Ortho versus α-Metalation of Ethyl Phenyl Sulfide by *n*-Butyllithium/*N,N,N′,N′*-Tetramethylethylenediamine: Synthesis, Reactivity, and Crystal Structures of (2-(Ethylthio)phenyl)- and (1-(Phenylthio)ethyl)lithium

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Metalation of ethyl phenyl sulfide by *n*-BuLi/tmeda (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) is strongly solvent dependent. In *n*-hexane and diethyl ether ortho lithiation took place, yielding (2-(ethylthio)phenyl)lithium, while in tetrahydrofuran (THF) α-lithiation occurred, yielding (1-(phenylthio)ethyl)lithium. From *n*-hexane solutions [{Li(C₆H₄SEt-2)-(tmeda)}₂] (**4**) was isolated as a white powder. Dissolution of **4** in THF resulted in isomerization, forming quantitatively the α-lithiated compound [Li(CHMeSPh)(tmeda)] (**5**). Compounds **4** and **5** reacted with *n*-Bu₃SnCl, yielding *n*-Bu₃Sn(C₆H₄SEt-2) (**1a**) and *n*-Bu₃-SnCHMeSPh (**2a**), respectively. The identities of **4**, **5**, **1a**, and **2a** were confirmed by ¹H, ¹³C, and ¹¹⁹Sn (**1a/2a**) NMR measurements. Single-crystal X-ray diffraction analysis of **4** showed it to be dimeric, with a nonplanar four-membered ring composed of two lithium atoms and two ortho phenyl carbon atoms. The distorted-tetrahedral donor set of Li is completed by two nitrogen atoms (tmeda). Furthermore, from solutions of **4** in *n*-hexane crystals of [{Li(CHMeSPh)(tmeda)}₂(*μ*-tmeda)] (**5′**) were obtained. X-ray structure analysis revealed the presence of centrosymmetric dimers. The primary donor set of Li is made up of one carbon atom and three nitrogen atoms, two of them from a chelating tmeda and the other from a bridging tmeda ligand.

Introduction

α-Functionalized alkyllithium compounds of the type LiCHRYR′_n (R = alkyl, H) with Lewis basic heteroatoms Y (YR′_n = NR′₂, PR′₂, OR′, SR′, F, Cl, ...; R′ = alkyl, aryl, H) cover a wide range of stabilities, structures, and reactivities.[1] This can be understood in terms of an electronic and/or steric influence of the Lewis basic YR′_n group upon the neighboring Li−C bond or directly upon the Li atom. Sulfur-functionalized methyl compounds of the type LiCH₂SR′ have been well studied.[2] Thus, only recently has a pronounced relationship between the mononuclear structure of [Li(CH₂SPh)-(pmdta)] (pmdta = *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine) and its carbenoid reactivity been shown.[3] Less investigated are analogous α-sulfur-functionalized alkyllithium compounds of the type LiCHRSPh (R = alkyl). This may be due to competitive ortho and α-metalation.[4] As early as 1940 Gilman showed for alkyl

phenyl sulfides that lithiation of methyl phenyl sulfide by *n*-BuLi in diethyl ether afforded LiCH₂SPh, whereas such reactions of phenyl sulfides containing higher alkyl groups resulted in ortho lithiation.[5] Such (2-(alkylthio)-phenyl)lithium compounds proved to be versatile reagents in organic synthesis.[6] Furthermore, better selectivities in ortho lithiation have been achieved while using *n*-BuLi/tmeda instead of *n*-BuLi.[6,7] Benzyl phenyl sulfide was found to react with *n*-BuLi/tmeda in hexane to give the ortho-metalated product,[6] whereas with *n*-BuLi in THF/hexane α-metalation of the benzyl group occurred.[8] We here report reactions of ethyl phenyl sulfide with *n*-BuLi/tmeda, which were investigated in order to determine what factors influence ortho versus α-lithiation.

Results and Discussion

The reaction of ethyl phenyl sulfide with an equimolar amount of *n*-BuLi/tmeda followed by addition of an

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Scheme 1

1a (R = Me), **1b** (R = H)   **2a** (R = Me), **2b** (R = H)   **3**
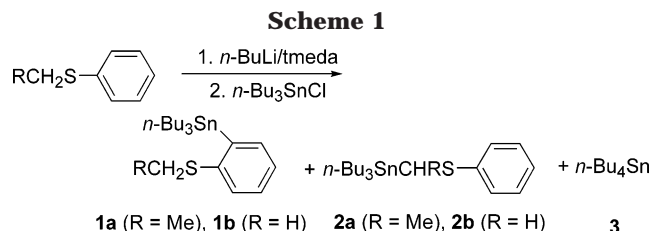
Table 1. Metalation of RCH₂SPh (R = Me, H) by
n-BuLi/tmeda According to Scheme 1[a]

R = Me

			product composition, mol %		
entry	solvent	time, h	**1a**	**2a**	**3**
1	n-hexane	24	70−75	5−10	0
2	n-hexane	1−2	10−20	1−2	75−85
3	Et₂O/n-hexane (4/1)	2[b]	70−80	8−12	5−10
4	THF/n-hexane (4/1)	1−2[b]	2−5	45−50	0

R = H

			product composition, mol %		
entry	solvent	time, h	**1b**	**2b**	**3**
5	n-hexane	24	0	90−95	0
6	n-hexane	1−2	<5	45−50	45−50

[a] The product composition is based on ¹¹⁹Sn spectroscopic investigations. [b] Addition of n-BuLi/tmeda at −78 °C.

equimolar amount of tri-n-butyltin chloride and analysis of the organotin product via ¹¹⁹Sn NMR spectroscopy showed a strong solvent influence on the course of the reaction (Scheme 1, Table 1). In n-hexane and diethyl ether ortho metalation was the predominant reaction; α-metalation occurred only to a minor extent. Comparison of entries 2 and 3 (Table 1) shows that in diethyl ether the reaction proceeded much faster. On the other hand, in tetrahydrofuran predominantly α-metalation occurred; the relatively low yield of about 50% resulted from the limited stability of n-BuLi/tmeda in THF.[9] For comparison, methyl phenyl sulfide was metalated with n-BuLi/tmeda in n-hexane under the same conditions. After 24 h only α-metalated product was observed. During shorter reaction times formation of smaller amounts of ortho-metalated product was observed, indicating that this is the kinetically favored process, as already stated in refs 1a and 7. Comparison of entries 6 and 2 (Table 1) shows that metalation of methyl phenyl sulfide proceeded faster than that of ethyl phenyl sulfide. Metalation of MeSPh in more polar solvents (ether, THF, tmeda) is known to proceed also by α-metalation.[5,10−12]

Cooling the reaction mixture of ethyl phenyl sulfide with n-BuLi/tmeda in n-hexane to −78 °C resulted in precipitation of the ortho-metalated product [{Li(C₆H₄-SEt-2)(tmeda)}₂] (**4**), which was isolated as a white powder in 60% yield (Scheme 2). In air **4** immediately went up in smoke. Even storage under argon at room temperature for 1 week resulted in decomposition, whereas at −40 °C no decomposition occurred over

several weeks. Solutions of **4** in n-hexane were not stable at room temperature, as indicated by a color change from yellowish via orange (after 1−2 h) and then to brown within several days. At −78 °C addition of a solution of n-Bu₃SnCl in n-hexane to a solution of [{Li-(C₆H₄SEt-2)(tmeda)}₂] (**4**) in n-hexane resulted in formation of n-Bu₃Sn(C₆H₄SEt-2) (**1a**), which was isolated in 49% yield as a colorless air-stable liquid: bp 135−142 °C at 0.02 Torr (Scheme 2).

The identities of **4** and **1a** were unambiguously proved by NMR spectroscopy, and that of **4** was also proved by a single-crystal X-ray diffraction analysis. ¹³C NMR spectra of **4** in perdeuterated n-hexane and benzene show six singlet resonances for aromatic C atoms, proving the presence of an unsymmetrically disubstituted benzene derivative. The two ipso C atoms were found to be strongly shifted to low field at 151.9/152.4 ppm (i-C$_{SEt}$, C₆D₁₄/C₆D₆) and 185.7/185.5 ppm (i-C$_{Li}$, C₆D₁₄/C₆D₆). In comparison with PhLi, the resonance of the ipso-C−Li atom is shifted to low field by about 14 ppm.[13] The presence of a nonlithiated α-methylene group is clearly indicated in ¹H NMR spectra, showing triplet and quadruplet resonances for CH₃CH₂S groups (CH₃, 1.43/1.29 ppm; CH₂, 2.89/2.79 ppm; C₆D₁₄/C₆D₆) with the correct 3:2 intensity ratio. The identity of the ortho-metalated tin compound **1a** was confirmed by ¹H and ¹³C NMR spectra. The magnitude of the coupling constant in **1a** (¹J(Sn, C$_{Bu}$) = 346.0 Hz) compared with that in the parent compound n-Bu₃SnPh (339.7 Hz)[14] indicates that o-SEt substitution results in a diminished electronic influence of the aryl ligand.[15]

Dissolving the ortho-lithiated compound **4** in THF-d_8 resulted immediately in nearly quantitative isomerization to the α-metalated lithium compound [Li-(CHMeSPh)(tmeda)] (**5**) (Scheme 2). As expected, reaction of **5** with n-Bu₃SnCl afforded n-Bu₃SnCHMeSPh (**2a**), which was isolated as a colorless air-stable liquid (bp 146−148 °C at 0.01 Torr) in 35% yield. The identities of compounds **5** and **2a** followed unambiguosly from the ¹H, ¹³C, and ¹¹⁹Sn NMR spectra. The ¹³C NMR spectrum of **5** shows four singlet resonances for aromatic carbon atoms, as expected for a monosubstituted benzene derivative. The resonance of the ipso carbon atom is essentially the same as that of the corresponding C atom in the ortho-metalated compound **4** (152.1 vs 152.4/151.9 ppm). α-Metalation results in a strong high-field shift of the methlyene carbon atom (27.6 ppm in PhSEt[16] vs 12.8 ppm in **5**) and in a strong low-field shift of the methyl carbon atom (14.3 ppm in PhSEt[16] vs 22.4 ppm in **5**). Further proof for α-metalation came from the ¹H NMR spectrum, showing for the SCHLiCH_3 unit doublet and quadruplet resonances in the correct 3:1 intensity ratio. In comparison with the nonmetalated thioether, the methine proton is shifted strongly to high field in **5** (2.94 versus 1.27 ppm). α-Metalation in the tin compound **2a** is clearly proved by the ¹H and ¹³C NMR spectra. The coupling constant ¹J(Sn, C$_{Bu}$) = 323.6 Hz in **2a** is smaller by 10.7 Hz than that in n-Bu₃SnCH₂-SPh (334.3 Hz).[17] Thus, as expected, substitution of H

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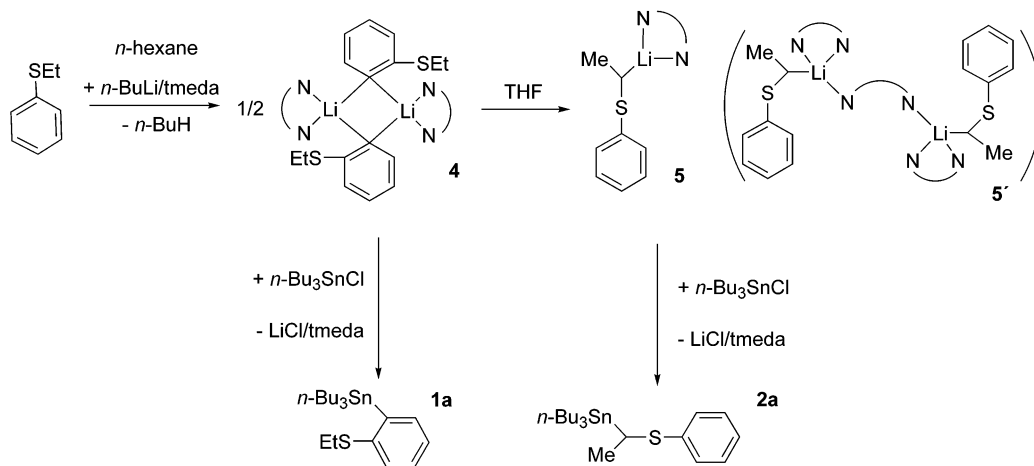(14) Al-Allaf, T. A. K. *J. Organomet. Chem.* **1986**, *306*, 337−346.
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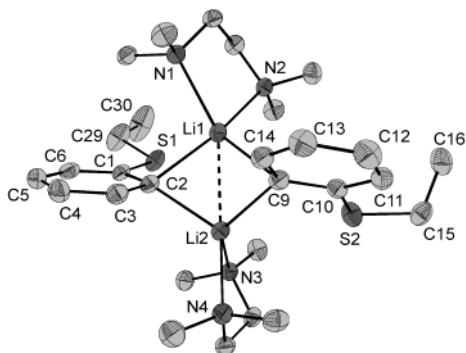(16) Linnert, M. Diplomarbeit, Universität Halle, 2002.
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Scheme 2

by Me in the methylene group ($SnCH_2S$ versus $SnCH-(Me)S$) results in an increased electronic influence of the α-thioalkyl ligand.

Crystals (colorless blocks) of compound **4** suitable for single-crystal X-ray diffraction analysis were grown from *n*-hexane solution at −40 °C. After several weeks (−40 °C) a few single yellowish crystals of [{Li-(CHMeSPh)(tmeda)}₂(μ-tmeda)] (**5′**) precipitated from these solutions. Compound **4** crystallized as isolated dimeric molecules without unusual short interactions (shortest contact between non-hydrogen atoms: C20···C21′ 3.401(5) Å). The molecular structure of the dimer is shown in Figure 1, and selected bond lengths and angles are given in Table 2. The central four-membered Li_2C_2 ring is not planar; the dihedral angle C2−Li1−Li2−C9 is −147.1(2)°. The Li−C bond lengths are between 2.247(5) and 2.292(6) Å. The Li1···Li2

distance is 2.568(6) Å. The structure of the Li_2C_2 ring in **4** is very similar to that in the parent compound [{LiPh(tmeda)}₂] (Li···Li = 2.490(6) Å; C_i−Li···Li′−C_i′ = −146.6°; interplanar angle Ph/Li_2C_i 80.7°).[18] It is worth noting that in other tmeda adducts [{Li(tmeda)}₂-(μ-R)₂] with four-membered Li_2C_2 rings the torsion angles C_i−Li···Li′−C_i′ were found to be between ±149.3 and 180.0° (median 159.9°, n = 8 observations).[19] Thus, the ring puckering in **4** (−147.1(2)°) is the largest one.

The phenyl rings include angles of 78.0(2) and 68.9-(2)° with the Li1Li2C2 and Li1Li2C9 planes, respectively. With respect to the central Li_2C_2 ring the two ethylthio substituents are in syn positions. Thus, dimer **4** is a typical representative of an electron-deficient bonding of the lithium atoms that are bridging between sp^2-hybridized carbon atoms. The carbon atoms which are bonded to Li have small C−C−C angles (C1−C2−C3/C10−C9−C14 = 111.9(3)/111.3(3)°), while the neighboring C atoms in the phenyl rings have large C−C−C angles (124.0(3)−125.6(3)°). The same distortions were found in structurally analogous aryllithium compounds (C_o−C_i−C_o, median 112.5°, lower/upper quartile 112.2/113.4°, n = 108 observations; C_m−C_o−C_b, median 124.5°, lower/upper quartile 123.8/125.4°, n = 216 observations), in particular in the parent compound [{LiPh-(tmeda)}₂] (C_o−C_i−C_o = 111.8(3)° versus C_m−C_o−C_i = 123.7(2)/125.5(3)°).[18] Unexpectedly, in the solvate-free polymeric LiPh all C−C−C angles were found to be 120.0(5)°.[20]

The shortest Li···S separations in **4** are Li1···S1/Li2···S2 = 3.457(5)/3.504(5) Å and do not indicate sulfur coordination. These are much longer than those in [Li-{CH(*t*-Bu)SPh}(μ-tmeda)_{1/2}] (**6**) forming in the crystal

Figure 1. Solid-state structure of [{Li(C_6H_4SEt-2)(tmeda)}₂] (**4**; thermal ellipsoids at 25% probability). Hydrogen atoms were omitted for clarity.

**Table 2. Selected Interatomic Distances (in Å) and Angles (in deg) in [{Li(C_6H_4SEt-2)(tmeda)}₂] (4)**

Li1−C2	2.256(6)	S1−C1	1.785(3)
Li1−C9	2.278(5)	S1−C29	1.795(4)
Li2−C2	2.247(5)	S2−C10	1.789(3)
Li2−C9	2.292(6)	S2−C15	1.812(4)
Li1···Li2	2.568(6)	Li−N	2.164(5)−2.285(5)
Li1−C2−Li2	69.5(2)	N1−Li1−N2	83.2(2)
Li1−C9−Li2	68.4(2)	N3−Li2−N4	84.0(2)
C2−Li1−C9	104.6(2)	C1−S1−C29	105.3(2)
C2−Li2−C9	104.4(2)	C10−S2−C15	108.0(2)
C1−C2−C3	111.9(3)	C10−C9−C14	111.3(3)
C2−C1−C6	124.0(3)	C9−C14−C13	125.6(3)
C2−C3−C4	125.4(3)	C9−C10−C11	125.4(3)

one-dimensional infinite chains by bridging tmeda

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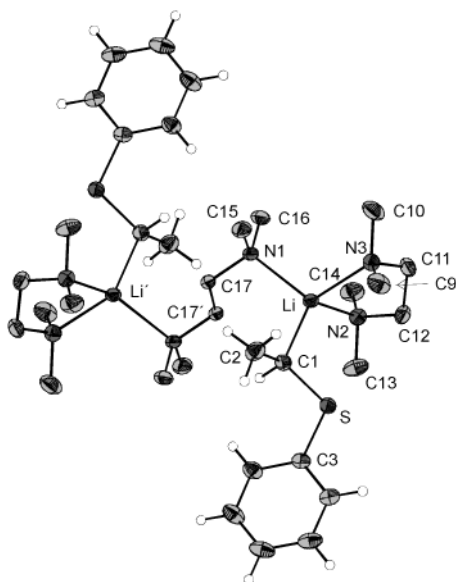
Figure 2. Solid-state structure of [{Li(CHMeSPh)(tmeda)}₂-(*u*−tmeda)] (**5′**; thermal ellipsoids at 25% probability). Hydrogen atoms of tmeda ligands were omitted for clarity. From disordered carbon atoms C11/C12 only the major occupied position (0.61) is shown.

Table 3. Selected Interatomic Distances (in Å) and Angles (in deg) in [{Li(CHMeSPh)(tmeda)}₂(*μ*-tmeda)] (5′)

Li−C1	2.184(2)	Li−N1	2.191(2)
S−C1	1.766(1)	Li−N2	2.183(2)
S−C3	1.779(1)	Li−N3	2.186(2)
C1−Li−N1	108.55(9)	N1−Li−N2	115.0(1)
C1−Li−N2	115.3(1)	N1−Li−N3	112.18(9)
C1−Li−N3	118.3(1)	N2−Li−N3	86.33(8)
C1−S−C3	110.18(6)		

ligands.[21] In **6** the Li atom has a distorted-tetrahedral coordination sphere consisting of two C atoms of phenyl rings, one N atom, and one S atom (Li−S = 2.712(5) Å).

Compound **5′** crystallized as isolated dimeric molecules. There are no unusual intermolecular contacts (shortest contact between non-hydrogen atoms: C10⋯C13″ = 3.635(3) Å). The dimer exhibits crystallographically imposed C_i symmetry. Its structure is shown in Figure 2. Selected bond lengths and angles are depicted in Table 3.

The lithium atoms are four-coordinate with a (distorted) tetrahedral coordination environment. The coordination tetrahedron is defined by one carbon atom and three nitrogen atoms belonging to a chelating and a bridging tmeda ligand. The chelating tmeda ligands form five-membered LiN₂C₂ rings exhibiting an approximate envelope conformation. Methylene carbon atoms C11/C12 of chelating tmeda ligands are disordered over two positions, corresponding to $\lambda\delta$ and $\delta\lambda$ isomers of the five-membered rings. Within the 3σ

criterion the Li−N bonds to the chelating and bridging tmeda ligands are of the same length (2.183(2)/2.186-(2) Å vs 2.191(2) Å). The (1-phenylthio)ethyl ligand is η¹ coordinated to Li with an Li−C1 distance of 2.184(2) Å.

The anion stabilizing effect of sulfur is mainly due to polarizability and negative hyperconjugation.[2,22] In accordance with that, α-lithiation gives rise to a substantial shortening of the S−C$_{alkyl}$ bond length (1.795(4)/1.812(4) Å in **4** versus 1.766(1) Å in **5′**). Although the lone pair on C1 is nearly in an antiperiplanar position to the σ*$_{S−Ph}$ orbital (Li−C1−S−C3 = −163.94(8)°), there is no lengthening of the S−C$_{Ph}$ bond (1.785(3)/1.789(3) Å in **4** vs 1.779(1) Å in **5′**). Analogous values were found in the solid-state structure of the monomeric [Li(CHPhSPh)(THF)₃] (S−C$_{benzyl}$ = 1.76(1) Å, S−C$_{Ph}$ = 1.771(9) Å)[8a] as well as in the parent compound LiCH₂-SPh with tmeda, pmdta, and THF coligands (S−CH₂ = 1.75(1)−1.780(7) Å, S−C$_{Ph}$ = 1.762(6)−1.81(2) Å).[3,11,23]

To summarize, the site of metalation of EtSPh by *n*-BuLi/tmeda is solvent dependent: in nonpolar and less polar solvents (*n*-hexane, Et₂O) ortho lithiation takes place, whereas in the more polar tetrahydrofuran α-lithiation occurs, yielding [{Li(C₆H₄SEt-2)(tmeda)}₂] (**4**) and [Li(CHMeSPh)(tmeda)] (**5**), respectively. For the first time, a solvent-induced isomerization of an ortho-metalated lithium compound into an α-metalated one (**4 → 5**) could be achieved. Recently, a slow THF-induced isomerization (at higher temperatures) of ortho-lithiated 1-methoxynaphthalene into the peri-lithiated species was observed.[24] Furthermore, to synthesize **5** via isomerization of **4** is superior to direct metalation of EtSPh by *n*-BuLi/tmeda in THF, due to its limited stability in this solvent. Investigations of the synthetic potential of this new route to synthesize α-sulfur-substituted alkyllithium compounds are in progress.

Experimental Section

All reactions and manipulations were carried out under purified argon using standard Schlenk techniques. Organotin compounds were handled in air. *n*-Hexane, THF-*d₈*, C₆D₆, and *n*-C₆D₁₄ were dried with LiAlH₄, and THF was distilled from sodium benzophenone ketyl. NMR spectra were recorded on Varian Gemini 200, Gemini 2000, and Unity 500 spectrometers using the protio impurities and the ¹³C resonances of the deuterated solvents as references for ¹H and ¹³C NMR spectroscopy, respectively. δ(¹¹⁹Sn) is relative to external SnMe₄ in C₆D₆.

General Procedure for Metalation of RCH₂SPh (R = Me, H). At 0 °C (using *n*-hexane) and −78 °C (using Et₂O/THF), respectively, to a stirred solution of *n*-BuLi in *n*-hexane (10 mmol, 1.5 M) was added the solvent (20−30 mL) listed in Table 1 and tmeda (10 mmol). Then, a solution of RCH₂SPh (10 mmol) in the solvent (5 mL) listed in Table 1 was added within 15 min. The mixture was warmed to room temperature and stirred for the time given in Table 1. A solution of *n*-Bu₃-SnCl (10 mmol) in the corresponding solvent (5 mL) was added at −78 °C, and the mixture was stirred for 24 h at room temperature. After the solvent was removed in vacuo, the residue was examined by ¹¹⁹Sn NMR spectroscopy in CDCl₃

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solution; proportionality between ^{119}Sn integrals and Sn portion was checked by measurements of pure tri-*n*-butyltin compounds as reference substances.

[{Li(C$_6$H$_4$SEt-2)(tmeda)}$_2$] (4). At 0 °C to a stirred solution of *n*-BuLi (50 mmol) in *n*-hexane (60 mL) was added dropwise a solution of tmeda (5.8 g, 50 mmol) in *n*-hexane (10 mL). After 15 min a solution of PhSEt (6.9 g, 50 mmol) in *n*-hexane (10 mL) was added dropwise. Stirring for 4 h gave a clear orange solution. Cooling to −78 °C resulted in precipitation of **4** as a white powder, which was filtered at that temperature, washed with *n*-hexane (2 × 10 mL), and dried in vacuo. Yield: 6.8 g (60%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.29 (t, $^3J_{H,H}$ = 7.47 Hz, 3H, C*H$_3$*CH$_2$S), 1.94−1.97 (m, 16H, tmeda), 2.79 (q, $^3J_{H,H}$ = 7.47 Hz, 2H, CH$_3$C*H$_2$*S), 6.98−7.13/8.07 (m/d, 3H/1H, C$_6$*H$_4$*). ^{1}H NMR (400 MHz, *n*-C$_6$D$_{14}$): δ 1.43 (t, $^3J_{H,H}$ = 7.47 Hz, 3H, C*H$_3$*CH$_2$S), 2.14 (s, C*H$_3$*N), 2.25 (s, C*H$_2$*N), 2.89 (q, $^3J_{H,H}$ = 7.47 Hz, 2H, CH$_3$C*H$_2$*S), 6.79/6.92/7.86 (m/t/d, 2H/1H/1H, C$_6$*H$_4$*). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 14.8 (s, *C*H$_3$CH$_2$S), 26.3 (s, CH$_3$*C*H$_2$S), 46.2 (s, *C*H$_3$N), 57.5 (s, *C*H$_2$N), 119.2/121.8/125.6/141.8 (s/s/s/s, C$_6$H$_4$), 152.4 (s, *i*-C$_{SEt}$), 185.5 (s, *i*-C$_{Li}$). ^{13}C NMR (100 MHz, *n*-C$_6$D$_{14}$): δ 14.8 (s, *C*H$_3$CH$_2$S), 26.6 (s, CH$_3$*C*H$_2$S), 46.3 (s, *C*H$_3$N), 57.7 (s, *C*H$_2$N), 119.2/121.7/125.3/141.4 (s/s/s/s, C$_6$H$_4$), 151.9 (s, *i*-C$_{SEt}$), 185.7 (s, *i*-C$_{Li}$). The powdery product contained smaller amounts of additional tmeda.

***n*-Bu$_3$Sn(C$_6$H$_4$SEt-2) (1a).** To **4** (100 mmol) in *n*-hexane (90 mL), cooled to −78 °C, was added dropwise a solution of *n*-Bu$_3$SnCl (30.0 g, 92 mmol) in *n*-hexane (20 mL). The reaction mixture was warmed to room temperature over 6 h and stirred overnight. A saturated aqueous solution of NH$_4$Cl (200 mL) was added at 0 °C. After phase separation, the aqueous phase was extracted with diethyl ether (3 × 100 mL). The combined organic phases were washed with water (3 × 50 mL) and dried (Na$_2$SO$_4$). Solvents were removed in vacuo, and the residue was fractionated (bp 135−142 °C at 0.02 Torr). Yield: 19.2 g (49%). Anal. Calcd for C$_{20}$H$_{36}$SSn (427.28): C, 56.22; H, 8.49; S, 7.50. Found: C, 56.54; H, 8.21; S, 7.12. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.89−0.94/1.12−1.16/1.30−1.40/1.52−1.61(m/m/m/m, ca. 30H, (C$_4$*H$_9$*)$_3$Sn + C*H$_3$*CH$_2$S), 2.94 (q, $^3J_{H,H}$ = 7.47 Hz, 2H, CH$_3$C*H$_2$*S), 7.13−7.18/7.24−7.32 (m/m, 1H/1H, *H*4 and *H*5 of Ph), 7.39 (m, 2H, *H*3 and *H*6 of Ph). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.7 (s, *C*H$_3$ of Bu), 27.5 (s+d, $^3J_{Sn,C}$ = 61.4 Hz, 3-*C*H$_2$ of Bu), 29.2 (s+d, $^2J_{Sn,C}$ = 19.6 Hz, 2-*C*H$_2$ of Bu), 11.0 (s+d, $^1J_{Sn,C}$ = 346.0 Hz, 1-*C*H$_2$ of Bu), 14.4 (s, *C*H$_3$CH$_2$S), 29.9 (s, CH$_3$*C*H$_2$S), 125.6 (s+d, $^2J_{Sn,C}$ = 38.3 Hz, *C*6 of Ph), 128.7 (s+d, $^4J_{Sn,C}$ = 8.8 Hz, *C*4 of Ph), 129.3/136.6 (s+d/s+d, $^3J_{Sn,C}$ = 29.1/30.3 Hz, *C*3 and *C*5 of Ph), 144.5 (s+d, $^2J_{Sn,C}$ = 22.7 Hz, *C*2 of Ph), 146.6 (s+d, $^1J_{Sn,C}$ = 388.6 Hz, *C*1of Ph). ^{119}Sn NMR (186 MHz, CDCl$_3$): δ −44.0 (s).

[Li(CHMeSPh)(tmeda)] (5) and *n*-Bu$_3$SnCHMeSPh (2a).
[Li(CHMeSPh)(tmeda)] (5). (a) To a stirred solution of *n*-BuLi (100 mmol) in *n*-hexane (60 mL)/THF (100 mL) was added tmeda (11.6 g, 100 mmol) at −78 °C. After 15 min of stirring PhSEt (13.8 g, 100 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred for 1−2 h.

(b) As shown by ^{1}H and ^{13}C NMR experiments, dissolution of [{Li(C$_6$H$_4$SEt-2)(tmeda)}$_2$] (**4**) (ca. 50 mg) in THF-*d$_8$* (ca. 1 mL) resulted in formation of **5**. ^{1}H NMR (400 MHz, THF-*d$_8$*): δ 1.27 (q, $^3J_{H,H}$ = 6.23 Hz, 1H, LiC*H*(CH$_3$)SPh), 1.53 (d, $^3J_{H,H}$ = 6.23 Hz, 3H, LiCH(C*H$_3$*)SPh), 2.18 (s, 12H, C*H$_3$*N), 2.32 (s, 4H, C*H$_2$*N), 6.69 (m, 1H, *p*-C*H*), 6.98/7.11 (m/m, 2H/2H, *o*-C*H* and *m*-C*H*). ^{13}C NMR (100 MHz, THF-*d$_8$*): δ 12.8 (s, LiCH-(CH$_3$)SPh), 22.4 (s, LiCH(*C*H$_3$)SPh), 46.2 (s, *C*H$_3$N), 58.7 (s, *C*H$_2$N), 120.9 (s, *p*-*C*), 125.5 (s, *m*-*C*), 127.6 (s, *o*-*C*), 152.1 (s, *i*-*C*).

***n*-Bu$_3$SnCHMeSPh (2a).** From [Li(CHMeSPh)(tmeda)] (**5**), prepared as described above, and *n*-Bu$_3$SnCl (30.0 g, 92 mmol) in THF (25 mL) at −10 °C tin compound **2a** was obtained by the same procedure as described for tin compound **1a** (bp 146−148 °C at 0.01 Torr). Yield: 13.6 g (35%). Anal. Calcd for C$_{20}$H$_{36}$SSn (427.28): C, 56.22; H, 8.49; S, 7.50. Found: C,

Table 4. Crystal Data and Structure Refinement for 4 and 5′

	4	**5′**
empirical formula	C$_{28}$H$_{50}$Li$_2$N$_4$S$_2$	C$_{34}$H$_{66}$Li$_2$N$_6$S$_2$
fw	520.72	636.93
T, K	223(2)	198(2)
cryst syst	triclinic	monoclinic
space group	*P*1̄	*P*2/*c*
a, Å	8.536(2)	13.382(5)
b, Å	10.612(3)	8.615(4)
c, Å	18.575(5)	18.031(6)
α, deg	90.78(3)	
β, deg	101.44(3)	103.36(3)
γ, deg	96.11(3)	
V, Å^3	1638.6(7)	2022.5(14)
Z	2	2
ρ$_{calcd}$, g/cm^3	1.055	1.046
μ(Mo Kα), mm^{-1}	0.183	0.160
F(000)	568	700
scan range, deg	2.20−25.00	1.56−24.96
no. of rflns collected	11 754	4798
no. of indep rflns	5431 (*R*$_{int}$ = 0.0841)	3547 (*R*$_{int}$ = 0.0242)
no. of params refined	325	219
goodness of fit on *F*^{2}	0.956	1.048
final *R* (*I* > 2σ(*I*))	R1 = 0.0575 wR2 = 0.1415	R1 = 0.0398 wR2 = 0.1023
R, all data	R1 = 0.0954 wR2 = 0.1639	R1 = 0.0499 wR2 = 0.1123
largest diff peak/hole, e/Å^3	0.477/−0.250	0.219/−0.222

56.36; H, 8,18; S, 7.17. ^{1}H NMR (200 MHz, CDCl$_3$): δ 0.89−1.06/1.11−1.18/1.27−1.41/1.45−1.62 (m/m/m/m, 30H, (C$_4$*H$_9$*)$_3$-Sn + C*H$_3$*), 2.91−3.01 (m, 1H, C*H*(CH$_3$)S), 7.10−7.17 (m, 1H, *p*-C*H*), 7.23−7.36 (m, 4H, *o*-C*H*/*m*-C*H*). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.7 (s, *C*H$_3$ of Bu), 27.4 (s+d, $^3J_{Sn,C}$ = 56.7 Hz, 3-*C*H$_2$ of Bu), 29.2 (s+d, $^2J_{Sn,C}$ = 20.7 Hz, 2-*C*H$_2$ of Bu), 9.3 (s+d, $^1J_{Sn,C}$ = 323.6 Hz, 1-*C*H$_2$ of Bu), 19.7 (s+d, $^2J_{Sn,C}$ = 10.0 Hz, CH(*C*H$_3$)S), 21.5 (s+d, $^1J_{Sn,C}$ = 250.2 Hz, *C*H(CH$_3$)S), 125.3 (s, *p*-*C*), 128.5/128.6 (s/s, *o*-*C* and *m*-*C*), 138.2 (s, *i*-*C*). ^{119}Sn NMR (186 MHz, CDCl$_3$): δ −7.9 (s).

Crystallographic Studies. Single crystals of **4** (colorless block, 0.60 × 0.60 × 0.21 mm) suitable for X-ray diffraction measurements were obtained from the reaction mixture stored for 1−2 days at −40 °C. From the same solutions very few crystals of **5′** were obtained after several weeks. Intensity data were collected on a STOE-STADI4 four-circle diffractometer (**5′**) and STOE-IPDS diffractometer (**4**), respectively, with Mo Kα radiation (0.710 73 Å, graphite monochromator). A summary of crystallographic data, data collection parameters, and refinement parameters is given in Table 4. The absorption correction for **4** was applied numerically (*T*$_{min}$/*T*$_{max}$ = 0.90/0.96) and for **5′** empirically via ψ-scans (*T*$_{min}$/*T*$_{max}$ = 0.68/0.85). The structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares routines against *F*^{2} using SHELXL-97.[25] Non-hydrogen atoms were refined with anisotropic and hydrogen atoms with isotropic displacement parameters. H atoms were added to the model in their calculated positions (riding model). In **5′** the ethylene bridge of the tmeda ligand shows a typical disorder (λδ). Thus, carbon atoms C11 and C12 are disordered over two positions with site occupancies of 0.61 and 0.39. The corresponding disorder of methyl carbon atoms C9/C10 and C13/C14 results in slightly larger displacement ellipsoids.

(25) Sheldrick, G. M. SHELXS-97 and SHELXL-97, Programs for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1990, 1997.

Supporting Information Available: X-ray crystallographic data are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) have been also deposited at the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-229877 (**4**) and

CCDC-229876 (**5′**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2, 1EZ, U.K. (fax, (internat.) +44(0)1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).