Ring Opening of Thiophene: Synthesis and Crystal Structure of Bis(diethyl ether)bis(μ_4-{(3,4-η)-4-[1,1,3,3-tetramethyl-3-(2-thienyl)disilazan-1-yl-κN:κN]but-1-en-3-yne-1-thiolato(2 –)-κS:κS:κS})tetralithium ([(C_4H_3S)$SiMe_2$–N(Li)–$SiMe_2$–C≡C–CH=CH–SLi · OEt_2]$_2$)

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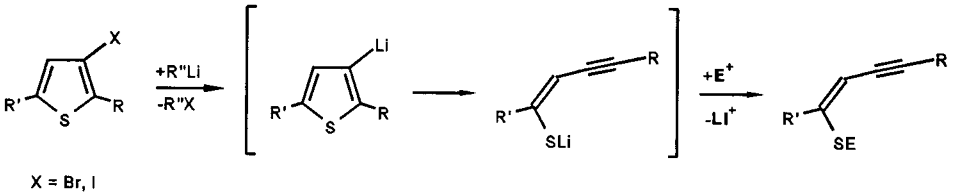
Double lithiation of *N*-[dimethyl(2-thienyl)silyl]-1,1-dimethyl-1-(2-thienyl)silanamine ((C_4H_3S)–$SiMe_2$–N(H)–$SiMe_2$–(C_4H_3S); **1**) leads, *via* ring opening of one thiophene moiety, to the title compound **2** ([(C_4H_3S)–$SiMe_2$–N(Li)–$SiMe_2$–C≡C–CH=CH–SLi · OEt_2]$_2$) which is characterized by an X-ray structure determination.

Introduction. – It has been well-established that 3-thienyllithium derivatives, prepared by halogen-metal exchange between the corresponding bromo- or iodo-substituted heterocycles and alkyllithium reagents, open up to thioenynes which can react with various electrophiles (*Scheme 1*) [1–3]. These ring-opening reactions occur regio- and stereospecifically which make them of synthetic value for highly unsaturated compounds [4][5]. It is astonishing that the key compounds of these reactions, the (enynethiolato)lithium derivatives have not been examined in more detail. To our knowledge, these intermediates have not been isolated so far, but were only treated *in situ* with alkylating reagents or other electrophiles (*Scheme 1*) [6]. Moreover, no crystal structure of any (enynethiolato)lithium derivative containing a –C≡C–C=C–S–Li fragment has been studied by X-ray structure analysis, until now.

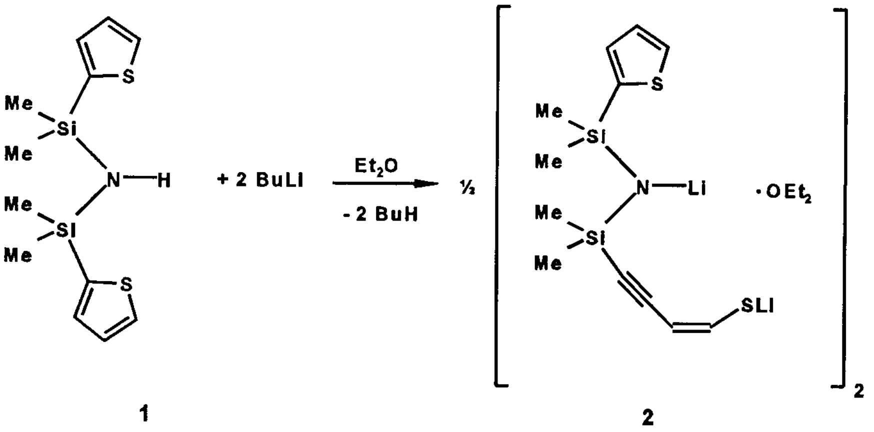
Scheme 1. *Ring Opening of Thiophene*



In connection with our studies on lithium coordination in chelating silazanes [7], we noticed an unprecedented reactivity of a second butyllithium molecule with the simple lithium amide. We succeeded to prepare the title compound **2** in high yield and to fully characterize it by an X-ray structure analysis.

Results and Discussion. – *Synthesis.* Compound **2** was synthesized by double lithiation of the corresponding silanamine **1** ((C_4H_3S)–$SiMe_2$–N(H)–$SiMe_2$–(C_4H_3S)) [7] at room temperature using Et_2O as a solvent (*Scheme 2*). Colorless needle-like crystals were obtained in high yield by crystallization from Et_2O/hexane. When hexane was used instead of Et_2O as a solvent, only the monolithiated compound (C_4H_3S)–$SiMe_2$–N(Li)–$SiMe_2$–(C_4H_3S) was obtained [7].

Scheme 2



X-Ray Structure Determination of **2**[1]). The procedure for the X-ray structure determination of **2** and some important crystal data are described in the *Exper. Part.* Compound **2** which almost has C_2 point symmetry originates from two enynethiolato ligands bridging four Li-atoms, two of the Li-atoms being also coordinated by Et_2O molecules (*Fig.*). The most important bond lengths and angles are collected in the *Table.* The N–Si–C≡C–C(H)=C(H)–S one-dimensional arrangement which is easily recognized by the C–C distances (see *Table*) is coordinated by Li-atoms in a quite astonishing way. The atoms Li(1) and Li(2) close the N–Si–C_4–S backbone to an eight-membered ring being chelated by the anionic termini of the ring. This $NSiC_4SLi$ ring is almost planar; the planarity seems to originate from a π interaction of the C≡C bond with the Li-atom across the ring (Li(1)–C(1) and Li(1)–C(2), Li(2)–C(13) and Li(2)–C(14): 2.280(8)–2.509(10) Å). Such interactions between Li-atoms and unsaturated systems have already been studied in various systems [8]. The two eight-membered $NSiC_4SLi$ rings are connected to each other at the mostly charged atoms N, Li, and S in such a way that oppositely charged atoms are always in direct connection incorporating the 'dangling' Li-atoms Li(3) and Li(4). Three four-membered cycles are formed by these interactions (a central Li_2S_2 ring and two similar NLi_2S rings) which build up a ladder-like structure.

The coordination spheres of the Li-atoms may be divided in pairs: Li(1) and Li(2) are in a distorted tetrahedral environment, whereas Li(3) and Li(4) are only three-coordinate. The atoms Li(1) and Li(2) are coordinated by two S-atoms, one N-atom, and the π-system of the triple bond, the angles around the Li-atoms deviating quite

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[1]) Crystallographic data (excluding structure factors) for the structure have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-101685. Copies of the data can be obtained, free of charge, on application to the *CCDC*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

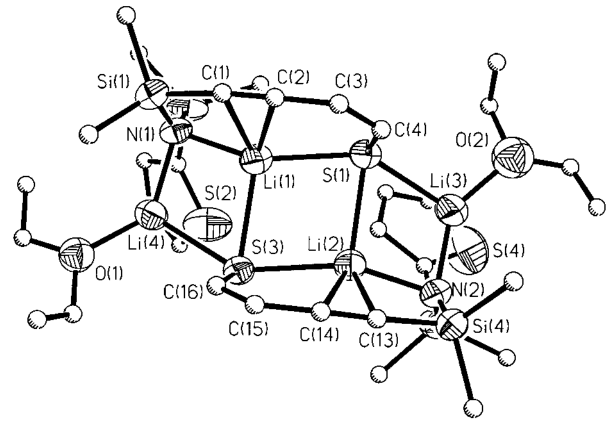

Figure. *ORTEP Plot of* **2** (50% probability thermal ellipsoids)

Table. *Selected Bond Lengths* [Å] *and Angles* [deg] *for* **2**

S(1)–Li(1)	2.462(8)	C(1)–C(2)	1.195(7)
S(1)–Li(2)	2.538(8)	C(2)–C(3)	1.407(7)
S(1)–Li(3)	2.459(8)	C(3)–C(4)	1.328(8)
S(2)–Li(4)	2.918(9)	C(13)–Li(2)	2.280(8)
S(3)–Li(1)	2.557(8)	C(14)–Li(2)	2.452(8)
S(3)–Li(2)	2.511(7)	C(13)–C(14)	1.213(7)
S(3)–Li(4)	2.512(8)	C(14)–C(15)	1.398(7)
N(1)–Li(1)	2.095(8)	C(15)–C(16)	1.329(7)
N(1)–Li(4)	2.034(9)	O(1)–Li(4)	1.919(9)
N(2)–Li(2)	2.099(8)	O(2)–Li(3)	1.928(10)
N(2)–Li(3)	1.992(9)	Li(1)–Li(4)	2.852(11)
C(1)–Li(1)	2.317(9)	Li(1)–Li(2)	3.195(10)
C(2)–Li(1)	2.509(10)	Li(2)–Li(3)	2.783(11)
C(2)–C(1)–Si(1)	166.0(4)	N(2)–Li(2)–C(13)	79.5(3)
C(1)–C(2)–C(3)	177.4(5)	C(13)–Li(2)–C(14)	29.42(18)
C(4)–C(3)–C(2)	122.3(5)	C(14)–Li(2)–S(3)	78.1(2)
C(3)–C(4)–S(1)	125.4(4)	N(2)–Li(2)–S(1)	99.9(3)
C(14)–C(13)–Si(3)	165.2(4)	S(3)–Li(2)–S(1)	100.6(3)
C(13)–C(14)–C(15)	177.8(6)	O(2)–Li(3)–N(2)	142.8(5)
C(16)–C(15)–C(14)	122.9(4)	O(2)–Li(3)–S(1)	109.2(4)
C(15)–C(16)–S(3)	126.0(4)	N(2)–Li(3)–S(1)	105.8(4)
N(1)–Li(1)–C(1)	79.2(3)	O(1)–Li(4)–N(1)	134.0(5)
C(1)–Li(1)–C(2)	28.32(18)	O(1)–Li(4)–S(3)	113.9(4)
S(1)–Li(1)–C(2)	77.1(3)	N(1)–Li(4)–S(3)	103.7(3)
N(1)–Li(1)–S(3)	100.4(3)		
S(1)–Li(1)–S(3)	101.4(3)		

remarkably from ideal tetrahedral geometry (91.5–152.2°). The atoms Li(3) and Li(4) are coordinated by one S-atom, one N-atom, and the O-atom of a diethyl-ether ligand. The angles around these Li-atoms sum up to 357.8° (Li(3)) and 351.6° (Li(4)), values which are not far from ideal trigonal planar geometry. The more pronounced pyramidality at Li(4) can be correlated to an approach of the atom S(2) of the undestroyed thiophene moiety (Li $\cdots$ S 2.918(9) Å), whereas the corresponding Li(3) $\cdots$ S(4) distance is longer than 3.5 Å. This different coordination behavior of the thiophene-ring atoms S(2) and S(4) can be deduced also from the orientation of the rings with respect to the polycyclic system (see *Fig.*). The Li(3) $\cdots$ S(4) and Li(4) $\cdots$ S(2) distances are nevertheless long compared to other structures including thiophen and Li-atoms without any interactions [9][10]. On the same line, a high thermal motion of the thiophene moiety in the crystal is observed (a split-atom model does not lead to a better structure).

The Li–S(1) and Li–S(3) bond lengths (2.459(8) – 2.557(8) Å) are in a range well-known for thiolato lithium compounds [11]; the Li–N (1.992(9) – 2.099(8) Å) and Li–O (1.919(9) – 1.928(10) Å) bond lengths are typical for lithium amides [12][13] or Li-atoms with Et_2O donor molecules [11], respectively.

The two C≡C bonds (mean: 1.204(7) Å) are not elongated compared to standard values (1.205 Å) [14], and the C=C bonds (mean: 1.328(8) Å) are in the expected range (1.338 Å) [14]. The unperturbed length of the C≡C bond is remarkable despite the fact that the Si–C≡C and C≡C–C angles deviate by 14.4°(Si) and 2.7°(C), respectively, from linearity due to the ring strain, and despite the fact that there are $\pi \rightarrow$Li interactions across the ring (see above). It is interesting to note that the dimeric molecule **2** has almost C_2 and not C_i symmetry. This may be ascribed to the special packing forces in the crystal of **2**, the energies of the two aggregates with C_2 or C_i symmetry being quite similar.

Experimental Part

General. Reactions were performed under purified N_2, using carefully dried solvents. NMR Spectra: δ in ppm rel. to $SiMe_4$ (= 0 ppm), J in Hz.

*Bis(diethyl ether)bis(μ₄-{(3,4-η)-4-[1,1,3,3-tetramethyl-3-(2-thienyl)disilazan-1-yl-κ*N : κN*]but-1-en-3-yne-1-thiolato(2 –)-κ*S : κS : κS*})tetralithium* (**2**). To *N*-[dimethyl(2-thienyl)silyl]-1,1-dimethyl-1-(2-thienyl)silanamine (**1**; 2.083 g, 7.0 mmol) in Et_2O (10 ml), 15% BuLi in hexane (9.5 ml, 2 mol-equiv.) was added dropwise at r.t. After 20 h stirring and concentration of the soln., colorless crystals were isolated: 1.634 g (75%) of **2**. ^{1}H-NMR (200 MHz, Et_2O/C_6D_6, 25°): 0.16 (*s*, Me_2Si); 0.30 (*s*, Me_2Si); 5.30 (*d*, $J = 8.6$, 1 H, CH=CH); 6.94 (*dd*, $J = 3.5$, 4.3, 1 H (C_4H_3S)); 7.05 (*d*, $J = 8.9$, 1 H, CH=CH); 7.20 (*d*, $J = 3.3$, 1 H (C_4H_3S)); 7.28 (*d*, $J = 4.6$, 1 H (C_4H_3S)). ^{13}C-NMR (55.0 MHz, Et_2O/C_6D_6, 25°): 5.4, 5.7 (Me_2Si); 101.1 (C≡C); 106.1 (CH=CH); 110.2 (C≡C); 128.6, 129.6, 133.0, 146.1 (C_4H_3S); 152.6 (CH=CH). ^{29}Si-NMR (39.7 MHz, Et_2O/C_6D_6, 25°): – 27.4, – 19.2. Anal. calc. for $C_{32}H_{54}Li_4N_2O_2S_4Si_4$: C 50.10, H 7.09, N 3.65; found: C 50.61, H 7.62, N 3.52. Measurement of M_e was precluded because of poor solubility of **2** in benzene.

Crystal Data of **2**. Colorless needles (0.60 × 0.50 × 0.35 mm), $C_{32}H_{54}Li_4N_2O_2S_4Si_4$, M_r 767.13, triclinic, space group $P\bar{1}$, $a = 9.037(2)$, $b = 15.310(3)$, $c = 18.058(4)$ Å; $\alpha = 111.68(3)$, $\beta = 92.55(3)$, $\gamma = 95.51(3)°$; $V = 2302.3(9)$ Å^3, $Z = 2$, $D_c = 1.107$ Mgm^{-3}; MoK_α radiation: $\lambda = 0.71073$ Å, $\mu = 0.337$ mm^{-1}. *Stoe-IPDS* diffractometer using a graphite monochromator, 293 K; 14772 reflections were collected, 6865 independent reflections (R_{int} 0.0396); 4861 ($I > 2\sigma(I)$) reflections were classified as observed. The structure was solved by heavy-atom methods and refined by full-matrix least-squares methods; anisotropic thermal parameters for all non-H-atoms in the final cycles; isotropic refinement of H-atoms positioned by geometry. R_1 0.0706 and wR_2 0.2038. SHELXS-97 and SHELXL-97 computer programs were used.

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