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A New Class of Organocopper and Organocuprate Compounds Derived from Copper(I) Arenethiolates

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Abstract: Organometallic reagents (ZR; Z = Li, Mg, or Cu; R = Me, CH$_2$SiMe$_3$, or C$_6$H$_2$Me$_3$-2,4,6) react with copper arenethiolates ([CuSAr]$_3$; SAr = SC$_6$H$_3$(CH(R′)NMe$_2$)-2-R″-3 (**1**, R′ = R″ = H; **2**, R′ = Me and R″ = H (*R*-configuration); **3**, R′ = H and R″ = Cl) to give well defined neutral species that have been isolated and characterized both in solution (mol wt determination by cryoscopy and microwave titration, both in benzene, and ^{1}H NMR) and in the solid state by X-ray crystallography. In these reactions the SAr groups on the copper array are substituted, through interaggregate exchange, by an organic group: [Cu$_3$Li(SAr)$_3$R] (**13**); [Cu$_3$(SAr)$_2$R]$_2$ (**4** and **5**); [Cu$_2$(SAr)R]$_2$ (**6**, **7**, and **11**); and [Cu$_4$R$_4$][μ-SAr]$_2$[MgSAr]$_2$ (**14**). Addition of a phosphine ligand to a solution of ZR and [CuSAr]$_3$ provides selective formation of [Cu$_3$(SAr)$_2$(R)(L)] (**8**, **9**, and **12**). The latter are postulated as models for the reactive species in the 1,4-addition reaction of organocuprates with α,β-unsaturated carbonyl compounds (L = alkene function). Crystals of [Cu$_2${SC$_6$H$_4$(CH$_2$NMe$_2$)-2}(C$_6$H$_2$Me$_3$-2,4,6)]$_2$ (**6**) are monoclinic with a = 13.774 (3) Å, b = 13.635 (1) Å, c = 19.977 (3) Å, β = 109.57 (1)°, V = 3535 (1) Å^3, space group $P2_1/n$, d_{calcd} = 1.550 g cm^{-3}, Z = 4, and R = 0.028 for 6493 reflections with $I \geq 2.5\sigma(I)$. Crystals of the benzene solvate of [Cu$_3${SC$_6$H$_3$(CH$_2$NMe$_2$)-2-Cl-3}$_2$(C$_6$H$_2$Me$_3$-2,4,6)(PPh$_3$)] (**9**) are monoclinic with a = 12.075 (1) Å, b = 12.888 (2) Å, c = 30.487 (3) Å, β = 93.65 (1)°, V = 4734 (1) Å^3, space group $P2_1/c$, d_{calcd} = 1.475 g cm^{-3}, Z = 4, and R = 0.047 for 7857 reflections with $I \geq 2.5\sigma(I)$. Crystals of the toluene solvate [Cu$_4$Mg$_2${SC$_6$H$_4$(CH(Me)NMe$_2$)-2}$_4$-(C$_6$H$_2$Me$_3$-2,4,6)$_4$] (**14**) are orthorhombic with a = 25.140 (3) Å, b = 19.026 (2) Å, c = 8.554 (1) Å, V = 4091.5 (8) Å^3, space group $P2_12_12$, d_{calcd} = 1.368 g cm^{-1}, Z = 2, and R = 0.056 for 3674 reflections with $I \geq 2.5\sigma(I)$. In solution the organo(arylthiolato)copper compounds **1–16** show fluxional behavior, which could be identified as combinations of three types of intramolecular processes, i.e., inversion of the sulfur configuration ($\Delta G^\ddagger$ = 48 kJ mol^{-1}), Cu–N dissociation/association ($\Delta G^\ddagger$ = 50–58 kJ mol^{-1}), and a boat-to-boat flip of Cu$_3$S$_2$C and Cu$_4$S$_2$C$_2$ units ($\Delta G^\ddagger$ = 40 kJ mol^{-1}), and one intermolecular process, i.e., an interaggregate exchange ($\Delta G^\ddagger$ = 70 kJ mol^{-1}).

Introduction

Synthetic and structural work in organocopper and organocuprate chemistry is primarily focussed on homoorganocopper and -cuprate species. It appears from the limited information available that in solution these species can undergo interaggregate exchange processes[1] and can react with metal salts to form new mixed aggregates. We have reported some products from reactions of the latter type arising from the interaction of pure homoaryl- and vinylcopper compounds with metal halides, e.g., [Cu$_6$R$_4$Br$_2$] (R = C$_6$H$_4$NMe$_2$-2),[2] [Au$_2$Cu$_4$Br$_2$R$_4$] (R = C$_6$H$_4$NMe$_2$-2),[1c] and [Cu$_4$Br$_2$R$_2$] (R = C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6,[3] (*Z*)-(2-Me$_2$NCH$_2$C$_6$H$_4$)C=C(Me)(C$_6$H$_4$Me-4)[4]). Recently, we also found that the reaction of copper benzoate [CuO$_2$CC$_6$H$_5$]$_4$ with pentameric mesitylcopper by a selective interaggregate exchange process leads to the formation of a trinuclear copper species, [Cu$_3$(O$_2$CC$_6$H$_5$)$_2$Mes] (Mes = C$_6$H$_2$Me$_3$-2,4,6).[5] A possible reason for the stability of this 40 electron cluster is that all copper(I) centers are linearly coordinated. These examples show that in these interaggregate exchange processes there is selective formation of only one of the possible mixed products.

The number of cuprate and organocopper compounds that have been characterized by X-ray analysis is now increasing rapidly.[6] The structure of the first neutral cuprate [Cu$_2$Li$_2${C$_6$H$_4$-(CH$_2$NMe$_2$)-2}$_4$], to which the later published diphenylcuprates bear analogy, has been used to develop a direct model for the reactive species in the 1,4-addition reaction of Cu$_2$Li$_2$Me$_4$ with enones.[7] Although it is feasible that ligands (as well as substrate molecules) influence the structure and constitution of organocopper and cuprate reagents[8] as well as the reactive species, little attention has been paid to this.[9]

We have now studied the reactivity of copper arenethiolates (CuSAr) toward organometallic reagents ZR (Z = Cu, Li, or MgX; R = organo group) to see whether these copper compounds can provide selective formation of heteroorganocuprates or het-

eroorganocopper compounds. Such a study is relevant because of the importance of heteroorganocuprate reagents CuZ(SAr)R in the specific alkyl and aryl group transfer in 1,4-addition reactions.[10] Our choice of the arenethiolate group (SAr) is based

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(8) (a) An example is the selective formation of tetranuclear [Cu$_4$-(Mes)$_4$(THT)$_2$] (THT = tetrahydrothiophene) from the reaction of pentanuclear [CuMes]$_5$ with THT reported by Floriani[8b] as well as the formation of [Cu$_4$(2-tolyl)$_4$(DMS)$_2$] (DMS = dimethyl sulfide).[6g] (b) Meyers, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

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Table I. Preparation of Heteroorganocopper and -cuprate compounds[a]

eq	reactants[b]	products	examples
	Organo(arenethiolato)copper		
1	2[CuSAr]₃ + 6CuR	→ 3[Cu₂(SAr)R]₂	6,[c] 7,[c] 11[d]
2	2[CuSAr]₃ + 6CuBr + 6LiMe	→ 3[Cu₂(SAr)(Me)]₂ + 6LiBr	10
3	2[CuSAr]₃ + 3CuBrL + 3LiMe	→ 3Cu₃(SAr)₂(Me)(L) + 3LiBr	12
4	2[CuSAr]₃ + 3CuBr + 3L + 3LiMe	→ 3Cu₃(SAr)₂(Me)(L) + 3LiBr	12
5	2[CuSAr]₃ + 3CuMe + 3L	→ 3Cu₃(SAr)₂(Me)(L)	8,[e] 9[f]
6	[Cu₂(SAr)(Mes)]₂ + L	→ Cu₃(SAr)₂(Mes)(L) + CuMes	8,[e] 9[f]
	Organo(arenethiolato)cuprates		
7	[CuSAr]₃ + LiMe	→ [Cu₃Li(SAr)₃R]	13
8	4[CuSAr]₃ + 6MgMes₂	→ 3[Cu₄Mes₄][μ-SAr]₂[MgSAr]₂	14

[a] The reactions were carried out at room temperature in toluene or benzene. [b] [CuSAr]₃ = [CuSC₆H₄(CH₂NMe₂)-2]₃, **1**; [CuSC₆H₄((R)-CH-(Me)NMe₂)-2]₃, **2**; [CuSC₆H₃(CH₂NMe₂)-2-Cl-3]₃, **3**. The CuR, MgR₂, and LiR compounds are not as is depicted monomers but are in fact part of homoorganometal aggregates. [c] R = mesityl, abbreviated as Mes (C₆H₂Me₃-2,4,6). [d] R = CH₂SiMe₃. [e] L = P(OMe)₃. [f] L = PPh₃.

on the fact that transferability decreases in the order alkyl > aryl > alkylthiolato > arenethiolato while the stabilization of the resulting heterocuprate can be anticipated to decrease in the reverse order.[10,11] As a special feature we have built into the SAr group a potentially coordinating ortho amino group CH(R′)NMe₂ which can be either chiral (R′ = Me) or achiral (R′ = H). Through coordination to reactive copper centers this amine group can stabilize unusual intermediates. Furthermore, it can direct the reactivity of the heterocuprates containing the SAr group. We have already found that the reaction of [CuSAr]₃ with LiC≡C*t*-Bu does not result in the formation of a cuprate species, but rather mixed organocopper compounds [Cu₃{SC₆H₄(CH(R)-NMe₂)-2}₂(C≡C*t*-Bu)]₂ (R = H (**4**) or Me (**5**)).[12]

In this paper we describe a number of unprecedented highly specific interaggregate exchange reactions of copper(I) arenethiolates, [CuSAr]₃, with organometallic reagents, ZR, and the influence of two-electron donors (e.g., PPh₃) on the course of these reactions. The successful application of the resulting cuprates and copper species in organic synthesis is the subject of a separate paper.[13]

Results

Starting from copper arenethiolates [CuSAr]₃ with an intramolecularly coordinating amino group a wide range of thermally stable, mixed organocopper compounds **6–14** can be synthesized. The results using [CuSC₆H₄(CH₂NMe₂)-2]₃ (**1**, R′ = R″ = H), [CuSC₆H₄((R)-CH(Me)NMe₂)-2]₃ (**2**, R′ = Me; R″ = H), and [CuSC₆H₃(CH₂NMe₂)-2-Cl-3]₃ (**3**, R′ = H; R″ = Cl) have been summarized in Table I containing the eqs 1–8. All compounds were identified by a combination of ¹H NMR, cryoscopy, and elemental analysis and the data are in accordance with the formulae given.

Mixed Aryl(arenethiolato)copper Compounds. A straightforward method to prepare mixed organo(arenethiolato)copper(I) compounds is by the interaggregate exchange reaction of a pure organocopper compound with a pure copper arenethiolate (eq 1). In this way the compounds [Cu₂{SC₆H₄(CH(R′)NMe₂)-2}(C₆H₂Me₃-2,4,6)]₂ (R′ = H, **6**; R′ = Me, **7**) were prepared, in benzene, from reactions of [CuC₆H₂Me₃-2,4,6]₅ with either **1** or **2**.

The preference for the formation of a heteroorganocopper compound **7** with a 1:1 SAr to mesityl ratio is also reflected in the result of a microwave titration of a solution of [CuC₆H₂Me₃-2,4,6]₅ in benzene with a benzene solution of **2**.[14] There is a point of equivalence when the concentration of **2** reaches 5/3 of the concentration of [CuC₆H₂Me₃-2,4,6]₅. No other points of equivalence are found, and this means that either free copper arenethiolate **2** or free [CuC₆H₂Me₃-2,4,6]₅ are present when one of them is in excess. This result is supported by ¹H NMR data where free **2** or free [CuC₆H₂Me₃-2,4,6]₅ is also seen in the spectra of mixtures of **2** and [CuC₆H₂Me₃-2,4,6]₅ in molar ratios other than 5:3.

Compounds **6** and **7** have a deep yellow color and are stable at room temperature when kept under a nitrogen atmosphere. They are readily soluble in benzene. Cryoscopy in benzene shows that **7** has a dimeric aggregation state in solution in the concentration range 0.124–0.030 mol kg⁻¹ benzene. Attempts to crystallize **7** failed, but it was possible to grow X-ray quality crystals of **6** in 72% yield by cooling the reaction mixture of achiral copper arenethiolate **1** with mesitylcopper in hot toluene.

It is possible to prepare the P(OMe)₃ adduct of **7**, [Cu₃-{SC₆H₄(CH(Me)NMe₂)-2}₂(C₆H₂Me₃-2,4,6){P(OMe)₃}] (**8**), in solution by several methods (eqs 3–6). The simple method of reacting P(OMe)₃ with **7** generated **8** and mesitylcopper, whereas the reaction of the pure copper arenethiolate **2** with mesitylcopper (2:1 ratio based on monomeric units) in the presence of P(OMe)₃ affords **8** exclusively (eq 5). Unfortunately, we have not found a suitable recrystallization solvent or a suitable workup procedure to isolate pure **8**.

The PPh₃ complex [Cu₃{SC₆H₃(CH₂NMe₂)-2-Cl-3}₂-(C₆H₂Me₃-2,4,6)(PPh₃)] (**9**), like **8**, could also be made in various ways (eqs 3–6). Of these methods the mixing of [CuSC₆H₃-(CH₂NMe₂)-2-Cl-3]₃, [CuC₆H₂Me₃-2,4,6]₅, and PPh₃ in the correct molar ratios in benzene is the most straightforward (eq 5). In contrast to **8**, compound **9** could be purified by crystallization. Yellow **9** is stable in air for months and has good solubility in benzene. Cryoscopy in benzene shows that in this solvent **9** exists as a monomer in the concentration range 0.022–0.155 mol kg⁻¹ benzene.

Mixed Alkyl(arenethiolato)copper Compounds. The above synthesis for mixed arylcopper arenethiolates has also been applied to the synthesis of the corresponding alkyl species **10–12**. Since the preparation of pure methylcopper is a dangerous undertaking (the solid is **explosive**), the synthesis of [CuSC₆H₄(CH(Me)-NMe₂)-2]₃·(CuMe)ₓ (**10**) was carried out by an in situ method (eq 2): the reaction of **2** with CuBr and LiMe affords **10** in solution and after filtration (**Careful**, methylcopper may be present in the residue) evaporation of the solvent affords the thermally stable yellow product. On exposure to air **10** decomposes within a few seconds. ¹H NMR data of **10** are consistent with the formulation of CuMe·[CuSC₆H₄((R)-CH(Me)NMe₂)-2]₂. Attempts to crystallize **10** from benzene resulted in crystallization of methylcopper itself. When the same reaction of CuBr and LiMe with **2** was carried out in toluene at room temperature, methylcopper precipitated in significant amounts; i.e., **10** is less stable in toluene than in benzene.

To avoid the solubility and purity problems encountered with methylcopper, similar reactions of **2** with the soluble alkylcopper, [CuCH₂SiMe₃]₄ (in pure form),[15] were carried out. In this case we could follow the direct interaggregate exchange reaction (similar to that described for **6** and **7**) which yielded [Cu₂-{SC₆H₄(CH(Me)NMe₂)-2}(CH₂SiMe₃)]ₙ (**11**) (eq 1). This compound, which is air- and light-sensitive, is dark yellow both in solution and in the solid state. With the very pure starting compounds used, no reaction other than the interaggregate ex-

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Table II. Relevant Bond Distances (Å) and Bond Angles (deg) in
[Cu₂{SC₆H₄(CH₂NMe₂)-2}(C₆H₂Me₃-2,4,6)]₂ (6)[a]

Cu1–S1	2.1928 (8)	Cu1–C10	2.022 (3)
Cu2–S1	2.2439 (9)	Cu2–Cl	2.005 (2)
Cu3–S2	2.1812 (9)	Cu3–Cl	2.019 (2)
Cu4–S2	2.2590 (9)	Cu4–C10	2.015 (3)
Cu2–N1	2.143 (2)	Cu4–N2	2.130 (2)
Cu1⋯Cu2	2.7952 (7)	Cu1⋯Cu3	2.6563 (7)
Cu1⋯Cu4	2.4075 (7)	Cu2⋯Cu3	2.3805 (7)
Cu2⋯Cu4	4.346 (1)	Cu3⋯Cu4	2.6983 (7)
Cu1–S1–Cu2	78.09 (2)	Cu3–S2–Cu4	74.82 (2)
Cu1–C10–Cu4	73.22 (9)	Cu2–Cl–Cu3	72.54 (8)
S1–Cu1–C10	143.89 (8)	Cu2–Cu1–S1	51.77 (2)
Cu4–Cu1–C10	53.26 (7)	S1–Cu2–N1	97.33 (6)
S1–Cu2–Cl	160.06 (7)	N1–Cu2–Cl	102.61 (9)
Cu1–Cu2–S1	50.14 (2)	Cu3–Cu2–Cl	54.02 (7)
S2–Cu3–Cl	141.28 (7)	Cu2–Cu3–Cl	53.44 (7)
Cu4–Cu3–S2	53.90 (2)	S2–Cu4–N2	97.82 (6)
S2–Cu4–C10	152.70 (8)	N2–Cu4–C10	106.6 (1)
Cu1–Cu4–C10	53.52 (7)	Cu3–Cu4–S2	51.28 (2)

[a] Uncertainties in the last significant digit are shown in parentheses.

change reaction occurred. The in situ prepared product gave ¹H NMR spectroscopic data for 11 (−0.07 (CH₂) and 0.29 ppm (SiMe₃)) together with signals of small amounts (<10%) of free [CuCH₂SiMe₃]₄ (−0.06 and 0.27 ppm). Unfortunately recrystallization proved impossible.

For the preparation of [Cu₃{SC₆H₄(CH(Me)NMe₂)-2}₂-(Me){P(OMe)₃}] (12) an in situ route starting from [CuBr{P-(OMe)₃}]₄ and methyllithium in the presence of the copper arenethiolate 2 in benzene (eq 3) was also used. Solutions of 12 in benzene show some decomposition after 30 min at room temperature. Solid 12 is stable for weeks at room temperature when kept under a nitrogen atmosphere.

Mixed Organo(arenethiolato)cuprates. From the reaction of 1 and LiMe (3:1 based on the monomeric units) in diethyl ether, yellow [Cu₃Li{SC₆H₄(CH₂NMe₂)-2}₃Me] (13) is obtained as a precipitate (eq 7). This solid is stable for months at room temperature when kept under a nitrogen atmosphere but decomposes rapidly on exposure to air. When 13 is dissolved in tetrahydrofuran (THF), a colorless solution is obtained from which a white solid is isolated upon evaporating the solvent. This material has not been fully characterized but is probably a THF adduct of 13. The white solid, unlike 13, is soluble in diethyl ether though after some minutes at room temperature pure yellow 13 precipitates from the solution. By using this intriguing behavior, 13 could be purified and isolated in 82% yield. The elemental analyses for 13 are correct for the sulfur and nitrogen, but those of carbon and hydrogen are low by an amount corresponding to ca. 0.6 mol equiv of methane. This result probably reflects the extreme sensitivity of 13 to moisture. The reaction of a THF solution of 13 with water yielded 1 equiv of methane. In the ¹H NMR spectrum of 13 the singlet resonance of the methyl carbanion at both 303 K (−0.51 ppm) and at 210 K (−0.95 ppm) is downfield with respect to both methylcuprates (−1.25 to −1.67 ppm) and methyllithium (−2.05 ppm).[16]

Reaction of 2 with pure [Mg(C₆H₂Me₃-2,4,6)₂(THF)₂] afforded quantitatively [Cu₄Mg₂{SC₆H₄(CH(Me)NMe₂)-2}₄(C₆H₂Me₃-2,4,6)₄] (14) (eq 8), which is stable in boiling toluene for long periods (>24 h).[17] Crystals of the solvate, 14·0.5toluene, were obtained on cooling a hot (100 °C) saturated toluene solution. The light yellow crystals of the solvate decompose within a few hours on exposure to air. At room temperature solid 14 and its solutions are stable for months under a nitrogen atmosphere.

Structures in the Solid State. The Tetranuclear Aryl(arenethiolate)copper 6. The molecular structure of [Cu₂{SC₆H₄-
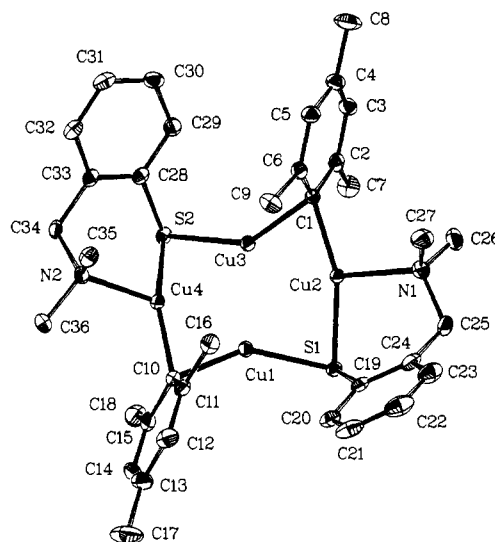
Figure 1. ORTEP drawing of [Cu₂{SC₆H₄(CH₂NMe₂)-2}(C₆H₂Me₃-2,4,6)]₂ (6) (with the exclusion of the hydrogen atoms) with the atom-labeling scheme. Ellipsoids are contoured at the 50% probability level.

(CH₂NMe₂)-2}(C₆H₂Me₃-2,4,6)]₂ (6) is depicted in Figure 1, and a list of relevant bond distances and angles is given in Table II. The structure consists of four copper atoms in a butterfly arrangement (the torsion angle Cu4–Cu1–Cu3–Cu2 is 159.61 (2)°) in which two mesityl groups bridge opposite Cu1⋯Cu4 and Cu2⋯Cu3 edges and the two SAr groups bridge, through sulfur, the Cu1⋯Cu2 and Cu3⋯Cu4 edges and also coordinate intramolecularly through the CH₂NMe₂ groups to opposite copper atoms Cu2 and Cu4. The bridging sulfur and C_ipso atoms are positioned on the inner and outer sides, respectively, of the butterfly with all the aryl groups on the "open" side of the Cu₄ array. The two copper atoms without nitrogen coordination are two-coordinate, while the two copper sites with nitrogen coordination are three-coordinate. The molecule contains a noncrystallographic C₂ axis which is perpendicular to both the Cu1–Cu3 and Cu2–Cu4 vectors.

The four copper atoms together with the two bridging sulfur atoms and the two ipso carbon atoms form an eight-membered Cu₄S₂C₂ ring that is in a twist-boat conformation with the aryl groups bonded to the sulfur atoms in equatorial positions (see Figure 7).

The mesityl groups bridge symmetrically between the copper atoms in a fashion typical for electron-deficient two-electron three-center bonding.[18] The separation between copper atoms bridged by the mesityl group are extremely short, i.e., 2.3805 (7) and 2.4075 (7) Å. The copper–copper distances of 2.7952 (7) and 2.6983 (7) Å between the atoms bridged by sulfur and the acute Cu–S–Cu angles of 74.82 (2)° and 78.09 (2)° are in the ranges expected for electron-deficient Cu₂S bonding.[18] The copper–sulfur bond distances (2.1928 (8) and 2.1812 (9) Å; 2.2439 (9) and 2.2590 (9) Å) are in agreement with the observed ranges of 2.14–2.18 and 2.22–2.33 Å, for di- and tricoordinate copper atoms, respectively.[18]

The overall structure of a tetranuclear copper cluster in a butterfly arrangement with two adjacent dicoordinate copper atoms and two-, three-, or four-coordinate copper atoms is one which is typical for pure homoarylcopper compounds, e.g., [Cu₄(Mes)₄(THT)₂] (THT = tetrahydrothiophene),[8b] [Cu₄-(C₆H₄Me-2)₄(SMe₂)₂],[6g] tetrameric 1-copper-8-(dimethyl-amino)naphthalene,[19] and 14 (vide supra). These basic structural

(16) The ¹H NMR data of pure LiMe as well as of mixtures of LiMe, CuMe, and LiI in different ratios in THF have been reported. The LiMe methyl group resonances is at −2.05 ppm while for mixtures of CuMe, LiMe, and LiI singlets lie between ~1.66 and −1.25 ppm. Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *J. Am. Chem. Soc.* 1985, *107*, 3197.

(17) Knotter, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* 1990, *112*, 5895.

(18) (a) Knotter, D. M.; van Maanen, H. L.; Spek, A. L.; Grove, D. M.; van Koten, G. *Inorg. Chem.* 1991, *30*, 3309. (b) *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 341. (c) This description is based on a localized picture and is therefore a first approximation. Computational studies on the bonding of the [Cuₙ₊ₘSₙCₘ]-skeleton of these organo(arenethiolate)copper clusters is underway: Dedieu, A. Unpublished results.

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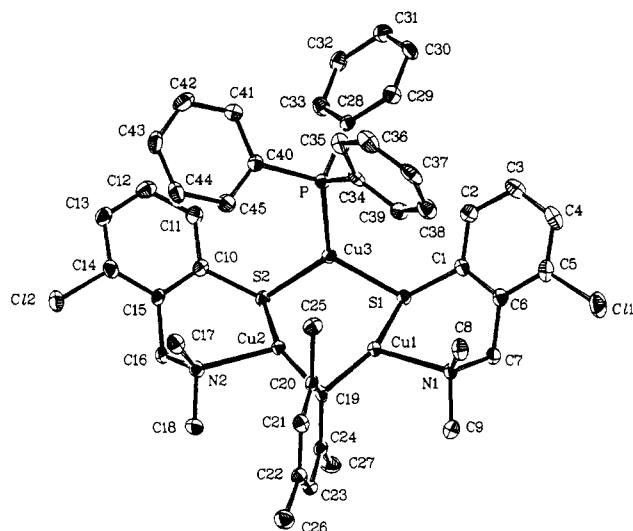
Copper(I) Arenethiolates

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Figure 2. ORTEP drawing of [Cu$_3${SC$_6$H$_3$(CH$_2$NMe$_2$)-2-Cl-3}$_2$-(C$_6$H$_2$Me$_3$-2,4,6)(PPh$_3$)] (**9**) (with the exclusion of the hydrogen atoms and the benzene molecule) with the atom-labeling scheme. Ellipsoids are contoured at the 50% probability level.

Table III. Relevant Bond Distances (Å) and Bond Angles (deg) in [Cu$_3${SC$_6$H$_3$(CH$_2$NMe$_2$)-2-Cl-3}$_2$(C$_6$H$_2$Me$_3$-2,4,6)(PPh$_3$)] (**9**)^a

Cu1–C19	2.021 (4)	Cu2–C19	2.040 (4)
Cu1–S1	2.246 (1)	Cu2–S2	2.234 (1)
Cu3–S1	2.267 (1)	Cu3–S2	2.280 (1)
Cu1–N1	2.150 (4)	Cu2–N2	2.187 (4)
Cu3–P	2.214 (1)	Cu1···Cu2	2.4361 (8)
Cu1···Cu3	2.8056 (9)	Cu2···Cu3	2.7525 (8)
Cu1–S1–Cu3	76.87 (4)	Cu2–S2–Cu3	75.13 (4)
Cu1–C19–Cu2	73.7 (1)	S1–Cu1–N1	97.5 (1)
S1–Cu1–C19	156.1 (1)	N1–Cu1–C19	105.1 (2)
Cu2–Cu1–C19	53.5 (1)	Cu3–Cu1–S1	51.90 (3)
S2–Cu2–N2	97.3 (1)	S2–Cu2–C19	156.9 (1)
N2–Cu2–C19	103.9 (2)	Cu1–Cu2–C19	52.8 (1)
Cu3–Cu2–S2	53.20 (3)	S1–Cu3–S2	104.11 (4)
S1–Cu3–P	128.01 (4)	S2–Cu3–P	126.94 (4)
Cu1–Cu3–S1	51.23 (3)	Cu2–Cu3–S2	51.67 (3)

^{a} Uncertainties in the last significant digit are shown in parentheses.

features are also met in some arylcuprates, e.g., [CuLi{C$_6$H$_4$-(CH$_2$NMe$_2$)-2}$_2$]$_2$[20] and [CuLi(phenyl)$_2$]$_2$·2OEt$_2$.[21] Thus, structures of **6** and homoarylcopper compounds can be directly related to those of arylcuprates in that the three- or four-coordinate copper centers are equivalent to the more highly coordinated lithium ion in the Cu$_2$Li$_2$ four-membered ring.

The Trinuclear Aryl(arenethiolato)(phosphine)copper Compound 9. Crystals of **9** were obtained from benzene as the solvate ([Cu$_3${SC$_6$H$_3$(CH$_2$NMe$_2$)-2-Cl-3}$_2$(C$_6$H$_2$Me$_3$-2,4,6)(PPh$_3$)]·C$_6$H$_6$). In the unit cell there are two mirror-related enantiomers of the molecule. The molecular structure of **9** is depicted in Figure 2, and relevant bond lengths and angles are given in Table III. Compound **9** is based on a six-membered Cu$_3$S$_2$C ring which has a boat-like conformation with pairs of copper atoms bridged by either sulfur of the arenethiolates or C$_{ipso}$ of the mesityl group. The aryl ring of the arenethiolates are bonded equatorially to the sulfur atoms with respect to the Cu$_3$S$_2$C ring. The amino groups are intramolecularly coordinated to the copper atoms (Cu1 and Cu2) that are bridged by C$_{ipso}$ of the mesityl group, while the phosphine ligand is coordinated to the unique copper atom (Cu3) that has two sulfur atoms attached to it. The amine and phosphine groups are bisectionally bound to the Cu$_3$S$_2$C ring.

All three copper atoms are thus three-coordinate with the sum of interligand angles around each copper atom being 359°. At

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(21) Lorenzen, N. D.; Weiss, E. *Angew. Chem.* **1990**, *102*, 322; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 300.

Table IV. Relevant Bond Distances (Å) and Bond Angles (deg) in {Cu$_4$Mg$_2${SC$_6$H$_4$((R)-CH(Me)NMe$_2$)-2}$_4$(C$_6$H$_2$Me$_3$-2,4,6)$_4$} (**14**)^a

Cu1–C1	1.981 (8)	Cu2–C1	2.064 (8)
Cu1'–C30	2.025 (8)	Cu2–C30	2.044 (8)
Cu1···Cu2	2.464 (1)	Cu1···Cu1'	2.700 (1)
Cu1···Cu2'	2.431 (1)	Cu2···Cu2'	4.079 (1)
Cu2–S1	2.389 (2)	Mg–S1	2.427 (4)
Mg–S2	2.376 (4)	Mg–N1	2.186 (8)
Mg–N2	2.180 (7)	Mg···Cu	4.472 (3)
Cu1–C1–Cu2	75.0 (3)	Cu1'–C30–Cu2	73.4 (3)
C1–Cu1–C30'	142.8 (3)	C1–Cu2–C30	168.1 (3)
S1–Cu2–C1	90.0 (2)	S1–Cu2–C30	101.4 (2)
Cu2–S1–C10	120.1 (3)	Cu2–S1–Mg	136.4 (1)
Mg–S1–C10	89.7 (3)	Mg–S2–C20	89.5 (3)
S1–Mg–S2	132.5 (5)	S1–Mg–N1	95.8 (2)
S2–Mg–N2	95.9 (2)	N1–Mg–N2	116.4 (3)
Cu2–Cu1–C1	54.0 (3)	Cu2'–Cu1–C30'	53.7 (2)
Cu1–Cu2–C1	51.0 (2)	Cu1'–Cu2–C30	53.0 (2)

^{a} Uncertainties in the last significant digit are shown in parentheses. Prime indicates symmetry operation $-x$, $-y$, z.

first sight the geometry of Cu1 and Cu2 copper atoms appears to be close to T-shaped and that of Cu3 appears to approximately trigonal. However, based on molecular orbital arguments (see Discussion), it can be shown that all copper atoms have in fact a trigonal coordination geometry. The Cu$_2$S units in **9** have acute Cu–S–Cu angles (76.87 (4) and 75.13 (5)°) and short copper–copper distances (2.8056 (9) and 2.7525 (8) Å), just like the electron-deficient Cu$_2$S units in **6**. The whole molecule is asymmetric due to unsymmetrical positioning of the phenyl groups of the triphenylphosphine ligand, with the phosphorus atom and the mesityl group lying on an approximate noncrystallographic mirror plane. The bond lengths and bond angles related to the Cu$_3$S$_2$C ring are similar to those in the monomeric units [Cu$_3${SC$_6$H$_4$-(CH(R)NMe$_2$)-2}$_2$(C≡Ct-Bu)]$_2$ (R = H (**4**) or Me (**5**)) whose structures have the same boat-like conformation.[12,22] The low temperature ^{1}H NMR spectrum of **9** is consistent with the solid state structure though the expected NOE interactions between the mesityl methyl and the amino methyl groups were not found in a ^{1}H–^{1}H NOE-2D experiment.

The Organocopper–Magnesium Arenethiolate Compound 14. Crystals of a solvate **14**·0.5toluene were used for an X-ray diffraction measurement. Figure 3 shows the molecular structure of **14**, while in Table IV the relevant bond lengths and interbond angles are given. The molecule contains a crystallographic C$_2$ rotation axis. The structure can be described as a [CuMes]$_4$ unit to which two Mg(SAr)$_2$ units are connected. The diamond-shaped central tetranuclear copper unit is essentially flat with each mesityl group bridging a Cu···Cu edge with C$_{ipso}$ (∠Cu–C–Cu = 73.4 (3) and 75.0 (3)°). The two copper atoms, Cu1, at the ends of the short diagonal (2.700 (1) Å) of the Cu$_4$-rhombic are only bonded to these mesityl groups and are thus two-coordinate. Each of the other two opposing copper atoms is also bonded to a Mg(SAr)$_2$ unit via a sulfur bridge and are three-coordinate. The coordination around each Mg comprises two S,N-chelating arenethiolate groups with one sulfur atom being involved in a bridging to the Cu$_4$ array.

There is significant asymmetry in the bonding mode for two of the aromatic groups (Cu1–C1 = 1.981 (8) Å and Cu2–C1 = 2.064 (8) Å), while the other two are bonded more symmetrically (Cu1'–C30 = 2.025 (8) Å and Cu2–C30 = 2.044 (8) Å); this asymmetry is probably induced by the steric demands of the Mg(SAr)$_2$ unit. The two Cu···Cu distances are typical for two-electron three-center carbon-bridged copper atoms (2.431 (1) and 2.464 (1) Å). The geometry of the two-coordinate copper atoms is nonlinear, ∠C1–Cu1–C30' = 142.8 (3)°, and the three-coordinate copper atoms, Cu2, have a planar distorted T-shaped geometry, ∠C1–Cu2–C30 = 168.1 (3)°, ∠S1–Cu2–C1 = 90.0 (2)°, ∠S1–Cu2–C30 = 101.4 (2)°. The sulfur atom that is two-electron two-center bonded to copper atom Cu2 has a Cu–S bond of 2.389 (2) Å. This distance is long when compared to Cu–S bonds in

(22) Knotter, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1989**, 1738.
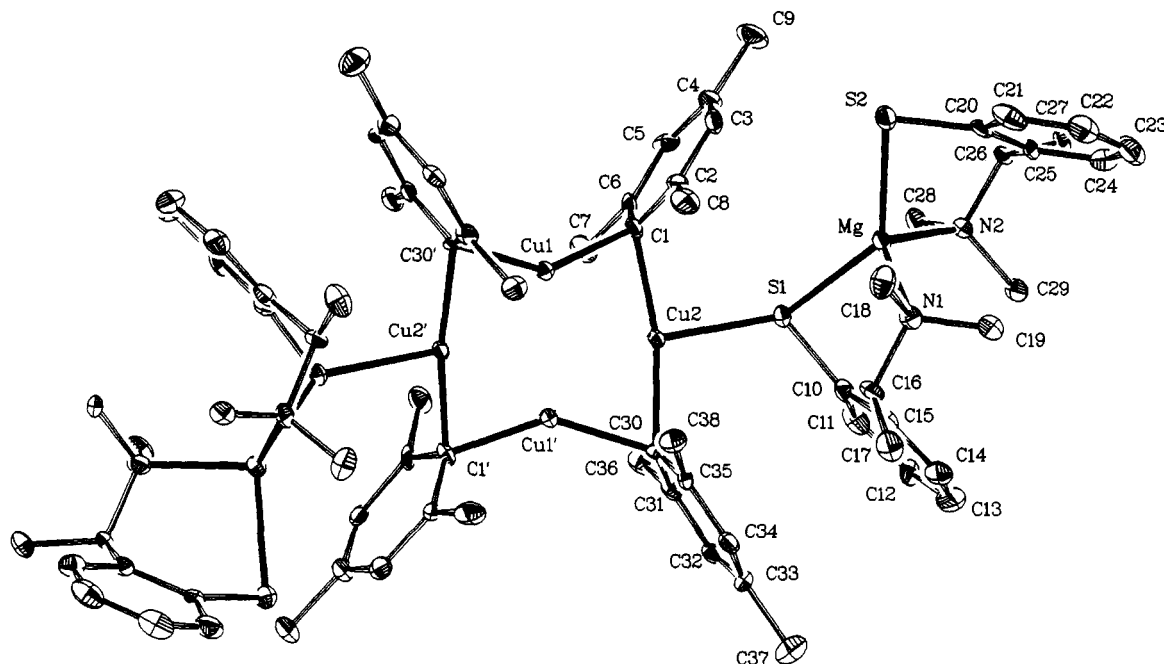
Figure 3. ORTEP drawing of [Cu$_4$Mg$_2${SC$_6$H$_4$(CH(Me)NMe$_2$)-2}$_4$(C$_6$H$_2$Me$_3$-2,4,6)$_4$] (**14**) (with the exclusion of the hydrogen atoms and the toluene molecule) with the atom-labeling scheme. Ellipsoids are contoured at the 50% probability level.

Table V. The Calculated Angles of the Bonding Copper Orbitals in (Organo)(arenethiolato)Copper Compounds[a]

compd[b]	Cu1	Cu2	Cu3	Cu4
4	106.0, 130.3, 121.9	73.0, 151.6, 131.6	112.9, 125.9, 121.3	
6	181.1	121.6, 119.0, 116.6	177.8	117.5, 119.1, 123.4
9	119.9, 120.1, 118.7	121.0, 118.9, 118.2	62.2, 149.1, 147.7	
14	174.8	137.9, 105.3, 116.3		

[a] These values are based on the structure in the solid state; eq 9 is used to calculated the position of the orbital involved in the two-electron three-center bond. [b] [Cu$_3${SC$_6$H$_4$(CH$_2$NMe$_2$)-2}$_2$(C≡C*t*-Bu)]$_2$ (**4**), [Cu$_2${SC$_6$H$_4$(CH$_2$NMe$_2$)-2}(C$_6$H$_2$Me$_3$-2,4,6)]$_2$ (**6**), [Cu$_3${SC$_6$H$_3$(CH$_2$NMe$_2$)-2-Cl-3}$_2$(C$_6$H$_2$Me$_3$-2,4,6)(PPh$_3$)} (**9**), and [Cu$_4$Mg$_2${SC$_6$H$_4$(CH(Me)NMe$_2$)-2}$_4$(C$_6$H$_2$Me$_3$-2,4,6)$_4$] (**14**).

which sulfur is bridge-bonded to two three-coordinate copper centers (2.22–2.33 Å).

A notable feature of the structure of **14** is the coordination around magnesium in which there are unprecedented Mg–S2 bonds. The Mg–S2 bond length is 2.375 (4) Å while the Mg–S1 bond which involves the sulfur bridging between the copper and the magnesium is somewhat longer at 2.427 (4) Å. The Mg–S–C bond angles are both very close to 90°. To our knowledge these are the first structural data for magnesium–sulfur interactions. Pappas has carried out ab initio calculations on Mg(SH)$^+$ and Mg(SH)$_2$ and found Mg–S bond distances of 2.264 and 2.324 Å, respectively, with a Mg–S–H bond angle of 95.2°.[23]

This structure of **14** in which the mesityl groups are bonded to the copper atoms and the magnesium ions to the sulfur ligand was totally unexpected since the strong Cu–S bond of **2** is not retained but is replaced by Mg–S bonding. The overall structure of the central tetranuclear arylcopper unit in **14** is comparable to **6**.

The Geometry of the Copper Atoms. The crystallographically found interatom geometries of copper atoms in aryl–copper arenethiolates are, at first sight, different to that expected for two- and three-coordinated copper atoms. However, the copper atoms are surrounded by 2e–3c bonded ligands that do not directly show the direction of the participating copper orbitals (see Figure 4a). In general in Cu$_2$X systems the binding orbital on a copper atom points between the neighboring copper atom and the bridging X atom, and we have developed a trigonometric method based on X-ray crystallographic data to determine this position. In this method we assume (i) that the vector of bonding orbital of the bridging ligand is perpendicular to the M$_c$–M$_n$ vector and is in the plane of M$_c$–M$_n$–L$_b$, and (ii) the metal orbitals are directed

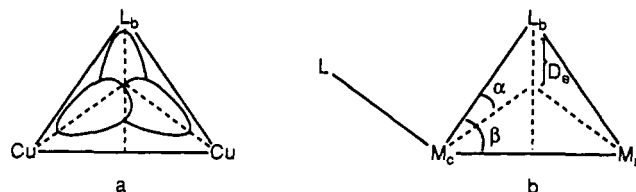(23) Pappas, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 6023.

Figure 4. Two-electron three-center (2e–3c) bonds. (a) The solid lines are the connections between the atoms found crystallographically, while the dotted lines are the direction of the orbitals which are indicative for the real geometry around the metal atoms. (b) A model for the calculation of the geometry around the metal center (M$_c$). The angle between two orbitals on M$_c$, which are responsible for bonding to ligand L and the bridging ligand L$_b$, is the summation of the angles α and L$_b$–M$_c$–L.

toward the point of the highest electron density of the bridging ligand orbital.

The model system considered (see Figure 4b) has central metal atom M$_c$ that is surrounded by a neighboring metal atom, M$_n$, a two-electron two-center bonded ligand, L, and a ligand L$_b$ which is bridging M$_c$ and M$_n$ in a 2e–3c bond. The position of the binding orbital on copper involved in the multicenter interaction is then defined as making an angle α with the M$_c$–L$_b$ bond; this angle is a fraction of the determined M$_n$–M$_c$–L$_b$ angle β. If the point of the highest electron density is at distance D_e away from the bridging atom, then eq 9 can be derived for the angle α.

$$\alpha = \beta - \arctan\left[\frac{d(M_cL_b)\sin\beta - D_e}{d(M_cL_b)\cos\beta}\right] \quad (9)$$

An estimate for D_e is obtained from half the bond distances of either C=C if a sp^2 carbon is bridging ($D_e = 0.669$ Å) or of S$_2$ if a sp^2 sulfur atom is bridging ($D_e = 0.994$ Å). The calculated values of α when added to the angle L–M$_c$–L$_b$ provide an estimate

Table VI. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes 6, 9, and 14

	6	9	14
(a) Crystal Data			
formula	$C_{36}H_{46}Cu_4N_2S_2$	$C_{45}H_{48}Cl_2Cu_3N_2PS_2 \cdot C_6H_6$	$C_{76}H_{100}Cu_4Mg_2N_4S_4 \cdot 2C_7H_8$
mol wt	825.08	1051.63	1684.97
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$ (Nr. 14)	$P2_1/c$ (Nr. 14)	$P2_12_12$ (Nr. 18)
a, Å	13.774 (3)	12.075 (1)	25.140 (3)
b, Å	13.635 (1)	12.888 (2)	19.026 (2)
c, Å	19.977 (3)	30.487 (3)	8.554 (1)
β, deg	109.57 (1)	93.65 (1)	90
V, Å^3	3535 (1)	4734 (1)	4091.5 (8)
Z	4	4	2
d_{calcd}, g·cm^{-3}	1.550	1.475	1.368
$F(000)$	1696	2168	1776
μ, cm^{-1}	25.2	16.1	11.9
cryst dimens, mm	0.5 × 0.45 × 0.38	0.60 × 0.25 × 0.12	0.08 × 0.13 × 0.90
(b) Data Collection			
temp, K	100	100	100
θ_{min}, θ_{max}, deg	1.08, 27.5	0.67, 30.2	0.81, 29.4
radiatn		Mo Kα (Zr filtered); λ = 0.71073 Å	
$\Delta\omega$, deg	0.65 + 0.35 tanθ	0.70 + 0.35 tanθ	0.65 + 0.35 tanθ
hor and vert aperture, mm	4.0, 5.0	3.0, 5.0	3.0, 5.0
X-ray exposure time (h)	130	199	94
linear decay, %	3.6	2.0	0.4
ref reflcn	2 3 0, −4 0 2, 0 2 −4	−3 0 4, 0 1 2, −3 −4 0	1 −1 0, 2 0 3
data set	h −17:0; k 0:17	h −16:0; k 0:17	h 0.34; k 0:26
	l 24:25	l 42:42	l 10:11
total data	8808	13260	6267
total unique data	8080	12098	6236
(c) Refinement			
no. of reflcns	6493	7857	3674
no. of refined params	428	551	470
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.00236F^2]$	$w = 1.0/[\sigma^2(F) + 0.000895F^2]$	$w = 1.0/[\sigma^2(F) + 0.00106F^2]$
final R, wR, S	0.028, 0.032, 1.69	0.047, 0.057, 3.07	0.056, 0.061, 3.18
isotr therm param H-atoms Å^2	0.044 (2)	0.035 (2)	0.058 (2)
$(\Delta/\sigma)_{av}$ in final cycle	0.200	0.021	0.047
min and max resd dens, e·Å^{-3}	−0.39, 0.42	−0.85, 0.88 (near Cu)	−0.58, 0.90 (near Cu)

for the interorbital angle that reflects the coordination geometry of copper. The viability of this method is illustrated by the results for the organocopper arenethiolates 4, 6, 9, and 14 in Table V. Most copper atoms in these compounds are found to have almost perfect trigonal or linear arrangement of their bonding orbitals, i.e., sp^2 or sp copper hybridization. In those instances where there is a large deviation from 120° the explanation can be found in steric strain caused by one or two of the ligands. For example, the triphenylphosphine on Cu3 in 9 which leads to a Y-shaped geometry.

^{1}H NMR (200 MHz) Studies. In solution each of the isolated (organo)copper arenethiolates 1–16 displays fluxional behavior which can be followed by variable temperature NMR spectroscopy. In a recent publication dealing with 1–5 we showed that fluxionality included inversion of the sulfur configuration, via a rotation process ($\Delta G^\ddagger$ = 50 kJ mol^{-1}), and an inversion at the nitrogen atom after a copper–nitrogen dissociation/association process ($\Delta G^\ddagger$ = 48 kJ mol^{-1}).[12,18] Furthermore, in [Cu$_3$-{SC$_6$H$_4$(CH(R)NMe$_2$)-2}$_2$(C≡Ct-Bu){P(OMe)$_3$}] (R = H (15) or Me (16)) we proved that there was a boat-to-boat conformation flip ($\Delta G^\ddagger$ = 40 kJ mol^{-1}) of the Cu$_3$S$_2$C ring.[12]

Fluxionality in Cu$_4$S$_2$C$_2$ Units. The ^{1}H NMR (toluene-d_8) spectrum of 6 at elevated temperature (333 K) shows only one ligand pattern for the arenethiolato groups as well as one singlet for both the ortho methyl groups and the meta aromatic protons of the mesityl groups. Several signals decoalesce on cooling. The first is that of the two benzylic protons on the arenethiolato group; this becomes two doublets (2.34 and 3.83 ppm; J_{AB} = 11 Hz) at 233 K, with a T_c of 310 K that corresponds to a $\Delta G^\ddagger$ of 58 kJ mol^{-1}. Further, the singlet signals of the ortho methyl groups and the meta protons on the mesityl group each decoalesce into two singlets at 290 K ($\Delta\nu$ = 98 Hz; $\Delta G^\ddagger$ = 57 kJ mol^{-1}) and 275 K ($\Delta\nu$ = 22 Hz; $\Delta G^\ddagger$ = 57 kJ mol^{-1}), respectively. Lastly, the signal of the amino methyl groups decoalesces into two singlets with a

T_c of 265 K ($\Delta\nu$ = 14 Hz; $\Delta G^\ddagger$ = 56 kJ mol^{-1}). The fact that all the $\Delta G^\ddagger$'s are approximately the same indicates that they all belong to one and the same fluxional process.

The ^{1}H NMR spectrum of 7 (R = mesityl)(toluene-d_8), like that of 6, displays one signal pattern for the arenethiolato groups above room temperature. In contrast, the methyl substituents of the mesityl group are all anisochronous and afford three singlets, and the mesityl aromatic protons appear as two singlets. Upon cooling the solution to 233 K, the signal for the amino methyl groups decoalesces into two singlets at 1.12 and 1.71 ppm (T_c = 300 K; $\Delta G^\ddagger$ of 58 kJ mol^{-1}). From these data for 7 and 6 we conclude that (i) there is no rotation around the C$_{ipso}$ of the mesityl group and (ii) a Cu–N dissociation/association process takes place with a relative high $\Delta G^\ddagger$. This high value reflects a strong Cu–N bond in an electron-poor cluster (13 valence electrons per copper atom); in [CuSAr]$_3$ and Cu$_3$(SAr)$_2$RL (14 valence electrons per copper atom) $\Delta G^\ddagger$ is ±48 kJ mol^{-1}. The fluxional processes in the Cu$_4$S$_2$C$_2$ unit are discussed later.

With compounds 10 (R = Me) and 11 (R = CH$_2$SiMe$_3$) ^{1}H NMR measurements were severely hampered by a number of practical problems, viz. the precipitation of methylcopper in the case of 10, the presence of free starting materials, and complex fluxional behavior. For both 10 (THF-d_8) and 11 (toluene-d_8) the spectrum at 303 K showed a single pattern for the arenethiolate ligand and for the organic group, Me and CH$_2$SiMe$_3$, respectively. For 10 the resonance of the methyl group decoalesced at 215 K into three signals at −0.08, −0.92, and −1.17 ppm in a 10:1:20 ratio. These values are more appropriate for CuMe units in a neutral array than for species of the type Cu$_m$Li$_{n-m}$Me$_n$.[16] At 215 K the arenethiolate region of the spectrum is very complicated, and some signals ascribable to free 2 are present. At 283 K, the ^{1}H NMR of 11 shows broadening of many signals, but, regrettably, the spectra at 223 K and at lower temperatures have proved to complex to unravel.
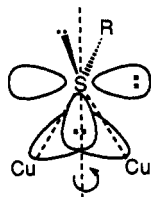
Figure 5. Schematic drawing of the Cu–S–Cu (Cu_2S) two-electron three-center (2e–3c) bond.

Fluxionality in Cu_3S_2C Units. In the ^1H NMR (toluene-d_8) spectrum of **8** (L = $POMe_3$; R = mesityl) at 296 K there are signals for three anisochronous mesityl methyl groups and one broad signal pattern for the SAr group. A low temperature (213 K) there are four ligand patterns for the SAr groups (ortho protons on the aromatic groups) and two doublet patterns in a one-to-two ratio for the $P(OMe)_3$ methyl groups ($^3J(H,P) = 11$ Hz), i.e., two species are present. In the aliphatic region the $CH(Me)NMe_2$ groups afford many broad signals. This behavior is similar to that of $[Cu_3(SAr)_2(C\equiv Ct\text{-}Bu)\{P(OMe)_3\}]$ **(16)**.[12]

The ^1H NMR (toluene-d_8) spectrum of **9** (L = PPh_3; R = mesityl) at 333 K (see Experimental Section) shows one ligand pattern for the arylthiolato group, a singlet for the amino methyl groups at 1.79 ppm and *one* signal for the ortho methyl groups of the mesityl group. On cooling the solution to 213 K, there is an AB pattern for the benzylic protons of the SAr group, two different amino methyl groups (1.51 and 1.88 ppm; T_c = 243 K), and *two* different ortho methyl groups of the mesityl group (2.03 and 2.68 ppm; T_c = 250 K). The $\Delta G^{\ddagger}$ value calculated for the methyl group processes is 48 kJ mol^{-1}.

The ^1H NMR spectrum in toluene-d_8 of **12** (L = $POMe_3$; R = Me) at room temperature shows one signal for the methyl group bound to the copper atom (0.12 ppm), and on cooling to 213 K this becomes four signals in a 1:4:16:20 ratio at 0.08, 0.13, 0.38, and −0.07 ppm. Further interpretation and assignment of this extremely complex spectrum was not possible. With a COSY 2D experiment the CH_3CH unit of the SAr group provided 12 cross-peaks, four of which could be assigned to a small amount of free **2**. We believe that this complexity is due to the presence of several conformers as found for **8** and **16**.[12]

Fluxionality in Cuprates. The ^1H NMR spectrum of **13** in THF-d_8 at room temperature shows one signal for the methyl anion at −0.51 ppm and one ligand pattern for the aryl group and the CH_2NMe_2 group (in a SAr/Me ratio of 3:1). At 210 K all the signals are broadened and there are three SAr group resonance patterns in a 1:1:1 ratio. The signals for the amino methyl group and the methyl anion remain singlets from 210–303 K. This behavior is related to movement of the methyl group over the Cu_3 array, see Discussion.

The ^1H NMR (toluene-d_8 or benzene-d_6, 297 K) spectrum of **14** is complicated by the presence of $[Cu_2\{SC_6H_4((R)\text{-}CH\text{-}(Me)NMe_2)\text{-}2\}(C_6H_2Me_3\text{-}2,4,6)]_2$, **7**, $[Mg\{SC_6H_4((R)\text{-}CH\text{-}(Me)NMe_2)\text{-}2\}_2]$, and $[CuC_6H_2Me_3\text{-}2,4,6]_5$. The ratio **7**:[Mg-$\{SC_6H_4(CH(Me)NMe_2)\text{-}2\}_2]$, calculated from the integrals of the ortho protons of the arenethiolato region, is solvent dependent; in toluene this ratio is 6:7 and in benzene it is 1:5. Upon warming the toluene-d_8 solution to 360 K the two ortho proton signals of the SAr groups of **7** and $[Mg\{SC_6H_4(CH(Me)NMe_2)\text{-}2\}_2]$ coalesce ($\Delta G^{\ddagger}$ = 70 kJ mol^{-1}); the methyl groups on the benzylic carbon atoms coalesce at 370 K ($\Delta G^{\ddagger}$ of 71 kJ mol^{-1}). The interaggregate exchange of SAr ligand between these two complexes almost certainly involves **14**.

Discussion

The Geometry of the Sulfur and Copper Atoms. In (aryl)–copper arenethiolates the Cu–S–Cu bond angle is acute (±76°), and the accompanying Cu⋯Cu distance (2.77 Å) is short. Recently, we proposed a description of such a localized Cu_2S unit in which the sulfur atom uses an sp^2 hybrid orbital to bind to the two copper atoms and so form a two-electron three-center (2e–3c) bond (see Figure 5).[18] This electron-deficient sulfur-to-copper bonding is analogous to the carbon-to-copper bonding in arylcopper species.
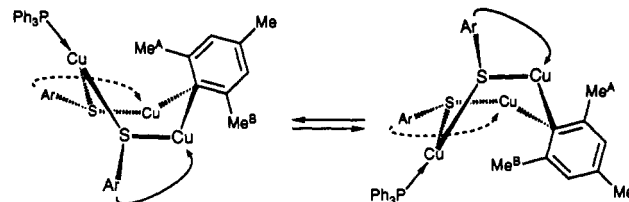

Figure 6. Boat-to-boat flip of the Cu_3S_2C ring with a concerted sulfur inversion; the mesityl *o*-methyl groups become isochronous when this process becomes fast on the NMR time scale.

The sp^2 hybridization of sulfur and sulfur anions is not unprecedented.[24] Since the p_z orbital has a higher electron density than the sp^2 orbitals it is a harder Lewis base. Consequently the way sulfur chooses to bond to a metal will depend on the Lewis acidity of the metal. The Mg–S–C bond angles of 90° in **14** indicates that the hard Lewis acid Mg^{2+} binds to the hard Lewis base site of the sulfur atom, i.e., the p_z orbital, whereas the Cu–S–C bond angle of 120° indicates that the soft Lewis acidic Cu^+ ion binds to the soft Lewis base sulfur sp^2 hybrid orbital.

On the basis of this description the Mg–S–Cu bond angle ought to be 90° rather than the observed 136.4 (1)°. There is a possible explanation for this discrepancy. If the angle were 90°, the Mg^{2+} and the Cu^+ cations would be separated by only 3.405 Å and this, without a ligand assisted metal–metal interaction, would lead to Coulomb repulsion between the two cations. This repulsion apparently results in the cations being driven apart to give a Cu⋯Mg distance of 4.472 (3) Å. This Cu⋯Mg separation (in a 4e–3c bond without a metal–metal bonding interaction) is much larger than in $[Cu_4MgPh_6\cdot OEt_2]$ (Cu⋯Mg = 2.754 Å) where the phenyl ipso carbon atom bridges in a 2e–3c bond which is bonding between the metal ions.[25]

In the complexes described in this paper, the copper(I) ion has either sp or sp^2 hybridization. But, not only the coordination geometry and the hybridization of the copper ion but also its Lewis character are important in determining its properties and reactivity. Most alkene groups in α,β-unsaturated ketones are soft Lewis bases, and the pure organocopper compounds $[Cu_2(SAr)R]_2$ described in this paper (**6**, **7**, and **10**) give, like cuprates, a 1,4-addition reaction to such ketones in the presence of a catalytic amount of Mg^{2+} salt.[13] A substrate–reagent complex is therefore likely to contain the alkene of the ketone coordinated to a soft Lewis acid copper center although we do not know whether the substrate reacts with $Cu_4(SAr)_2R_2$ or with $Cu_3(SAr)_2R$ in an associative or dissociative mechanism, respectively. This complexation is analogous to the situation in the $[Cu_3(SAr)_2R(L)]$ species **4**, **5**, and **9** where the soft Lewis acid copper center is the one not bonded to the carbon atom of the organic group, i.e., the copper bonded to two sulfur atoms, and this center does not coordinate to hard Lewis bases such as amines.[26] Ullenius et al. have proposed, based on NMR results, that alkene coordination occurs in the initial stages of 1,4-addition reactions with cuprates.[7]

Intramolecular Processes. Some new fluxional processes in complexes **6**, **7**, and **9** that have not been described[12,18] earlier, merit a discussion.

In $[Cu_3(SAr)_2(Mes)(PPh_3)]$, **9**, a fluctional process is active which results in the two ortho methyl mesityl groups becoming equivalent at elevated temperatures ($\Delta G^{\ddagger}$ = 48 kJ mol^{-1}). This process is not likely to be due to simple rotation of the mesityl group around C_{ipso}, since this phenomenon is not found at all in the sterically less hindered mesityl group in $[Cu_2(SAr)Mes]_2$, **7**. Furthermore, a simple boat-to-boat flip of the Cu_3S_2C ring or inversion of configuration at the sulfur atom does not make the ortho methyl groups equivalent. We propose that the observed fluxionality is a combined boat-to-boat flip and inversion of the sulfur configuration (see Figure 6), in which the aryl groups on

(24) (a) Coppens, P.; Yang, Y. W.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* **1977**, *99*, 760. (b) Guru Row, T. N.; Parthasarathy, R. *J. Am. Chem. Soc.* **1981**, *103*, 477.
(25) Khan, S. I.; Edwards, P. G.; Yuan, H. S. H.; Bau, R. *J. Am. Chem. Soc.* **1985**, *107*, 1682.
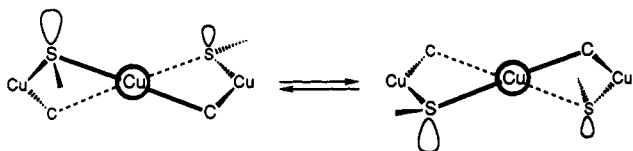(26) Pearson, R. G. *Coord. Chem. Rev.* **1990**, *100*, 403.

Copper(I) Arenethiolates

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Figure 7. Projection of the two enantiomers of $Cu_4(SAr)_2C_2$ unit in **6** along the axis through the two two-coordinate copper atoms.
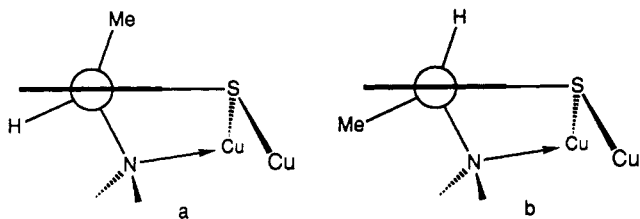

Figure 8. Newman projection of the $C_6H_4CH(Me)NMe_2$ group along the bond of the benzylic carbon to the aromatic group: (a) methyl group out of plane and (b) methyl group in plane.

the sulfur atoms remain in equatorial positions. Since the $\Delta G^{\ddagger}$ found for this process is the same as that for the inversion of the sulfur configuration found in $[CuSAr]_3$ and related compounds,[12,18] the rate-determining step is likely to be inversion of the sulfur configuration that allows the lower energy boat-to-boat flip process ($\Delta G^{\ddagger}$ = 40 kJ mol^{-1} in $[Cu_3\{SC_6H_4(CH(Me)NMe_2)\text{-}2\}_2(C\equiv Ct\text{-}Bu)\{P(OMe)_3\}]$, **16**).[12]

For **6** and **7**, $[Cu_2(SAr)R]_2$, the basic structure is a $Cu_4S_2C_2$ ring in a twisted boat conformation with chirality. The line between the two-coordinate copper atoms is a chiral axis, and Figure 7 shows a schematic view of the two possible enantiomeric $Cu_4S_2C_2$ rings along this axis. Since **7** has two chiral SAr groups (i.e., $SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2$) the enantiomeric $Cu_4S_2C_2$ rings are diastereoisomers and would be NMR distinguishable. The NMR data of **7** show the presence of only one diastereoisomer; the one in which the benzylic methyl group is in the aryl plane (see Figure 8b) would for steric reasons be energetically unfavorable and is not present in solution. For **6** (SAr = SC_6H_4-(CH_2NMe_2)-2) the two enantiomers have identical NMR patterns.

The fluxionality of the tetranuclear complexes **6** and **7** has a $\Delta G^{\ddagger}$ equivalent to a Cu–N dissociation/association process but the spectral data and the chirality of these species allow us to identify further intramolecular fluxionality, probably with a lower $\Delta G^{\ddagger}$, based on the $Cu_4S_2C_2$ ring.

The high temperature ^1H NMR spectrum of **6**, in which the ortho methyl group protons coalesce, cannot be explained solely by Cu–N dissociation. The process that needs to be invoked is a boat-to-boat flip of the $Cu_4S_2C_2$ ring with a concerted inversion of the sulfur configuration as illustrated in Figure 7; this exchange process between enantiomeric species is similar to that found for the Cu_3S_2C ring in **9** and **16**.

Another possibility that could also lead to exchange between enantiomers would be recoordinated of dissociated nitrogen atoms to formerly two-coordinate copper centers, but in this process the ortho methyl mesityl groups do not interchange—the orientation of the methyl groups relative to the sulfur lone-pair remains unchanged. For **6** the presence or absence of this process cannot be determined by NMR. However, for **7** where NMR measurements show the methyl mesityl groups to be anisochronous over the temperature range from 203 to 333 K the occurrence of nitrogen coordination/decoordination can be definitely excluded. If a boat-to-boat flip with a concerted inversion of the sulfur configuration were to take place in **7**, the formation of the unfavorable diastereoisomer would occur followed by a movement of a donor amine group from a three- to the two-coordinate copper atom. This sequence would have given rise to the coalescence of the ortho methyl mesityl protons. Apparently, during the fluxional process of **6** and **7**, each nitrogen atom remains in the neighborhood of the same copper atom.

Structures and Interrelations. The present results show that with a properly designed SAr group and/or organic group highly

selective interaggregate exchange reactions can be achieved. Scheme I gives an overview and schematic structures of compounds **1–16** that have been isolated from the reaction of the copper arenethiolates **1–3** with organometallic reagents. The ratio inorganic to organic ligands on the copper array of these compounds decreases from 1:0 for $[CuSAr]_3$, through 3:1 for $[Cu_3(SAr)_3R]^-$, 2:1 for $[Cu_3(SAr)_2R]$, and 1:1 for $[Cu_2(SAr)R]_2$, to 0:1 for $[CuR]_5$.

The properties of the trimeric copper arenethiolates **1–3** ($[CuSAr]_3$) with a Cu_3S_3 six-membered ring in the chair conformation are published elsewhere.[18] In the Cu_3 array each sulfur atom bridges two copper atoms and donates two electrons, each intramolecularly coordinating amine group also donates two electrons; i.e., each SAr group is able to donate four electrons while occupying three coordination sites.

The product of 1 equiv of LiMe and 1 equiv of $[CuSAr]_3$ is a so-called higher order heteroorganocuprate $[Cu_3Li(SAr)_3(Me)]$ **(13)** that probably has a basic structure $[Cu_3(SAr)_3Me]^-Li^+$ similar to $[CuSAr]_3$, but with a methyl group bridging over two copper atoms of the Cu_3 array. At higher temperatures the methyl group shows fluxionality (^1H NMR data) and the average structure that results from this process has a 2e–4c methyl group bridging over three copper atoms.

Corresponding $[Cu_3(SAr)_3(C\equiv Ct\text{-}Bu)]Li$ is not stable and elimination of LiSAr affords a neutral species, which forms a dimer $[Cu_3(SAr)_2(C\equiv Ct\text{-}Bu)]_2$ **(4 and 5)**.[12] A compound $[Cu_3(SAr)_2(R)]$ is electron-deficient compared to $[CuSAr]_3$ and one of its copper atoms is coordinatively unsaturated. Monomeric $[Cu_3(SAr)_2(C\equiv Ct\text{-}Bu)]$ finds its stabilization by dimerization through occupation of the electron deficient coordination site by the π-electrons of the alkynyl group of a second identical species.

The species $[Cu_3(SAr)_2(R)]$ (R = methyl or mesityl), in which the R groups cannot provide internal stabilization like $C\equiv Ct\text{-}Bu$, can be stabilized by coordination of an appropriate ligand to the reactive (Lewis acidic) copper site. The compounds $[Cu_3\text{-}(SAr)_2(R)(L)]$ are stable (coordinatively and electronically saturated) and unreactive. For example, **9** is a discrete species in solution and ligand exchange reactions between **9** and added $[CuMes]_5$ or $[CuSAr]_3$ are not observable on the NMR time scale.

The tetranuclear compounds $[Cu_2(SAr)(R)]_2$ can be prepared from the reaction of either $[CuSAr]_3$ with $[CuR]_n$ or of $[CuSAr]_3$ with ZR (Z = MgR or Li). How $[Cu_2(SAr)(R)]_2$ is formed from trinuclear species is not known. Formally they could result from either an associative reaction of $[Cu_3(SAr)_2(R)]$ or $[Cu_3\text{-}(SAr)_2(R)(L)]$) with a CuR unit or from an association of two $[Cu_3(SAr)_2(R)]$ species followed by the dissociation of two $[CuSAr]$ units. For the former the reverse reaction is known; addition of PPh_3 to $[Cu_2(SAr)(Mes)]_2$ leads to the formation of $[Cu_3(SAr)_2(Mes)(PPh_3)]$ and $[CuMes]_n$, i.e., the copper cluster completely changes upon interaction with the 2e-donating ligand.

To date we have not been able to characterize products arising from reaction of either $[CuSAr]_3$ with alkylcopper, CuR, due to either spectral complexity (R = CH_2SiMe_3) or to the insolubility of CuR (R = Me) that shifts the equilibrium from mixed aggregates to the free $[CuSAr]_3$ and methylcopper.
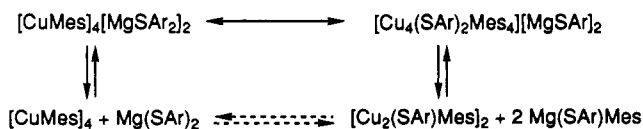
The attempted synthesis of a mixed heteroorganocuprate from a typical cuprate mixture of $MgMes_2$ and $[CuSAr]_3$ afforded a crystalline material **14** with a typical cuprate stoichiometry, i.e., $[Cu_2Mg(SAr)_2(Mes)_2]$. However, this compound has a structure $[(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ and is unprecedented in the way the ligands are bonded to the metal ions. The structure can be described as a pure organocopper compound $[CuMes]_4$ with two $Mg(SAr)_2$ molecules coordinated to it or alternatively as a cuprate, $[Cu_4(SAr)_2R_4]^{2-}$, with two $[MgSAr]^+$ cations coordinated to it (Scheme II). Both the structural data and the properties of **14** in solution are consistent with both descriptions.

In fact **14** in solution is not discrete and species such as $[CuMes]_n$[8b] (formed from the organocopper compound $[CuMes]_5$), $Mg(SAr)_2$, and $[Cu_2(SAr)(Mes)]_2$, **7**, dominate. The latter two exchange their SAr groups with a $\Delta G^{\ddagger}$ of 70 kJ mol^{-1}; this is a high energy process which is consistent with metal–ligand bond breaking and formation steps. It is likely that the equilibrium

Scheme I. Interrelations of Arenethiolatocoppers [CuSAr]$_3$ and Organocopper [CuR]$_n$

R = alkyl, aryl, alkynyl; M = Li, MgX, Cu; $\curvearrowleft_S$ = [SC$_6$H$_3${CH(R)NMe$_2$}-2-R'-6]$^-$
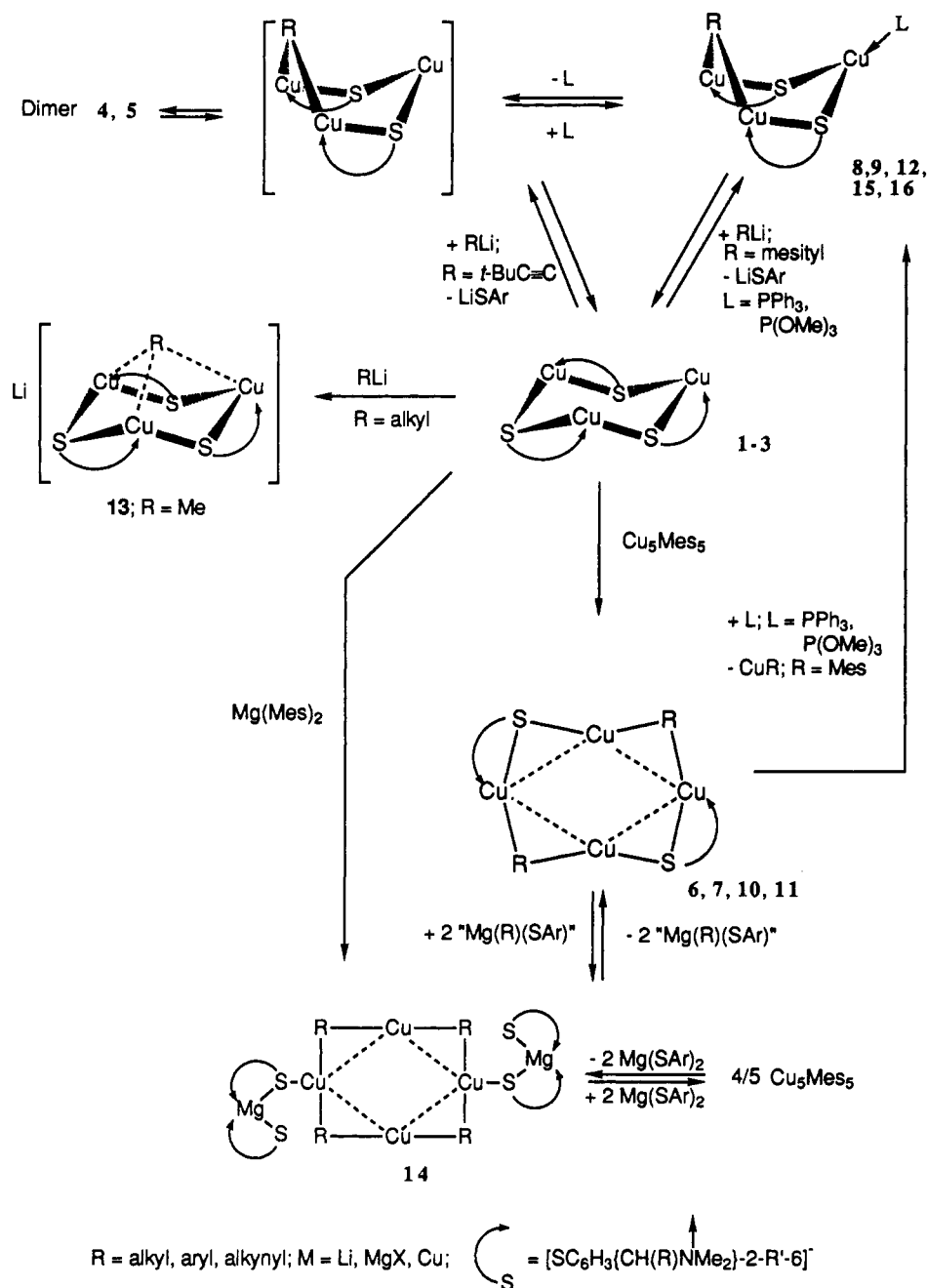
Scheme II. Equilibrium between [CuMes]$_5$ and [Cu$_4$(SAr)$_2$Mes$_2$] (7) with **14** as Intermediate

[CuMes]$_4$[MgSAr$_2$]$_2$ ⟷ [Cu$_4$(SAr)$_2$Mes$_4$][MgSAr]$_2$

⇅   ⇅

[CuMes]$_4$ + Mg(SAr)$_2$ ⇌ [Cu$_2$(SAr)Mes]$_2$ + 2 Mg(SAr)Mes

between **7** and Mg(SAr)$_2$ involves **14** in the manner illustrated in Scheme II.

Conclusions

The strategy of using arenethiolate anions, SAr$^-$, as information-carrying co-ligands has been successfully applied to the synthesis of new mixed heteroorganocopper. The results concerning the structure and constitution, interconversion and equilibria of cuprates and organocopper compounds indicate that care must be taken in the identification of the reactive species in cuprate solutions. The reactivity and selectivity of cuprate reagents

will depend on the ligands surrounding the reactive copper center which needs to have the proper Lewis acidity to anchor a substrate molecular such as an α,β-unsaturated carbonyl compound.

A possible model for a reagent–substrate complex comprising more than one copper center is [Cu$_3$(SAr)$_2$(R)(L)], which is formed from a reassembly reaction of tetranuclear [Cu$_2$(SAr)(R)]$_2$ with a substrate molecule, L, see eq 6 in Table I. Both species contain the SAr group with the chiral information, which is of great importance in the case of their use in enantioselective synthesis.[13a] It should be possible using arenethiolates with the proper choice of intramolecularly coordinating substituent to control the Lewis basicity of the reactive copper centers and as illustrated by [(CuMes)$_4$(μ-SAr)$_2$(MgSAr)$_2$] to influence the undesirable formation of nonchiral reactive species in cuprate solutions.

That the above outlined strategy can be successful is indicated by the following preliminary results. The reaction of LiMe with benzylideneacetone (*trans*-4-phenyl-but-3-en-2-one) in the presence of **2** results, up to a ratio of LiMe-to-[CuSAr]$_3$ of 6:1 with ex-

clusively formation of the 1,4-addition product 4-phenylpentan-2-one. The fact that at higher ratios in THF exclusively the 1,2-addition product *trans*-2-methyl-4-phenyl-but-3-en-2-ol is formed shows that well-defined polynuclear [CuSAr]$_3$[LiMe]$_n$ cuprate species are present in solution in the range n = 3–6, i.e., the formation of kinetically highly reactive homocuprates, [Cu-LiMe$_2$]$_n$, is effectively suppressed by the use of the arenethiolate anion, SAr. However, no enantiomeric excess has been found in any of these reactions.

In contrast to this lack of enantioselectivity in the LiMe–[CuSAr]$_3$ system the reaction of benzylideneacetone with a preformed complex of MgIMe and [CuSAr]$_3$ in diethyl ether afforded the 1,4-addition product in 57% ee.[13b] Even more interesting is the finding that the reaction of MgIMe with a diethyl ether solution of benzylideneacetone and 3 mol% of [CuSAr]$_3$ at 0 °C gives rise to the formation of the 1,4-addition product in 57% ee. Although this enantioselectivity needs further improvement, this result represents to the best of our knowledge one of the first reported examples of the catalytic use of both the copper salt and the chiral auxiliary in an enantioselective 1,4-addition reaction of cuprate reagents.

$$80\ \%;\ 57\ \%\ \text{e.e.}\quad (10)$$
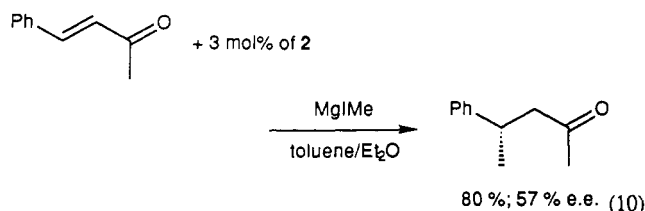
Experimental Section

Syntheses were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Solvents were carefully dried and distilled prior to use. [CuSC$_6$H$_4$(CH$_2$NMe$_2$)-2]$_3$ (1),[18] [CuSC$_6$H$_4$((*R*)-CH(Me)NMe$_2$)-2]$_3$ (2),[18] [CuSC$_6$H$_3$(CH$_2$NMe$_2$)-2-Cl-3]$_3$ (3),[18] [CuC$_6$H$_2$Me$_3$-2,4,6]$_5$,[8b,27] LiMe (0.98 M in ether), [CuBr-{P(OMe)$_3$}],[28] and [CuCH$_2$SiMe$_3$]$_4$[15] were prepared according to literature methods.

^{1}H NMR spectra were recorded on a Bruker AC-200P spectrometer.[29a] Cryoscopic molecular weight determinations were carried out in benzene under dry oxygen-free nitrogen.[29b,c] Elemental analyses were carried out by the section for Elemental Analysis of ITC/TNO Zeist, The Netherlands. GC/MS analyses were carried out at the Analytical Chemical Laboratory of the University of Utrecht. Microwave titration was done by a literature method with home-built apparatus.[14] Membrane filters (type RC 60; 1.0 µm, diameter 25 mm) were purchased from Schleicher & Schuell.

Synthesis of [Mg(C$_6$H$_2$Me$_3$-2,4,6)$_2$(THF)$_2$]. To magnesium turnings (6.48 g, 0.28 mol) in THF (25 mL) was added dropwise a solution of mesityl bromide (30 mL, 39.0 g, 0.20 mol) in THF (120 mL). After refluxing for 1 h, the solution was cooled to room temperature, and dioxane (100 mL) was added. The magnesium salts were separated by centrifugation, and the supernatant collected. The salts were washed with THF (100 mL) and again centrifuged. The combined supernatants were evaporated to dryness in vacuo, and the solid was crystallized from a minimum of hot toluene (∼50 mL): yield 28.5 g, 77% of [Mg-(C$_6$H$_2$Me$_3$-2,4,6)$_2$(THF)$_2$]: ^{1}H NMR (toluene-d_8, 313 K) δ 6.86 (s, 2 H, *H*-Mes), 3.43 (m, 2 H, THF-OC*H*$_2$), 2.42 (s, 6 H, *o*-CH$_3$), 2.27 (s, 3 H, *p*-CH$_3$), 1.19 (m, 4 H, THF-C*H*$_2$).

Synthesis of [Cu$_2${SC$_6$H$_4$(CH$_2$NMe$_2$)-2}(C$_6$H$_2$Me$_3$-2,4,6)]$_2$, 6. In boiling toluene (40 mL) were dissolved 1 (2.29 g, 3.3 mmol) and [CuC$_6$H$_2$Me$_3$-2,4,6]$_5$ (1.82 g, 2.0 mmol). On cooling the solution to room temperature crystals of 6 precipitated. These were filtered off and

washed three times with 10-mL portions of toluene: yield 2.95 g, 72%; ^{1}H NMR (toluene-d_8, 333 K) δ 8.11 (d, 1 H, *J* = 7 Hz, *o*-*H*-ArS), 6.95 (m, 3 H, *H*-ArS), 6.64 (s, 2 H, *H*-Mes), 3.18 (s, 2 H, NC*H*$_2$), 2.32 (s, 6 H, *o*-CH$_3$), 2.06 (s, 3 H, *p*-CH$_3$), 1.61 (s, 6 H, NC*H*$_3$); ^{1}H NMR (toluene-d_8, 233 K) δ 8.34 (d, 1 H, *J* = 7 Hz, *o*-*H*-ArS), 6.95 (m, 3 H, *H*-ArS), 6.71 (s, 1 H, *H*-Mes), 6.60 (s, 1 H, *H*-Mes), 3.83 (d, 1 H, *J* = 11 Hz, NC*H*-Ar), 2.67 (s, 3 H, *o*-CH$_3$), 2.34 (d, 1 H, *J* = 11 Hz, NC*H*-Ar), 2.18 (s, 6 H, *p*-CH$_3$ and *o*-CH$_3$), 1.53 (s, 3 H, NC*H*$_3$), 1.46 (s, 3 H, NC*H*$_3$). Anal. Calcd for C$_{36}$H$_{46}$Cu$_4$N$_2$S$_2$: C, 52.40; H, 5.63; N, 3.40. Found: C, 52.29; H, 5.54; N, 3.40.

Synthesis of [Cu$_2${SC$_6$H$_4$((*R*)-CH(Me)NMe$_2$)-2}(C$_6$H$_2$Me$_3$-2,4,6)]$_2$, 7. In benzene (20 mL) were mixed 2 (2.67 g, 3.03 mmol) and [CuC$_6$H$_2$Me$_3$-2,4,6]$_5$ (0.83 g, 0.91 mmol). After evaporating the benzene in vacuo the resulting yellow oil was suspended in pentane (20 mL) and stirred until the product solidified. The pentane was distilled off in vacuo to leave 7 as a clear yellow solid: molecular weight (cryoscopy in benzene in concentration range: 0.030–0.124 mol kg^{-1} benzene); 813 g mol^{-1} (calcd for [C$_{19}$H$_{25}$Cu$_2$NS]$_2$; 852 g mol^{-1}); ^{1}H NMR (toluene-d_8, 313 K) δ 7.89 (d, 1 H, *J* = 8 Hz, 6-*H*-ArS), 6.9 (m, 5 H, Ar-*H*), 2.76 (s, 3 H, *o*-CH$_3$), 2.48 (q, 1 H, *J* = 7 Hz, *H*-CMe), 2.31 (s, 3 H, *o*-CH$_3$), 2.12 (s, 3 H, *p*-CH$_3$), 1.60 (d, 3 H, *J* = 7 Hz, Ar-C-CH$_3$), 1.49 (s, 6 H, N(CH$_3$)$_2$); ^{1}H NMR (toluene-d_8, 233 K) δ 7.93 (d, 1 H, *J* = 8 Hz, 6-*H*-ArS), 7.06 (dt, 1 H, J_t = 8 Hz, J_d = 1 Hz, 5-*H*-ArS), 6.91 (dt, 1 H, J_t = 8 Hz, J_d = 1 Hz, 4-*H*-ArS), 6.82 (s, 1 H, *H*-Mes), 6.61 (d, 1 H, *J* = 8 Hz, 3-*H*-ArS), 6.53 (s, 1 H, *H*-Mes), 2.82 (s, 3 H, *o*-CH$_3$), 2.63 (q, 1 H, *J* = 7 Hz, *H*-CMe), 2.33 (s, 3 H, *o*-CH$_3$), 2.11 (s, 3 H, *p*-CH$_3$), 1.71 (s, 3 H, NC*H*$_3$), 1.54 (d, 3 H, *J* = 7 Hz, Ar-C-CH$_3$), 1.12 (s, 3 H, NC*H*$_3$).

In Situ Preparation of 7 from the Reaction of [CuC$_6$H$_2$Me$_3$-2,4,6]$_5$ with 2 Followed by Microwave Titration.[14] In 65 mL (*V*$_0$) of benzene was dissolved [CuC$_6$H$_2$Me$_3$-2,4,6]$_5$ (0.7429 g, 4.08 mmol monomer). The solution was put in a glass cell which was connected to the microwave transmitter and receiver. The continuously stirred solution was thermostatically kept at 25 °C, and the microwave transmission was measured (*E*$_0$). A solution of 2 (2.25 g, 9.24 mmol monomer) in benzene (30 mL) was added by means of a gas-tight piston burette in 0.3-mL portions. After each portion the solution was equilibrated and the new transmission (*E*$_i$) of the microwaves was measured. The absorption (Δ*c*$_i$) was calculated and corrected for volume changes

$$\left(\Delta c_i = \frac{V_i}{V_0}\left[\sqrt{\frac{E_0}{E_i}} - 1 \right] \right)$$

An X–Y plot with millimoles of added monomeric 2 divided by 4.08 (X-axis) against Δ*c*$_i$ values (Y-axis) showed an excellent linearity for *x* = 0 to *x* = 1. At *x* = 1 there was an change in the slope to a slope which for *x* > 1 was the same as that found for the addition of 2 to pure benzene.

Synthesis of [Cu$_3${SC$_6$H$_4$((*R*)-CH(Me)NMe$_2$)-2}$_2$(C$_6$H$_2$Me$_3$-2,4,6){P-(OMe)$_3$}], 8. In benzene (15 mL) were mixed [CuC$_6$H$_2$Me$_3$-2,4,6]$_5$ (0.82 g, 0.90 mmol), 2 (2.20 g, 1.5 mmol), and P(OMe)$_3$ (0.53 mL, 0.56 g, 4.5 mmol). The benzene was distilled off, and the resulting yellow oil stirred in pentane until it solidified. The volatiles were evaporated in vacuo to afford 3.5 g of solid 8: ^{1}H NMR (benzene-d_8, 296 K) δ 7.83 (d, 1 H, *J* = 8 Hz, *o*-*H*-ArS), 6.9 (m, 6 H, Ar-*H*), 6.76 (s, 1 H, *H*-Mes), 6.66 (s, 1 H, *H*-Mes), 3.48 (d, 3 H, *J* = 11 Hz, P(OCH$_3$)$_3$), 3.45 (br s, 2 H, *H*-C-Me), 2.20 (s, 3 H, *o*-CH$_3$), 2.18 (s, 12 H, N(CH$_3$)$_2$), 2.14 (s, 6 H, *p*-CH$_3$ and *o*-CH$_3$), 1.52 (d, 6 H, *J* = 7 Hz, Ar-C-CH$_3$). For low temperature ^{1}H NMR data see results.

Synthesis of [Cu$_3${SC$_6$H$_4$(CH$_2$NMe$_2$)-2-Cl-3}$_2$(C$_6$H$_2$Me$_3$-2,4,6)(PPh$_3$)], 9. In benzene (100 mL) were mixed 3 (4.40 g, 5.55 mmol), [CuC$_6$H$_2$Me$_3$-2,4,6]$_5$ (1.45 g, 1.59 mmol), and triphenylphosphine (2.08 g, 7.95 mmol). The benzene was evaporated slowly with a nitrogen stream at 50 °C until ca. 40 mL remained and crystals appeared. A hexane layer (60 mL) was carefully put on top of the benzene layer, and the system was allowed to stand for 2 days in order for solvents to mix by diffusion. The yellow crystals which formed were filtered off and washed twice with 20-mL portions of hexane. Volatiles were removed in vacuo: yield 7.09 g, 85% of 9·C$_6$H$_6$; mp 125 °C (dec). Solvent free 9 can be obtained by heating the solvate at 80 °C, in vacuo: molecular weight (cryoscopy in benzene in concentration range: 0.022–0.115 mol kg^{-1} benzene) 1077 g mol^{-1} (calcd for [C$_{51}$H$_{54}$Cl$_2$Cu$_3$N$_2$PS$_2$] (including the solvated benzene) 1045 g mol^{-1}); ^{1}H NMR (toluene-d_8, 333 K) δ 7.00 (m, 23 H, Ar*H*), 3.72 (s, 4 H, C*H*$_2$N), 2.34 (s, 6 H, *o*-CH$_3$), 2.11 (s, 3 H, *p*-CH$_3$), 1.79 (s, 12 H, NC*H*$_3$); ^{1}H NMR (toluene-d_8, 213 K) δ 7.80 (br s, 1 H, P-Ar-*H*), 7.26 (d, 2 H, *J* = 9 Hz, *o*-*H*-ArS), 6.5–7.1 (m, 19 H, Ar-*H*), 6.02 (t, 1 H, P-Ar-*H*), 3.80 (d, 2 H, *J* = 13 Hz, Ar-C*H*$_2$-N), 3.63 (d, 2 H, *J* = 13 Hz, Ar-C*H*$_2$-N), 2.68 (s, 3 H, *o*-CH$_3$), 2.13 (s, 3 H, *p*-CH$_3$), 2.03 (s, 3 H, *o*-CH$_3$), 1.88 (s, 6 H, N(CH$_3$)), 1.51 (s, 6 H, N(CH$_3$)). Anal. Calcd for C$_{51}$H$_{54}$Cl$_2$Cu$_3$N$_2$PS$_2$: C, 58.29; H, 5.14; N,

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(29) (a) Abbreviations and techniques used in the text include the following: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet, br = broad; COSY = correlation spectroscopy; and NOESY = nuclear Overhauser enhancement spectroscopy. With COSY phase-sensitive 2D experiments shift correlation by homonuclear scalar couplings are found. Eyring equation: Δ*G*‡ = −*RT*$_c$ ln [2πh(Δν)/*kT*$_c$√3] with Δ*G*‡ = free energy of activation (*J*); *T*$_c$ = coalescence temperature (*K*); Δν = chemical shift difference (Hz); the other symbols have their usual meaning. (b) Dilts, J. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1968**, *90*, 5769. (c) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972.

2.67; S, 6.09. Found: C, 58.34; H, 5.20; N, 2.57; S, 5.91.

Reaction of [CuSC₆H₄((R)-CH(Me)NMe₂)-2]₃ with in Situ Prepared CuMe. Formation of 10. To a suspension of CuBr (1.20 g, 8.4 mmol) and **2** (2.04 g, 2.8 mmol) in benzene was added LiMe (8.4 mmol) in diethyl ether (8.5 mL). The solution immediately turned yellow. The suspension was filtered off with a 1 μm membrane filter (**Caution**: the residue contains CuMe and can explode when dry. Immediately after the filtration the filter was put into an aqueous NH₄Cl solution). The benzene was distilled off in vacuo to yield a yellow compound, CuMe·[CuSC₆H₄((R)-CH(Me)NMe₂)-2]₂ (**10**): ¹H NMR (THF-d₈, 307 K) δ 7.56 (d, 2 H, J = 7 Hz, o-H-ArS), 6.00 (m, 6 H, Ar-H), 3.65 (br s, 2 H, Ar-CH), 2.50 (s, 18 H, NCH₃), 1.69 (d, 6 H, J = 6 Hz, ArCCH₃), −0.51 (s, 3 H, CH₃Cu). For low temperature ¹H NMR data, see results.

Synthesis of [Cu₂{SC₆H₄((R)-CH(Me)NMe₂)-2}(CH₂SiMe₃)]ₙ, 11. In benzene (20 mL) were mixed [CuCH₂SiMe₃]₄ (1.24 g, 2.06 mmol) and **2** (2.00 g, 2.74 mmol). After evaporating the benzene in vacuo the resulting dark yellow sticky oil was suspended in pentane (50 mL) until the product solidified. The volatiles were evaporated to leave **11** as a dark yellow solid: ¹H NMR (toluene-d₈, 303 K) δ 7.78 (d, 2 H, J = 8 Hz, o-H-ArS), 6.7–7.0 (m, 3 H, Ar-H), 3.23 (br s, 1 H, Ar-C-H), 2.14 (s, 6 H, N(CH₃)₂), 1.50 (d, 3 H, J = 7 Hz, Ar-C-CH₃), 0.29 (s, 9 H, Si(CH₃)₃), −0.07 (s, 2 H, CH₂-Cu). For low temperature ¹H NMR data, see results.

Synthesis of [Cu₃{SC₆H₄((R)-CH(Me)NMe₂)-2}₂Me{P(OMe)₃}], 12. To a solution of **2** (2.60 g, 10.7 mmol) and [CuBr{P(OMe)₃}] (1.43 g, 5.3 mmol) in benzene (20 mL) was added LiMe (5.3 mmol) in diethyl ether (5.34 mL). LiBr was filtered off with a 1 μm membrane filter (**Caution**: the residue contains CuMe and can explode when dry. Immediately after the filtration the filter was put into an aqueous NH₄Cl solution). The benzene was distilled off in vacuo, and the remaining oil was stirred in pentane until it solidified. The pentane was distilled off to leave **12** as a yellow solid: yield 2.77 g, 76%; ¹H NMR (toluene-d₈, 296 K) δ 7.82 (dd, 2 H, o-H-ArS), 6.9 (m, 6 H, Ar-H), 3.6 (br s, 2 H, Ar-C-H), 3.14 (d, 9 H, J(H,P) = 11 Hz, P-OCH₃), 2.12 (s, 12 H, NCH₃), 1.43 (d, 6 H, J = 7 Hz, Ar-C-CH₃), 0.12 (s, 3 H, CH₃-M). For low temperature ¹H NMR data, see results.

Synthesis of [Cu₃Li{SC₆H₄(CH₂NMe₂)-2}₃Me], 13. To **1** (4 g, 5.82 mmol) dissolved in diethyl ether (50 mL) was added LiMe (5.82 mmol) in diethyl ether (5.8 mL). The mixture was stirred for 1.5 h whereafter the yellow solid was filtered off and washed twice with 20-mL portions of diethyl ether and once with 20 mL of pentane. The solid was dissolved in THF, and the THF was then distilled off. The resulting white solid was dissolved in diethyl ether and stirred for 15 min while a yellow precipitate of the product formed. This was filtered off and washed twice with 20-mL portions of diethyl ether. The solid was dried in vacuo to yield 3.4 g of **13** (82%): ¹H NMR (THF-d₈, 297 K) δ 7.98 (d, 3 H, J = 7 Hz, o-H-ArS), 7.24 (m, 9 H, Ar-H), 4.00 (s, 6 H, Ar-CH₂), 2.56 (s, 18 H, NCH₃), −0.59 (s, 3 H, CH₃M); ¹H NMR (THF-d₈, 193 K) δ 7.93 (br d, o-H-ArS), 7.73 (br d, o-H-ArS), 7.56 (br d, o-H-ArS), 2.14 (br s, N(CH₃)₂), −0.95 (br s, CH₃M); ¹³C NMR (THF-d₈, 297 K) δ 124.99, 129.97, 133.60, 137.61, 138.96, 146.64 (aromatic carbons), 68.80 (Ar-C-N), 48.56 (N(CH₃)₃), −11.52 (H₃CM). Anal. Calcd for C₂₈H₃₉Cu₃LiN₃S₃: C, 47.29; H, 5.49; N, 5.91; S, 13.51. Found: C, 46.25; H, 5.12; N, 5.94; S, 13.49. Hydrolysis of a solution of **13** in THF yielded 1 equiv of gas.

Synthesis of [Cu₄Mg₂{SC₆H₄((R)-CH(Me)NMe₂)-2}₄(C₆H₂Me₃-2,4,6)₄], 14. In boiling toluene (75 mL) were mixed **2** (2.70 g, 11.08 mmol monomer) and [Mg(C₆H₂Me₃-2,4,6)₂(THF)₂] (1.85 g, 5.54 mmol), and the solution was kept at reflux for ca. 15 min until all solids

were dissolved. The toluene solution was concentrated to 65 mL by distillation, so removing THF, and the solution cooled to room temperature, whereupon crystals slowly separated. The crystals were filtered off, washed with pentane (~25 mL), and dried in vacuo: yield 3.01 g of **14**·0.5toluene (73%); dec > 185 °C. Anal. Calcd for C₇₆H₁₀₀Cu₄Mg₄N₄S₄·0.5toluene: C, 59.86; H, 6.82; N, 3.51; S, 8.04. Found: C, 59.44; H, 6.60; N, 3.47; S, 8.16. For ¹H NMR data, see results.

Structure Determination and Refinement of 6, 9, and 14. Crystal data and numerical details of the structure determinations are given in Table VI. The crystals were glued on top of a glass fiber and transferred immediately into the cold nitrogen stream of the low temperature unit of an Enraf-Nonius CAD4F diffractometer for data collection. Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 25 reflections and were checked for the presence of higher lattice symmetry.[30] All data were collected with ω/2θ scan mode. Data were corrected for Lp and for the observed linear decay of the reference reflections but not for absorption. The structures were solved with either standard Patterson methods (**14**) or with direct methods (**6** and **9**) (SHELXS86; ref 31) and subsequent difference Fourier synthesis. Refinement of F was carried out by full matrix least squares techniques. H-atoms were introduced on calculated positions [C–H = 0.98 Å] and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; H-atoms were refined with one common isotropic thermal parameter. Weights were introduced in the final refinement cycles. Refinement of **14** with opposite anomalous dispersion factors (-if") resulted in a significantly higher R value (0.063). Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables VII, VIII, and IX. Neutral atom scattering factors were taken from Cromer and Mann[32] and corrected for anomalous dispersion.[33] All calculations were performed with SHELX76 (ref 34) and the EUCLID package[35] (geometrical calculations and illustrations) on a Micro VAX cluster.

Supplementary Material Available: Tables (S1–S14) of refined hydrogen coordinates, thermal parameters, and bond distances and angles (29 pages); listings of observed and calculated structure factors (161 pages). Ordering information is given on any current masthead page.

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