The Presence of [Ar$_2$Cu]$^-$ and [(RC≡C)$_2$Cu]$^-$ Homocuprate Moieties in the Neutral Mixed Cuprate [Cu$_2$Li$_2$(C≡CR)$_2$Ar$_2$] (Ar = C$_6$H$_4${CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$}-2; R = C$_6$H$_4$Me-4 or C$_6$H$_4$SiMe$_3$-4)

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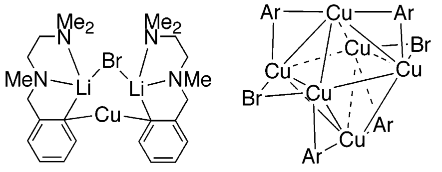
The neutral, mixed 2:2 aryl-alkynyl-cuprates [Cu$_2$Li$_2$(C≡CR)$_2$Ar$_2$] (Ar = [C$_6$H$_4${CH$_2$N(Me)CH$_2$-CH$_2$NMe$_2$}-2]$^-$; R = C$_6$H$_4$Me-4 (**3a**) or C$_6$H$_4$SiMe$_3$-4 (**3b**)) are the first examples of cuprates that contain two different organic homocuprate parts ([Ar−Cu−Ar]$^-$ and [(RC≡C)−Cu−(C≡CR)]$^-$) in one assembled structure. Each part has a two-coordinate Cu atom in linear geometry. They are held together by Li−C$_{ipso}$ interactions to two Li atoms. Tetrahedral four-coordination at the Li centers is completed by N,N′-chelation of the *ortho*-diamine substituent of the Ar ligand. Compound **3** is formed as the only reaction product in almost quantitative yield when LiAr and Cu(C≡CR) aggregates are mixed together in equimolar amounts. This cuprate is an example of ion-pairing between two different homocuprate anions and two Li cations.

Introduction

Although the influence of the nature of organic and inorganic anions, ligands, and solvents on the formation of pure organocopper(I) compounds has been studied extensively,[1−8] our understanding of the influence of these factors on the self-assembling process that gives rise to the actual organocopper(I) species is still in its infancy. Organocopper species commonly are polynuclear compounds of type Cu$_n$R$_n$ which are formed by self-assembly of a number of monomeric CuR species. This process may involve other moieties present in solution, e.g., a metal salt MX or another organometallic species MR′, and we have extensively demonstrated that the formation of self-assembled species such as CuR/MX or CuR/MR′ may interfere with the preparation of pure organocopper compounds.[9−13] Some examples are [CuLi$_2$BrAr$_2$] (**1**)[13] (Ar = C$_6$H$_4${CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$}-2) and [Cu$_6$Br$_2$Aryl$_4$] (**2**)[10] (Aryl = C$_6$H$_4$NMe$_2$-2); see Figure 1.



1 **2**

Figure 1. Schematic representation of the arylbromocuprate [CuLi$_2$BrAr$_2$] (**1**) (Ar = C$_6$H$_4${CH$_2$N(Me)CH$_2$CH$_2$-NMe$_2$}-2) and the hetero-organocopper compound [Cu$_6$Br$_2$-Aryl$_4$] (**2**) (Aryl = C$_6$H$_4$NMe$_2$-2).

These species, which are both relevant to the present study, are neutral and formed directly from the reaction of the corresponding aryllithium compound with copper

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bromide. These reagents have to be used in the proper 2:1 ratio to obtain $[CuLi_2BrAr_2]$ (**1**), but $[Cu_6Br_2Aryl_4]$ (**2**) is always formed initially, irrespective of the ratio of the two reactants. The organocopper compound $[CuAryl]_n$ is formed only after prolonged reaction of copper bromide with aryllithium.

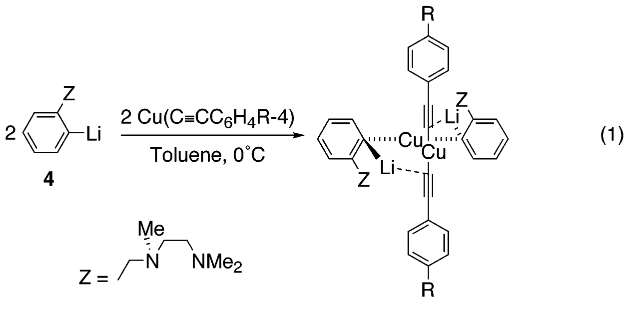
The two bromide ions in **2** can be replaced by other halide or also alkynyl anions while the overall $[Cu_6X_2Aryl_4]$ structure is retained.[10] These observations point to a considerable stability of the $[Cu_6Aryl_4]^{2+}$ skeleton, which obviously can be formed by self-assembly from various combinations of reagents.

The present paper describes a study of reactions of $[CuLi_2BrAr_2]$ (**1**) with organolithium compounds, in particular lithium acetylides, which were aimed at preparing the first examples of organocuprates containing different organic anions. In fact, **1** is the first example of a neutral heterocuprate with a $CuLi_2$ structural motif that has been used in computational studies of reactions of higher-order cuprates.[14] Structural information on related hetero-organocuprates would greatly assist these latter studies.

We here report the synthesis and characterization of novel mixed cuprate complexes $[Cu_2Li_2(C{\equiv}CR)_2Ar_2]$ (**3**) ($Ar = C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}$-2), which have been obtained both from the stoichiometric reaction of [LiAr] with $[Cu(C{\equiv}CR)]$ ($R = C_6H_4Me$-4 or $C_6H_4SiMe_3$-4) and from the reaction of $[CuLi_2BrAr_2]$ with $[Li(C{\equiv}CR)]$.

Results and Discussion

Preparation of the 2:2 Mixed Bisaryl-, Bis(alkynyl)cuprates $[Cu_2Li_2(C{\equiv}CC_6H_4R\text{-}4)_2Ar_2]$ ($Ar = [C_6H_4\text{-}\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2]^-$, R = Me (3a) or $SiMe_3$ (3b)). Addition of an equimolar amount of $[Li_2(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (**4**) to copper(I) *p*-tolylacetylide $[CuC{\equiv}CC_6H_4Me\text{-}4]$[15] or copper(I) *p*-trimethylsilylphenylacetylide $[CuC{\equiv}CC_6H_4SiMe_3\text{-}4]$ in toluene at 0 °C gives the 2:2 complexes containing two different homocuprate units $[Cu_2Li_2(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2(C{\equiv}CC_6H_4R\text{-}4)_2]$ (**3a** and **3b**, respectively) as the only reaction product (eq 1). Complexes **3** are obtained as off-white powders, which are extremely sensitive toward air. The solid immediately turns yellow upon exposure to air. They are soluble in toluene, benzene, and THF and slightly soluble in diethyl ether and pentane.



3a R = Me
3b R = $SiMe_3$

That the formation of **3** is driven by thermodynamics became evident from the observation that irrespective of the ratio of the starting materials, $[Li_2(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ and $[CuC{\equiv}CC_6H_4R\text{-}4]$, **3** is always formed, with one of the unreacted starting materials remaining that was present in excess. This was furthermore confirmed by the observation that the attempted substitution of the bromide anion in $[CuLi_2Br(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (**1**) with a stoichiometric amount of $[LiC{\equiv}CC_6H_4R\text{-}4]$ (eq 2) leads to the formation of **3** and $[Li_2(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$. These observations indicate that among other aggregates that might be formed during the synthesis of **3** it is **3** that is thermodynamically the most stable one.

$$CuLi_2BrR_2 \xrightarrow[-\ LiBr]{LiC{\equiv}CR'} 1/2\ \mathbf{3a} + LiR \qquad (2)$$

$R = C_6H_4[CH_2N(Me)CH_2CH_2NMe_2\text{-}2]$

$R' = C_6H_4Me\text{-}4$ or $C_6H_4SiMe_3\text{-}4$

Solid State Structure of 3a and 3b. Both for **3a** and **3b** the crystal structures were determined, showing that their overall structural geometries are identical; see Figure 2. Selected bond distances, angles, and torsion angles are given in Table 1. Only slight but not significant differences were observed in bond distances and angles; therefore the structure of **3a** is described below in detail. Corresponding bond distances and angles for **3b** are given in Table 1 and the Supporting Information.

Compound **3a** contains two linear anionic units, $[Ar{-}Cu{-}Ar]^-$ and $[(RC{\equiv}C){-}Cu{-}(C{\equiv}CR)]^-$, linked together by two lithium cations. These two lithium cations are tetrahedral four-coordinated by N,N′-chelate coordination of the diamine functionalities of the *ortho*-$CH_2N(Me)CH_2CH_2NMe_2$ substituent and by C_{ipso} atoms of one aryl and one acetylide anion. Thus the alkynyl and aryl units each bridge one Cu and one Li atom. The centrosymmetric unit cell of the solid state structure of **3a** contains an S_NS_N/R_NR_N enantiomeric pair. Figure 2 shows the S_NS_N stereoisomer (vide infra).[18]

The two linear anionic units, $[Ar{-}Cu{-}Ar]^-$ and $[(RC{\equiv}C){-}Cu{-}(C{\equiv}CR)]^-$, are mutually orthogonally oriented. The two Cu atoms and the two Li atoms are nearly in one plane ($\angle Cu(1){-}Li(1){-}Cu(2){-}Li(2) = 2.17(13)°$). This in-plane position of the metal atoms is comparable to that found in $[Cu_2Li_2Aryl_4]$ ($Aryl = C_6H_4\text{-}CH_2NMe_2\text{-}2$) ($\angle Cu(1){-}Li(1){-}Cu(2){-}Li(2) = 0.448°$).[17]

The (aryl)$C_{ipso}{-}Cu$ bonds are significantly longer than the (acetylide)$C^{\alpha}{-}Cu$ bonds (*d*(mean) 1.933 and 1.869 Å, respectively) which reflects the differences in s-character (sp^2 vs sp) and steric influences of C_{ipso} in the

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[18] Upon nitrogen to lithium coordination of the −N(Me) group, this nitrogen atom becomes a stereogenic center. The stereochemistry of cuprates of type $CuLi_2BrAr_2$ is described in ref 13.

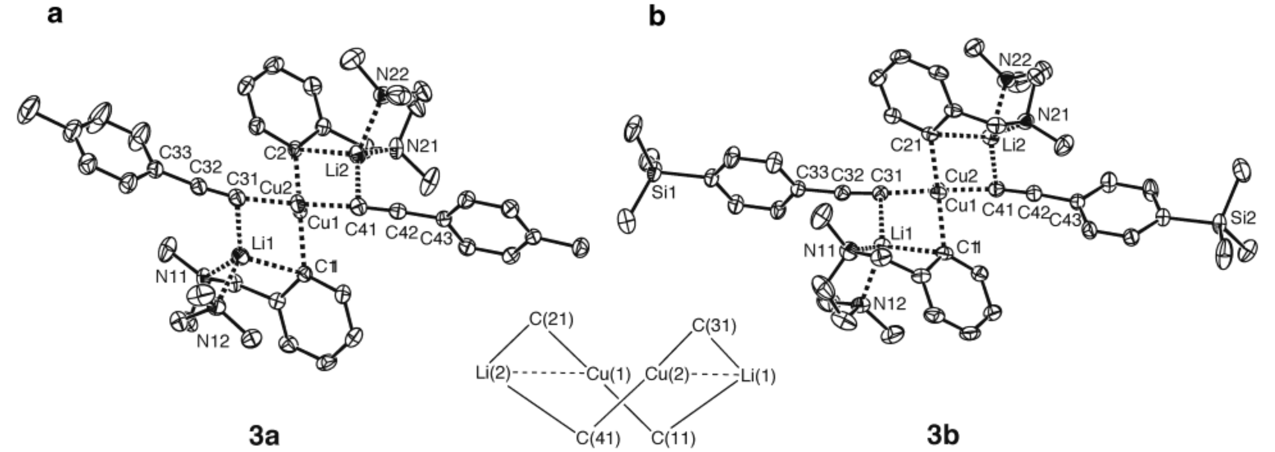

Figure 2. (a) Displacement ellipsoid plot (50% probability) of **3a**. Hydrogen atoms are omitted for clarity. Only the major disorder component of the *ortho*-diamine substituent (N11 → N12) is shown. (b) Displacement ellipsoid plot (50% probability) of **3b**. Hydrogen atoms and benzene solvent molecules are omitted for clarity.

Table 1. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for 3a and 3b[a]

	3a	3b
C31−C32	1.219(3)	1.218(3)
C41−C42	1.217(3)	1.220(3)
Cu1−C11	1.932(2)	1.943(2)
Cu1−C21	1.933(2)	1.940(2)
Cu2−C31	1.871(2)	1.868(2)
Cu2−C41	1.868(2)	1.869(2)
Li1−C11	2.513(4)	2.432(5)
Li2−C21	2.498(4)	2.435(4)
Li1−C31	2.219(4)	2.258(4)
Li2−C41	2.233(4)	2.241(4)
Cu1−Cu2	2.6723(4)	2.6282(4)
Li1−N11	2.045(4)	2.102(4)
Li1−N12	2.056(4)	2.088(4)
Li2−N21	2.094(4)	2.091(4)
Li2−N22	2.096(4)	2.095(4)
Cu1−Li1	2.678(4)	2.750(4)
Cu1−Li2	2.764(4)	2.706(4)
Cu2−Li1	2.686(4)	2.903(4)
Cu2−Li2	2.755(4)	2.813(4)
C11−Cu1−C21	166.91(9)	165.10(9)
C31−Cu2−C41	173.15(9)	176.43(9)
Cu1−C11−Li1	72.76(11)	77.00(12)
Cu1−C21−Li2	76.01(11)	75.45(11)
Cu2−C31−Li1	81.63(12)	88.91(13)
Cu2−C41−Li2	83.90(12)	85.88(13)
Cu2−C31−C32	169.5(2)	175.7(2)
Cu2−C41−C42	176.1(2)	169.7(2)
Li2−Cu2−Li1−Cu1	2.17(13)	−2.26(12)

[a] The estimated standard deviations are given in parentheses.

Cu−C bonding. The two different C−Cu−C units have bond angles of 166.91(9)° (∠C_{ipso}(11)−Cu(1)−C_{ipso}(21)) and 173.15(9)° (∠C^{α}(31)−Cu(2)−C^{α} (41)), respectively. The angle in the [alkynyl−Cu−alkynyl] anion is closer to 180° than found in the [Ar−Cu−Ar] anion. The (aryl)-C_{ipso}−Li distances in **3a** are longer than those reported for the related arylcuprate $[Cu_2Li_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_4]$[17] (2.513(4) and 2.498(4) versus 2.385(7) Å) and much longer than the (acetylide)C^{α}−Li distances (2.219(3) and 2.233(4) Å). The Cu−(aryl)C_{ipso}−Li angles in **3a** (72.76(11)° and 76.01(11)° are comparable to those in $[CuLi_2BrAr_2]$ (**1**) (77.63°).[13] Finally, the Cu−Cu distance found in **3a** (2.6723(4) Å) is longer than the ca. 2.39 Å found in the organoiodocuprate $[Cu_2I_2(2,6\text{-}Mes_2C_6H_3)][Li(THF)_4]$ (Mes = $C_6H_2Me_3$-2,4,6)[7] but comparable with the Cu−Cu distances in the 1:1 cyanocuprate $[(t\text{-Bu})Cu(CN)Li(Et_2O)_2]_{\infty}$ (ca. 2.71 Å)[19] (Table 2).

Table 2. Cu--Cu Distances (Å) in a Series of Aryl-, Alkyl-, and Mixed Aryl-alkynylcuprates.

entry	compound	*d*(mean) Cu−Cu	ref
1	$[Cu_6(C{\equiv}CC_6H_4Me\text{-}4)_2Aryl_4]$	2.47−2.85	11
2	$[Cu_2Li_2(C{\equiv}CC_6H_4Me\text{-}4)_2Ar_2]$ (**3**)	2.67	*a*
3	$[Cu_3\{SC_6H_4(CH_2NMe_2)-2\}_2(C{\equiv}Ct\text{-}Bu)]_2$	2.46−2.84	20a
4	$[Cu_3(S\text{-}1\text{-}C_{10}H_6NMe_2-8)_2(C{\equiv}Ct\text{-}Bu)]_2$	2.47−2.69	20b
5	$[Cu_2Li_2(C_6H_4\{CH_2NMe_2\}-2)_4]$	2.67	17
6	$[CuLi(CN)t\text{-}Bu]_{\infty}$	2.71	19
7	$[Cu_2I_2(C_6H_3Mes_2-2,6)][Li(THF)_4]$	2.39	7

[a] Present work.

An interesting aspect of the molecular structure of **3a** is the relatively short Cu−C^{α} bond of 1.869 Å (mean), which is also shorter than the corresponding bonds for previously reported mixed organoalkynylcopper compounds[11,20] (Table 2). In the compounds in entries 3 and 4 of Table 2 two different types of bonding for the C≡C*t*-Bu units are present. One alkynyl unit in these cuprates is μ_3-η^1 coordinated (end-on). The other unit is μ_3-η^2 bonded (side-on) to the other Cu atom. Such side-on coordination results in an elongated Cu−C^{α} distance. The Cu−Cu distances found, in **3a** (2.6723(4) Å) and **3b** (2.6282(4) Å) are similar to that in the neutral arylcuprate $[Cu_2Li_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_4]$[17] (2.666 Å) and somewhat smaller than that found in Boche's 1:1 cyanocuprate $[CuLi(CN)(t\text{-}Bu)]_2$[19] (2.713 Å) (entry 6 in Table 2). Following this author's view of Cu(d^{10})−Cu(d^{10}) bonding in such cuprates,[19] which contain a perpendicular arrangement of two organocopper units, compound **3a** could be another example of a cuprate containing such Cu(d^{10}) interactions.

Another interesting aspect of the structure of the mixed 2:2 aryl-alkynyl-cuprate **3a** concerns the fact that the C_{ipso}−Li bond distances in **3a** are ca. 0.2 Å larger (2.498(4) and 2.513(4) Å) than in the aryl-bromocuprates. These observations suggest that the electron-deficient type of bonding of C_{ipso} between copper and

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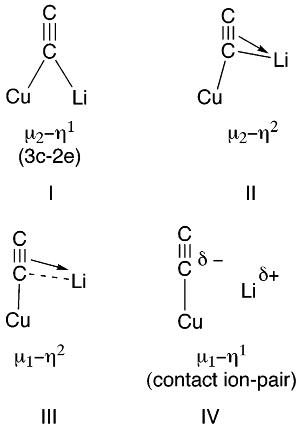

Figure 3. Possible bonding modes of an alkynyl group bonded to copper and lithium.

lithium is far less pronounced in **3a** than in other known neutral cuprates.[13,17] This supports our idea that **3a** can be best seen as consisting of two anionic homocuprate parts, namely, [Ar−Cu−Ar] and [RC≡C−Cu−C≡CR], with the two Li cations acting as bridges between the anionic parts.

The Cu−C^{α}−Li angle is almost rectangular (81.63(12)° and 83.90(12)°), while the acetylene-copper (Cu−C^{α}−C^{β}) units are almost linear (169.5(2)° and 176.1(2)° for Cu(2)−C(31)−C(32) and Cu(2)−C(41)−C(42), respectively). Bridge-bonding of an alkynyl unit between copper and lithium can be realized in various ways[21] (Figure 3). The actual interaction may differ in the number of atoms (one or two) bonded to the C^{α} atom of the alkynyl group (μ_1 or μ_2 type) and in the way the triple bond participates in the bonding to lithium (η^1 or η^2 type). At first sight, the bridging of the *p*-tolylacetylene unit between copper and lithium seems to be of 3c-2e character (μ_2-η^1, Type I in Figure 3).

In the ^{13}C NMR spectrum (vide infra) of **3a**, however, two distinct broad resonances with a line width of ca. 20 Hz are observed, which point to coupling of both the C^{α} and C^{β} with lithium ($^1J(^{13}C-^7Li = 7$ Hz). The bonding of both C^{α} and C^{β} to lithium suggests a side-on coordination mode of the acetylene unit to lithium (as in Type II and III in Figure 3). Such an interaction between lithium and *p*-tolylacetylene would rule out the possibility of a contact ion pair interaction or electrostatic π-contacts[21] (Type IV in Figure 3). Supporting evidence for at least partial side-on coordination follows from the solid state structure of **3a**, where the distances between lithium and the C^{α} and C^{β} atoms of the *p*-tolylacetylene group are quite close, i.e. ca. 2.2 and 2.7 Å, respectively. Moreover, the short Cu−C^{α} bond distances of 1.868(2) and 1.871(2) Å suggest that, despite the interaction between lithium and C^{α}, the interaction between copper and C^{α} can be best described in terms of two-center−two-electron (2c-2e) bonding. This sp-character also appears from the Cu−C^{α}−C^{β} angles (176.1(2)° and 169.5(2)°) (vide supra). In conclusion, the bridging of the *p*-tolylacetylene ligand can be considered to be intermediate between Type II and III (Figure 3).

Structure of 3a in Solution. The ^{1}H NMR spectrum (benzene-d_6, 298 K) of the mixed 2:2 aryl-alkynylcuprate **3a** shows one resonance pattern with two distinct singlet resonances ($\Delta\delta$ ca. 1 ppm) for the NMe_2 groups of the aryl ligands and one AB pattern for the benzylic protons. These observations indicate that at room temperature both the benzylic (NMe) and dimethylamino (NMe_2) nitrogen atoms coordinate to a lithium atom. The presence of single resonance patterns, for both the aryl ligands and the *p*-tolylacetylene ligands, points to the presence of an inversion center in **3a** in solution, which implies that the structure of **3a** found in the solid state is retained in solution. The $^{13}C_{ipso}$ resonance of **3a** (benzene-d_6, 298 K) has a line width of 15 Hz. From this, and data obtained for species such as **1** ($^1J(^{13}C_{ipso}-^7Li) = 7$ Hz),[13] it follows that an average $^1J(^{13}C_{ipso}-^7Li)$ of about 5 Hz is present in **3a**. Both ^{13}C signals of the C≡C units are broad (line width ca. 20 Hz), which is in accord with a ^{13}C nucleus being coupled to one ^{7}Li nucleus with an average $^1J(^{13}C^{\alpha}-^7Li)$ of about 7 Hz. Attempts to resolve the expected quartet multiplicity (1:1:1:1 intensity distribution) failed (toluene-d_8, 243 K, 75 MHz).

Coordination of the benzylic nitrogen (NMe) to lithium turns the N^{Me} atom into a stereogenic center. As a result, **3a** may exist as four diastereoisomers and in the solid state it appears to be the S_NS_N/R_NR_N enantiomeric pair. Since for both the aryl and *p*-tolylacetylene ligands only one distinct signal is observed in the NMR spectrum, one can conclude that also in solution only one diastereoisomeric pair is present (no decision can be made whether this is the racemic or meso compound). Variable-temperature NMR investigations do not provide any evidence for interconversion of these stereoisomers in solution.[13,18] Upon cooling to 233 K, no significant alterations in the resonance pattern were observed. The ^{1}H NMR spectrum at elevated temperature (333 K) shows coalescence of the NMe_2 methyl resonances to one singlet, showing that the N^{Me2}−Li coordination−dissociation process has become fast on the NMR time scale. The benzylic protons are still represented by a distinct AB pattern, even at 333 K, pointing to N^{Me}−Li coordination, which is rigid on the NMR time scale. Above 333 K, decomposition of cuprate **3a** occurs.

Both in the solid state (Nujol) and in solution (benzene), the IR spectrum of **3** shows a C≡C stretching vibration at 2076 cm^{-1}. This suggests identical structural features in solution and in the solid state. Conclusive evidence for a dimeric structure in solution is provided by cryoscopic molecular weight determination in benzene (calcd for **3a**, 752.80; found, 670).

Concluding Remarks

The neutral heterocuprates **3** are the first cuprates in which two different homocuprate anionic moieties ($[Ar-Cu-Ar]^-$ and $[RC{\equiv}C-Cu-C{\equiv}CR]^-$)(Ar = $[C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2]^-$) and [CuC≡CR] (R = C_6H_4-Me-4 or $C_6H_4SiMe_3$-4) are combined. Both lithium cations function as bridges between the two homocuprate anionic parts and are stabilized by the N,N′-chelating function of the *ortho*-diamino substituent of the Ar ligand.

The intrinsic stabilities of the $[Aryl_4Cu_6]^{2+}$ cationic skeleton as found in $[Cu_6Br_2Aryl_4]$, **2**,[10] and that of the $[Ar_2Cu]^-$ anion in $[CuLi_2BrAr_2]$, **1**,[13] critically affect the

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[21] The various possibilities involving π-interactions of acetylenes with alkali metal cations have been discussed earlier; see: Goldfuss, B.; Schleyer, P. Von R.; Hampel, F. *J. Am. Chem. Soc.* **1997**, *119*, 1080.

type and stability of the copper compounds formed during substitution reactions. As an example, the substitution of bromide by acetylide occurs only on a stable cationic moiety as is seen in compound **2**. Another example is the selective synthesis of the relatively stable, mixed 2:2 aryl-alkynyl-cuprate **3** from [LiAr] and different combinations of [CuC≡CR]. An alternative view of the formation of **3** is that it occurs by a substitution of Br^- in **1** by a $[RC{\equiv}C{-}Cu{-}C{\equiv}CR]^-$ anion.

Experimental Section

General Comments. All experiments were carried out under a completely dry and oxygen-free nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried and distilled prior to use. All reactions concerning organocuprate and -lithium syntheses were carried out in flame-dried Schlenk flasks. The starting materials $[CuLi_2Br(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (**1**),[13] $[Li_2(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (**4**),[22] $[LiC{\equiv}C(C_6H_4Me\text{-}4)]$,[15] and $[CuC{\equiv}C(C_6H_4Me\text{-}4)]_\infty$[15] were prepared according to literature procedures. $[CuC{\equiv}C(C_6H_4SiMe_3\text{-}4)]_\infty$ was prepared starting from $HC{\equiv}C(C_6H_4SiMe_3\text{-}4)$[16] according to the procedure described for $[CuC{\equiv}C(C_6H_4Me\text{-}4)]_\infty$. 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. For calibration, naphthalene was used to give the cryoscopic constant $K_f = 5.54$ K·kg·mol^{-1}. IR spectra were recorded on a Mattson Galaxy FTIR 5000 spectrometer and on a Mettler Toledo ReactIR 1000 FTIR spectrometer with a K6 conduit, 6 bounce SiComp probe, Nickelson Interferrometer, and MCT Midband detector.

$[Cu_2Li_2(C{\equiv}CC_6H_4Me\text{-}4)_2(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (3a). To a stirred suspension of $[CuC{\equiv}CC_6H_4Me\text{-}4]_\infty$ (369 mg; 2.07 mmol based on monomer) in toluene (40 mL) was slowly added dropwise a solution of $[Li_2(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (**4**) (0.41 g; 2.07 mmol of monomer) in toluene (25 mL) at 0 °C. After additional stirring for 1 h at 0 °C the temperature was raised to ambient temperature, upon which the reaction mixture turned into a clear yellow solution. After stirring for another 30 min at room temperature the solvent was evaporated in vacuo, leaving the crude product as an off-white powder. After subsequent washing with pentane (3 × 15 mL) **3** was obtained as an almost white powder (0.74 g, 95%; 0.98 mmol based on dimer). Crystals (ca. 65%) suitable for X-ray structure determination were obtained by crystallization from benzene/pentane (1:1) at room temperature.

^1H NMR (C_6D_6, 300.105 MHz, 298 K): δ (in ppm) 1.05 (bs, 6H, NMe_2) 1.42 (m, 4H, $N(Me)CH_2CH_2N$), 1.79 (m, 2H, $N(Me)CH_2CH_2N$), 2.04 (s, 12H, NMe_2 and $CH_2N(Me)$). 2.20 (s, 6H, $C_6H_4(CH_3)$), 2.36 (m, 2H, $N(Me)CH_2CH_2N$), 2.77 (d, 2H, $^2J = 10.80$ Hz, $ArCH_2N$), 4.12 (d, 2H, $^2J = 10.80$ Hz, $ArCH_2N$), 6.90 (d, 4H, *p*-Tol*H*(*2,6*)), 6.95 (d, 2H, Ar*H*(*3*)), 7.18 (t, 2H, Ar*H*(*4*)), 7.51 (bt, 2H, Ar*H*(*5*)), 7.64 (d, 4H, *p*-Tol*H*(*3,5*)), 9.34 (bs, 2H, Ar*H*(*6*)). ^{13}C NMR (C_6D_6, 75.469 MHz, 298 K): δ (in ppm) 21.16 (*p*-Tol(CH_3)), 42.7 (b, NMe_2), 46.1 ($N(Me)CH_2CH_2N$), 47.5 (b, NMe_2), 52.6 ($N(Me)CH_2CH_2N$), 57.3 ($N(Me)$), 70.9 ($ArCH_2$), 111.6, 120.2 (b, $J^1(^{13}C{-}^7Li)$ = ca. 6.7 Hz,$C{\equiv}C$), 123.54, 124.7 (Ar(*3,4*), 125.3, 129.1, 131.7 (*p*-Tol), 135.3, 144.9, 149.2 (Ar), 166.6 ($J^1(^{13}C{-}^7Li)$ = ca. 5 Hz, $Ar(C_{ipso})$. IR (**3** in Nujol): 2076 cm^{-1}; (**3** in C_6H_6) 2076 cm^{-1}. Anal. Calcd for $C_{42}H_{52}Cu_2Li_2N_4$: C, 66.92; H, 6.95; N, 7.43. Found: C, 67.11; H, 6.82; N, 7.34. Molecular weight determination by cryoscopy (0.44 g in 16.19 g of C_6H_6). Calcd for $C_{21}H_{26}CuLiN_2$: 376.40. Found: 670.

Table 3. Experimental Data for the X-ray Diffraction Studies of 3a and 3b

	3a	**3b**
formula	$C_{42}H_{52}Cu_2Li_2N_4$	$C_{46}H_{64}Cu_2Li_2N_4Si_2\cdot 0.56C_6H_6$
M_r	753.84	913.89
cryst size [mm^3]	0.60 × 0.12 × 0.12	0.63 × 0.18 × 0.18
cryst color	yellow	yellow
temp [K]	150(2)	150(2)
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a [Å]	12.7340(2)	11.8848(2)
b [Å]	12.8276(1)	13.3156(2)
c [Å]	14.2614(2)	18.6519(3)
α [deg]	97.7242(7)	81.5370(7)
β [deg]	103.7379(6)	78.6000(7)
γ [deg]	114.7861(7)	69.5940(6)
V [Å^3]	1980.83(4)	2702.06(7)
Z	2	2
ρ [g/cm^3]	1.264	1.123
μ [mm^{-1}]	1.11	0.86
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.65	0.65
no. of reflns (measd/unique)	45 664/9004	55 863/12 163
abs corr	PLATON (MULABS)	PLATON (MULABS)
transmn	0.78−0.91	0.76−0.88
no. of params/restraints	469/8	559/12
R1/wR2 [$I > 2\sigma(I)$]	0.0378/0.0867	0.0380/0.1284
R1/wR2 [all reflns]	0.0522/0.0933	0.0440/0.1328
S	1.040	1.103
res dens [e/Å^3]	−0.41/0.73	−0.57/0.87

$[Cu_2Li_2(C{\equiv}CC_6H_4SiMe_3\text{-}4)_2(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (3b). The synthetic procedure is identical to that described for **3a**, starting from $[Cu(C{\equiv}CC_6H_4SiMe_3\text{-}4)]$ (0.53 g; 2.24 mmol) and $[Li_2\{C_6H_4(CH_2N(Me)CH_2CH_2NMe_2)\text{-}2\}_2]$ (**4**) (0.44 g; 2.24 mmol) in toluene (50 mL). Analytically pure **3b** was obtained by crystallization from benzene/pentane at room temperature. Yield: 0.38 g (39%).

^1H NMR (C_6D_6, 300.105 MHz, 298 K): δ (in ppm) 0.16 (s, 18H, $Si(Me_3)$), 1.04 (bs, 6H, NMe_2), 1.38 (m, 4H, $N(Me)CH_2CH_2N$), 1.75 (t, 2H, $N(Me)CH_2CH_2N$), 2.08 (bs, 6H, NMe_2), 2.21 (s, 6H, $CH_2N(Me)$), 2.30 (m, 2H, $N(Me)CH_2CH_2N$), 2.75 (d, 2H, $^2J = 10.80$ Hz, $ArCH_2$), 4.11 (d, 2H, $^2J = 10.80$ Hz, $ArCH_2$), 6.94 (d, 2H, Ar*H*(*3*)), 7.16 (t, 2H, Ar*H*(*4*)), 7.37 (d, 4H, *p*-Si(Me_3)Ar*H*(*2,6*)), 7.53 (bt, 2H, Ar*H*(*5*)), 7.74 (d, 4H, *p*-Si(Me_3)Ar*H*(*3,5*)), 9.34 (bs, 2H, Ar*H*(*6*)). ^{13}C NMR (C_6D_6, 75.469 MHz, 298 K): δ (in ppm) −1.23 ($Si(Me_3)$), 42.5 (NMe_2), 46.1 ($N(Me)CH_2CH_2N$), 47.5 (NMe_2), 51.6 ($N(Me)CH_2CH_2N$), 56.6 ($N(Me)$), 70.9 ($ArCH_2$), 111.1 (b, $ArC{\equiv}C$), 121.2 (b, $ArC{\equiv}C$), 125.4, 125.8 (Ar(*3,4*), 127.3, 128.4, 131.5, 133.8 (*p*-$Me_3Si{-}Ar(1{-}6)$, 138.3, 144.8, 149.2 (Ar(*2,5,6*), 166.7 ($Ar(C_{ipso})$). Anal. Calcd for $C_{46}H_{64}N_4Cu_2Li_2Si_2$: C, 63.49; H, 7.41; N, 6.44. Found: C, 63.56; H, 7.21; N, 6.30.

Structure Determinations and Refinement of 3a and 3b. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ = 0.71073 Å). The structures were solved with direct methods (SHELXS97[24] for **3a** and SIR97[23] for **3b**) and refined with SHELXL97[24] against F^2 of all reflections. One of the *ortho*-diamine substituents in **3a** was refined with a disorder model. There are two crystallographically independent benzene solvent molecules present in **3b**, which were refined with an stoichiometry of 26% and 30% with respect to the main molecule. Molecular illustrations,

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structure checking, and calculations were performed with the PLATON package.[25] Further details are given in Table 3.

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Supporting Information Available: X-ray crystallographic data of **3a** and **3b** (also CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM030082A

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