

Induction of Chirotopicity in the Self-Assembly Process of Heterocuprates: Structural and Stereochemical Aspects of Neutral $\text{CuLi}_2\text{BrAr}_2$ Aggregates

Claudia M. P. Kronenburg,[†] Cateljine H. M. Amijs,[†]
Johann T. B. H. Jastrzebski,[†] Martin Lutz,[‡] Anthony L. Spek,^{‡,§} and
Gerard van Koten^{*,†}

Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University,
Padualaan 8, 3584 CH Utrecht, The Netherlands, and Bijvoet Center for Biomolecular
Research, Crystal and Structural Chemistry, Utrecht University,
Padualaan 8, 3584 CH Utrecht, The Netherlands

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Self-assembling reactions of the *ortho*-diamine chelated aryllithium dimers of type $[\text{Li}(\text{C}\wedge\text{N}\wedge\text{N}')_2]$ with 1 equiv of CuBr resulted in the selective formation of hetero cuprates **1**, **2**, **3a**, and **3b**, respectively, which all have $[\text{CuLi}_2\text{Br}(\text{C}\wedge\text{N}\wedge\text{N}')_2]$ stoichiometry ($\text{C}\wedge\text{N}\wedge\text{N}' = \text{Ar}$, $[\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]^-$ (**1**); Naph , $[\text{1-C}_{10}\text{H}_6(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]^-$ (**2**); (*R*)- Ar , (*R*)- $[\text{C}_6\text{H}_4(\text{CH}(\text{Me})\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]^-$ (**3a**); or *rac*- Ar , *rac*- $[\text{C}_6\text{H}_4(\text{CH}(\text{Me})\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]^-$ (**3b**)). The structure of **1** and **2** in the solid state comprises $[(\text{C}\wedge\text{N}\wedge\text{N}')_2\text{Cu}]^-$ and $[\text{Li}_2\text{Br}]^+$ fragments which are joined by intramolecular *N,N*-chelation of the *ortho*-diamine ligand to lithium, thus forming an, overall neutral, 2:1 cuprate species. The coordinated benzylic nitrogen centers (N^{Me}) in these trinuclear CuLi_2 aggregates have a stable configuration, R_N or S_N . In fact, **1** and **2** exist in the solid state as $R_N R_N$ and $S_N S_N$ diastereoisomers, respectively. Accordingly, the halocuprates **1** and **2** can serve as model complexes for investigation of the structure of corresponding 2:1 cyanocuprates in solution. Reactions of both **1** and **2** with excess CuBr results in the formation of mixed $(\text{C}\wedge\text{N}\wedge\text{N}')\text{-Cu-CuBr}$ aggregates of formula $[\text{Cu}_3\text{Br}(\text{C}\wedge\text{N}\wedge\text{N}')_2]$ and $[\text{Cu}_4\text{Br}_2(\text{C}\wedge\text{N}\wedge\text{N}')_2]$, respectively. Interestingly, multinuclear NMR spectra of **3a** and **3b** are similar and show only one resonance pattern for the aryl ligands, which resembles that of **1** and **2** in solution. From this it follows that **3a** possesses either a $R_C S_N, R_C S_N$ or a $R_C R_N, R_C R_N$ configuration. Consequently, cuprate **3b** is formed as either the $S_C R_N, S_C R_N / R_C S_N, R_C S_N$ or the $R_C R_N, R_C R_N / S_C S_N, S_C S_N$ enantiomeric pair. The formation of cuprates **3a** and **3b** provides excellent examples of highly specific enantioselective recognition during the self-assembly of aryllithium and -cuprate species containing an *ortho*-diamine chelating $\text{C}\wedge\text{N}\wedge\text{N}'$ -type of ligand.

Introduction

The building-up of discrete molecular entities from smaller units is interesting because such assemblies may show interesting chemical, physical, or mechanical properties.¹ Self-assembling processes may involve either metal-,² ligand-,³ or anion-assisted⁴ assembly to supramolecular architectures. Many of the polynuclear

ligands used in these processes contain a multidentate functionality in which nitrogen or oxygen atoms act as potential binding sites.

Most of the metal assemblies reported so far^{2,3} belong to the class of coordination compounds. Examples of organometallic assemblies in which metal-to-carbon bonds are present are still relatively scarce.⁴ The development of monoanionic bi- or terdentate ligands of the type $\text{C}\wedge\text{N}$ ($[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]^-$), $\text{N}\wedge\text{C}\wedge\text{N}$ 'pincer' ($[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]^-$), or $\text{C}\wedge\text{N}\wedge\text{N}'$ ($[\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]^-$) (cf. Figure 1) in our group allowed the synthesis of stable, well-defined transition metal and main-group metal complexes containing metal-to-

* To whom correspondence should be addressed. E-mail: g.vankoten@chem.uu.nl. Fax: +31 30 252 3615.

[†] Debye Institute.

[‡] Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry.

[§] To whom correspondence on crystallographic studies should be addressed.

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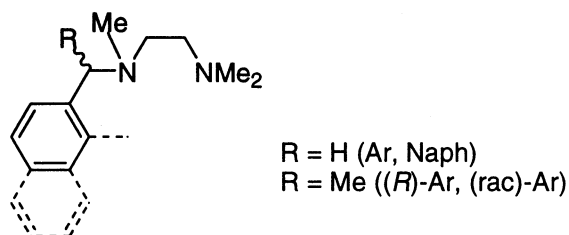


Figure 1. Selected monoanionic diamine chelating aryl ligands of type $C^A N^A N'$. Either enantiomerically pure R or racemic $C^A N^A N'$ ($R = Me$) has been used: throughout the text the configuration of the benzylic carbon atom is labeled with either R_C or S_C , while the configuration of the coordinated benzylic nitrogen atom is labeled with either R_N or S_N .

carbon bonds.⁵ We^{6,7} and others⁸ have shown that the built-in coordination properties of these (di)amine chelated aryl ligands play a dominant role in the formation of well-defined polynuclear aryllithium and -copper assemblies. The known structures of $Li_2(C^A N^A N')$ ⁶ and $Cu_3Br(C^A N^A N')$ ⁷ show that the combination of two monomeric $Li(C^A N^A N')$ units into one dimer and of a $[(C^A N^A N')_2 Cu]^-$ anion with a $[Cu_2 Br]^+$ cation into one monomer will lead to the formation of stereoisomers as a result of Li–N or Cu–N coordination. As a result of this coordination, the benzylic nitrogen atoms (N^{Me}) of the $(C^A N^A N')$ ligand become stereogenic. Relevant for the present study is that whereas $Cu_3 Br(C^A N^A N')$ ₂ can exist in two possible enantiomeric pairs of diastereoisomers, only the $R_N R_N / S_N S_N$ enantiomeric pair is formed (vide infra for a stereochemical analysis). This indicates that these diastereoisomeric aggregates, which are formed under thermodynamic control, have considerable energy differences.

In our studies of the monoanionic C,N - and S,N -chelating ligands $[C_6H_4(CH_2NMe_2)_2]^-$ and $[SC_6H_4(CH_2NMe_2)_2]^-$, we have explored the effect of the introduction of a stereogenic benzylic C atom in these ligands, via vicinal interactions, on the coordination of the NMe_2 group.⁹ The approach of stabilizing the various stereoisomers in polynuclear aryl–copper and –cuprate aggregates by intramolecular metal–nitrogen coordination has been used by our group since 1979.¹² For example, the chiral, tetranuclear organocopper compound (*S*)- $[(Cu_4\{C_6H_4(CH(Me)NMe_2)_2\}_4)]$ and the corresponding -ate compounds (*S*)- $[M_2Li_2\{C_6H_4(CH(Me)$

$NMe_2)_2\}_4]$ ($M = Cu, Ag, Au$) selectively self-assemble in unique copper- or metal-lithium aggregates. This illustrates the profound influence of chiral *ortho*- $CH(Me)NMe_2$ substituents on the stereochemistry of the resulting arylmetal aggregate (induction of chirotopicity).¹² This induction of chirotopicity concept also could lead to stereoselective self-assembly in organolithium and heterocuprate chemistry. To this end we recently prepared the chiral, monoanionic diamine chelating aryl ligands (*R*)- $[C_6H_4(CH(Me)N(Me)CH_2CH_2NMe_2)_2]^-$ ((*R*)-Ar) and its racemic form (*rac*-Ar)¹³ as well as two achiral analogues ($[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)_2]^- = Ar^6$ and $[C_{10}H_6(CH_2N(Me)CH_2CH_2NMe_2)_2]^- = Naph^7$) (see Figure 1, abbreviated as $C^A N^A N'$) and applied them to the synthesis of organoheterocuprate compounds.

We here report the synthesis of novel cuprates of type $[CuLi_2Br(C^A N^A N')_2]$ (**1–3**) with the monoanionic aryl ligands ($[C_6H_4(CH(R)N(Me)CH_2CH_2NMe_2)_2]^-$ ($R = H$ (Ar), (*R*)-Me ((*R*)-Ar) or *rac*-Me (*rac*-Ar)) or $[C_{10}H_6(CH_2N(Me)CH_2CH_2NMe_2)_2]^-$ (Naph)). The cuprate $[CuLi_2BrAr_2]$ **1** seems to act as an intermediate in the formation of $[Cu_3BrAr_2]$, which is a bis(organocopper) copper bromide aggregate.⁷ Also, **1** can be seen as a model for 2:1 cyanocuprates. Previous findings in our group on selective decomposition of well-defined mixed organocopper aggregates of type $[Cu_4Br_3Ar_2]$, $[Cu_4Br_3Naph_2]$,⁷ and $[Cu_6Br_2Aryl_2]$ (aryl = $[C_6H_4(CH_2NMe_2)_2]^-$)¹⁴ into biaryl derivatives point to a possible role of such aggregates in aryl-to-aryl coupling reactions.¹⁵ Also, we report that self-assembly of a cuprate compound of formula $[CuLi_2Br(C^A N^A N')_2]$ from the (a)chiral and racemic aryllithium derivatives with CuBr results in transfer of the chosen chirality of the benzylic carbon atom in the $C^A N^A N'$ ligand to its neighboring epimeric N(Me) center.

Results

Preparation of Mixed 2:1 Aryl- and Naphthylbromocuprates $[CuLi_2BrAr_2]$ (1**) and $[CuLi_2BrNaph_2]$ (**2**) (Ar = $[C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)_2]^-$, Naph = $[1-C_{10}H_6(CH_2N(Me)CH_2CH_2NMe_2)_2]^-$).** The heterogeneous reaction of dimeric $[LiAr]_2$ with CuBr in exact 2:1 molar ratio, based on the monomeric aryllithium complex, in Et₂O at –30 °C affords the 2:1

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(9) For example, the enantioselectivity arising in reactions catalyzed by (*R*)- $[CuSc_6H_4(CH(Me)NMe_2)_2]_2$ (1,4-addition)¹⁰ and (*R*)- $[ZnSc_6H_4(CH(Me)NMe_2)_2]_2$ (alkyl reduction of C=O)¹¹ was ascribed to induction of chirotopicity from the benzylic stereogenic center, via the coordinated NMe_2 group, to the catalytically reactive metal center.

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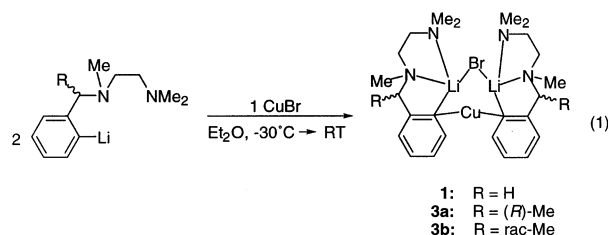
(12) In the case of the enantiomerically pure organocopper aggregate (*S*)- $[Cu_4\{C_6H_4(CH(Me)NMe_2)_2\}_4]$, selective formation of diastereoisomeric tetranuclear copper aggregates with either α - or β -helicity as a result of intramolecular Me_2N -copper coordination has been observed. When the bridging C_{1ps} atom of the unsymmetrically substituted aryl ring is bonded via a 3c-2e bond to two different metal atoms, the C_{1ps} atom turns into a chiral center. The butterfly arrangement of the Cu_4 core in combination with the distinct chirality at the benzylic carbon center gives rise to two helicity forms, α and β . NMR studies point to a loss of the helicity as a chiral element at room temperature. See also: (a) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1979**, *101*, 6593. (b) van Koten, G.; Jastrzebski, J. T. B. H. *Tetrahedron* **1989**, *45*, 569. (c) van Koten, G.; Leusink, A. J.; Noltes, J. G. *Chem. Commun.* **1970**, 1107. (d) van Koten, G.; Noltes, J. G. *Chem. Commun.* **1972**, 940. (e) van Koten, G.; Jastrzebski, J. T. B. H.; Müller, F.; Stam, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 697. (f) van Koten, G.; Jastrzebski, J. T. B. H. *J. Am. Chem. Soc.* **1984**, *106*, 1880.

(13) (*R*)- and (*rac*)- $[LiC_6H_4(CH(Me)N(Me)CH_2CH_2NMe_2)_2]_2$ were prepared according to the procedure reported for $[LiC_6H_4(CH_2N(Me)CH_2CH_2NMe_2)_2]_2$,⁶ starting from the corresponding bromo compounds and *n*-BuLi.

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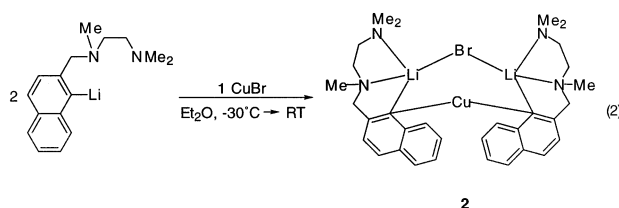
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organocuprate lithium bromide aggregate $[\text{CuLi}_2\text{BrAr}_2]$ (**1**) as the only reaction product (eq 1).



Complex **1** is an off-white, air- and moisture-sensitive solid, which is very soluble in benzene, toluene, and THF, but poorly soluble in Et_2O and almost insoluble in pentane or hexane.

Similar reaction of the more bulky naphthyllithium derivative $[\text{LiNaph}]_2$ with CuBr gives the analogous 2:1 naphthylcuprate lithium bromide (**2**) (eq 2). Cuprate **2**



shows the same solubility properties as **1**. When stored in a nitrogen atmosphere, solutions of **1** and **2** in benzene or toluene are stable at room temperature for at least several days. The release of poorly soluble lithium bromide during this storage has not been observed. In the solid state, both **1** and **2** readily turn green upon exposure to air. These novel compounds were fully characterized by elemental analysis, single-crystal X-ray structure determinations, and NMR spectroscopy.

Synthesis of Chiral and Racemic 2:1 Aryl-cuprates $[\text{CuLi}_2\text{Br}(\text{R})\text{-Ar}_2]$ (3a**) and $[\text{CuLi}_2\text{Br}(\text{rac-Ar})_2]$ (**3b**) (Ar = $[\text{C}_6\text{H}_4(\text{CH}(\text{Me})\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2]$). Cuprates **3a** and **3b** were prepared according to the method described for **1** and **2** involving reaction of 1 equiv of CuBr with 2 equiv of enantiopure (*R*)- $[\text{LiAr}]_2$ and (*rac*)- $[\text{LiAr}]_2$,¹³ respectively, in Et_2O at -50°C (eq 1). The cuprates **3a** and **3b** were isolated as slightly yellowish to green-colored solids as the only reaction product. Interestingly, whereas (*R*)-**3a** is extremely sensitive toward air and moisture, (*rac*)-**3b** is significantly less reactive to air and moisture and can be stored at room temperature in a nitrogen atmosphere for weeks.**

Solid State Structures of $[\text{CuLi}_2\text{BrAr}_2]$ (1**) and $[\text{CuLi}_2\text{BrNaph}_2]$ (**2**).** The molecular structure of **1** ($1/2\text{C}_6\text{H}_6$) consists of a monomeric cuprate unit containing one two-coordinate copper atom and two four-coordinate lithium atoms (Figure 2). Selected bond distances and angles are listed in Table 1.

Complex **1** can be regarded as consisting of an anionic $[\text{Ar}_2\text{Cu}]^-$ bisarylcopper entity and a cationic $[\text{Li}_2\text{Br}]^+$ unit, jointly forming a neutral, trinuclear, monomeric bromolithium cuprate species. The two-coordinated copper atom has a bent linear geometry with a $\text{C}(1)\text{-Cu}(3)\text{-C}(13)$ angle of $163.84(7)^\circ$. The structure of **1** shows an almost planar $[\text{C}_{\text{ipso}}\text{-Cu-C}_{\text{ipso}}][\text{Li-Br-Li}]$

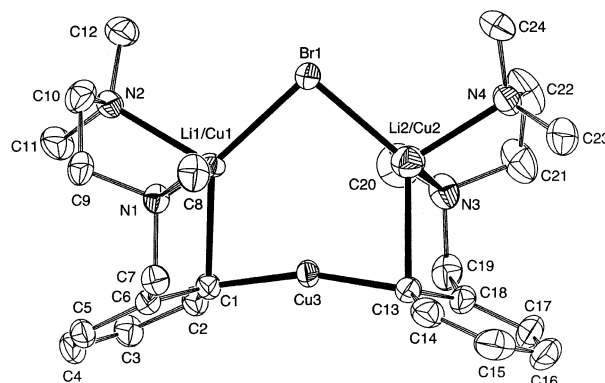


Figure 2. Displacement ellipsoid plot (50% probability level) of **1**. The positions of Li1 and Li2 are occupied by 97% Li and 3% Cu, respectively. Hydrogen atoms and benzene solvent molecules have been omitted for clarity.

Table 1. Selected Bond Distances (Å), Angles, and Torsion Angles (deg) for **1** and **2**^a

	1	2		1	2
C1—Cu3	1.9291(17)	C1—Cu3	1.9516(19)		
C13—Cu3	1.9274(18)	C17—Cu3	1.9434(19)		
Li1 ^a —Cu3	2.6519(19)	Li1 ^a —Cu3	2.6382(17)		
Li2 ^a —Cu3	2.750(3)	Li2—Cu3	2.833(3)		
Cu3—Br1	3.6299(3)	Cu3—Br1	3.7562(3)		
N1—Li1 ^a	2.139(2)	N1—Li1 ^a	2.156(2)		
N2—Li1 ^a	2.189(2)	N2—Li1 ^a	2.183(2)		
N3—Li2 ^a	2.113(3)	N3—Li2	2.073(3)		
N4—Li2 ^a	2.149(3)	N4—Li2	2.167(3)		
Li1 ^a —Br1	2.4108(19)	Li1 ^a —Br1	2.4155(16)		
Li2 ^a —Br1	2.430(2)	Li2—Br1	2.453(3)		
Li1 ^a —C1	2.305(2)	Li1 ^a —C1	2.316(2)		
Li2 ^a —C13	2.393(3)	Li2—C17	2.500(4)		
C1—Cu3—C13	163.84(7)	C1—Cu3—C17	163.57(8)		
Li1 ^a —Br1—Li2 ^a	95.67(8)	Li1 ^a —Br1—Li2	93.26(8)		
Li1 ^a —Cu3—Li2 ^a	83.21(7)	Li1 ^a —Cu3—Li2	80.52(7)		
N1—Li1 ^a —N2	85.85(9)	N1—Li1 ^a —N2	85.12(9)		
N3—Li2 ^a —N4	87.43(11)	N3—Li2—N4	88.18(13)		
C2—C1—C6	115.05(16)	C2—C1—C9	116.02(17)		
C14—C13—C18	115.26(18)	C18—C17—C25	115.66(19)		
Li1 ^a —C1—Cu3	77.00(8)	Li1 ^a —C1—Cu3	75.83(7)		
Li2 ^a —C13—Cu3	78.25(9)	Li2—C17—Cu3	78.11(10)		
Cu3—Li1 ^a —Br1—Li2 ^a	7.67(8)	Cu3—Li1 ^a —Br1—Li2	0.38(8)		
N1—C9—C10—N2	60.1(2)	N1—C13—C14—N2	56.9(2)		
N3—C21—C22—N4	59.6(3)	N3—C29—C30—N4	-59.5(4)		

^a The lithium positions Li1 and Li2 in **1** and Li1 in **2** are partially occupied by copper. The given values are average values including the contribution of the copper.

arrangement. The $\text{Cu-C}_{\text{ipso}}\text{-Li}$ angles in **1** are $77.0(8)^\circ$ and $78.25(9)^\circ$, respectively. Such small angles are typical for a three-center–two-electron (3c-2e) type of bonding of C_{ipso} between copper and lithium.¹⁶ The presence of asymmetry in this 3c-2e bonding appears from the relatively long $\text{Li-C}_{\text{ipso}}$ distances of 2.305(2) Å ($\text{Li}(1)\text{-C}(1)$) and 2.393(3) Å ($\text{Li}(2)\text{-C}(13)$) and the short $\text{Cu-C}_{\text{ipso}}$ bond lengths of 1.928 Å (mean). These are of the same order of magnitude as those reported for the ion-separated cuprates $[\text{CuPh}_2]^-$ (1.93(1) Å),¹⁸ $[\text{CuMes}_2]^-$ (1.915(9) Å),¹⁶ and $[\text{CuLi}_2(\text{CN})\{\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\}_2]_\infty$ (1.917(2) Å)¹⁷ and somewhat shorter than reported for the neutral homocuprate $[\text{Cu}_2\text{Li}_2\{\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\}_2]_4$

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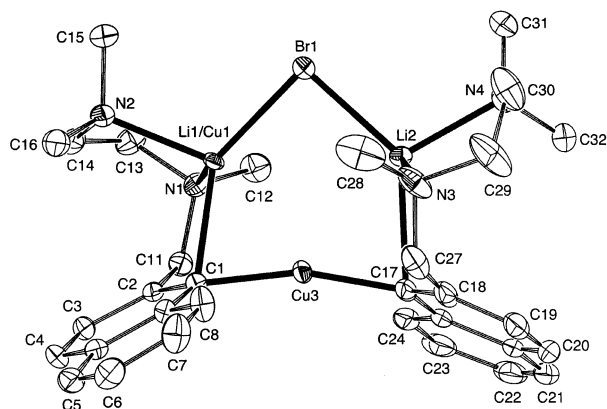
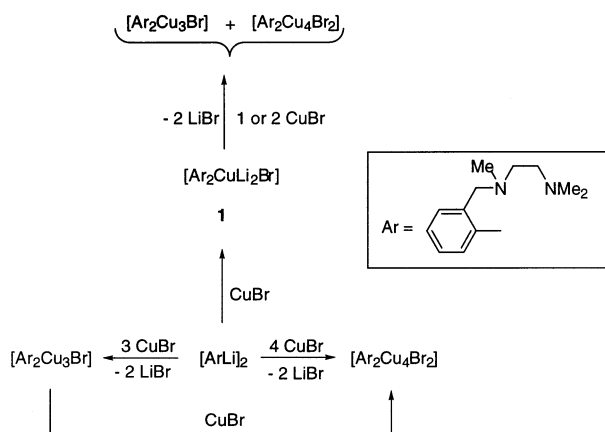


Figure 3. Displacement ellipsoid plot (50% probability level) of **2**. The position of Li1 is occupied by 94% Li and 6% Cu. Hydrogen atoms and benzene solvent molecules have been omitted for clarity.

Scheme 1. Schematic Representation of Self-Assembling Reactions of ArLi with CuBr in Et₂O (Ar = [C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2]⁻)



(1.942 Å (mean)).^{12e} The bromide anion bridges between the two lithium atoms ($\angle\text{Li}(1)-\text{Br}-\text{Li}(2)$ 95.67(8)°). The two nitrogen donor atoms of each of the aryl ligands coordinate to the same lithium atom, resulting in a distorted tetrahedral four-coordination of lithium through N,N'-chelation. Interestingly, the $\text{C}_{\text{ipso}}-\text{Cu}-\text{C}_{\text{ipso}}$ angle is less bent in **1** than this angle in known $[\text{Cu}_3\text{BrAr}_2]$ ⁷ (163.84(7)° versus 159.5°). It must be noted that in ion-separated cuprates the $\text{C}_{\text{ipso}}-\text{Cu}-\text{C}_{\text{ipso}}$ angle is 180°.¹⁷⁻²⁰

The molecular structure of **2** ($3 \cdot (3/2\text{C}_6\text{H}_6)$) shows structural features identical to those found for **1** (Figure 3). Selected bond distances and angles for **2** are given in Table 1. The $\text{C}_{\text{ipso}}-\text{Cu}-\text{C}_{\text{ipso}}$ angle of 163.57(8)° found in **2** is in close agreement with the one found for **1** (163.84(7)°, *vide supra*), indicating comparable cuprate character in **1** and **2**.

In the crystal structure refinement it turned out that the Li positions in **1** and **2** are partly occupied by Cu atoms instead of Li atoms. The occupancies were refined as 97% Li and 3% Cu in **1** (on positions Li1 and Li2, respectively) and in **2** 94% Li and 6% Cu (on position Li1). This implies that part of the solid state structures can be regarded as consisting of the known bis(aryl)-copper copper bromide aggregate $[\text{Cu}_3\text{BrAr}_2]$ ⁷ (cf. Scheme 1) and eventually of unknown $[\text{Cu}_2\text{LiBrAr}_2]$.

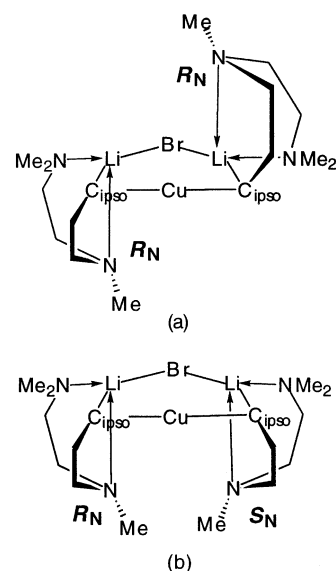


Figure 4. Symmetry in the two diastereoisomers of **1** and **2** (phenyl rings are omitted for clarity): (a) $R_N R_N$ enantiomer with C_2 symmetry ($S_N S_N$ enantiomer not shown). (b) $R_N S_N$ diastereoisomer with mirror plane symmetry ($S_N R_N$ not shown).

Structure of 1 and 2 in Solution: Stereochemical Aspects. To gain insight into the structure of the cuprates **1** and **2** in solution, a multinuclear NMR investigation was carried out. At room temperature, both the ¹H and ¹³C NMR spectra of solutions of **1** and **2** in benzene-*d*₆ show one single resonance pattern for Ar and Naph, respectively. It has to be noted that the partial occupation of the Li positions by Cu atoms and vice versa in **1** and **2** is not supported by NMR, since this occupancy is less than 5% (*vide infra*). The ¹H NMR spectrum comprise two distinct singlet resonances at 1.01 and 2.06 ppm for the NMe₂ functionality of the aryl ligands. In addition, for the CH₂N(Me)CH₂CH₂NMe₂ group only one characteristic AB pattern is found for the benzylic protons. From these observations it follows that at room temperature both nitrogen functionalities of one Ar ligand coordinate to the same lithium atom. The ¹³C NMR spectrum of **1** shows only one quartet resonance (1:1:1:1 intensity ratio) for the C_{ipso} carbon atom. This is characteristic for coupling between one C_{ipso} atom and one lithium atom ($^1J(^{13}\text{C}-^7\text{Li}) = 7$ Hz). For **2**, one broad resonance for the C_{ipso} carbon atoms is observed in the ¹³C NMR spectrum. The line width of 30 Hz is consistent with a $^{13}\text{C}_{\text{ipso}}-^7\text{Li}$ coupling constant of 7.5 Hz, which is again characteristic for a single C_{ipso} -lithium bond. Attempts to resolve the quartet multiplicity at low temperature failed.

Since the N^{Me} group becomes stereogenic upon coordination to lithium and the structures of **1** and **2** contain two aryl ligands, two diastereoisomers of **1** and **2** are possible with $R_N R_N$ (or its $S_N S_N$ enantiomer) or $R_N S_N$ chirality (Figure 4; the configuration of the nitrogen center is indicated by either R_N or S_N). The crystal structure determinations of **1** and **2** reveal that the centrosymmetric unit cells contain pairs of $R_N R_N/S_N S_N$ diastereoisomers. In Figures 2 and 3 only the $S_N S_N$

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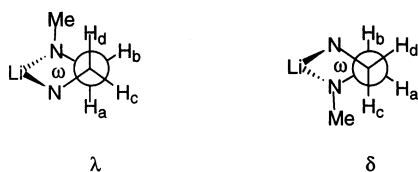


Figure 5. Possible λ and δ conformations of the two $[\text{Li}(\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)]$ fragments encountered in **1** and **2**.

enantiomer of **1** and the $R_N R_N$ enantiomer of **2**, respectively, are depicted.

The presence of a mirror plane in the $R_N S_N$ diastereoisomer renders the two Ar ligands equivalent, which likewise would give rise to one resonance pattern. This would, however, differ from the resonance pattern observed for the ligands in the $R_N R_N / S_N S_N$ enantiomers. Consequently, interconversion between diastereoisomers via either epimerization at the N centers or via interaggregate exchange could thus be monitored by a change in the ligand resonance pattern. For the arylcopper copper bromide analogue $[\text{Cu}_3\text{BrAr}_2]$ such interconversion has been reported to occur at or above 263 K in toluene- d_8 .⁷ At 193 K to room temperature the ^1H and ^{13}C NMR spectra of **1** and **2** in toluene- d_8 reveal only one ligand resonance pattern. At elevated temperature (363 K) the ^1H NMR spectrum of **1** and **2** in toluene- d_8 shows coalescence of the two NMe₂ resonances to one broad signal. However, at 363 K coalescence of the AB pattern (sharp at room temperature) of the benzylic $\text{CH}_2\text{N}(\text{Me})$ hydrogens of either **1** or **2** is not observed. This implies that at 363 K the $\text{N}^{\text{Me}} \rightarrow \text{Li}$ chelate coordination remains rigid on the NMR time scale. Apparently, the coordinative bonding to lithium is stronger for the N^{Me} than for the N^{Me_2} nitrogen atoms (two fused five-membered chelate rings), which could explain the partly coalesced NMe₂ resonance pattern at 363 K. These observations indicate that, indeed, the structural features of **1** and **2** in solution are identical to those observed in the solid state and exist as either the $R_N R_N$ or $S_N S_N$ stereoisomer.

A Karplus analysis^{21,22} of the vicinal proton–proton coupling constants within the $\text{NCH}_2\text{CH}_2\text{N}'$ multiplets of **1** indicates that N,N'-chelate binding to Li results in a five-membered chelate ring with predominantly (94.2%) λ -conformation (Figure 5). The calculated torsion angle (ω) is 58.2° . This value is in close agreement with the one found in the solid state structure of **1** (59.8° (mean)). Of note is that the results of this Karplus analysis of **1** are consistent with those obtained for the naphthyl-lithium dimer $[\text{LiNaph}]_2$ ($\omega = 60 \pm 2^\circ$)⁷ and the aryllithium dimer $[\text{LiAr}]_2$ ($\omega = 59.1(8)^\circ$, from X-ray).⁶ The conformation of the NCCN' chelation ring in the latter two dimers is also of λ -type. Unfortunately, a Karplus analysis of the $\text{NCH}_2\text{CH}_2\text{N}'$ unit in **2** proved to be impossible due to the broadness of the $\text{NCH}_2\text{CH}_2\text{N}'$ resonances. (For details, see the Experimental Section.)

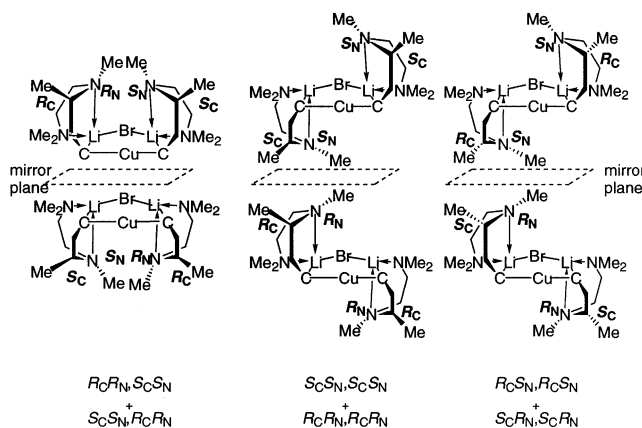


Figure 6. Schematic representation of six possible diastereoisomers of **3a** and **3b** (phenyl rings are omitted for clarity, C is C_{ipso} of the aryl group).

Structural and Stereochemical Aspects of Cuprates **3a and **3b** in Solution.** The ^1H and ^{13}C NMR spectra of enantiopure (R_C)-**3a** (the configuration at the benzylic carbon atom is indicated by R_C or S_C) and (rac)-**3b** in toluene- d_8 are completely identical in the temperature range 193–313 K and show only one single resonance pattern for the $\text{C}\wedge\text{N}\wedge\text{N}'$ ligands. The ^1H NMR spectra between 193 K and ambient temperature show two distinct singlets for the NMe₂ groupings, indicating rigid coordination of the NMe₂ group to lithium as found for **1** and **2**. Raising the temperature above 313 K results in decomposition of these cuprates, which is indicated by dark green coloring of the solution. The ^{13}C NMR spectra (benzene- d_6 , 298 K) of **3a** and **3b** show one characteristic quartet resonance (1:1:1:1 intensity ratio) for the two C_{ipso} atoms. This is consistent with a coupling of C_{ipso} with one ^7Li ($I = 3/2$; $^1J(^{13}\text{C}-^7\text{Li}) = 7.3$ Hz), so each C_{ipso} center is bonded to one Li center. These observations are in accord with the schematic structures of **1** and **2** in solution as well as in the solid state (vide supra).

In cuprate **3a**, the benzylic carbon atom has the, chosen, (R)-configuration. In principle, the C_{ipso} atoms can also be regarded as stereogenic centers as they bridge between one copper and one lithium; the aryl ring is *ortho*-substituted and is held in a position out of the $\text{LiC}_{\text{ipso}}\text{Cu}$ plane.¹² This provides C_{ipso} with a pseudo-tetrahedral coordination geometry. In the case of the (R)-Ar ligand only the benzylic carbon atom has a chosen (R)-configuration, whereas the configuration at C_{ipso} and the benzylic N atom are derived therefrom.²³ Accordingly the configuration of the C_{ipso} atom is not included in the notation of configuration of the cuprates.

In the $[\text{CuLi}_2\text{Br}((R)\text{-Ar})_2]$ (**3a**) aggregate the number of possible diastereoisomers is three, i.e., $R_C R_N, R_C R_N, R_C S_N, R_C S_N$, and $R_C S_N, R_C R_N$. The single $\text{C}\wedge\text{N}\wedge\text{N}'$ ligand pattern observed in the NMR spectra of both **3a** and **3b** points to the presence of a C_2 axis in the aggregate and rules out the $R_C S_N, R_C R_N$ diastereoisomer for **3a**, as these would show two unequal resonance patterns for the two aryl ligands. Consequently, only the $R_C R_N, R_C R_N$ and $R_C S_N, R_C S_N$ diastereoisomers are plausible structures for **3a** in solution (Figure 6).

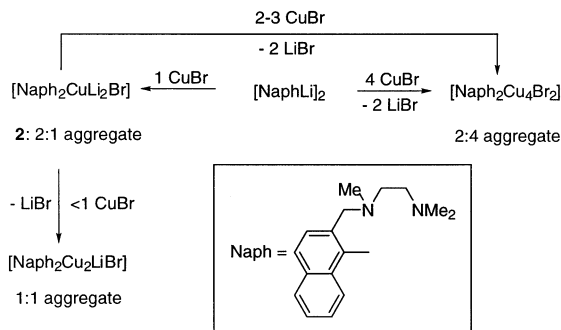
The fact that one resonance pattern is observed in a wide temperature range (193–313 K) strongly suggests

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Scheme 2. Schematic Representation of Self-Assembling Reactions of NaphLi with CuBr in Et₂O (Naph = [1-C₁₀H₆(CH₂N(Me)CH₂CH₂Me₂)-2]⁻)



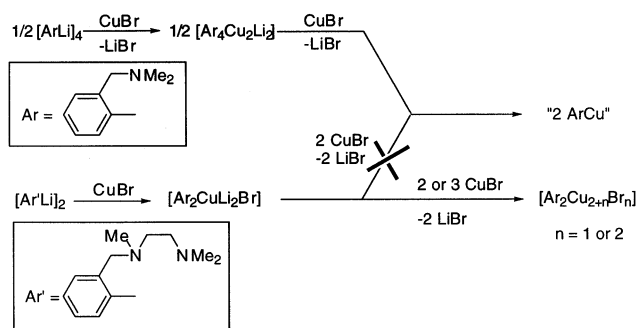
that interconversion of diastereoisomers does not take place. Interconversion of one diastereoisomer into another would require epimerization at the N^{Me} center, which is highly unlikely, *vide supra*. Moreover, molecular models suggest that the $R_C R_N, R_C R_N$ configuration for **3a** is favored over the $R_C S_N, R_C S_N$ configuration.

In the case of (*rac*)-**3b** 16 diastereoisomers are theoretically possible.¹³ However, only one resonance pattern for the aryl ligands of (*rac*)-**3b** is observed and again a restricted number of diastereoisomers can explain these NMR observations, i.e., the pairs of enantiomers $R_C R_N, R_C R_N$ (and $S_C S_N, S_C S_N$) and $R_C S_N, R_C S_N$ (and $S_C R_N, S_C R_N$). An essential difference between the $R_C S_N, R_C S_N/S_C R_N, S_C R_N$ enantiomeric pair and the $R_C R_N, R_C R_N/S_C S_N, S_C S_N$ pair is that in the former pair the α -Me groups point toward each other. This must result in decisive steric hindrance and makes this aggregate less likely. A comparison of the ¹H and ¹³C NMR spectra indicates that in solutions of **3b** indeed the $R_C R_N, R_C R_N$ aggregate (**3a**) and its enantiomer are dominant. Some additional resonances and line broadening strongly suggest that in solutions of **3b** also other aggregates are present in minor amounts.

Reaction of 1 and 2 with Excess CuBr: Formation of [Cu₃BrNaph₂] and [Cu₄Br₂Naph₂] Aggregates. As mentioned above, some of the lithium positions in the solid state structures of **1** are occupied by copper atoms. This suggests the presence of the [Cu₃BrAr₂] aggregate⁷ as an impurity in the crystal lattice. This is not surprising, as it is known that reaction of aryl- and naphthyl-lithiums with excess copper(I) bromide results in the formation of stable [Cu₃BrAr₂] and [Cu₄Br₂Naph₂] aggregates.⁷ For this reason, the use of an exact 2:1 Li-to-Cu ratio is of crucial importance for any successful synthesis of **1** and **2**. To study the course of the self-assembling of aryl- and naphthyllithiums with copper(I) bromide, model experiments were conducted in which **1** and **2** were reacted with CuBr. The type of aggregate formed turns out to depend markedly on the type of aryl ligand present. Addition of more than 1 equiv of CuBr to arylcuprates **1** gives a mixture of the known [Cu₃BrAr₂] and [Cu₄Br₂Ar₂] aggregates⁷ (Scheme 1).

Obviously, a bromocuprate like **1** but with a Li:Cu ratio of 1:2 is thermodynamically unfavored. On the contrary, addition of more than 1 equiv of CuBr to the naphthylcuprate **2** predominantly results in the formation of the [Cu₄Br₂Naph₂] aggregate (Scheme 2). Interestingly, addition of 0.8 molar equiv of copper bromide

Scheme 3. Differences in Reactivity of Monoanionic, Amine Chelated, and Diamine Chelated Aryllithium Derivatives toward Copper Bromide



to **2** results in the formation of a highly unstable, bright yellow compound. The ¹H NMR spectrum of this unstable compound (benzene-*d*₆, 298 K) shows two resonance patterns for the naphthyl ligand. This suggests the formation of an unsymmetrical cuprate with a Li:Cu ratio of 1:2 (Scheme 2).

Discussion

It is obvious that during copper-mediated organic syntheses new organocopper species and copper or metal salts are gradually formed and consumed. Such organocopper species have aggregated structures which can be subject to exchange processes with other organometallic species (e.g., organolithium, organomagnesium) and metal salts.^{6,23,24} As a result, during the reaction organocopper and cuprate intermediates may react with each other to form new mixed organocopper and/or cuprate species. As a consequence, a complex pattern of equilibria may form in solution which makes identification of such newly formed aggregates in organic reaction mixtures difficult.

The syntheses of the bromocuprates **1**, **2**, and **3** via self-assembly in a reaction of ArLi and CuBr in a 2:1 molar ratio is therefore not as straightforward as one might think. The formation of the bromocuprates seems to be the major reaction product; that is, all other possible cuprate species are less stable than these 2:1 cuprates. It appears that the type of reaction product(s) strongly depends on the type of aryl ligand used. For example, in the case of the related monoanionic aryllithium ligand [C₆H₄CH₂NMe₂]⁻ the analogous reaction using a 2:1 copper-to-lithium ratio yields the neutral 1:1 cuprate [Cu₂Li₂{C₆H₄CH₂NMe₂-2}].^{12e} Addition of a second equivalent of CuBr to this cuprate generates the pure, tetrameric organocopper compound [Cu₄{C₆H₄CH₂NMe₂-2}].²⁵ On the contrary, reaction of the bromocuprates **1** and **2**, which have *ortho*-diamine chelating CH₂N(Me)CH₂CH₂NMe₂ substituents, with excess CuBr results in the formation of mixed aryl- or naphthylcopper/copper bromide aggregates of type [Cu_{n+m}Br_mAr_n] (Scheme 3). These examples point to an essential difference in the tuning of the aryl ligand during the self-assembling process.

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The bromocuprates **1** and **2** contain a $[\text{R}_2\text{Cu}]^-$ cuprate anionic part, which is combined with a $[\text{Li}_2\text{Br}]^+$ cation. This formulation links the structural motifs of **1** and **2** in a direct way to the recently reported solid state structures of 2:1 cyanocuprates of type $[\text{CuLi}_2(\text{C}\equiv\text{N})\text{R}_2]$,^{17,26} as these structures likewise comprise $[\text{R}_2\text{Cu}]^-$ anions and $[\text{Li}_2\text{CN}]^+$ cations. The difference is that **1** and **2** represent neutral structures, whereas the above-mentioned cyanocuprates have ion-separated structures. It is interesting to note that Hartree–Fock and DFT calculations on dimethylchlorocuprates by Nakamura et al. point out that a so-called closed structure as found in **1** and **2** is more favorable than the open “higher-order” structure of halocuprates of type $[\text{Cu}(\text{X})\text{R}_2]^{2-}$.²⁷ This comparison also reveals the different roles that the *ortho*-amine chelating substituents play in the assembling of the aggregates. In **1** and **2** it is the N,N'-chelate functionality of the *ortho*-diamine substituent that assembles the Li_2X cation. The structural features of **1** and **2** match those found in $[\text{Cu}_3\text{BrAr}_2]$ and $[\text{Cu}_4\text{Br}_2\text{Naph}_2]$ aggregates.^{7,16,28} In $[\text{Cu}_3\text{BrAr}_2]$ and $[\text{Cu}_4\text{Br}_2\text{Naph}_2]$ the *ortho*-N,N'-chelates assemble a $[\text{R}_2\text{Cu}]^-$ anion and a $[\text{Cu}_{n+1}\text{Br}_n]^+$ ($n = 1, 2$) cation. The halide ion in the $[\text{Cu}_{n+1}\text{Br}_n]^+$ cation plays an important role by providing a cation of proper size (CuBrCu or CuBrCuBrCu)⁷ that can span between the two N,N'-chelates. The Cu–Br–Cu angles in these cations are $85.75(3)^\circ$ and $67.30(4)^\circ$ (mean), respectively. Some other examples of neutral aggregates in which a $[\text{R}_2\text{Cu}]^-$ anion assembles with $[\text{Cu}_{n+1}\text{Br}_n]^{x+}$ cations through chelate bonding are $[\text{Cu}(\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6})_2]^- [\text{Cu}_3\text{Br}_2]^+$,²⁸ $[\text{Cu}(2\text{-NMe}_2\text{C}_6\text{H}_4\text{CMe}=\text{CHpTol})_2]^- [\text{Cu}_3\text{Br}_2]^+$,²⁹ and $2[\text{Cu}(\text{C}_6\text{H}_4\text{NMe}_2)_2]^- [\text{Cu}_4\text{Br}_2]^{2+}$.³⁰ The corresponding $[\text{LiBrLi}]^+$ cations in **1** and **2** span a shorter distance, but this is most likely compensated for by the Li–N,N' bonding, which is much stronger than the corresponding bonding with Cu^I . The Li–Br–Li angles in **1** and **2** are $95.67(8)^\circ$ and $93.26(8)^\circ$, respectively. The partial occupation of the Li positions by Cu in the structure of **1** suggests that also mixed $[\text{CuLiX}]^+$ cations can function as a bridge (cf. the partial occupation of Li by Cu in the structure of **1** in the solid state, *vide supra*). However, ¹H NMR studies of solutions of **1** and **2** show that assembling $[\text{Cu}_2\text{X}]^+$ cations with a $[\text{R}_2\text{Cu}]^-$ anion results in (thermodynamically) more stable aggregates. These observations underline the role metal salts, present in solution during reaction of cuprates in organic synthesis, may play in stabilizing or activating aggregated intermediates. They do this by affecting the preequilibria leading to the kinetically most active species in the key reaction step. It also provides experimental evidence for the existence of the $[\text{Cu}_m\text{Li}_n\text{X}_{m+n-1}]^{(n+m)-(m+n-1)+}$ ($m =$

1, 2; $n = 0, 1, 2$; X = Br, CN) cations encountered in computational studies of cuprate reactions.²⁷

The aryl ligands in **1** and **2** each bridge one copper atom and one lithium atom. The corresponding Li–C_{ipso}–Cu angles are acute ($77.00(8)^\circ$ and $78.25(9)^\circ$ in **1** and $75.83(7)^\circ$ and $78.11(10)^\circ$ in **2**). Such acute angles have been earlier explained by an electron-deficient (3c-2e) bonding of C_{ipso} between lithium and copper.¹⁶ The favored perpendicular positioning of the aryl rings with respect to the Cu⋯Li vector is supported by the (relatively bulky) *ortho*-amine substituents. The fact that the naphthylbromocuprate **2** is significantly more thermally stable than the arylbromocuprate **1** is of interest. This difference in stability can be accounted for by the better electron-donating properties of the naphthyl ligand compared to the aryl ligand. In addition, it has to be noted that the more bulky naphthyl ligand stabilizes the perpendicular rotamer conformation of the NaphCuLi entity, thus effecting that through bonding and back-bonding a higher electron density may result in the C_{ipso}CuLi unit. The relatively high thermal stability observed is in agreement with our previous finding that the stability of arylcuprates increases with the introduction of substituents either with or without coordination properties *ortho* to the C_{ipso} carbon bonded to copper.^{16,25,31}

These structural features are similar to those encountered in the neutral 1:1 cuprates $[\text{Cu}_2\text{Li}_2\text{Ph}_4(\text{OEt})_2]$ ³² and $[\text{Cu}_2\text{Li}_2\{\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\}_2]$,^{12e} in which likewise each aryl group is 3c-2e bonded to one Cu and one Li atom (*vide supra*). In both the solid state and solution (benzene and Et₂O) these cuprates exhibit distinct covalent bonding between C_{ipso} and Cu and Li. Although this binding is highly asymmetric in the direction of a 2e-2c C_{ipso}–Cu and a π C_{ipso}–Li bond, no evidence has been found that this cuprate can be considered as a contact (or tight) ion pair (CIP) type of structure.^{33c,34} In the case of the series of -ate complexes $[\text{MLi}_2\text{XAr}_2]$ (M = Cu, Ag, Au; X = Br, CN) this was demonstrated by the presence of distinct ⁷Li–¹³C couplings³⁵ and the same is true for the Cu–C_{ipso}–Li bonding in **1** and **2**. Despite the fact that in those cuprates ionic parts $[\text{Ar}-\text{Cu}-\text{Ar}]^-$ and $[\text{Li}-\text{Br}-\text{Li}]^+$ can be recognized, cuprates **1** and **2** are best described as distinctly neutral aggregates, which consist of building blocks of opposite polarity combined through N,N'-chelation. This is the case not only in the solid state but also in benzene/toluene and diethyl ether. This is in line with the findings of Boche et al., who describe cuprates $[\text{Cu}_2\text{Li}_2\text{Ph}_4]$ in Et₂O solution as CIPs as well as bonding possibilities ranging from SSIP in very polar solvents via CIP to neutral assemblies in apolar solvents.³³ The structural features of **1** and **2** in more polar solvents are currently being investigated.

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Stereochemical Aspects of Cuprates 3a and 3b.

The experiments with chiral *ortho*-diamine chelating CHMeN(Me)CH₂CH₂NMe₂ substituents led to the selective formation of chiral bromocuprates **3a** and **3b**, which have [CuLi₂BrAr₂] structural features similar to **1** and **2**. However, in the case of **3a** a unique, enantiomerically pure structure and for **3b** an enantiomeric pair of the same diastereoisomers is formed. In particular the single resonance pattern observed for the aryl units is in agreement with the occurrence of a stereoselective self-assembling process of [R₂Cu]⁻ and [LiBrLi]⁺ units during cuprate formation, induced by the specific configuration of the benzylic center. In this way, the configuration at the N^{Me} centers (R_N or S_N) created during this assembling process is based on the chosen R_C chirality of the benzylic carbon position. As a consequence in (*R*)-**3a**, only the R_CR_N, R_CR_N enantiomer is present in solution. In the same way, of all theoretically possible diastereoisomers of cuprate *rac*-**3b**, only the R_CR_N, R_CR_N/S_CS_N, S_CS_N enantiomeric pair is present in solution. Molecular modeling (DFT; Gaussian98: B3LYP/LANL2DZ) of the possible structures showed that in the alternative R_CS_N, R_CS_N/S_CR_N, S_CR_N pair the α-Me groups are pointing toward each other,²³ causing some steric interference, which is absent in the R_CR_N, R_CR_N/S_CS_N, S_CS_N pair. Indeed the calculated energy difference between these enantiomeric pairs reveals that the R_CR_N, R_CR_N/S_CS_N, S_CS_N enantiomeric pair is ca. 20 kcal/mol more stable than the R_CS_N, R_CS_N/S_CR_N, S_CR_N pair. To the best of our knowledge this is the first demonstration of stereoselective aggregate formation in organocopper chemistry.

Concluding Remarks

The results presented in this paper show that the stoichiometric ratio of ArLi to CuBr (i.e., 2:1, 2:3, or 2:4 Li-to-Cu ratio) critically determines which thermodynamically favored copper species is formed. The halocuprates **1** and **2** can be seen as intermediates in the synthesis of the [Cu₃BrAr₂] and [Cu₄Br₂Naph₂] aryl(naphthyl)copper aggregates.

Furthermore, the present results show for the first time that chirality present at the *ortho*-position of the Ar ligand is very effectively transmitted during the selective formation of halocuprates of type [CuLi₂XAr₂] (X = halide) and is under thermodynamic control. We are currently studying the structures of related cyanocuprates in which instead of the Li₂Br cation as in **1–3** a Li₂(CN) cation is present. Both the latter cyanocuprates^{17,34,35} and the bromocuprates **1–3** are the first heterocuprates existing as neutral species (or tight ion-pairs, as has been recently postulated for the Gilman type of cuprates by Boche et al.)³³ in solution, of which the structural features and self-assembling behavior have been fully elucidated.

Experimental Section

All experiments were carried out under a dry, oxygen-free, nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. All standard chemicals were purchased from ACROS and Aldrich Chemical Co. and used as received, except for NET₃, which was distilled from CaH₂ prior to use. All reactions involving organocuprate and -lithium syntheses were carried out in flame-dried Schlenk flasks. The starting materials (*R*)- and (*rac*)-[LiC₆H₄(CH(Me)-

N(Me)CH₂CH₂NMe₂)-2]₂,¹³ [LiC₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2]₂,⁶ [LiC₁₀H₆(CH₂N(Me)CH₂CH₂NMe₂)-2]₂,⁷ and dry CuBr³⁶ were prepared according to literature procedures. ¹H, ¹³C, and ⁶Li NMR spectra were recorded on a 300 MHz spectrometer at ambient temperature unless otherwise stated. Chemical shifts (δ) are given in ppm relative to SiMe₄ as an internal standard. Coupling constants are in Hz. Melting points are uncorrected. Elemental analyses were obtained from Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Cryoscopic measurements were carried out using a S2541 thermolyzer and a metal-mantled Pt-100 sensor.³⁷ For calibration, naphthalene was used to determine the cryoscopic constant K_f = 5.54 K·kg·mol⁻¹.

[CuLi₂Br{C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2]₂ (**1**). To a stirred solution of [Li₂{C₆H₄(CH₂N(Me)-CH₂CH₂NMe₂)-2]₂ (1.61 g; 8.12 mmol of monomer) in Et₂O (30 mL) at -30 °C was added CuBr (0.58 g; 4.06 mmol) as a solid. After the reaction mixture was stirred at -30 °C for 1.5 h the suspension was slowly warmed to room temperature. After the suspension was stirred for an additional 1 h at ambient temperature, all volatiles were removed in vacuo. The remaining slightly white-brownish solid was dissolved in toluene (30 mL) and filtered over a glass filter covered with dry Celite (to remove Cu⁰ particles) to give an almost colorless solution. Evaporation of the solvent in vacuo gave 1.79 g of **1** as a white powder (82%, 3.32 mmol). Crystals suitable for X-ray structure determination were obtained by crystallization from benzene/pentane at room temperature.

¹H NMR (C₆D₆, 300.105 MHz, 298 K): δ (in ppm) 1.01 (s, 3H, NMe₂), 1.46 (ddd, 1H, ²J = 12.82 Hz, ³J = 3.36 Hz, ³J = 3.05 Hz, CH₂CH^HNMe₂), 1.50 (ddd, 1H, ²J = 12.82 Hz, ³J = 3.36 Hz, ³J = 3.05 Hz, CH₂CH^HNMe₂), 1.68 (ddd, 1H, ²J = 13.73 Hz, ³J = 3.36 Hz, ³J = 3.35 Hz, CH^HCH₂NMe₂), 1.72 (ddd, 1H, ²J = 13.73 Hz, ³J = 3.36 Hz, ³J = 3.35 Hz, CH^HCH₂-NMe₂), 1.92 (td, 1H, ²J = 12.82 Hz, ³J = 9.46 Hz, ³J = 3.05 Hz, CH₂CH^HNMe₂), 1.92 (td, 1H, ²J = 12.82 Hz, ³J = 9.76 Hz, ³J = 3.05 Hz, CH₂CH^HNMe₂), 2.06 (s, 3H, NMe₂), 2.33 (td, 2H, ²J = 13.13 Hz, ³J = 10.07 Hz, ³J = 3.66 Hz, CH^HCH₂-NMe₂), 2.54 (s, 3H, N(Me)CH₂CH₂NMe₂), 2.93 (d, 2H, ²J = 11.6 Hz, ArCH₂), 4.29 (d, 2H, ²J = 11.9 Hz, ArCH₂), 6.95 (d, 2H, ³J = 7.33 Hz, ArH(3)), 7.12 (dt, 2H, ³J = 7.33 Hz, ArH(4)), 7.25 (dt, 2H, ³J = 7.02 Hz, ³J = 7.33 Hz, ArH(5)), 8.36 (dd, 2H, ³J = 7.02 Hz, ArH(6)). ¹³C NMR (C₆D₆, 75.469 MHz, 298 K): δ (in ppm) 42.3 (NMe₂), 46.6 (NMe), 47.7 (NMe₂), 53.1 (CH₂CH₂-NMe₂), 57.1 (CH₂CH₂NMe₂), 70.9 (ArCH₂), 125.5, 125.6 (2x Ar(3)), 127.5, 128.5 (Ar(4–5)), 143.6 (Ar(6)), 149.9 (Ar(2)), 166.9 (Ar(*J*)_{ipso}). Mp: 115 °C (dec). Anal. Calcd for C₂₄H₃₈BrCuLi₂N₄: C, 53.39; H, 7.09; N, 10.38. Found: C, 53.30; H, 7.16; N, 10.27.

[CuLi₂Br{1-C₁₀H₆(CH₂N(Me)CH₂CH₂NMe₂)-2]₂ (**2**). The synthesis of **2** is identical to that of **1**, starting from [Li₂{1-C₁₀H₆(CH₂N(Me)CH₂CH₂NMe₂)-2]₂ (1.23 g; 4.96 mmol of monomer) and CuBr (357 mg; 2.49 mmol). Complex **2** was obtained as a yellow solid (1.32 g, 84%). Crystals suitable for X-ray structure determination were obtained by crystallization from benzene/pentane at room temperature.

¹H NMR (C₆D₆, 300.105 MHz, 298 K): δ (in ppm) 0.55 (s, 6H, NMe₂), 1.14, 1.58 (2 × m, 4H, N(Me)CH₂CH₂N), 1.90 (s + m, 8H, N(Me)CH₂CH₂N) and NMe₂), 2.38 (m, 2H, N(Me)CH₂-CH₂N), 2.67 (s, 3H, CH₂N(Me)), 3.08 (d, 2H, ²J = 11.7 Hz, ArCH₂), 4.86 (d, 2H, ²J = 11.4 Hz, ArCH₂), 6.9–7.09, 7.14–7.30, 7.41–7.63 (3 × m, 8H, ArH(3–6)), 7.79 (d, 2H, ²J = 7.8 Hz, ArH(7)), 9.17 (d, 2H, ²J = 8.1 Hz, ArH(8)). ¹³C NMR (C₆D₆, 75.469 MHz, 298 K): δ (in ppm) 42.6 (NMe₂), 46.1 (N(Me)), 47.7 (NMe₂), 52.2, 58.9 (N(Me)CH₂CH₂N), 69.9 (ArCH₂), 120–138 (Ar(3–10)), 147.7 (Ar(2)), 172.2 (Ar(Cipso)). Mp: 126 °C

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Table 2. Experimental Data for the X-ray Diffraction Studies of 1 and 2

	1	2
formula	C ₂₄ H ₃₈ BrCu _{1.07} Li _{1.93} N ₄ ·0.5C ₆ H ₆	C ₃₂ H ₄₂ BrCu _{1.06} Li _{1.94} N ₄ ·1.5C ₆ H ₆
fw	582.93	760.58
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)
cryst size [mm ³]	0.67 × 0.37 × 0.37	0.30 × 0.21 × 0.09
cryst color	colorless	yellow
temp [K]	150(2)	100(2)
λ [Å]	0.71073	0.71073
a [Å]	16.9805(1)	44.1343(9)
b [Å]	10.6531(1)	10.4437(2)
c [Å]	16.5938(1)	16.8488(3)
β [deg]	92.0821(5)	90.7910(8)
V [Å ³]	2999.75(4)	7765.3(3)
Z	4	8
D _{calc} [g/cm ³]	1.291	1.301
μ [mm ⁻¹]	2.128	1.656
abs corr	PLATON (MULABS)	PLATON (MULABS)
transmn range	0.35–0.46	0.77–0.88
sin(θ/λ) _{max} [Å ⁻¹]	0.65	0.65
no. of reflns measd/unique	69 696/6878	56 447/8905
R _{int}	0.063	0.041
no. of params/restraints	453/0	448/0
R1 (obsd/all reflns)	0.0253/0.0352	0.0342/0.0417
wR2 (obsd/all reflns)	0.0701/0.0765	0.0796/0.0835
GoF	0.769	1.024
ρ(min/max) [e/Å ³]	–0.46/0.94	–0.62/1.70

(dec). Anal. Calcd for C₃₂H₄₂N₄BrCuLi₂: C, 60.05; H, 6.61; N, 8.75. Found: C, 59.89; H, 6.55; N, 8.64.

[CuLi₂Br{C₆H₄(CH(Me)N(Me)CH₂CH₂NMe₂-(R))-2}]₂ (3a). The synthesis of **3a** is identical to that of **1**, starting from (*R*)-[LiC₆H₄(CH(Me)N(Me)CH₂CH₂NMe₂)-2]₂ (0.68 g; 3.05 mmol) and CuBr (218 mg; 1.52 mmol) in Et₂O (50 mL) at –50 °C. Cuprate **3a** is obtained as a slightly greenish to white solid. Yield: 0.61 g (68%).

¹H NMR (C₆D₆, 300.105 MHz, 298 K): δ (in ppm) 0.91 (s, 6H, NMe₂), 1.11 (d, 4H, ³J = 6.9 Hz, ArCH(*Me*)), 1.2, 1.34 (2 × m, 4H, NCH₂CH₂N), 2.13 (s, 6H, NMe₂), 2.18, 2.36 (2 × m, 4H, NCH₂CH₂N), 2.58 (s, 6H, N(*Me*)), 2.73 (q, 2H, ³J = 6.9 Hz, ArCH(*Me*)), 6.98 (d, 2H, ArH(*3*)), 7.16 (t, 2H, ArH(*4*)), 7.26 (t, 2H, ArH(*5*)), 8.41 (d, 2H, ArH(*6*)). ¹³C NMR (C₆D₆, 75.469 MHz, 298 K): δ (in ppm) 7.66 (CH(*Me*)), 41.2 (NMe₂), 42.5, 45.1 (NCH₂CH₂N), 48.9 (NMe₂), 56.7 (N(*Me*)), 69.8 (ArCH), 123.5, 125.5, 125.8 (Ar(*3,4,5*)), 143.5 (Ar(*6*)), 153.6 (Ar(*2*)), 169.0 (ArC_{ipso}). [α]_D²⁰ = –221.1° (c 0.1 (C₆H₆)). Elemental analysis was not possible due to the thermal instability of the product.

[CuLi₂Br{C₆H₄(CH(Me)N(Me)CH₂CH₂NMe₂)-2}]₂ (3b). The synthesis of **3b** is identical to that of **1**, starting from [LiC₆H₄(CH(Me)N(Me)CH₂CH₂NMe₂)-2]₂ (1.21 g; 5.70 mmol) and CuBr (409 mg; 2.85 mmol) in Et₂O (50 mL) at –50 °C. Cuprate **3b** is obtained as an almost white solid. Yield: 1.34 g (80%).

¹H and ¹³C NMR are identical to that of cuprate **3a**. Elemental analysis was not possible due to the thermal instability of the product.

Conformational Analysis of the LiN(Me)CH₂CH₂NMe₂ Chelate Ring. ¹H NMR spectra of compound **1** in C₆D₆ were analyzed after resolution enhancement by Gaussian multiplication. The mole fraction of the λ conformation (*n*_λ) was determined by solving the following equations: *n*_λ = [X cos² ω – cos² (120 – ω)]/[α cos² (120 + ω) – cos² (120 – ω)] and *n*_λ = [Y cos² ω – α cos² (120 + ω)]/[cos² (120 – ω) – α cos² (120 + ω)], where X = J_{ad}/((J_{ac} + J_{bd})/2), Y = J_{bc}/((J_{ac} + J_{bd})/2) and α is the ratio of the Karplus coefficients A₁ and A₂. It was assumed in these calculations that α = 1.2 and ω_δ = ω_λ = ω. The value of 1.2 for α has been used previously for chelate ring systems and is obtained from the average of a number of literature values for J_{trans}/J_{gauche} coupling constants in metal–diamine systems.^{21,22}

Reaction of 1 with 1 or 2 Equiv of CuBr. To a stirred solution of **1** (0.98 g, 1.82 mmol) in a benzene/Et₂O mixture (1:1, v/v) was added 1 or 2 equiv of CuBr (0.26 g, 1.82 mmol or 0.52 g, 3.64 mmol) as a solid. After stirring for 5 h all solvents were removed in vacuo. Subsequent extraction of the remaining solid with benzene (3 × 20 mL) gave a green-yellowish powder (ca. 1.3 g). The ¹H NMR (benzene-*d*₆) spectrum of the reaction products obtained reveals the presence of a mixture of the 2:3 and 2:4 arylcopper copper bromide aggregates [Cu₃Br{C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}]₂ and [Cu₄Br₂{C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}]₂ upon comparison with authentic samples of these aggregates.⁷

Reaction of 2 with 0.8 Equiv of CuBr. To a stirred suspension of **2** (0.25 g, 0.39 mmol) in Et₂O (50 mL) was added CuBr (46 mg, 0.31 mmol) as a solid at –60 °C. After 2 h, the suspension was allowed to warm to room temperature and stirred for an additional 2 h, after which all volatiles were removed in vacuo. The remaining bright yellow powder was dissolved in toluene (50 mL) and filtered over dry Celite. The solvent was removed in vacuo. A yellow residue remained, which was washed with pentane (2 × 15 mL), leaving an unstable bright yellow powder.

¹H NMR (benzene-*d*₆, 300.105 MHz, 298 K): δ in ppm 0.50 (s, 3H, NMe₂), 1.91 (s, 3H, NMe₂), 2.18 (s, 3H, NMe₂), 2.71 (bs, 6H, NMe), 2.83 (s, 3H, NMe), 2.96 (d, 1H, ²J = 11 Hz, ArCH₂), 3.21 (d, 1H, ²J = 13 Hz, ArCH₂), 4.65 (d, 1H, ²J = 11 Hz, ArCH₂), 4.72 (d, 1H, ²J = 12 Hz, ArCH₂), 6.87 (d, 1H, ³J = 8 Hz, ArH-3), 6.92 (d, 1H, ³J = 8 Hz, ArH-3), 7.05 (d, 1H, ³J = 8 Hz, ArH-3), 7.32 (m, ArH-6,7), 7.47 (d, 1H, ³J = 8 Hz, ArH-5), 7.61 (d, 1H, ³J = 8 Hz, ArH-4), 7.70 (m, ArH-4), 8.85 (d, 1H, ³J = 8 Hz, ArH-8), 8.95 (d, 1H, ³J = 9 Hz, ArH-8). The signals from the CH₂CH₂ groups of both species reside between 1.1 and 2.6 ppm.

Reaction of 2 with 1.9 Equiv of CuBr. The procedure was identical to that described for the reaction of **2** with 0.8 equiv of CuBr, starting from **2** (0.32 g, 0.50 mmol) and CuBr (0.14 g, 0.96 mmol). The ¹H NMR (benzene-*d*₆) spectrum showed the product to be a mixture of the 2:4 mixed naphthylcopper–copper bromide aggregate [Cu₄Br₂{1-C₁₀H₆(CH₂N(Me)CH₂CH₂NMe₂)-2}]₂⁷ and an unidentified product. Crystallization from a 1:1 v/v mixture of benzene/pentane afforded yellow crystals, which were identified by single-crystal X-ray diffraction as [Cu₄Br₂Naph₂].⁷

X-ray Crystal Structure Determinations of **1 and **2**.** Intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (Mo K α). Structure **1** was solved with Patterson methods (DIRDIF-97),³⁸ and structure **2** with direct methods (SIR-97).³⁹ Both structures were refined with the program SHELXL-97⁴⁰ against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters; hydrogen atoms were refined as rigid groups. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON.⁴¹ The lithium positions Li1 and Li2 in **1** and Li1 in **2** were partially occupied by copper atoms. The lithium atoms

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and the corresponding copper atoms were constrained to the same coordinates and the same anisotropic displacement parameters. Then the corresponding partial occupancies were refined with the criterion that the total occupancy remains 1.0. Besides the main molecules, the unit cells of **1** and **2** additionally contain benzene solvent molecules. Further experimental details are given in Table 2.

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Supporting Information Available: ¹H and ¹³C NMR spectra of **3a** and **3b**. X-ray crystallographic data of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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