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Synthesis and Molecular Structure of Copper(I) and Organozinc(II) Arenethiolates with Chelating Amino and Ether Groups: X-ray Structure of $[CuSC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2]_4$ and $[Zn(Me)\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_2$

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The syntheses of some (trimethylsilyl)arenethiolates $Me_3SiSC_6H_4(CH(R')N(Me)R)$-2 (R = CH_2CH_2OMe, R' = H, Me; R = R' = Me) are described. These arenethiolates (Me_3SiSAr), which contain potentially coordinating amine (and ether) functions, have been used to prepare pure metal arenethiolates $[CuSAr]_n$ and $[Zn(Me)(SAr)]_2$ in high yield from their reaction with CuCl and ZnMeCl, respectively. The X-ray structures of a tridentate arenethiolate copper(I) compound, $[CuSC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2]_4$ (**6a**), and of $[Zn(Me)\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_2$ (**7**) have been solved. Crystals of **6a** are triclinic, space group $P\bar{1}$, with $a = 12.826$ (1) Å, $b = 14.057$ (2) Å, $c = 16.301$ (3) Å, $\alpha = 108.64$ (1)°, $\beta = 106.37$ (1)°, $\gamma = 99.93$ (1)°, $V = 2558.3$ (7) Å^3, $Z = 2$, and final $R = 0.031$ for 9440 reflections with $I \geq 2.5\sigma(I)$ and 566 variables. The copper arenethiolate **6a** is a tetramer having a noncrystallographic S_4 symmetry. Four copper atoms are in a flattened butterfly arrangement with a bridging sulfur atom over each Cu⋯Cu (average 2.693 (9) Å) edge; the sulfur atoms are alternately above and below the copper array. The amine groups each coordinate intramolecularly to a tricoordinate copper atom, which as a result becomes stereogenic, while the ether functions do not coordinate. Crystals of **7** are monoclinic, space group $P2_1$, with $a = 8.651$ (2) Å, $b = 13.876$ (2) Å, $c = 10.181$ (2) Å, $\beta = 99.82$ (1)°, $V = 1204.2$ (4) Å^3, $Z = 2$, and final $R = 0.044$ for 3645 reflections with $I \geq 2.5\sigma(I)$ and 259 variables. This compound is a dimer with two zinc atoms bridged by two sulfur atoms. Each zinc atom is bound to two sulfur atoms, one methyl group, and one intramolecularly coordinating amine group. The described metal arenethiolates are fluxional in solution.

Introduction

Recently, we published the synthesis of a new type of copper(I) arenethiolates, $[CuSAr]_3$, with a (chiral) intramolecularly coordinating amino group ortho with respect to the sulfur atom; i.e. $[CuSC_6H_4(CH(R')NMe_2)\text{-}2]_3$ (R' = H, Me) and $[CuSC_6H_3(CH_2NMe_2)\text{-}2\text{-}Cl\text{-}3]_3$.[1] From these compounds, the first examples of stable heteroorganocopper and heteroorganocuprate compounds could be synthesized and characterized (eqs 1–3).[2]

$$\tfrac{2}{3}[CuSAr]_3 + \tfrac{2}{5}[CuMes]_5 \rightarrow [Cu_2(SAr)(Mes)]_2 \qquad (1)$$

$$\tfrac{2}{3}[CuSAr]_3 + \tfrac{1}{5}[CuMes]_5 + PPh_3 \rightarrow [Cu_3(SAr)_2(Mes)(PPh_3)] \qquad (2)$$

$$\tfrac{4}{3}[CuSAr]_3 + 2[MgMes_2] \rightarrow [Cu_2Mg(SAr)_2(Mes)_2]_2 \qquad (3)$$

Furthermore, chiral copper(I) complexes can be used as catalysts for the enantioselective, conjugated 1,4-addition reaction of organolithium and organomagnesium reagents to α,β-unsaturated carbonyl compounds.[3-7] Surprisingly, in a Mg^{2+} salt catalyzed reaction, $[Cu_2(SAr)(Mes)]_2$ itself transfers a mesityl group to benzylideneacetone at 70 °C to form 1-mesityl-1-phenyl-3-butanone in 79% yield.[4] This result is unexpected as this reaction is usually found for reagents derived from organocopper and organolithium or -magnesium reagents and not for reagents based on copper alone. To successfully extend the scope of this latter reaction to other functionalized arenethiolates it is first necessary to ensure that no lithium or magnesium salts are present in the copper arenethiolates, since these salts even in catalytic amounts could be responsible for the observed 1,4-addition reaction. We have therefore searched for preparative routes for copper arenethiolates that do not involve lithium or magnesium reagents in the final stage.

A strategy based on the method used by Fenske et al. for the synthesis of metal sulfides, selenides, and tellurides, $[ME_{m/2}]_n$ (E = S, Se, Te), from the reaction of a metal halide with $E(SiMe_3)_2$ seems attractive (eq 4),[8] since the only byproduct is volatile (i.e. easy to remove) $XSiMe_3$.

$$MX_m + (m/2)E(SiMe_3)_2 \rightarrow (1/n)[ME_{m/2}]_n + mXSiMe_3 \qquad (4)$$

M = metal; X = Cl, Br, I; E = S, Se, Te

This paper describes the development of a synthetic route for the preparation of copper- and zinc arenethiolates that employs the reaction of (trimethylsilyl)arenethiolates with copper(I) and zinc(II) halides. The structural aspects of these metal arenethiolates, both of which belong to a new class of compounds, have been studied by NMR spectroscopy and by X-ray structure determinations of two representative species.

Experimental Section

Syntheses were carried out by using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Solvents were carefully dried and distilled prior to use. ^{1}H NMR spectra were recorded on a Bruker AC-200P spectrometer. Cryoscopic molecular weight determinations were carried out in benzene under dry oxygen-free nitrogen. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands. GC/MS analyses were carried out at the Analytical Chemical Laboratory of the University of Utrecht.

Synthesis of $C_6H_5CH_2N(Me)CH_2CH_2OMe$ (1a). A 1-L glass flask fitted with a Dean-Stark distillation apparatus was charged with $MeOCH_2CH_2NH_2$ (45.8 mL, 0.53 mol), benzaldehyde (55.2 mL, 0.54 mol), and 300 mL of benzene. The mixture was heated to reflux, and when no more water collected (ca. 10 mL), the benzene was distilled off

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in vacuo. The residue was dissolved in 100 mL of diethyl ether and the solution added slowly to a suspension of $\mathrm{LiAlH_4}$ (25 g, 0.66 mol) in 400 mL of diethyl ether. After 1 h, unreacted $\mathrm{LiAlH_4}$ was destroyed by slow addition of 50 mL of water. The aluminum salts were partly dissolved by the addition of 200 mL of 10 M aqueous KOH. The two-phase solution was filtered and the solid residue washed three times with 100-mL portions of diethyl ether. The ether layer of the combined filtrate and washings was separated from the water layer and the latter was then extracted three times with 300-mL portions of diethyl ether. The combined ether layers were dried on $\mathrm{MgSO_4}$, and after filtration, the ether was distilled off in vacuo to afford $\mathrm{C_6H_5CH_2N(H)CH_2CH_2OMe}$ as a colorless oil.

To this oil at 0 °C were added 42.0 mL of 37% aqueous formaldehyde solution (0.56 mol) and formic acid (20.5 mL, 0.54 mol). The mixture was heated at reflux for 3 h and then, after being cooled to room temperature, acidified by the addition of 53.0 mL of 10 M aqueous hydrochloric acid. The resulting solution was then washed three times with 80-mL portions of diethyl ether. To the acidic solution was added 100 mL of 10 M aqueous KOH, and the basic solution was extracted with three 100-mL portions of diethyl ether. The combined ether layers were dried on $\mathrm{MgSO_4}$, and after filtration the solvents were removed in vacuo. The crude product **1a** was then distilled in vacuo: yield 74.3 g (78%); bp 61 °C (0.3 mmHg); $n_{\mathrm{D}}^{18} = 1.5003$. ^{1}H NMR (benzene-$d_6$): δ 7.36 (d, 2 H, *J* = 6.9 Hz, *o*-Ar*H*), 7.15 (m, 3 H, Ar*H*), 3.40 (s, 2 H, CH_2Ar), 3.35 (t, 2 H, *J* = 5.8 Hz, CH_2O), 3.08 (s, 3 H, CH_3O), 2.55 (t, 2 H, *J* = 5.8 Hz, CH_2N), 2.15 (s, 3 H, CH_3N).

Synthesis of ((*R*)-1-(Methylamino)ethyl)benzene (3). A 2-L glass flask fitted with a Dean–Stark distillation apparatus was charged with (*R*)-α-methylbenzylamine (100.5 g, 0.83 mol), benzaldehyde (88.2 g, 0.83 mol), and 300 mL of benzene. The mixture was heated to reflux, and when no more water collected (ca. 15 mL), the reaction mixture was cooled to room temperature and the Dean–Stark distillation apparatus replaced by a reflux condenser. To this mixture was then added 236 mL of dimethyl sulfate (2.49 mol of $\mathrm{Me_2SO_4}$) in 500 mL of benzene. This mixture was cautiously heated until an exothermic reaction started; an ice bath was employed to control the vigor of the reaction. After 5 min, the initial reaction subsided and the mixture was heated at reflux for 16 h. After the mixture was cooled to room temperature, 150 mL of water was slowly added and the heating at reflux continued for 1 h. The reaction mixture was cooled to room temperature and the acidic water layer was separated and washed with two 100-mL portions of diethyl ether. The aqueous solution was made alkaline with 10 M aqueous NaOH, and $\mathrm{Na_2SO_4}$ deposited. The solution was filtered and the residue washed with two 100-mL portions of diethyl ether. The ether layer of the combined filtrate and washings was separated from the water layer, and the latter was then extracted three times with 150-mL portions of diethyl ether. The combined ether layers were dried on $\mathrm{MgSO_4}$ and after filtration the solvents removed in vacuo. The crude product **3** was then distilled in vacuo: yield 93.0 g (83%); bp 53 °C (2 mmHg); $[\alpha]_{\mathrm{D}}^{22} = +77.8°$ neat; $n_{\mathrm{D}}^{20} = 1.5118$. ^{1}H NMR (benzene-$d_6$): δ 7.2 (m, 5 H, Ar*H*), 3.40 (q, 1 H, *J* = 7 Hz, ArC*H*), 2.12 (s, 3 H, CH_3N), 1.17 (d, 3 H, *J* = 7 Hz, CH_3C), 0.68 (br s, 1 H, N*H*). Mass spectrum [*m*/*z* (relative intensity)]: 135 (2) [M$^+$, calcd 135]; 120 (100).

Synthesis of $\mathrm{C_6H_5}$-(*R*)-CH(Me)N(Me)$\mathrm{CH_2CH_2OH}$ (4). To **3** (41.0 g, 0.30 mol) in THF (400 mL) at −40 °C was added *n*-BuLi (205 mL in hexane, 0.32 mol). The solution was heated to 35 °C, and a reflux condenser filled with dry ice/ethanol was connected to the reaction vessel. Ethylene oxide (13.48 g, 0.31 mol) in THF (75 mL) was added while the temperature of the reaction mixture was kept below 45 °C with a water bath. The mixture was stirred for 2 h at 52 °C, after which 200 mL of water was added and the mixture stirred overnight. The water layer was separated and extracted three times with 200-mL portions of hexane. The combined organic layers were dried on $\mathrm{MgSO_4}$ and after filtration the volatiles removed in vacuo. The crude product **4** was then distilled in vacuo: yield 38.7 g (71%); bp 80–84 °C (0.6 mmHg); $n_{\mathrm{D}}^{18} = 1.5287$; ^{1}H NMR (benzene-$d_6$, 297 K): δ 7.1 (m, 5 H, Ar*H*), 3.42 (t, 2 H, *J* = 5.8 Hz, *J* = 5.2 Hz, CH_2O), 3.35 (q, 1 H, *J* = 7 Hz, ArC*H*), 2.56 (br s, 1 H, O*H*), 2.30 (dt, 1 H, *J* = 12.6 Hz, *J* = 5.8 Hz, *J* = 5.2 Hz, C*H*HN), 2.16 (dt, 1 H, *J* = 12.6 Hz, *J* = 5.8 Hz, *J* = 5.2 Hz, C*H*HN), 1.89 (s, 3 H, CH_3N), 1.11 (d, 3 H, *J* = 7 Hz, CH_3C). Mass spectrum [*m*/*z* (relative intensity)]: 179 (10) [M$^+$, calcd 179]; 105 (100).

Synthesis of $\mathrm{C_6H_5}$-(*R*)-CH(Me)N(Me)$\mathrm{CH_2CH_2OMe}$ (1b). To a solution of KO-*t*-Bu (18.8 g, 0.17 mol) in THF (150 mL) at room temperature was added a solution of **4** (15.8 g, 87.9 mmol) in THF (50 mL). After 10 min, a solution of dimethyl sulfate (17 mL, 179.7 mmol) in THF (50 mL) was slowly added. After 20 min, the mixture was poured onto ice (100 g) and made alkaline with 10 M aqueous KOH. The water solution was extracted three times with 100-mL portions of diethyl ether. The combined ether layers were dried on $\mathrm{MgSO_4}$ and after filtration the solvents removed in vacuo. The crude product **1b** was then distilled in vacuo: yield 10.8 g (64%); bp 75 °C (0.9 mmHg); $n_{\mathrm{D}}^{20} = 1.5027$. ^{1}H NMR (benzene-$d_6$): δ 7.33 (d, 2 H, *J* = 7.0 Hz, *o*-Ar*H*), 7.14 (m, 3 H, Ar*H*), 3.45 (q, 1 H, *J* = 6.7 Hz, ArC*H*), 3.33 (t, 2 H, *J* = 6.1 Hz, *J* = 6.2 Hz, CH_2O), 3.08 (s, 3 H, CH_3O), 2.63 (dt, 1 H, *J* = 13.0 Hz, *J* = 6.1 Hz, *J* = 6.2 Hz, C*H*HN), 2.51 (dt, 1 H, *J* = 13.0 Hz, *J* = 6.1 Hz, *J* = 6.2 Hz, C*H*HN), 2.17 (s, 3 H, CH_3N), 1.22 (d, 3 H, *J* = 6.7 Hz, CH_3C). Mass spectrum [*m*/*z* (relative intensity)]: 193 (11) [M$^+$, calcd 193]; 105 (100).

Synthesis of $\mathrm{Me_3SiSC_6H_4(CH_2N(Me)CH_2CH_2OMe)}$-2 (5a). To **1a** (15.0 g, 84 mmol) dissolved in hexane (30 mL) at 0 °C was added a solution of *n*-BuLi in hexane (56 mL, 84 mmol of *n*-BuLi). The resulting mixture was stirred for 16 h at room temperature. The white precipitate that formed was separated from the solution by centrifugation and subsequent decantation. The solid $\mathrm{LiC_6H_4(CH_2N(Me)CH_2CH_2OMe)}$-2 was washed twice with 30 mL of pentane and dried in vacuo; yield 11.7 g (63 mmol, 76%).

$\mathrm{LiC_6H_4(CH_2N(Me)CH_2CH_2OMe)}$-2 (11.7 g, 63 mmol) dissolved in THF (100 mL) was slowly added to a suspension of sublimed sulfur (2.03 g, 63 mmol) in THF (100 mL) at −50 °C. The solution was warmed to room temperature, and trimethylchlorosilane (8.5 mL, 67.3 mmol) was added. The crude product **5a** was distilled in vacuo: yield 3.4 g (19%); bp 104 °C (0.5 mmHg). ^{1}H NMR (benzene-d_6): δ 7.75 (d, 1 H, *J* = 6.9 Hz, 6-Ar*H*), 7.52 (d, 1 H, *J* = 8.6 Hz, 3-Ar*H*), 7.12 (t, 1 H, *J* = 6.9 Hz, 5-Ar*H*), 6.97 (t, 1 H, *J* = 8.6 Hz, 4-Ar*H*), 3.89 (s, 2 H, CH_2Ar), 3.39 (t, 2 H, *J* = 5.7 Hz, CH_2N), 3.10 (s, 3 H, CH_3O), 2.66 (t, 2 H, *J* = 5.7 Hz, CH_2O), 2.24 (s, 3 H, CH_3N), 0.17 (s, 9 H, (CH_3)$_3$Si).

Synthesis of $\mathrm{Me_3SiSC_6H_4}$((*R*)-CH(Me)N(Me)$\mathrm{CH_2CH_2OMe}$)-2 (5b). The synthetic procedure is the same as that described for **5a**, but starting from **1b** (21.9 g; 0.11 mol): yield of $\mathrm{LiC_6H_4}$((*R*)-CH(Me)N(Me)-$\mathrm{CH_2CH_2OMe}$)-2 19.2 g (85%); yield of **5b** 13.0 g (45%); bp 114 °C (0.08 mmHg). ^{1}H NMR of two diastereomers (1:4), which are present due to a second chiral center (benzene-d_6, 297 K): δ 7.70 (d 2×, 1 H, *J* = 7.7 Hz; *J* = 1.6 Hz, Ar*H*), 7.50 (d 2×, 1 H, *J* = 7.6 Hz; *J* = 1.4 Hz, Ar*H*), 7.10 (t 2×, 1 H, *J* = 7.4; *J* = 1.3 Hz, Ar*H*), 6.92 (t 2×, 1 H, *J* = 7.5 Hz; *J* = 1.6 Hz, Ar*H*), 4.52 (q 2×, 1 H, *J* = 6.5 Hz, ArC*H*), 3.39 (t 2×, 1 H, *J* = 6.3 Hz, C*H*HO), 3.38 (t 2×, 1 H, *J* = 5.9 Hz, C*H*HO), 3.09, 3.06 (s 2×, 3 H, CH_3O), 2.78 (dt 2×, 1 H, *J* = 13.0 Hz, *J* = 5.9 Hz, *J* = 6.3 Hz, C*H*HN), 2.64 (dt 2×, 1 H, *J* = 13.0 Hz, *J* = 5.9 Hz, *J* = 6.3 Hz, C*H*HN), 2.29, 2.26 (s 2×, 3 H, CH_3N), 1.30, 1.28 (d 2×, 3 H, *J* = 6.6 Hz, CH_3C), 0.19, 0.16 (s 2×, 9 H, (CH_3)$_3$Si). Anal. Calcd for $\mathrm{C_{15}H_{27}NOSSi}$: C, 60.55; H, 9.15; N, 4.71. Found: C, 60.42; H, 9.15; N, 4.67.

Synthesis of $\mathrm{Me_3SiSC_6H_4}$((*R*)-CH(Me)$\mathrm{NMe_2}$)-2 (5c). The synthetic procedure is the same as that described for **5a**, but starting from $\mathrm{LiC_6H_4}$((*R*)-CH(Me)$\mathrm{NMe_2}$)-2 (13.9 g; 89 mmol):[6] yield of **5c** 16.5 g (73%); bp 87 °C (0.5 mmHg). ^{1}H NMR (benzene-d_6): δ 7.76 (dd, 1 H, *J* = 6.4 Hz, *J* = 1.4 Hz, 6-Ar*H*), 7.50 (dd, 1 H, *J* = 6.6 Hz, *J* = 1.1 Hz, 3-Ar*H*), 7.10 (dt, 1 H, *J* = 7.4 Hz; *J* = 1.1 Hz, 5-Ar*H*), 6.92 (dt, 1 H, *J* = 7.4 Hz, *J* = 1.5 Hz, 4-Ar*H*), 4.24 (q, 1 H, *J* = 6.6 Hz, ArC*H*), 2.19 (s, 6 H, (CH_3)$_2$N), 1.29 (d, 3 H, *J* = 6.6 Hz, CH_3C), 0.19 (s, 9 H, (CH_3)$_3$Si). Anal. Calcd for $\mathrm{C_{13}H_{23}NSSi}$: C, 61.59; H, 9.15; N, 5.53. Found: C, 61.19; H, 9.27; N, 5.39.

Synthesis of $\mathrm{[CuSC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2]_4}$ (6a). To a suspension of CuCl (1.17 g, 11.8 mmol) in 30 mL of toluene at room temperature was added **5a** (3.38 g, 11.8 mmol) in 40 mL of toluene. The volatiles were removed in vacuo, and the crude product was crystallized from $\mathrm{CH_2Cl_2}$/hexane at −20 °C to afford colorless crystals of **6a**: yield 3.2 g (99%); mp 98–108 °C dec. ^{1}H NMR (toluene-d_8, 297 K): δ 7.87 (d, 1 H, *J* = 7.2 Hz, 6-Ar*H*), 6.98 (t, 1 H, *J* = 7.2 Hz, 5-Ar*H*), 6.83 (t, 1 H, *J* = 6.9 Hz, 4-Ar*H*), 6.71 (d, 1 H, *J* = 6.2 Hz, 3-Ar*H*), 3.65 (br s, 2 H, CH_2N), 3.45 (s, 2 H, CH_2Ar), 3.03 (s, 3 H, CH_3O), 2.46 (s, 2 H, CH_2O), 2.24 (s, 3 H, CH_3N). Anal. Calcd for $\mathrm{C_{11}H_{16}CuNOS}$: C, 48.24; H, 5.89; N, 5.11. Found: C, 48.45; H, 6.13; N, 4.96. Molecular weight cryoscopy of $\mathrm{[CuSC_6H_4(CH_2NMe(CH_2CH_2OMe))\text{-}2]}_n$ (concentration 3.1–11.9 g kg^{-1} of benzene): n = 1.65–2.19.

Synthesis of $\mathrm{[CuSC_6H_4}$((*R*)-CH(Me)N(Me)$\mathrm{CH_2CH_2OMe)\text{-}2]}_n$ (6b). The synthetic procedure is the same as that described for **6a**, but starting from **5b** (12.3 g; 41 mmol). Yield after crystallization from warm toluene/hexane was 11.2 g (95%); ^{1}H NMR (benzene-d_6, 345 K): δ 7.88 (d, 1 H, *J* = 7.4 Hz, 6-Ar*H*), 6.9 (m, 3 H, Ar*H*), 4.04 (q, 1 H, *J* = 6.5 Hz, ArC*H*), 3.62 (t, 1 H, *J* = 5.8 Hz, C*H*HO), 3.61 (t, 1 H, *J* = 5.6 Hz, *J* = 5.8 Hz, C*H*HO), 3.11 (s, 3 H, CH_3O), 2.83 (dt, 1 H, *J* = 13.2 Hz, *J* = 5.6 Hz, *J* = 5.8 Hz, C*H*HN), 2.68 (dt, 1 H, *J* = 13.2 Hz, *J* = 5.6 Hz, *J* = 5.8 Hz, C*H*HN), 2.32 (s, 3 H, CH_3N), 1.43 (d, 3 H, *J* = 6.8 Hz, CH_3C). Anal. Calcd for $\mathrm{C_{12}H_{18}CuNOS}$: C, 50.07; H, 6.30; N, 4.87. Found: C, 49.21; H, 6.18; N, 4.73.

Alternative Synthesis of $\mathrm{[CuSC_6H_4}$((*R*)-CH(Me)$\mathrm{NMe_2)\text{-}2]_3}$ (6c).[1] The synthetic procedure is the same as that described for **6a**, but starting from **5c** (4.70 g; 18.5 mmol). Isolated yield after crystallization from THF was 4.4 g (90%) of yellow triboluminescent **6c**·THF.

Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **6a** and **7**

	6a	**7**
formula	$C_{44}H_{64}Cu_4N_4O_4S_4$	$C_{22}H_{34}N_2S_2Zn_2$
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1$
cell params		
a, Å	12.826 (1)	8.651 (2)
b, Å	14.057 (2)	13.876 (2)
c, Å	16.301 (3)	10.181 (2)
α, deg	108.64 (1)	
β, deg	106.37 (1)	99.82 (1)
γ, deg	99.93 (1)	
V, Å^3	2558.3 (7)	1204.2 (4)
Z	2	2
d_{calcd}, g cm^{-3}	1.422	1.438
μ, cm^{-1}	18.4	22.2
T, K	100	100
radiation	Mo Kα (Zr filtered); λ = 0.71073 Å	
final R, R_w, S	0.031, 0.040, 1.31	0.044, 0.043, 1.19

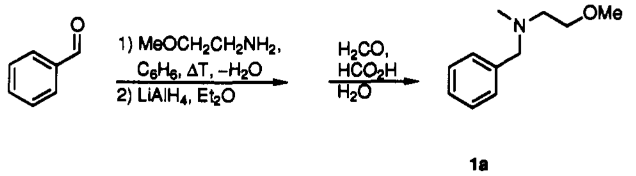
Synthesis of [Zn(Me){SC_6H_4((*R*)-CH(Me)NMe_2)-2}]$_2$ (7). To a suspension of $ZnCl_2$ (0.75 g, 5.50 mmol) in toluene (3.1 mL) at room temperature was added a solution of Me_2Zn (5.50 mmol) in hexane. To this mixture was added **5c** (2.80 g, 11.1 mmol) in 20 mL of toluene. After the mixture was stirred for 0.5 h, the resulting solution was filtered and all volatiles removed in vacuo. Crystallization of the solid gray residue from warm toluene yielded slightly gray crystals of **7**; yield 2.7 g (94%). ^1H NMR (toluene-d_8, 325 K): δ 6.6–7.7 (m, 4 H, Ar*H*), 2.09 (s, 6 H, $(CH_3)_2N$), 1.73 (br s, 1 H, ArC*H*), 1.35 (d, 3 H, J = 5.9 Hz, CH_3C), –0.57 (s, 3 H, CH_3Zn). Anal. Calcd for $C_{11}H_{17}NSZn$: C, 50.68; H, 6.57; N, 5.37. Found: C, 49.86; H, 6.33; N, 5.29. Molecular weight cryoscopy of [Zn(Me){SC_6H_4((*R*)-CH(Me)NMe_2)-2}]$_n$ (concentration 5.12–8.67 g kg^{-1} of benzene): n = 2.9–3.3.

Structure Determination and Refinement of [$CuSC_6H_4$(CH_2N(Me)-CH_2CH_2OMe)-2]$_4$ (6a). A greenish block-shaped crystal (0.78 × 0.53 × 0.49 mm) was glued on a glass-fiber and transferred to an Enraf-Nonius CAD4 diffractometer for data collection. Unit cell parameters at 100 K were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with 13.8 < θ < 17.7°. The unit cell parameters were checked for the presence of higher lattice symmetry.[9] Intensity data of 12625 reflections were collected in the range 1.41 < θ < 28.47° and corrected for *Lp* and for a linear decay (3.0%) of the intensity control reflections during the 121 h of X-ray exposure time but not for absorption (a 360° ψ scan for the –4,–1,0 reflection, showed intensity variations less than 5%). The structure was solved with direct methods (SHELXS86)[10] and subsequent difference Fourier syntheses. Refinement on *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-H atoms were refined with anisotropic thermal parameters, H atoms with one common isotropic thermal parameter (U = 0.038 (1) Å^2). A solvate molecule (located on an inversion symmetry site and tentatively interpreted as *n*-hexane) could not be located from difference Fourier maps unambiguously and was taken into account in the structure factor and refinement calculations by direct Fourier transformation of the electron density in the cavity, following the BYPASS procedure.[11] Weights were introduced in the final refinement cycles, convergence was reached at R = 0.031, R_w = 0.040 [$w = 1/(\sigma^2(F) + 0.000519F^2)$] for 9440 reflections with $I > 2.5\sigma(I)$ and 566 parameters. A final difference Fourier map revealed features within the range –1.40 to +0.82 e/Å^3 located near Cu atoms.

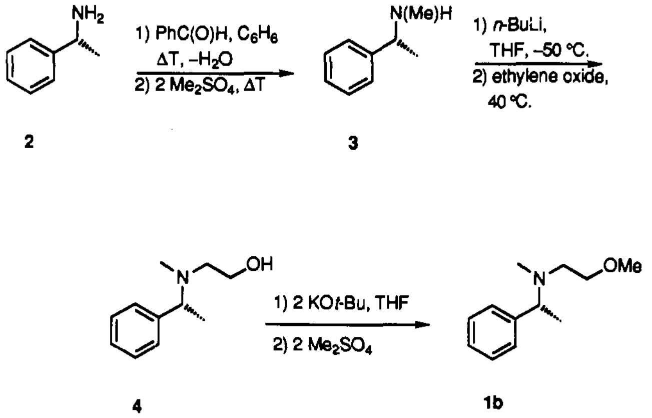
Crystal data and numerical details of the structure determination are given in Table I. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table II.

Neutral atom scattering factors were taken from Cromer and Mann[12] and corrected for anomalous dispersion.[13] All calculations were performed with SHELX76[14] and the EUCLID package[15] (geometrical calculations and illustrations) on a Micro VAX cluster.

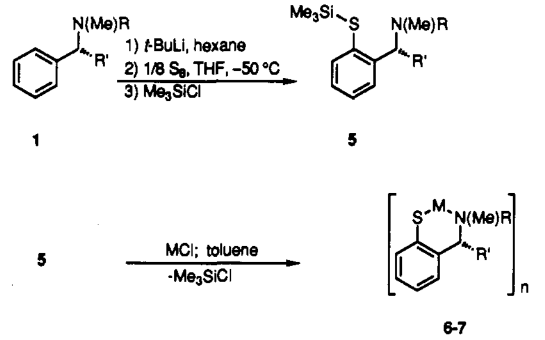
Scheme I



Scheme II



Scheme III



6a, M = Cu, R = CH_2CH_2OMe, R' = H, n = 4; **6b**, M = Cu, R = CH_2CH_2OMe, R' = Me, n = 4; **6c**, M = Cu, R = R' = Me, n = 3; **7**, M = ZnMe, R = R' = Me, n = 2.

Structure Determination and Refinement of [Zn(Me){SC_6H_4((*R*)-CH(Me)NMe_2)-2}]$_2$ (7). A transparent colorless crystal of dimensions 0.25 × 0.33 × 0.50 mm was mounted on the end of a glass fiber. The lattice parameters at 100 K were determined by a least-squares fit to the setting angles of 25 independent reflections (14 < θ < 19.4°), and refinement was by SET4 scans performed on a Enraf-Nonius CAD4 four-circle diffractometer. A unit cell check showed no presence of any higher lattice symmetry.[9] A total of 5682 reflections were collected in the range 0.1 < θ < 34°. The three reflections monitored after every 1 h indicated that after a total of 90 h of X-ray exposure time no decomposition had occurred. The data were corrected for Lorentz and polarization effects and absorption (DIFABS).[16] The structure was solved by Patterson routine with SHELXS86.[10] All subsequent least-squares refinements were executed by using SHELX76.[14] The hydrogen atoms were added at calculated positions (C–H = 1.08 Å) and their thermal parameters were refined as a common group factor (U = 0.043 (3) Å^2). The absolute configuration was established by using the coordinates sign change routine.[14] In the final full-matrix least-squares calculation, all the non-hydrogen atoms were modeled anisotropically by using neutral atom scattering factors.[12] R and R_w converged at 0.044 and 0.043, respectively, while the weighting scheme employed converged at $w = 1.28/[\sigma^2(F) + 0.000972F^2]$, for 3645 reflections with $I > 2.5\sigma(I)$ and 259 parameters.

The remaining electron density features range from –0.73 to +1.03 e/Å^3 with the largest peak located near carbon atom C(22).

The crystal data and other details are given in Table I. The final coordinates and equivalent isotropic thermal parameters are given in

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Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for **6a**

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Cu(1)	0.15940 (2)	0.27723 (2)	0.31845 (2)	0.0186 (1)
Cu(2)	−0.04108 (2)	0.17808 (2)	0.31775 (2)	0.0183 (1)
Cu(3)	−0.12790 (2)	0.17435 (2)	0.14493 (2)	0.0177 (1)
Cu(4)	0.03343 (2)	0.35857 (2)	0.21351 (2)	0.0185 (1)
S(1)	0.08754 (5)	0.32671 (5)	0.42731 (4)	0.0201 (2)
S(2)	−0.07570 (5)	0.04665 (5)	0.18591 (4)	0.0191 (2)
S(3)	−0.14898 (5)	0.33243 (5)	0.20039 (4)	0.0187 (2)
S(4)	0.15772 (5)	0.27688 (5)	0.18067 (4)	0.0195 (2)
O(1)	0.5589 (2)	0.3683 (2)	0.4496 (1)	0.0323 (6)
O(2)	−0.1213 (2)	0.0802 (2)	0.5507 (2)	0.0568 (9)
O(3)	−0.4510 (2)	−0.0624 (2)	−0.1039 (1)	0.0365 (6)
O(4)	0.0240(2)	0.6319 (2)	0.1117 (2)	0.0372 (7)
N(1)	0.2693 (2)	0.1918 (2)	0.3672 (1)	0.0234 (6)
N(2)	−0.1954 (2)	0.1440 (2)	0.3444 (1)	0.0233 (7)
N(3)	−0.1743 (2)	0.1400 (2)	−0.0011 (1)	0.0194 (6)
N(4)	0.1350 (2)	0.5194 (2)	0.2821 (2)	0.0234 (6)
C(1)	0.1629 (2)	0.2932 (2)	0.5189 (2)	0.0216 (7)
C(2)	0.1666 (2)	0.3524 (2)	0.6076 (2)	0.0282 (8)
C(3)	0.2150 (3)	0.3283 (2)	0.6829 (2)	0.0354 (9)
C(4)	0.2635 (3)	0.2480 (3)	0.6724 (2)	0.040 (1)
C(5)	0.2644 (3)	0.1916 (2)	0.5860 (2)	0.0339 (9)
C(6)	0.2144 (2)	0.2123 (2)	0.5085 (2)	0.0247 (7)
C(7)	0.2126 (2)	0.1405 (2)	0.4160 (2)	0.0263 (8)
C(8)	0.2650 (3)	0.1077 (2)	0.2828 (2)	0.0325 (8)
C(9)	0.3882 (2)	0.2516 (2)	0.4276 (2)	0.0264 (8)
C(10)	0.4443 (2)	0.3214 (2)	0.3893 (2)	0.0323 (9)
C(11)	0.6182 (3)	0.4382 (3)	0.4209 (2)	0.0363 (9)
C(12)	−0.2022 (2)	−0.0468 (2)	0.1670 (2)	0.0214 (7)
C(13)	−0.2134 (3)	−0.1512 (2)	0.1149 (2)	0.0295 (8)
C(14)	−0.3095 (3)	−0.2305 (2)	0.0930 (2)	0.0359 (9)
C(15)	−0.3968 (3)	−0.2071 (2)	0.1216 (2)	0.0355 (9)
C(16)	−0.3858 (2)	−0.1046 (2)	0.1743 (2)	0.0322 (9)
C(17)	−0.2891 (2)	−0.0230 (2)	0.1986 (2)	0.0235 (7)
C(18)	−0.2884 (2)	0.0866 (2)	0.2519 (2)	0.0247 (8)
C(19)	−0.2146 (3)	0.2459 (2)	0.3858 (2)	0.0338 (9)
C(20)	−0.1998 (2)	0.0836 (2)	0.4030 (2)	0.0302 (8)
C(21)	−0.0970 (2)	0.1266 (2)	0.4920 (2)	0.0315 (9)
C(22)	−0.0331 (3)	0.1183 (3)	0.6375 (2)	0.061 (1)
C(23)	−0.2236 (2)	0.3553 (2)	0.1018 (2)	0.0208 (7)
C(24)	−0.2911 (2)	0.4225 (2)	0.1165 (2)	0.0255 (8)
C(25)	−0.3481 (2)	0.4512 (2)	0.0470 (2)	0.0313 (9)
C(26)	−0.3401 (2)	0.4122 (2)	−0.0393 (2)	0.0332 (9)
C(27)	−0.2766 (2)	0.3428 (2)	−0.0558 (2)	0.0284 (8)
C(28)	−0.2172 (2)	0.3129 (2)	0.0133 (2)	0.0209 (7)
C(29)	−0.1440 (2)	0.2425 (2)	−0.0098 (2)	0.0219 (7)
C(30)	−0.0974 (2)	0.0813 (2)	−0.0316 (2)	0.0267 (8)
C(31)	−0.2938 (2)	0.0815 (2)	−0.0611 (2)	0.0216 (7)
C(32)	−0.3371 (2)	−0.0138 (2)	−0.0432 (2)	0.0253 (8)
C(33)	−0.5046 (2)	−0.1451 (2)	−0.0859 (2)	0.0319 (9)
C(34)	0.2803 (2)	0.3758 (2)	0.2016 (2)	0.0204 (7)
C(35)	0.3454 (2)	0.3442 (2)	0.1478 (2)	0.0265 (8)
C(36)	0.4457 (2)	0.4117 (2)	0.1600 (2)	0.0307 (9)
C(37)	0.4823 (2)	0.5131 (2)	0.2254 (2)	0.0333 (9)
C(38)	0.4167 (2)	0.5467 (2)	0.2775 (2)	0.0269 (8)
C(39)	0.3156 (2)	0.4797 (2)	0.2670 (2)	0.0230 (7)
C(40)	0.2531 (2)	0.5208 (2)	0.3299 (2)	0.0254 (7)
C(41)	0.0924 (3)	0.5689 (2)	0.3549 (2)	0.0337 (9)
C(42)	0.1347 (2)	0.5800 (2)	0.2227 (2)	0.0285 (8)
C(43)	0.0168 (2)	0.5643 (2)	0.1589 (2)	0.0307 (9)
C(44)	−0.0838 (3)	0.6202 (3)	0.0491 (3)	0.045 (1)

[a] *U*(eq) = one-third of the trace of the orthogonalized **U** matrix.

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for **7**

atom	*x*	*y*	*z*	*U*(eq), Å^2
Zn(1)	0.23321 (6)	0.5	0.10162 (5)	0.0164 (2)
Zn(2)	0.22790 (7)	0.52727 (5)	0.40518 (6)	0.0181 (2)
S(1)	0.2118 (1)	0.6438 (1)	0.2263 (1)	0.0175 (3)
S(2)	0.2453 (2)	0.3819 (1)	0.2824 (1)	0.0183 (3)
N(1)	−0.0062 (5)	0.4888 (3)	0.0203 (4)	0.018 (1)
N(2)	0.4649 (5)	0.5307 (4)	0.4982 (4)	0.020 (1)
C(1)	0.0079 (6)	0.6730 (4)	0.2095 (5)	0.018 (1)
C(2)	−0.0329 (7)	0.7302 (4)	0.3105 (6)	0.024 (2)
C(3)	−0.1851 (8)	0.7619 (5)	0.3083 (7)	0.031 (2)
C(4)	−0.3020 (7)	0.7343 (5)	0.2011 (7)	0.032 (2)
C(5)	−0.2619 (6)	0.6766 (5)	0.1023 (6)	0.025 (2)
C(6)	−0.1091 (6)	0.6442 (4)	0.1029 (5)	0.019 (1)
C(7)	−0.0812 (6)	0.5854 (4)	−0.0177 (5)	0.020 (1)
C(8)	0.0100 (7)	0.6437 (4)	−0.1068 (6)	0.027 (2)
C(9)	−0.0114 (8)	0.4265 (5)	−0.0970 (6)	0.031 (2)
C(10)	−0.0994 (6)	0.4412 (4)	0.1109 (6)	0.024 (2)
C(11)	0.3953 (6)	0.4932 (4)	−0.0193 (5)	0.019 (1)
C(12)	0.4472 (6)	0.3526 (4)	0.3009 (5)	0.019 (1)
C(13)	0.4950 (6)	0.3019 (4)	0.1957 (5)	0.022 (2)
C(14)	0.6501 (7)	0.2746 (5)	0.2002 (6)	0.026 (2)
C(15)	0.7591 (7)	0.2986 (4)	0.3109 (6)	0.026 (2)
C(16)	0.7147 (7)	0.3492 (5)	0.4145 (5)	0.024 (2)
C(17)	0.5571 (6)	0.3755 (4)	0.4131 (5)	0.020 (1)
C(18)	0.5101 (7)	0.4274 (4)	0.5330 (5)	0.021 (1)
C(19)	0.6337 (7)	0.4179 (5)	0.6586 (5)	0.030 (2)
C(20)	0.4586 (7)	0.5894 (5)	0.6187 (6)	0.029 (2)
C(21)	0.5727 (6)	0.5792 (5)	0.4205 (6)	0.026 (2)
C(22)	0.0623 (5)	0.5304 (4)	0.5276 (4)	0.015 (1)

Table III. The geometrical calculations and diagrams were made by using the EUCLID package.[15]

Results

The synthetic route used to prepare copper and zinc complexes containing the novel anionic N-S ligands $\{SC_6H_4(CH(R')N(Me)R)\text{-}2\}^-$ (R = CH_2CH_2OMe, R′ = H, Me; R = R′ = Me) is outlined in Schemes I–III. The first stage is the synthesis of the compounds $C_6H_5(CH(R')N(Me)CH_2CH_2OMe)$ (**1a**, R′ = H; **1b**, R′ = Me, (*R*)-configuration) for which two different approaches were used. Compound **1a** can be easily prepared in two steps from benzaldehyde and $MeOCH_2CH_2NH_2$ in 78% yield (Scheme I). Compound **1b** can be prepared by the route shown in Scheme II that starts from commercially available enantiomerically pure (*R*)-(+)-α-methylbenzylamine (**2**). The primary amine function is first protected with benzaldehyde and then monomethylated to afford the secondary amine C_6H_5-(*R*)-CH(Me)NH(Me) (**3**).[7] The nitrogen atom is further functionalized with ethylene oxide to afford C_6H_5((*R*)-CH(Me)N(Me)CH_2CH_2OH) (**4**), which is converted to product **1b** by an ether synthesis. The overall yield of **1b** based on α-methylbenzylamine is 38%. We found this route to **1b** to be preferable to a more direct synthesis from acetophenone using the method employed for **1a**; this latter method provides racemic **1b**, which then requires an additional optical resolution step.

The second stage is the synthesis of the (trimethylsilyl)arenethiolates, $Me_3SiSC_6H_4(CH(R')N(Me)R)$-2 (**5a**, R = CH_2CH_2OMe, R′ = H; **5b**, R = CH_2CH_2OMe, R′ = Me; **5c**, R = Me = Me, (*R*)-configuration), shown in Scheme III. First, the reaction of **1a–c** with *t*-BuLi or *n*-BuLi provides *o*-lithio derivatives, which are then converted with sulfur to the corresponding lithium arenethiolates. Finally, the unstable arenethiolates are quenched with Me_3SiCl to afford the required (trimethylsilyl)arenethiolates (**5a–c**) which, unlike the corresponding arenethiols, can be purified by distillation. The (trimethylsilyl)arenethiolates **5a–c** are very moisture-sensitive liquids; the corresponding thiols crystallize out if they are exposed to air.

The copper arenethiolates $[CuSC_6H_4(CH(R')N(Me)R)\text{-}2]_n$ (**6a**, R = CH_2CH_2OMe, R′ = H; **6b**, R = CH_2CH_2OMe, R′ = Me; **6c**, R = R′ = Me, (*R*)-configuration) were subsequently prepared from the reaction of **5a–c** with a suspension of CuCl in toluene. The insoluble CuCl dissolves immediately when 1 equiv of the (trimethylsilyl)arenethiolates **5a–c** is added and the pure copper(I) arenethiolates **6a–c** were obtained in almost quantitative yield by removing the solvent and volatile Me_3SiCl in vacuo.

There is an alternative preparation method for **6c**.[1] Hydrolysis of the intermediate lithium arenethiolate $LiSC_6H_4(CH(Me)NMe_2)$-2 affords the arenethiol $HSC_6H_4(CH(Me)NMe_2)$-2. This crude arenethiol, when reacted directly with copper(I) oxide, yields **6c**, which can be purified by extraction and crystallization. The synthesis of pure **6a** and **6b** by this route proved impossible because the lithium salts formed during the hydrolysis step could not be removed even by extraction with water.

Compounds **6a,b** are white solids that form light-sensitive solutions. The molecular weight of **6a**, in a benzene solution, is

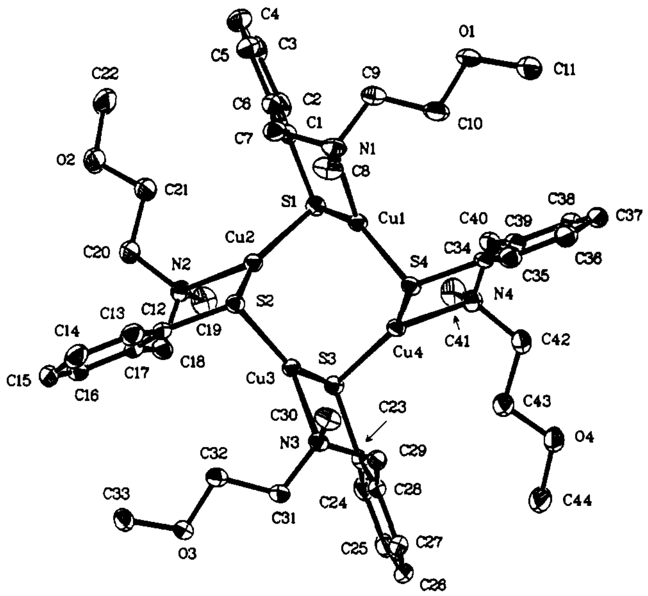

Figure 1. ORTEP drawing (drawn at 50% probability level) of $[CuSC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2]_4$ (**6a**) (with the exclusion of the hydrogen atoms) with the atom-labeling scheme.

concentration dependent (concentration range 3.13–11.92 g kg^{-1} of benzene) with the aggregation state varying between 1.65 and 2.19. The ^{1}H NMR spectra (200 MHz, toluene-d_8) of **6a**,**b** are temperature dependent. Below 345 K the signals broaden and a very complex spectrum with many overlapping ligand patterns is obtained at 213 K. It was impossible to reach the slow-exchange limit for some of these patterns, and this has hampered the assignment of the ^{1}H NMR spectra. The fluxional behavior of **6c**, which was reported earlier,[1b] has been intensively studied and was shown to involve an inversion of configuration at sulfur and Cu–N bond dissociation/association processes. We believe that the complex patterns observed in ^{1}H NMR spectra of **6a** and **6b** are due to the presence of species with different aggregation states and conformations.

The new method, described above, involving the use of (trimethylsilyl)arenethiolates for the preparation of **6a–c** is not restricted to the preparation of copper(I) arenethiolates. The same method can be used for the preparation of zinc, tungsten, gold, and titanium complexes containing bi- and tridentate (N–S and N–S–O) arenethiolate ligands. One example is the preparation of methylzinc arenethiolate, $[Zn(Me)\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_n$ (**7**), from the 1:1 reaction of ZnClMe (prepared in situ from $ZnMe_2$ and $ZnCl_2$) and **5c** in 94% yield (after crystallization).

The methylzinc arenethiolate **7** is grayish white and is air-sensitive. The aggregation state of **7** in benzene solution varies between 2.9 and 3.3 (benzene; concentration range 5.12–8.67 g kg^{-1} of benzene). In the ^{1}H NMR spectrum of **7** (200 MHz, toluene-d_8), broad signals are present at room temperature. At 325 K, the ^{1}H NMR spectrum shows sharp signals for the ligands and the integral indicates that the methyl group on the zinc and the arenethiolate ligand are present in a 1:1 ratio. The complex overlap of the signals in the 213 K ^{1}H NMR spectrum prevented us from carrying out structural investigations on this compound in solution. However, between +0.1 and −0.5 ppm there are at least eight signals for the methyl group bound to zinc.

Structure of $[CuSC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2]_4$ (6a). The X-ray crystal structure determination of **6a** established that in the solid state this compound has a tetrameric structure. A ORTEP plot of **6a** with the adopted numbering scheme is to be found in Figure 1, and Table IV contains relevant bond distances and angles. The molecule has a noncrystallographic 4-fold rotation mirror axis, i.e. S_4 symmetry. The four copper atoms are in a flattened butterfly arrangement (dihedral angle Cu(1)–Cu(2)–Cu(4)–Cu(3) = 47.47 (2)°) with a thiolate sulfur atom bridging each Cu···Cu edge. The sulfur atoms are alternately above and below the copper array. The copper and the sulfur atoms form an eight-membered Cu_4S_4 ring in a twist–boat conformation with the four aryl groups in equatorial positions.

The two Cu–S bond distances (one short, average = 2.206 (5) Å; one normal, average = 2.243 (4) Å) are comparable to those found in **6c**. The acute Cu–S–Cu angle (average = 74.5 (3)°) and the short Cu···Cu distance (average 2.693 (9) Å) indicate that each sulfur atom forms together with two copper atoms an electron-deficient two-electron–three-center bond.[1b] The average sum of the bond angles at the S atoms amounts to 287.9°. Each amino nitrogen atom coordinates intramolecularly to one copper atom (average Cu–N = 2.149 (2) Å) to provide a six-membered CuSCCCN chelate ring. As a consequence, each copper center has a distorted-trigonal coordination geometry (with a sum of the interligand angles amounting to an average value of 359.98°), and the nitrogen atoms are centers of chirality. In the molecule shown in Figure 1, two adjacent nitrogen atoms have an *R* configuration (N(1) and N(3)) while the other two have the *S* configuration (N(2) and N(4)). The potentially coordinating ether group in this molecule does not coordinate at all.

Table IV. Important Bond Distances (Å) and Bond Angles (deg) in $[CuSC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2]_4$ (**6a**)[a,b]

	range[b]	av
Cu–S[c]	2.1991 (8)–2.2111 (9)	2.206 (5)
Cu–S′[d]	2.2384 (8)–2.2463 (9)	2.243 (4)
Cu–N	2.146 (2)–2.150 (2)	2.149 (2)
S–C	1.778 (3)–1.783 (3)	1.781 (3)
Cu···Cu	2.6784 (6)–2.7012 (6)	2.693 (9)
S–Cu–S	143.08 (3)–145.11 (3)	144 (1)
S–Cu–N	102.05 (7)–103.19 (6)	102.7 (5)
S′–Cu–N	111.65 (6)–114.86 (7)	113 (1)
Cu–S–Cu	74.12 (2)–74.82 (2)	74.4 (3)
Cu–S–C	105.80 (9)–108.23 (8)	106.7 (9)
Cu–N–CH_2Ar	105.2 (2)–107.5 (2)	106.4 (9)
Cu–N–CH_3	105.6 (2)–106.1 (2)	105.9 (2)
Cu–N–CH_2R	116.2 (2)–117.5 (2)	117.0 (6)

[a] Uncertainties in the last significant digit are shown in parentheses. [b] The range of the four (crystallographically nonequivalent) subunits. [c] Within the six-membered Cu–S–C–C–C–N rings. [d] Nonchelating Cu–S distances.

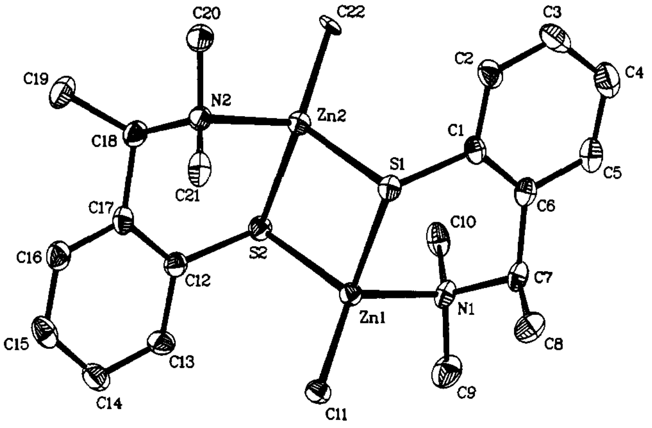

Figure 2. ORTEP drawing (drawn at 50% probability level) of $[Zn(Me)\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_2$ (**7**) (with the exclusion of the hydrogen atoms) with the atom-labeling scheme.

Structure of $[Zn(Me)\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_2$ (7). The molecular structure of **7** and the adopted numbering scheme are shown in Figure 2, and a list of relevant bond distances and angles is given in Table V. The compound is dimeric with a central almost planar Zn_2S_2 unit in which the zinc atoms are bridged by the two sulfur atoms which both have a clear pyramidal coordination with $\sum\angle S$ of about 286.4°. The aryl group bonded to each sulfur atom coordinates intramolecularly through the amino group to a zinc atom that carries a methyl group. Within the dimer one aryl group and one methyl group are positioned to each side of the Zn_2S_2 plane. Because the benzylic carbon atoms both

Table V. Important Bond Distances (Å) and Bond Angles (deg) in $[Zn(Me)\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_2$ (**7**)[a]

Zn(1)–S(1)	2.389 (1)	Zn(1)–S(2)	2.453 (2)
Zn(2)–S(2)	2.390 (1)	Zn(2)–S(1)	2.422 (2)
Zn(1)–C(11)	2.020 (5)	Zn(2)–C(22)	2.053 (4)
Zn(1)–N(1)	2.101 (4)	Zn(2)–N(2)	2.107 (4)
Zn(1)···Zn(2)	3.1216 (8)	S(1)···S(2)	3.6822 (9)
S(1)–Zn(1)–S(2)	98.99 (5)	S(1)–Zn(2)–S(2)	99.84 (5)
Zn(1)–S(1)–Zn(2)	80.91 (5)	Zn(1)–S(2)–Zn(2)	80.25 (5)
S(1)–Zn(1)–N(1)	96.3 (1)	S(2)–Zn(1)–N(1)	99.2 (1)
S(2)–Zn(2)–N(2)	96.4 (2)	S(1)–Zn(2)–N(2)	104.5 (1)
S(1)–Zn(1)–C(11)	119.2 (2)	S(2)–Zn(1)–C(11)	118.8 (2)
S(2)–Zn(2)–C(22)	116.6 (2)	S(1)–Zn(2)–C(22)	119.1 (2)
N(1)–Zn(1)–C(11)	119.8 (2)	N(2)–Zn(2)–C(22)	116.9 (2)
Zn(1)–S(1)–C(1)	107.6 (2)	Zn(2)–S(1)–C(1)	98.8 (2)
Zn(2)–S(2)–C(12)	106.7 (2)	Zn(1)–S(2)–C(12)	98.5 (2)

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

have an (*R*)-configuration, the molecule does not contain any symmetry element. The overall structure is similar to that of $[Cu\{OC_6H_4(CH_2NMe_2)\text{-}2\}\{P(OMe)_3\}]_2$, which we recently reported.[18]

The zinc atoms have a distorted tetrahedral geometry with S–Zn–S angles of 98.99 (5)° and 99.84 (5)°. The Zn···Zn distance is 3.1216 (8) Å, which is considered to be nonbonding. The Zn–S–Zn angles are rather acute (80.91 (5) and 80.25 (5)°), and this reflects the more flexible geometry of sulfur compared to zinc. The internal angles in the Zn_2S_2 unit are comparable to those in Zn_2O_2 units found in molecules like $[Zn(Et)\{Et(t\text{-}Bu)NCH{=}C(Me)\text{-}O\}]_2$.[19]

One benzylic methyl group (C(19)) is almost in the plane of the aromatic ring (C(16)–C(17)–C(18)–C(19) = −17.4 (8)°; C(16)···C(19) = 2.858 (8) Å), while the other benzylic methyl group (C(8)) is out of the aromatic plane (C(5)–C(6)–C(7)–C(8) = 107.3 (6)°). The asymmetry caused by the former is reflected in the geometry around Zn(2) where the S(1)–Zn(2)–N(2) and S(2)–Zn(2)–C(22) angles (104.5 (1) and 116.6 (2)°) deviate significantly from the other three S–Zn–N and S–Zn–C angles.

There are two other organozinc structures known in which a direct zinc–sulfur bond is present, i.e. $[Zn(Me)(S\text{-}i\text{-}Pr)]_8$ and $[Zn(Me)(S\text{-}t\text{-}Bu)]_5$.[20] Compared to these structures, two zinc–sulfur bond distances in **7** (Zn(1)–S(1) = 2.389 (1) and Zn(2)–S(2) = 2.390 (1) Å) are short while the zinc–carbon bond distances (Zn(1)–C(11) = 2.020 (5) and Zn(2)–C(22) = 2.053 (4) Å) are slightly longer. Compared to many other organozinc compounds, the Zn–C bond lengths in **7** are long.

Steric strain in the conformation of the methylzinc arenethiolate **7** in the solid state is likely to be relieved in solution by the formation of higher aggregates. This behavior, supplemented by the chirality of the benzylic carbon atom, explains the many ligand signals in the low-temperature ^1H NMR spectrum of this complex.

Discussion

The new synthetic method for the preparation of metal arenethiolates from (trimethylsilyl)arenethiolates and metal halides is very versatile and can be applied to a variety of functionalized arenethiolates and metal ions. A significant advantage of this method over the use of lithium and magnesium reagents is that the metal arenethiolates are obtained pure and do not require separation from salts; the latter separation is often very difficult or even impossible.

The overall structure of the copper arenethiolate **6a** is similar to that of tetranuclear organocopper compounds, e.g. $[CuC_6H_4(CH_2NMe_2)\text{-}2\text{-}Me\text{-}5]_4$;[17] structural similarity between copper arenethiolates and organocopper compounds is often found.[2c,d] In contrast to **6c**, which is a trimer, **6a** is a tetramer in the solid state.[1] This difference may be caused by the increased steric bulk of the substituents on the nitrogen atom in **6a**. In **6c** the dimethylamino group has already some steric interactions with neighboring aromatic groups that cause destabilization of the conformation found, and increasing the bulk of the amino nitrogen substituents as in **6a** is likely to destabilize the trimeric aggregation state even more.[1b] In solution, **6c** is a trimer over a large concentration range while the tetrameric aggregation state of **6a** is not stable and, surprisingly, lower aggregates are present. ^1H NMR data of **6a** suggest that the ether function of the ligand can coordinate to a copper center (the signal of the *O*-methyl group decoalesces at low temperatures into several signals) and possibly has a stabilizing influence on lower aggregates.

An interesting aspect of the copper arenethiolates **6** is that they catalyze the 1,4-addition of MgIMe to benzylideneacetone. For example, if one uses the chiral copper thiolate **6c** as catalyst, this reaction in diethyl ether gave after hydrolysis the 1,4-addition product in near-quantitative yield with an enantiomeric excess (ee) of 60%.[4] Preliminary studies indicate that this interesting ee value emerges from reactions of "lower order" type cuprates, $[Cu(SC_6H_4CH(Me)NMe_2\text{-}2]_n\cdot[MeMgI]_m$ ($n = m$), with the enone. In contrast when "higher order" type cuprates ($m > n$) are used, 1,4-addition is also obtained but with negligible ee values. With the introduction of an ether function in the copper arenethiolates **6a** and **6b**, cuprate species can be obtained that contain a specific extra binding site for magnesium (and lithium) cations. The enone can bind to this coordinated Lewis acidic metal ion via its carbonyl function.[5] Preliminary studies show that the ether function CH_2CH_2OMe in the copper thiolates binds magnesium and lithium salts very well. Studies on chiral copper thiolates as catalysts in the enantioselective 1,4-addition reaction to α,β-unsaturated ketones are current.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, bond distances, bond angles, torsion angles, and crystallographic data for **6a** and **7** (19 pages); listings of observed and calculated structure factor amplitudes for **6a** and **7** (79 pages). Ordering information is given on any current masthead page.

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