Novel Asymmetrical Dianionic Polyimido-Sulfur(IV)-Ylides

Carola Selinka and Dietmar Stalke

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg

Reprint requests to Prof. Dr. D. Stalke and C. Selinka. Tel. +49(0)931-888-4783; Fax +49(0)931-888-4619; E-mail: dstalke@chemie.uni-wuerzburg.de

Sulfurdiimides RN=S=NR react in donating solvents with two equivalents of lithiumalkyls to give the dimeric *C,N*-dilithium-methylenediimidosulfite solvent adducts [(Et$_2$O)Li$_2$\{H$_2$CS-(NSiMe$_3$)(N^{t}Bu)\}]$_2$ (**1**) and [(thf)Li$_2$\{H$_8$C$_4$S(N^{t}Bu)$_2$\}]$_2$ (**2**). Firstly, addition of a lithiumalkyl to sulfurdiimide gives the diimidosulfinates [RS(NR′)$_2$]$^-$ (**1**: R = Me, R′ = ^{t}Bu, SiMe$_3$; **2**: R = nBu; R′ = ^{t}Bu) while in a second step the α-carbon atom in R is metalated with one equivalent of lithiumalkyl to give the asymmetric S-ylides. The reaction of 3-bromothiophene with one equivalent of *n*BuLi and one of sulfurdiimide ^{t}BuN=S=N^{t}Bu resulted in the dilithium-3-thiophenylenediimidosulfite [(thf)Li$_2$\{(SC$_4$H$_2$)S(N^{t}Bu)$_2$\}]$_2$ (**3**). It can be regarded as the first example of a dianionic S(IV)-β-ylide. This class of compounds can be rationalised as sulfite analogues, where two oxygen atoms are isoelectronically replaced by a NR group each and the remaining oxygen atom is replaced by a CR$_2$ group. The rich coordination chemistry of the triimidosulfites is extended by the introduction of a hard carbanionic centre.

Key words: Chiral Auxiliaries, Sulfur Ylides, Wittig Reactions

Introduction

Isoelectronic replacement [1] of the oxygen atoms in the simple p-block element oxoanions by a NR imido group is currently a flourishing area of main group chemistry [2].

Although our research focused so far on sulfur nitrogen compounds like S(NR)$_2$, [S(NR)$_3$]$^{2-}$, S(NR)$_3$ and [S(NR)$_4$]$^{2-}$ [4], more recently the oxygen centres in sulfur oxoanions can also be replaced isoelectronically by alkylene groups (= CR$_2$) [5]. C$_\alpha$-deprotonation of the S-bound substituents in diimidosulfinates R$_2$(H)CS(NR)$_2^-$ [6] and methyltriimidosulfonates H$_3$CS(NR)$_3^-$ [7] yields the dianionic alkylenediimidosulfites R$_2$CS(NR)$_2^{2-}$ [8] or methylenetriimidosulfates R$_2$CS(NR)$_3^{2-}$ [9], the carba/imido analogues of SO$_3^{2-}$ and SO$_4^{2-}$. Similar to *Wittig's* phosphonium ylides R$_3$P$^+$–$^-$CR$_2$ these molecules contain a positively charged hetero-atom (sulfur in analogy to phosphorus) next to a carbanionic centre (Scheme 1). The first S-ylide was prepared by Ingold and Jessop in 1930 [10] and the synthetic potential of R$_2$(O)S$^+$–$^-$CR$_2$ was mainly elaborated by Corey [11]. Today sulfur ylides are mainly used in catalytic asymmetric synthesis of epoxides starting from aldehyds [12] and in the synthesis of substituted indoles [13].
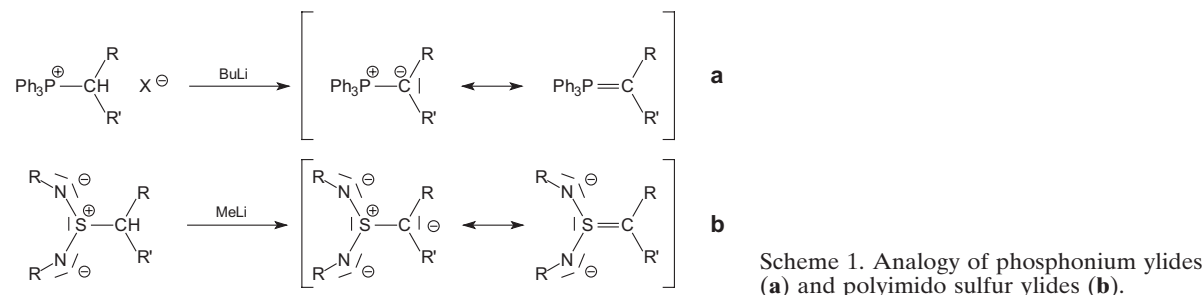
In this paper we present the C- and S-asymmetric S-ylides [(Et$_2$O)Li$_2$\{H$_2$CS(NSiMe$_3$)(N^{t}Bu)\}]$_2$ (**1**) and [(thf)Li$_2$\{H$_8$C$_4$S(N^{t}Bu)$_2$\}]$_2$ (**2**) and the unprecedented dianionic S(IV)-β-ylide dilithium-3-thiophenylenediimidosulfite [(thf)Li$_2$\{(SC$_4$H$_2$)S(N^{t}Bu)$_2$\}]$_2$ (**3**).

Results and Discussion

Synthesis of **1** *and* **2**. The direct chemical replacement of an oxygen atom of sulfates or an

Table 1. Some imido analogues of p-block oxoanions [3].

Group 13	Group 14	Group 15	Group 16
[B(NR)$_3$]$^{3-}$[3a]	[C(NR)$_3$]$^{2-}$[3b]		
	[Si(NR)$_3$]$^{2-}$[3c]	[P(NR)$_3$]$^-$[3e]	[S(NR)$_3$]$^{2-}$[3j]
	[Si(NR)$_4$]$^{4-}$[3d]	[P(NR)$_4$]$^{3-}$[3f]	[S(NR)$_4$]$^{2-}$[3k]
		[As(NR)$_3$]$^{3-}$[3g,h]	[Se(NR)$_3$]$^{2-}$[3l]
		[Sb(NR)$_3$]$^{3-}$[3i]	[Te(NR)$_3$]$^{2-}$[3m]

Scheme 1. Analogy of phosphonium ylides (**a**) and polyimido sulfur ylides (**b**).

imido group of polyimidosulfates by the CR_2 group is precluded. However, the following synthetic route provides access to those compounds: In the first step addition of one equivalent of a lithium alkyl to sulfurdiimide leads to the alkyldiimidosulfinates [6] [RS(N^{t}Bu)(NR$^\prime$)]$^-$. In the second step the α-carbon atom of the S-bound alkyl residue is metalated with one equivalent of lithium alkyl and the dianionic S-ylides are obtained (Scheme 2).

In this work we aimed to introduce asymmetry to the diimido sulfur ylides. In principle this can

either be achieved at the sulfur atom while starting from an asymmetrically substituted sulfurdiimide RN=S=NR$^\prime$ or by the S-bound alkyl group to give a chiral carbanionic centre upon lithiation. The resulting ligands might serve as chiral auxiliaries in metal coordination to give asymmetrical induction in Wittig type >C=C< or >C=N– bond formation or in catalysis.

$[(Et_2O)Li_2\{H_2CS(NSiMe_3)(N^tBu)\}]_2$ (**1**) is the product from the first approach obtained in a one-pot reaction. Two equivalents of ^{t}BuN=S=NSiMe$_3$ reacted with four equivalents of methyllithium to give the S-ylide **1** as a dimer in the solid state. Chirality at the carbanionic centre in $[(thf)Li_2\{H_8C_4S(N^tBu)_2\}]_2$ (**2**) was introduced by addition of nBuLi to S(N^{t}Bu)$_2$ followed by lithiation with a second equivalent of nBuLi. Unfortunately all attempts to deprotonate other asymmetric alkyldiimidosulfinates like *e.g.* $[(Et_2O)Li\{H_3CS(NSiMe_3)(NC_6H_{11})\}]_2$ with MeLi so far failed under various reaction conditions.

Crystal structures of **1** *and* **2**. The crystal structure of $[(Et_2O)Li_2\{H_2CS(NSiMe_3)(N^tBu)\}]_2$ (**1**) consists of two distorted $SN_2C_2Li_3$ cubes with a common C_2Li_2 face (Fig. 1). The asymmetrical substitution of the NSN backbone, compared to the bis-*tert*-butyl substituted species $[(thf)Li_2\{H_2CS$-$(N^tBu)_2\}]_2$ [8] has only a marginal effect on the geometric properties in **1**. The S–N bond lengths (av. 165 pm) are in the same range as in $[(thf)Li_2\{H_2CS(N^tBu)_2\}]_2$ (av. 166 pm) and $[(thf)Li_2\{(Et)(Me)CS(N^tBu)_2\}]_2$ (av. 165 pm) [8]. The S–C bond length of 177.7(3) pm in **1** is as long as the S–C single bond found in alkyldiimidosulfinates (~181 pm) or alkyltriimidosulfonates (~179 pm). No bond shortening, anticipated from a charge delocalisation and S=C double bond character in an ylenic canonical formula (**a** in Chart 1) is ascertained. The S–N and S–C bond
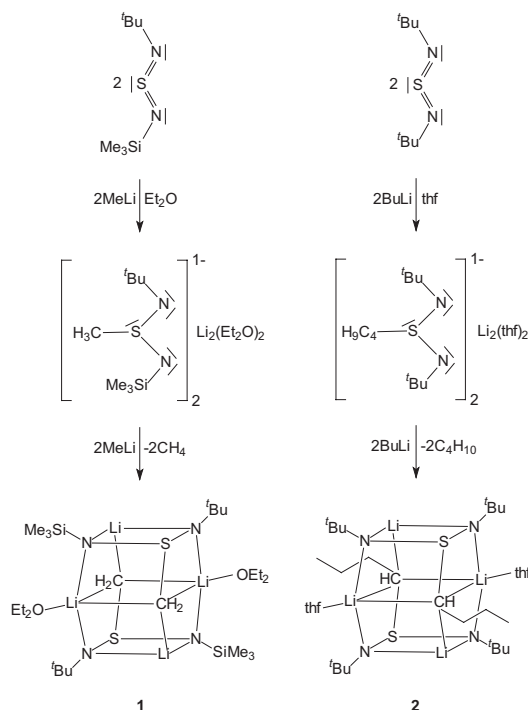
Scheme 2. Synthesis of the C- and S-asymmetric substituted diimido S-ylides $[(Et_2O)Li_2\{H_2CS(NSiMe_3)$-$(N^tBu)\}]_2$ (**1**) and $[(thf)Li_2\{H_8C_4S(N^tBu)_2\}]_2$ (**2**).

lengths indicate that one negative charge is shared by the two nitrogen atoms of the SN_2 backbone, while the second negative charge is localised at the carbon atom. These findings confirm the assumption, that the ylidic type resonance formula (**b** in Chart 1) describes the bonding in the molecule best.
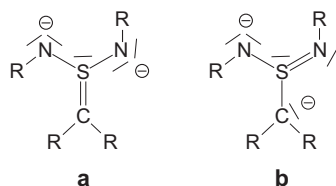

Chart 1. Ylenic (**a**) and ylidic (**b**) canonical formula of alkylenediimidosulfites.

Since a centre of inversion is located in the middle of the C_2Li_2 four membered ring, **1** crystallises as a racemate. In addition, in the solid state structure the $SiMe_3$ group and the ^tBu group are disordered in a ratio of ¼ to ¾ in site occupation factors.

The structure of $[(thf)Li_2\{H_8C_4S(N^tBu)_2\}]_2$ (**2**) is isomorphous, but not isostructural to **1**. The main structural features of both are similar. The av. S–N bond length in **2** of 166 pm is almost identical to that found in **1** (av. 165 pm). The replacement of the methylene group in $[(thf)Li_2\{H_2CS(N^tBu)_2\}]_2$ by the bulkier butylene group in **2** has only little effect on the S–C bond length. In $[(thf)Li_2\{H_2CS(N^tBu)_2\}]_2$ the S–C bond length is 178.6(3) pm while in **2** it is slightly longer (179.9(2) pm). The structures of the alkylenediimidosulfites are only marginally affected by the different substituents at the nitrogen and carbon atoms, respectively. In any case the double-cubic
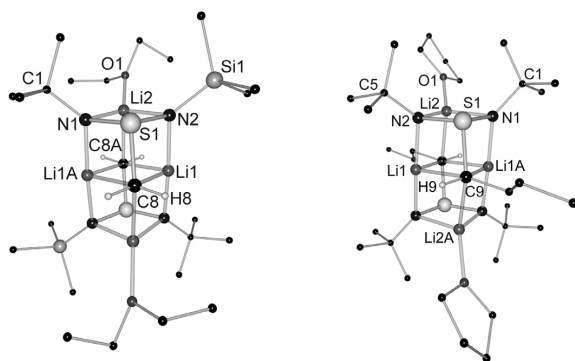

Fig. 1. Solid state structures of $[(Et_2O)Li_2\{H_2CS(NSiMe_3)(N^tBu)\}]_2$ (**1**) and $[(thf)Li_2\{H_8C_4S(N^tBu)_2\}]_2$ (**2**).

Table 2. Selected bond lengths [pm] and angles [°] of $[(Et_2O)Li_2\{H_2CS(NSiMe_3)(N^tBu)\}]_2$ (**1**) and $[(thf)Li_2\{H_8C_4S(N^tBu)_2\}]_2$ (**2**).

Atom	1	2
S1–N1	163.9(3)	165.41(19)
S1–N2	165.0(3)	166.28(19)
S1–C8/9	177.7(3)	179.9(2)
N1–Li1A	198.2(6)	198.1(4)
N1–Li2	208.2(6)	209.9(5)
N2–Li1	200.0(6)	198.9(4)
N2–Li2	208.5(7)	205.4(4)
C8/9–Li1	238.0(7)	244.2(5)
C8/9–Li1A	240.4(7)	236.0(4)
C8/9–Li2A	229.3(6)	230.2(5)
N1–S1–N2	104.45(14)	104.55(10)
N1–S1–C8/9	100.16(16)	98.99(10)
N2–S1–C8/9	100.04(15)	99.88(10)
N2–Li1–N1A	176.4(4)	177.6(2)
S1–C8/9–Li2A	144.0(2)	142.82(16)
S1–N1–Li2	89.4(2)	87.89(14)
S1–N2–Li2	89.0(2)	89.20(14)
Li1–C8/9–Li1A	69.3(2)	68.34(17)
C8/9–Li1–C8A/9A	110.6(3)	111.66(17)

structure is retained. The conversion of a hexagonal prismatic structure in $[Li_2\{N^tBu\}_3S]_2$ [3j] (Chart 2, left) into two distorted $SN_2C_2Li_3$ cubes with a common C_2Li_2 face in **1** and **2** (Chart 2, right) can be rationalised by the contraction caused by the formation of two additional Li–C bonds across the six-membered Li_2N_3S rings. **2** is an intermediate case. The C9–Li1 distance of 244.2(5) pm is very long, indicating that **2** is 'on the way' to a hexagonal prismatic structure.
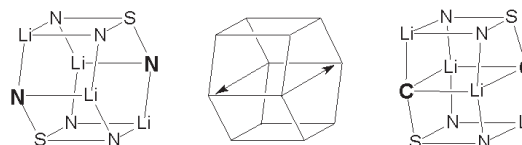

Chart 2. The replacement of a single NR group in $S(NR)_3^{2-}$ by a CR_2 group in $S(NR)_2(CR_2)^{2-}$ causes the hexagonal prismatic dimer to change into two face connected cubes (R groups on N and C are omitted).

A database search for C–Li distances [14] reveals that the C8/9–Li1 bond length of 236.0(4) to 244.2(5) pm fall at the long end of the range covered by C–Li bonds (Scheme 3).

Synthesis of **3**. For the preparation of $[(thf)Li_2\{(SC_4H_2)S(N^tBu)_2\}]_2$ (**3**) two equivalents of *n*BuLi and 3-bromothiophene [15] are added *in situ* to the sulfurdiimide. In the product the thiophenyl substituent is added in the 3-position to the
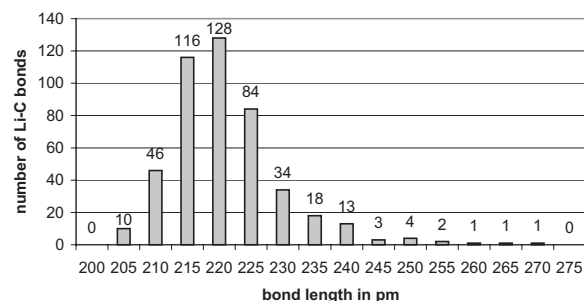
Scheme 3. Distribution and frequency of C–Li bond lengths [pm] in the CCDC.

sulfur atom and deprotonated in the 2-position. Hence, two reaction mechanisms are plausible. First the thiophene starting material is metalated twice in the 2- and 3-position and subsequently reacts at its 3-position with the formal S=N double bond of the sulfurdiimide. The second possibility is the selective single metalation of the 3-position of the ring, addition of the thiophenyl substituent to the sulfurdiimide and subsequent metalation of the 2-position. The first option should mainly give the 2-substituted and 3-deprotonated product, because of the higher nucleophilic character of the 2-position. However, we never observed this product. Therefore the second route with a selective single metalation of the 3-position, addition onto sulfurdiimide and subsequent metalation of the 2-position seems the most likely pathway. The lithiation of the heteroaryl ring can either be accomplished by nBuLi or 3-lithiothiopene (Scheme 4). This reaction sequence is further substantiated by the similar lithiation reaction of bis(trimethylsilyl)-methylphenylsulfone, which yielded 1,o-dilithio-bis(trimethylsilyl)methylphenylsulfon [16].
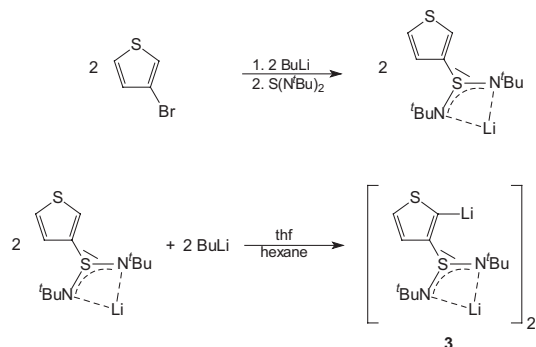
Scheme 4. Proposed reaction pathway to **3**.

The structure of $[(thf)Li_2\{(SC_4H_2)S(N^tBu)_2\}]_2$ (**3**), adopts in analogy to the known triimidosulfites [3j], triimidoselenites [3l], triimidotellurites [3m] and alkylene-diimidosulfites [8] a dimeric aggregation (Fig. 2). Both tripodal ligands are facing each other with their concave sites in a staggered conformation. This cyclic ladder cage was first observed with lithium amides [17] and differs considerably from the face-connected cubes of sulfur(IV)-α-ylides. The closest structural relationship to **3** is found in $[Cl_3Sn\{(N^tBu)_2S(fc)\}]$ [18] (fc = ferrocenyl). The monomeric anion shows the anticipated $\eta^5\pi$-coordination of a Cp ring at the sulfur rather than the $\mu^2\varrho$-bonding of the thiophenyl substituent in the dianion of **3**. The bite of the tripodal dianion in **3** is remarkably wide because the anionic ring-C does not directly bind to the sulfur atom. The sum of distances from the centre of the N1, N2, C9 triangle to the coordinating nitrogen and carbon atoms in **3** (512.0 pm) is 60–70 pm longer than in the alkylene diimidosulfites $R_2CS(NR)_2^{2-}$ (454.4 pm) [8] and triimidosulfite $S(NR)_3^{2-}$ (441.7 pm) [3j], respectively. The S–N bonds (av. 164 pm) in **3** are longer than typical formal S=N double bonds determined by topological analysis while the S–C bond (av. 180 pm) is shorter than a typical S–C single bond [19]. The C9–C10 and C21–C22 (av. 139 pm) bonds are 3 pm longer than the other ring double bonds. This clearly indi-
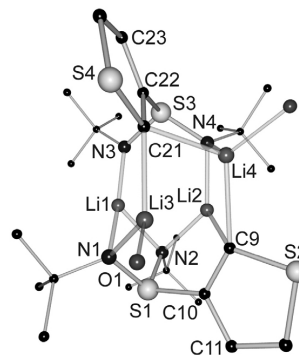

Fig. 2. Solid state structure of $[(thf)Li_2\{(SC_4H_2)S-(N^tBu)_2\}]_2$ (**3**); selected bond lengths [pm] and angles [°]. S1–C10 179.4(2), S1–N1 163.68(18), S1–N2 164.40(19), C10–C9 138.8(3), C11–C12 136.0(3), N1–Li1 207.0(4), N1–Li3 201.9(4), N2–Li1 205.5(5), N2–Li2 199.6(4), C9–Li2 222.8(5), C9–Li4 232.4(4), C9⋯Li3 240.3(5), S3–N3 162.50(19), S3–N4 164.51(18), S3–C22 179.7(2), C21–C22 138.4(3), C23–C24 135.2(3), N1–S1–N2 102.34(9), N1–S1–C10 101.49(10), N2–S1–C10 103.05(10), N3–S3–N4 106.59(9), N3–S3–C22 105.98(10), N4–S3–C22 101.15(10).
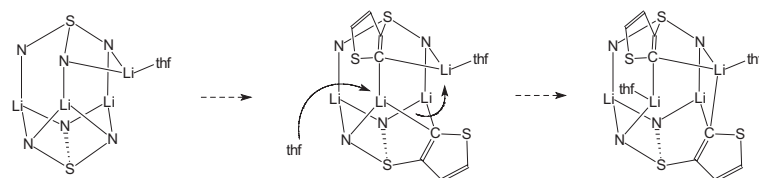
Scheme 5. Structural deduction of the cage found in **3** from the thf adduct of triimidosulfite (^{t}butyl groups are omitted for clarity).

cates a charge transfer from the metalated ring carbon atom to the SN_2-unit. The rationalisation of **3** as a sulfur(IV)-β-ylide like $[O(MeN)(MeHC)(H_4C_6)S]^{2-}$ [20] seems valid.

The structure of the β-ylide resembles more the structure of the triimidosulfite thf-adduct [3j], an open hexagonal prism (see Scheme 5), than the double-cubic structures of **1** and **2**. The complete structure can be deduced from the thf adduct of the triimidosulfite $[(thf)Li_4\{(N^tBu)_3S\}_2]$ by addition of another thf to Li3 inducing bond cleavage of Li3–C9 and bond formation of C9–Li4.

^{7}Li NMR spectroscopic investigations of **3**. As can be seen from the solid state structure depicted in Fig. 2, each of the four lithium cations in $[(thf)Li_2\{(SC_4H_2)S(N^tBu)_2\}]_2$ (**3**) adopts its own chemical and hence magnetical environment. There-

fore, in non-donating solvents, anticipating that the solid-state structure is retained, a Li NMR spectrum should ideally resolve the four different sites of the lithium cations. Variable temperature ^{7}Li NMR spectra of **3** in d_8-toluene were recorded and gave the results shown in Fig. 3.

At room temperature only one peak for the different lithium environments could be obtained. The small peak at 1.45 ppm vanishing upon cooling is attributed to an impurity. The coalescence point is reached at 273 K and at 263 K two signals are deconvoluted. The broad one at 3.38 ppm is assigned to the trigonally coordinated lithium atoms Li1 and Li2, the sharp peak at 2.07 ppm to the distorted tetrahedrally coordinated Li3 and Li4, where an additional thf is coordinated to lithium (for Li3···C9 a bonding interaction is assumed in solution). It was not possible
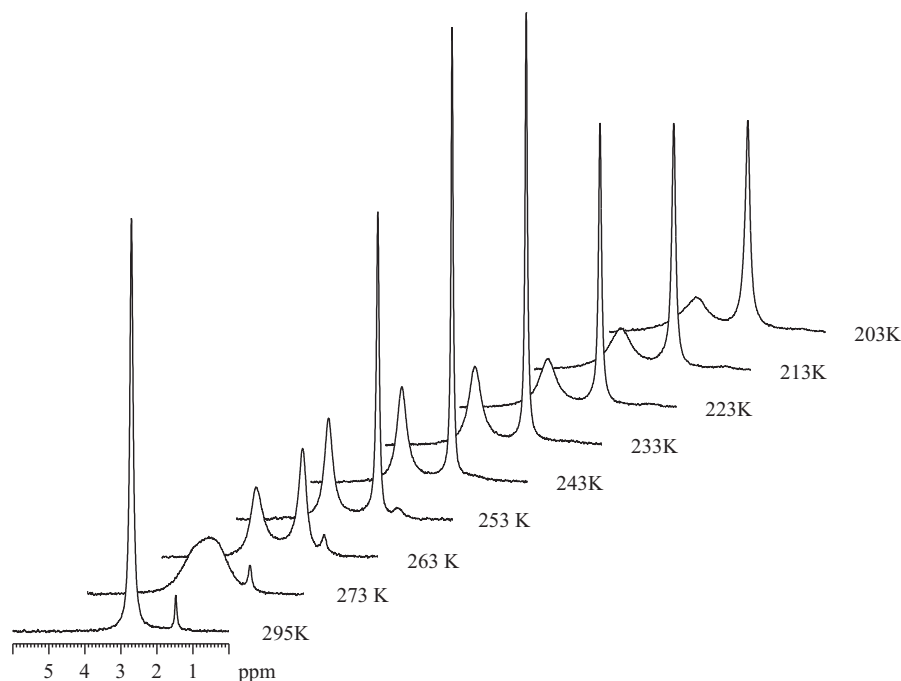

Fig. 3. ^{7}Li NMR spectra of $[(thf)Li_2\{(SC_4H_2)S(N^tBu)_2\}]_2$ (**3**) at different temperatures in d_8-toluene.

Table 3. Chemical shifts of $[(thf)Li_2\{(SC_4H_2)S(N^tBu)_2\}]_2$ (**3**) at different temperatures in d_8-toluene.

T [K]	Li–thf (Li1/Li2)	Li–trigonal (Li3/Li4)	Integration
RT		2.70	4
273		2.62	4
263	2.07	3.38	2/2
253	2.07	3.42	2/2
243	2.07	3.48	2/2
233	2.08	3.52	2/2
223	2.10	3.59	2/2
213	2.13	3.63	2/2
203	2.14	3.57	2/2

to resolve the signals for all four different lithium environments, either due to the line broadening in the standard ^{7}Li NMR spectrum or the equilibration of the four sites to give only two in solution.

Conclusion

In conclusion the deprotonation of the α-carbon atoms in S-alkyl-diimidosulfinates $[H_3CS(NSiMe_3)(N^tBu)]^-$ and $[H_9C_4S(N^tBu)_2]^-$ with lithiumorganics opens an easy synthetic route to two new classes of compounds. The asymmetric alkylene diimidosulfites $[H_2CS(NSiMe_3)(N^tBu)]^{2-}$ and $[H_8C_4S(N^tBu)_2]^{2-}$ can be rationalised as S-ylides or the carba-/diimido-analogues of sulfite SO_3^{2-}. $[(SC_4H_2)S(N^tBu)_2]^{2-}$ is the first dianionic sulfur(IV)-β-ylide that contains a thiophenyl substituent connected to the sulfur atom in the 3-position and deprotonated in the 2-position. Apart from the synthetic potential in analogy to the well established Wittig phosphonium ylides these molecules broaden the rich coordination chemistry of the triimidosulfites by the introduction of a carbon centre. The dianionic sulfur(IV)-β-ylide provides the opportunity to connect SN$_2$ chelates *via* conjugated spacers with a potential metal S-donor centre.

Experimental Section

General. All manipulations were performed under inert-gas atmosphere of dry N$_2$ with Schlenk techniques or in an argon glovebox. All solvents were dried over Na/K alloy and distilled prior to use. ^{1}H, ^{7}Li and ^{13}C NMR spectra were recorded in C$_6$D$_6$ (^{1}H: C$_6$HD$_5$: δ = 7.15; ^{13}C: C$_6$D$_6$: δ = 128.0) using a Bruker AMX 400 spectrometer. Elemental analyses were performed by the Microanalytisches Labor der Universität Würzburg.

Synthesis of $[(Et_2O)Li_2\{H_2CS(NSiMe_3)(N^tBu)\}]_2$ (**1**). A solution of methyllithium in diethyl ether (1.6 M, 5.25 mmol, 3.28 ml) was added dropwise to a solution of N-*tert*-butyl-N′-trimethylsilylsulfurdiimide (5.25 mmol, 1.00 g) in 5 ml diethyl ether at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. A second equivalent of methyllithium in diethyl ether (1.6 M, 5.25 mmol, 3.28 ml) was added to the solution at −78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. Colourless crystals were obtained directly from the reaction mixture upon 7 days storage at −36 °C. (yield: 1.25 g, 81%). – M.p. 117 °C (dec.). – ^{1}H NMR (300.4 MHz, C$_6$D$_6$): δ = 0.32 (s, 9 H, SiMe$_3$), 1.08 (t, 6 H, O(CH$_2$Me)$_2$), 1.13 (s, 2 H, SCH$_2$), 1.33 (s, 9 H, CMe$_3$), 3.25 (q, 4H, O(CH_2Me)$_2$). – ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 1.36 (Si*Me$_3$*), 15.04 (O(CH$_2$*Me*)$_2$), 33.49 (C*Me$_3$*), 42.92 (SCH$_2$), 52.32 (*C*Me$_3$), 65.18 (O(*C*H$_2$Me)$_2$); ^{7}Li (155.5 MHz, ext. sat. LiCl solution): δ = 3.00. – ^{29}Si NMR (60 MHz, C$_6$D$_6$): δ = −2.1, −4.5. – C$_{24}$H$_{60}$Li$_4$N$_4$O$_2$S$_2$Si$_2$ (584.43): calcd. C 49.29, H 10.34, N 9.58, S 10.96; found C 45.98, H 9.09, N 9.47, S 9.33.

Synthesis of $[(thf)Li_2\{H_8C_4S(N^tBu)\}]_2$ (**2**). A solution of *n*-butyllithium in hexane (1.6 M, 11.47 mmol, 7.17 ml) was added dropwise to a solution of N,N′bis(*tert*-butyl)sulfurdiimide (5.7 mmol, 1.00 g) in 5 ml thf and 1.7 ml tmeda and stirred for 12 h. Colourless crystals were obtained directly from the reaction mixture upon 7 days storage at +6 °C (yield: 0.63 g, 35%). M.p.: 50 °C. – ^{1}H NMR (300.4 MHz, C$_6$D$_6$): δ = 0.87 (m, 1 H, S–C*H*LiCH$_2$CH$_2$Me), 1.11 (t, 3 H, S–CHLiCH$_2$CH$_2$Me), 1.30 (qi, 4 H, O(CH$_2$C*H$_2$*)$_2$), 1.38 + 1.40 (s, 18 H, CMe$_3$), 1.49 (m, 2 H, S–CHLiCH$_2$C*H$_2$*Me), 1.57 (m, 2 H, S–CHLiC*H$_2$*CH$_2$Me), 3.59 (t, 4 H, (O(C*H$_2$*CH$_2$)$_2$). – ^{13}C-NMR (100 MHz, C$_6$D$_6$): δ = 14.58 (S–CHLiCH$_2$CH$_2$Me), 25.32 ((*C*H$_2$CH$_2$)$_2$O), 27.40 (S–CHLiCH$_2$*C*H$_2$Me), 33.78 (S–*C*H$_2$CH$_2$CH$_2$Me), 34.04 + 34.30 (C*Me$_3$*), 52.01 + 52.29 (*C*Me$_3$), 52.14 (S–C*H*LiCH$_2$CH$_2$Me), 68.57 (O(*C*H$_2$CH$_2$)$_2$). – ^{7}Li (155.5 MHz, ext. sat. LiCl solution): δ = 2.42, 2.51. – C$_{32}$H$_{68}$Li$_4$N$_4$O$_2$S$_2$ (632.54): calcd. C 60.74, H 10.83, N 8.85, S 10.13; found C 59.09, H 10.23, N 8.96, S 9.44.

Synthesis of $[(thf)Li_2\{(SC_4H_2)S(N^tBu)_2\}]_2$ (**3**). To a solution of 3-bromothiophene (10 mmol, 1.63 g) in 15 ml hexane a solution of *n*-butyllithium in hexane (1.6 M, 10.56 mmol, 6.6 ml) was dropped slowly at −40 °C. 2 ml thf were added and the suspension was stirred 15 min. 5 ml hexane were added to the suspension and warmed to room temperature. Subsequently N,N′-bis(*tert*-bu-

tyl)sulfurdiimide (10 mmol, 1.75 g) was added. The suspension was heated instantaneously till the white precipitate dissolved. Storage of the solution for 10 min afforded colourless crystals. (yield: 0.376 g, 22%). M.p. 94 °C (dec). – ^{1}H NMR (400 MHz, C_6D_6): δ = 1.27 (qi, 4 H, $O(CH_2CH_2)_2$), 1.36 (s, 18 H, CMe_3), 3.41 (t, 4 H; $O(CH_2CH_2)_2$), 7.48 (d, 1 H, C_4H_2S), 7.66 (d, 1 H, C_4H_2S). – ^{13}C NMR (100 MHz, C_6D_6): δ = 25.36 ($O(CH_2CH_2)_2$), 33.17, 33.49 ((CMe_3), 54.15, 54.55 (CMe_3), 68.41 ($O(CH_2CH_2)_2$), 125.64, 127.16, 132.33, 165.67 (C_4H_2S). – ^{7}Li NMR (116.7 MHz, ext. sat. LiCl solution) RT: δ = 2.54 (s, 2Li); –30 °C: δ = 2.07 (s, 1 Li), 3.48 (s, 1 Li). – $C_{32}H_{56}Li_4N_4O_2S_4$ (684.82): C 56.12, H 8.24, N 8.18, S 18.73; found C 55.54, H 8.12, N 8.19, S 18.23.

Crystal structure determination of **1–3**. Crystal data for the structures **1–3** are presented in Table 4. Data were collected from shock-cooled crystals on a BRUKER SMART-APEX diffractometer (graphite-monochromated Mo-K$_\alpha$ radiation, λ = 71.073 pm) equipped with a low temperature device [21]. Data collection was performed in the ω-scan mode with step widths of 0.3°. The program SAINT-NT [22] was employed for integration of the frames. The obtained data were empirically absorption corrected applying SADABS2 [23]. The structures were solved by direct methods (SHELXS-97) [24] and refined by full-matrix least squares methods against F^2 (SHELXL-97) [25]. R values defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, w = $[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2, 0) + 2F_c^2]$. The H-atoms at C8 in **1** and that one at C9 in **2** were located by difference Fourier synthesis and refined freely. The disordered *tert*-butyl- and trimethylsilyl-groups of the sulfurdiimide backbone in **1** were refined using distance restraints (SAME) to split occupancies of 0.76/0.24. The disordered Et_2O molecule at Li1 was refined using distance restraints (SADI) to split occupancies of 0.81/0.19. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. see Table 3. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)336-033; e-mail: deposit@ccdc. cam.ac.uk].

Table 4. Crystal data of **1–3**.

	1	**2**	**3**
Formula	$C_{24}H_{60}Li_4N_4O_2S_2Si_2$	$C_{32}H_{68}Li_4N_4O_2S_2$	$C_{32}H_{56}Li_4N_4O_2S_4$
CCDC-no.	198108	198109	189363
M_r	584.82	632.78	684.81
T [K]	173(2)	173(2)	100(2)
Crystal size [mm]	$0.4 \times 0.3 \times 0.3$	$0.3 \times 0.3 \times 0.2$	$0.3 \times 0.2 \times 0.2$
Space group	$C2/c$	$P2_1/n$	$P2_1/c$
a [pm]	2381.34(5)	1114.81(12)	1394.75(6)
b [pm]	992.41(2)	1608.21(17)	1828.08(8)
c [pm]	1741.51(4)	1200.07(13)	1511.86(7)
β [°]	111.306(2)	108.072(2)	91.7140(10)
V [nm³], Z	3.83436(14), 8	2.04540(63), 4	3.8531(3), 4
ϱ_{calcd} [mg/m³]	1.013	1.027	1.181
μ [mm^{-1}]	0.224	0.159	0.279
$F(000)$	1280	696	1472
θ Range [°]	1.84–24.97	2.18–25.03	1.75–25.03
No. of refl. measd.	21110	19882	41531
No. of unique refl.	3369	3616	6796
R(int)	0.0483	0.0293	0.0635
Data/restraints/param.	3369/232/302	3616/0/209	6796/0/427
GooF on F^2	1.283	1.193	1.017
$R1$ [$I > 2\sigma(I)$]	0.0765	0.0610	0.0425
$wR2$ (all data)	0.1796	0.1520	0.1055
$g1/g2$	0.0717/5.0436	0.0648/1.1846	0.0483/2.7500
Largest diff. peak/hole [e nm^{-3}]	554/−232	462/−281	542/−297

[1] I. Langmuir, J. Am. Chem. Soc. **41**, 868 and 1543 (1919).

[2] Reviews: a) M. A. Beswick and D. S. Wright, Coord. Chem. Rev. **176**, 373 (1998); b) T. Chivers and J. K. Bask, Angew. Chem. **113**, 4082 (2001), Angew. Chem. Int. Ed. **40**, 3988 (2001); b) G. M. Aspinall, M. C. Copsey, A. P. Leedham, and C. A. Russel, Coord. Chem. Rev. **227**, 217 (2002).

[3] a) $B(NR)_3^{3-}$: U. Braun, T. Habereder, H. Nöth, H. Piotrowski, and M. Warchhold, Eur. J. Inorg. Chem. **5**, 1132 (2002); b) $C(NR)_3^{2-}$: T. Chivers, M. Parvez, and G. Schatte, J. Organomet. Chem. **550**, 213 (1998); c) $Si(NR)_3^{2-}$: M. Veith and R. Lisowsky, Angew. Chem. **102**, 1124 (1988); Angew. Chem. Int. Ed. **27**, 1087 (1988); d) $Si(NR)_4^{4-}$: J. K. Brask, T. Chivers, and M. Parvez, Inorg. Chem. **39**, 2505 (2000); e) $P(NR)_3^{-}$: E. Niecke, M. Frost, M. Nieger, V. v. d. Gönna, A. Ruban, and W. W. Schoeller, Angew. Chem. **106**, 2170 (1994); Angew. Chem. Int. Ed. **33**, 2111 (1994); f) $P(NR)_4^{3-}$: P. R. Raithby, C. A. Russell, A. Steiner, and D. S. Wright, Angew. Chem. **109**, 676 (1997); Angew. Chem. Int. Ed. **36**, 649 (1997); g) $As(NR)_3^{3-}$: M. A. Beswick, S. J. Kidd, M. A. Paver, P. R. Raithby, A. Steiner, and D. S. Wright, Inorg. Chem. Comm. **2**, 612 (1999); h) L. T. Burke, J. C. Jeffery, A. P. Leedham, and C. A. Russell, J. Chem. Soc. Dalton Trans. 423 (2001); i) $Sb(NR)_3^{3-}$: A. J. Edwards, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell, and D. S. Wright, Angew. Chem. **106**, 1334 (1994); Angew. Chem. Int. Ed. **33**, 1277 (1994); j) $S(NR)_3^{2-}$: R. Fleischer, S. Freitag, F. Pauer, and D. Stalke, Angew. Chem. **108**, 208 (1996); Angew. Chem. Int. Ed. **35**, 204 (1996); k) $S(NR)_4^{2-}$: R. Fleischer, A. Rothenberger, and D. Stalke, Angew. Chem. **109**, 1140 (1997); Angew. Chem. Int. Ed. **36**, 1105 (1997); l) $Se(NR)_3^{2-}$: T. Chivers, M. Parvez, and G. Schatte, Inorg. Chem. **35**, 4094 (1996); m) $Te(NR)_3^{3-}$: T. Chivers, X. Gao, and M. Parvez, Angew. Chem. **107**, 2756 (1995); Angew. Chem. Int. Ed. **34**, 2549 (1995).

[4] Reviews: a) R. Fleischer and D. Stalke, Coord. Chem. Rev. **176**, 431 (1998); b) D. Stalke, Proc. Indian Acad. Sci. **112**, 155 (2000).

[5] D. Hänssgen, H. Hupfer, M. Nieger, M. Pfendtner, and R. Steffens, Z. Anorg. Allg. Chem. **627**, 17 (2001).

[6] a) D. Hänssgen and R. Steffens, J. Organomet. Chem. **236**, 53 (1982); b) D. Hänssgen and R. Steffens, Z. Naturforsch. **40b**, 919 (1985); c) F. Pauer and D. Stalke, J. Organomet. Chem. **416**, 127 (1991); d) F. Pauer, J. Rocha, and D. Stalke, J. Chem. Soc. Chem. Commun. 1477 (1991); e) F. T. Edelmann, F. Knösel, F. Pauer, D. Stalke, and W. Bauer, J. Organomet. Chem. **438**, 1 (1992); f) S. Freitag, W. Kolodziejski, F. Pauer, and D. Stalke, J. Chem. Soc. Dalton Trans. 3779 (1993).

[7] a) R. Fleischer, B. Walfort, A. Gburek, P. Scholz, W. Kiefer, and D. Stalke, Chem. Eur. J. **4**, 2266 (1998); b) B. Walfort, A. P. Leedham, C. A. Russell, and D. Stalke, Inorg. Chem. **40**, 5668 (2001).

[8] B. Walfort, R. Bertermann, and D. Stalke, Chem. Eur. J. **7**, 1424 (2001).

[9] B. Walfort and D. Stalke, Angew. Chem. **113**, 3965 (2001); Angew. Chem. Int. Ed. **40**, 3846 (2001).

[10] C. K. Ingold and J. A. Jessop, J. Chem. Soc. 713 (1930).

[11] a) E. J. Corey and T. Durst, J. Am. Chem. Soc. **88**, 5656 (1966); b) E. J. Corey and T. Durst, J. Am. Chem. Soc. **90**, 5548 (1968).

[12] J. Zanardi, C. Leriverend, D. Aubert, K. Julienne, and P. Metzner, J. Org. Chem. **66**, 5620 (2001).

[13] A. R. Cennedy, M. H. Taday, and J. D. Rainier, Org. Letters **3**, 2407 (2001).

[14] a) Cambridge Structural Database, May 2002; b) F. H. Allen and O. Kennard, Chem. Des. Automat. News **8**, 131 (1993).

[15] A. T. Jeffries, K. C. Moore, D. M. Ondeyka, and W. V. Morgantown, J. Org. Chem. **46**, 2885 (1981).

[16] W. Hollstein, K. Harms, M. Marsch, and G. Boche, Angew. Chem. **99**, 1279 (1987); Angew. Chem. Int. Ed. **26**, 1287 (1987).

[17] a) D. R. Armstrong, D. Barr, W. Clegg, R. E. Mulvey, D. Reed, R. Snaith, and K. Wade, J. Chem. Soc. Chem. Commun. 869 (1989); b) K. Gregory, P. v. R. Schleyer, and R. Snaith, Adv. Inorg. Chem. **37**, 47 (1991); c) R. E. Mulvey, Chem. Soc. Rev. **20**, 167 (1991); d) R. E. Mulvey, Chem. Soc. Rev. **27**, 339 (1998); e) A. Downard and T. Chivers, Eur. J. Inorg. Chem. 2193 (2001).

[18] H. W. Roesky, A. Grünhagen, F. T. Edelmann, and M. Noltemeyer, Z. Naturforsch. **44b**, 1365 (1989).

[19] D. Leusser, B. Walfort, and D. Stalke Angew. Chem. **114**, 2183 (2002); Angew. Chem. Int. Ed. **41**, 2079 (2002).

[20] a) J. F. K. Müller, M. Neuburger, and B. Spingler, Angew. Chem. **111**, 3766 (1999); Angew. Chem. Int. Ed. **38**, 3549 (1999); b) J. F. K. Müller, M. Neuburger, and M. Zehnder, Helv. Chim. Acta **80**, 2182 (1997).

[21] a) D. Stalke, Chem. Soc. Rev. **27**, 171 (1998); b) T. Kottke, R. J. Lagow, and D. Stalke, J. Appl. Crystallogr. **29**, 465 (1996); c) T. Kottke and D. Stalke, J. Appl. Crystallogr. **26**, 615 (1993).

[22] Bruker AXS, Inc. Madison WI 2000, Program for data processing.

[23] SADABS2: G. M. Sheldrick, Universität Göttingen 2000, Program for empirical absorption correction.

[24] G. M. Sheldrick, Acta Crystallogr. Sect. **A 46**, 467 (1990).

[25] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, 1993, University of Göttingen.