** after addition of two equivalents of THF- d_6 .

clusters in general. Since an uncoordinated CH_2NMe_2 ortho substituent can clearly be seen to produce a very bulky aryl group a tetrameric aggregate would in the first instance be anticipated to be less favoured than a dinuclear unit. Indeed, the structure of *1a* shows that N–Li coordination compensates for the steric bulk a free CH_2NMe_2 group otherwise would represent. In contrast, the structure of *14* shows that in case the solvent molecules take over from N coordination, the dinuclear structures (with three center, two electron bonded aryl groups) have bridging configurations that provide room for the free CH_2NMe_2 substituent, i.e. those rotamers that have the aryl's plane close to or exactly perpendicular to the Li...Li axis. It must be expected that it is also this aryl orientation which provides optimum orbital interaction in a three center, two electron $\text{C}(1)\text{Li}_2$ bond, cf, ref. 30a.

This novel idea concerning the influence of ortho substituents on the aggregate stability of aryllithium compounds is further substantiated by the following observations:

- i. The presence of two ortho- CH_2NMe_2 substituents as in *15* (see Table 1) stabilizes the dinuclear aryllithium structure. The aryl groups are three center, two electron bonded to the Li_2 pair like in *14* (For a figure, see ref. 10). Both N donor atoms coordinate to lithium. Their excellent positioning for this coordination is reflected by the fact that neither Et_2O nor THF can compete for the coordination sites at the Li atoms.
- ii. The preference for the dinuclear structure in the presence of coordinating solvents is less pronounced for unsubstituted phenyllithium. Even for o-tollythium equilibrium mixtures of the tetra- and dinuclear aggregates are observed at low temperature. However, when two ortho groups are present, as in xylyllithium, tetranuclear aggregates can not be detected at all and in THF the dinuclear aggregate $\text{Li}_2(\text{xylyl})_2 \cdot 4\text{THF}$ is observed.

Full details of this study will be published shortly (14).

B. Arylmetal IB Compounds (3)

Structural data in the solid exist for $\text{Cu}_4(\text{C}_6\text{H}_3\text{CH}_2\text{NMe}_2-2-\text{Me}-5)_4$, *5b*, and a schematic structure is shown in Figure 3. The actual structure contains the four copper atoms in a butterfly arrangement with a short bridged Cu...Cu distances of 2.37 Å (3,31). The aryl groups are three center, two electron bonded and the N donor atoms coordinate only weakly to the Cu centers.

Reasons for the observed differences in stereochemistry at C(1) (i.e. 4c,2e vs. 3c,2e bridging in *1* and *5b*, respectively) and at the metal atoms between these aryllithium and -copper(I) species are not apparent. Earlier we proposed (10) as a possible factor the much stronger preference of Li for N coordination that would thus stabilize the Li_4C_4 core of *1*. This explanation seems now to have been rendered invalid by the recent structure of unsubstituted phenyllithium etherate (13) and the

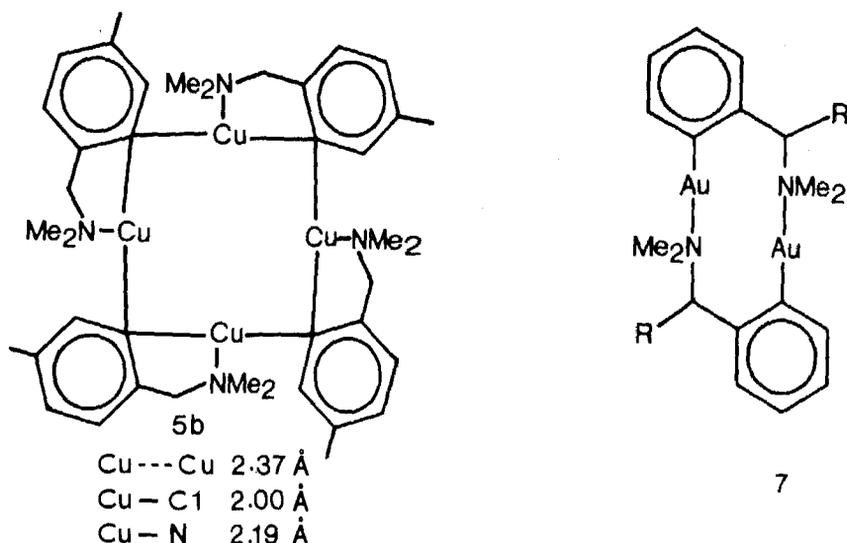


Figure 3. Schematic structures of two arylmetal IB compounds **5b** (for X-ray see ref. 31) and **7** (20).

results of our NMR study of the solution behaviour of various aryllithium compounds, vide supra.

Comparison of the known aryllithium and -copper structures shows that although both Li and Cu(I) have vacant *s* and *p* orbitals for bonding it is the Li atom which favours the higher number of bonding interactions, cf. Figures 2 and 3. This is a generally observed phenomenon since tetrahedral structures (with four center, two electron bonded organo groups) for various other alkyl- (24) and alkynyllithium (26) compounds have also been reported. In contrast in most of the known arylcopper(I) structures (as well as $\text{Cu}_4(\text{CH}_2\text{SiMe}_3)_4$) (32) the copper(I) atoms show linear bonding and three center, two electron bonded aryl groups, e.g. in $\text{Cu}_5(\text{mesityl})_5$ (33), while in a few cases three bonding interactions are present, e.g. in **5b** and in $\text{Cu}_6\text{Br}_2(\text{C}_6\text{H}_4\text{NMe}_2-2)_4$ (16).

It must be noted that in a three center, two electron bonding situation the aryl ring is perpendicular to the Cu...Cu axis. This is the groundstate situation especially preferred when ortho-substituents are present because in this rotamer the interaction between these substituents and the bridged Cu atoms is at its minimum, see discussions in refs. 3 and 34. Accordingly, it is not the (weak) (34b) coordination of the donor atom with the Cu atom that stabilizes the Cu-C bond in **7**. It is more particularly the bulkiness of this ortho-substituent which stabilizes the perpendicular rotamer and thus the C(1)Cu₂ bonding. This is nicely reflected in the structures of recently reported mesityl metal IB compounds. Both linear bonding at each metal IB atom and the perpendicular mesityl groups are present and this leads to the flat $\text{M}_n\text{C}(1)_n$ (*M*=Cu, Ag or Au) cores in these $\text{M}_n(\text{mesityl})_n$ structures (33).

Finally it is tempting to speculate as to whether the structure of $\text{Li}_4(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$, **1a**, mimics the transition state of an intramolecular exchange route for the aryl groups in $\text{Cu}_4(\text{C}_6\text{H}_3\text{CH}_2\text{NMe}_2-2-\text{R}-5)_4$, **5**. This process would involve folding of the butterfly Cu_4 arrangement into a tetrahedral one (cf. **1a** in Figure 2) and concomitant change of the aryl bonding from a three center, two electron into a four center, two electron one. The reversed process, but now involving opening of a different set of Cu_2 edges, would lead to intramolecular exchange.

The aryl silver species (**6**) have most probably Ag_4R_4 structures similar to those found for the corresponding copper compounds **5**. The gold compound $\text{AuC}_6\text{H}_4\text{CH}_2\text{NMe}_2-2$, **7**, has a dinuclear structure. Based on molecular weight measurements, ^1H and ^{13}C NMR data and on ^{197}Au Mössbauer data the structure shown in Figure 3 has been proposed (20).

C. Arylmetal IB Lithium (Ate) Compounds

The tetranuclear structures, $\text{M}_2\text{Li}_2\text{R}_4$, have been proposed for the neutral ate compounds **2-4**, **10** and **11** in solution (see Figure 4) on the basis of molecular weight data (cryoscopic in benzene) as well as ^1H and ^{13}C NMR data (10,11,20,30b).

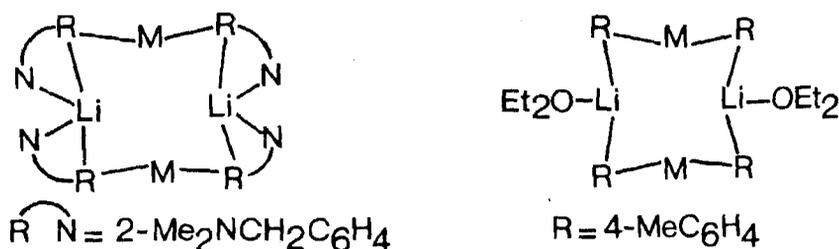


Figure 4. Schematic structures of A **2-4** and B **10,11** series complexes in solution.

In particular the ^{13}C NMR spectra of the $\text{Ag}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$ **3a** compound in toluene- d_8 provided definite proof for the three center, two electron bonding of each aryl group via C(1) to a AgLi pair. Figure 5 shows a recently recorded ^{13}C NMR spectrum of **3a** using the J modulated ECHO sequence (49) which allows a pairwise discrimination of the C, CH, CH_2 and CH_3 ^{13}C nuclei in the structure and thus a complete assignment (35). An interesting feature is the multiplicity of C(1) as a result of $J(^{107}\text{Ag}, ^{13}\text{C}(1))$, $J(^{109}\text{Ag}, ^{13}\text{C}(1))$, and $J(^7\text{Li}, ^{13}\text{C}(1))$ (see also ref. 21).

Furthermore, $J(^{107,109}\text{Ag}, ^{13}\text{C})$ (36) is also present on C(2), C(6) and even on the benzylic C resonance.

The ^{109}Ag INEPT NMR spectrum (37) using the $^3J(^{107,109}\text{Ag}, ^1\text{H}(6))$ (-7.1 Hz) (21) is shown in Figure 6a. It reveals a single line which is in accord with the proposed structure in which $\text{Ag}\dots\text{Ag}$ interactions are absent (38) The coupling pattern of

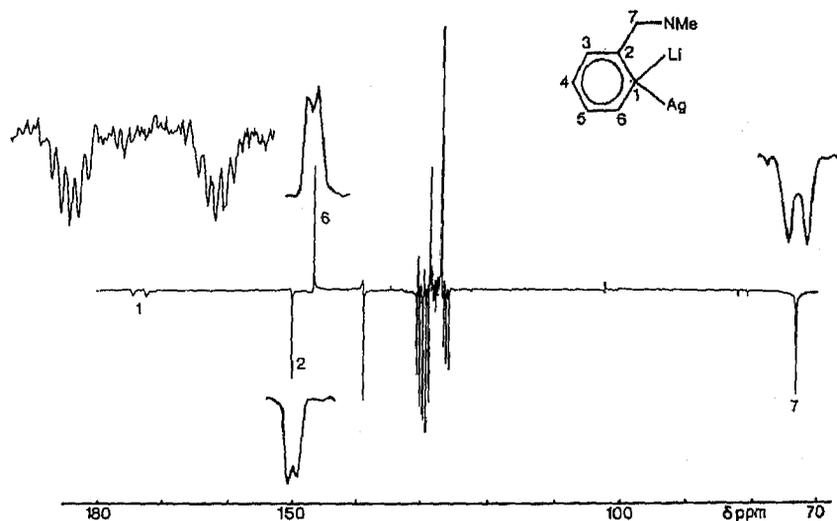


Figure 5. J modulated ECHO ^{13}C NMR spectrum of $\text{Ag}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$ **3a** at 293 K. $J(^{109}\text{Ag}, ^{13}\text{C}(1))$ is 136.0 ± 0.8 ; $J(^7\text{Li}, ^{13}\text{C}(1))$ is 7.2 ± 0.2 Hz.

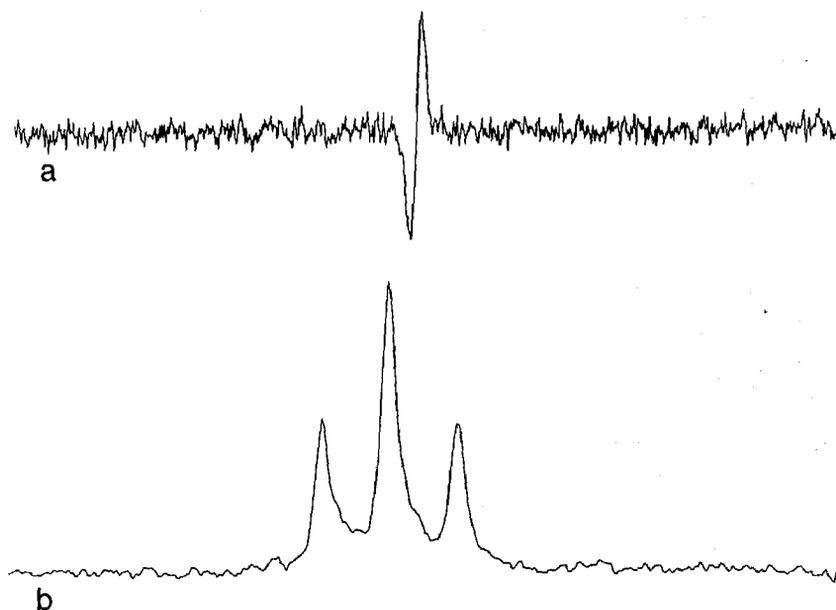


Figure 6. a. ^1H coupled ^{109}Ag INEPT NMR spectrum of **3a** in toluene- d_8 at 293 K. $\delta^{109}\text{Ag}$ is 897.7 ppm (1 M $\text{AgNO}_3/\text{D}_2\text{O}$ external reference). b. ^6Li NMR spectrum of **3a** in toluene- d_8 at 293 K. $\delta^6\text{Li}$ is -0.10 ppm (1M $\text{LiCl}/\text{D}_2\text{O}$ external reference), $J(^{107,109}\text{Ag}, ^7\text{Li})$ is 3.91 and $J(^{107,109}\text{Ag}, ^6\text{Li})$ is 1.46 Hz.

^{109}Ag with Li is not observed because of line broadening of the Ag resonance due to small long range $^{109}\text{Ag}-^1\text{H}$ couplings and to the multiplicity of the $^{109}\text{Ag}-^6\text{Li}$.

However, when we recorded the ^6Li NMR spectrum of **3a** the triplet pattern shown in Figure 6b was obtained. The 1:2:1 intensity ratio arises from coupling of the Li nuclei with two neighboring $^{107,109}\text{Ag}$ (38) nuclei (vide infra).

The importance of these results goes beyond the confirmation of the structural features of these ate complexes in solution. It demonstrates clearly the power of the multinuclear NMR approach for the study of cluster structures in solution. Even in the present case where a heavy metal nucleus like Ag with a low γ value (e.g. γ ^{109}Ag is -1.2449) is involved.

After many attempts (39) we succeeded in growing single crystals of the cuprate **2a** and aurate **4a**, which were suitable for an X-ray structure determination. Both structures are shown in Figure 7 together with some relevant bond distances and angles.

To our knowledge these structures are the first examples of a structural investigation of a neutral cuprate with characteristic 1/1 Cu/Li atomic ratio (see Introduction) as well as of a neutral aurate. Two other cuprate structures have been reported, i.e. $[\text{Cu}_5\text{Ph}_6][\text{LiTF}_4]$ which in fact is an anionic arylocopper structure (7b,41) and $[\text{Li}_2\text{Cu}_3\text{Ph}_6]_2[\text{Li}_4\text{Cl}_2(\text{Et}_2\text{O})_{10}]$ in which the Cu/Li ratio in the anionic cluster is 3/2 (7a). The present discussion will be concentrated on the structural features of the cuprate **2** in the solid because the aurate **4** has been the subject of a recent communication (42).

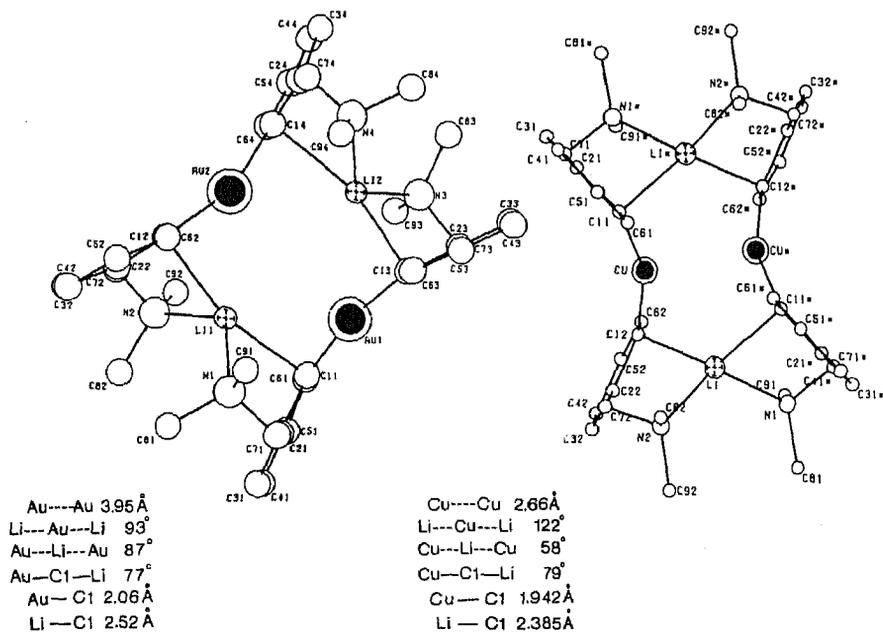


Figure 7. Structures of the neutral cuprate **2a** and aurate **4a** in the solid. \odot is the metal IB nucleus and \oplus the lithium.

The copper and lithium atoms in **2** are in one plane with Cu–Li distances of 2.755 Å (mean). The aryl groups each bridge a CuLi pair with expected Cu–C(1) and Li–C(1) bond lengths (see Figure 7). These values are comparable with those distances found in the $\text{Cu}_3\text{Li}_2\text{Ph}_6$ anion (**7a**) (Cu–C(1) 1.923 Å and Li–C(1) 2.240 Å). The four N-donor atoms are exclusively coordinated to lithium with a Li–N distance of 2.139(6) Å.

The bridging configuration of the aryl groups in the various homonuclear aryllithium and -copper compounds is essentially perpendicular (about 80–85°) to the M...M vectors. This has also been found for the $[\text{Cu}_3\text{Ph}_6]$ -anion in which the aryl groups are likewise bridging equivalent metal atoms. The symmetric configuration of the metal-aryl-metal bridges is as expected from the proposed bonding scheme (see Figure 8: A and B): (31,34b) i.e., a combination of three center interactions consisting of the two metal centers and the carbon sp^2 orbital (A) and an antibonding combination of the metal orbitals and the carbon p orbital (B). It is the contribution of the latter interaction B which stabilizes the aryl- M_2 bonding (cf. the role of ortho-substituents in aryllithium and -copper compounds).

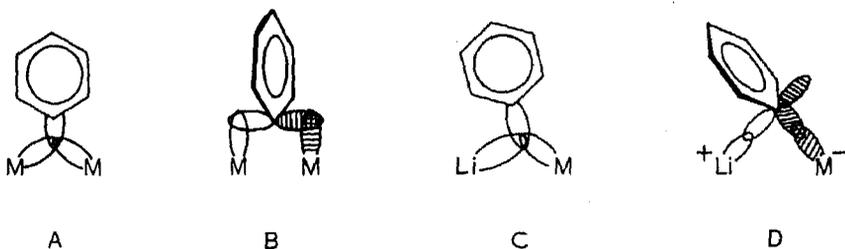


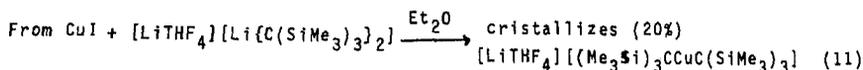
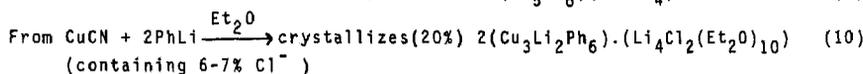
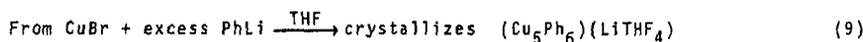
Figure 8. The various bonding interactions of the aryl C(1) sp^2 and metal orbitals $\text{M}=\text{Cu}(\text{I}), \text{Ag}(\text{I})$ or $\text{Au}(\text{I})$.

The cuprate structure of **2** shows a less symmetric configuration for the aryl bridges. This is as expected when the different orbital sizes and energies of copper and lithium are taken into account. The tilting of the aryl ring into the direction of the lithium indicates a better overlap of the carbon sp^2 and copper orbitals (C). However, it must be noted that any contribution of interaction C still implies a bonding between the carbon sp^2 and lithium orbitals. This is supported by the $J(^{13}\text{C}(1), ^7\text{Li})$ of 7.0 Hz indicating that s electron density is still present in the C–Li interaction of **2**. Furthermore, interaction C comprises a bonding combination of M and Li orbitals which is reflected by the $J(^{107,109}\text{Ag}, \text{Li})$ (see Figure 6) observed in the Li spectra of the neutral silver lithium compound **3**.

The same asymmetric bridging configuration for the aryl bridges has been found in $[\text{Cu}_3\text{Li}_2\text{Ph}_6]$ cuprate anion (**7a**) and it is plausible to assume that this will be a general feature of bridging organo groups (e.g. alkyls, aryls, alkynyls, etc) in cuprates. Accordingly, we propose that $\text{Cu}_2\text{Li}_2(\text{p-tolyl})_4 \cdot 2\text{Et}_2\text{O}$ (see Figure 4) has structural features similar to those observed for **2a** (see Figure 7): i.e. a planar Cu_2Li_2 arrangement with the p-tolyl groups asymmetrically bridging between Cu and Li. Since

coordinating substituents are absent coordination of a solvent molecule to each of the lithium centers is required. In this respect it is relevant to recall our observation described above for the dissolution of $\text{Cu}_2\text{Li}_2(\text{p-tolyl})_4$ in toluene on addition of 2 equivalents of diethyl ether (i.e. formation of $\text{Cu}_2\text{Li}_2(\text{p-Tol})_4 \cdot 2\text{Et}_2\text{O}$; see eqn. (7)). Strong coordination of these Et_2O molecules is indicated by the large ^1H NMR chemical shift changes of the ether's CH_2 and CH_3 protons (22). Likewise the structure of $\text{Cu}_2\text{Li}_2\text{Me}_4$ in Et_2O most probably consists of the same basic $\text{Cu}_2\text{Li}_2\text{C}(1)_4 \cdot 2\text{Et}_2\text{O}$ framework present in **2a**, i.e., a planar Cu_2Li_2 arrangement with the methyl groups bridging asymmetrically between Cu and Li via a three center, two electron interaction. It is interesting to note here that Pearson et al. (43) reported that using solution X-ray scattering data the Cu...Cu distances in $\text{Cu}_2\text{Li}_2\text{Me}_4$ in diethyl ether can be estimated at 4.4 Å. This is not at all in agreement with the Cu...Cu distance of 2.6660(8) Å (44) in our cuprate **2**, thus substantiating earlier questioning (47) of the interpretation of these X-ray scattering data.

There is strong evidence that in coordinating solvents the neutral lithium cuprate structure disintegrates. This is caused by solvent coordination of the free lithium cation which competes with the intramolecular stabilization of the cationic lithium centers in the neutral cuprate structures. This leads to the anionic cuprate species with Cu/Li ratios larger than one, see eqns. 9-11:



In the latter example (45) the monomeric linear structure with two center, two electron Cu—C bonding is most likely due to the steric bulk of the $\text{C}(\text{SiMe}_3)_3$ groups which prevents bridge bonding.

In a recent study (14) of the solution behaviour of $\text{Cu}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$, **2a**, we have found that in toluene the tetranuclear structure remains whereas in THF this complex also exists as an anionic $[\text{Cu}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_2]$ species with $[\text{LiTHF}_4]$ cations (46). However, on crystallization of **2a** from THF the tetranuclear species was recovered. These results indicate that the role of the N donors in the aryl cuprate **2a** on the structure is that of a well-positioned "intramolecular solvent" for which Li coordination has a favourable entropy factor.

Comparison of the cuprate and aurate structures **2a** and **4a**, see Figure 7, shows that the lithium-aryl-metal IB bridge becomes increasingly asymmetric going down the series Cu(I), Ag(I) to Au(I). For the Au(I) compound **4a** this aryl-metal interaction (in the solid) is better described as a two center, two electron aryl-gold(I) interaction; i.e. in this structure the aryl sp^2 lone pairs are almost exclusively bonded to the Au atoms (see Figure 8D). The lithium sites are the electropositive centers to which the

heteroatoms are coordinated. This bonding description is supported by the trend in ^6Li chemical shift data of the series $\text{M}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$, **2a-4a** (14).

In toluene- d_8 **2a-4a** give a single line whose chemical shift was temperature independent (-60 – 30°). Whereas $\delta^6\text{Li}$ of $\text{Li}_4(\text{C}_6\text{H}_3\text{NMe}_2-2-\text{Me}-5)_4$, was observed at 3.58 ppm the resonances of the ate complexes appeared upfield ranging from 0.35 for **2a**, -0.10 for **3a** to -1.25 ppm for the aurate **4a**. There is also a marked difference in $J(^{13}\text{C}(1), ^7\text{Li})$ values of these species, i.e., 7.0 **2a**, 7.2 **3a** and 4 Hz for the aurate **4a**. Both results strongly suggest that the lithium centers become increasingly cationic going from Cu(I) and Ag(I) to the Au(I) lithium species. However, further work is clearly needed to further substantiate these observations.

The neutral cuprate and aurate structures, **2a** and **4a**, are interesting models for, on the one hand, the reactive organocuprates and, on the other hand, the transient (organocuprate-substrate) species that are postulated (47) to be formed in reactions of simple organocuprates (e.g. $\text{Cu}_2\text{Li}_2\text{Me}_4$) with, for example, α,β -unsaturated ketones. Structural changes from C to D (see Figure 8) which enhance the nucleophilicity of the copper center are feasible with retention of the square-planar Li_2M_2 structure. The present results suggest that such ketones anchor via the O donor to the lithium center in the neutral cuprate. However, alternative mechanisms have been proposed and the results of a recent ^{13}C NMR study of the $\text{Cu}_2\text{Li}_2\text{Me}_4$ /t-butyl-cinnamate system were interpreted in terms of an initial formation of an olefin-copper(I) π -complex (48).

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$$\text{Cu}_4\text{R}_4 + \text{Cu}_4\overset{\text{C}_6\text{H}_6}{\text{R}}_4 \rightleftharpoons \text{Cu}_4\text{R}_3\overset{\text{C}_6\text{H}_6}{\text{R}} + \text{Cu}_4\text{R}_2\overset{\text{C}_6\text{H}_6}{\text{R}}_2 + \text{Cu}_4\overset{\text{C}_6\text{H}_6}{\text{R}}_3$$

5a **5b**
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