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The First Homologous Series of Self-Assembled Aryl Bromo- and Aryl Cyanocuprates, -Argentates, and -Aurates; MLi$_2$XAr$_2$ (M = Cu^{I}, Ag^{I}, Au^{I}; X = Br, C≡N; Ar = [C$_6$H$_4$CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$-2]$^-$)

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Received May 17, 2002

Abstract: Reaction of 2 molar equiv of the diamine chelated aryllithium dimers Li$_2$(C$_6$H$_4${CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$}-2)$_2$ (Li$_2$Ar$_2$) with the appropriate metal bromide allows the synthesis of the first homologous series of monomeric group 11 bromoate complexes of type MLi$_2$BrAr$_2$ (M = Cu (**7**), Ag (**8**), Au (**9**)). Both in the solid state and in solution, the bromocuprate **7** is isostructural with the bromoargentate **8**. The crystal structures of **7** and **8** consist of a MLi$_2$ core, and each of the two aryl ligands bridges via electron-deficient bonding between the group 11 metal and one Li atom (d(C$_{ipso}$−M) = 1.941(4) (mean) and 2.122(4) (mean) Å, for **7** and **8**, respectively). The bromine atom exclusively bridges between the two lithium atoms. Each of the *ortho*-CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$ moieties is *N*,*N′*-chelate bonded to one lithium (d(N−Li) = 2.195(5) and 2.182(0) (mean) Å for **7** and 2.154(8) and 2.220(1) (mean) Å for **8**). Although the MLi$_2$BrAr$_2$ compounds are neutral higher-order -ate species, the structure can also be regarded as consisting of a contact ion pair consisting of two ionic fragments, [Li−Br−Li]$^+$ and [Ar$_2$M]$^-$, which are interconnected by both Li-*N*,*N′*-chelate bonding and a highly polar C$_{ipso}$−Li interaction. On the basis of NMR and cryoscopic studies, the structural features of the bromoaurate **9** are similar to those of **7** and **8**. A multinuclear NMR investigation shows that the bonding between the [Li−Br−Li] and [Ar$_2$M] moieties is intermediate between ionic and neutral with an almost equally polarized C$_{ipso}$−Li bond in **7**, **8**, and **9**. Similar reactions between M(C≡N) and 2 molar equiv of LiAr yield the analogous 2:1 cyanoate complexes of type MLi$_2$(C≡N)Ar$_2$ (M = Ag (**10**), Au (**11**)). Multinuclear NMR studies show that the cyanoate complexes **10** and **11** are isostructural with the bromoate complexes **7**, **8**, and **9**. This paper illustrates that these cyanoaurates may serve as excellent model complexes to gain more insight into the structure of 2:1 cyanocuprates in solution.

Introduction

Organocopper(I) complexes, especially cuprates [CuLi$_n$R$_{n+1}$] and [CuLi$_n$XR$_n$] (n = 1,2), are widely used, often as in situ prepared reagents, in organic synthesis.[1] Along with the development of synthetic applications, interest in the structural features both in the solid state and in solution is increasing as well. Although a number of pure halocuprates (X = Cl, Br, I)[2] and cyanocuprates[3,4] have been reported, particularly the structural aspects of cyanocuprates (X = CN) are subject to extensive, ongoing discussions in the literature.[5,6] We have set out to concentrate our synthetic and structural studies on haloaryl and cyanoaryl cuprates containing monoanionic, *ortho*-mono-, and -diamine chelating aryl ligands; see Scheme 1. The use of these *ortho*-amine aryl ligands allows the formation of stable, well-defined organocopper aggregates of which the neutral

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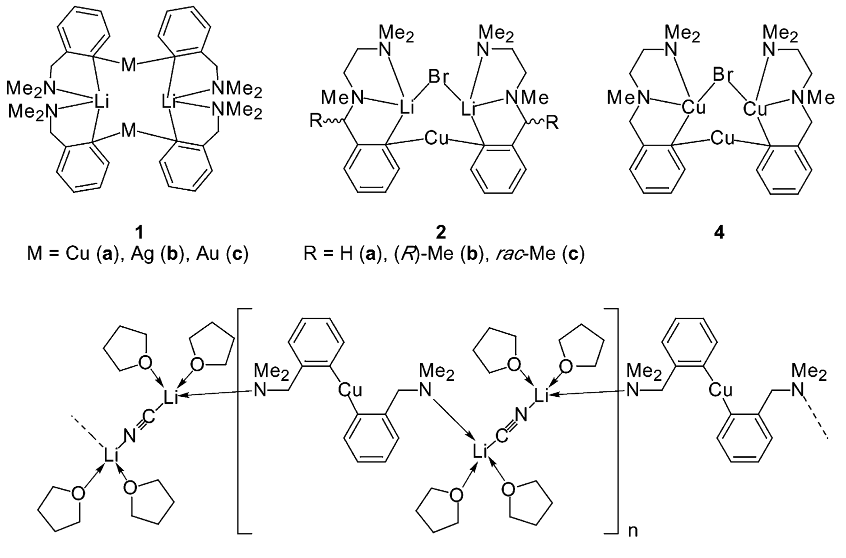
10.1021/ja026945t CCC: $22.00 © 2002 American Chemical Society

Scheme 1



1
M = Cu (**a**), Ag (**b**), Au (**c**)

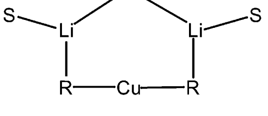
2
R = H (**a**), (*R*)-Me (**b**), *rac*-Me (**c**)

4

3

bromocuprate $[CuLi_2Br(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (**2a**) (vide infra, Scheme 1) is an interesting example.[7] In the complexes **1** and **2**, the *ortho*-amine substituents represent suitably positioned donor atoms[8] which contribute, by forming additional N−Li or N−Cu bonds, to the overall (thermodynamic) stability of the resulting cuprate aggregate. Recently, we have also reported the synthesis and characterization of a stable, polymeric 2:1 cyanocuprate $[Cu(C_6H_4\{CH_2NMe_2\}\text{-}2)_2]^-[Li_2(CN)\cdot(THF)_4]^+$ (**3**) (vide infra, Scheme 1).[3] The solid-state structure of **3** reveals an ionic structure comprising distinct, anionic $[R_2Cu]^-$ moieties with a linear C−Cu−C arrangement and $[Li_2(CN)]^+$ countercations. In this structure, the amino-to-Li coordination occurs between both ionic species.

Despite the disclosure of this solid-state structure of a 2:1 cyanocuprate, the structures of such cuprates in solution remain uncertain. Recent NMR studies by Gschwind et al.[5e] reveal that organocuprates exist in solution either as contact ion pairs (CIP) or as solvent-separated ion pairs (SSIP), depending on the nature of the solvent. The neutral bromocuprates **2** (achiral, **2a**, enantiomerically pure, **2b**, and racemic, **2c**), which we recently reported, may be regarded as comprising $[R_2Cu]^-$ and $[Li_2Br]^+$ ionic fragments (vide infra).[5,7] They occur as discrete neutral monomers $CuLi_2BrR_2$, both in the solid state and in apolar solutions; see Figure 1.[7] This unique feature prompted us to attempt the synthesis of the corresponding aryl cyanocuprate, -argentate, and -aurate complexes. The resulting $[MLi_2(CN)R_2]$ species, when accessible, may serve as model complexes for an important class of organo cyanocuprates ($M = Cu^I$) which has been used as a starting point in a number of computational studies;[6b−f] see Figure 1. The synthesis of the corresponding argentate(I) and aurate(I) complexes would give the first series of homologous 2:1 heteroate complexes in group 11 organometallic chemistry. An early example of such a series in group 11 alkyl and aryl chemistry is the neutral 1:1 homoate complexes $[Li_2M_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_4]$ for $M = Cu^I$ (**1a**),[9] Ag^I (**1b**),[10] and Au^I (**1c**)[11] (cf., Scheme 1).[12]



S = suitable solvent
a X = $[RCuR]^-$
b X = Br^- or CN^-

Figure 1. Schematic representations of organocuprates. a, homocuprates; b, heterocuprates.

The present study describes the synthesis and isolation of the homologous series of aryl bromo- and cyanoate complexes $[MLi_2X(C_6H_4\{CH_2N(Et)CH_2CH_2NEt_2\}\text{-}2)_2]$ ($M = Cu^I$, X = Br (**7**); $M = Ag^I$, X = Br (**8**); $M = Au^I$, X = Br (**9**); $M = Ag^I$, X = CN (**10**); and $M = Au^I$, X = CN (**11**)).[21] These are the first

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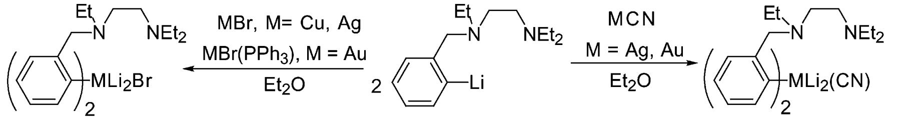
Scheme 2



M = Cu, **7**; Ag, **8**; Au, **9**   **6**   M = Ag, **10**; Au, **11** (Cu, **12**)

compounds that substantiate the $CuLi_2XR_2$ structural motif that has been discussed in computational studies.[6b−f] In fact, the structural similarities of the heterocuprate **7**, heteroargentate **8**, and the bromocopper compound **4** show that the $[R_2Cu]^-$, $[R_2Ag]^-$, and $[R_2Au]^-$ building blocks can self-assemble with any suitable $[M_2X]^+$ cation to give stable, overall neutral species.

Results

Syntheses. *N*-(2-Bromobenzyl)-*N*,*N′*,*N′*-triethyl-1,2-diaminoethane $[C_6H_4BrCH_2N(Et)CH_2CH_2NEt_2\text{-}2]$ (**5**) was prepared via amination of 2-bromobenzyl bromide with $(HN(Et)CH_2CH_2NEt_2)$ analogous to the synthesis of $[C_6H_4BrCH_2N(Me)CH_2CH_2NMe_2\text{-}2]$.[22] Lithiation of **5** by slow addition of an equimolar amount of *n*-BuLi in pentane at −78 °C gave dimeric $[Li(C_6H_4\{CH_2N(Et)CH_2CH_2NEt_2\}\text{-}2)]_2$ (**6**) in 85% yield. The heterogeneous reaction of **6** in diethyl ether with insoluble copper(I) bromide resulted in selective formation of the neutral aryl bromocuprate $[CuLi_2Br(C_6H_4\{CH_2N(Et)CH_2CH_2NEt_2\}\text{-}2)_2]$ (**7**) (Scheme 2). Compound **7**, which was isolated as a colorless solid in 85% yield, is air- and moisture-sensitive, and crystalline material immediately turns green upon exposure to air. It is very soluble in benzene, toluene, and THF and slightly soluble in diethyl ether, pentane, and hexane. A successful cuprate synthesis requires following a strict synthetic protocol, and the synthesis of **7** is no exception. The temperature at which the cuprate formation begins should be below −30 °C. At higher temperatures, cuprate formation is accompanied by reductive side reactions giving metallic copper particles which are known to cause subsequent autocatalytic decomposition.[23−25] As the formation of copper metal cannot be completely avoided, its removal from the cuprate solution via a quick filtration through Celite is essential (details can be found in the Experimental Section). In the absence of metallic copper, the cuprate **7** is relatively stable. Also, the stoichiometry of the starting materials, that is, the Li:Cu atomic ratio, must be exactly 2:1.

The analogous aryl bromoargentate $[AgLi_2Br(C_6H_4\{CH_2N(Et)CH_2CH_2NEt_2\}\text{-}2)_2]$ (**8**) and -aurate $[AuLi_2Br(C_6H_4\{CH_2N(Et)CH_2CH_2NEt_2\}\text{-}2)_2]$ (**9**) were prepared by reacting equimolar amounts of **6** with AgBr or $AuBr(PPh_3)$, using similar synthetic procedures (Scheme 2). In both cases, the -ate formation should begin at or below −78 °C. Argentate **8** was obtained in reasonable yield as a cream-colored powder which is air- and moisture-sensitive. The powder readily turns dark brown-to-black upon exposure to light for periods ranging from several minutes to 1 h. The aryl bromoaurate **9** is obtained as a pink/white solid which is slightly light sensitive; after exposure to light for a period of 6 h, its color had slowly changed to purple/black. The argentate **8** is easily soluble in THF but only slightly so in benzene and toluene. It is almost insoluble in diethyl ether, pentane, and hexane. Aurate **9** shows the same solubility behavior as cuprate **7** (vide supra).

The reaction of **6** with silver(I) or gold(I) cyanide in diethyl ether affords the analogous aryl cyanoargentate $[AgLi_2(C{\equiv}N)(C_6H_4\{CH_2N(Et)CH_2CH_2NEt_2\}\text{-}2)_2]$ (**10**) or -aurate $[AuLi_2(C{\equiv}N)(C_6H_4\{CH_2N(Et)CH_2CH_2NEt_2\}\text{-}2)_2]$ (**11**) as the major reaction products (Scheme 2). Both **10** and **11** are highly air-, moisture-, and light-sensitive white solids, which are soluble in benzene, toluene, and diethyl ether and slightly soluble in pentane and hexane. The similar reaction of **6** with copper(I) cyanide resulted in the formation of a solid material that partially redissolved in all common solvents after separation (vide infra).

Crystallographic Studies of -Ate Complexes 7 and 8. Suitable crystals for X-ray diffraction were grown by vapor diffusion of pentane into benzene solutions of **7** and **8** at room temperature and at 0 °C, respectively. Both compounds appeared to be isomorphous in the solid state, which implies that they crystallize in the same monoclinic space group $P2_1/c$ with essentially the same cell parameters and atomic positions. The small deviations observed can be explained by the different measurement temperatures of 150 K for **7** and 125 K for **8**, and by the slightly different radii of the Cu^I and Ag^I atom (0.60 versus 0.81 Å, for coordination number 2[26]). Isomorphism is a common phenomenon among Cu^I and Ag^I compounds (for examples, see refs 27, 28).

In the crystal structures of **7** and **8**, part of the Li sites are occupied by Cu and Ag atoms, respectively. The occupancies were refined as 9 and 4% Cu in **7** on positions Li1 and Li2, respectively, and 2.3 and 2.9% Ag in **8**, on positions Li1 and Li2. This implies that the corresponding Cu_3 and Ag_3 complexes also have to be isomorphous, which is a prerequisite for the formation of such substitutional solid solutions. We can assume that the *N*,*N′*-chelated site can be occupied by Li, Cu, and Ag in any ratio without changing the crystal structure. This interpretation of the electron density is supported by the knowledge that tetrahedral geometries are quite common in Cu^I and Ag^I complexes.[32]

The molecules are discrete, neutral $[MLi_2BrR_2]$ species in the solid state (Figure 2). The bond lengths and angles given

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(21) So far, all attempts to prepare suitable crystals of the corresponding arylcyanocuprate of **2** for an X-ray structure determination had failed. For this reason, we decided to replace the methyl groups in the *ortho*-diamine chelating substituent of the aryl ligand in **2** by ethyl groups which enhance the Lewis basicity of the N-donor sites leading to a stronger N−Li coordination.

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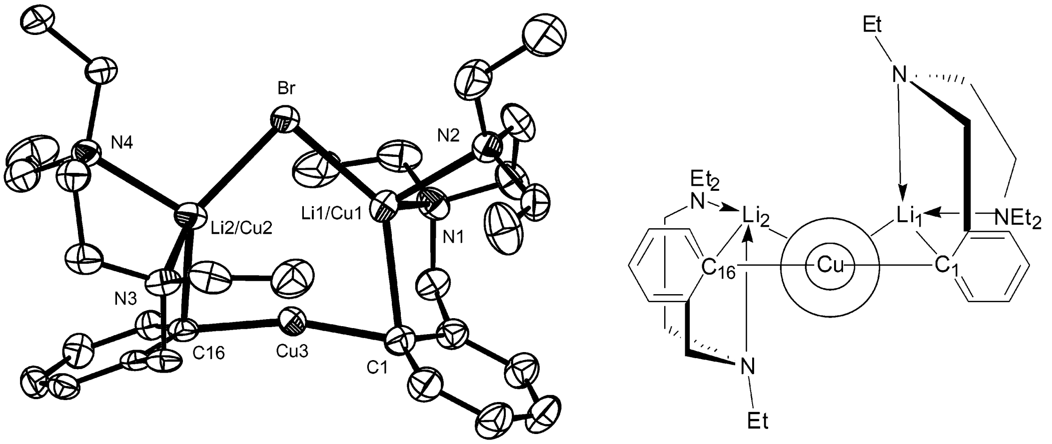

Figure 2. Displacement ellipsoid plot (50% probability level) of **7**. The position of Li1 is occupied by 91% Li and 9% Cu. The position of Li2 is occupied by 96% Li and 4% Cu. The crystal structures of the Cu compound **7** and the Ag compound **8** are isostructural. A schematic Newman projection along the Cu−Br axis is depicted as well. Torsion C1−Cu3−Br−Li2, 155.72(19)°.

for Li are averaged, including the contribution of Cu and Ag, respectively. The transition-metal atom is bonded to both anionic aryl units and is therefore two-coordinate ($\angle C_{ipso}-M-C_{ipso} = 165.13(15)°$ for **7** and 168.08(14)° for **8**). The two-coordinate bromide anion links the two lithium centers ($\angle Li1-Br-Li2 = 94.53(12)°$ and 99.97(17)° for **7** and **8**, respectively). Additional chelate bonding of the two amine-nitrogen atoms of the *ortho*-diamine substituent and C_{ipso} of the same aryl group completes the coordination environment of each of the lithium centers, which is best described as distorted tetrahedral. In particular, the N−Li−N angles (85.41(16)° and 86.6(2)° for Li1 in **7** and **8**, respectively) are significantly distorted by chelate-ring formation and much smaller than the ideal tetrahedral value. Table 1 summarizes the geometrical details of the molecular structures of **7** and **8**.

The molecules can be considered to consist of a cationic $[Li-Br-Li]^+$ fragment and an anionic $[Ar-Cu-Ar]^-$ (**7**) or $[Ar-Ag-Ar]^-$ (**8**) fragment, which are connected by chelate *N*,*N*′-Li binding to form a neutral molecule with approximate, noncrystallographic C_2 symmetry. Deviations from C_2 symmetry are mainly caused by conformational differences between the ethyl groups.

Upon coordination of the benzylic N^{Et} atoms to lithium, these nitrogen groups become stereogenic. The centrosymmetric structures of both **7** and **8** contain the R_NR_N/S_NS_N enantiomeric pair in the unit cell. The alternative R_NS_N/S_NR_N stereoisomers are not only absent from the solid state but also from solution as appears from variable-temperature NMR experiments (vide infra). The bonding of the *ipso*-carbon atom of the aryl group to the two metals is highly asymmetric; the bonds to the lithium atoms are significantly longer (C−Li 2.402(5) and 2.361(5) Å in **7**, C−Li 2.502(6) and 2.396(6) Å in **8**) than the bonds to the group 11 metal (C−Cu 1.940(4) and 1.942(4) in **7**, 2.118(4) and 2.126(3) in **8**). The C_{ipso}−Cu and −Ag bonds are in the expected range for σ C_{sp2}−M bonds.[29,30] Monoanionic $[Ag_3Li_2Ph_6]^{-}$[31], in which the lithium atoms are only coordinating to aryl anions, contains significantly shorter C−Li distances (2.188−2.332 Å). The C_{ipso}−Cu bond distances are comparable to those found in the neutral homocuprate $[Cu_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$ (**1a**) (d(mean) = 1.942 Å)[32] and in $[CuLi_2Br(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (**2a**) (d(mean) = 1.928 Å).[7] Also, the trinuclear neutral heteroorganocopper compound $[Cu_3Br(C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2)_2]$ (**4**),[32] which is structurally closely related to **7**, shows similar C_{ipso}−Cu bond lengths (d(mean) = 1.968 Å). These structures, **1a**, **2a**, **4**, and **7**, have asymmetric C_{ipso}CuLi bonding in common, which suggests the presence of 3c−2e bonding or 2c−2e C_{ipso}−Cu bonding complemented by a polar C_{ipso}−Li interaction. It is interesting to note that the C_{ipso}−Cu bond distances in the ionic cyanocuprate $[CuLi_2(C{\equiv}N)(C_6H_4\{CH_2NMe_2\}\text{-}2)_2(THF)_4]$ (**3**), which only contains 2c−2e C−Cu bonds, are slightly shorter (d(mean) = 1.917 Å).[3] Finally, the Ag−C_{ipso} and Ag−Li distances in **8** are about 0.1 Å longer than the corresponding Cu−C_{ipso} and Cu−Li distances in **7**, which is in agreement with the smaller ionic radius of Cu^I (0.60 Å) versus Ag^I (0.81 Å).

Table 1. Selected Bond Distances, Angles, and Torsion Angles for **7** and **8**[a]

	7; M = Cu	**8**; M= Ag
C1−M3	1.940(4)	2.118(4)
C16−M3	1.942(4)	2.126(3)
Li1[b]−M3	2.621(3)	2.789(5)
Li2[c]−M3	2.807(4)	2.828(5)
M3−Br	3.6702(7)	3.6632(5)
N1−Li1[b]	2.197(4)	2.154(6)
N2−Li1[b]	2.193(4)	2.155(6)
N3−Li2[c]	2.159(5)	2.220(6)
N4−Li2[c]	2.203(5)	2.218(5)
Li1[b]−Br	2.408(3)	2.417(5)
Li2[c]−Br	2.412(4)	2.395(5)
Li1[b]−C1	2.402(5)	2.502(6)
Li2[c]−C16	2.361(5)	2.369(6)
C1−M3−C16	165.13(15)	168.08(14)
Li1[b]−Br−Li2[c]	94.53(12)	99.97(17)
Li1[b]−M3−Li2[c]	81.35(11)	82.02(14)
N1−Li1[b]−N2	85.41(16)	86.6(2)
N3−Li2[c]−N4	85.84(19)	84.2(2)
C2−C1−C6	114.7(3)	114.8(3)
C17−C16−C21	115.0(3)	114.9(3)
N1−C10−C11−N2	59.3(5)	53.1(6)
N3−C25−C26−N4	62.2(4)	62.2(4)

[a] The estimated standard deviations are given in parentheses. [b] 9% occupation of Cu1 for **7** and 2.9% of Ag1 for **8**. [c] 4% occupation of Cu2 for **7** and 2.3% of Ag2 for **8**.

Structure of the Aryl Bromoate Complexes 7, 8, and 9 in Solution. Molecular weight determinations by cryoscopy in

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(32) Janssen, M. D.; Corsten, M. A.; Spek, A. L.; Grove, D. M.; van Koten, G. *Organometallics* **1996**, *15*, 2810.

benzene showed that all three complexes exist in solution as distinct neutral species with stoichiometry MLi_2BrAr_2. This indicates that the MLi_2BrAr_2 stoichiometry found in the solid state has been retained in benzene solution.

The ^1H NMR spectra of these -ate complexes are more complex than those reported earlier for the corresponding complex **2**,[7] which contains the $[C_6H_4\{CH_2N(Me)CH_2CH_2NMe_2\}\text{-}2]^-$ ligand. This is due to the presence of N-bound Et groups. ^1H, ^{13}C, and ^6Li NMR spectra in toluene-d_8 in the temperature range from 193 to 378 K provided unambiguous evidence that these MLi_2BrAr_2 compounds have identical connectivity patterns between M (Cu, Ag, or Au), Li, and C_{ipso} of the Ar ligand. The ^1H and ^{13}C NMR spectra of solutions of **7**, **8**, and **9** in the temperature range from 233 to 378K showed for all compounds only one single resonance pattern for the two $[C_6H_4CH_2N(Et)CH_2CH_2NEt_2]^-$ ligands. The ^1H NMR spectra below 233 K show a rigid coordination of the $Li-NEt_2$ units on the NMR time scale, as two distinct resonances are observed for the CH_3 groups of the NEt_2 units, and also at this temperature an AB pattern is observed for the benzylic CH_2 groups in both **7** and **9**. Unfortunately, the solubility of aryl bromoargentate **8** in toluene-d_8 was too low to record ^1H NMR spectra below 253 K. At this temperature, the CH_3 groups of the NEt_2 units are still observed as two very broad resonances. The ^1H NMR spectra in benzene-d_6 at 298 K of **7**, **8**, and **9** show one broad signal for the CH_3 groups of the NEt_2 groupings, indicating a Li−N bond dissociation/association process which is in the intermediate exchange limit. Above 333 K, this process becomes faster as indicated by sharpening of the (triplet) resonance of the CH_3 moieties of these NEt_2 units. At room temperature, the $ArCH_2N$ methylene hydrogen atoms are diastereotopic and still appear as an AB pattern which unambiguously proves that $N^{Et}-Li$ coordination is present and renders the N^{Et} center stereogenic. At 373 K, the coordination of the N^{Et} group is still rigid (and inert) on the NMR time scale, although the AB pattern has broadened slightly. These observations show that the MLi_2Br core has C_2 symmetry along the axis through Br and Cu atoms (see Newman projection in Figure 2) and only one of the possible stereoisomeric pairs, that is, R_NR_N/S_NS_N, is present in solution.[7]

The ^{13}C NMR spectra of **7** in benzene-d_6 at room temperature showed the expected quartet multiplicity (equal intensity) for the C_{ipso} carbon resonance as a result of the $^{13}C-^7Li$ coupling ($^1J(^{13}C-^7Li) = 6.9$ Hz) (cf., $^1J(^{13}C-^7Li) = 7.0$ Hz for $[Cu_2Li_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_4]$).[9] The ^6Li NMR spectrum shows one singlet resonance at −1.08 ppm, which is in agreement with the presence of two structurally equivalent Li nuclei in the molecule.

Because of the low solubility of **8** in toluene, spectra with only partly resolved fine structures were obtained. However, the ^{13}C NMR spectrum of **8** in toluene-d_8 at 253 K shows clearly two (broad) C_{ipso} resonances at 168.7 and 170.5 ppm. This can be explained by coupling of $^{13}C_{ipso}$ with both isotopes ^{107}Ag and ^{109}Ag ($J(^{13}C-^{107,109}Ag)$), resulting in an average value of 135 Hz (gyromagnetic ratio: $^{107}Ag/^{109}Ag = 1.14$). The ^{107}Ag and ^{109}Ag couplings are not resolved (natural abundances: $^{107}Ag = 51.8\%$; $^{109}Ag = 48.2\%$).[33] Likewise, the quartet multiplicity resulting from the corresponding $J(^{13}C-^7Li)$ coupling in **8** is not resolved, cf., the well-resolved $^{13}C-^7Li$ coupling observed for the aryl bromocuprate **7**. However, the line width of each of the two signals (31 Hz) is in agreement with a $J(^{13}C-^7Li)$ coupling of about 7.8 Hz (vide supra). Unambiguous proof for the bridging of the aryl group via the C_{ipso} atom between one Ag and one Li nucleus in **8** is obtained from the ^6Li NMR spectrum (benzene-d_6, 298 K). A single broadened doublet resonance is observed. This multiplicity is characteristic for a silver−lithium coupling $^2J(^6Li-^{107,109}Ag)$ of 1.3 Hz (average). Further evidence for connectivities in the $AgLi_2Br$ core is provided by ^1H NMR experiments. In the ^1H NMR spectrum, at 298 K a triplet of doublets is observed for the *ortho*-H (i.e., H(6)) of the aryl ring. The triplet splitting (6.6 Hz) arises from the coupling of H(6) with both H(5) and $^{107,109}Ag$. Evidence for the silver-proton coupling is provided by proton spin-decoupling. Irradiation at H(5) results in collapse of the H(6) pattern to a doublet resulting from the proton-silver coupling $^3J(^1H - ^{107,109}Ag)$ of 6.6 Hz (average).[10,33−35]

The ^{13}C NMR spectrum (benzene-d_6, 283 K) of the aryl bromoaurate **9** shows a relatively sharp C_{ipso} resonance at 176.0 ppm with a line width of 16 Hz. This indicates a $^1J(^{13}C-^7Li)$ coupling constant of ∼5 Hz, which is considerably smaller that those in **7** and **8**. The chemical shifts of the C_{ipso} resonances of **7**, **8**, and **9** closely match those of the previously reported -ate compounds of type $[M_2Li_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_4]$ (M = Cu (168.1 ppm); Ag (ca. 170 ppm); and Au (174.4 ppm)).[9−11]

These NMR experiments show that all three MLi_2BrAr_2 compounds, **7**, **8**, and **9**, have a MLi_2Br core which is rigid on the NMR time scale as intermolecular exchanges between similar cores or aggregates with different compositions would remove the coupling information. In particular, the $^{13}C-^{107,109}Ag$ coupling is extremely sensitive to that.[34]

Structural Aspects of the *ortho*-Diamine Chelated Aryl Cyanoate Complexes 10 and 11 in Solution. Solid **12** obtained from the synthesis of the cuprate redissolves only partly in solvents such as diethyl ether, benzene, or toluene. This hampered meaningful NMR analysis and cryoscopic molecular weight determinations. Unfortunately, so far, also attempts to obtain suitable single crystals for the X-ray determination of cyanocuprate **12**, cyanoargentate **10**, and cyanoaurate **11** failed. However, the molecular weight determination of cyanoargentate **10** by cryoscopy in benzene was successful and indicated that this compound exists in solution as a species with $R_2MLi_2(C{\equiv}N)$ stoichiometry.

^1H and ^{13}C NMR studies (toluene-d_8, 213−373 K) of the cyanoargentate **10** and the cyanoaurate **11** revealed that these compounds have structural features in common with bromoargentate **8** and bromoaurate **9**. The ^{13}C NMR spectra of **10** and **11** both contain a resonance at 168 ppm, which indicates the presence of a CN group in the structure. The same shift value of a $C{\equiv}N$ group has been found earlier in cyanocuprate **3**,[3] in which the cyanide anion bridges exclusively between two Li centers and has no further contact with Cu-sites. The coupling patterns of the C_{ipso} atoms in both **10** and **11** are equal to those found for the bromo analogues **8** and **9**, vide supra. For example, the line width of the $^{13}C_{ipso}$ resonance (ca. 13 Hz) of cyanoaurate **11** closely resembles that found for the bromoaurate **9** (16 Hz).

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(33) Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987.

(34) Brevard, C.; van Stein, G. C.; van Koten, G. *J. Am. Chem. Soc.* **1981**, *103*, 6746.

(35) van Koten, G.; Jastrzebski, J. T. B. H.; Stam, C. H.; Brevard, C. In *Copper Coordination Chemistry; Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, New York, 1985; p 267.

IR spectra of **10** in the solid state (recorded in Nujol) showed a weak ν_{CN} at 2149 cm^{-1} which is similar to that found for **10** in benzene solution (2150 cm^{-1}). In contrast, when **10** is dissolved in a polar solvent like THF, the ν_{CN} shifts considerately to lower frequencies (2114 cm^{-1}, sh 2146 cm^{-1}). The latter value is the same as that found for a THF solution of cyanocuprate **3** ($\nu_{CN} = 2114$ cm^{-1}), which in THF is a solvent-separated ion pair (SSIP) comprising $[Li{-}C{\equiv}N{-}Li]^+$ cations.[3]

Discussion

The formation of a homologous series of aryl bromoate complexes **7**, **8**, and **9** and their silver and gold cyano analogues **10** and **11**, by reacting 2 equiv of aryllithium compound **6** with 1 equiv of the appropriate metal salt, shows that in solution stable and unique aggregates are formed. This can be seen as an example of ligand-directed self-assembling because only one type of thermodynamically stable aggregate is formed independent of the nature of metal (Cu, Ag, or Au) in the precursor salt. The ^{13}C NMR spectra of the bromoate complexes illustrate changes in the nature of the metal$-C_{ipso}$ bond within a series. The C_{ipso} atoms of bromocuprate **7** and bromoargentate **8** both show an upfield shift (**7**, 167.1 ppm; **8**, 169.5 ppm) as compared to that of C_{ipso} in the bromoaurate **9** (176 ppm). This suggests a more covalent bonding of Au with C_{ipso}.

Similar effects are found in the solid-state structure of the known aurate $[Au_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4]$, where the lithium and gold atoms are bridged by the C_{ipso} carbon.[11] The bridge bond in this aurate is more asymmetric ($d(Au{-}C_{ipso}) = 2.06$ Å; $d(Li{-}C_{ipso}) = 2.58$ Å) than that in the analogous cuprate **1** (vide supra). Furthermore, the ^6Li NMR spectrum of aurate **9** shows a larger upfield shift (-1.67 ppm) than that found for cuprate **7** and argentate **8** (-1.08 and -1.17 ppm, respectively), while the $^1J(^{13}C{-}^7Li)$ for **9** is smaller (4 Hz) than that for **7** and **8** (7.0 and 7.8 Hz, respectively). A similar trend has been reported by Van Koten et al. for homoate compounds of type $[M_2Li_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_4]$ (M = Cu, Ag, Au).[35] It is suggested that these differences largely originate from the differences of the $M{-}C_{ipso}$ (M = Cu, Ag, Au) bond character; that is, the $Cu{-}C_{ipso}$ and $Ag{-}C_{ipso}$ bonds are more ionic than the $Au{-}C_{ipso}$ bond.[36]

The ^1H, ^{13}C, and ^6Li NMR spectra of cyanoargentate **10** show related coupling patterns indicating an electron-deficient type of bonding mode of the $Li{-}C_{ipso}{-}Ag$ unit as is found for **8**. The coupling constants between ^{13}C and ^7Li (7.3 Hz) still imply a bonding with considerable s character between C_{ipso} with lithium. This is also supported by the $^6Li{-}^{107,109}Ag$ coupling observed in the Li spectrum of **10**. For cyanoaurate **11**, an even smaller line width (ca. 13 Hz) for the $^7Li{-}^{13}C$ coupling has been found, suggesting a further distortion of the unsymmetrical electron-deficient bonding mode in the direction of a more covalent bonding between C_{ipso} and Au. This observation suggests that the extent of charge separation between the [ArAuAr] and [Li(X)Li] (X = Br, **9**; CN, **11**) increases going from **9** to **11**.

A further interesting aspect of the ethyl-substituted $C{\wedge}N{\wedge}N$ ligand is that it allows the formation of distinct cyanoate complexes **10** and **11**. So far, no clear indication has been obtained about the nature of the cyanocopper species formed. A possible reason for a structural difference between the cyanoargentate, -aurate, and -cuprate and therefore for the low stability of **3** may be the larger ionic radii of Ag^I and Au^I as compared with that of Cu^I.[37] As a consequence of this, the distance between the *N,N′*-chelating donor atoms in the ArMAr anion which coordinate the $[Li(X)Li]^+$ cationionic unit will vary and, in the case of the cyanocuprate, is too small to accommodate the [Li(X)Li] cation for X = CN, whereas for X = Br this cation fits well (cf., **8**).

The bonding mode of the cyanide anion can be either end-on (via N or C) or side-on (linearly, N,C-bridged). The latter $C{\equiv}N$ bonding mode is present in the solid-state structure of the related ionic 2:1 cyanocuprates **3**[3] and $[(t\text{-}Bu)_2Cu]^-$ $[Li_2(C{\equiv}N)pmdeta_2(THF)_2]^+$.[4] Because no distinct difference is found between the cyanide ^{13}C NMR resonances in **10** and **11**, we believe that the cyanide is side-on bonded between the two lithium atoms. This idea is corroborated by our IR results. Previous IR studies of cyanocuprates reported that there is a significant difference between ν_{CN} of an end-on coordinated $C{\equiv}N$ group (2034 cm^{-1}) and a side-on bonded $C{\equiv}N$ group (2163 cm^{-1}).[39] The differences observed in our data (in benzene versus in THF) may result from the fact that in THF, solvated $[(THF)_nLi{-}C{\equiv}N{-}Li(THF)_n]^+$ ions are present with five-coordinated Li atoms ($n = 4$). This high coordination number may lower the ν_{CN} by 20−40 cm^{-1} for each added ligand to the metal.[39] It has to be noted that in benzene the Li atoms of **10** (ν_{CN} 2149 cm^{-1} in Nujol and benzene) are four coordinated (cf., the structure of **7**).

The bonding types found in bromoaurate **9** and cyanoaurate **11** can be best described as contact ion pair (CIP) for **9** and solvent-separated ion pair (SSIP) for **11** (Figure 3). In **11**, the nitrogen atoms can be seen as the solvent molecules, and the $[Li{-}(C{\equiv}N){-}Li]^+$ is captured in the cavity formed by these four nitrogen atoms. Earlier results by Boche et al. demonstrated that in polar (i.e., well-solvating) solvents, lithium cuprates are present as solvent-separated ion pairs, whereas in poorly solvating solvents such as diethyl ether and benzene they are present as contact ion pairs.[5e,40] The NMR results presented in this paper and those reported earlier by Van Koten et al.[9−11] provide evidence that in less polar solvents such as diethyl ether and benzene, the ionic units as identified in neutral *ortho*-amine chelated aryllithium cuprates and argentates are not separated from each other. The strongest evidence is provided by the observation of both the Li−C and the Li−Ag couplings in the corresponding argentates.

Experimental Section

General Data. All experiments were carried out under a strictly dry, oxygen-free nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried and distilled prior to use. All standard

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(36) One of the reviewers is thanked for his work which has been based on the results of a series of calculated structures.[6g]

(37) Recently, it was found that the ionic radius of gold(I) is ca. 7% smaller than that of silver.[38] Therefore, one would assume less interaction between Li and Ag/C_{ipso} as compared with Li and Au/C_{ipso} in the bromo- and cyanoate compounds **10** and **11**. The results presented in this paper are not consistent with this earlier finding.[38] However, they are in close agreement with the findings presented by our group in 1985.[35]

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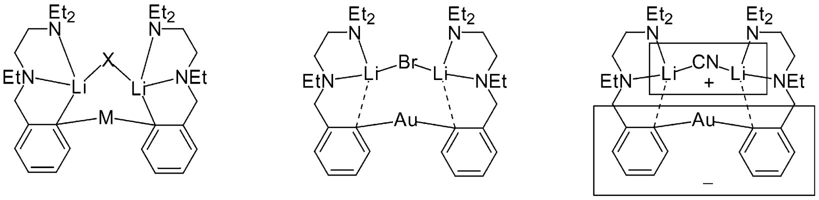

M = Cu; X = Br
M = Ag; X = Br, CN

7, 8, 10 **9** **11**

Figure 3. Schematic representation of the structures of **7**, **8**, **9**, **10**, and **11**. For compound **11**, both the intramolecular [Li−(CN)−Li]$^+$ moiety located within the cavity of the aryldiamine framework and the [Ar$_2$Au]$^-$ fragment are framed.

chemicals were purchased from ACROS and Aldrich Chemical Co. and used as received. The starting materials [AuCl(PPh$_3$)][41] and water-free Cu^{I}Br[42] were prepared according to literature procedures, and Cu^{I}Br was stored in a nitrogen atmosphere. ^{1}H, ^{13}C, and ^{6}Li NMR spectra were recorded at 300 MHz at ambient temperature unless otherwise stated, and a full description of the NMR data can be found in the Supporting Information. Chemical shifts (δ) for ^{1}H and ^{13}C spectra are given in ppm relative to the internal standard SiMe$_4$. Coupling constants are given in Hz. Chemical shifts (δ) for ^{6}Li spectra are given in ppm relative to LiCl (1.0 M in D$_2$O) as an external standard. 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. For calibration purposes, naphthalene was used to calculate the cryoscopic constant K_f (5.54 K Kg mol^{-1}). IR measurements 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 Interferometer and MCT Midband detector. All reactions involving silver(I) and gold(I) chemistry were carried out under exclusion of light by wrapping the Schlenk flasks in aluminum foil.

[C$_6$H$_4$BrCH$_2$N(Et)CH$_2$CH$_2$NEt$_2$-2] (5). To a solution of *N,N,N′*-triethylethanediamine (10.0 mL, 55.73 mmol) and triethylamine (25 mL) in C$_6$H$_6$ (80 mL) was added a solution of 2-bromobenzyl bromide (13.73 g, 54.94 mmol) in C$_6$H$_6$ (60 mL) dropwise. After 5 h, the resulting white suspension (indicating the formation of HNEt$_3$Br) was filtered off and extracted with C$_6$H$_6$ (25 mL). The filtrate was concentrated by removal of the solvent in vacuo. The crude product was obtained as a yellow oil, which was purified by a short-path distillation at reduced pressure to yield **1** as a colorless oil, yield 12.94 g (75%). ^{1}H NMR (C$_6$D$_6$, 300.105 MHz, 298 K): δ (in ppm) 0.86 (dt, 9H, N(CH$_2$C*H*$_3$)$_2$ and CH$_2$N(CH$_2$C*H*$_3$)), 2.32 (q, 4H, N(C*H*$_2$CH$_3$)$_2$), 2.50 (m, 6H, CH$_2$N(C*H*$_2$CH$_3$)C*H*$_2$C*H*$_2$N(Et$_2$)), 3.65 (s, 2H, ArC*H*$_2$N(Et)), 6.73 (t, 1H, ^2J = 7.80 Hz, Ar*H*(4)), 7.02 (t, 1H, ^2J = 7.80 Hz, Ar*H*(5)), 7.35 (d, 1H, ^2J = 7.80 Hz, Ar*H*(3)), 7.60 (d, 1H, ^2J = 7.80 Hz, Ar*H*(6)). ^{13}C NMR (C$_6$D$_6$, 75.469 Hz, 298 K): δ (in ppm) 12.4 (CH$_2$N(CH$_2$*C*H$_3$)), 12.5 (N(CH$_2$*C*H$_3$)$_2$), 47.8 (N(*C*H$_2$CH$_3$)$_2$), 48.6 (CH$_2$N(*C*H$_2$CH$_3$)), 52.0, 52.6 (N*C*H$_2$*C*H$_2$N(Et$_2$)), 58.6 (Ar*C*H$_2$), 124.2, 128.1, 128.2, 130.7, 132.6 (Ar(*2−6*)), 140.3 (Ar(*1*)). Anal. Calcd for C$_{15}$H$_{25}$BrN$_2$: C, 57.50; H, 8.04; N, 8.94. Found: C, 57.63; H, 8.11; N, 9.04.

[Li(C$_6$H$_4${CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$}-2)]$_2$ (6). This was prepared according to a published procedure for the synthesis of [Li(C$_6$H$_4${CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$}-2)]$_2$,[22] starting from **5** (6.71 g; 21.44 mmol) in pentane and *n*-BuLi (13.6 mL of a 1.6 M solution in hexane; 21.8 mmol), yield 85% (4.38 g; 18.22 mmol). ^{1}H NMR (C$_6$D$_6$, 300.105 MHz, 298 K): δ (in ppm) 0.59−1.20 (bm, 9H, CH$_2$N(CH$_2$C*H*$_3$) and N(CH$_2$C*H*$_3$)$_2$), 1.54−3.00 (bm, 8H, N(C*H*$_2$CH$_3$)$_2$ and CH$_2$N(Et)C*H*$_2$C*H*$_2$N(Et)$_2$), 3.00−3.15 (bm, 2H, CH$_2$N(C*H*$_2$CH$_3$)), 3.48 (d, 1H, ^2J = 11.4 Hz, ArC*H*$_2$), 4.22 (d, 1H, ^2J = 11.4 Hz, ArC*H*$_2$), 7.13−7.30 (m, 3H, Ar*H*(*3,4,5*)), 8.32 (bs, 1H, Ar*H*(*6*)). ^{13}C NMR (C$_6$D$_6$, 75.469 MHz, 298 K): δ (in ppm) 8.12 (CH$_2$N(CH$_2$*C*H$_3$)), 10.1 (b, 2 × N(CH$_2$*C*H$_3$)$_2$), 45.3 (b, 2 × N(*C*H$_2$CH$_3$)$_2$), 45.6, 46.0 (2 × N*C*H$_2$*C*H$_2$N), 51.7 (CH$_2$N(*C*H$_2$CH$_3$)), 68.8 (Ar*C*H$_2$N), 124.0 (2×), 125.8, 142.9, 150.9 (Ar*(2,3,4,5)*), (ArC$_{ipso}$ not observed, probably too broad). Anal. Calcd for C$_{15}$H$_{25}$N$_2$Li: C, 74.97; H, 10.49; N, 11.66. Found: C, 77.06; H, 10.72; N, 11.88.

[CuLi$_2$Br(C$_6$H$_4${CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$}-2)$_2$] (7). To a stirred solution of **6** (2.00 g, 8.32 mmol of monomer) in Et$_2$O (80 mL) at −78 °C was added CuBr (0.60 g, 4.16 mmol) as a solid. After the reaction mixture had been stirred between −40 and −30 °C for 1.5 h, the suspension was allowed to warm slowly to room temperature. After the suspension had been stirred for 1.5 h at ambient temperature, all volatiles were removed in vacuo. The remaining slightly white/brownish solid was dissolved in toluene (40 mL) and filtered over a glass filter covered with dry Celite (to remove Cu^0), leaving an almost colorless solution. Warning: The Celite has to be thoroughly dried. Evaporation of the solvent in vacuo and subsequently washing with pentane (2 × 15 mL) yielded 1.60 g of **7** as a cream-colored powder (2.56 mmol, 62%). Suitable crystals for X-ray diffraction were obtained by crystallization from benzene/pentane at room temperature. ^{1}H NMR (C$_6$D$_6$, 300.105 MHz, 298 K): δ (in ppm) 0.68 (bs, 12H, N(CH$_2$C*H*$_3$)$_2$), 1.20−1.40 (bm, 4H, N(C*H*$_2$CH$_3$)$_2$), 1.51 (t, 6H, CH$_2$N(CH$_2$C*H*$_3$)), 1.86 (m, 2H, NC*H*$_2$CH$_2$N(Et$_2$)), 2.10 (dm, 4H, NC*H*$_2$C*H*$_2$N(Et$_2$)), 2.49 (m, 2H, NCH$_2$C*H*$_2$N(Et$_2$)), 2.73 (m, 4H, CH$_2$N(C*H*$_2$CH$_3$) and N(C*H*$_2$CH$_3$)$_2$), 2.87 (m, 2H, N(C*H*$_2$CH$_3$)$_2$), 2.91 (d, 2H, ^2J = 11.4 Hz, ArC*H*$_2$N), 3.06 (m, 2H, CH$_2$N(C*H*$_2$CH$_3$)), 4.47 (d, 2H, ^2J = 11.4 Hz, ArC*H*$_2$N), 7.00 (d, 2H, ^3J = 7.50 Hz, Ar*H(3)*), 7.14 (t, 2H, ^3J = 7.50 Hz, Ar*H(4)*), 7.22 (t, 2H, ^3J = 7.2 Hz, Ar*H(5)*), 8.30 (d, 2H, ^3J = 6.90 Hz, Ar*H(6)*). ^{13}C NMR (C$_6$D$_6$, 75.469 MHz, 298 K): δ (in ppm) 6.77, 8.85 (2 × b, N(CH$_2$*C*H$_3$)$_2$), 11.9 (CH$_2$N(CH$_2$*C*H$_3$)), 42.4, 45.2 (2 × b, N(*C*H$_2$CH$_3$)$_2$), 47.6, 48.2 (2 × N*C*H$_2$*C*H$_2$N), 52.2 (CH$_2$N(*C*H$_2$CH$_3$)), 67.4 (Ar*C*H$_2$N), 125.4, 128.0, 143.7, 149.9 (Ar*(2,3,4,5)*), 167.2 (ArC$_{ipso}$). ^{6}Li NMR (C$_6$D$_6$, 44.165 MHz, 298 K): δ (in ppm) −1.08 (s, 2Li). Mp. (dec) 150−155 °C. Anal. Calcd for C$_{30}$H$_{50}$BrCuLi$_2$N$_4$: C, 57.74; H, 8.08; N, 8.98. Found: C, 57.59; H, 7.96; N, 8.88. Molecular weight determination by cryoscopy (0.40 g (0.64 mmol) in 12.98 g of C$_6$H$_6$). Calcd for C$_{30}$H$_{50}$BrCuLi$_2$N$_4$ (**7**): 624.09. Found: 699.70.

[AgLi$_2$Br(C$_6$H$_4${CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$}-2)$_2$] (8). To a stirred solution of **6** (1.70 g, 7.07 mmol of monomer) in Et$_2$O (80 mL) at −78 °C was added solid AgBr (0.66 g, 3.54 mmol). After the reaction mixture had been stirred at −78 °C for 45 min, the suspension was allowed to warm slowly to room temperature and was subsequently stirred for 1.5 h at ambient temperature, after which all volatiles were removed in vacuo. The slightly gray solid obtained was dissolved in toluene (40 mL) and filtered over a glass filter filled with dry Celite (to remove Ag^0), leaving a light brown solution. Evaporation of the solvent in vacuo and subsequent washing with pentane (2 × 15 mL) gave 1.58 g of **8** as a light brown powder (2.36 mmol, 67%). Suitable crystals for X-ray diffraction were obtained by a slow diffusion of pentane into a solution of **8** in benzene at 0 °C. ^{1}H NMR (C$_6$D$_6$, 300.105 MHz, 298 K): δ (in ppm) 0.62 (bs, 12H, N(CH$_2$C*H*$_3$)$_2$), 1.10−1.43

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(bm, 4H, N(CH_2CH$_3$)$_2$), 1.50 (t, 6H, ^3J = 6.90 Hz, CH$_2$N(CH$_2$CH_3)), 1.79 (m, 2H, NCH_2CH$_2$N(Et$_2$)), 1.94 (m, 2H, NCH_2CH$_2$N(Et$_2$)), 2.06 (m, 2H, NCH$_2$CH_2N(Et$_2$)), 2.37 (m, 2H, NCH$_2$CH_2N(Et$_2$)), 2.45 (m, 4H, CH$_2$N(CH_2CH$_3$) and N(CH_2CH$_3$)$_2$), 2.61 (m, 2H, N(CH_2CH$_3$)$_2$), 2.81 (d, 2H, ^2J = 11.4 Hz, ArCH_2N), 2.93 (m, 2H, CH$_2$N(CH_2CH$_3$)), 4.30 (d, 2H, ^2J = 11.4 Hz, ArCH_2N), 7.03 (d, 2H, ^3J = 7.80 Hz, Ar*H-(3)*), 7.12 (t, 2H, ^3J = 7.50 Hz, Ar*H(4)*), 7.24 (t, 2H, ^3J = 6.90 Hz, Ar*H(5)*), 8.26 (t, 2H, $^3J_{\mathrm{HH}}$ = 6.60 Hz, $^3J_{\mathrm{HAg}}$ = 7.3 Hz, ArH*(6)*). ^{13}C NMR (C$_6$D$_6$, 75.469 MHz, 298 K): δ (in ppm) 6.80, 10.7 (2 × b, N(CH$_2$CH_3)$_2$), 12.4 (CH$_2$N(CH$_2$CH_3)), 42.3, 45.3 (2 × b, N(CH_2CH$_3$)$_2$), 50.8, 50.9 (2 × NCH_2CH_2N), 52.3 (CH$_2$N(CH_2CH$_3$)), 67.7 (d, $^3J_{\mathrm{CAg}}$ = ca. 4 Hz, ArCH_2N), 125.1 (d, $^2J_{\mathrm{CAg}}$ = 6.7 Hz, Ar*(6)*), 125.6, 127.1, 145.1 (Ar*(3,4,5)*), 150.1 (d, $^2J_{\mathrm{CAg}}$ = 4.2 Hz, Ar*(2)*), 168.7, 170.5 (2 × b, $^1J_{\mathrm{CAg}}$ = 135 Hz, ArC$_{\mathrm{ipso}}$). ^{6}Li NMR (C$_6$D$_6$, 44.165 MHz, 298 K): δ (in ppm) −1.17. (d, 2Li, $^2J_{\mathrm{LiAg}}$ = 1.30 Hz). mp. (dec) 165−170 °C. Anal. Calcd for $C_{30}H_{50}BrAgLi_2N_4$: C, 53.91; H, 7.54; N, 8.38. Found: C, 54.06; H, 7.63; N, 8.31. Molecular weight determination by cryoscopy (0.51 g (0.76 mmol) in 17.00 g of C$_6$H$_6$). Calcd for $C_{30}H_{50}BrAgLi_2N_4$ (**8**): 668.41. Found: 608.80.

[AuBr(PPh$_3$)]. To a stirred solution of [AuCl(PPh$_3$)] (0.36 g, 0.78 mmol) in 10 mL of CH$_3$Cl was added 22 mL of a saturated solution of NaBr in a mixture of EtOH/H$_2$O (1:1 v/v). The solution was stirred for 2 h at ambient temperature, after which all solvents were removed by rotary evaporation at 50 °C. The remaining solid was extracted with CH$_2$Cl$_2$ (6 × 25 mL). The CH$_2$Cl$_2$ fractions were collected, dried over Na$_2$CO$_3$, and concentrated to ca. 10 mL. Next, an equal amount of hexane was added. Crystallization from this solvent mixture at −30 °C afforded 0.25 g (0.46 mmol, 59% (first batch of crystals)) of [AuBr-(PPh$_3$)] as colorless crystals. ^{31}P NMR (C$_6$D$_6$/CDCl$_3$ (1:1 v/v), 88.016 MHz, 298 K): δ (in ppm) 35.76.[43,44]

[AuLi$_2$Br(C$_6$H$_4${CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$}-2)$_2$] (9). The synthetic procedure is identical to that described for the argentate **8**, starting from **6** (0.23 g, 0.95 mmol of monomer) in Et$_2$O (30 mL) and [AuBr(PPh$_3$)] (0.24 g, 0.47 mmol). Yield 0.28 g of **9** as slightly pink powder (0.38 mmol, 80%). ^{1}H NMR (C$_6$D$_6$, 300.105 MHz, 298 K): δ (in ppm) 0.62 (t, ^3J = 6.90 Hz, 12H, N(CH$_2$CH_3)$_2$), 1.44 (bm, 2H, N(CH_2CH$_3$)$_2$), 1.47 (t, 6H, ^3J = 6.90 Hz, CH$_2$N(CH$_2$CH_3)), 1.84 (m, 4H, NCH_2CH$_2$N-(Et$_2$)), 2.02 (dm, 6H, NCH_2CH_2N(Et$_2$) and N(CH_2CH$_3$)$_2$), 2.38 (m, 4H, NCH$_2$CH_2N(Et$_2$) and CH$_2$N(CH_2CH$_3$)), 2.67 (m, 4H, N(CH_2CH$_3$)$_2$), 2.75 (d, 2H, ^2J = 11.4 Hz, ArCH_2N), 3.02 (m, 2H, CH$_2$N(CH_2CH$_3$)), 4.61 (d, 2H, ^2J = 11.4 Hz, ArCH_2N), 7.01 (d, 2H, Ar*H(3)*), 7.31 (m, Ar*H-(4,5)*), 8.14 (d, 2H, ^3J = 6.90 Hz, Ar*H(6)*). ^{13}C NMR (C$_6$D$_6$, 75.469 MHz, 283 K): δ (in ppm) 6.70, 10.7 (2 × b, N(CH$_2$CH_3)$_2$), 12.2 (CH$_2$N-(CH$_2$CH_3)), 43.0, 47.8 (2 × b, N(CH_2CH$_3$)$_2$), 50.5, 50.8 (2× NCH_2CH_2N), 52.6 (CH$_2$N(CH_2CH$_3$)), 66.1 (ArCH_2N), 125.2, 126.1, 129.4, 143.9, 149.0 (Ar*(2,3,4,5)*), 176.0 (ArC$_{\mathrm{ipso}}$). ^{6}Li NMR (C$_6$D$_6$, 44.165 MHz, 298 K): δ (in ppm) −1.67 (s, 2Li). mp. 188−190 °C. Anal. Calcd for $C_{30}H_{50}BrAuLi_2N_4$: C, 47.57; H, 6.65; N, 7.40. Found: C, 47.63; H, 6.64; N, 7.28. Molecular weight determination by cryoscopy (0.20 g (0.26 mmol) in 11.20 g of C$_6$H$_6$). Calcd for $C_{30}H_{50}BrAuLi_2N_4$ (**9**): 757.55. Found: 638.20.

Table 2. Experimental Data for the X-ray Diffraction Studies of **7** and **8**

	7	**8**
formula	$C_{30}H_{50}BrCu_{1.13}Li_{1.87}N_4$	$C_{30}H_{50}Ag_{1.05}BrLi_{1.95}N_4$
formula weight	631.29	673.70
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
crystal size [mm^3]	0.32 × 0.28 × 0.03	0.51 × 0.12 × 0.06
crystal color	colorless	colorless
temp [K]	150	125
λ [Å]	0.71073	0.71073
a [Å]	12.6266(5)	12.6609(3)
b [Å]	31.1512(11)	31.2622(8)
c [Å]	8.6751(4)	8.5488(2)
β [°]	109.3060(7)	107.7146(10)
V [Å^3]	3220.3(2)	3223.24(14)
Z	4	4
D_{calc} [g/cm^3]	1.302	1.388
μ [mm^{-1}]	2.03	1.92
abs. correction	PLATON (MULABS)	PLATON (MULABS)
transmission range	0.66−0.94	0.82−0.91
$\sin(\theta/\lambda)_{\max}$ [Å^{-1}]	0.57	0.65
refl. meas./unique	20 853/5044	24 973/7340
R_{int}	0.078	0.056
param./restraints	343/0	351/0
R1 (obs./all refl.)	0.0445/0.0594	0.0448/0.0734
wR2 (obs./all refl.)	0.1127/0.1305	0.0938/0.1056
GOF	1.085	1.045
ρ (min/max) [e/Å^3]	−1.25/0.82	−0.77/1.20

[AgLi$_2$(C≡N)(C$_6$H$_4${CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$}-2)$_2$] (10). The synthetic procedure is identical to that described for the argentate **8**, starting from **6** (1.22 g, 5.08 mmol of monomer) in Et$_2$O (30 mL) and AgCN (340 mg, 2.54 mmol). Yield 1.12 g of **10** as a white powder (1.83 mmol, 72%). ^{1}H NMR (C$_6$D$_6$, 300.105 MHz, 298 K): δ (in ppm) 0.56 (bs, 12H, N(CH$_2$CH_3)$_2$), 1.10−1.60 (bm, 4H, N(CH_2CH$_3$)$_2$), 1.51 (t, 6H, ^3J = 6.90 Hz, CH$_2$N(CH$_2$CH_3)), 1.73 (m, 2H, NCH_2CH$_2$N(Et$_2$)), 1.85 (m, 2H, NCH_2CH$_2$N(Et$_2$)), 1.97 (m, 2H, NCH$_2$CH_2N(Et$_2$)), 2.20−2.60 (m, 2H, NCH$_2$CH_2N(Et$_2$); m, 6H, CH$_2$N(CH_2CH$_3$) and N(CH_2-CH$_3$)$_2$), 2.79 (d, 2H, ^2J = 11.7 Hz, ArCH_2N), 2.84 (m, 2H, N(CH_2-CH$_3$)$_2$), 4.33 (d, 2H, ^2J = 11.7 Hz, ArCH_2N), 7.03 (d, 2H, ^3J = 7.50 Hz, Ar*H(3)*), 7.13 (t, 2H, ^3J = 7.20 Hz, Ar*H(4)*), 7.27 (t, 2H, ^3J = 6.90 Hz, Ar*H(5)*), 8.33 (t, 2H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $^2J_{\mathrm{HAg}}$ = 7.6 Hz, ArH*(6)*). ^{13}C NMR (C$_6$D$_6$, 75.469 MHz, 298 K): δ (in ppm) 7.49, 10.1 (2 × b, N(CH$_2$CH_3)$_2$), 12.4 (CH$_2$N(CH$_2$CH_3)), 42.4, 45.3 (2 × b, N(CH_2CH$_3$)$_2$), 50.4, 50.8 (2 × NCH_2CH_2N), 51.8 (CH$_2$N(CH_2CH$_3$)), 67.1 (ArCH_2N), 125.12 (d, $^2J_{\mathrm{CAg}}$ = 7.3 Hz, Ar*(6)*), 125.5, 128.9, 145.2 (Ar*(3,4,5)*), 149.8 (d, $^2J_{\mathrm{CAg}}$ = 4.2 Hz, Ar*(2)*), 168.5 (*C*≡N), 169.9, 171.7 (2 × b, $^1J_{\mathrm{CLi}}$ = 7.3 Hz, $^1J_{\mathrm{CAg}}$ = 134 Hz, ArC$_{\mathrm{ipso}}$). ^{6}Li NMR (C$_6$D$_6$, 44.165 MHz, 298 K): δ (in ppm) −1.85 (d, 2Li, $^2J_{\mathrm{LiAg}}$ = 1.30 Hz). IR (solid): C≡N 2149 cm^{-1}; (C$_6$H$_6$): C≡N 2150 cm^{-1}; (THF): C≡N 2114 cm^{-1}. Anal. Calcd for $C_{31}H_{50}AgLi_2N_5$: C, 60.59; H, 8.20; N, 11.40. Found: C, 60.68; H, 8.16; N, 11.40. Molecular weight determination by cryoscopy (0.43 g (0.70 mmol) in 13.45 g C$_6$H$_6$). Calcd for $C_{31}H_{50}AgLi_2N_5$ (**10**): 614.52. Found: 598.05.

[AuLi$_2$(C≡N)(C$_6$H$_4${CH$_2$N(Et)CH$_2$CH$_2$NEt$_2$}-2)$_2$] (11). The synthetic procedure is identical to that described for the argentate **8**, starting from **6** (0.36 g, 1.50 mmol of monomer) in Et$_2$O (30 mL) and AuCN (167 mg, 0.75 mmol). Yield 0.27 g of **11** as a white powder (0.38 mmol, 51%). ^{1}H NMR (toluene-d_8, 300.105 MHz, 298 K): δ (in ppm) 0.59 (bs, 12H, N(CH$_2$CH_3)$_2$), 1.43 (t, 6H, ^3J = 6.90 Hz, CH$_2$N-(CH$_2$CH_3)), 1.85 (m, 2H, NCH_2CH$_2$N(Et$_2$)), 1.98 (m, 2H, NCH_2CH$_2$N-(Et$_2$)), 2.06 (m, 2H, NCH$_2$CH_2N(Et$_2$)), 2.37−2.44 (m, 2H, NCH$_2$CH_2N-(Et$_2$)); 2.55−2.80 (m, 6H, CH$_2$N(CH_2CH$_3$) and N(CH_2CH$_3$)$_2$), 2.70 (d, 2H, ArCH_2N), 2.94 (m, 2H, N(CH_2CH$_3$)$_2$), 4.55 (d, 2H, ^2J = 11.4 Hz, ArCH_2N), 7.07 (bm, 4H, Ar*H(3,4)*), 7.33 (m, 2H, Ar*H(5)*), 8.03 (d, 2H, $^3J_{\mathrm{HH}}$ = 6.90 Hz, ArH*(6)*). ^{13}C NMR (toluene-d_8, 75.469 MHz, 248 K): δ (in ppm) 6.71, 10.6 (2 × b, N(CH$_2$CH_3)$_2$), 12.5 (CH$_2$N-(CH$_2$CH_3)), 41.5, 45.1 (2 × b, N(CH_2CH$_3$)$_2$), 50.3, 50.5 (2 × NCH_2CH_2N), 51.8 (CH$_2$N(CH_2CH$_3$)), 65.1 (ArCH_2N), 125.7, 129.4, 143.7 (Ar*(3,4,5)*), 148.6 (Ar*(2)*), 167.8 (*C*≡N), 175.8 (ArC$_{\mathrm{ipso}}$). Anal.

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(43) The ^{31}P NMR spectrum of [AuCl(PPh$_3$)] in CDCl$_3$ showed a singlet at 33.84 ppm, which is in accordance with literature values. A mixture of [AuBr(PPh$_3$)] and [AuCl(PPh$_3$)] showed two singlet resonances in the ^{31}P NMR spectrum, indicating that the single resonance in **5** can be assigned to pure [AuBr(PPh$_3$)] and not a mixture of the Cl and Br compounds.

Calcd for $C_{31}H_{50}AuLi_2N_5$: C, 52.92; H, 7.16; N, 9.95. Found for (**11**): C, 53.06; H, 7.05; N, 9.86.

We have tried to prepare the copper analogue of **10** and **11**, $[CuLi_2(C{\equiv}N)(C_6H_4\{CH_2N(Et)CH_2CH_2NEt_2\}\text{-}2)_2]$ (**12**), by the same procedure as has been described for **7**, that is, starting from **6** (1.07 g, 4.46 mmol of monomer) in Et_2O and CuCN (199 mg, 2.23 mmol). However, a suspension was formed, which was not fully soluble in benzene or toluene. A NMR spectrum of the reaction mixture in benzene-d_6 showed a mixture of at least four complex resonance patterns.

X-ray Crystal Structure Determinations of 7 and 8. Intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (Mo Kα). The structures were solved by Patterson methods (DIRDIF-97[45]) and refined with the program SHELXL-97[46] 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.[47] The lithium positions in both structures were partially occupied by copper atoms (compound **7**) or silver atoms (compound **8**). The lithium atoms and the heavy atom were constrained to the same coordinates and the same anisotropic displacement parameters. The corresponding partial occupancies were then refined with the criterion that the total occupancy remains 1.0. Further experimental details are given in Table 2.

Acknowledgment. This work was supported in part (M.L., A.L.S.) by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (CW-NWO).

Supporting Information Available: X-ray crystallographic data **7** and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA026945T

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