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New Chelating Ligands Based on S-Organosulfurdiimides: Synthesis and Single Crystal X-ray Structures of their Lithium Complexes

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Three new diimidosulfinates, $[\mathrm{TMSCH_2S(N^tBu)_2Li}]_2$ (**1**), $[\mathrm{2\text{-}PyCH_2S(N^tBu)_2Li}]_2$ (**2**), and $[\{\mathrm{PhCH_2S(N^tBu)_2Li}\}_2\cdot\mathrm{THF}]$ (**3**) (TMS = trimethylsilyl; Py = 2-pyridyl), have been synthesized by the reaction of functionalized α-$\mathrm{CH_2}$-organolithium compounds with *bis-tert*-butylsulfurdiimide. These new organolithium chelates are characterized by NMR (^{1}H, ^{13}C, ^{7}Li, and ^{29}Si) spectroscopy and single-crystal X-ray diffraction analyses. Compounds **1** and **2** crystallize as dimers without donor molecules, whereas one of the lithium atoms in **3** is coordinated by a single THF molecule. The crystal structure of **1** shows significant intramolecular proximity between one methyl group of the trimethylsilyl (TMS) and one lithium atom, which could be described as an electrostatic Li···C interaction. The coordination sphere of each lithium atom in **2** is completed by donation from the nitrogen atom of the pyridyl ring; however, one of the lithium atoms in **3** is coordinated by a THF molecule. In addition, the first mixed sulfurdiimide species containing a diimidosulfinate and a diimidosulfite fragment, $[\{\mathrm{PhCHS(N^tBu)_2Li_2(THF)_2}\}\{\mathrm{MeS(N^tBu)_2Li(THF)}\}]$ (**4**), was isolated by deprotonation of the α-$\mathrm{CH_2}$ group in **3**. The single-crystal X-ray structure of **4** revealed two different S-bound substituents coexisting in one dimer and two asymmetrically coordinated lithium atoms.

Introduction

In consideration of the sterical demand, bidentate S-alkyl diimidosulfinates resemble cyclopentadienyl ligands, and with regard to the coordination behavior toward metal atoms, this type of compounds exhibits a similar bidentate N-centered donor site to that of β-diketiminate ligands.[1] Furthermore, S-alkyl diimidosulfinates have been widely used in main group and transition metal chemistry,[2] especially owing to their high solubility in common hydrocarbon solvents. A literature survey reveals that an addition of lithium organics to sulfurdiimides is known[3] and has been investigated since the 1970s. A variety of diimidosulfinate compounds have been synthesized using commercially available lithium organics,[4] and the emphasis has been given to nucleophilic substrates like $\mathrm{TMSCH_2Li}$ (TMS = trimethylsilyl), $\mathrm{2\text{-}PyCH_2Li}$ (Py = 2-pyridyl), and $\mathrm{PhCH_2Li}$ (Ph = phenyl) to examine the influence on the coordinating behavior toward metal atoms. The TMS group is renowned to stabilize β-carbocation intermediates in organic chemistry[5] and may be useful to strengthen the S−C bond. Our principal strategy is to develop ligands which bear different coordination sites for both hard and soft metal centers.[6,7] It is expected that such organometallic systems will provide a rigid and well-defined coordination geometry leading to interesting chemical properties and reactivity patterns. The modification of classical chelating ligands to produce novel and fluxional multidentate system has already opened up an exciting area of research in the past few years.[8] We have already carried out investigations on heteroaromatic diimidosulfinate derivatives for the reason that a coupling of diimidosulfinate units *via* a conjugated organic substituent seems advantageous to facilitate electronic communication between two $\mathrm{S(NR)_2}$ moieties since polyimido sulfur compounds are exposed to SET processes.[9,10] Our efforts to coordinate a metal atom with the S-bound substituent have produced rather promising results, and during the present course of investigations, 2-picoline was introduced as a heteroaromatic substituent with the motif to provide a flexible third coordination site for an

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intramolecular coordination, which could be achieved for the first time. Furthermore, S-phenyldiimidosulfinates have been reported which show π interactions between the phenyl ring and alkaline and alkaline earth metals, except for the small lithium atom;[11,12] however, this could not be achieved by the more flexible benzyl substituent. Furthermore, our group has extensively examined the deprotonation of S-bound α-CH_2 groups with appropriate reagents to obtain diimidosulfites,[10,13] which are comparable with Corey's ylides.[14] It is clear from recent breakthroughs about bonding properties in diimidosulfinates and -sulfites by experimental charge density studies based on high-resolution X-ray data that promising results are likely to occur in this area of research.[13,15,16] Herein, we report on the synthesis, characterization, and structural elucidation of three new diimidosulfinates, $[TMSCH_2S(N^tBu)_2Li]_2$ (**1**), $[2\text{-}PyCH_2S(N^tBu)_2Li]_2$ (**2**), and $[\{PhCH_2S(N^tBu)_2Li\}_2\cdot THF]$ (**3**) (TMS = trimethylsilyl; Py = 2-pyridyl), and the first mixed sulfurdiimide species containing both a diimidosulfinate and diimidosulfite fragment, $[\{PhCHS(N^tBu)_2Li_2(THF)_2\}\{MeS(N^tBu)_2Li(THF)\}]$ (**4**).

Results and Discussion

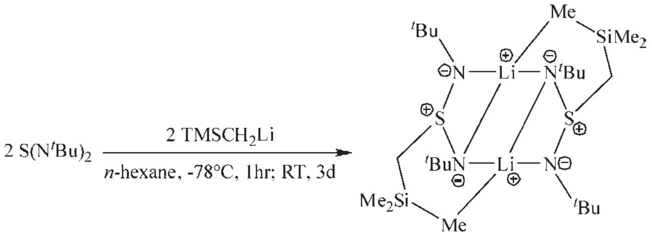
The synthesis of diimidosulfinates is usually achieved by the addition of lithium organics to the electropositive sulfur atom of sulfurdiimides which leads, in general, to dimeric species.[4] Compound **1** was isolated in fair overall yield by an equimolar reaction of $TMSCH_2Li$ with *bis*-*tert*-butylsulfurdiimide, $S(N^tBu)_2$, in *n*-hexane at −78 °C (Scheme 1).

For the synthesis of the compounds **2** and **3**, 2-picoline and toluene were first metalated with *n*-BuLi to form $[2\text{-}PyCH_2Li\cdot TMEDA]_2$[17] and $[PhCH_2Li\cdot THF\cdot TMEDA]$,[18] respectively. These were added to a solution of *bis*-*tert*-butylsulfurdiimide, $S(N^tBu)_2$, in *n*-hexane at −78 °C, which resulted in the formation of $[2\text{-}PyCH_2S(N^tBu)_2Li]_2$ (**2**) and $[\{PhCH_2S(N^tBu)_2Li\}_2\cdot THF]\cdot$(**3**) (Scheme 2).

These compounds were obtained in satisfying overall yields and afforded suitable crystals for X-ray diffraction analyses. It turned out that the dimers of **1** and **2** contain no donor molecules, although the reactions were carried out in the presence of THF or diethyl ether. This is due to the existence of intramolecular interactions between the S-bound organic substituents and the lithium atoms. Even TMEDA as a bidentate donor and being present in the reaction mixtures has no impact on the crystallization of **2** and **3**. However, the benzyl substituents in **3** are arranged at the outer region of the molecule core causing enough space for one THF molecule to coordinate one of the lithium atoms.

$[\{PhCHS(N^tBu)_2Li_2(THF)_2\}\{MeS(N^tBu)_2Li(THF)\}]$ (**4**) is the first mixed dimer of a diimidosulfite and a diimidosulfinate fragment and furthermore the first structure with two different S-bound organyl substituents coexisting in one dimer. In addition, it represents the first deprotonated sulfurdiimide species bearing an aromatic group. The formation of **4** can be envisaged in a two step reaction. First, compound **3** was prepared by the reaction between $[PhCH_2Li\cdot THF\cdot TMEDA]$ and $S(N^tBu)_2$ in *n*-hexane at −78 °C followed by deprotonation with MeLi, forming compound **4** (Scheme 3).

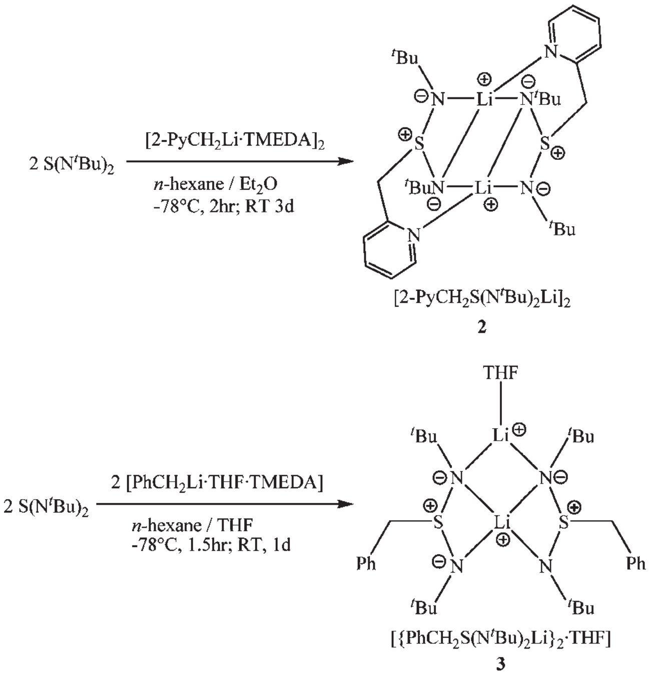
Scheme 1. Synthesis of $[TMSCH_2S(N^tBu)_2Li]_2$ (**1**)



$[TMSCH_2S(N^tBu)_2Li]_2$

1

Scheme 2. Synthesis of $[2\text{-}PyCH_2S(N^tBu)_2Li]_2$ (**2**) and $[\{PhCH_2S(N^tBu)_2Li\}_2\cdot THF]$ (**3**)



The planned synthesis should have yielded a dimeric diimidosulfite with both S-bound benzyl substituents being deprotonated, but since MeLi is also known to be a good nucleophilic reagent[19−21] and the benzyl substituent is a good leaving group, a substitution reaction at the electropositive sulfur atom hence presumably led to the mixed derivative.

Single-Crystal X-Ray Structures

$[TMSCH_2S(N^tBu)_2Li]_2$. Compound **1** crystallizes from *n*-hexane in the monoclinic space group $P2_1/c$ (Figure 1)

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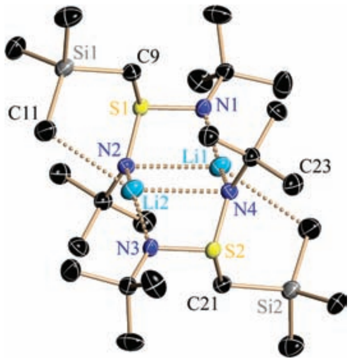
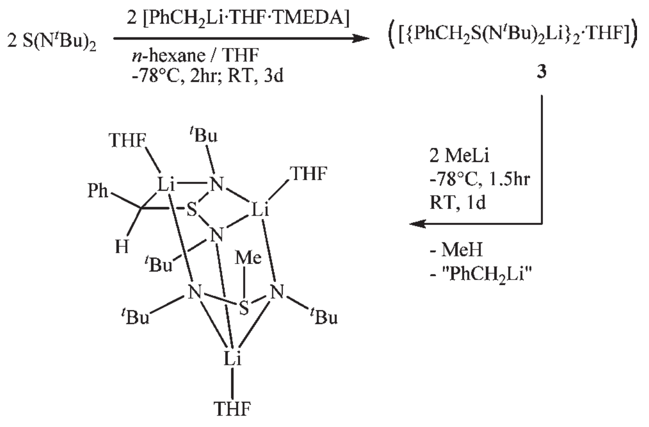


Figure 1. Molecular structure of [TMSCH$_2$S(N^{t}Bu)$_2$Li]$_2$ (**1**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: S1−N1 1.616(1), S1−N2 1.637(1), S1−C9 1.814(1), Li1−N1 1.919(3), Li1−N2 2.435(3), Li1−N4 1.965(3), Li1−C23 2.902(3), Li2−C11 2.787(3), S1−N1−C1 117.0(1), S1−N1−Li1 98.5(1), S1−N2−C2 113.8(1), S1−N2−Li2 124.7(1), Li1−N2−Li2 76.8(1), N1−S1−N2 105.0(1), N1−S1−C9 105.0(1), N2−S1−C9 98.2(1), N1−Li1−N4 146.4(2), N2−Li1−N4 105.5(1), N2−Li1−N1 71.6(1), N2−Li1−C23 42.5(1), N2−Li2−N3 144.3(2), N2−Li2−N4 103.1(1), N4−Li2−C11 40.8(1).

Scheme 3. Formation of [{PhCHS(N^{t}Bu)$_2$Li$_2$(THF)$_2$}{MeS(N^{t}Bu)$_2$-Li(THF)}] (**4**)



[{PhCHS(N^{t}Bu)$_2$Li$_2$(THF)$_2$}{MeS(N^{t}Bu)$_2$Li(THF)}]
4

and has a dimeric and centrosymmetric step-shaped structure of three fused four-membered rings like other known diimidosulfinates. The lithium atoms are 4-fold coordinated by three nitrogen atoms and additionally coordinated by long-range Li···C interactions leading to distorted tetrahedral coordination geometry. The distances between Li2 and the methyl carbon atom C11 (2.787(3) Å) and Li1 and C23 (2.902(3) Å) are in the range of weak Li···C interactions.[22] Additionally, an unusual inclination of the trimethylsilyl group in the direction of the corresponding lithium atom supports the suggested interactions. This is verified by unequal N−S1−C9 angles with an aberration of 7°, which could also relate to different N−S bonding situations and associated orbital arrangements involved in the N−S bonds given the different N coordination types. The distortion of the four-membered ring core (Li1−N2−Li2−N4) serves as an additional authentication. Compared to [^{t}BuS(N*t*Bu)$_2$Li]$_2$ (113.2°),[11] which shows even longer Li···C distances and [PhS(NSiMe$_3$)$_2$Li·thf]$_2$ (101.5°)[12] with THF coordinated lithium atoms, the N2−Li2−N4 angle of 103.1(1)° in compound **1** illustrates that a less-stretched four-membered ring core is indicating stronger Li···C interaction. The environment of Li1 reveals two short Li−N distances (1.919(3) Å/1.965(3) Å) and a longer one (2.435(3) Å), which represents a horizontal "bevel" of the step. An unusual widening of the N1−Li1−N4 angle up to 146.4(1)° is caused by a distinct vicinity between the TMS group and Li1 or rather by the sterical effects of the N1-bound *tert*-butyl group.

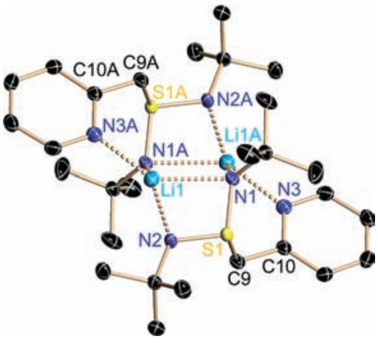


Figure 2. Molecular structure of [2-PyCH$_2$S(N^{t}Bu)$_2$Li]$_2$ (**2**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: S1−N1 1.625(2), S1−N2 1.610(2), S1−C9 1.859(2), Li1−N1 2.281(4), Li1−N2 1.979(4), Li1−N1A 2.074(3), Li1−N3A 2.118(4), C9−C10 1.487(3), S1−N1−C1 111.8(1), S1−N1−Li1 85.2(1), S1−N2−C2 117.9(1), S1−N2−Li1 96.5(1), Li1−N1−Li1A 81.5(2), N1−S1−N2 103.5(1), N1−S1−C9 99.3(1), N2−S1−C9 104.2(1), N1−Li1−N1A 98.5(2), N2−Li1−N1A 126.8(2), N2−Li1−N1 72.8(1), N2−Li1−N3A 127.7(2).

The averaged S−N distances, akin to the N−C distances (1.627 Å/1.485 Å), differ only slightly from other diimidosulfinates. The previous studies verify diverse S−C bond lengths depending on the S-bound substituent.[4] The longest S−C bond is reported for [^{t}BuS(N^{t}Bu)$_2$Li]$_2$ (1.857 Å),[11] while the shortest bond is known for [EtS-(N^{t}Bu)$_2$Li]$_2$ (1.810 Å).[23] Surprisingly, the S1−C9 bond in **1** (1.814(1) Å) lies in between, although the TMS group is even larger than the *tert*-butyl group. This clarifies a more stable S−C bond caused by the positive inductive effect of the substituent. With regard to the lone pair, a tetrahedral geometry and sp^3-hybridization for the sulfur atoms is obvious.

[2-PyCH$_2$S(N^{t}Bu)$_2$Li]$_2$ (2). Despite a moderate solubility of the precursor [2-PyCH$_2$Li·TMEDA]$_2$ in *n*-hexane, the synthesis of [2-PyCH$_2$S(N^{t}Bu)$_2$Li]$_2$ (**2**) was performed in this solvent and the residue of the product was redissolved for crystallization along with diethyl ether. The use of THF has led to degradation as indicated by the NMR spectra. Compound **2** crystallizes in the monoclinic space group *C*2/*c* and shows a dimeric and centrosymmetric step-shaped structure similar to **1** (Figure 2). The heteroaromatic 2-picolyl substituent clearly coordinates to the

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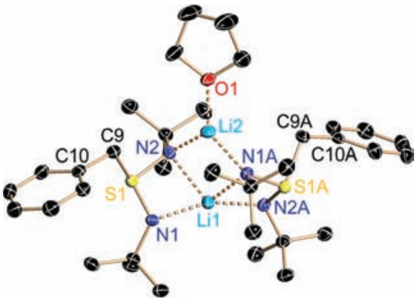

Figure 3. Molecular structure of [$\{PhCH_2S(N^tBu)_2Li\}_2\cdot THF$] (**3**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: S1−N1 1.613(2), S1−N2 1.634(2), S1−C9 1.839(2), Li1−N1 2.050(2), Li1−N2 2.160(3), Li2−N2 1.988(3), Li2−O1 1.870(5), C9−C10 1.496(3), S1−N1−C1 115.7(1), S1−N1−Li1 92.5(1), S1−N2−C5 113.9(1), S1−N2−Li1 88.0(1), S1−N2−Li2 122.0(1), Li1−N2−Li2 73.9(2), N1−S1−N2 104.0(1), N1−S1−C9 105.6(1), N2−S1−C9 98.9(1), N1−Li1−N2 74.8(1), N1−Li1−N1A 159.4(3), N1−Li1−N2A 119.5(1), N2−Li1−N2A 99.8(2), N2−Li2−N2A 112.4(2), N2−Li2−O1 123.8(1).

corresponding lithium atom, which is affirmed by a Li1−N3A distance of 2.118(4) Å. The weak Li···C interaction in **1** is replaced by a Li−N donor bond, and both lithium atoms are 4-fold coordinated by nitrogen atoms leading to distorted tetrahedral geometries. The S−N and N−C bond lengths comply with the literature reports.[4] The S−C bond in **2** (1.859(2) Å) is much longer compared to those in **1**. This is due to the negative inductive effect of the pyridyl ring and the internal coordination. Anyhow, the Li1−N3A vector still protudes out of the pyridyl mean plane by 22°. Similar to **1**, the N−S1−C9 angles differ by 5°, indicating a distortion of the 2-picolyl substituent in the direction of the coordinated lithium atom. One of the *tert*-butyl groups in **2** is shifted away from the nearby situated 2-picolyl substituent, although it shows attractive CH/π interactions with the ring with an average distance of 3.03 Å. Additionally, the polarized charge density of the pyridyl rings leads to attractive π/π interactions[24] with an intermolecular pyridyl−pyridyl distance of 3.7 Å in the packing.

[$\{PhCH_2S(N^tBu)_2Li\}_2\cdot THF$]. Compound **3** crystallizes from a mixture of *n*-hexane and THF in the monoclinic space group *C*2/*c* (Figure 3). Compound **3** does not crystallize in a step-shaped structure like **1** and **2**, but in a twisted tricyclic structure with two different coordination environments around the two lithium atoms. Li1 shows a trigonal distorted coordination polyhedron with two nitrogen atoms of the diimidosulfinate and one oxygen atom of the THF molecule, whereas Li2 exhibits a tetrahedrally distorted coordination made up by the four nitrogen atoms of both diimidosulfinates moieties in the dimer. Incidentally, an analogous structural type is also reported for diimidosulfinate derivatives,[2] and obviously, the missing two Li−N donor bonds from the isosterical 2-pyridyl substituents in **2** cause the additional coordination of a donor molecule. Weak Li···C interactions as observed in **1** are less favorable than a single donor base. Li···π (arene) interactions are known to be very weak and the present structural rearrangement is favored. Metal atoms like sodium or potassium show stronger metal···π (arene) interactions,[25] and as a consequence, donor molecules are missing in S-phenyl diimidosulfinate metal complexes, for example.[11] In compound **3**, N2 is coordinated to both lithium atoms (Li1−N2 2.160(3) Å and Li2−N2 1.988(3) Å), whereas N1 is only bonded to Li1 (Li1−N1 2.050(2) Å). The S1−C9 distance of 1.839(2) Å is due to the impact of the negative inductive effect of the S-bound subtituent as in **2**. Surprisingly, the N−S1−C9 angles also differ by 7° like in **1** and **2**, while there are no interactions between the substituent and the lithium atoms. The crystal structure reveals CH/π interactions between the N1-bound *tert*-butyl group and the phenyl ring (3.08 Å).

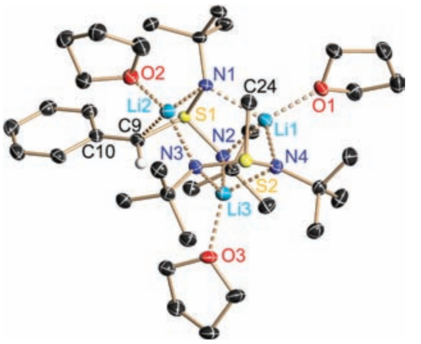

Figure 4. Molecular structure of [$\{PhCHS(N^tBu)_2Li_2(THF)_2\}\{MeS(N^tBu)_2Li(THF)\}$] (**4**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, and all hydrogen atoms have been omitted for clarity, except the freely refined benzylic hydrogen atom bonded to C9. Selected bond lengths [Å] and angles [deg]: S1−N1 1.679(1), S1−N2 1.665(1), S1−C9 1.716(1), Li1−N1 2.100(2), Li1−N2 2.080(2), Li1−N4 2.166(2), Li1−O1 2.008(2), C9−C10 1.426(2), C9−H9 0.94(2), Li2−N1 2.040(2), Li2−N3 2.079(2), Li2−C9 2.409(3), Li2−O2 1.978(2), Li3−N2 2.063(2), Li3−N3 2.230(2), Li3−N4 2.123(3), Li3−O3 1.998(2), S2−C24 1.808(1), S1−N1−C1 110.7(1), S1−N1−Li1 91.1(1), S1−N2−C2 111.4(1), S1−N2−Li1 92.2(1), S1−N2−Li3 111.7(1), Li1−N1−Li2 107.6(1), N1−S1−N2 99.8(1), N1−S1−C9 107.0(1), N2−S1−C9 108.1(1), N1−Li1−N2 75.5(1), N1−Li1−N4 116.9(1), N2−Li1−N4 101.2(1), N1−Li1−O1 119.3(1), N1−Li2−N3 112.9(1), N1−Li2−C9 75.2(1), N1−Li2−O2 124.5(1), C9−Li2−O2 120.6(1), N3−Li2−O2 113.8(1), N3−Li3−N4 72.4(1), N3−S2−C24 103.8(1), N4−S2−C24 103.5(1), N3−S2−N4 104.0(1).

[$\{PhCHS(N^tBu)_2Li_2(THF)_2\}\{MeS(N^tBu)_2Li(THF)\}$]. Compound **4** crystallizes from a mixture of *n*-hexane and THF in the monoclinic space group *C*2/*c* (Figure 4). Unlike the precursor **3**, the coordination type of **4** correlates with the dimeric tub-shaped structure of a previously described ethyl derivative.[23] The molecular aggregate is made up of a diimidosulfur ylide $PhCHS(N^tBu)_2^{2-}$ dianion and a diimidosulfinate $MeS(N^tBu)_2^{-}$ monoanion. The three lithium cations are coordinated by a THF donor base each. The ylide is (*N*,*N*) chelating Li1 and (*N*,*C*) chelating Li2. The sulfinate (*N*,*N*) chelates Li3. Li1 and Li3 provide the link between the two anions. The known structural core of compound **1** and **2** ($S_2N_4Li_2$) is still present, but in a *syn* arrangement, which is caused by the contact of N3 and Li2.

Hence, all lithium atoms show distorted tetrahedral coordination geometry. In addition to the oxygen atom of the donor base, Li1 and Li3 are coordinated by three nitrogen atoms. Li2, however, is the only cation that shows a contact to the carbanionic C9 atom. Compound

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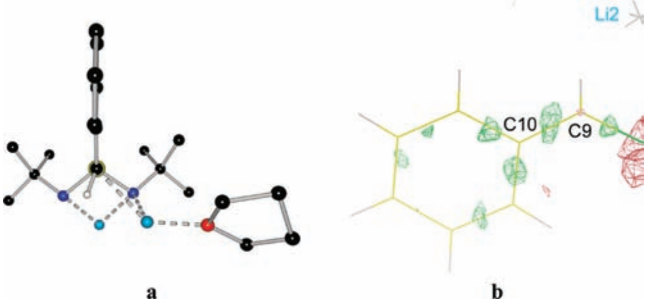

Figure 5. The ylidic $\mathrm{PhCHS(N^tBu)_2}^{2-}$ dianion in **4** with the benzylic mean plane orthogonal and with a view along the C9–S1 bond (a) and the residual electron density plot around C9 and in the aromatic system with the benzylic mean plane in the paper plane (b). Green areas indicate charge accumulation, which is due to bonding electrons.

4 is a rare example of a molecule containing an asymmetrically coordinated lithium atom.[26] Since **4** crystallizes in a centrosymmetric space group, both enantiomers are present in the solid state.

The S1–C9 bond is located in the mean plane of the phenyl ring, preventing any interaction with a lithium atom, but an interesting electronic coupling between the ring and sulfurdiimide is thereby enabled, which leads to a highly delocalized negative charge.[27] This is also demonstrated by a distorted phenyl ring with three nearly equivalent C–C bond lengths (1.422–1.426 Å) around the *ipso* carbon atom (C10). The deformation caused by transferring negative charge into the phenyl ring through the overlapping π orbitals implies an increased chinoidal character of the substituent.[28] The shortening of the S1–C9 bond to 1.716(1) Å in **4** compared to **3** (1.839(2) Å) is mainly attributed to the higher polarity of the bond. The involved effects have already been examined in a detailed charge density study of an α-lithiated benzylsilane[26] and apply analogously to the structure of **4**. The carbanionic atom C9 shows a virtually trigonal planar environment, not taking the Li–C contact into account (Figure 5a),[17] because the sum of the bond angles around C9 adds up to 356.8°. The position of the remaining hydrogen atom was taken from the final residual density map and refined freely. The benzyl mean plane almost ideally bisects the NSN angle, and there is no noticeable lone pair character at C9 (Figure 5b). Although the carbanionic charge is not located in a stereochemically active lone pair, the long Li···C contact of 2.409(3) Å represents an attractive interaction with the lithium cation Li2.

Conclusion

The research work presented in this paper is an interplay between the oriented synthesis and the structural characterization of sulfurdiimide compounds. The results have clearly indicated that the coupling of reactive lithium organics with sulfurdiimides is quite feasible and enables a versatile application of these derivatives. Compound **1** shows intramolecular interactions including the TMS group, while in the case of **2**, the donation of one lithium atom is facilitated by the nitrogen atom present in the heteroaromatic 2-picolyl substituent. If there is no chance of any intramolecular donation, a THF molecule coordinates one of the lithium atoms (as can be seen in **3**) instead. Although only lithium complexes of the described ligands could be isolated up to now, earlier studies in our working group concerning additional side arm coordination suggest that metal exchange reactions should be unproblematic.[29]

The deprotonation of α-carbon atoms in S-aryl-diimidosulfinates like $[\mathrm{PhCH_2S(N^tBu)_2}]^-$ opens a synthetic route to new class of compounds. Compound **4** is a rare molecule having both diimidosulfite and diimidosulfinate fragments together in one dimer. This is also the first deprotonated sulfurdiimide species bearing an aromatic group. Further, the lithium atoms in **4** are asymmetrically coordinated, and therefore, the formation of **4** generates lots of expectation for new promising asymmetric molecules, which can find application as important synthons in future asymmetric organic and inorganic synthesis. Unfortunately, the synthesis of **4** is not quite understood, and the nonreproducibility detains its common use, but we are working on the problem to obtain this new compound in a satisfying synthetic pathway.

Experimental Section

All experimental manipulations were performed either in an inert gas atmosphere of purified dry nitrogen or argon with standard Schlenk techniques or in an argon glovebox. The glassware was dried at 140 °C, assembled hot, and cooled down under a vacuum. All solvents were dried over a sodium–potassium alloy, distilled, and degassed prior to use. The reactants were commercially available or synthesized according to the literature reports ($\mathrm{S(N^tBu)_2}$).[30] All NMR spectra were either recorded on a Bruker Avance DPX 300 MHz or Bruker Avance DRX 500 MHz spectrometer using TMS (^{1}H and ^{13}C) and LiCl (^{7}Li) as an external reference and the protons of THF-d^8 as an internal standard. Elemental analyses (C, H, N, and S) were carried out at the Mikroanalytisches Labor, Institut für Anorganische Chemie, Universität Göttingen.

$[\mathrm{TMSCH_2S(N^tBu)_2Li}]_2$ (1). A 1.06 M solution of $\mathrm{TMSCH_2Li}$ (4.72 mL, 5.00 mmol) in *n*-hexane was added dropwise to a solution of $\mathrm{S(N^tBu)_2}$ (0.872 g, 5.00 mmol) in 20 mL of *n*-hexane at −78 °C over a period of 30 min. The colorless reaction mixture turned to pale yellow after an additional 30 min of stirring at −78 °C, which was then stirred overnight at room temperature. Subsequently, two-thirds of the solvent was removed under reduced pressure. This afforded crystals suitable for X-ray analysis after storing at −30 °C for two days. The product was separated from the mother liquor and washed with cold *n*-hexane (2 × 5 mL), which yielded 1.94 g (3.61 mmol, 72%) of overall pure material. Anal. Calcd for $\mathrm{C_{24}H_{58}Li_2N_4S_2Si_2}$ (mol wt 536.92): C, 52.1; H, 11.1; N, 10.1; S, 12.4. Found: C, 53.7; H, 10.9; N, 10.4; S, 11.9. M.P.: 140 °C (dec.). ^{1}H NMR (300 MHz, THF-d^8): δ 2.66 (s, 2H, $\mathrm{SC\mathit{H}_2Si(CH_3)_3}$), 1.33 (s, 18H, $\mathrm{S(NC(C\mathit{H}_3)_3)_2}$), 0.20 (s, 9H, $\mathrm{Si(C\mathit{H}_3)_3}$). ^{13}C NMR (125 MHz, THF-d^8): δ 56.9 (s, $\mathrm{S(N\mathit{C}(CH_3)_3)_2}$), 53.8 (s, $\mathrm{S\mathit{C}H_2Si(CH_3)_3}$), 33.9 (s, $\mathrm{S(NC(\mathit{C}H_3)_3)_2}$), −0.3 (s, $\mathrm{SCH_2Si(\mathit{C}H_3)_3}$). ^{7}Li NMR (194 MHz, THF-d^8): δ 2.45 (s). ^{29}Si NMR (99 MHz, THF-d^8): δ −4.09 (s). EI-MS *m*/*z* (%): 537 (1) $[\mathrm{M}]^+$, 449 (30) $[\mathrm{M-CH_2SiMe_3}]^+$,

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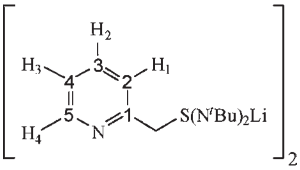
275 (100) [M − $(\mathrm{CH_2SiMe_3})_2$ − ^{t}Bu − $\mathrm{Me_2}]^+$/[$\mathrm{Li_2}$(N^{t}Bu)$_2$SCH$_2$SiMe$_3]^+$, 190 (20) [(N^{t}Bu)SCH$_2$SiMe$_3]^+$, 188 (26) [Li$_2$(N^{t}Bu)$_2$S]$^+$, 181 (28) [Li(N^{t}Bu)$_2$S]$^+$, 131 (24) [Li$_2$(N^{t}Bu)SN]$^+$, 119 (20) [SCH$_2$SiMe$_3$]$^+$, 73 (51) [SiMe$_3$]$^+$.

[2-PyCH$_2$S(N^{t}Bu)$_2$Li]$_2$ (2). S(N^{t}Bu)$_2$ (1.31 g, 7.50 mmol) was added dropwise to a red solution of [2-PyCH$_2$Li·TMEDA]$_2$[17] (1.70 g, 3.95 mmol) in 60 mL of *n*-hexane over a period of one hour. After additional stirring for one hour at −78 °C, the reaction mixture was further stirred for three days at room temperature. The yellow precipitate thus formed was filtered off, washed with *n*-hexane (2 × 10 mL), and dried *in vacuo*. The residue was dissolved in an adequate amount of diethyl ether and kept at −30 °C for three days, which afforded pale-yellow crystals suitable for X-ray analysis. Overall yield: 2.52 g (4.61 mmol, 61%) of pure material. Anal. Calcd for $\mathrm{C_{28}H_{48}Li_2N_6S_2}$ (mol wt 546.73): C, 61.5; H, 9.3; N, 15.4; S, 11.5. Found: C, 61.5; H, 8.9; N, 15.4; S, 11.7. M.P.: 130 °C (dec.). ^{1}H NMR (300 MHz, THF-d^8): δ 8.60 (H$_4$, 1H, ddd, $^3J_{\mathrm{HH}} = 0.9$ Hz, $^4J_{\mathrm{HH}} = 1.8$ Hz, $^5J_{\mathrm{HH}} = 5.0$ Hz), 7.73 (H$_2$, 1H, ddd, $^3J_{\mathrm{HH}} = 7.7, 7.7$ Hz, $^4J_{\mathrm{HH}} = 1.8$ Hz), 7.31 (H$_3$, 1H, ddd, $^3J_{\mathrm{HH}} = 7.7, 0.9$ Hz, $^4J_{\mathrm{HH}} = 1.2$ Hz), 7.22 (H$_1$, 1H, ddd, $^3J_{\mathrm{HH}} = 7.7$ Hz, $^4J_{\mathrm{HH}} = 1.2$ Hz, $^5J_{\mathrm{HH}} = 5.0$ Hz), 4.08 (s, 2H, 2-PyC*H*$_2$S), 1.12 (s$_{\mathrm{br}}$, 18H, S(NC(C*H*$_3$)$_3$)$_2$). ^{13}C NMR (75 MHz, THF-d^8): δ 56.6 (s, 1-C), 149.3 (s, 5-C), 138.1 (s, 3-C), 124.9 (s, 2-C), 122.2 (s, 4-C), 69.1 (s, 2-Py*C*H$_2$S), 54.1 (s, S(N*C*(CH$_3$)$_3$)$_2$), 34.2 (s, S(NC(*C*H$_3$)$_3$)$_2$). ^{7}Li NMR (117 MHz, THF-d^8): δ 2.38 (s). EI-MS *m*/*z* (%): 454 (4) [M − PyCH$_2$]$^+$, 304 (3) [M − ^{t}Bu$_3$ − N^{t}Bu]$^+$, 280 (12) [PyCH$_2$S(N^{t}Bu)$_2$Li$_2$]$^+$, 266 (10) [PyCH$_2$S(N^{t}Bu)$_2$]$^+$, 181 (18) [S(N^{t}Bu)$_2$Li]$^+$, 103 (96) [S(N^{t}Bu)]$^+$.



[{PhCH$_2$S(N^{t}Bu)$_2$Li}$_2$·THF] (3). A 0.19 M solution of [PhCH$_2$Li·THF·TMEDA][18] (8.47 mL, 1.61 mmol) in THF was added dropwise to a solution of S(N^{t}Bu)$_2$ (0.262 g, 1.50 mmol) in 20 mL of *n*-hexane at −78 °C over a period of 30 min. After an additional stirring for one hour at −78 °C, the orange colored reaction mixture was stirred overnight at room temperature. Subsequently, two-thirds of the solvents were removed under reduced pressure, and the contents were kept at −30 °C for two months, which afforded pale-yellow crystals suitable for X-ray analysis. The product was separated from the mother liquor, washed with *n*-hexane (2 × 5 mL), and dried under a vacuum yielding 0.75 g (0.99 mmol, 66%) of pure material. Anal. Calcd for $\mathrm{C_{42}H_{74}Li_2N_4O_3S_2}$ (mol wt 761.07): C, 62.4; H, 8.8; N, 8.4; S, 10.5. Found: C, 66.3; H, 9.8; N, 7.4; S, 8.4. ^{1}H NMR (500 MHz, THF-d^8): δ 7.30−7.15 (m, 5H, phenyl), 3.91 (s, 2H, PhC*H*$_2$S), 3.58 (s, 5H, THF), 1.73 (s, 7H, THF), 1.10 (s, 18H, S(NC(C*H*$_3$)$_3$)$_2$). ^{13}C NMR (75 MHz, THF-d^8): δ 134.8 (s, C$_{\mathrm{ipso}}$), 131.6 (s, C$_{\mathrm{para}}$), 128.6 (s, C$_{\mathrm{meta}}$), 127.9 (s, C$_{\mathrm{ortho}}$), 67.4 (THF), 66.0 (s, Ph*C*H$_2$S), 54.1 (s, S(N*C*(CH$_3$)$_3$)$_2$), 32.5 (s, S(NC(*C*H$_3$)$_3$)$_2$), 25.2 (THF). EI-MS *m*/*z* (%): 195 (11) [PhCH$_2$S(N^{t}Bu)]$^+$, 175 (54) [S(N^{t}Bu)$_2$ + H]$^+$, 119 (42) [NS(N^{t}Bu) + 2H]$^+$, 91 (100) [PhCH$_2$]$^+$, 57 (44) [^{t}Bu]$^+$.

[{PhCHS(N^{t}Bu)$_2$Li$_2$(THF)$_2$}{MeS(N^{t}Bu)$_2$Li(THF)}] (4). A 0.19 M solution of [PhCH$_2$Li·THF·TMEDA][18] (21.6 mL, 4.00 mmol) in THF was added dropwise to a solution of S(N^{t}Bu)$_2$ (0.697 g, 4.00 mmol) in 40 mL of *n*-hexane at −78 °C over a period of one hour. The orange colored reaction mixture was stirred for one hour at −78 °C followed by stirring at room temperature for three days. Now, the reaction mixture was cooled again to −78 °C and a 1.60 M solution of MeLi (2.56 mL, 4.10 mmol) in Et$_2$O added dropwise over a period of 30 min. The yellow colored contents were stirred for one hour at this temperature followed by stirring overnight at room temperature. Subsequently, about 80% of the solvent was evaporated under reduced pressure, and the contents were kept at 3 °C for two days, which afforded pale-yellow crystals suitable for X-ray analysis. The crystals were separated from the mother liquor, washed with *n*-hexane (2 × 5 mL), and dried under a vacuum yielding 0.13 g (0.19 mmol, 10%) of crystalline material. No further analyses could be performed due to the high reactivity of the compound and the nonreproducibility of the synthesis, so far.

Single Crystal Structural Analysis

The data for **1**−**4** were collected from shock-cooled crystals at 100.0(5) K. All data sets were collected on Bruker SMART-APEX II diffractometers with D8 goniometers. For the data collections of **1** and **2**, a Bruker TXS-Mo rotating anode was used as an X-ray source; for **4**, an Incoatec microfocus source;[31] and for **3**, a fine-focused sealed tube was utilized. All diffractometers were equipped with a low-temperature device[32,33] and used monochromated Mo K$_\alpha$ radiation, $\lambda = 0.71073$ Å. The Bruker TXS-Mo rotating anode and the Incoatec microfocus source used mirror optics as radiation monochromator, whereas the sealed tube device used a graphite monochromator. The data sets were integrated with SAINT,[34] and an empirical absorption correction (SADABS/TWINABS) was applied.[35,36] All structures were solved by direct methods (SHELXS-97)[37] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[38,39] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were either refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms or found freely in the residual density map. Disordered moieties were refined using bond length restraints and isotropic displacement parameter restraints.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data, and experimental details for the X-ray measurements are listed below. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[TMSCH$_2$S(N^{t}Bu)$_2$Li]$_2$ (1). $\mathrm{C_{24}H_{58}Li_2N_4S_2Si_2}$, CCDC number: 751245, $M = 536.92$, monoclinic, space group $P2_1/n$, $a = 9.658(1)$ Å, $b = 16.723(2)$ Å, $c = 21.316(2)$ Å, $\alpha = 90°$, $\beta = 100.350(1)°$, $\gamma = 90°$, $V = 3.3865(6)$ nm^3, $Z = 4$, 76 006 reflections measured, 7188 independent reflections ($R_{\mathrm{int}} = 0.0397$), 347 parameters, R_1 (all data) = 0.0410, $R_1[\mathrm{I} > 2\sigma(\mathrm{I})] = 0.0328$, w$R_2$ = (all data) = 0.0911, w$R_2[\mathrm{I} > 2\sigma(\mathrm{I})] = 0.0837$, GoF = 1.071, largest diff. peak and hole 0.471 and −0.287 eA^{-3}.

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[2-PyCH$_2$S(N^{t}Bu)$_2$Li]$_2$ (2). $C_{28}H_{48}Li_2N_6S_2$, CCDC number: 751246, M = 546.73, monoclinic, space group $C2/c$, a = 9.883(3) Å, b = 18.001(5) Å, c = 17.611(5) Å, α = 90°, β = 91.175(4)°, γ = 90°, V = 3.1324(16) nm^3, Z = 4, 69 271 reflections measured, 3814 independent reflections (R_{int} = 0.1689), 179 parameters, R_1 (all data) = 0.0492, R_1[I > 2σ(I)] = 0.0449, wR_2 = (all data) = 0.1033, wR_2[I > 2σ(I)] = 0.1011, GoF = 1.179, largest diff. peak and hole 0.453 and −0.371 eA^{-3}.

[{PhCH$_2$S(N^{t}Bu)$_2$Li}$_2$·THF] (3). $C_{42}H_{74}Li_2N_4O_3S_2$, CCDC number: 751247, M = 761.07, monoclinic, space group $C2/c$, a = 16.322(1) Å, b = 12.276(1) Å, c = 26.994(2) Å, α = 90°, β = 94.091(1)°, γ = 90°, V = 5.3950(6) nm^3, Z = 4, 35 720 reflections measured, 4948 independent reflections (R_{int} = 0.0518), 299 parameters, R_1 (all data) = 0.0649, R_1[I > 2σ(I)] = 0.0440, wR_2 = (all data) = 0.1105, wR_2[I > 2σ(I)] = 0.0996, GoF = 1.027, largest diff. peak and hole 0.385 and −0.251 eA^{-3}.

[{PhCHS(N^{t}Bu)$_2$Li$_2$(THF)$_2$}{MeS(N^{t}Bu)$_2$Li(THF)}] (4). $C_{36}H_{69}Li_3N_4O_3S_2$, CCDC number: 751248, M = 690.89, monoclinic, space group $C2/c$, a = 15.284(3) Å, b = 17.129(3) Å, c = 31.676(5) Å, α = 90°, β = 94.386(2)°, γ = 90°, V = 8.268(2) nm^3, Z = 8, 58 843 reflections measured, 8756 independent reflections (R_{int} = 0.0247), 450 parameters, R_1 (all data) = 0.0395, R_1[I > 2σ(I)] = 0.0330, wR_2 = (all data) = 0.0866, wR_2[I > 2σ(I)] = 0.0829, GoF = 1.044, largest diff. peak and hole 0.282 and −0.0.279 eA^{-3}.

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