A New Class of Dianionic Sulfur-Ylides: Alkylenediazasulfites

Bernhard Walfort, Rüdiger Bertermann, and Dietmar Stalke*[a]

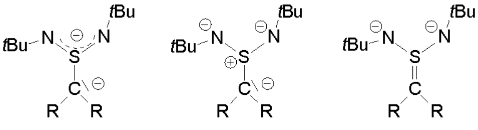
Abstract: The compounds $[\{(thf)Li_2[H_2CS(NtBu)_2]\}_2]$ (**1**) and $[\{(thf)Li_2[(Et)(Me)CS(NtBu)_2]\}_2]$ (**2**) can be synthesized in a two-step reaction. Firstly addition of an alkyllithium to sulfur diimide gives the diazaalkylsulfinate $[RS(NtBu)_2]^-$ (R = Me, *s*Bu). In a second step the α-carbon atom in R is metalated with one equivalent of methyllithium to give the *S*-ylides. This new class of compounds can be rationalized as sulfite analogues, in which two oxygen atoms are each isoelectronically replaced by a N*t*Bu group and the remaining oxygen atom is replaced by a CR_2 group. Similar to Corey's *S*-ylides $(R_2(O)S^{+}{-}^{-}CR_2)$ and Wittig's phosphonium ylides $(R_3P^{+}{-}^{-}CR_2)$, these molecules contain a positively charged sulfur atom next to a carbanionic center. Therefore nucleophilic addition reactions of the carbon atom are feasible. The reaction of a sulfur diimide with the anionic carbon center in $[H_2CS(NtBu)_2]^{2-}$ gives the intermediate alkylbis(diazasulfinate) $[(tBuN)_2SCH_2S(NtBu)_2]^{2-}$. The acidity of the hydrogen atoms at the bridging CH_2 group is high enough to give, upon deprotonation, the $[(tBuN)_2SCHS(NtBu)_2]^{3-}$ trianion in $[\{(thf)Li_3[(tBuN)_2SCHS(NtBu)_2]\}_2]$ (**3**). In $[(Et)(Me)CS(NtBu)_2]^{2-}$ the nucleophilic carbon atom is sterically hindered and transimidation instead of deprotonation is observed. In a complex redox process $[(thf)_6Li_6S\{(NtBu)_3S\}_2]$ is recovered. The two new classes of compounds broaden the rich coordination chemistry of the triazasulfites by the introduction of a hard carbon center.

Keywords: lithiation · lithium · nucleophilic addition · sulfur · sulfur ylides

Introduction

During the last years we were interested in the syntheses and coordination chemistry of polyimido sulfur anions like $S(NR)_3^{2-}$,[1] $S(NR)_4^{2-}$,[2] $RS(NR)_2^{-}$[3] or $RS(NR)_3^{-}$,[4] the aza analogues of the well-established oxo anions SO_3^{2-}, SO_4^{2-}, RSO_2^{-}, and RSO_3^{-}. The extensive interest in polyimido anions of the p-block elements is evident from the syntheses of most $E(NR)_x^{n-}$ anions during the last five to six years (E = S,[1–4] Se,[5] Te,[6] P,[7] As,[8] Sb,[9] C,[10] Si,[11], Sn[12]; x, $n = 1-4$) and is still fuelled by various applications. Here we present the syntheses and structures of $[\{(thf)Li_2[H_2CS(NtBu)_2]\}_2]$ (**1**) and $[\{(thf)Li_2[(Et)(Me)CS(NtBu)_2]\}_2]$ (**2**), the first carb/diaza analogues of SO_3^{2-}, in which two oxygen atoms are isoelectronically replaced by a N*t*Bu group each and the third oxygen atom is substituted by a CR_2 group. The resulting alkylene diazasulfite dianions can be envisaged in three different resonance forms (**A**–**C**).

As visualized in structures **A**–**C**, there is a close relationship between Corey's sulfur ylides and the alkylene diazasulfites dianions reported in this paper. As in sulfur ylides there is a positively charged sulfur atom in compounds **1** and **2** adjacent to a carbanionic center. Therefore we expect a similar reactivity for the alkylene diazasulfites and the *S*-ylides. A nucleophilic addition reaction of the deprotonated carbon atom seems feasible. Addition of an equivalent sulfur diimide to **1** gives the intermediate alkylbis(diazasulfinate) $[(tBuN)_2SCH_2S(NtBu)_2]^{2-}$. Deprotonation of this intermediate gives dimeric $[\{(thf)Li_3[(tBuN)_2SCHS(NtBu)_2]\}_2]$ (**3**), which contains the $[(RN)_2SCHS(NR)_2]^{3-}$ trianion.



A B C

delocalised ylidic ylenic

Results and Discussion

Synthesis of *S*-methylene-*N*,*N*′-di(*tert*-butyl)diazasulfite $[H_2CS(NR)_2]^{2-}$ in 1 and *S*-*sec*-butylene-*N*,*N*′-di(*tert*-butyl)-diazasulfite $[(H_5C_2)(H_3C)CS(NR)_2]^{2-}$ in 2: Compounds $[\{(thf)Li_2[H_2CS(NtBu)_2]\}_2]$ (**1**) and $[\{(thf)Li_2[(Et)(Me)CS(NtBu)_2]\}_2]$ (**2**) can be synthesized in a two-step reaction: first the alkyl diazasulfinate is generated in an addition reaction of the corresponding organolithium to *N*,*N*′-di-(*tert*-butyl)sulfur diimide [Eq. (1)]. In a second step the α-carbon atom is

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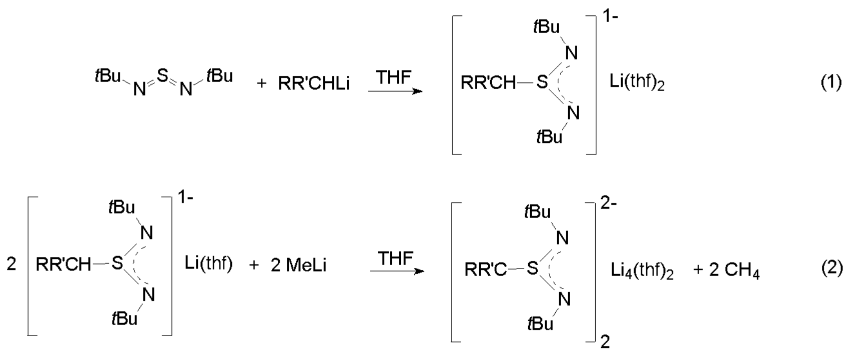


1 and **2**

	R	R'
1	H	H
2	Et	Me

deprotonated by one equivalent of methyllithium to give the sulfite analogues in good yields (60–80%) [Eq. (2)].

Deprotonation reactions of an α-carbon atom next to a sulfur atom in general are well established. Most widespread is the synthesis of sulfur ylides,[13] but also they are employed in the synthesis of sulfines and sulfenes by HCl elimination from $RCH_2S(O)Cl$[14] or more recently in asymmetric C–C coupling reactions with sulfoximines.[15] In all these known compounds the sulfur atom is neutral or positively charged. The alkyl diazasulfinates discussed in this paper are the first examples of anions capable of generating *S*-ylides. Unlike in the carboxylates with α-CH functions, in which the negative charge prevents the formation of enolates, the negative alkyl diazasulfinates can be deprotonated with the strong base MeLi to give the *S*-methylene-*N*,*N'*-di(*tert*-butyl)diazasulfite $[H_2CS(NR)_2]^{2-}$ in **1** and the *S*-*sec*-butylene-*N*,*N'*-di(*tert*-butyl)diazasulfite in **2**. Attempts to deprotonate the alkyl diazasulfinates with metal amides or metal alkoxides failed. This seems to be more a kinetic effect than the lack of basicity.

Abstract in German: *Die Verbindungen* $[\{(thf)Li_2[H_2CS(NtBu)_2]\}_2]$ *(**1**) und* $[\{(thf)Li_2[(Et)(Me)CS(NtBu)_2]\}_2]$ *(**2**) sind leicht in einer zweistufigen Synthese zugänglich. Im ersten Schritt erhält man Diazaalkylsulfinate* $[RS(NtBu)_2]^-$ *(R = Me, sBu) durch Addition eines Lithiumalkyls an ein Schwefeldiimid. Im zweiten Syntheseschritt wird das α-Kohlenstoffatom in R mit einem Äquivalent Methyllithium metalliert und ergibt die neuartigen S-Ylide. Diese neuen Verbindungen können ebenfalls als Sulfitanaloga beschrieben werden, wobei zwei Sauerstoffatome isoelektronisch durch eine NtBu Gruppe ersetzt werden und das verbleibende Sauerstoffatom durch eine* CR_2 *Gruppe ersetzt wird. Analog zu Corey's S-Yliden* $(R_2(O)S^{+}{-}^{-}CR_2)$ *und Wittig's Phosphor-Yliden* $(R_3P^{+}{-}^{-}CR_2)$ *besitzten diese Moleküle ein positiv geladenes Schwefelatom in direkter Nachbarschaft zu einem carbanionischen Zentrum. Folglich sind nucleophilen Additionsreaktionen mit dem Kohlenstoffatom möglich. Die Reaktion eines Schwefeldiimids mit dem anionischen Kohlenstoffatom in* $[H_2CS(NtBu)_2]^{2-}$ *ergibt intermediär Alkylbis(diazasulfinat)* $[(tBuN)_2SCH_2S(NtBu)_2]^{2-}$*. Die Azidität der Wasserstoffatome der verbrückenden* CH_2 *Gruppe ist groß genug, so daß nach Deprotonierung das Trianion* $[(tBuN)_2SCHS(NtBu)_2]^{3-}$ *als* $[\{(thf)Li_3[(tBuN)_2SCHS(NtBu)_2]\}_2]$ *(**3**) erhalten wird. In* $[(Et)(Me)CS(NtBu)_2]^{2-}$ *ist das carbanionische Zentrum sterisch gehindert, und man beobachtet Transimidierung statt einer Addition des Kohlenstoffatoms an ein Schwefeldiimid. Im anschließenden Redoxprozess erhält man das bekannte Triazasulfit-Adukt des Lithiumsulfids* $[(thf)_6Li_6S\{(NtBu)_3S\}_2]$*. Die beiden neu gewonnenen Verbindungsklassen erweitern die bereits reichhaltige Koordinationschemie der Triazasulfite durch das eingeführte harte Kohlenstoffzentrum.*

Crystal structures of $[\{(thf)Li_2[H_2CS(NtBu)_2]\}_2]$ (1) and $[\{(thf)Li_2[(Et)(Me)CS(NtBu)_2]\}_2]$ (2): By isoelectronic replacement of an imide group from the triazasulfite $[Li_4\{(NtBu)_3S\}_2]$[1] by a CH_2 group in $[\{(thf)Li_2[H_2CS(NtBu)_2]\}_2]$ (**1**) the degree of aggregation is maintained in the solid state (Figures 1 and 2). Both structures are dimers. The additional charge does not appear to affect the S–N bond lengths in **1**, on average 165.8(2) pm and which are in the same range as those in $S(NR)_3^{2-}$ [1] (~167 pm) or $RS(NR)_2^-$ [3] (~165 pm), or the S–C bond length. The S–C bond length of 178.6(3) pm in **1** is as long as a S–C single bond found in alkyl diazasulfinates[3] (~181 pm) or alkyl triazasulfonates[4] (~179 pm). No bond shortening, anticipated from a Lewis diagram with a S=C double bond is detected. This findings favour the ylidic **B**-type

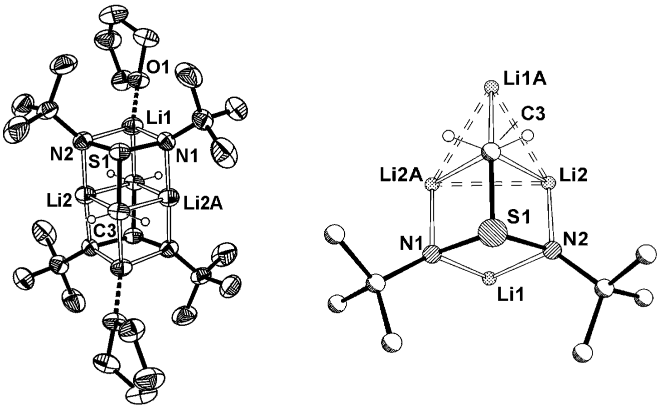


Figure 1. Solid-state structure of $[\{(thf)Li_2[H_2CS(NtBu)_2]\}_2]$ (**1**) (thermal elipsoids drawn at 50% probability, left) and the coordinating features of the ligand (right); selected bond lengths [pm] and angles [°]: S1–N1 165.9(2), S1–N2 165.6(2) S1–C3 178.6(3), N1–Li1 203.4(5), N1–Li2A 202.6(6), N2–Li1 210.1(6), N2–Li2 198.4(6), C3–Li1A 230.5(6), C3–Li2 237.2(6), C3–Li2A 235.1(6); N1-S1-N2 103.0(1), N1-S1-C3 100.7(1), N2-S1-C3 99.2(2), N2-Li2-N1A 177.8(3).

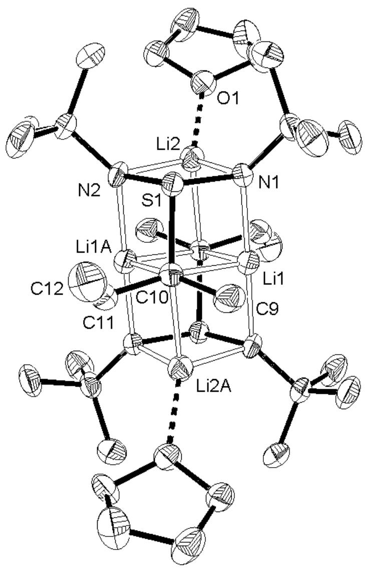


Figure 2. Solid-state structure of [{(thf)Li$_2$[(Et)(Me)CS(N*t*Bu)$_2$]}$_2$] (**2**) (thermal ellipsoids drawn at 50% probability); selected bond lengths [pm] and angles [°]: S1–N1 165.2(2), S1–N2 164.9(2), S1–C10 181.7(3), N1–Li1 201.2(5), N1–Li2 209.4(5), N2–Li2 207.5(5), N2–Li1A 201.9(5), C10–Li1 237.2(5), C10–Li1A 241.0(6), C10–Li2A 236.8(5); N1-S1-N2 104.48(11), N1-S1-C10 99.88(11), N2-S1-C10 99.64(12), N1-Li1-N2A 178.8(3).

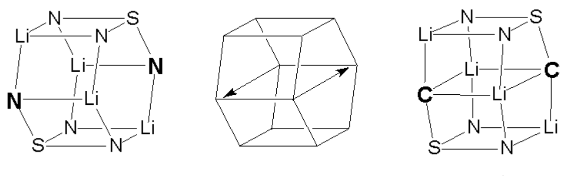
resonance formula. The S–N and S–C bond lengths indicate that one negative charge is delocalized over the SN$_2$ backbone, while one negative charge is localized at the carbon atom. The contribution of the ylenic form **C** is insignificant.

The carbanion C3 is coordinated at the center of a triangle made up by three lithium atoms, a structural motif well known in lithium alkylides (Figure 1, right).[17] All lithium atoms are coordinated by four atoms. Li1 and Li1A are coordinated tetrahedrally by two nitrogen atoms, one carbon atom, and one THF donor molecule. Li2 and Li2A are located at the apical position of a distorted square pyramid with two nitrogen atoms and two carbon atoms in the basal positions.

The structure of [{(thf)Li$_2$[(Et)(Me)CS(N*t*Bu)$_2$]}$_2$] (**2**) is isomorphous, but not isostructural to **1**. The main structural features of both are the same. The average S–N bond length of 165.0(2) pm is almost identical to that found in **1** (165.8(2) pm). The replacement of the methylene group in **1** by the much bulkier *sec*-butylene group in **2** induces a 3 pm longer S–C bond length (S–C 181.7(3) in **2** vs. 178.6(3) pm in **1**). The Li$_3$LCR$_2$ structural motif from organolithium complexes is present, and the mesomeric form **B** describes the bonding best. One negative charge is delocalized over the SN$_2$ backbone and one is localized at the α-carbon atom.

Similar to [Li$_4${(NtBu)$_3$S}$_2$] both crystal structures of **1** and **2** are dimeric. The first adopts a distorted hexagonal prismatic arrangement, made up from two stacked SN$_3$Li$_2$ six-membered rings (Scheme 1, left).[1] Replacement of a NR group by a CR$_2$ (bolt) group causes two additional Li–C bonds across the six-membered rings to be formed. Hence the hexagonal prismatic structure changes to two distorted SN$_2$C$_2$Li$_3$ cubes with a common C$_2$Li$_2$ face (Scheme 1, right).

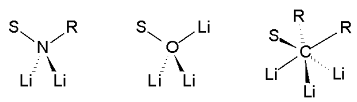
Chivers et al. recently reported the syntheses and structure of the heteroleptic oxodiazasulfite [Li$_2${(N*t*Bu)$_2$SO}].[16] The



Scheme 1. The replacement of a single NR group in S(NR)$_3$$^{2-}$ by a CR$_2$ group in S(NR)$_2$(CR$_2$)$^{2-}$ causes the hexagonal prismatic dimer to change into two face connected cubes (R groups on N and C are omitted).

replacement of one NR group by a single oxygen atom results in complete structural rearrangement. The hexagonal prismatic structure from the triazasulfite is opened and trimerization to a hexameric array is detected. All oxygen atoms in this aggregate are coordinated to three lithium atoms.

A comparison of the structures of the aza/oxo/carba sulfites reveals that the structures are determined by the preferred coordination mode of the corresponding heteroatom. Nitrogen prefers a tetrahedral coordination mode with two lithium atoms. Oxygen also prefers a tetrahedral environment; this results in the coordination of three lithium atoms. By contrast, the carbon atom prefers a distorted octahedral coordination sphere. As in the organolithium compounds reported here one triangular face of the octahedron is formed by three lithium atoms (Scheme 2).



Scheme 2. Different coordination modes of the aza/oxo/carba analogues of the sulfites.

The two-dimensional ^{7}Li MQMAS NMR spectrum of **1** clearly shows two well-resolved peaks at isotropic shifts of $\delta_{\text{iso}} = 2.4$ and 3.1.[18] The shape of the contour plot in Figure 3

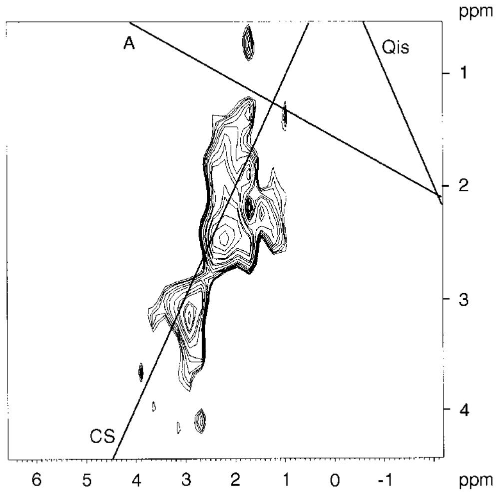
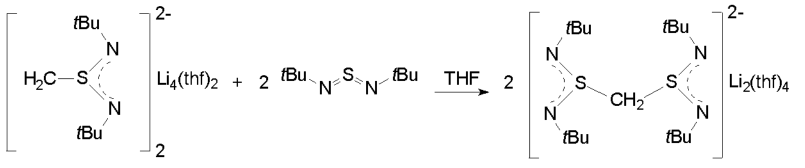


Figure 3. Unsheared 3Q MQMAS ^{7}Li solid-state NMR spectrum of **1** showing two ^{7}Li sites with an intensity ratio of approximately 1:1. Additional axes are included for interpretation: **A** is the anisotropic axis with the slope of $-7/27$, **Qis** is the quadrupolar induced shift axis, and **CS** is the chemical shift axis.

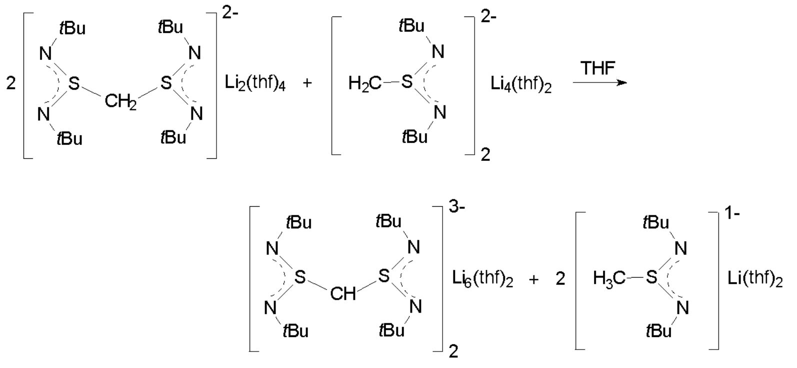
indicates that the sites are well defined because the signals show neither a distribution of chemical shifts nor of quadrupolar couplings. The result of the ^{7}Li MQMAS is consistent with the single-pulse high-power decoupled ^{6}Li MAS experiment, which also exhibits two well-defined sites for sample **1** in the ratio 1:1.

Addition reactions of [{(thf)Li$_2$[H$_2$CS(N*t*Bu)$_2$]}$_2$] (1) and [{(thf)Li$_2$[(Et)(Me)CS(N*t*Bu)$_2$]}$_2$] (2) to a sulfur diimide: To elucidate the reactivity of **1** and **2** we tried to add the nucleophilic carbanionic center to the electrophilic sulfur atom in sulfur diimide. With **1** this addition works. In a first step the addition gives the intermediate [(thf)$_4$Li$_2${((N*t*Bu)$_2$-S)$_2$CH$_2$}] [Eq. (3)]. The acidity of the hydrogen atoms of the bridging CH$_2$ group is so high that this product is deprotonated by **1** before the addition of **1** to the sulfur diimide is completed. As a result [{(thf)Li$_3$[(*t*BuN)$_2$SCHS(N*t*Bu)$_2$]}$_2$] (**3**), which contains the [(*t*BuN)$_2$SCHS(N*t*Bu)$_2$]$^{3-}$ trianion and the known methyl diazasulfinate [(thf)$_2$Li{(N*t*Bu)$_2$SCH$_3$}], is obtained [Eq. (4)].



1

(3)

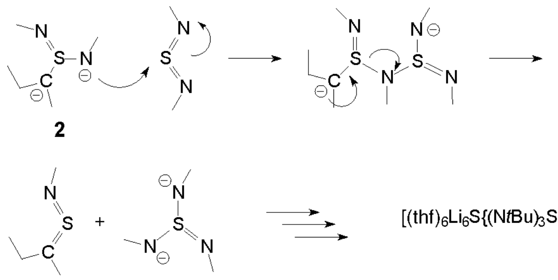


3

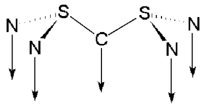
(4)

In compound **2** the nucleophilic carbon atom is sterically hindered and the addition reaction is prevented. Instead a sterically less crowded, but also negatively charged, nitrogen atom adds in a first step to the electrophilic sulfur atom of the sulfur diimide. In the subsequent step the imido group is completely transferred to the sulfur diimide and the triazasulfite is formed. The sulfur carbylenimine initially present then decomposes in a complex redox process to give sulfide anions and other unidentified products. However, the lithium sulfide adduct of the triazasulfite [(thf)$_6$Li$_6$S{(N*t*Bu)$_3$S}$_2$], as described earlier,[19] crystallizes from solution at −20° C in 35% yield (Scheme 3).

Crystal structure of [{(thf)Li$_3$[(*t*BuN)$_2$SCHS(N*t*Bu)$_2$]}$_2$] (3): The complex [{(thf)Li$_3$[(*t*BuN)$_2$SCHS(N*t*Bu)$_2$]}$_2$] (**3**) could only be crystallized by the addition of lithium chloride to the reaction mixture.[20] In the structure one equivalent of LiCl is co-coordinated to the dimer (Figure 4). In the structure the two [(*t*BuN)$_2$SCHS(N*t*Bu)$_2$]$^{3-}$ trianions face each other with their diconcave sites accommodating the six lithium cations between them (Scheme 4). The ligand coordinates as two tripodal caps coupled through C100 to give a pentacoordinate system.



Scheme 3. Transfer of an imido group in **2** to the sulfur diimide and formation of a lithium sulfide adduct of triazasulfite, [(thf)$_6$Li$_6$S-{(N*t*Bu)$_3$S}$_2$].



Scheme 4. Coordinating mode of the metallated bis-diazasulfinate.

The lithium coordination in the two SN$_2$C tripods of the corner-shared caps is quite different. While three lithium cations are in almost ideal staggered arrangement relative to the two nitrogen atoms and the CH function (relative to S1 in Figure 4, bottom), they are much more distorted in the second cap (relative to S2 in Figure 4, bottom). All the nitrogen atoms as well as the two carbanionic-bridging CH groups are coordinated to two lithium atoms each. While Li1, Li4, Li5, and Li6 are coordinated tetrahedrally, Li2 and Li3 have a trigonal pyramidal coordination environment. The chlorine atom is coordinated by Li4 and Li5 from the complex and by Li7 from a pendant Li(thf)$_3$ fragment. The average S–N bond length of 165.0(3) pm in **3** is identical to that in complex **2**. The S–C bond of 179.1(3) pm (on average) again is fairly long, an indication of insignificant double bond character. This ligand along with the recently prepared azadisulfite[21] dianion [O$_2$S(μ-NPh)SO$_2$]$^{2-}$ is of potential interest as a multidentate ligand.[22]

Conclusion

[H$_2$CS(NR)$_2$]$^{2-}$ and [(Et)(Me)CS(NR)$_2$]$^{2-}$ can be synthesized through deprotonation of the related alkyl diazasulfinates. They can be rationalized as sulfite analogues, in which two

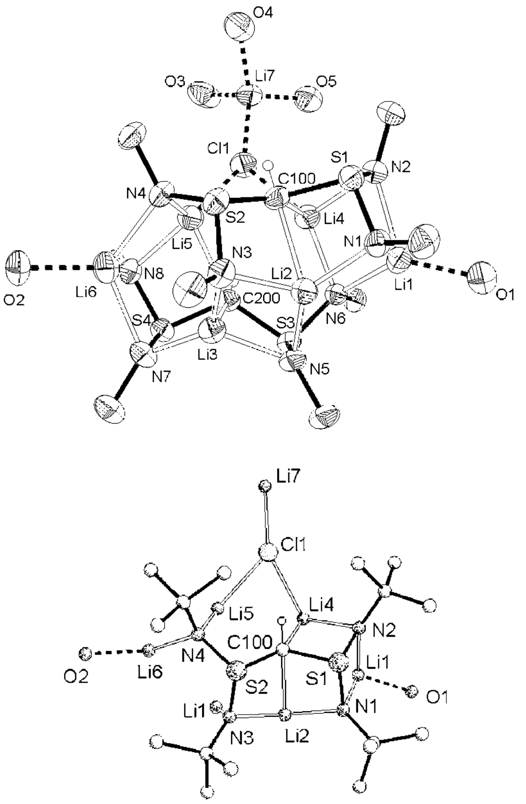


Figure 4. Solid-state structure of $[\{(thf)Li_3[(tBuN)_2SCHS(NtBu)_2]\}_2]\cdot LiCl(thf)_3$, (**3**$\cdot$LiCl(thf)$_3$, top) and coordination mode of one ligand (bottom). Carbon atoms of the coordinated THF molecules and primary carbon atoms of the *t*Bu groups are omitted for clarity; selected bond lengths [pm] and angles [°]: S1–N1 163.8(3), S1–N2 165.4(3), S2–N3 163.8(3), S2–N4 166.9(3), S1–C100 179.4(3), S2–C100 178.7(3), C100–Li2 230.1(6), C100–Li4 223.2(6), Li–Cl 247.4(5), S1-C100-S2 121.20(18), N1-S1-N2 105.74(14), N3-S2-N4 109.48(13), N1-S1-C100 100.77(15), N2-S1-C100 95.59, N3-S2-C100 99.84(15), N4-S2-C100 100.44(14).

oxygen atoms are isoelectronically replaced by N*t*Bu groups and one oxygen is replaced by a CR_2 group. Like in sulfur ylides there is a positively charged sulfur atom next to a carbanionic center. The ylidic or ionic form describes the S–C bonding best. The ylenic form does not seem to contribute. Nucleophilic addition reactions of the carbon atom are possible. The dialkyl diazasulfinates $[(RN)_2SCH_2S(NR)_2]^{2-}$ can be synthesized in an addition reaction of sulfur diimide to the anionic carbon center of $[H_2CS(NR)_2]^{2-}$. $[\{(thf)Li_3\{[(NtBu)_2S]_2CH\}\}_2]$, which contains the $[(tBuN)_2SCHS(NtBu)_2]^{3-}$ trianion, can be generated. This ligand coordinates as two tripodal caps coupled through a CH group to give a pentacoordinate system. The two new classes of compounds broaden the varied coordination chemistry of the triazasulfites by inclusion of a hard carbon center. The latter with five coordination centers may be a useful ligand in mixed-metal complexes and in catalytic reactions.

Experimental Section

All experiments were performed under a nitrogen atmosphere either by using modified Schlenk techniques or in a drybox. Solvents were freshly distilled from sodium-potassium alloy prior to use. ^1H, ^7Li, and ^{13}C NMR spectra were recorded in C_6D_6 (^1H, C_6HD_5: $\delta = 7.15$; ^{13}C, C_6D_6: $\delta = 128.0$) with a JEOL Lambda 300 and a Bruker AMX 400 spectrometer. The solid-state ^6Li MAS and ^{13}C CP/MAS NMR experiments were performed with a Bruker DSX 400 spectrometer, while the two-dimensional ^7Li MQMAS was recorded on a Bruker MSL 400 spectrometer. Melting (decomposition) points were determined by using a MEL TEMP II melting point apparatus. Elemental analysis were performed by the analytical laboratory of the Department of Inorganic Chemistry at Würzburg. The complex $[(thf)_2Li\{(NtBu)_2SMe\}]$ was prepared by the literature procedure.[3]

Compound 1: MeLi (1.6 M, 5.5 mL, 8.82 mmol) was added slowly to a solution of $[(thf)_2Li\{(NtBu)_2SMe\}]$ (3.0 g, 8.82 mmol) in THF (20 mL) at −78 °C. Immediately evolution of methane gas started. The solution was stirred for another two hours at room temperature. The solvent was removed in vacuum, and the white precipitate was dissolved in warm hexane. Storage of the solution for several days at −5 °C afforded colorless crystals suitable for X-ray crystallography, (2.1 g, 86 %). M.p. 114 °C (decomp); ^1H NMR (300 MHz, C_6D_6): $\delta = 0.97$ (s, 4H; S-CH$_2$), 1.22 (m, 8H; THF), 1.44 (s, 36H; C(CH$_3$)$_3$), 3.48 (m, 8H; THF); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 25.42$, 68.70 (THF), 33.85 (C(*C*H$_3$)$_3$), 52.58 (*C*(CH$_3$)$_3$); ^7Li NMR (116.7 MHz, external saturated LiCl solution): $\delta =$ 1.67, 2.73 (2 s, 4 Li); ^6Li MAS NMR (58.9 MHz, external solid LiCl): $\delta = 1.9$, 2.9 (2s, 1:1; 4 Li); ^{13}C CP/MAS NMR (100.6 MHz, external TMS): $\delta =$ −13.9 (S-*C*H$_2$), 25.8, 26.0, 26.2, 69.0 (THF), 34.2, 34.3, 34.8 (4(C(*C*H$_3$)$_3$), 52.8, 53.2 (*C*(CH$_3$)$_3$); elemental analysis calcd (%) for $C_{26}H_{56}Li_4N_4O_2S_2$ (548.63): C 56.92, H 10.29, N 10.21, S 11.69; found C 54.67, H 9.89, N 10.43, S 10.70.

Compound 2: MeLi (1.6 M, 35.5 mL, 57.37 mmol) was added slowly to a solution of $[(thf)_2Li\{(NtBu)_2SCH(CH_3)(C_2H_5)\}]$ (22 g, 57.37 mmol) in THF (35 mL) at −78 °C. Immediately evolution of methane gas started. The solution was stirred for another two hours at room temperature. The solvent was removed in vacuum, and the white precipitate was dissolved in warm hexane. Storage of the solution for several days at −36 °C afforded colorless crystals suitable for X-ray crystallography, (12.7 g, 71 %). M.p. 132 °C (decomp); ^1H NMR (300 MHz, C_6D_6): $\delta = 1.43$ (4H; S-CC*H$_2$*CH$_3$), 1.46 (6H; S-CCH$_2$C*H$_3$*), 1.60 (s, 3H; S-CCH$_3$), 1.33 (m, 8H; THF), 1.48 (s, 36H; C(CH$_3$)$_3$), 3.60 (m, 8H; THF); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 25.52$, 68.29 (THF), 33.11, 33.44, 34.27 (S-C*C*H$_2$CH$_3$ or S-CCH$_2$*C*H$_3$ or S-C*C*H$_3$), 34.51 (C(*C*H$_3$)$_3$), 53.56, 53.63 (*C*(CH$_3$)$_3$); ^7Li NMR (116.7 MHz, external saturated LiCl solution) $\delta = 1.92$ (s, 4 Li); elemental analysis calcd (%) for $C_{32}H_{68}Li_4N_4O_2S_2$ (632.78) C 56.92, H 10.29, N 10.21, S11.69; found C 54.67, H 9.89, N 10.43, S 10.70.

Compound 3: *N,N'*-Di-*tert*-butyl sulfur diimide (0.38 g, 2.2 mmol) was added slowly to a solution of **1** (1.05 g, 2.2 mmol) in THF (10 mL) at room temperature. At first the color of the solution turned from yellow to red. At the end of the addition the color had returned to yellow. After stirring the solution for two hours at room temperature, the THF was removed in vacuum, and the white precipitate was solved in warm hexane. Storage of the solution for several days at −36 °C afforded colorless crystals suitable for X-ray crystallography (0.9 g, 67 %). M.p. 68 °C (decomp); ^1H NMR (300 MHz, C_6D_6): $\delta = 1.33$ (m, 8H; THF), 1.34 (s, 36H; C(CH$_3$)$_3$), 3.57 (m, 8H; THF), 1.54 (s, 2H; SCH$_2$S); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 25.34$, 68.67 (THF), 34.22 (C(*C*H$_3$)$_3$), 52.63 (*C*(CH$_3$)$_3$) 64.00 (S-*C*H$_2$-S); ^7Li NMR (116.7 MHz, external satuarated LiCl solution) $\delta = 1.58$, 2.06.

Crystallographic measurements: Crystal data for the structures **1**, **2**, and **3** are presented in Table 1. Data for the structures **1** and **2** were collected at low temperature (173(2) K) on oil-coated shock-cooled crystals[23] on a Stoe IPDS diffractometer with monochromated $Mo_{K\alpha}$ radiation ($\lambda =$ 71.073 pm). The data for structure **3** was collected on a Enraf-Nonius CAD4 diffractometer with κ geometry in $\omega/2\Theta$ scan mode. The structures were solved by Patterson or direct methods with SHELXS-NT 97.[24] All structures were refined by full-matrix least-squares procedures on F^2 with SHELXL-NT 97.[25] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. The positions of the important hydrogen atoms at the metalated carbon atoms in **1**, **2**, and **3** were taken from the difference Fourier map and refined freely. The disordered THF molecule in **2** was refined to split occupancy of 0.57/0.43 (O1 – C28). In **3** one *tert*-butyl group and eight THF molecules (five coordinated to the complex and three additional lattice solvents) were disordered and were refined to split occupancies: 0.48/0.52 (C71 – C73), 0.48/0.52 (O1t – C14t), 0.39/0.61 (O2t – C24t), 0.65/0.35 (O3t – C34t), 0.31/0.69 (O4t – C44t), 0.6/0.4 (O5t – C54t), 0.53/0.47 (O6t – C64t), 0.5/0.5 (O7t – C74t), 0.64/0.36 (O8t – C84t). All disordered groups were

Table 1. Crystal data and structure refinement for **1**, **2**, and **3**.

	1	**2**	**3**
formula	$C_{26}H_{56}Li_4N_4O_2S_2$	$C_{32}H_{68}Li_4N_4O_2S_2$	$C_{66}H_{138}ClLi_7N_8O_8S_4$
M_r	548.63	632.78	1384.11
crystal size [mm]	0.2 × 0.2 × 0.1	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.2
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [pm]	960.89(19)	1057.3(2)	1521.27(10)
b [pm]	1884.0(4)	1216.0(2)	1537.61(10)
c [pm]	1008.0(2)	1612.7(3)	1934.79(10)
α [°]	90	97.99(3)	83.588(10)
β [°]	111.06(3)	91.47(3)	79.912(10)
γ [°]	90	106.92(3)	68.434(10)
V [nm^3]	1702.9(6)	1959.7(7)	4.1383(4)
Z	2	2	2
ρ_{calcd} [Mg m^{-3}]	1.070	1.072	1.111
μ [mm^{-1}]	0.182	0.166	0.197
$F(000)$	600	696	1512
Θ range [°]	2.42–24.75	2.34–24.71	3.04–22.48
reflections measured	11032	12756	11685
unique reflections	2909	6274	10751
R(int)	0.0994	0.0675	0.0258
data/restraints/parameters	2909/77/186	6274/30/459	10751/1690/1278
goodness-of-fit on F^2	0.879	0.933	1.020
$R1$[a] [$I > 2\sigma(I)$]	0.0442	0.0567	0.0480
$wR2$[b] (all data)	0.0971	0.1582	0.1226
g_1/g_2[c]	0.0376/0.0000	0.1004/0.0000	0.0541/2.2189
largest difference peak/hole [e nm^{-3}]	198/−254	1182/−434	254/−213

[a] $R1 = \Sigma \|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] $w = 1/\sigma(F_o^2) + (g_1P)^2 + g_2P$; $P = [\max(F_o^2,0) + 2F_c^2]/3$.

refined with distance and similarity restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151664 (**1**), CCDC-151663 (**2**) and CCDC-151662 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[18] The two-dimensional ^{7}Li solid-state NMR spectrum of **1** was recorded on a Bruker MSL400 spectrometer with a two-pulse sequence by using time-proportional phase incrementation (TPPI). The experiment was performed with a 4 mm double bearing CP/MAS probe at 155.5 MHz and the sample was spun at MAS speed of 10 kHz. The 90° degree nonselective pulse length was 3.8 µs measured on saturated aqueous LiCl solution. The experiment was performed by using a calculated pulse length of 10.1 µs for the first pulse and 2.3 µs for the second pulse. 600 scans were accumulated for each F_1 increment, for 128 increments were measured. In F_2 a time domain of 2048 points was used. The recycle delay was 1 s, and the depicted spectrum is not sheared.

[19] R. Fleischer, Ph.D. Dissertation **1997**, Universität Würzburg; direct synthesis of $[(\mathrm{thf})_6\mathrm{Li}_6\mathrm{S}\{(\mathrm{N}t\mathrm{Bu})_3\mathrm{S}\}_2]$: *N,N'*-di-*tert*-butyl sulfur diimide (8.72 g, 50 mmol) was added to freshly cut lithium (0.347 g, 50 mmol) in THF (10 mL). After 3 h stirring, the lithium was completely dissolved. Crystallization from the deep red THF solution at room temperature gave colorless crystals. After the reaction solution was decanted, the volume was reduced by half, and an additional batch of crystals was obtained. $M = 997.36$; yield: 7.3 g (88%); m.p. 111 °C (135 °C decomp.); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.38$ (m, 4H; THF), 1.40 (s, 9H; $C(CH_3)_3$), 3.56 (m, 4H; THF); ^{7}Li NMR (100 MHz, C_6D_6): $\delta = 2.83$ (s); crystal data: rhombohedral, space group $R\bar{3}$, $a = 1791.0(3)$, $c = 2350.8(5)$ pm, $V = 6.530(2)$ nm^3, $Z = 3$.

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