Structural Aspects of Lithium Arenethiolate Complexes with Intramolecular Coordinating Amine Donors[†]

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Received January 24, 1996[⊗]

Reaction of aryllithium reagents LiR (R = $C_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2$ (**1a**), $C_6H_3(CH_2NMe_2)_2\text{-}2,6$ (**1b**), $C_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2$ (**1c**)) with 1 equiv of sulfur (1/8 S_8) results in the quantitative formation of the corresponding lithium arenethiolates $[Li\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_6$ (**3**), $[Li\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_6$ (**4**), and $[Li\{SC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2\}]_2$ (**5**). Alternatively, **3** can be prepared by reacting the corresponding arenethiol $HSC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2$ (**2**) with ^nBuLi. X-ray crystal structures of lithium arenethiolates **3** and **4**, reported in abbreviated form, show them to have hexanuclear prismatic and hexanuclear planar structures, respectively, that are unprecedented in lithium thiolate chemistry. The lithium arenethiolate $[Li\{SC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2\}]_2$ (**5**) is dimeric in the solid state and in solution, and crystals of **5** are monoclinic, space group $P2_1/c$, with $a = 17.7963(9)$ Å, $b = 8.1281(7)$ Å, $c = 17.1340(10)$ Å, $\beta = 108.288(5)°$, $Z = 4$, and final $R = 0.047$ for 4051 reflections with $F > 4\sigma(F)$. Hexameric **4** reacts with 1 equiv of lithium iodide and 2 equiv of tetrahydrofuran to form the dinuclear adduct $[Li_2(SAr)(I)(THF)_2]$ (**6**). Crystals of **6** are monoclinic, space group $P2_1/c$, with $a = 13.0346(10)$ Å, $b = 11.523(3)$ Å, $c = 16.127(3)$ Å, $\beta = 94.682(10)°$, $Z = 4$, and final $R = 0.059$ for 3190 reflections with $F > 4\sigma(F)$.

Introduction

Arenethiolate ligands are widely used in organometallic and inorganic chemistry, and their complexes are usually quite stable toward protic media.[1] Since sulfur atoms are easily polarized, these ligands can adopt various kinds of coordination.[2] Our work involves the use of aryl, phenolate, and arenethiolate ligands with tertiary amine substituents which, through intramolecular coordination, can stabilize reaction intermediates or change the reactivity of the metal center by blocking specific coordination sites.[3] As an example, we reported copper(I) arenethiolates as catalysts for selective group transfer of RMgX reagents to various substrates, *i.e.,* selective conjugate 1,4- and 1,6-additions to cyclic or acyclic α,β-unsaturated enones and $\alpha,\beta,\gamma,\delta$-unsaturated alkynylenones, as well as selective α- or γ-alkylation of allylic substrates.[4] Very recently, we have also found that zinc(II) arenethiolate complexes can be used as catalysts in the enantioselective addition of ZnR_2 to various aldehydes.[5]

To understand the coordination behavior and reactivity of arenethiolate ligands with potentially coordinating donor substituents, we have isolated the corresponding lithium complexes and studied their structure and reactivity. Here, we report the syntheses of lithium complexes containing such ligands (Figure 1) and show how the positioning of the intramolecularly coordinating functions can affect their aggregation state and structure.

The arenethiolate ligands described in this work are all related in having an *o*-amino substituent that can generate a six-membered chelate ring on coordination through sulfur and nitrogen to a metal center. The first of these monoanionic ligands $SC_6H_4(CH(Me)NMe_2)\text{-}2$ (**a** in Figure 1) has, besides the anionic sulfur atom and the neutral nitrogen donor atom, a chiral element which has found use in catalytic studies.[4,5] The

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[†] Dedicated to Prof. Hans Georg von Schnering on the occasion of his 65th birthday.

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) CuSAr can resist up to 0.1 N HCl solutions in water. (a) SAr = $SC_6H_4\text{-}CH(R)NMe_2\text{-}2$ (R = H, Me): Knotter, D. M.; van Maanen, H. L.; Grove, D. M.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1991**, *30*, 3309−3317. (b) $SC_6H_4(CH(R)N(Me)CH_2CH_2OMe)\text{-}2$ (R = H, Me): Knotter, D. M.; Janssen, M. D.; Grove, D. M.; Smeets, W. J. J.; Horn, E.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1991**, *30*, 4361−4366. (c) $SC_6H_4NMe_2\text{-}2$ and $S\text{-}1\text{-}C_{10}H_6NMe_2\text{-}8$: Janssen, M. D.; Donkervoort, J. G.; van Berlekom, S. B.; Spek, A. L.; Grove, D. M.; van Koten G. *Inorg. Chem.* **1996**, *35*, 4752−4763.

(2) Cu−S−Cu angles in copper(I) arenethiolates are reported in the range 67.8−135.5°. See ref 1a. Moreover, arenethiolates have been reported to bind to various copper atoms in several ways. (a) η^1: Janssen, M. D.; Herres, M.; Zsolnai, L.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 2476−2483. (b) μ^2: Togni, A.; Rihs, G.; Blumer, R. E. *Organometallics* **1992**, *11*, 613−621. (c) μ^3: Block, E.; Gernon, M.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 1263−1271. (d) μ^4 in $[Cu_8(SAr)_3Br_5]$: Janssen, M. D.; Spek, A. L.; Grove, D. M.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 4078−4081.

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(4) (a) van Koten, G. *Pure Appl. Chem.* **1994**, *66*, 1455−1462. 1,4-Addition: (b) Lambert, F.; Knotter, D. M.; Janssen, M. D.; van Klaveren, M.; Boersma, J.; van Koten, G. *Tetrahedron: Asymmetry* **1991**, *2*, 1097−1100. (c) van Klaveren, M.; Lambert, F.; Eijkelkamp, D. J. F. M.; Grove, D. M.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 6135−6138. 1,6-Addition: (d) Haubrich, A.; van Klaveren, M.; van Koten, G.; Handke, G.; Krause, N. *J. Org. Chem.* **1993**, *58*, 5849−5852. Substitution: (e) van Klaveren, M.; Persson, E. S. M.; Grove, D. M.; Bäckvall, J.-E.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 5931−5934. (f) van Klaveren, M.; Persson, E. S. M.; Grove, D. M.; Bäckvall, J. E.; van Koten, G. *Chem.—Eur. J.* **1995**, *1*, 351−359.

(5) Rijnberg, E.; Jastrzebski, J. T. B. H.; Janssen, M. D.; Boersma, J.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 6521−6524.

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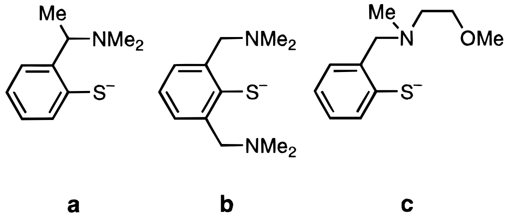

Figure 1. Arenethiolate ligands with potential for intramolecular coordination.

second arenethiolate system $SC_6H_3(CH_2NMe_2)_2$-2,6 (**b** in Figure 1) has two neutral nitrogen donor sites and is a potentially terdentate *trans*-spanning ligand. Finally, $SC_6H_4(CH_2N(Me)CH_2CH_2OMe)$-2 (**c** in Figure 1), which is also a potentially terdentate ligand, has an additional possibility for oxygen to metal coordination through the presence of a CH_2CH_2OMe group on the N donor atom, and this can lead to the formation of a five-membered chelate ring.

Experimental Section

Syntheses were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen free nitrogen. Toluene, benzene, hexane, pentane, Et_2O (predried on CaH_2), and tetrahydrofuran (THF) were carefully dried and distilled from sodium benzophenone−ketyl prior to use. CH_2Cl_2 was distilled from calcium hydride. Commercial ^{n}BuLi (1.67 M solution in hexane) was used. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200P or a Bruker AC-300P spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. $[Li\{C_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_4$ (**1a**),[6a] $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$ (**1b**),[6b] $[Li\{C_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2\}]_n$ (**1c**),[1b] and $HSC_6H_4((R)\text{-}CH(Me)NMe_2)$-2 (**2**)[1a] were prepared according to literature procedures. The succesful sulfur insertion reaction of **1a** affording **3** *in situ* has been reported previously.[1b]

$[Li\{SC_6H_4((R)\text{-}CH(Me)NMe_2)\text{-}2\}]_6$ (3). To a suspension of $HSC_6H_4((R)\text{-}CH(Me)NMe_2)$-2 (0.58 g, 3.20 mmol) in benzene (25 mL) was added ^{n}BuLi (2.0 mL of a 1.6 M solution in hexane, 3.20 mmol). On addition of the ^{n}BuLi, the reaction mixture immediately became a clear yellow solution. After stirring for 15 min, the volatiles were removed *in vacuo*, yielding 0.68 g of crude **3** still containing both benzene and hexane. Crystals could be obtained by slowly cooling a saturated hexane solution of **2** to −20 °C. Because crystalline material afforded irreproducible microanalysis data, powdered crystals were evacuated (10^{-3} mmHg) for 24 h to afford analytically pure solvent free material. ^{1}H NMR (toluene-d_8, 353 K; ppm): δ 1.72 (d, 3H, $^{3}J = 6$ Hz, CMe), 2.06 (s, 6H, NMe_2), 3.0 (br s, 1H, CH), 6.74 (m, 2H, ArH), 6.96 (m, 1H, ArH), 7.75 (d, 1H, ArH-6). ^{1}H NMR (toluene-d_8, 233 K; ppm): δ 1.71 (s, 3H, NMe), 1.93 (d, 3H, $^{3}J = 6$ Hz, CMe), 2.41 (s, 3H, NMe), 2.67 (br q, 1H, $^{3}J = 6$ Hz, CH), 6.68 (d, 1H, $^{3}J = 7$ Hz, ArH-3), 6.83 (t, 1H, $^{3}J = 7$ Hz, ArH-4), 7.11 (t, 1H, $^{3}J = 8$ Hz, ArH-5), 7.92 (d, 1H, $^{3}J = 7$ Hz, ArH-6). Signal assignments for ArH-4 and ArH-5 are tentative. ^{13}C NMR (toluene-d_8, 263 K; ppm): δ 17.2 (Me), 46.2 (NMe_2), 73.9 (C(H)), 122.01, 127.0, 131.9, 137.3, 143.5, 144.7 (Ar). Anal. Calcd for $C_{60}H_{84}N_6S_6Li_6$: C, 64.15; H, 7.54; N, 7.48. Found: C, 64.22; H, 7.59; N, 7.55.

$[Li\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_6$ (4). To a well-stirred solution of $LiC_6H_3(CH_2NMe_2)_2$-2,6 (**1b**) (4.65 g, 23.5 mmol) cooled at −78 °C was added in one portion sublimed sulfur (0.76 g, 23.7 mmol). The reaction mixture was allowed to warm to room temperature, and the stirring was continued for another 5 h, whereafter all volatiles were removed *in vacuo*. The remaining solid was washed with pentane (twice 25 mL) and dried *in vacuo*. Yield: 4.77 g (88%) of creamy-white powder. Crystals could be obtained by slow diffusion of pentane into a concentrated toluene solution of **4**; mp 130 °C (dec). ^{1}H NMR (benzene-d_6, 320 K; ppm): δ 1.96 (br s, 12H, NMe_2), 3.57 (br s, 4H, CH_2), 6.73 (t, 1H, $^{3}J = 7$ Hz, Ar*H*-4), 6.92 (d, 2H, $^{3}J = 7$ Hz, Ar*H*-3,5). Anal. Calcd for $C_{72}H_{114}N_{12}S_6Li_6{\cdot}2C_7H_8$: C, 65.96; H, 8.37; N, 10.73. Found: C, 65.73; H, 8.92; N, 10.37.

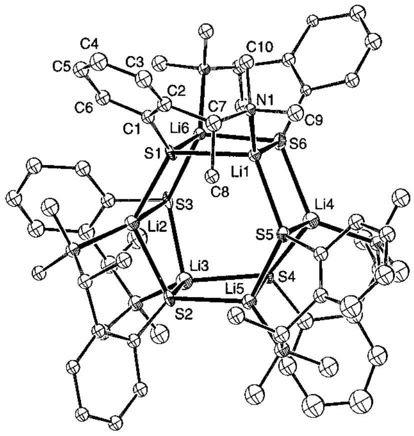

Figure 2. ORTEP drawing at 30% probability level of **3** (with the exclusion of the hydrogen atoms). Selected ranges of bond lengths (Å) and angles (deg): (within top and bottom layers) Li−S = 2.34(2)−2.51(2), Li···Li = 4.13(3)−4.37(3), Li−N = 2.04(2)−2.16(2), S−C = 1.72(2)−1.77(1), Li−S−Li = 117.4(7)−134.3(8), S−Li−S = 97.8(9)−120.2(8); (between top and bottom layers) Li−S = 2.43(3)−2.73(2), Li···Li = 3.21(3)−3.51(3), Li−S−Li (within the chelate) = 77.5(8)−83.8(8), Li−S−Li (to neighboring chelate) = 81.6(8)−89.7(8), S−Li−S (within the chelate) = 93.0(8)−102.5(9), S−Li−S (to neighboring chelate) = 87.8(7)−96.6(9).

$[Li\{SC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2\}]_2$ (5). To a THF (60 mL) solution of **1c** (7.43 g, 40 mmol) cooled at −40 °C was added in one portion sublimed sulfur (1.29 g, 40 mmol). After being stirred for 20 min, the reaction mixture was allowed to warm to room temperature. Stirring for another 2 h, evaporating all volatiles *in vacuo*, and subsequent washing of the solid with pentane (twice 30 mL) yielded 8.41 g (39 mmol, 98%) of **5**. Transparent white crystals could be obtained by slow diffusion of pentane into a saturated THF/toluene solution of **5**; mp 198 °C (dec). ^{1}H NMR (dichloromethane-d_2, 200 MHz, 223 K; ppm): δ 2.07 (s, 3H, NMe), 2.51 (td, 1H, $^{2}J = -13.32$ Hz, $^{3}J = 11.06$ Hz, $^{3}J = 2.68$ Hz, NCH_2), 2.57 (d, 1H, $^{2}J = 11$ Hz, $ArCH_2$), 3.00 (td, 1H, $^{2}J = -13.32$ Hz, $^{3}J = 3.11$ Hz, $^{3}J = 1.65$ Hz, NCH_2), 3.17 (s, 3H, OMe), 3.53 (dt, 1H, $^{2}J = -9.15$ Hz, $^{3}J = 3.11$ Hz, $^{3}J = 2.68$ Hz, CH_2O), 3.96 (td, 1H, $^{2}J = -9.15$ Hz, $^{3}J = 11.06$ Hz, $^{3}J = 1.65$ Hz, CH_2O), 4.38 (d, 1H, $^{2}J = 11$ Hz, $ArCH_2$), 6.76 (t, 1H, $^{3}J = 7$ Hz, ArH-4), 6.85 (d, 1H, $^{3}J = 7$ Hz, ArH-3), 6.93 (t, 1H, $^{3}J = 7$ Hz, ArH-5), 7.30 (d, 1H, $^{3}J = 7$ Hz, ArH-6). Anal. Calcd for $C_{22}H_{32}N_2O_2S_2Li_2$: C, 60.68; H, 7.41; N, 6.36. Found: C, 60.81; H, 7.42; N, 6.45.

$[Li_2\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}(I)(THF)_2]$ (6). To a solution of **4** (0.54 g, 2.34 mmol) in benzene (30 mL) was added LiI (0.31 g, 2.34 mmol) in one portion. After stirring for 1 h, all volatiles were removed *in vacuo*, resulting in crude **6** as a cream solid. Crystallization by diffusion of pentane into a toluene solution (a few drops of THF added to solubilize all material) yielded 0.77 g (91%) of brownish crystals; mp 119 °C (dec). ^{1}H NMR (toluene-d_8, 200 K; ppm): δ 1.38 (br m, 8H, THF), 2.10 (s, 6H, NMe), 2.15 (s, 6H, NMe), 2.58 (d, 2H, $^{2}J = 10$ Hz, CH_2), 3.71 (m, 8H, THF), 4.63 (d, 2H, $^{2}J = 10$ Hz, CH_2), 6.7−7.4 (m, 3H, ArH). ^{13}C NMR (toluene-d_8; ppm): δ 25.7 (THF), 46.6 (br s, NMe_2), 66.8 (br s, CH_2), 68.5 (THF), 120.2 (Ar-2,6), 131.7 (Ar-4), 137.5 (Ar-3,5), 139.3 (Ar-1). Anal. Calcd for $C_{20}H_{35}N_2O_2SLi_2I$: C, 47.25; H, 6.94; N, 5.51. Found: C, 47.06; H, 6.91; N, 5.56.

Structure Determination and Refinement of 3−6. Full experimental data for the X-ray single crystal diffraction studies of **3** and **4** are to be found in the deposited Supporting Information; selected geometrical data are included in the captions to Figures 2 and 3, respectively. X-ray data (total/unique reflections: 11351/5396 with $-22 \leq h \leq 21$, $-10 \leq k \leq 0$, $-22 \leq l \leq 23$ for **5** and 3951/3556 with $0 \leq h \leq 15$, $-13 \leq k \leq 0$, $-18 \leq l \leq 18$ for **6**) were collected on an Enraf-Nonius CAD4T rotating anode diffractometer for a colorless (0.40 × 0.50 × 0.60 mm for **5**) or brownish (0.80 × 0.80 × 0.90 mm for **6**) block-shaped crystal glued on top of a glass fiber. Accurate unit-cell parameters and an orientation matrix were derived from the setting angles of 25 well-centered reflections (SET4)[7] in the range $8° < \theta <$

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(6) (a) Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490−5492. (b) Jastrzebski, J. T. B. H; van Koten, G. *Inorg. Synth.* **1989**, *26*, 150−155.

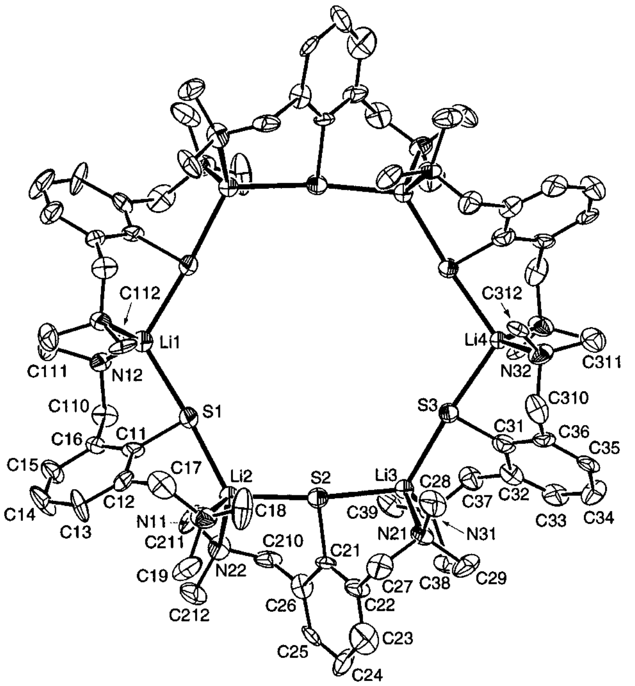


Figure 3. ORTEP drawing at 50% probability level of **4** (with the exclusion of the hydrogen atoms). Selected bond lengths (Å) and angles (deg): Li1−S1 = 2.426(10), Li2−S1 = 2.401(15), Li2−S2 = 2.417(13), Li3−S2 = 2.392(13), Li3−S3 = 2.403(15), Li4−S3 = 2.401(10), Li1−N12 = 2.138(13), Li2−N11 = 2.17(2), Li2−N22 = 2.160(19), Li3−N21 = 2.173(17), Li3−N31 = 2.116(17), Li4−N32 = 2.124(13), Li1−S1−Li2 = 175.7(5), Li2−S2−Li3 = 170.6(6), Li3−S3−Li4 = 171.2(4), S1−Li1−S1a = 117.5(8), S1−Li1−N12 = 97.5(2), S1−Li1−N12a = 116.9(3), N12−Li1−N12a = 115.8(9), S1−Li2−S2 = 118.6(6), S2−Li3−S3 = 125.5(6), S3−Li4−S3a = 110.3(7).

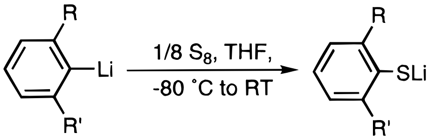
14°. The unit-cell parameters were checked for the presence of higher lattice symmetry.[8] Data were corrected for Lorentz and polarization effects. Anisotropic scaling was applied for both **5** and **6** (DIFABS[9] as implemented in PLATON[10]). The structures were solved by direct methods and subsequent difference Fourier techniques (SHELXS86[11] for **5**; DIRDIF92[12] for **6**). Refinement of the structures of **5** and **6** was carried out on F^2 by full-matrix least-squares techniques (SHELXL93[13]); no observance criterion was applied during refinement (number of least-squares parameters: 275 and 258 for **5** and **6**, respectively). In the structure determinations of **5** and **6** all non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were introduced on calculated positions (C−H = 0.98 Å) and refined by riding on their carrier atoms with a fixed isotropic atomic displacement parameter amounting to 1.5 or 1.2 times the value of the equivalent isotropic atomic displacement parameter of their carrier atom. An extinction correction was not found to be necessary. Weights were optimized in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography.[14] Geometrical calculations and illustrations were performed with PLATON;[10] all calculations were performed on a DEC5000 cluster. Collected data and details of data collection and refinement of **5** and **6** are in Table 1.

Table 1. Experimental Data for the X-ray Diffraction Studies of **5** and **6**

	5	**6**
formula	$C_{22}H_{32}Li_2N_2O_2S_2$	$C_{20}H_{35}ILi_2N_2O_2S$
fw	434.52	508.36
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
cryst syst	monoclinic	monoclinic
Z	4	4
a (Å)	17.7963 (9)	13.0346 (10)
b (Å)	8.1281 (7)	11.523 (3)
c (Å)	17.1340 (10)	16.127 (3)
β (deg)	108.288 (5)	94.682 (10)
vol (Å^3)	2353.3 (3)	2414.2 (8)
d_{calc} (g·cm^{-3})	1.226	1.399
μ(Mo Kα) (cm^{-1})	2.3	14.1
radiation (Å)	Mo Kα (0.710 73)[a]	Mo Kα (0.710 73)[a]
temp (K)	150	150
R^b	00.047	0.059
R_{w2}	0.138	0.170

[a] Graphite monochromator. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. Refinement on F^2: $R_{w2} = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Scheme 1. Synthesis of Lithium Arenethiolates **3**−**5**



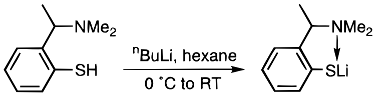
3: R = CH(Me)NMe$_2$, R' = H
4: R = R' = CH$_2$NMe$_2$
5: R = CH$_2$N(Me)CH$_2$CH$_2$OMe, R' = H

Results

Reaction of the known aryllithium reagents LiC$_6$H$_4$((*R*)-CH-(Me)NMe$_2$)-2 (**1a**), LiC$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6 (**1b**), and LiC$_6$H$_4$-(CH$_2$N(Me)CH$_2$CH$_2$OMe)-2 (**1c**) with 1 equiv of sulfur (1/8 S$_8$) in THF at low temperature (Scheme 1) results in virtually quantitative formation of the corresponding lithium arenethiolates [Li{SC$_6$H$_4$((*R*)-CH(Me)NMe$_2$)-2}]$_6$ (**3**), [Li{SC$_6$H$_3$(CH$_2$-NMe$_2$)$_2$-2,6}]$_6$ (**4**), and [Li{SC$_6$H$_4$(CH$_2$N(Me)CH$_2$CH$_2$OMe)-2}]$_2$ (**5**). These new complexes have a strong tendency to incorporate THF (a Lewis base), and *via* this route complex **3** could in fact only be isolated as a THF adduct [Li{SC$_6$H$_4$((*R*)-CH(Me)NMe$_2$)-2}]·*n*THF in which *n* is not precisely defined but lies between 1 and 3.

For the success of this synthetic procedure it is of utmost importance that the reagents are very thoroughly mixed; poor stirring of the reaction mixture leads to the formation of unwanted byproducts such as polysulfido complexes, whose presence complicates the isolation of the desired lithium arenethiolate.

Another synthetic route to lithium arenethiolates such as **3**−**5**, which has been used before in metal thiolate chemistry, is deprotonation of an arenethiol.[15] This route was necessary for the preparation of pure solvent-free **3**; reaction of the arenethiol HSC$_6$H$_4$((*R*)-CH(Me)NMe$_2$)-2 (**2**) with 1 equiv of ^{n}BuLi in hexane affords **3** in high yield (eq 1).



(1)

2 **3**

In principle this method is also suitable for the synthesis of **4** and **5**, but the corresponding arenethiols are difficult to obtain

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(11) Sheldrick, G. M. *SHELXS86. Program for crystal structure determination*, University of Göttingen: Göttingen, Germany, 1986.
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(14) Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.
(15) Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 4231−4234.

in pure form and the preferred synthetic method is the sulfur insertion with aryllithium reagents (Scheme 1). Compounds **4** and **5** obtained by this former route, when first isolated, also contain THF, but in these cases the pure THF-free complexes can be obtained by repeated washings with pentane.

The pure THF-free lithium arenethiolates **3**−**5** are yellowish, off-white powders which, although slightly hygroscopic, can be handled safely in air for several minutes. Their solutions slowly decompose upon exposure to air. Complexes **3**−**5** are readily soluble in Et_2O and THF and somewhat less soluble in benzene and toluene. The lithium arenethiolates **3** and **4** are also slightly soluble in hexane, whereas **5** is insoluble in both pentane and hexane.

Solid State Structures of 3 and 4. The natures of **3** and **4** in the solid state have been determined by X-ray crystallography, but because of the rather low quality of the data sets and the presence of disordered solvent (**4**), only a brief description of these structures is provided here. Further details are available in the Supporting Information.

The molecular structure of **3** (Figure 2) shows it to be a hexameric cage aggregate which comprises six lithium arenethiolate moieties arranged such that the Li and S atoms form a distorted hexagonal prism. In this aggregate there are two layers of cyclohexane-like Li_3S_3 six-membered rings, with alternating Li and S atoms that are both in a chair conformation. The aryl rings of the arenethiolate ligands occupy equatorial positions with respect to the Li_3S_3 rings, and within each Li_3S_3 layer the arenethiolate ligands intramolecularly coordinate through the CH(Me)NMe_2 group to the neighboring lithium atom. Each sulfur atom is bonded not only to two lithium neighbors within each Li_3S_3 ring but also to one lithium atom from the opposite Li_3S_3 layer, resulting in a μ^3-bonding of each arenethiolate ligand. Through this bonding and the intramolecular CH(Me)NMe_2 coordination, the lithium atoms are tetrahedrally coordinated. Complex **3** was synthesized with an enantiopure arenethiolate ligand, and each Li_3S_3 layer has identical propeller-type chirality. This structure has various features present in the nonameric copper(I) arenethiolate $[Cu\{S\text{-}1\text{-}C_{10}H_6NMe_2\text{-}8\}]_9$ and the *N*-chelated aryllithium complexes $[Li\{C_6H_4CH_2NMe_2\text{-}2\}]_4$ [6b] and $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$.[16]

Lithium arenethiolate **4** (Figure 3) has an hexameric structure based on a central essentially planar Li_6S_6 12-membered ring in which there are alternating Li and S atoms. This structure contrasts dramatically with the prismatic structure of **3**. The most striking feature in the structure of **4** is that the central hexagonally shaped Li_6S_6 ring contains arenethiolate sulfur atoms that have a T-shaped geometry as a result of bonding to two lithium atoms and the C_{ipso} atom of the ligand system. In **4** the arenethiolate ligands *S*-bridge between neighboring lithium centers whose coordination sphere is completed by N-coordination of two CH_2NMe_2 substituents from different ligand systems. The orientation of the aryl ring in the ligands with respect to the Li_6S_6 ring provides an overall "propeller-like" aggregate with each hexamer having screw-type chirality. Due to crystallographic symmetry both enantiomers are present in the crystal.

Solid State Structure of 5. The molecular structure of complex **5**, $[Li\{SC_6H_4(CH_2N(Me)CH_2CH_2OMe)\text{-}2\}]_2$, as determined by X-ray diffraction, shows **5**, in contrast to the hexamers **3** and **4**, to be a dimer in the solid state (Figure 4). Selected bond distances and bond angles are listed in Table 2.

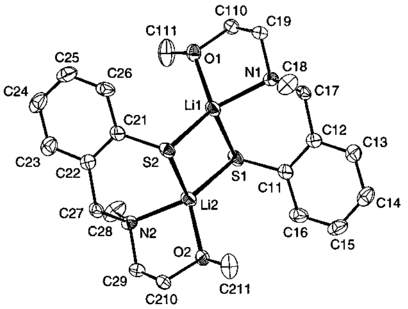

Figure 4. ORTEP drawing at 50% probability level of **5** (with the exclusion of the hydrogen atoms).

Table 2. Selected Geometrical Details of **5**[a]

Bond Distances (Å)			
Li1−S1	2.424(3)	Li1−O1	1.974(4)
Li1−S2	2.430(2)	Li2−O2	1.960(4)
Li2−S1	2.426(3)	Li1···Li2	2.899(4)
Li2−S2	2.427(3)	S1−C11	1.768(2)
Li1−N1	2.068(4)	S2−C21	1.761(2)
Li2−N2	2.068(4)		
Bond Angles (deg)			
Li1−S1−Li2	73.41(10)	S1−Li1−N1	100.56(13)
Li1−S2−Li2	73.29(11)	S2−Li2−N2	100.44(14)
S1−Li1−S2	106.61(11)	Li1−S1−C11	95.50(10)
S1−Li2−S2	106.66(12)	Li2−S1−C11	98.36(10)

[a] The estimated standard deviations of the last significant digits are shown in parentheses.

The structure of **5** comprises two arenethiolate ligands which each S-bridge two lithium atoms, thereby forming a planar central Li_2S_2 moiety (the largest deviation from planarity is 0.011(4) Å). The aryl substituents of these ligands are positioned above and below the two sulfur atoms of the Li_2S_2 plane, as is shown by the angles Li1−S1−C11, Li2−S1−C11, Li1−S2−C21, and Li2−S2−C21, which are 95.50(10), 98.36(10), 96.60(10), and 97.73(10)°, respectively. Additionally, the nitrogen and oxygen atoms from one arenethiolate ligand coordinate to the same lithium atom, thus resulting in S, S, N, O tetrahedrally coordinated lithium atoms. The tetrahedral geometry around lithium is not regular but has distortion that arises from the restrictions of the five- and six-membered chelate rings that have been formed, *i.e.*, Li−O−C−C−N and Li−S−C−C−C−N; illustrative angles are S1−Li1−N1, S2−Li2−N2, N1−Li1−O1, and N2−Li2−O2, which are 100.56(13), 100.44(14), 87.62(12), and 87.52(14)°, respectively.

The Li-S distances within the Li_2S_2 moiety are Li1−S1 = 2.424(3), Li1−S2 = 2.430(2), Li2−S1 = 2.426(3), and Li2−S2 = 2.427(3) Å, respectively, and these clearly point to a symmetrical binding of the sulfur atom of the arenethiolates to the lithium atoms. Moreover, these Li−S distances are comparable to those in the structures of **3** and **4**. In contrast to the latter structures, the angles Li1−S1−Li2 and Li1−S2−Li2 in **5** of 73.41(10) and 73.29(11)° are remarkably acute and similar to the acute Cu−S−Cu angles often encountered in copper(I) arenethiolate structures. In copper arenethiolate chemistry the acute Cu−S−Cu angles have been ascribed to the formation of two-electron three-center bonds.[1]

Solution Structures of 3−**5.** The ^1H NMR spectra of **3** in toluene-d_8 are temperature dependent. Above 343 K, the ^1H NMR spectrum of **3** is simple and consists of characteristic resonances for the arenethiolate ligand: *i.e.*, a doublet for the α-methyl protons, a broad singlet for the dimethylamino protons, a very broad signal for the benzylic proton, and a set of aromatic resonances. The proton which is positioned *ortho* to the sulfur atom is observed as a characteristic doublet at 7.75 ppm in a position that is significantly low-field of the resonance of the corresponding proton of (*R*)-α-methyl-*N*,*N*-dimethylbenzylamine. A low-field shift for the *ortho*-proton is typical for

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(16) (a) van der Zeijden, A. A. H.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 431−433. (b) Smeets, W. J. J.; Spek, A. L.; van der Zeijden, A. A. H.; van Koten, G. *Acta Crystallogr.* **1987**, *C43*, 1429−1430.

this type of arenethiolate ligand and is also observed for the starting arenethiol[1a] and for other metal arenethiolates.[1,5,17,18]

On cooling down from 343 K, there are significant changes of which the most striking is that the dimethylamino signal becomes broader and starts to decoalesce at 313 K into two singlets at 283 K (one singlet is initially hidden underneath the α-methyl signal). The slow-exchange spectrum is reached at 253 K. Both the high- and low-temperature spectra of **3** are in agreement with a highly symmetric structure as only one ligand pattern is observed over the whole temperature range of 203−353 K. This is in agreement with the hexagonal prismatic structure of **3** found in the solid state (Figure 2). The two singlet signals for the dimethylamino group found in the low-temperature ^{1}H NMR spectrum of **3** is typical for this type of benzylamine ligand when lithium−nitrogen coordination is present on the NMR time scale. At higher temperatures the signal broadening is the result of N donor association/dissociation processes, and the calculated energy barrier ($\Delta G^{\ddagger}$) for this is 61 kJ/mol.[19]

For the lithium arenethiolate **4**, the ^{1}H NMR spectrum at elevated temperatures (320 K) in toluene-d_8 consists of a set of well-resolved resonances from the aromatic protons and broad singlets for the CH_2 and NMe_2 groups of the arenethiolate ligands. Upon cooling, the ^{1}H NMR spectrum of **4** changes significantly: at first the two well-resolved aromatic resonances broaden, and upon further cooling the CH_2 resonance decoalesces (305 K) into two broad signals at 4.5 and 2.4 ppm. The dimethylamino resonance decoalesces at 275 K into several broad resonances. At low temperature the broad signal patterns are consistent with a planar hexameric structure like that in the solid state. We believe that the fluxional processes occurring in solution involve N → Li association/dissociation similar to that found in **3**. Unfortunately, due to the broadness of the signals in the ^{1}H NMR spectra of **4**, the calculated energy barrier $\Delta G^{\ddagger}$ could only be estimated and is approximately 55 kJ/mol.

The ^{1}H NMR data of lithium arenethiolate **5** in solution are slightly different from those of **3** and **4**. At 297 K, the ^{1}H NMR spectrum of **5** in CD_2Cl_2 comprises sharp singlet resonances for the methylamino (NMe) and the methoxy (OMe) groups (2.06 and 3.30 ppm, respectively), six broad multiplet patterns in the region of 2.0−4.5 ppm arising from the benzylic protons (AB system) and the protons in the 2-methoxyethylamine chelate ring (ABCD pattern), and a set of well-resolved signals for the aromatic protons: one triplet of doublets at 6.72 ppm (ArH-4), one doublet of doublets, and one triplet of doublets (partially overlapping) at 6.88 (ArH-5) and 7.02 (ArH-3) ppm, respectively, and finally one doublet of doublets at 7.37 ppm from the hydrogen atom positioned *ortho* to the sulfur (ArH-6). Upon cooling, the NMe, OMe, and aromatic signals remain virtually identical to those observed at 297 K. However, the initially broad signals from the benzylic protons become resolved at 223 K as two doublets, while, simultaneously, the protons in the 2-methoxyethylamine chelate ring provide what appears to be two doublets and two triplets. In fact the latter signals are ddd and td patterns, respectively, similar to those observed in ethanediamine chelates.[20] The NCH_2CH_2O multiplet resonances in the spectrum of **5** at 223 K are sufficiently resolved so that, after trapezoidal and Gaussian multiplication, the vicinal coupling constants ^3J(H,H) can be measured (see Experimental Section).

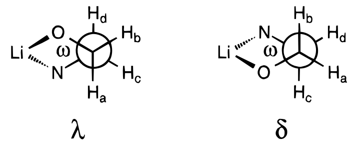


Figure 5. Newman projections along the C−C bond of the 2-methoxyethylamine chelate ring for the λ- and δ-conformations.

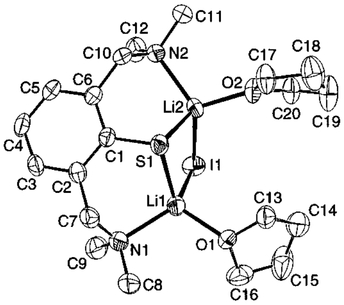
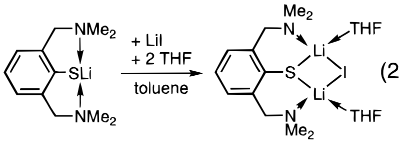


Figure 6. ORTEP drawing at 50% probability level of **6** (with the exclusion of the hydrogen atoms).

These ^{1}H NMR coupling data were, after spectral simulation and iteration,[21] used to obtain further information as to the structure of **5** in solution. Use of the Karplus equations[22] allows a conformational analysis of the λ (δ) conformation of the five-membered Li−O−C−C−N ring. For **5**, it is found that the ring is primarily ($n_\lambda = 0.99$) in the λ-conformation (Figure 5) in full agreement with the solid state structure, though the calculated value for ω of 65° is significantly larger than that of 57.3(2)° observed in the crystal.

Reaction of 4 with Lithium Iodide. Reaction of **4** with 1 equiv of LiI in toluene leads to the formation of $[Li\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}\cdot LiI]_n$, which, initially soluble in toluene, precipitates upon cooling. Crystallization by slow diffusion of pentane into a toluene solution at −20 °C (THF is added to solubilize all material) results in $[Li_2\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}(I)(THF)_2]$ (**6**) in quantitative yield (eq 2).



(2)

4 **6**

The mixed aggregate **6** is a beige, slightly hygroscopic solid which is soluble in most hydrocarbon solvents (Et_2O, THF, benzene, toluene, $CHCl_3$, and CH_2Cl_2) but insoluble in pentane and hexane.

Solid State Structure of 6. An X-ray diffraction study of **6** shows it to be a dinuclear mixed aggregate $[Li_2(SAr)(I)(THF)_2]$ (Figure 6, Table 3). The structure contains two lithium atoms that are bridged by the sulfur atom of the arenethiolate ligand and by one iodide, with one molecule of THF bonded to each lithium (Li1−O1 = 1.925(11) Å, Li2−O2 = 1.917(11) Å). Each lithium coordination sphere is completed by intramolecular

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(17) Janssen, M. D.; Grove, D. M.; van Koten, G.; Spek, A. L. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 286−292.

(18) Rijnberg, E.; Janssen, M. D.; Jastrzebski, J. T. B. H.; Boersma, J.; Spek, A. L.; van Koten, G. To be published.

(19) Eyring equation: $\Delta G^{\ddagger} = -RT_c \ln[2\pi h(\Delta\nu)/kT_c\sqrt{3}]$ with $\Delta G^{\ddagger}$ = free energy of activation (J), T_c = coalescence temperature (K), $\Delta\nu$ = chemical shift difference (Hz), and the other symbols have their usual meaning.

(20) Alsters, P. A.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831−1844.

(21) Using the simulation program gNMR by Cherwell Scientific Publishing.

(22) Karplus equations: $n_\lambda = [X\cos^2\omega - \cos^2(120 - \omega)]/[\alpha\cos^2(120 + \omega) - \cos^2(120 - \omega)]$; $n_\lambda = [Y\cos^2\omega - \alpha\cos^2(120 + \omega)]/[\cos^2(120 - \omega) - \alpha\cos^2(120 + \omega)]$; $n_\lambda + n_\delta = 1$; n_λ (n_δ) is the mole fraction of the λ (δ) conformation; $X = J_{a,d}/J_{a,c}$; and $Y = J_{b,c}/J_{a,c}$. A value of 1.208 was previously determined for α. (a) Sudmeier, J. L.; Blackmer, G. L. *Inorg. Chem.* **1971**, *10*, 2010. (b) Hawkins, C. J.; Peachey, R. M. *Aust. J. Chem.* **1976**, *29*, 33.

Table 3. Selected Geometrical Details of **6**[a]

Bond Distances (Å)			
Li1−S1	2.405(11)	Li1−N1	2.085(11)
Li2−S1	2.415(10)	Li2−N2	2.067(11)
Li1−I1	2.802(10)	Li1−O1	1.925(11)
Li2−I1	2.718(10	Li2−O2	1.917(11)
Li1···Li2	3.074(14)	S−C	1.770(6)
Bond Angles (deg)			
Li1−S1−Li2	79.3(3)	S1−Li1−N1	100.4(4)
Li1−I1−Li2	67.7(3)	S1−Li2−N2	100.8(4)
Li1−S1−C	93.7(3)	O1−Li1−N1	113.7(5)
Li2−S1−C	93.5(3)	O2−Li2−N2	110.6(5)

[a] The estimated standard deviations of the last significant digits are shown in parentheses.

N-donor ligation of one dimethylamino group from the SAr ligand (Li1−N1 = 2.085(11) Å, Li2−N2 = 2.067(11) Å).

In the structure of **6** the angle Li1−S1−Li2 of 79.3(3)° is acute and similar to those found in **5** (73.41(10) and 73.29(11)°). The Li−S distances of 2.405(11) and 2.415(11) Å are comparable to those in the other lithium arenethiolates in this study. The Li−I distances and the angle Li1−I−Li2 are 2.802(10), 2.718(10) Å and 67.7(3)°, respectively; these data are not unlike the distances and angles observed in the analogous complex $[Li_2\{OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4\}(I)]_2$, where they are 2.738(9), 2.814(8) Å and 61.6(3)°, respectively.[23]

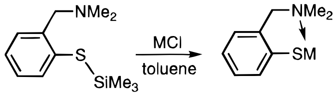
Solution Structure of 6. Variable-temperature ^1H NMR measurements of **6** are in agreement with the dinuclear structure observed in the solid state. The fast exchange spectrum (above 260 K) of **6** comprises a triplet and a doublet from the aromatic protons, a singlet for the CH_2 protons which lies with a multiplet from the THF molecules at 3.71 ppm, a singlet for the NMe_2 protons, and a second THF multiplet at 1.47 ppm. Upon lowering the temperature, the CH_2 signal at 3.71 decoalesces into two doublets (240 K), while the NMe_2 signal decoalesces (230 K) into two singlet signals. At 200 K the (slow-exchange) ^1H NMR spectrum shows two singlets for the NMe_2 entities and an AB pattern for the CH_2 moiety (two doublet signals), indicative of coordination of nitrogen to the lithium atoms. This leads to asymmetry within the CH_2NMe_2 substituent due to a different positioning of the methylenic hydrogen atoms in the chelate ring, but, due to an apparent mirror plane through the middle of the Li···Li vector and the atoms S1, C1, C4, and I1, the two CH_2NMe_2 substituents on the aryl nucleus remain equivalent. The calculated energy barrier ($\Delta G^{\ddagger}$) for the fluxionality in this complex that is believed to be based on N → Li association/dissociation processes is 46 KJ/mol.

Discussion

Synthetic Aspects. The insertion of elemental sulfur into the lithium carbon bond of an aryllithium reagent as described in this study is generally a straightforward method for the preparation of corresponding lithium arenethiolates such as **3**−**5**. The alternative synthetic procedure by deprotonation of arenethiols has been reported to give access to lithium, magnesium, and zinc arenethiolates but is limited to cases where the arenethiols are commercially or synthetically accessible.[15]

The major advantage of the sulfur insertion method over deprotonation is the enlarged accessible set of lithium arenethiolates, as the synthesis of aryllithium reagents is well-developed,[24] but it does have the minor disadvantage that donor solvent molecules may be retained by the lithium arenethiolate product. It is apparent from the series **3**−**6** that this tendency to retain coordinated solvent molecules decreases when more intramolecularly coordinating ligands are present. Actually, it proved impossible to isolate pure **3** from the sulfur insertion pathway since THF is used as a solvent in this route, and this complex was only prepared in a pure THF-free form *via* a deprotonation pathway. In contrast, **4** could only be successfully prepared by the sulfur insertion pathway. The alternative pathway to **4** from the corresponding arenethiol, *i.e.* $HSC_6H_3(CH_2NMe_2)_2\text{-}2,6$, is not applicable because it is difficult to extract from the aqueous media in which it is generated (from **4**). As already briefly mentioned, lithium arenethiolate complexes such as **3**−**6** are easily converted into the corresponding arenethiols by reaction with hydrochloric acid, and the sulfur insertion route may thus possess a very interesting synthetic potential for new thiol molecules. In this respect, the tendency of **3** and other related species to retain solvent molecules such as THF would not hamper its use for preparing the pure arenethiol.[1a]

We reported earlier that *in situ* prepared lithium arenethiolates ($[LiSAr]_n$) react with chlorotrimethylsilane to give trimethylsilylarenethioethers,[1b] Me_3SiSAr, and indeed when **3**−**5** are reacted with Me_3SiCl, the corresponding (trimethylsilyl)arene thioethers can be isolated pure in high yield. (Trimethylsilyl)arene thioethers are excellent starting materials for the preparation of various salt-free metal arenethiolate complexes (eq 3),[1b,c,5,17] and, moreover, their reaction with methyllithium can be used to generate the corresponding lithium arenethiolates.



(3)

MCl = CuCl, Zn(Me)Cl, 1/2 $ZnCl_2$, $PdCl_2$, Pd(SAr)Cl, 1/2 $PdCl_2$

Structures of 3−6 in the Solid State. From the structures of **3**−**6** it is clear that the structure and the aggregation state of lithium arenethiolates are very sensitive to changes in the chelating properties of the ligand. Similar structural sensitivity has been observed with phenolate ligands and, for example, the bidentate ligand $OC_6H_4(CH_2NMe_2)\text{-}2$ affords hexameric $[Na\{OC_6H_4(CH_2NMe_2)\text{-}2\}]_6$, while related $OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4$, with an extra nitrogen donor function, affords tetrameric $[Na\{OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4\}]_4$.[25] Moreover, the aggregation state of lithium arenethiolates and arenetellurolates is also very sensitive to the addition of external donor ligands such as THF or dimethoxyethane and recently a lithium arenetellurolate derived from ((dimethylamino)methyl)ferrocene was reported to be monomeric as a result of auxiliary coordination of dimethoxyethane.[26] Furthermore, pure lithium thiophenolate is polymeric, but addition of donor molecules such as THF and pyridine can result both in polymers with a lower bridging character of the arenethiolate sulfur atom, *e.g.*, $[(py)Li(\mu^3\text{-}SPh)]_\infty$ and $[(py)_2Li(\mu^2\text{-}SCH_2Ph)]_\infty$ or in formation of discrete aggregates such as $[(py)_3LiSC_6H_4Me\text{-}2]$.[27]

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Hexagonal prismatic structures such as that found for **3** are known for some lithium enolates,[28] but few precedents exist for hexagonal planar structures like that of **4**. To our knowledge the only related example is that of the lithium phenolate $[Li\{OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4\}]_3$, which forms a structure having a planar Li_3O_3 6-membered ring.[23] Dimeric structures such as that of **5** are more common.

Bonding in Lithium Arenethiolates. *Ab initio* calculations by Pappas[29] on complexes MSH (M = Li, Na, K, Be, Mg, Ca) indicate that the lithium−sulfur interaction is a typically ionic one in which almost no charge transfer occurs and where no covalent character is present. Typical bond distances and bond angles calculated for these systems are 2.198 Å for Li−S and 97.2° for Li−S−H,[29] although X-ray powder diffraction studies on metal methyl mercaptides, $MSCH_3$ (M = Li, Na, K),[31] as well as crystal structures of THF or pyridine solvated lithium thiolates indicate that a longer Li−S distance of about 2.4(2) Å is normal.[27]

The theoretical calculations imply that the structures of **3**−**6** are best described as cation−anion pairs $(Li^+)_6(SAr^-)_6$ (**3** and **4**), $(Li^+)_2(SAr^-)_2$ (**5**), and $(Li^+)_2(SAr^-)(I^-)(THF)_2$ (**6**), respectively, in which the lithium and sulfur atoms are held together by electrostatic attraction augmented by intramolecular Li−N coordination. The Li−S distances of **3**−**6** are normal for lithium thiolate structures, and comparison of these distances with those reported for other lithium thiolate structures shows that the Li−S distance is hardly influenced by the organic residue attached to sulfur.[27]

Although in some cases (*e.g.*, $[Li\{OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4\}]_3$) the explanation of flat $(ME)_n$ entities (M = Li, Zn; E = O, N) has been given in terms of quasi-aromaticity (since the M−E and $E-C_{ipso}$ distances are relatively short),[31] it is unlikely that the flat Li_6S_6 entity in **4** arises from quasi-aromaticity, since the Li−S distances as well as the $S-C_{ipso}$ distances are normal for lithium thiolates.

A more plausible explanation for occurrence of the Li_6S_6 cores in **3** and **4**, as well as for the T-shaped geometry of the arenethiolate sulfur atoms in **4**, is the involvement of sp^2-hybridized sulfur atoms in these structures, in combination with steric hindrance of the coordinating *ortho*-substituents and the rigidity of the Li−S−C−C−C−N chelates (only Li and N can move out of the plane of the aromatic ring) that leave little freedom in the positioning of the lithium atoms with respect to the sulfur atoms. It may thus be assumed that the polarizability of the sulfur atoms in combination with the design of the arenethiolate ligand dictates the aggregation state and resulting structure of the lithium arenethiolate complexes.

In contrast to the situation in **3** and **4**, the bonding mode of the arenethiolate ligand in **5** and **6** is best explained by a two-electron three-center (2e−3c) description as proposed for the structures of copper(I) arenethiolate complexes. In these latter cases the nature of the arenethiolate ligand is also found to have a great influence on the structure of the complex.[1]

Structures of 3−6 in Solution. As described in the results section, the lithium arenethiolates **3**−**6** have overall structures in solution that correspond to those in the solid state. However, the N → Li coordination is not particularly strong, and in solution one observes fluxional processes similar to those found for amine-coordinated aryllithium compounds.[32] We believe that this fluxional behavior is based on lithium−nitrogen association/dissociation processes which have also been described for the aryllithium and lithium phenolate analogues, **1b**[6] and $[Li\{OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4\}]_3$.[23] This is furthermore corroborated by the observation that small amounts of THF result in broad NMe_2 and CH_2 signals in the ^1H NMR spectra of **4** (even at low temperature), *i.e.*, THF competes with the nitrogen coordination in **4**. However, the presence of other chelation isomers formed by selective THF coordination to lithium, as recently established by Reich and Gudmundsson with ^{15}N NMR spectroscopy, cannot be excluded.[33]

Conclusions

The results presented on aggregates **3**−**6** represent the first detailed structural studies of lithium arenethiolates with intramolecular coordination, and they nicely demonstrate the variety of coordination that is possible with substituted arenethiolate ligands. Moreover, the design of the arenethiolate ligand is crucial in determining the aggregation state and the structure of the resulting complex, both in the solid state and in solution. To explain various structural features in these complexes, we propose bonding models involving different types of sulfur hybridization.

The lithium arenethiolate complexes are excellent starting materials for the synthesis of trimethylsilyl-arenethioethers and thereby also for a diversity of salt-free metal arenethiolates.

Acknowledgment. This work was supported in part (A.L.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supporting Information Available: Tables of data and details of the structure determination, all atomic positional parameters, thermal parameters, bond lengths, and bond angles (32 pages). Ordering information is given on any current masthead page.

IC960075X

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